

# Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water

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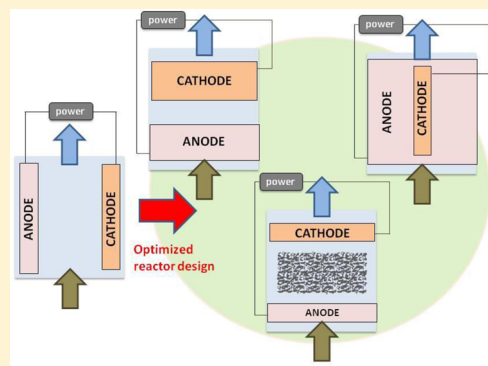
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## S Supporting Information

**ABSTRACT:** Electrochemical processes have been extensively investigated for the removal of a range of organic and inorganic contaminants. The great majority of these studies were conducted using nitrate-, perchlorate-, sulfate-, and chloride-based electrolyte solutions. In actual treatment applications, organic and inorganic constituents may have substantial effects on the performance of electrochemical treatment. In particular, the outcome of electrochemical oxidation will depend on the concentration of chloride and bromide. Formation of chlorate, perchlorate, chlorinated, and brominated organics may compromise the quality of the treated effluent. A critical review of recent research identifies future opportunities and research needed to overcome major challenges that currently limit the application of electrochemical water treatment systems for industrial and municipal water and wastewater treatment. Given the increasing interest in decentralized wastewater treatment, applications of electrolytic systems for treatment of domestic wastewater, greywater, and source-separated urine are also included. To support future adoption of electrochemical treatment, new approaches are needed to minimize the formation of toxic byproducts and the loss of efficiency caused by mass transfer limitations and undesired side reactions. Prior to realizing these improvements, recognition of the situations where these limitations pose potential health risks is a necessary step in the design and operation of electrochemical treatment systems.



## INTRODUCTION

Electrochemical processes have gained increasing interest in recent years for the treatment of polluted waters. They are considered to be versatile and capable of degrading a wide range of contaminants, including refractory carboxylic acids<sup>1,2</sup> and even perfluorocarboxylic acids.<sup>3,4</sup> Electrochemical systems offer several advantages over other approaches, such as operation at ambient temperature and pressure as well as robust performance and capability to adjust to variations in the influent composition and flow rate. They generally require no auxiliary chemicals and do not produce waste. Electrochemical processes can be adapted to various applications, and can be easily combined with other technologies.<sup>5</sup> The modular design and small footprint of electrochemical systems also make them attractive for decentralized wastewater treatment. However, application of electrochemical treatment has been slowed down by the relatively high costs of electrodes and concerns about the presence of toxic byproducts in the treated water.

Numerous bench-scale studies have demonstrated the ability of electrochemical processes to remove organic contaminants from an electrolyte solution (see refs 6–11 for recent reviews of electrochemical advanced oxidation processes). While these studies provide an understanding of the effects of operational variables on process performance, the importance of these effects, as well as reaction kinetics, mechanisms, and expected

byproducts are likely to differ when electrochemistry is used to treat real waste streams.<sup>12</sup> In particular, chlorine and bromine species formed at the anode can produce toxic organic chlorine- and bromine-containing transformation products.<sup>13,14</sup> Furthermore, the presence of chloride in wastewater may yield toxic chlorate and perchlorate.<sup>15,16</sup> Most studies that have been conducted in authentic wastewater have focused on the removal of chemical oxygen demand (COD), ammonia, color, and dissolved organic carbon (DOC).<sup>11,17</sup>

To gain insight into the use of electrochemical treatment under conditions likely to be encountered in industrial wastewater and water recycling systems, recent research on electrochemical treatment was reviewed. The main focus was placed on anodic oxidation because it is the most mature of the approaches employed for water treatment. Cathodic reduction, electrodialysis and related processes were also considered as alternatives for specific applications. Considering the importance of electrode materials to system performance and cost, a brief overview was made of the most commonly used anodes before assessing treatment applications.

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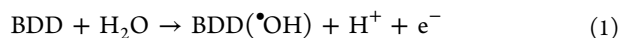
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## ELECTRODE MATERIALS AND ELECTROCHEMICAL OXIDATION MECHANISMS

The choice of electrode material will determine the efficiency of electrochemical treatment processes as well as the potential formation of toxic byproducts. Electrochemical oxidation can proceed via direct and indirect electrolysis. Direct electrolysis requires adsorption of pollutants onto the electrode, and can occur at relatively low potentials (i.e., prior to the O<sub>2</sub> evolution). The rates of direct electrolysis are affected by diffusion limitations, slow reaction kinetics and a decrease in the catalytic activity of the electrode in the presence of dissolved solutes (i.e., poisoning).<sup>18</sup> Indirect electrolysis relies on the production of oxidizing species at the electrode that mediate the transformation of contaminants. The nature of these electrochemically produced species is affected by the electrode material, such as the O<sub>2</sub> overpotential and adsorptive properties of the electrode surface.

Mixed metal oxide (MMO) electrodes, known under the trade name Dimensionally Stable Anodes (DSA), have been commercially available for almost 30 years. They consist of corrosion-resistant base material, such as titanium or tantalum, coated with a layer of metal oxides (e.g., RuO<sub>2</sub>, IrO<sub>2</sub>, PbO<sub>2</sub>, SnO<sub>2</sub>). Comninellis<sup>19</sup> classified anodes into active and nonactive, characterized by a strong and weak interaction of electrogenerated hydroxyl radicals (<sup>•</sup>OH) with the electrode surface, respectively. Active anodes (e.g., IrO<sub>2</sub>, RuO<sub>2</sub>) have a low overpotential for O<sub>2</sub> evolution, and consequently exhibit low capability for transformation of recalcitrant organic compounds. Nonactive anodes (e.g., PbO<sub>2</sub>, SnO<sub>2</sub>) exhibit lower electrochemical activity for O<sub>2</sub> evolution and therefore have a higher efficiency for oxidation of recalcitrant organic compounds. Because of the limited ability of MMO electrodes to oxidize and mineralize the organics, they have mostly been applied for the treatment of pollutants in the presence of chloride.

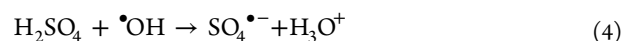
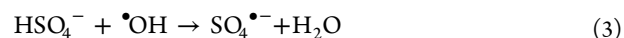
Boron-doped diamond (BDD) electrodes have been studied extensively in recent years. The distinct features of BDD electrodes, such as high O<sub>2</sub> overpotential, make them better suited for the direct oxidation of contaminants than metal oxide anodes. The high activity of BDD anode toward organics oxidation has been explained by the presence of weakly adsorbed <sup>•</sup>OH formed by water electrolysis at the anode surface<sup>19</sup>



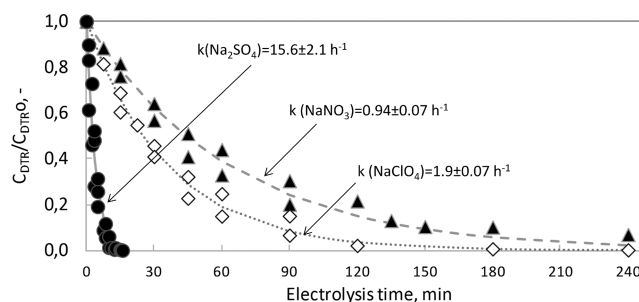
The nature of the BDD(<sup>•</sup>OH) is still a subject of scientific debate, as there is no clear spectroscopic evidence of free <sup>•</sup>OH radicals.<sup>20,21</sup> Some authors have hypothesized that, because of the high reactivity of BDD(<sup>•</sup>OH), oxidation reactions are confined to an adsorbed film adjacent to the electrode surface.<sup>20,22</sup> Kapalka et al.<sup>23,24</sup> suggested the participation of molecular oxygen in radical chain reactions, evidenced by the formation of C<sup>18</sup>O<sub>2</sub> and C<sup>16</sup>O<sup>18</sup>O when BDD anodes were used for electrooxidation of acetic acid in a solution saturated with labeled <sup>18</sup>O<sub>2</sub>. Electrogenerated <sup>•</sup>OH may trigger the formation of organic radicals (R<sup>•</sup>), which in the presence of O<sub>2</sub>, form organic peroxy radicals (ROO<sup>•</sup>).<sup>23</sup> Peroxy radicals can initiate subsequent chain reactions leading to a non-Faradaic enhancement of the rate of electrooxidation of organic compounds.

In addition to oxidizing organic contaminants, BDD anodes can generate ozone, H<sub>2</sub>O<sub>2</sub>, as well as ferrate.<sup>25,26</sup> BDD can also produce peroxydicarbonate (C<sub>2</sub>O<sub>6</sub><sup>2-</sup>), peroxydiphosphate

(P<sub>2</sub>O<sub>8</sub><sup>4-</sup>) and peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) in the presence of carbonate, phosphate, and sulfate ions, respectively.<sup>26–30</sup> The formation of peroxydisulfate is thought to proceed in two stages: i) formation of sulfate radical (SO<sub>4</sub><sup>•-</sup>) by direct, one-electron oxidation of sulfate ion at the anode, or by the reaction of H<sub>2</sub>SO<sub>4</sub> or HSO<sub>4</sub><sup>-</sup> with the electrogenerated <sup>•</sup>OH and (ii) recombination of two SO<sub>4</sub><sup>•-</sup> radicals to yield peroxydisulfate.<sup>29,30</sup>



The rate of persulfate generation at BDD anode is affected by the condition of the electrode surface: up to 50 times lower rates of persulfate formation were observed on an aged BDD compared to a new electrode.<sup>31</sup> Although SO<sub>4</sub><sup>•-</sup> and other inorganic radicals are considered to be the intermediates responsible for the formation of peroxy-species, some studies have suggested their participation in the oxidation of organics.<sup>32–34</sup> For example, significantly faster oxidation rates of the X-ray contrast agent diatrizoate and several other organic compounds were observed when a BDD anode was used in a sulfate electrolyte, relative to perchlorate or nitrate electrolyte (Figure 1).<sup>35</sup> The presence of SO<sub>4</sub><sup>•-</sup> and other inorganic radicals on conductive diamond anodes has not been confirmed through spectroscopic methods.



**Figure 1.** Disappearance of diatrizoate (DTR, 2 μM) during electrooxidation at boron-doped diamond (BDD) anode in NaNO<sub>3</sub> (60 mM), NaClO<sub>4</sub> (74 mM), and Na<sub>2</sub>SO<sub>4</sub> (40 mM) analytes of same initial conductivity (9 mS cm<sup>-1</sup>) and pH (pH 2.0), and first-order decay rates calculated by nonlinear regression using Aqsim. Adapted from 35. Copyright 2015 American Chemical Society.

The main impediment to large-scale application of BDD electrodes is the high cost of the substrate onto which the BDD film is deposited (Nb, W, Ta), and its poor mechanical strength in the case of Si substrate. In addition, chemical vapor deposition (CVD) manufacturing of synthetic diamond is still limited to small-scale production. The price of conductive diamond electrodes is currently about ten times higher than that of MMO electrodes, in the range 12 000–18 000 € m<sup>-2</sup>.<sup>36</sup> As a result of advances in manufacturing, the price is expected to drop by approximately half in the next decade, but it will remain expensive for the foreseeable future. While titanium possesses all the necessary features of a good substrate material (i.e., good electrical conductivity, mechanical strength and

**Table 1. Reported Formation of Inorganic and Organic Halogenated Byproducts and Effluent Toxicity in Electrochemical Oxidation of Contaminated Water of Different Origin<sup>a</sup>**

wastewater	ClO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	ClO <sub>4</sub> <sup>-</sup> (mg L <sup>-1</sup> )	tTHMs (mg L <sup>-1</sup> )	tHAAs (mg L <sup>-1</sup> )	AOX (mg L <sup>-1</sup> )	bTEQ (mg L <sup>-1</sup> )
ROC, landfill	5–30 (MMO) <sup>48,67</sup>		0.080–0.3 (MMO) <sup>48</sup>	0.23–0.7 (MMO) <sup>48</sup>	0.9–33 (BDD) <sup>45,46</sup>	150–210 (MMO) <sup>13,68</sup>
leachate	70–350 (BDD) <sup>49,66,67</sup>		0.05–2 (BDD) <sup>45,49,50</sup>	1.8–3.1 (BDD) <sup>45</sup>		2–4 (BDD) <sup>46</sup>
municipal/domestic wastewater	33–117 (BDD) <sup>47</sup>	8–99 (BDD) <sup>47</sup>			0.2–1.2 (BDD) <sup>47,73</sup>	
greywater					0.7–1.7 (MMO) <sup>118</sup>	

<sup>a</sup>ROC, reverse osmosis concentrate; MMO, mixed metal oxide anode; BDD, boron-doped diamond anode; tTHM, total trihalomethanes; tHAA, total haloacetic acids; AOX, adsorbable organic halogen; bTEQ-baseline-toxic equivalent concentration, derived from a baseline toxicity quantitative structure–activity relationship (QSAR) model using a virtual compound with octanol–water partition coefficient (log  $K_{OW}$ ) of 3 and molecular weight (MW) of 300 g mol<sup>-1</sup> as a reference, which equates to an EC<sub>50</sub> of 12 mg L<sup>-1</sup>.<sup>79</sup>

electrochemical inertness), the deposition of stable BDD films on Ti has not been achieved.<sup>37</sup>

Ebonex, a low-cost ceramic material comprised of Magneli phase titanium oxides (i.e., Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>5</sub>O<sub>9</sub>) has been investigated as an anode for organics oxidation due to its high overpotential for O<sub>2</sub> evolution.<sup>38,39</sup> Ebonex exhibits conductivity comparable to that of graphite and can be produced in a number of forms. When polarized anodically, it behaves as a nonactive anode that is capable of oxidizing organic compounds.<sup>21,40</sup> Yet, it is still uncertain how the electrocatalytic activity of Ebonex compares to other anodes with high O<sub>2</sub> overpotential (e.g., BDD, SnO<sub>2</sub>, PbO<sub>2</sub>). Considering that Ebonex is produced from inexpensive starting materials (titania and hydrogen), has excellent corrosion resistance, and has good electrical conductivity, this material may be well suited for treatment of highly acidic and basic solutions, where the lifetime of conventional electrode materials is significantly shortened.<sup>39</sup> Further research is needed to assess the possibilities of using this material as an anode for wastewater treatment.

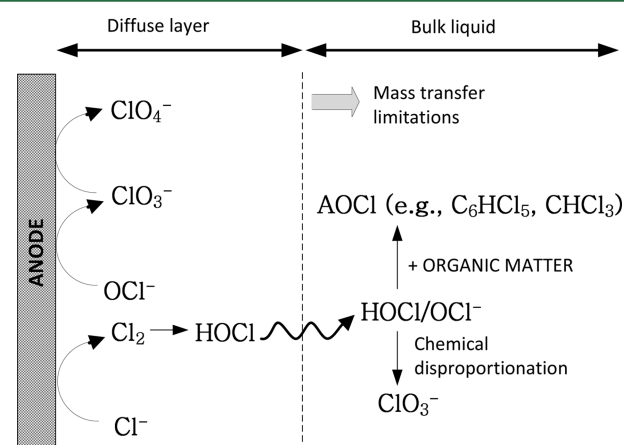
A recent study<sup>41</sup> reported the synthesis of a new electrode material, a dark blue TiO<sub>2</sub> nanotube array (NTA). The electrocatalytic activity of the blue TiO<sub>2</sub> NTA electrode for chlorine and •OH production was observed to be comparable to the commercial DSA and BDD anodes, respectively. Given the simple fabrication of the electrode by cathodic polarization of an anatase TiO<sub>2</sub> NTA, this material has the potential to become a cost-effective anode material for industrial and environmental applications. Nevertheless, further research is required to determine the capability of the blue TiO<sub>2</sub> NTA anode to oxidize the organic contaminants. Also, the long-term performance of the blue TiO<sub>2</sub> NTA has not been assessed under conditions relevant to water treatment.

## ■ FORMATION OF HALOGENATED BYPRODUCTS AND OTHER TOXIC BYPRODUCTS

As mentioned previously, the formation of halogenated byproducts during electrooxidation is a serious concern due to the toxicity of many of the compounds.<sup>42,43</sup> To assess the potential risks of forming toxic halogenated byproducts during electrooxidation, available data from studies conducted in authentic wastewater and chloride-containing solutions (Table 1, Table S1) were reviewed and categorized related to conditions typically observed in different matrices.

Electrochemical oxidation of chloride-containing water produces chlorine (Cl<sub>2</sub>) and hypochlorous acid/hypochlorite

(HOCl/OCl<sup>-</sup>) and other reactive halogens (Figure 2). Hypochlorous acid reacts with unsaturated bonds and



**Figure 2.** Participation of chloride ions in electrochemical oxidation. Formation of chlorine radicals has not been included as the mechanisms are yet unknown.

electron-rich moieties (e.g., reduced sulfur moieties, aliphatic amines, phenols, and other aromatics)<sup>44</sup> to form halogenated products that are often more persistent and toxic than the parent compound. Up to 33 mg L<sup>-1</sup> and 1.2 mg L<sup>-1</sup> of organohalogen byproducts measured as adsorbable organic halogen (AOX) were formed during electrooxidation of brine<sup>45,46</sup> and municipal wastewater effluent,<sup>47</sup> respectively, with a BDD electrode. Trihalomethanes (THMs) and haloacetic acids (HAAs) were formed at concentration ranging from 0.05 to 2 mg L<sup>-1</sup><sup>45,48–50</sup> and 0.2 to 3 mg L<sup>-1</sup>,<sup>45,48</sup> respectively, in electrooxidation of brine and landfill leachate. These values exceed the World Health Organization (WHO) drinking water guidelines for THMs (i.e., 0.06–0.3 mg L<sup>-1</sup>).<sup>51</sup> In the presence of ammonium, especially in the case of high-strength wastewater (e.g., landfill leachate, effluents from food, pharmaceutical, and fertilizer industries), oxidation of organic matter is affected by the rapid conversion of free chlorine into less reactive chloramines.

In most studies employing MMO anodes, free available chlorine is considered to be the main oxidant in the presence of chlorides.<sup>48,52</sup> Recent studies<sup>53–55</sup> suggest the formation of more potent chlorine radicals (i.e., Cl<sub>2</sub><sup>•-</sup>, Cl<sup>•</sup>) when bismuth-doped TiO<sub>2</sub> anodes (BiO<sub>x</sub>/TiO<sub>2</sub>) are used to treat wastewater. In solution, chloride radical (Cl<sup>•</sup>) has similar properties to

•OH; it can undergo rapid addition, hydrogen abstraction and direct electron transfer reactions with aromatics at second-order rate constants ranging from  $10^8$  to  $10^9$   $M^{-1} s^{-1}$ .<sup>56</sup> Chloride radical is converted to dichloride radical anion ( $Cl_2^{\bullet-}$ ) in the presence of higher background chloride concentration.  $Cl_2^{\bullet-}$  reacts with organic compounds similar to  $Cl^{\bullet}$  but typically at rates that are two to 4 orders of magnitude slower.<sup>53,56</sup> Park et al.<sup>53</sup> reported a correlation between the oxidation rates of organic compounds on  $BiO_x/TiO_2$  anode and their relative bimolecular rate constants of reaction with  $Cl_2^{\bullet-}$  in 50 mM NaCl solution. Further research is needed to verify the presence of reactive chlorine radicals during electrooxidation reactions under conditions of interest for wastewater treatment.

Similar to chloride, bromide can be oxidized at the anode to bromine ( $Br_2$ ) and hypobromous acid (HOBr), which react rapidly with the bulk organics.<sup>13,45</sup> In the presence of chloride, bromide can also be oxidized by HOCl/OCl<sup>-</sup> to hypobromous acid in the bulk liquid.<sup>44</sup> HOBr may be more reactive than hypochlorous acid with some organic compounds, for example with phenolic compounds.<sup>57</sup> Bromide is also an important scavenger of •OH ( $k = 1.1 \times 10^{10} M^{-1} s^{-1}$ ).<sup>58,59</sup>

The formation of chlorate, perchlorate and bromate are also of great concern as these chemicals are suspected carcinogens and mutagens.<sup>15,60,61</sup> In electrooxidation systems, chlorate can be formed both chemically and electrochemically, and it was observed at both conductive diamond and metal oxide-coated electrodes.<sup>62</sup> Perchlorate generation is strictly electrochemical (i.e., limited to the oxidation of chlorate at the anode surface) and seems to occur only at highly oxidizing BDD anodes.<sup>15,16,62,63</sup> Up to 120 and 100 mg L<sup>-1</sup> of chlorate and perchlorate were formed, respectively, in electrooxidation of sewage effluent at a BDD anode.<sup>47</sup> Higher formation of chlorate and perchlorate was observed at BDD compared with MMO anodes.<sup>64</sup> Similar to chlorate, bromate can be formed at both MMO<sup>65</sup> and BDD anodes,<sup>66</sup> although its expected concentrations will be in the low microgram per liter range because of the low bromide concentrations in most wastewaters.

In most studies where formation of chlorine, chlorate or perchlorate was identified as an issue, the applied current densities were in the range from 50 to 300 A m<sup>-2</sup>.<sup>13,45–48,67–69</sup> For more contaminated wastewater, such as landfill and olive pomace leachate, higher current densities have been applied (i.e., 1.2–2.6 kA m<sup>-2</sup>).<sup>70</sup> The formation of perchlorate at BDD anodes can be controlled by working at lower current densities, which can range from 100 to 300 A m<sup>-2</sup>, depending on the type of wastewater.<sup>47,71</sup> Further lowering of the current density ( $\leq 50$  A m<sup>-2</sup>) may minimize the detrimental effect of chlorides, but it also limits the oxidation performance of the treatment because of pronounced charge transfer limitations and decreased formation of •OH radicals.<sup>72</sup> The formation of chlorine is difficult to avoid, as oxygen evolution reaction is associated with a higher overpotential than chlorine evolution reaction.<sup>73</sup> Moreover, AOX formation in electrooxidation at BDD anodes increases linearly with charge density.<sup>45,74</sup> Thus, the amount of chlorinated organic byproducts may be minimized by applying short electrolysis time while targeting a suitable degree of removal of contaminants. Also, decreasing the interelectrode distance may reduce the mass transfer limitations of the contaminants toward the electrode surface and enhance their electrochemical transformation.<sup>75,76</sup> Nevertheless, high electrode surface/reactor volume ratio also implies an increase in the capital costs of the treatment.

The reaction kinetics of chloride and bromide will be affected by the presence of organic matter, ammonia and other inorganic anions. Thus, formation of inorganic and organic halogenated byproducts should be evaluated on a case-by-case basis, and used to assess the suitability of electrochemical treatment for environmental applications. If formed oxidation byproducts are of concern, they could be removed by sorption to activated carbon, similar to full-scale ozonation systems. Compared to activated carbon alone, electrochemical process provides disinfection of the treated effluent, and oxidative degradation of the organic matter. However, although halogenate and perhalogenate species adsorb on the activated carbon, the treatment efficiency is highly dependent on the composition of source water and modification of carbon surface may be required to achieve satisfactory performance.<sup>61,77</sup> A range of other treatment techniques has been explored to date for the removal of chlorate, perchlorate, and bromate, such as ion-exchange, membrane filtration, and microbial, chemical, and electrochemical reduction.<sup>61,77</sup> Yet, further development of these techniques is required prior to their full-scale use.

## ■ FIGURES-OF-MERIT FOR ELECTROCHEMICAL TREATMENT PROCESSES

The technical feasibility of electrochemical oxidation of wastewater is often based on the removal of COD, ammonia and/or specific target organic contaminants. The removed COD can be converted to the portion of electrical current that results in decreases in solute concentrations by use of current efficiency (i.e., coulombic efficiency, Faradaic yield). Current efficiency is defined as the ratio of the electricity consumed by the electrode reaction of interest divided by the total electricity passed through the circuit. In anodic oxidation, current efficiency for COD removal can be expressed using general current efficiency ( $GCE_{COD}$ ).<sup>8,78</sup>

$$GCE_{COD} = n_{O_2} FV \frac{COD_0 - COD_t}{M_{O_2} I t} \quad (6)$$

where  $n_{O_2}$  is the number of electrons required for water oxidation ( $n = 4$ ,  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ),  $F$  is the Faraday constant ( $96487$  C mol<sup>-1</sup>),  $V$  the electrolyte volume (L),  $COD_0$  and  $COD_t$  are COD values measured at time  $t = 0$  and time  $t$  (in g O<sub>2</sub> L<sup>-1</sup>),  $M_{O_2}$  is the molecular weight of oxygen ( $32$  g mol<sup>-1</sup>),  $I$  is the applied current (A), and  $t$  is the time over which treatment occurs (s). An analogous approach can be used for ammonia or organic contaminants, with values of  $n$  adjusted accordingly.

In situations where target contaminants are present at low concentrations, a more appropriate parameter for estimating the energy efficiency of electrochemical treatment may be electric energy per order ( $E_{EO}$ ).  $E_{EO}$  expresses the electric energy (in kWh m<sup>-3</sup>) required to reduce the concentration of a contaminant by 1 order of magnitude in a unit volume of contaminated water.<sup>79</sup>  $E_{EO}$  can be calculated as

$$E_{EO} = \frac{Pt}{V \log\left(\frac{C_0}{C}\right)} \text{ for batch processes} \quad (7)$$

$$E_{EO} = \frac{P}{q \log\left(\frac{C_0}{C}\right)} \text{ for flow-through processes} \quad (8)$$

where  $P$  is the rated power of the system (kW),  $V$  is volume of water (L) treated in time  $t$  (h),  $q$  is the water flow rate ( $\text{m}^3 \text{h}^{-1}$ ),  $C_0$  and  $C$  are initial and final (or influent and effluent) contaminant concentrations. Equations 8 and 9 are valid only for perfectly mixed batch and plug-flow flow-through processes. For an electrochemical treatment process,  $E_{\text{EO}}$  will depend on the treatment efficiency of the process and the concentrations of other solutes (e.g., COD) that undergo reactions.

The energy efficiency of electrochemical treatment is often determined using the specific energy consumption ( $E_{\text{SP}}$ ), expressed per kg of COD removed<sup>80</sup>

$$E_{\text{SP}} = \frac{1}{3600} \frac{FV_{\text{CELL}}}{8ACE_{\text{COD}}} \quad (9)$$

where  $V_{\text{CELL}}$  is the total cell potential (V), 8 is the equivalent mass of oxygen (32 g  $\text{O}_2$  per 4 mol  $\text{e}^-$ ), and  $ACE_{\text{COD}}$  is the average current efficiency of COD removal.

Given the reactor-specific nature of the figures-of-merit used in electrochemical systems and the effect of water composition on treatment efficiency, it is difficult to compare the operational costs among existing publications. Most studies employ a batch mode of operation, using an external reservoir. Under these conditions, the ratio of the reactor volume (active volume,  $V_{\text{ACT}}$ ) and total volume of the electrolyte ( $V_{\text{TOT}}$ ), as well as electrode surface/reactor volume ratio ( $A_{\text{EL}}/V_{\text{ACT}}$  or  $A_{\text{EL}}/V_{\text{TOT}}$ ) will play a critical role in treatment efficiency. Furthermore, electrolysis experiments are typically performed in the galvanostatic mode. In many cases, current density is reported, but anodic potentials are measured very rarely, and in some cases information about the reference electrode is omitted. This information is crucial for gaining insight into the possible generation of oxidant species at the anode surface, particularly when comparing electrodes of different resulting potentials for a given applied current (e.g., active vs nonactive anodes). Therefore, we recommend that it should always be reported. Thus, it is crucial to provide complete information on the reactor design (e.g., interelectrode distance,  $A_{\text{EL}}/V_{\text{ACT}}$  ratio,  $V_{\text{ACT}}/V_{\text{TOT}}$  ratio for the batch mode), operational parameters (e.g., electrode potential and current, electrolyte flow rate), electrolyte characteristics (conductivity, presence of chloride and bromide) and full composition of the test to enable comparisons with the reported data.

## ■ APPLICATION OF ELECTROCHEMICAL WATER TREATMENT PROCESSES

There are very few examples in which electrochemical treatment has been applied successfully in full-scale treatment applications. Use of electrooxidation for disinfection of swimming pool water is widely applied.<sup>7</sup> Electrochemical treatment is also one of the ballast water treatment technologies approved by International Maritime Organization.<sup>81</sup> BDD anodes have also been employed in some situations for the on-site disinfection of rainwater, sewage and industrial process water.<sup>82</sup> Anodic oxidation has been applied for the treatment of effluents from tanneries, petrochemical plants, dairies, and pulp and papermills.<sup>83–86</sup> These industrial wastewaters, which often contain high concentrations of refractory organics, also contain elevated concentrations of chloride. As a result, indirect electrochemical oxidation with active halogen species is typically responsible for much of the removal of COD and ammonia.<sup>83,87</sup> As previously discussed, this mode of anodic treatment is also likely to yield chlorinated byproducts that

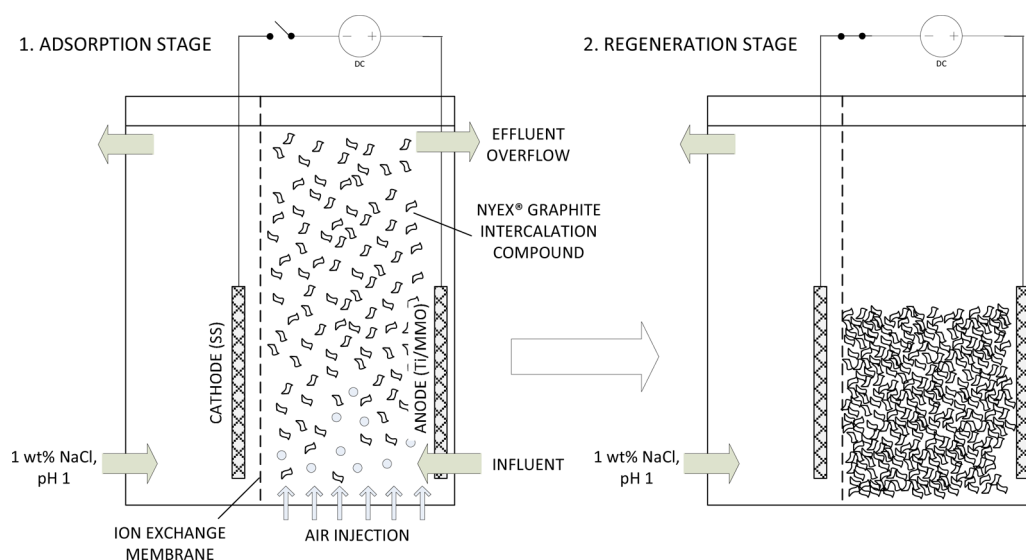
increase the toxicity of the water.<sup>88</sup> Activated carbon was used in some studies to lower the concentration of halogenated byproducts in the effluent.<sup>89,90</sup>

Some of the major impediments to the commercialization of electrochemical processes include low current efficiencies and limited space-time yields (i.e., quantities of removed contaminant per unit volume and unit time), which consequently lead to high energy consumption. To obtain adequate removal kinetics under conditions encountered in wastewater, high current densities are often applied, leading to a drastic increase in energy consumption. For example, the energy consumption of pilot-scale system that used BDD electrode to oxidize organic matter in landfill leachate ranged from approximately 22 kWh  $\text{kg}_{\text{COD}}^{-1}$  at high current efficiency (charge transfer controlled regime) to 95 kWh  $\text{kg}_{\text{COD}}^{-1}$  at high current densities where mass transfer controlled regime occurred.<sup>91</sup> To lower the overall energy consumption current modulation can be used, based on the stepwise lowering of current to values close to the limiting current for organics oxidation.<sup>92</sup>

Mass transfer limitations in electrochemical systems are exacerbated by the use of plate-and-frame filter press reactors. When plate electrode reactors are operated in a flow-by mode, the current flow direction is perpendicular to the electrolyte flow direction, and the reactions rates are subject to strong mass transfer limitations due to the presence of a thin stagnant boundary layer at the electrode surface. Flow-through electrochemical reactors partially overcome this limitation through enhanced convective transport of the contaminants to the electrode surface due to cross-flow filtration.<sup>93,94</sup> However, many industrial electrochemical processes use a channel flow between two plane, parallel electrodes,<sup>95</sup> and this is also a common configuration for environmental applications.

To enhance the process performance and increase the current efficiency, porous three-dimensional electrodes can be employed in the flow-through mode.<sup>90,91</sup> For example, efficient phenol removal by electrochemical adsorption and oxidation was achieved in a cross-flow electrochemical filtration unit equipped with porous Ebonex anode.<sup>96</sup> Electrochemical carbon nanotube (CNT) filters were applied for the removal of dyes by their direct oxidation at CNTs.<sup>94,97</sup> Also, CNT membrane stack was used for flow-through electro-Fenton degradation of persistent contaminants.<sup>98</sup> The sequential in situ generation of  $\text{H}_2\text{O}_2$  at the first CNT network cathode,  $\text{H}_2\text{O}_2$  reduction to  $\bullet\text{OH}$  at the subsequent Fe-coated CNT network cathode, and oxidation at the CNT network anode yielded 4-fold greater reaction rate for oxalate oxidation compared to the sum of individual anodic oxidation at CNT and Fenton oxidation processes. Nevertheless, when porous electrodes are employed in actual waste treatment, bed blocking, increases in back pressure due to bubble generation and corrosion of carbonaceous material may lead to diminished performance.

As an alternative, three-dimensional particle and granular electrodes can be employed for combined adsorption-electrochemical oxidation. By loading a conventional two-dimensional plate and frame reactor with granular or particulate electrode material, such as granular activated carbon (GAC) or graphite, granules act as bipolar electrodes and promote oxidative degradation of the adsorbed contaminants. The mass transfer of contaminants is greatly increased due to a large specific surface area, thus reducing the energy consumption. For example, use of GAC and quartz sand filling between a MMO anode and a stainless steel cathode lowered the energy consumption for industrial wastewater treatment from 300 kWh  $\text{kg}_{\text{COD}}^{-1}$  to 180



**Figure 3.** Schematic diagram of combined adsorption-electrochemical regeneration system for the removal of low concentrations of pollutants. Adapted from refs 101 and 103. Copyrights 2013 and 1998, respectively, Elsevier.

$\text{kWh kg}_{\text{COD}}^{-1}$ .<sup>99</sup> Electrocatalysis at activated carbon granules enhances the oxidation performance of the treatment and increases the adsorption capacity and effective lifetime of carbon because of continuous oxidation of the contaminants adsorbed on the GAC filling.<sup>100</sup> In addition to direct electrooxidation on the polarized GAC, adsorbed organic pollutants can be oxidized by the in situ generated oxidants (e.g.,  $\text{H}_2\text{O}_2$ ,  $\cdot\text{OH}$ ,  $\text{Cl}_2/\text{HOCl}$ ).<sup>101</sup> Hydrogen peroxide formed by oxygen reduction at the cathode side of GAC particles can be decomposed to  $\cdot\text{OH}$  at the activated carbon and thus promote indirect oxidation of contaminants.<sup>100,102,103</sup> Three-dimensional electrochemical reactors with carbon-based fillings merit further research, as they could be well suited for the treatment of wastewater with a high potential of formation of halogenated organics byproducts.<sup>104</sup>

Complete regeneration of GAC is difficult to achieve due to the slow desorption of the contaminants from a large internal surface area of the adsorbent.<sup>105</sup> To minimize the intraparticle diffusion and increase the efficiency of electrochemical regeneration of the adsorbent, researchers at the University of Manchester, UK, used a nonporous, highly conducting graphite adsorbent Nyex. The process was based on the adsorption of contaminants, and desorption and oxidation by applying current (Figure 3).<sup>104,106,107</sup> With this approach, a pilot-scale system was capable of removing low  $\mu\text{g L}^{-1}$  levels of pesticides from groundwater, with an estimated energy consumption of  $55 \text{ kWh kg}_{\text{COD}}^{-1}$ .<sup>106</sup> The authors emphasized that the process may not be economic for effluents with high organic load due to the high recycle rate of the adsorbent.

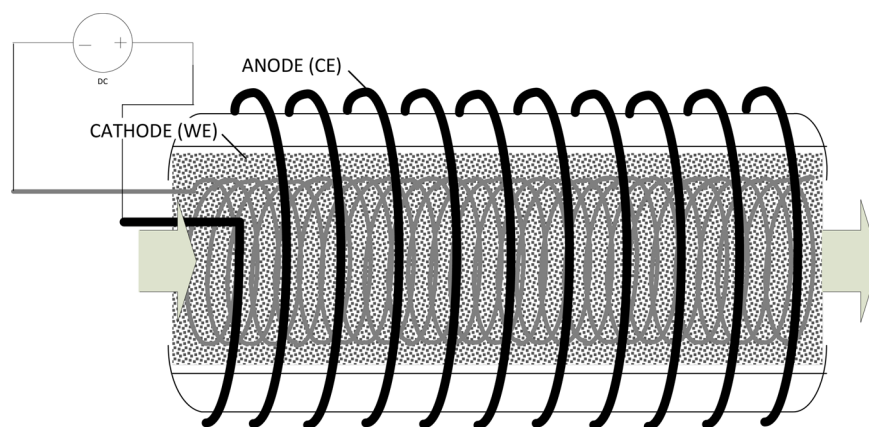
More widespread application of electrochemical systems require advances in operational issues such as electrode fouling. Several researchers have reported the formation of deposits of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the treatment of real waste streams in electrolytic cells.<sup>46,108,109</sup> The most simple and effective method to prevent the cathode scaling in practical applications of electrochemical reactors is polarity reversal. For example, in an on-site electrochemical treatment of wastewater at MMO anodes, cathode scaling was overcome by applying polarity reversal, with an estimated lifetime of 6 years for Ta/Ir and Pt/Ir electrodes. Also, periodical dosing of acid generated at the anode when the reactor is not treating wastewater (e.g., during

the night) to the cathode compartment could be used as an alternative to frequent polarity switching. In addition, when high electric charge density is applied, an imbalance between protons and hydroxyl ions formed by water electrolysis can lead to a change in pH, particularly in the case of membrane-divided electrolytic cells. Thus, prior to discharge of electrochemically treated water the properties of the influent (i.e., pH, redox potential) need to be restored.

## ■ DECENTRALIZED TREATMENT

Electrochemical processes may be particularly well suited for decentralized water treatment because the mechanisms through which electrochemical processes are controlled, electrode potential and cell current, are easier to control remotely than conventional chemical and biological processes.<sup>110</sup> Furthermore, electrochemical treatment systems are compact and are easier to adjust to variations in influent water composition than most existing technologies. Conventional chemical treatment, such as chlorination and ozonation, have intrinsic limitations to small-scale operation related to the possible buildup of toxic levels of ozone or chlorine in small enclosures typical of decentralized treatment systems. Given the growing interest in decentralized wastewater treatment and source separation, interest has been growing in the use of electrochemical systems for the treatment of potable water, greywater, source-separated urine, settled sewage, hospital wastewater, and point-of-use drinking water systems.<sup>110</sup>

The formation of toxic disinfection byproducts (DBPs) is a major challenge in drinking water treatment. The existing strategies aiming at minimization of DBPs are only partially efficient and expensive.<sup>111</sup> Electrochemical treatment may be applied for the removal of residual chlorine and disinfection byproducts (DBPs) as a point-of-use treatment of water intended for direct consumption. Reductive dehalogenation of THMs and HAAs was achieved at carbon-based and metal electrodes polarized at around  $-1 \text{ V}$  vs standard hydrogen electrode (SHE).<sup>112–115</sup> Moreover, electrochemical reduction may also be applied for the removal of bromate.<sup>116,117</sup> Yet, the reaction rates are significantly limited by the low concentration of DBPs and low conductivity of tap water.<sup>113</sup> The process



**Figure 4.** Three-dimensional reactor for the treatment of low-conductivity drinking water; working electrode (WE): metal-impregnated activated carbon or carbon fiber cathode with spiral metal wire to ensure the even distribution of the applied potential, counter electrode (CE): Pt wire anode. Adapted from ref 110. Copyright 2013 IWA Publishing.

performance can be improved by using three-dimensional reactors. For example, Sonoyama et al.<sup>112,113</sup> used column-type carbon fiber and activated carbon electrodes for reductive electrochemical removal of THMs from low conductivity tap water (Figure 4). Greater contact between the fluid and the electrode alleviates the detrimental effects of low conductivity and low contaminant concentration on the process performance.<sup>118–120</sup>

Electrochemical systems may be an attractive option for the decentralized treatment of greywater. Prior to land application or indirect reuse, it may be necessary to treat greywater to remove chemical contaminants. Electrochemical oxidation of greywater at Pt, Pt/Ir, and Ru/Ir anodes removed personal care and household products (e.g., bisphenol A, triclosan, parabens), without the formation of high concentrations of halogenated organic byproducts (AOX < 2 mg L<sup>-1</sup>).<sup>121</sup> Free chlorine was measured at a relatively high bulk concentration (35 mg L<sup>-1</sup>) compared to the typical chlorine doses for municipal wastewater disinfection (i.e., 5–20 mg L<sup>-1</sup> with a 30–60 min contact time).<sup>122</sup> The energy consumed by the electrochemical system was approximately 0.66 kWh m<sup>-3</sup>.

Source-separated urine has attracted considerable interest, both as a source of fertilizer and as a means of reducing nutrient loading to municipal wastewater. Unfortunately, the unpleasant odor and corrosion due to the release of ammonia from urea are impediments to application of the technology. Electro-oxidation at a Pt/Ir anode resulted in a reduction in odor due to reactions of urease with reactive halogen species that prevented the hydrolysis of urea to ammonia.<sup>123</sup> Alternatively, electrochemical processes have been used to recover nutrients from urine. For example, the recovery of NH<sub>4</sub>-N, phosphate, potassium, sodium, sulfate and chloride from urine could be achieved by electrodialysis. The process also removed organic contaminants such as ethinylestradiol, diclofenac and carbamazepine.<sup>124</sup>

Using a similar strategy, ammonia also have been recovered from anaerobic digestate with cation exchange membrane-divided electrolytic cell.<sup>125,126</sup> Under the high pH conditions in the cathode compartment efficient stripping and absorption of dissolved ammonia was achieved. In addition, oxidation of sulfide at the anode resulted in a significantly lower H<sub>2</sub>S concentrations in the biogas.<sup>126</sup>

Electrochemical oxidation also has been used for municipal wastewater treatment.<sup>54,74,127</sup> Electrogeneration of chlorine at

BDD anodes enabled efficient disinfection of domestic wastewater, while the amount of chlorinated byproducts could be minimized by applying low charge densities.<sup>74</sup> For example, 0.25 Ah L<sup>-1</sup> of applied charge density yielded a 4-log reduction of total coliforms and approximately 0.4 mg L<sup>-1</sup> of AOX, which met the German discharge standard for AOX in municipal wastewater (i.e., 1 mg L<sup>-1</sup>).<sup>128</sup>

To lower operational costs electrochemical reactors can be coupled to photovoltaic cells.<sup>129,130</sup> For example, an electrolysis cell equipped with a bismuth-doped TiO<sub>2</sub> anode and a stainless steel cathode, and powered by photovoltaic cells was used for the treatment of wastewater.<sup>54</sup> The energy consumption of the 20 L prototype photovoltaic-powered reactor was 13 kWh m<sup>-3</sup> when it was operated with a 4 h hydraulic retention time.

## RECOMMENDATIONS AND FUTURE RESEARCH DIRECTIONS

One critical challenge to wider adoption of electrochemical treatment of industrial and environmental applications is a need to reduce energy consumption and cost. This may be possible through the use of flow-through reactors with three-dimensional electrodes: an approach that has shown significantly enhanced performance compared to the conventional two-dimensional reactor design at bench-scale. Also, improving the long-term stability and electrocatalytic performance, and lowering the cost of electrode materials is a critical area of research where new developments in materials science and nanotechnology may be important.

Another challenge for electrochemical treatment is a need to control the formation of toxic byproducts when treating halide-containing wastewater. When electrochemical treatment systems are developed, bench-scale studies should be performed with authentic water samples and, when oxidation occurs, measurements of AOX, toxicity, chlorate, and perchlorate are needed. Given that most contaminants are present at low concentrations, their electrochemical reactivity will be subject to mass transfer limitations. Thus, research on electrochemical treatment systems should be redirected toward the actual conditions that occur in wastewater (e.g., concentrations of contaminants that are lower than those of dissolved salts and organic matter). To facilitate further research, evaluation of electrochemical treatment systems should report appropriate figures of merit and provide

complete information on the reactor configuration, operational parameters, and electrolyte composition.

Electrochemical systems are particularly well suited for the treatment of hazardous organic waste. For example, anodes made of materials such as BDD and Ti/SnO<sub>2</sub> can be used for the treatment of aqueous film-forming foams that contain high concentrations of fluorinated surfactants. In the case of wastewater with high concentration of halides, electrooxidation may be coupled or integrated with GAC, to minimize the release of chlorinated organic byproducts. Nevertheless, for some waste streams electrochemical treatment may not be technically and economically feasible due to increased toxicity of the treated effluent.

Electrolytic cells offer multiple technical benefits, including a lack of need for storage and handling of chemicals, easily automated operation, compact and modular reactor design, and an ability to adjust to variable organic loads in wastewater. Because of these intrinsic advantages, electrochemical processes may find their greatest applications in decentralized treatment of water and wastewater, as well as in distributed point-of-entry and point-of-use water treatment.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02414.

Summary of studies reporting the formation of inorganic and organic halogenated byproducts and effluent toxicity in electrooxidation treatment of waste streams (PDF)

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### Notes

The authors declare no competing financial interest.

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