Toxic Byproduct Formation during Electrochemical Treatment of Latrine Wastewater

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ABSTRACT: Electrochemical systems are an attractive option for onsite latrine wastewater treatment due to their high efficiency and small footprint. While concerns remain over formation of toxic byproducts during treatment, rigorous studies examining byproduct formation are lacking. Experiments treating authentic latrine wastewater over variable treatment times, current densities, chloride concentrations, and anode materials were conducted to characterize byproducts and identify conditions that minimize their formation. Production of inorganic byproducts (chlorate and perchlorate) and indicator organic byproducts (haloacetic acids and trihalomethanes) during electrolysis dramatically exceeded recommendations for drinking water after one treatment cycle (~10–30 000 times), raising concerns for contamination of downstream water supplies. Stopping the reaction after ammonium was removed (i.e., the chlorination breakpoint) was a promising method to minimize byproduct formation without compromising disinfection and nutrient removal. Though treatment was accelerated at increased chloride concentrations and current densities, byproduct concentrations remained similar near the breakpoint. On TiO2/IrO2 anodes, haloacetic acids (up to ~50 μM) and chlorate (up to ~2 μM) were of most concern. Although boron-doped diamond anodes mineralized haloacetic acids after formation, high production rates of chlorate and perchlorate (up to ~4 and 25 μM) made them inferior to TiO2/IrO2 anodes in terms of toxic byproduct formation. Organic byproduct formation was similar during chemical chlorination and electrolysis of wastewater, suggesting that organic byproducts are formed by similar pathways in both cases (i.e., reactions with chloramines and free chlorine).

INTRODUCTION

Onsite electrochemical systems show promise for providing wastewater treatment to the billions of people lacking access to adequate wastewater treatment,1 and these systems are currently being commercialized for application in both rural communities (e.g., rural schools in South Africa) and urban communities (e.g., apartment buildings in India). Electrochemical systems can be powered by solar energy and do not require external water inputs, as treated water can be recycled for flushing.2 However, in addition to being recycled within the system, once storage tanks are full, treated water is also discharged to the environment due to system users’ urine input. Ensuring a high level of wastewater treatment is therefore critical to protecting the receiving environment as well as human health if discharged water reaches drinking water sources or system users come in contact with recycled flushing water.

Electrochemical treatment systems have been shown to provide effective treatment of latrine wastewater. Greater than 5-log inactivation of bacterial and viral indicator organisms is achieved via production of reactive chlorine species from chloride (15–20 mM) within 1 h at 4 V applied cell potential.3 A combination of reactive chlorine species and direct oxidation provide reduction of chemical oxygen demand (COD)4 and transformation of trace organic contaminants within 4 h (3.5–4.5 V applied cell potential)5 with rates enhanced at elevated chloride concentrations (up to 75 mM). Under similar operating conditions, ammonium removal occurs via breakpoint chlorination,6 and phosphorus can be precipitated as hydroxyapatite.9

Unfortunately, strongly oxidizing conditions in the presence of the high concentrations of chloride and organic matter typical of latrine wastewater also result in formation of toxic byproducts.10 While wastewater disinfection is essential to protecting human health, an ideal electrochemical system should also be designed to minimize toxic byproduct formation.11 Chloride enhances electrochemical treatment via formation of reactive chlorine species (e.g., hypochlorous acid, chloramines, and chlorine radicals).5,6,7,12,13 However, electrochemical oxidation of chloride also produces the toxic byproducts chlorate and, on “nonactive” anodes that preferentially form hydroxyl radical (e.g., boron-doped diamond (BDD)),...
perchlorate. For example, chlorate and perchlorate concentrations 1000 to more than 100 000 times higher than World Health Organization (WHO) and United States Environmental Protection Agency (US EPA) health guidelines were measured during electrochemical treatment of reverse osmosis retentate, urine, and latrine wastewater (see Table SI 1 for health guidelines and Table SI 2 for a summary of previous electrochemical byproduct studies). Though less toxic, nitrate may also be produced during electrochemical treatment. Electrochemical bromate production is limited by the low bromide concentrations typical of latrine wastewater.

A wide array of halogenated organic byproducts is also produced by reaction of chlorine species with wastewater, which contains organic compounds known to form disinfection byproducts (i.e., carbohydrates, amino acids, and proteins). Only a few indicator compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs) or the bulk parameter adsorbable organic chlorine (AOCl) are commonly monitored, however. For example, electrolysis of latrine wastewater and reverse osmosis retentate produced THMs and HAAs at concentrations 10–50 times higher than those of drinking water regulations (Tables SI 1 and 2). Halogenated organic byproducts have also been measured during treatment of domestic wastewater, latrine wastewater, urine, and surface water. While it is known that these toxic byproducts are produced during electrochemical treatment, a comprehensive study of the effects of electrochemical operating conditions on byproduct formation, with an aim of limiting byproduct formation while ensuring adequate wastewater treatment, is lacking.

The purpose of this study was for the first time to rigorously evaluate the formation of potentially hazardous byproducts during electrochemical treatment of latrine wastewater. The inorganic byproducts nitrate, chloride, and perchlorate were measured as well as the commonly observed organic byproducts THMs (chloroform, bromodichloromethane, dichlorobromomethane, and bromoform) and chlorinated HAAs (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA)), which were used as indicators of halogenated organic byproduct formation. Byproduct formation in authentic latrine wastewater was evaluated under a range of treatment times, current densities, chloride concentrations, and anode compositions. Operating parameters were then identified that could be adjusted to minimize toxic byproduct formation while maintaining efficient wastewater treatment.

## MATERIALS AND METHODS

### Materials

All reagents were purchased from Sigma-Aldrich at reagent-grade purity or higher. Solutions were prepared using ≥18 MΩ Milli-Q water from a Millipore system.

**Latrine Wastewater.** Latrine wastewater was collected from a previously described recycling electrochemical toilet system located at Caltech (Pasadena, CA). Wastewater from an adjacent toilet was macerated and stored by the system, treated electrochemically (3.5–4.0 V applied cell voltage; 4 h batch treatment cycle), and then recycled for use as flushing water. Latrine wastewater was collected from the untreated water storage tank and filtered prior to use to enhance stability between experiments (2.5 mm; see Table 1 for water quality parameters). Wastewater was amended with sodium chloride to select experiments.

### Table 1. Typical Latrine Wastewater Properties

| property        | latrine wastewater |
|-----------------|--------------------|
| pH              | 8.6 ± 0.2          |
| conductivity (mS cm⁻¹) | 7 ± 2            |
| TOC (mg C L⁻¹) | 154 ± 13           |
| TIC (mM)       | 52 ± 2             |
| COD (mg O₂ L⁻¹) | 500 ± 60           |
| [Cl⁻] (mM)     | 33–100             |
| [Br⁻] (μM)     | 5 ± 1              |
| [NH₄⁺] (mM)    | 34 ± 2             |

**Wastewater Electrolysis.** Wastewater was treated electrochemically under conditions similar to those employed in the Caltech electrochemical toilet system. Either mixed-metal oxide anodes (TiO₂/Ir-Ta₂O₅/Ti; referred to as TiO₂/IrO₂ below for simplicity; purchased from Nanopac, South Korea) or BDD anodes (purchased from NeoCoat, Switzerland) were coupled to stainless steel counter electrodes. TiO₂/IrO₂ anodes (14 cm²) were configured as previously reported, sandwiched between two cathodes in 80 mL of wastewater. BDD anodes (6.3 cm²) were paired with a single cathode in 25 mL of wastewater as only one side of the anode was active. Electrochemical cells were undivided, and electrodes were separated by 3 mm. Electrolysis current was held constant at 2.5–7.5 A L⁻¹ (14–45 mA cm⁻², 3.6–4.4 V cell voltage for TiO₂/IrO₂; 15 mA cm⁻², 6.5 V cell voltage for BDD) using a potentiostat (Neware, China). Solutions were stirred (400 rpm) in uncovered beakers to simulate pilot-scale systems which are left uncovered or actively vented to prevent accumulation of hydrogen gas. The chlorination breakpoint time (i.e., when ammonium removal was complete) was identified by a peak in the measured voltage due to changes in solution conductivity at the breakpoint (e.g., Figure SI 1) as well as by monitoring ammonium and total chlorine concentrations.

### Halocetic Acid Electrolysis

Electrolysis of individual chlorinated HAAs (~1 mM) was evaluated in buffered solutions (30 mM sodium borate; pH 8.7) using TiO₂/IrO₂ and BDD anodes. Electrolysis conditions were as described above, except anodes were held at 7.5 V versus the cathode, which was similar to the voltage measured during latrine wastewater treatment with BDD anodes. In addition to HAA concentrations, total organic carbon (TOC), chlorine, chloride, and perchlorate concentrations were measured to determine if HAAs were mineralized during electrolysis. Parachlorobenzoic acid (pCBA) was added to select electrolysis experiments (100 μM) to estimate hydroxyl radical steady state concentrations.

### Chlorination of Wastewater

To compare byproduct concentration profiles during chemical chlorination of latrine wastewater to those observed during electrochemical treatment, sodium hypochlorite (~5%) was added to stirred latrine wastewater (20 mL) in uncovered beakers using a peristaltic pump (0.47 mL h⁻¹). Sodium hypochlorite was added at a rate similar to the initial rate of chlorine production during electrochemical treatment (~16 mM h⁻¹).

**Analytical Methods.** Total organic and inorganic carbon concentrations were measured using a TOC analyzer (Aurora...
1030; College Station, TX). Samples for ion analysis, including ammonium, chloride, nitrate, chlorate, and perchlorate, were diluted 25 times upon sampling and were quantified by ion chromatography (Dionex ICS 2000; Sunnyvale, CA). Total chlorine and COD were measured within 5 min of sampling by standard methods using commercially available kits (Hach; Loveland, CO).

Organic disinfection byproducts were extracted immediately upon sampling. THMs (1 mL sample aliquots) were extracted using pentane (2 mL), and the organic phase was collected using a glass transfer pipet for analysis following centrifugation (5000 rpm, 5 min). HAA samples (1 mL) were amended with Na2SO4 (0.5 g), acidified (0.1 mL conc. H2SO4), and extracted using methyl tert-butyl ether (2 mL). HAAs were converted to their corresponding methyl esters by addition of 10% H2SO4 in methanol (1 mL) at 50 °C (2 h). After conversion, samples were cleaned with 10% Na2SO4 in water (4 mL), and the organic phase was collected for analysis.

HAAs and THMs were analyzed by gas chromatography coupled to a mass spectrometer (GC/MS; HP 6890 GC/HP 5973 MS; Palo Alto, CA) in selected ion monitoring mode (SIM) using previously reported methods that were modified slightly. Details are provided in the Analytical Methods section of the Supporting Information text.

■ RESULTS AND DISCUSSION

Byproduct Formation during Wastewater Electrolysis. With TiO2/IrO2 anodes, electrolysis of latrine wastewater that was amended with chloride (100 mM total Cl−) to simulate salt accumulation during treated water recycling nearly completely removed COD (Table SI 3). Electrolysis also produced chloramines, resulting in conversion of ammonium to nitrogen gas (i.e., breakpoint chlorination; Figure 1). Similar to breakpoint chlorination via chlorine addition, about 5% of ammonium was converted to nitrate (2 mM).

Prior to the breakpoint, hypochlorous acid reacted rapidly with ammonia (4.4 × 106 M−1 s−1) to form chloramines, preventing the formation of chlorate on active anodes. Following ammonium removal (~3.5 h), chlorate production could be modeled as a series of reactions forming hypochlorous acid and subsequently chlorate (Figure SI 2):

\[
2\text{Cl}^- + H_2O \rightarrow \text{OCl}^- + \text{Cl}^- + 2H^+ + 2e^- \\
\text{OCl}^- + 2H_2O \rightarrow \text{ClO}_3^- + 4H^+ + 4e^- \\
k_1 = 0.35 \text{ M}^{-1} \text{ (Ah L}^{-1})^{-1}; k_2 = 0.030 \text{ (Ah L}^{-1})^{-1}
\]

Free chlorine concentrations reached a maximum of about 40 mM at 6 to 8 h, and the majority of chlorine was converted to chlorate by 12 h (75 mM). Oxidation of chloride to perchlorate was not detected on TiO2/IrO2 anodes (i.e., <0.01 mM). The sum of chloride, chlorate, and total chlorine was always within ~10% of the initial chlorine concentration (Figure 1).

As expected, given the low bromide concentration (Table 1), chloroform was the predominant measured THM, accounting for greater than 95% of the total THMs measured (Figure SI 3). Chloroform concentrations increased until the breakpoint, after which time concentrations decreased slowly (Figure 1). Chloroform loss was attributed to volatilization, as this loss was also observed in the absence of applied current (data not shown). Chloroform volatilization highlighted the need for proper venting and possibly filtering the exhaust of electrochemical treatment systems.

In contrast to THMs, the nonvolatile chlorinated HAAs accumulated throughout 12 h of electrolysis (Figure 1; formation rates: MCAA: 0.5 ± 0.1 μM (Ah L−1)−1; DCAA: 1.4 ± 0.1 μM (Ah L−1)−1; TCAA: 0.6 ± 0.1 μM (Ah L−1)−1). HAAs were dominated by DCAA, which is typical during chloramination of wastewater. After the breakpoint when free chlorine was present, TCAA formation rates increased slightly (~25%), while DCAA and MCAA formation rates remained constant or declined slightly. The increase in TCAA formation rates may be explained by free chlorine’s preferential production of TCAA. Sustained accumulation of DCAA and TCAA suggested that their organic precursors were not significantly depleted during 12 h of electrolysis.

Maximum chlorate, chloroform, and HAA concentrations were significantly higher (~10–50 times) than previously measured during electrolysis of reverse osmosis retentate and latrine wastewater (Table SI 2). The sum of chloride, chlorate, and total chlorine was always within ~10% of the initial chlorine concentration (Figure 1).

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Minimizing the formation of toxic byproducts therefore requires that electrolysis time be limited to the shortest time necessary to achieve treatment goals. Chloroform was an exception, as it was removed with further electrochemical treatment. However, chloroform concentrations were generally of less concern compared to drinking water regulations than...
other byproducts (see below), and chloroform concentrations would also be reduced post-treatment via volatilization in treated water storage tanks.

Complete ammonium removal is a reasonable treatment goal to protect the aquatic environment and prevent accumulation of ammonium within the system, which can hamper treatment efficiency by scavenging reactive chlorine species. Further, disinfection and color removal are completed prior to ammonium removal, although achieving complete COD removal may require pretreatment or longer treatment times (Table SI 3). Halting treatment near the breakpoint will also minimize residual free chlorine that may produce toxic byproducts post-treatment (i.e., during storage of treated water). Electrolysis byproduct formation was thus evaluated at the breakpoint under a variety of operating conditions to optimize treatment while minimizing byproduct formation.

**Current Density.** Ammonium removal rates increased approximately proportionally with increasing current densities with the breakpoint being reached at about 50 Ah L$^{-1}$ at current densities of both 5.0 and 7.5 A L$^{-1}$ (the breakpoint was not reached within 12.5 h at 2.5 A L$^{-1}$; Figure SI 4). Organic and inorganic byproduct formation typically also increased in proportion to current density (Figures 2 and SI 4). Chlorate formation, however, was reduced at lower current densities (i.e., ~65% lower concentrations after 60 Ah L$^{-1}$ at 5.0 A L$^{-1}$ than at 7.5 A L$^{-1}$), suggesting that chlorate formation is favored at higher current densities and potentials.

**Chloride Concentration.** As treated wastewater is recycled in onsite treatment systems, chloride concentrations may approach that of urine (i.e., 50 to >100 mM), depending on factors such as the extent to which additional water is added by system users (e.g., hand washing or bidet water), evaporation, and formation of halogenated byproducts. Higher chloride concentrations may enhance electrolysis efficiency due to increased reactive chlorine species concentrations but may also be expected to increase chlorinated byproduct formation.

Overall, while higher current densities may reduce treatment times, similar concentrations of disinfection byproduct concentrations will be formed at a given level of treatment (e.g., degree of ammonium removal). The same conclusion was previously reached for AOX production during treatment of domestic wastewater.

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Increased chloride concentrations in latrine wastewater resulted in higher steady-state total chloride concentrations (~0.5 mM with 30 mM Cl$^{-}$; ~0.8 mM with 65 mM Cl$^{-}$; ~1 mM with 100 mM Cl$^{-}$) during electrolysis and thus more rapid ammonium removal (i.e., the breakpoint was reached at 4.5 h with 30 mM Cl$^{-}$; 3.6 h with 65 mM Cl$^{-}$; 2.8 h with 100 mM Cl$^{-}$; Figure SI 5).

Despite differences in total chlorine concentrations, byproduct concentrations near the breakpoint were typically within a factor of 2 (Figures 3 and SI 5), as the breakpoint was reached sooner with higher chloride concentrations. Nitrate was an exception, as formation rates were similar at all chloride concentrations throughout the electrolysis. Although organic byproduct concentrations increased dramatically following the breakpoint, after 6 h of treatment, they reached similar concentrations at all chloride concentrations tested.
Therefore, with the exception of nitrate, higher chloride concentrations may enhance treatment efficiency, but they should not be expected to significantly affect byproduct concentrations near the breakpoint.

**Anode Material.** In contrast to “active” oxygen-generation anodes (e.g., TiO₂/IrO₂ mixed-metal oxide), “nonactive” anodes (e.g., BDD) produce relatively high concentrations of hydroxyl radical and low concentrations of hypochlorous acid.¹⁹ This may result in mineralization of a greater proportion of organic matter as opposed to accumulation as chlorinated byproducts.

Electrolysis of latrine wastewater with BDD anodes produced concentrations of toxic inorganic byproducts significantly higher than those produced by treatment with TiO₂/IrO₂ anodes. In contrast to TiO₂/IrO₂ anodes, chlorate was formed on BDD anodes throughout the electrolysis process, even in the presence of ammonium (Figure 4). Chlorate was therefore produced directly via oxidation of hypochlorous acid at the anode,⁴¹ whereas hypochlorous acid in the bulk solution reacted rapidly with ammonia to form chloramines that are not directly oxidized to form chlorate.⁴² This was in contrast to previous studies with Pt/Ti anodes in the absence of ammonium that found direct oxidation of chloride to be only a minor pathway for chlorate formation.⁴³ Chlorate was further oxidized to perchlorate, which accounted for greater than 95% of the initial chloride concentration (29 mM) after 6 h of electrolysis. Chloride, chloride, and perchlorate concentrations throughout electrolysis could be fit relatively well by a series of first-order reactions (Figure SI 6):

\[
\text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^-
\]

\[
\text{ClO}_3^- + \text{H}_2\text{O} \rightarrow \text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^-
\]

\[
k_1 = 0.17 \text{ (Ah L}^{-1})^{-1}; \ k_2 = 0.087 \text{ (Ah L}^{-1})^{-1}
\]

However, the model could not explain the lag in perchlorate formation before 2 h. This lag may have been a result of initially high chloride and organic matter concentrations, both of which can inhibit electrochemical oxidation of chlorate.⁴⁴ Nonetheless, the sum of chloride-containing species was within 10% of the initial chloride concentration throughout electrolysis (Figure 4).

Ammonium removal was limited to about 50% after 6 h of electrolysis, as chloride oxidation to chlorate and perchlorate competed with production of hypochlorous acid. Of the ammonium that was removed, more than 60% was converted to nitrate (∼20 mM).

As on TiO₂/IrO₂, chloroform was the predominant measured THM formed during electrolysis of latrine wastewater on BDD anodes (∼99% of THMs). Initial chloroform formation rates on a charge density basis were similar on BDD anodes and TiO₂/IrO₂ anodes (∼1 µM (Ah L⁻¹)⁻¹). However, peak chloroform concentrations were reached much more rapidly on BDD anodes (BDD at ∼6 Ah L⁻¹; TiO₂/IrO₂ at ∼30 Ah L⁻¹). This may have been due to rapid mineralization of organic precursors on BDD anodes (i.e., BDD: >90% TOC removal; TiO₂/IrO₂: ∼30% TOC removal; Table SI 3). As on TiO₂/IrO₂ anodes, chloroform was volatilized following its formation.

HAAs were initially formed at faster rates on a charge density basis on BDD anodes as compared to TiO₂/IrO₂ anodes (i.e., BDD: ∼1–4 µM (Ah L⁻¹)⁻¹; TiO₂/IrO₂: ∼0.5–1.5 µM (Ah L⁻¹)⁻¹). This resulted in concentrations up to 2 times higher at a similar level of treatment (∼10 Ah L⁻¹). As on TiO₂/IrO₂ anodes, DCAA dominated HAA production.

In contrast to treatment with TiO₂/IrO₂ anodes, on BDD anodes, chlorinated HAAs reached a peak concentration between 1 and 2 h, after which time they were attenuated. This implied that on BDD anodes, organic precursors were removed, and HAAs were further oxidized. HAA attenuation was pseudo first-order (R² = 0.94–0.99), and all HAAs were removed at similar rates (MCAA: 12.7 ± 0.4 × 10⁻² (Ah L⁻¹)⁻¹; DCAA: 8.2 ± 1.0 × 10⁻² (Ah L⁻¹)⁻¹; 8.4 ± 2.5 × 10⁻² (Ah L⁻¹)⁻¹; Table SI 4). This may have been due to continued HAA formation in latrine wastewater after attaining a peak concentration at 2 h. Perchlorate formation and loss of TOC accounted for greater than 95% of the initial HAA chlorine and carbon content, suggesting that perchlorate and carbon dioxide were the primary products of HAA electrolysis on BDD anodes.

Electrolysis of HAAs in Borate Buffered Solutions. Electrolysis of individual chlorinated HAAs in borate buffered solutions confirmed that these compounds could be attenuated on BDD anodes (Figure 5). As in latrine wastewater, removal was pseudo first-order (R² > 0.99), and removal rates were 2–4 times higher than those observed in latrine wastewater (MCAA: 26 ± 1 × 10⁻² (Ah L⁻¹)⁻¹; DCAA: 25 ± 1 × 10⁻² (Ah L⁻¹)⁻¹; 35 ± 1 × 10⁻² (Ah L⁻¹)⁻¹; Table SI 4). This may have been due to continued HAA formation in latrine wastewater after attaining a peak concentration at 2 h. Perchlorate formation and loss of TOC accounted for greater than 95% of the initial HAA chlorine and carbon content, suggesting that perchlorate and carbon dioxide were the primary products of HAA electrolysis on BDD anodes.

Electrolysis rates were 50–125 times faster than expected for reaction with hydroxyl radical (k₉,h₉HAA = (<6.0–9.2) × 10⁷ M⁻¹ s⁻¹)⁴⁵ based on steady-state hydroxyl radical concentrations calculated using pCBA as a probe ([OH]₉HAA ≈ 3 × 10⁻¹⁴
M; Figure SI 7). Therefore, HAA electrolysis most likely occurred via direct electron transfer at the BDD anode. Conversely, on TiO2/IrO2 anodes coupled to stainless steel cathodes in borate buffered solutions, TCAA and DCAA were reduced to MCAA but not further transformed (Figure 5). DCAA and TCAA could not be reformed from MCAA, as released chloride was oxidized to chlorate. MCAA has also previously been reported to be resistant to reduction on gold and copper cathodes.46

Chlorination of Wastewater. With the exception of MCAA, slow addition of hypochlorite solutions to latrine wastewater (∼16 mM h⁻¹) produced maximum halogenated organic byproduct concentrations within a factor of 2 of maximum concentrations measured during electrochemical treatment with TiO2/IrO2 anodes (Figure 5). When normalized to percent ammonium removed (i.e., progress toward breakpoint), byproduct time profiles were also similar (Figure 6).

The similarity in organic byproduct profiles suggested that HAAs and THMs were formed by similar pathways during electrolysis and chlorination, namely reaction with chloramines and, after the breakpoint when ammonia was no longer present to react with chlorine, free chlorine. As discussed above, the predominance of DCAA prior to the breakpoint agreed with previous studies showing that DCAA production is favored by chloramines.4,36,39,47 It is unclear why MCAA formation was slower during chlorine addition than electrolysis of latrine wastewater. One possibility is that MCAA production was enhanced during electrolysis via cathodic reduction of DCAA and TCAA (see above). Organic byproduct formation on BDD anodes was also initially similar to byproduct formation during chlorine addition, although byproducts were subsequently removed on BDD anodes.

Chlorate concentration profiles during chlorine addition of wastewater differed dramatically from those during electrolysis. During chlorine addition, chlorate accumulated linearly, as chlorate was present in hypochlorite solutions as a decomposition product (data not shown). Chlorate formation during electrolysis was due to anodic oxidation of chloride and hypochlorous acid following the breakpoint and was therefore delayed.

Minimizing Electrochemical Byproducts’ Health Impacts. As discussed above, complete ammonium removal (breakpoint chlorination) is a reasonable goal when electrochemically treating latrine wastewater. Disinfection occurs well before the breakpoint,⁷ while formation of toxic byproducts is generally minimized prior to the breakpoint. Stopping treatment at the breakpoint may be achieved during batch operation using an automated control system that monitors oxidation−reduction potential (ORP), which increases dramatically at the breakpoint (Figure SI 1) and is measurable with robust and inexpensive sensors.

To gain insight into the potential for byproducts of electrochemical latrine wastewater treatment to contaminate drinking water supplies, contaminant concentrations at the breakpoint after one treatment cycle were compared to drinking water guidelines (Table SI 1). Byproduct concentrations after treatment with TiO2/IrO2 were typically 2 to 200 times above WHO drinking water guidelines. Nitrate was an exception, as it was always below WHO guidelines (Figure 7). Chlorate, MCAA, and DCAA posed the greatest risks to human health, exceeding guidelines by more than 100 times. Trends were similar when comparing byproduct concentrations to US EPA drinking water limits and advisories (Figure SI 8), and TCAA (see above). Organic byproduct formation on BDD anodes was also initially similar to byproduct formation during chlorine addition, although byproducts were subsequently removed on BDD anodes.

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To gain insight into the potential for byproducts of electrochemical latrine wastewater treatment to contaminate drinking water supplies, contaminant concentrations at the breakpoint after one treatment cycle were compared to drinking water guidelines (Table SI 1). Byproduct concentrations after treatment with TiO2/IrO2 were typically 2 to 200 times above WHO drinking water guidelines. Nitrate was an exception, as it was always below WHO guidelines (Figure 7). Chlorate, MCAA, and DCAA posed the greatest risks to human health, exceeding guidelines by more than 100 times. Trends were similar when comparing byproduct concentrations to US EPA drinking water limits and advisories (Figure SI 8), and TCAA (see above). Organic byproduct formation on BDD anodes was also initially similar to byproduct formation during chlorine addition, although byproducts were subsequently removed on BDD anodes.

Chlorate concentration profiles during chlorine addition of wastewater differed dramatically from those during electrolysis. During chlorine addition, chlorate accumulated linearly, as chlorate was present in hypochlorite solutions as a decomposition product (data not shown). Chlorate formation during electrolysis was due to anodic oxidation of chloride and hypochlorous acid following the breakpoint and was therefore delayed.

Minimizing Electrochemical Byproducts’ Health Impacts. As discussed above, complete ammonium removal (breakpoint chlorination) is a reasonable goal when electrochemically treating latrine wastewater. Disinfection occurs well before the breakpoint,⁷ while formation of toxic byproducts is generally minimized prior to the breakpoint. Stopping treatment at the breakpoint may be achieved during batch operation using an automated control system that monitors oxidation−reduction potential (ORP), which increases dramatically at the breakpoint (Figure SI 1) and is measurable with robust and inexpensive sensors.
IrO₂ anodes (TiO₂/IrO₂ are therefore preferable for their ability to limit expensive anode material. Mixed-metal oxide anodes such as volume, further increasing the capital costs of using an already also necessitate an increase in treatment times and/or reactor ammonium removal was maximized (i.e., point where chloride oxidation was nearly complete and before complete ammonium removal was achieved. At the energy concentrations may therefore change treatment time and breakthrough. Changes in current densities and chloride concentrations produced slightly lower byproduct concentrations were significantly lower than those near the chlorination breakpoint ([byproduct]BP) exceeded WHO drinking water (DW) guidelines with different anodes, current densities, and chloride concentrations after one treatment cycle. For treatment with BDD anodes, concentrations at complete chloride removal were used, as complete ammonium removal was not achieved. Although byproduct to regulation ratios were higher (10−1000) because EPA limits and advisories are generally more stringent than WHO guidelines.

While treatment at low current densities or at high chloride concentrations produced slightly lower byproduct concentrations, differences were only within a factor of 2 to 3 at the breakpoint. Changes in current densities and chloride concentrations may therefore change treatment time and energy efficiency but do not substantially affect byproduct formation if treatment is stopped near the breakpoint.

BDD anodes oxidized chloride to chlorate and perchlorate before complete ammonium removal was achieved. At the point where chloride oxidation was nearly complete and ammonium removal was maximized (i.e., ∼4 h), organic byproduct concentrations were significantly lower than those during treatment with TiO₂/IrO₂ anodes and were only about 20 times above WHO guidelines (Figure 7). However, inorganic byproduct concentrations were much higher, with perchlorate concentrations more than 10,000 times above WHO guidelines.

Treatment with BDD anodes may instead be targeted toward complete COD removal, which is more rapid than on TiO₂/IrO₂ anodes (∼2 h; Table SI 3), or removal of regulated byproducts (∼6 h). Even so, at these end points, chloride and perchlorate concentrations exceeded WHO guidelines by more than 1000 times (Figure SI 9). Operating at lower current densities may reduce perchlorate formation, but this would also necessitate an increase in treatment times and/or reactor volume, further increasing the capital costs of using an already expensive anode material. Mixed-metal oxide anodes such as TiO₂/IrO₂ are therefore preferable for their ability to limit perchlorate and chloride formation, despite their inability to attenuate HAAs after formation. Bromate also may be produced on BDD anodes, although formation will be limited by the low bromide concentrations typical of latrine wastewater (i.e., ∼5 μM; maximum of ∼60 times WHO and EPA guidelines).

If electrochemically treated latrine wastewater is recycled as flushing water in an onsite system, discharged treated water will undergo multiple treatment cycles depending on flushing water volumes and other water inputs to the system (on average about 11 cycles; see Supporting Information text for calculation). With the exception of the volatile THMs, byproduct concentrations in discharged water will therefore be about 11 times higher than those after a single treatment cycle, depending on variations between treatment cycles (e.g., chloride concentrations). Water discharged from onsite latrine wastewater electrolysis systems will thus require additional treatment before it can safely be used for human consumption.

The control of byproduct formation during electrochemical treatment is complicated by the presence of both inorganic and organic byproducts, although with additional research, certain strategies may be efficacious. Judicious siting of electrochemical latrine wastewater treatment systems is a simple strategy which may ensure discharged water is sufficiently diluted in drinking water sources (more than 1000 times), thereby protecting downstream consumers’ health. A second strategy commonly used during drinking water treatment is to provide pretreatment of latrine wastewater to remove organic byproduct precursors. Finally, use of novel electrode materials and reactor designs may limit byproduct formation. For example, activated carbon cathodes have been shown to capture and reduce organic byproducts during treatment. Alternatively, latrine wastewater may be treated via reactive oxygen species such as activated hydrogen peroxide produced at the cathode, eliminating the formation of chlorinated byproducts. If appropriately designed and operated, the dramatic decrease in acute risk of disease provided by disinfecting latrine wastewater will likely outweigh the long-term health implications of chemical contamination of treated water.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b01002.

Additional materials and methods, discussion, tables, and figures (PDF)

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