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Disparities between Experimental and Environmental Conditions: Research Steps Towards Making Electrochemical Water Treatment a Reality

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Abstract

Electrochemical water treatment is one of the key topics of environmental electrochemistry. Identifying electrocatalytic materials capable of electrogenerating high oxidant species *in situ* seems to have catalyzed researchers' interest in these processes. While most studies have focused on ideal lab-made solutions, translation to higher technology readiness levels and commercialization requires reframing research questions in context of real water matrices. In this *current opinion,* we discuss disconnects that may occur when focusing on synthetic solutions treatment rather than real waters. Future research can fill the gaps identified herein, thus facilitating application of electrochemical water treatment technologies.

Keywords

Electocatalytic water treatment; electrochemical advanced reduction processes; electrochemical advanced oxidation processes; boron-doped diamond electrode; magneli Ti_4O_7, persistent organic pollutants; oxyanions

1. Introduction

Electrocatalytic processes are emerging as reliable treatment technologies for recalcitrant pollutants present at low concentrations in heterogeneous and complex industrial wastewater and drinking water matrices [1••]. Inspired to treat the broad spectrum of environmental pollutants, development of electrochemically-driven treatment processes has blossomed over the past few decades. It is among the hottest environmental treatment research topics [2••,3••], as illustrated by the exponential increase in annual publications from only ninety articles in the year 2000 to over a thousand articles in 2019. The research momentum during the last five years can be attributed to a clear market opportunity for compact, easily automatable, and chemical-free technologies to commercially purify water [4••,5••]. The growing market demand for new technology stems from an increasing public awareness of water quality effects on human health coupled with ecological concerns due to anthropogenic pollution. For example, the market alone for point-of-use drinking water purification systems for home use is projected to exceed $32 billion by 2023 [6]. Industrial wastewater pretreatment prior to municipal sewer discharge is also a growing market for electrocatalytic treatment as discharges are often regulated for chemical oxygen demand (COD) from organic and inorganic chemicals [7•,8•]. This *current opinion* envisions a future where electrochemical systems rapidly emerge from lab-scale curiosities to widespread commercial application that solve growing environmental pollution problems. Towards this, we explore actual, and often neglected, needs that may have to be fulfilled by electrochemical advanced oxidation processes (EAOPs) and electrochemical advanced reduction processes (EARPs) before full-scale commercial implementation can become a reality.

2. How do electrocatalytic technologies efficiently clean pollutants in water?

Electrocatalytic water treatment oxidative and reductive processes transform target pollutants to innocuous species (*e.g.*, transformation/mineralization of organic pollutants to low molecular weight, readily biodegradable products and/or carbon dioxide; reduction of nitrate to nitrogen gas) [9••–11]. Pollutant transformations occur via two fundamentally different pathways: direct charge transfer or indirect electrochemical processes [12••,13]. Direct charge transfer involves pollutant reduction or oxidation at the surface of the cathode or anode, respectively. In contrast, indirect electrochemical reactions are governed by a sequential two-step process: (i) the electrogeneration of redox mediators at the electrode surface followed by (ii) the reaction between the redox mediator with the target pollutant. Most EAOPs are based on the *in situ* electrogeneration of hydroxyl radical ($^{\bullet}OH$) mediators because they have higher standard reduction potentials when compared with other reactive oxygen species, including superoxide radical, ozone, hydrogen peroxide, or sulfate radical [14,15•]. Electrochlorination is another oxidation process that converts chloride ions to active chlorine-based redox mediators (*e.g.*, $Cl^{\bullet}$, Cl_2, $HClO/ClO^-$) [16,17•]. EARPs exploit the reductant activity of different electrogenerated redox mediators (*e.g.,* adsorbed monoatomic hydrogen, sulfite radical, and solvated electrons) that electrochemically reduce target pollutants [3,18,19]. Faradaic efficiencies differ among the spectrum of available electrocatalytic materials, electrochemical operational conditions (*e.g.*, applied voltage), and presence of other non-target solutes. Several review articles provide a thorough discussion of electrocatalytic water treatment fundamentals [1–5].

A recent techno-economic analysis benchmarked EAOPs as point-of-use drinking water devices against commercial carbon adsorption-based products for the abatement of the pesticide atrazine [20••]. Figure 1 shows the annual total cost of ownership per device depends strongly on the atrazine removal kinetics rate constant (k_1). Obtained from lab-scale experimentation, k_1 is the major driver for operational expenditure (*opex*) because it directly dictates the required time necessary to decrease target pollutant in water below the defined regulatory goal. k_1 is also important to calculate electrical energy per order (E_{EO}), which is a common engineering figure of merit. E_{EO} defined by IUPAC as a tool to comparison the energy requirements of different water treatment technologies to reduce target pollutant concentration one order of magnitude, as defined by equation (1) [21••,22••].

$$E_{EO}\ (\mathrm{kWh\ m^{-3}\ order^{-1}}) = \frac{6.4 \times 10^{-4}\, E_{cell}\, I}{V_s\, k_1} \qquad (1)$$

where 6.4×10^{-4} is a conversion factor (1 h / 3600 s / 0.4343), E_{cell} is the cell potential (V), I is the current (A), V_s is the volume of the solution (L), and k_1 (s^{-1}).

Within this evaluation framework, an essential question is, '*what variables affect the experimental kinetic constant observed in electrochemical water treatment technologies?*' The quick answer that will come to most readers is, of course, the applied current density. Current density (j) defines the number of electrons delivered into the system by unit of time per unit of electrode area (*e.g.*, mA cm^{-2}) [23,24]. While j directly impacts the charge transfer rate possible at the operational electrode potential, it remains a controllable operational variable that can be optimized [25,26•]. In contrast, variables such as pollutant concentration and water matrix also have a significant impact on process performance but cannot be controlled or selected when treating drinking water or industrial wastewaters. The interplay of these competing factors is addressed in the following sections.

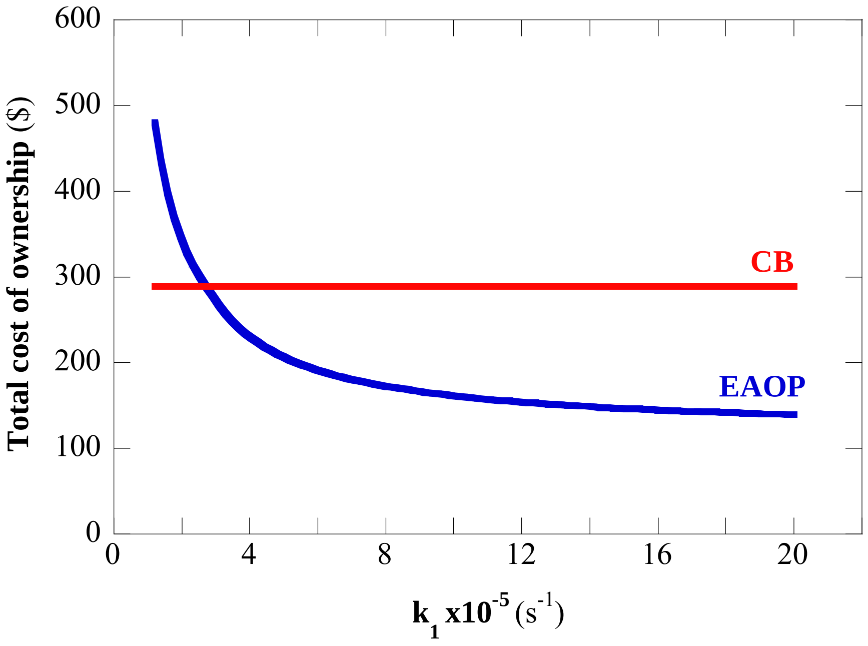

Figure 1 – Effect of the pseudo-first order rate constant of atrazine degradation on the total cost of ownership (TCO) of EAOP devices using boron-doped diamond electrodes. The cost is benchmarked to a carbon block (CB) adsorption device with a constant TCO of $289 [20••].

3. How do disparities between laboratory and environmental pollutant concentrations limit commercialization of EAOP and EARP?

Electrocatalytic water treatment processes occur near or at the electrode surface [2••,27]. Consequently, these heterogeneous reactions are nearly always mass transfer limited and thus influenced by transport rates towards, from, or through electrodes of electroactive species (*e.g.*, target pollutant and redox mediator). Fickian diffusion rates are a function of the pollutant diffusivity and pollutant concentration gradient between the bulk solution and surface. In a typical EAOP study (*e.g.*, electrochemical oxidation [28,29], electro-Fenton processes [30•,31], photoelectrocatalytic processes [32,33]), initial reactant concentration is often systematically varied to probe its influence on the observed reaction kinetics. When mass transport rates have a similar order of magnitude to the direct or indirect chemical reaction rates, which can be inferred from Damköhler numbers, then the observed reaction kinetics implicitly are due not only to chemical reaction rates. Unfortunately, most of target pollutant concentration ranges in studies using synthetic lab-prepared solutions are orders of magnitude higher than real world scenarios and do not consider the water matrix constituents in real water. Figure 2 illustrates the orders-of-magnitude disparity between pollutants concentrations found in environmental samples and typical synthetic solutions reported in literature [12••,33–45]. The difference in concentrations means the diffusion mass transport rates will be dramatically different between lab and field applications, and the ratio of surface pollutants to redox mediators present near electrode surfaces may also not be representative of field conditions.

Only a few studies have evaluated the effects of target pollutant concentration beyond experimental removal percentages and kinetic constants by implementing detailed analyses of engineering figures of merit [47•,48•]. Recent research suggests that chemical-based advanced oxidation processes (AOPs; *e.g.*, UV/H_2O_2. H_2O_2/O_3, UV/HOCl) are more sensitive to the increase in pollutant concentration than electrochemical oxidation [49••]. These results highlight how EAOPs become more competitive than their chemical AOP counterparts at higher pollutant concentration. However, few studies evaluate treatment efficiencies under real-world environmental conditions.

There is a pressing need to reconcile implicit significance stemming from large concentration differences to provide more mechanistically-relevant and realistically meaningful electrochemical process assessments. It is true that drastically reducing the organic pollutant concentration to ppb and ppt values will dramatically decrease mineralization current efficiencies, but it also emerges as an opportunity to redefine research questions to overcome realistic challenges. Not to be overlooked, environmental pollutants often occur at low concentrations in the presence of other solutes that may compete for electrons delivered or oxidants electrogenerated (*i.e.*, scavenging) [50•,51•]. High target pollutant concentrations increases mass transport to electrodes surface and likely increases selectivity (*i.e.*, less competition by other solutes) [52–54], which results in artificially higher k_1 values.

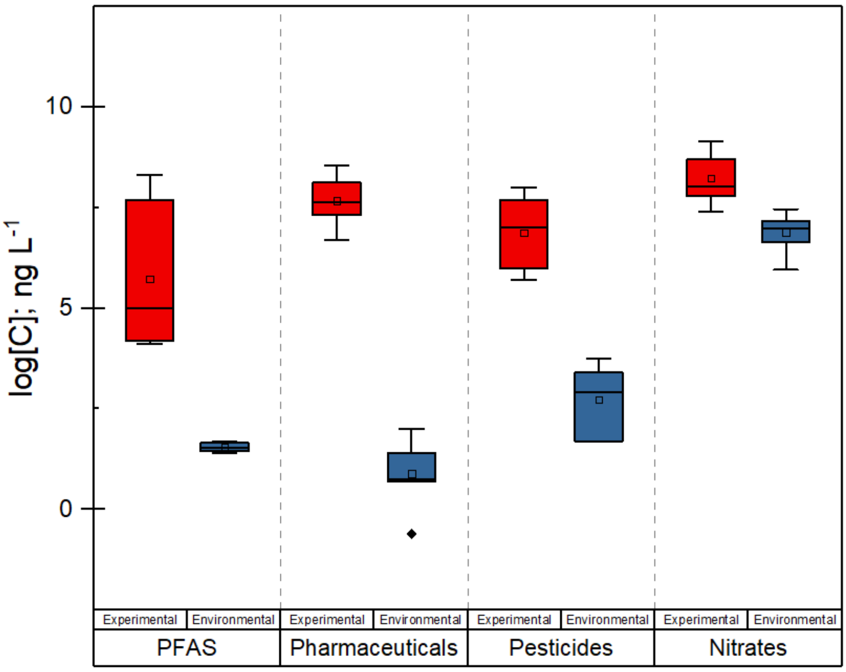

Figure 2 – Box-and-whisker plot comparing concentration ranges of target pollutants found in true environmental concentrations (🟦) vs. synthetic solutions (🟥) treated in the lab. Pollutants are classified by pollutant class: Per- and polyfluoroalkine substances (PFAS), pharmaceuticals, pesticides, and nitrates. Central mark (☐) of box represents the median value, bottom and top edges are 25th and 75th percentiles, respectively. Whiskers extend to extremes not considered outliers. Outliers (◆) are points greater than (Q1+ 1.5(Q3-Q1)) and less than (Q1-1.5(Q3-Q1)), where Q is quartile.

Other critical research needs are to discover strategies to overcome mass transport limitations arising from low pollutant concentrations and to modulate near-electrode surface concentrations of target pollutants or redox mediators that effectively increase k in realistic water matrices. Specifically, the authors believe that the engineering development of “trap-n-zap” inspired electrode geometries is a promising strategy. The novel concept of “trap-n-zap” considers two steps in pollutant destruction that may occur simultaneously or sequentially. The initial step selectively attracts the target pollutant to the electrode surface via adsorption [55], molecular sieving [56•], or molecular identification via electrodes imprinting [57•]. This “trapping” step overcomes mass transfer limitations by increasing target pollutant concentration close to the electrode surface and diminishes competitive/scavenging reactions due to increased selectivity towards the target pollutant over other solutes. The second step of “zapping” consists of the direct or indirect electrochemically induced transformations of selectively “trapped” pollutants. Research is needed to study necessary cycle times between the trapping and zapping steps. It is important to assure that by-products do not poison the electrode surface and can readily diffuse back into solution. Interfacial materials or processes commensurate with this promising trap-n-zap strategy can improve system efficiency even when low target pollutant concentrations exist in solution or even when competing solutes are present. So far, little has been done to consider electrochemical re-generation of carbonaceous adsorbents via electrochemical processes [58•,59], and to date, existing processes still lack the selectivity component that will have to be overcome at low environmental concentrations (see Fig. 2).

4. Which background solutes in water matrices require more attention by researchers?

Conducting research in synthetic matrices has been essential to develop our mechanistic understanding of electrochemical principles for treating drinking waters and/or wastewaters. However, the focus on fundamentals in the thousands of papers published annually may be missing the actual barriers limiting more widespread adoption of electrocatalytic processes in commercial applications. All drinking waters and industrial wastewaters are complex, heterogeneous mixtures of solutes and often contain pH buffers that limit the economic flexibility of readily modulating pH to optimal levels reported in lab-scale experiments [60•,61••] and vary in water hardness [62]. Such barriers go beyond decreased efficiency due to concentration-dependent mass transport or competitive species on the electrode surface, as discussed previously. Because electrocatalytic processes are driven by reactions on electrode surfaces, the accessibility and long-term stability of the electrode surface is essential to ensuring continuous, sustained operation. As such, it is surprising that there is limited research evaluating electrode scaling and fouling [63–66]. For example, Figure 3a depicts an electrochemical reactor whose performance was inhibited after a couple of days under continuous flow operation of real groundwater with high hardness (~350 mg L^{-1} as $CaCO_3$). Inorganic scale deposition (mostly calcium carbonate) is promoted by the high alkaline pH localized at the cathodic surface due to water reduction reaction ($H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$). Additionally, fouling occurs due to irreversible adsorption of ions on electrode surfaces and can happen rapidly (*e.g.*, sulfidation) or may only become apparent in longer-term studies as background organics (*e.g.*, natural organic matter), and biofilms accumulate on surfaces such as electrodes [67]. Figure 3b illustrates a bacteriological biofilm of *Pseudomonas aeruginosa* formed on an electrode surface [64••]. Biofilms not only reduce mass transport coefficients of target pollutants and decrease electrochemical treatment performance, but they also pose a health risk due to their potential to harbor microbial pathogens. Common strategies to mitigate or remove these foulants in other water treatment technologies involve chemicals (*e.g.*, surfactants, acids, bases, oxidants), which limit claims that electrochemically-driven processes can be chemical-free technologies. Yet, opportunities exist to minimize the stabilization of foulants on the electrode surfaces through improved electrochemical reactor design. For example, inducing localized high-energy hydrodynamic shear can remove biofilms. Electrochemists often say controlling fouling or aging can be readily accomplished by alternating electrode polarity. While true for some foulants, continuous operation under reverse polarity can dissolve inorganic scaling due to the high induced acidity of anodic surfaces but requires chemical stable electrode materials whether exposed to anodic or cathodic potentials.

Another commonly overlooked, but critical aspect is the presence of realistic ranges of electrolytes in water containing target pollutants. Salt levels in waters, measured as conductance (mS m^{-1}) or total dissolved solids (TDS, mg L^{-1}) are usually much lower in "real" waters compared with electrolyte concentrations (e.g., 0.5M Na_2SO_4) commonly used in electrochemical lab-studies. For example, conductivity values range between 5-50 mS m^{-1} for drinking waters with TDS below 100 mg L^{-1} [68], which equates to ionic strengths of roughly 0.0025M and far lower than used in most lab-studies. Water conductivity has a direct impact on electrocatalytic activity since defines applied current (delivery of electrons) for a given applied cell potential [2,12]. Adding high salts to drinking waters is not a feasible solution because it affects tastes and exceeds WHO water quality guidelines [68], apart from playing against one of the said "benefits" of electrochemical processes as "chemical-free" technologies. Reactor designs may contribute to overcome this "salty" challenge by implementing ionomer membranes [49••,69•] or using microfluidic devices that diminish ohmic drop [52•,70•]. The overlooked aspect of salt does not create and unsurpassable obstacle for electrochemical processes, but it will contribute to narrow down options to identify where electrocatalysis makes sense in terms of performance and competitiveness.

While some salts are good, and improve conductance in water, the presence of halogens nearly in all “real” waters can lead to formation of toxic by-products such as halogenated organics and oxyhalides (i.e. chlorate, perchlorate, bromate, iodate). In most waters, chloride occurs at roughly 300 times higher mass concentrations than bromide, the same ratio of these halogens present in seawater. Chloride (Cl^-) can be oxidized to active chlorine species (e.g., HOCl, OCl^-) or generate chloramines (e.g., NH_2Cl) when ammonium ion co-occurs [17•,71•,72•]. Further oxidation can lead to electrogeneration of chlorate and perchlorate [73,74••], which are regulated in drinking waters. Active chlorine species can react with background organics present in all waters, and generate halogenated organics which pose additional health concern [75••]. For example, electrochemical treatment of a secondary effluent containing low levels of contaminants of emerging concern produced 0.1-1.0 mM ClO_4^- and 15 μM of adsorbable organic chloride (AOCl) species and 5 μM or below detectable levels of adsorbable organic bromide (AOBr) and iodide (AOI), respectively [76••]. Despite relatively low levels, low molecular weight halogenated compounds can pose highly toxic and carcinogenic effects [75••]. Importantly, halogenated compounds increase their health risk in the following order AOI > AOBr > AOCl [77–79]. Electrochemical approaches should be developed to avoid the generation of such toxic species by controlling operational variables and electrode design. If the generation of these species cannot be selectively controlled, it will be required the development of coupled technologies (i.e. electrochemical dehalogenation, electrochemical reduction, adsorption of organic precursors or by-products) that circumvent this limitation and reduce undesired health risks [9,80••]. Nevertheless, it is important to start considering these alternatives and approaches now, before these become an actual barrier or a completely neglected issue that has to be quickly solved when electrochemical technologies are implemented.

Taken together, there is a clear need to realign priorities on the treatment of actual water samples to set the stepstones required for technology translation to commercialization.

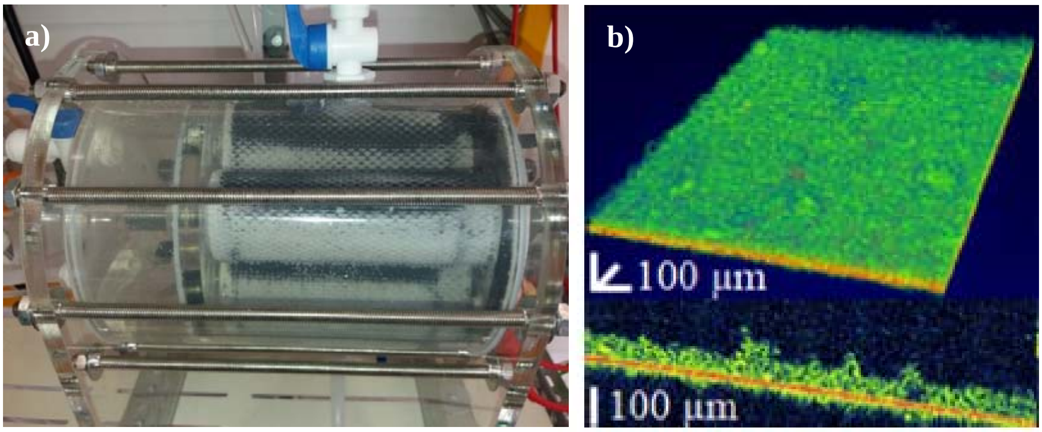

Figure 3 – (a) Inorganic scaling on electrodes during electrocatalytic treatment of real groundwater (hardness: ~350 mg L^{-1} as $CaCO_3$). (b) Biofouling on boron-doped diamond electrodes by *Pseudomonas aeruginosa* seen by optical coherence tomography microscopy [64••].

5. Conclusions and key insights

Electrochemically-driven technologies are gaining relevance due to promising results reported in the treatment of synthetic lab-made solutions often containing a single target pollutant. While expanding fundamental knowledge related to mechanisms underlying discovery of novel electrode materials or architectures remains necessary, systems-level research priorities are also needed to bridge the gap between laboratory findings and application of electrocatalytic technologies to solve real world challenges. The first step is recognition that large discrepancies (*i.e.,* several orders of magnitude) exist between actual environmental concentrations of target pollutants and those tested in lab settings, which should motivate researchers to better understand the consequences of competitive and target solute concentrations on observed rate constants or figures of merit. Continuing research in ultrapure waters with a single target pollutant masks the engineering challenges that must be solved prior implementation. Further, excessive technology hype can blind well-informed engineering decisions that are instrumental to ensure commercial success. A lack of understanding in the mechanisms of electrode scaling and fouling has occurred in part because most research is conducted in batch reactors rather than continuous flow reactors where solutes and bacteria that detrimentally impact system performance pass by electrode surfaces. Future research must confront the elephant in the room, the treatment of more realistic water matrices (*i.e.*, composition and concentration). This will help to identify fit-for-purpose and niche opportunities for electrochemically-driven technologies.

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References

Papers of particular interest, published within the period of review, have been highlighted as:
•Paper of special interest
••Paper of outstanding interest

••[1] B.P. Chaplin, The prospect of electrochemical technologies advancing worldwide water treatment, Acc. Chem. Res. 52 (2019) 596–604.
This account provides an overview on the processes and discusses critical prospects for electrochemical technologies.

••[2] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, Appl. Catal. B Environ. 202 (2017) 217–261.

This review discusses fundamental aspects of different electrochemical advanced oxidation technologies.

••[3] S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski, P. Westerhoff, Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications, Appl. Catal. B Environ. 236 (2018).

This is a referent text that provides a mechanistic description of nitrate electrocatalytic reduction as well as a comprehensive description of electrocatalytic materials and processes.

••[4] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: A critical review, Chem. Rev. 115 (2015) 13362–13407.

This review focuses on electrochemical reactor advances.

••[5] J. Radjenovic, D.L. Sedlak, Challenges and opportunities for electrochemical processes as next- generation technologies for the treatment of contaminated water, Environ. Sci. Technol. 49 (2015) 11292–11302.

This referent article identifies clear challenges to overcome for technology translation.

[6] Point-of-Use Water Treatment Systems Market by Device (Tabletop, Faucet-mounted, Countertop, Under-the-sink) Technology (RO, Ultrafiltration, Distillation, Disinfection, Filtration), Application (Residential, Non-residential), & Region - Forecast to 2023 , n.d. https://www.marketsandmarkets.com/PressReleases/point-of-use-water-treatment-systems.asp.

•[7] C.L. Coonrod, Y.B. Yin, T. Hanna, A. Atkinson, P.J.J. Alvarez, T.N. Tekavec, M.A. Reynolds, M.S. Wong, Fit-for-purpose treatment goals for produced waters in shale oil and gas fields, Water Res. (2020).

This article describes fit-for-purpose technologies for oil and gas industry, including electrochemical processes.

•[8] E. Mousset, Z. Wang, H. Olvera-Vargas, O. Lefebvre, Advanced electrocatalytic pre-treatment to improve the biodegradability of real wastewater from the electronics industry — A detailed investigation study, J. Hazard. Mater. 360 (2018) 552–559.

This article provides a perspective on possibility of electrochemical technologies to control COD levels.

••[9] K.N. Heck, S. Garcia-Segura, P. Westerhoff, M.S. Wong, Catalytic Converters for Water Treatment, Acc. Chem. Res. 52 (2019) 906–915.

This account discusses the application of different catalytic technologies using catalytic converters for water treatment.

[10] N. Barhoumi, N. Oturan, S. Ammar, A. Gadri, M.A. Oturan, E. Brillas, Enhanced degradation of the antibiotic tetracycline by heterogeneous electro-Fenton with pyrite

catalysis, Environ. Chem. Lett. 15 (2017) 689–693.

[11] S. Garcia-Segura, J. Anotai, S. Singhadech, M.-C. Lu, Enhancement of biodegradability of o-toluidine effluents by electro-assisted photo-Fenton treatment, Process Saf. Environ. Prot. 106 (2017).

••[12] S. Garcia-Segura, J.D. Ocon, M.N. Chong, Electrochemical oxidation remediation of real wastewater effluents — A review, Process Saf. Environ. Prot. 113 (2018).

This article focuses on the exhaustive revision of works that have reported electrochemical oxidation of real water effluents

[13] A. Thiam, R. Salazar, E. Brillas, I. Sirés, Electrochemical advanced oxidation of carbofuran in aqueous sulfate and/or chloride media using a flow cell with a RuO_2-based anode and an air-diffusion cathode at pre-pilot scale, Chem. Eng. J. 335 (2018) 133–144.

[14] J. Cai, M. Zhou, Y. Liu, A. Savall, K. Groenen Serrano, Indirect electrochemical oxidation of 2,4-dichlorophenoxyacetic acid using electrochemically-generated persulfate, Chemosphere. 204 (2018) 163–169.

•[15] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, Treatment of real effluents from the pharmaceutical industry: A comparison between Fenton oxidation and conductive-diamond electro-oxidation, J. Environ. Manage. 195 (2017) 216–223.

This is a valuable report regarding the treatment of real wastewater containing pharmaceuticals.

[16] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, Novel electrodialysis-electrochlorination integrated process for the reclamation of treated wastewaters, Sep. Purif. Technol. 132 (2014) 362–369.

•[17] E. Mostafa, P. Reinsberg, S. Garcia-Segura, H. Baltruschat, Chlorine species evolution during electrochlorination on boron-doped diamond anodes: In-situ electrogeneration of Cl_2, Cl_2O and ClO_2, Electrochim. Acta. 281 (2018).

This article provides insight in the mechanistic evolution of chlorine volatile species, which are relevant components in electrochlorination treatments.

[18] T. Liu, J. Luo, X. Meng, L. Yang, B. Liang, M. Liu, C. Liu, A. Wang, X. Liu, Y. Pei, J. Yuan, J. Crittenden, Electrocatalytic dechlorination of halogenated antibiotics via synergistic effect of chlorine-cobalt bond and atomic H*, J. Hazard. Mater. 358 (2018) 294–301.

[19] H. Liu, J. Han, J. Yuan, C. Liu, D. Wang, T. Liu, M. Liu, J. Luo, A. Wang, J.C. Crittenden, Deep dehalogenation of florfenicol using crystalline CoP nanosheet arrays on a Ti plate via direct cathodic reduction and atomic H, Environ. Sci. Technol. 53 (2019) 11932–11940.

••[20] R. Stirling, W.S. Walker, P. Westerhoff, S. Garcia-segura, Techno-economic analysis to identify key innovations required for electrochemical oxidation as point-of-use treatment systems, Electrochim. Acta 338 (2020) 135874.

This article presents a techno-economic analysis of electrochemical technologies to understand research needs to attain high level of competitiveness respect commercially available

••[21] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and

solar-driven systems (IUPAC Technical Report), Pure Appl. Chem. 73 (2001) 627–637.
This is a referent article that defines engineering figures of merit that must be used to benchmark different technologies in terms of energy requirements and cost.

••[22] S. Garcia-Segura, E. Brillas, Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters, J. Photochem. Photobiol. C Photochem. Rev. 31 (2017) 1–35.
This review article describes fundamentals of photoelectrocatalytic technologies and identifies challenges in the future research roadmaps.

[23] E. Mousset, L. Frunzo, G. Esposito, E.D. Van Hullebusch, N. Oturan, M.A. Oturan, A complete phenol oxidation pathway obtained during electro-Fenton treatment and validated by a kinetic model study, Appl. Catal. B Environ. 180 (2016) 189–198.
[24] A. Schranck, K. Doudrick, Effect of reactor configuration on the kinetics and nitrogen byproduct selectivity of urea electrolysis using a boron doped diamond electrode, Water Res. 168 (2020) 115130.
[25] V. Poza-Nogueiras, M. Pazos, M.Á. Sanromán, E. González-Romero, Double benefit of electrochemical techniques: Treatment and electroanalysis for remediation of water polluted with organic compounds, Electrochim. Acta. 320 (2019) 1–13.
•[26] C. Candia-Onfray, N. Espinoza, E.B. Sabino da Silva, C. Toledo-Neira, L.C. Espinoza, R. Santander, V. García, R. Salazar, Treatment of winery wastewater by anodic oxidation using BDD electrode, Chemosphere. 206 (2018) 709–717.
This is an example of applying electrochemcial technology in the food industry.

[27] A.S. Fajardo, A.J. dos Santos, E.C.T. de Araújo Costa, D.R. da Silva, C.A. Martínez-Huitle, Effect of anodic materials on solar photoelectro-Fenton process using a diazo dye as a model contaminant, Chemosphere. 225 (2019) 880–889.
[28] F. Sopaj, M.A. Rodrigo, N. Oturan, F.I. Podvorica, J. Pinson, M.A. Oturan, Influence of the anode materials on the electrochemical oxidation efficiency . Application to oxidative degradation of the pharmaceutical amoxicillin, Chem. Eng. J. 262 (2015) 286–294.
[29] H. Lebik-Elhadi, Z. Frontistis, H. Ait-Amar, S. Amrani, D. Mantzavinos, Electrochemical oxidation of pesticide thiamethoxam on boron doped diamond anode: Role of operating parameters and matrix effect, Process Saf. Environ. Prot. 116 (2018) 535–541.
•[30] V. Poza-Nogueiras, E. Rosales, M. Pazos, E. Rosales, M.Á. Sanromán, Current advances and trends in electro-Fenton process using heterogeneous catalysts – A review, Chemosphere. 201 (2018) 399–416.
This revision provides a robust discussion on the combination of heterogeneous catalysts with electrochemically-driven generation of H_2O_2.

[31] A. Thiam, I. Sirés, R. Salazar, E. Brillas, On the performance of electrocatalytic anodes for photoelectro-Fenton treatment of synthetic solutions and real water spiked with the herbicide chloramben, J. Environ. Manage. 224 (2018) 340–349.
[32] G.A. Cerrón-Calle, A.J. Aranda-Aguirre, C. Luyo, S. Garcia-Segura, H. Alarcón, Photoelectrocatalytic decolorization of azo dyes with nano-composite oxide layers of ZnO nanorods decorated with Ag nanoparticles, Chemosphere. 219 (2019) 296–304.
[33] G.G. Bessegato, J.C. Cardoso, B.F. da Silva, M.V.B. Zanoni, Combination of photoelectrocatalysis and ozonation: A novel and powerful approach applied in Acid

Yellow 1 mineralization, Appl. Catal. B Environ. 180 (2016) 161–168.
[34] M.S. Díaz-Cruz, D. Barceló, Trace organic chemicals contamination in ground water recharge, Chemosphere. 72 (2008) 333–342.
[35] M.F. Garcia-Montoya, S. Gutierrez-Granados, A. Alatorre-Ordaz, R. Galindo, R. Ornelas, J.. Peralta-Hernandez, Application of electrochemical/BDD process for the treatment wastewater effluents containing pharmaceutical compounds, J. Ind. Eng. Chem. 31 (2015) 238–243.
[36] A. Jurado, E. Vàzquez-Suñé, J. Carrera, M. López de Alda, E. Pujades, D. Barceló, Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context, Sci. Total Environ. 440 (2012) 82–94.
[37] F. Nantaba, J. Wasswa, H. Kylin, W.U. Palm, H. Bouwman, K. Kümmerer, Occurrence, distribution, and ecotoxicological risk assessment of selected pharmaceutical compounds in water from Lake Victoria, Uganda, Chemosphere. 239 (2020) 124642.
[38] M. Zheng, K.D. Daniels, M. Park, A.B. Nienhauser, E.C. Clevenger, Y. Li, S.A. Snyder, Attenuation of pharmaceutically active compounds in aqueous solution by UV/CaO_2 process: Influencing factors, degradation mechanism and pathways, Water Res. 164 (2019) 114922.
[39] L. Boulard, G. Dierkes, M.P. Schlüsener, A. Wick, J. Koschorreck, T.A. Ternes, Spatial distribution and temporal trends of pharmaceuticals sorbed to suspended particulate matter of German rivers, Water Res. 171 (2020) 115366.
[40] D. Fatta-Kassinos, S. Meric, A. Nikolaou, Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research, Anal. Bioanal. Chem. 399 (2011) 251–275.
[41] WHO, Pharmaceuticals in drinking-water, 2012.
[42] C.E. Schaefer, C. Andaya, A. Urtiaga, E.R. McKenzie, C.P. Higgins, Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acod (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs), J. Hazard. Mater. 295 (2015) 170–175.
[43] P.C. Rumsby, C.L. McLaughlin, T. Hall, Perfluoroctane sulphonate and perfluorooctanoic acid in drinking and environmental waters, Phil. Trans. R. Soc. A. 367 (2009) 4119–4136.
[44] M.J.M. De Vidales, M. Millán, C. Sáez, P. Cañizares, M.A. Rodrigo, What happens to inorganic nitrogen species during conductive diamond electrochemical oxidation of real wastewater?, Electrochem. Commun. 67 (2016) 65–68.
[45] C.E. Schaefer, C. Andaya, A. Burant, C.W. Condee, A. Urtiaga, T.J. Strathmann, C.P. Higgins, Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanims and application to groundwater treatment, Chem. Eng. J. 317 (2017) 424–432.
[46] M. Ghazouani, H. Akrout, L. Bousselmi, Nitrate and carbon matter removals from real effluents using Si/BDD electrode, Environ. Sci. Pollut. Res. 24 (2017) 9895–9906.
• [47] M. Lanzarini-Lopes, S. Garcia-Segura, K. Hristovski, P. Westerhoff, Electrical energy per order and current efficiency for electrochemical oxidation of p -chlorobenzoic acid with boron-doped diamond anode, Chemosphere. 188 (2017) 304–311.
Reports a comprehensive study on the effect of operational variables on the energy requirements of electrochemical oxidation water treatment.

•[48] Y. Wang, M. Chen, C. Wang, X. Meng, W. Zhang, Z. Chen, J. Crittenden, Electrochemical degradation of methylisothiazolinone by using Ti/SnO_2-Sb_2O_3/A, B-PbO_2 electrode: Kinetics, energy efficiency, oxidation mechanism and degradation pathway, Chem. Eng. J. 374 (2019) 626–636.

Interesting discussion regarding energy efficiency of electrochemical systems.

••[49] X. Meng, Z. Chen, C. Wang, W. Zhang, K. Zhang, S. Zhou, J. Luo, N. Liu, D. Zhou, D. Li, J. Crittenden, Development of a three-dimensional electrochemical system using a blue TiO_2/SnO_2 −Sb_2O_3 anode for treating low-ionic-strength wastewater, Environ. Sci. Technol. 53 (2019) 13784–13793.

This article compares energy requirements of electrochemcial systems with different advanced oxidation processes.

•[50] N.E. Pica, J. Funkhouser, Y. Yin, Z. Zhang, D.M. Ceres, T. Tong, J. Blotevogel, Electrochemical oxidation of hexafluoropropylene oxide dimer acid (GenX): mechanistic insights and efficient treatment train with nanofiltration, Environ. Sci. Technol. 53 (2019) 12602–12609.

This ariticle identifies concentration challenges, which are relevant for per- and polyfluoroalkyl substances found in concentrations of ppb-ppt.

•[51] Z. Frontistis, S. Meriç, The role of operating parameters and irradiation on the electrochemical degradation of tetracycline on boron doped diamond anode in environmentally relevant matrices, J. Chem. Technol. Biotechnol. 93 (2018) 3648–3655.

Article that evaluates effects of environmental water matrices.

•[52] E. Mousset, M. Puce, M.N. Pons, Advanced electro-oxidation with Boron-Doped Diamond for acetaminophen removal from real wastewater in a microfluidic reactor: Kinetics and mass-transfer studies, ChemElectroChem. 6 (2019) 2908–2916.

Article that proposes the use of microfluidic devices.

[53] S.N. Misal, M.H. Lin, S. Mehraeen, B.P. Chaplin, Modeling electrochemical oxidation and reduction of sulfamethoxazole using electrocatalytic reactive electrochemical membranes, J. Hazard. Mater. 384 (2019) 121420.

[54] R. Xie, X. Meng, P. Sun, J. Niu, W. Jiang, L. Bottomley, D. Li, Y. Chen, J. Crittenden, Electrochemical oxidation of ofloxacin using a TiO_2-based SnO_2-Sb/polytetrafluoroethylene resin-PbO_2 electrode: Reaction kinetics and mass transfer impact, Appl. Catal. B Environ. 203 (2017) 515–525.

[55] S. Almassi, Z. Li, W. Xu, C. Pu, T. Zeng, B.P. Chaplin, Simultaneous adsorption and electrochemical reduction of N-Nitrosodimethylamine using carbon-Ti_4O_7 composite reactive electrochemical membranes, Environ. Sci. Technol. 53 (2019) 928–937..

•[56] S.A. Hawks, M.R. Cerón, D.I. Oyarzun, T.A. Pham, C. Zhan, C.K. Loeb, D. Mew, A. Deinhart, B.C. Wood, J.G. Santiago, M. Stadermann, P.G. Campbell, Using ultramicroporous carbon for the selective removal of nitrate with capacitive deionization, Environ. Sci. Technol. 53 (2019) 10863–10870.

Example of how nano-structures can act as molecular sievers to enhance selectivity.

•[57] B. Tang, J. Zhang, N. Yang, G. Zhao, Selective photoelectrocatalytic removal of environmental pollutants on molecular imprints decorated TiO_2 single crystalline nanoarrays, Chem. Eng. J. 383 (2019) 123188.

Example demonstrting selectivity enhancement through molecular imprinting recognition.

•[58] C. Trellu, N. Oturan, F.K. Keita, C. Fourdrin, Y. Pechaud, M.A. Oturan, Regeneration of activated carbon fiber by the electro-Fenton process, Environ. Sci. Technol. 52 (2018) 7450–7457.

One of the few works that explores adsorbent regeneration by in situ electrochemical treatment.

[59] F. Sharif, E.P.L. Roberts, Anodic electrochemical regeneration of a graphene/titanium dioxide composite adsorbent loaded with an organic dye, Chemosphere. 241 (2020) 125020.

•[60] A. Schranck, R. Marks, E. Yates, K. Doudrick, Effect of urine compounds on the electrochemical oxidation of urea using a nickel cobaltite catalyst: An electroanalytical and spectroscopic investigation, Environ. Sci. Technol. 52 (2018) 8638–8648.

Well-executed study on the effect of different urine compounds interaction with electrode surfaces.

••[61] E. Brillas, S. Garcia-Segura, Benchmarking recent advances and innovative technology approaches of Fenton , photo-Fenton , electro-Fenton , and related processes : A review on the relevance of phenol as model molecule, Sep. Purif. Technol. (2019) 116337.

Critical revision on the advances of Fenton and electrochemically-driven Fenton technologies and the need to benchmark and compare such advances.

[62] A.J. Dos Santos, M.D. De Lima, D.R. Da Silva, S. Garcia-Segura, C.A. Martínez-Huitle, Influence of the water hardness on the performance of electro-Fenton approach: Decolorization and mineralization of Eriochrome Black T, Electrochim. Acta. 208 (2016).

[63] C.A. Cid, J.T. Jasper, M.R. Hoffmann, Phosphate recovery from human waste via the formation of hydroxyapatite during electrochemical wastewater treatment, ACS Sustain. Chem. Eng. 6 (2018) 3135–3142.

••[64] D. Rice, P. Westerhoff, F. Perreault, S. Garcia-segura, Electrochemical self-cleaning anodic surfaces for biofouling control during water treatment, Electrochem. Commun. 96 (2018) 83–87.

First report that analyzes in situ biofilm disruption with a combined electrochemical - optical coherence tomography microscope. Relevant for fundamental understanding of self-cleaning properties of electrodes with high overpotential of oxygen evolution.

[65] M.-H. Lin, S. Mehraeen, G. Cheng, C. Rusinek, B.P. Chaplin, The role of near electrode solution chemistry on bacteria attachment and inactivation at low applied potentials, Environ. Sci. Technol. 54 (2019) 446–455.

[66] R.E. Wilson, I. Stoianov, D. O'Hare, Biofouling and in situ electrochemical cleaning of a boron-doped diamond free chlorine sensor, Electrochem. Commun. 71 (2016) 79–83.

[67] C.Y. Kim, X. Zhu, M. Herzberg, S. Walker, D. Jassby, Impact of Physical and Chemical Cleaning Agents on Specific Biofilm Components and the Implications for Membrane Biofouling Management, Ind. Eng. Chem. Res. 57 (2018) 3359–3370.

[68] WHO, Total dissolved solids in Drinking-water, 1996. doi:10.1080/10417943609370625.

•[69] A.L. Tasca, M. Puccini, D. Clematis, M. Panizza, Electrochemical removal of Terbuthylazine:Boron-Doped Diamond anode coupled with solid polymer electrolyte, Environ. Pollut. 251 (2019) 285–291.

Interesting article that proposes the use of solid polymer electrolyte in reactor configurations.

••[70] P. Ma, H. Ma, S. Sabatino, A. Galia, O. Scialdone, Electrochemical treatment of real wastewater. Part 1: Effluents with low conductivity, Chem. Eng. J. 336 (2018) 133–140.

Excellent article on strategies to overcome low conductivity challenges during electrochemical water treatment.

•[71] S. Garcia-Segura, E. Mostafa, H. Baltruschat, Electrogeneration of inorganic chloramines on boron-doped diamond anodes during electrochemical oxidation of ammonium chloride, urea and synthetic urine matrix, Water Res. 160 (2019) 107–117.

Demonstrates in situ formation of chloramines during electrochemical oxidation in different water matrices including urine.

•[72] M. Murata, T.A. Ivandini, M. Shibata, S. Nomura, A. Fujishima, Y. Einaga, Electrochemical detection of free chlorine at highly boron-doped diamond electrodes, J. Electroanal. Chem. 612 (2008) 29–36.

Well-executed study that evaluates formation of soluble ionic chlorine species.

[73] M.E.H. Bergmann, J. Rollin, Product and by-product formation in laboratory studies on disinfection electrolysis of water using boron-doped diamond anodes, Catal. Today. 124 (2007) 198–203.

••[74] M.E.H. Bergmann, J. Rollin, T. Iourtchouk, The occurrence of perchlorate during drinking water electrolysis using BDD anodes, Electrochim. Acta. 54 (2009) 2102–2107.

First report on the formation of perchlorates during anodic oxidation on BDD electrodes.

••[75] S.D. Richardson, T.A. Ternes, Water Analysis: Emerging Contaminants and Current Issues, Anal. Chem. 90 (2018) 398–428.

Excellent perspective on current challenges and issues in water quality.

••[76] S. Garcia-Segura, J. Keller, E. Brillas, J. Radjenovic, Removal of organic contaminants from secondary effluent by anodic oxidation with a boron-doped diamond anode as tertiary treatment, J. Hazard. Mater. 283 (2015) 551–557.

Comprehensive study on the treatment of a real water collected from a wastewater treatment plan with a complex mixture of trace contaminants of emerging concern. It reports formation of halogenated organics and oxyhalides.

[77] N. Sharma, T. Karanfil, P. Westerhoff, Historical and future needs for geospatial iodide occurrence in surface and groundwaters of the United States of America, Environ. Sci. Technol. Lett. 6 (2019) 379–388. doi:10.1021/acs.estlett.9b00278.

[78] S.D. Richardson, F. Fasano, J.J. Ellington, F.G. Crumley, K.M. Buettner, J.J. Evans, B.C. Blount, L.K. Silva, T.J. Waite, G.W. Luther, A.B. Mckague, R.J. Miltner, E.D. Wagner, M.J. Plewa, Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water, Environ. Sci. Technol. 42 (2008) 8330–8338.

[79] M.J. Plewa, J.E. Simmons, S.D. Richardson, E.D. Wagner, Mammalian cell cytotoxicity and genotoxicity of the haloacetic acids, a major class of drinking water disinfection by-products, Environ. Mol. Mutagen. 51 (2010) 871–878.

••[80] Q. Yang, F. Yao, Y. Zhong, D. Wang, F. Chen, J. Sun, S. Hua, S. Li, X. Li, G. Zeng, Catalytic and electrocatalytic reduction of perchlorate in water – A review, Chem. Eng. J. 306 (2016) 1081–1091.

Complete reviw article on the reduction of perchlorate in water.