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# **A Review of Electrochemical Reduction Processes to Treat Oxidized Contaminants in Water**

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## **Abstract**

This purpose of this review is to provide a short overview of electrochemical reduction processes for oxidized contaminants in water. The major parameters affecting the electro-reduction mechanisms and the impact of electrode choice are discussed with reference to both inorganic and organic pollutants that are either regulated or emerging (e.g., non-metal oxyanions, per- and polyfluoroalkyl substances (PFAS)). To conclude, a discussion is presented on the future directions and challenges that must be addressed to develop these electrochemical reduction processes at a larger, commercialized scale.

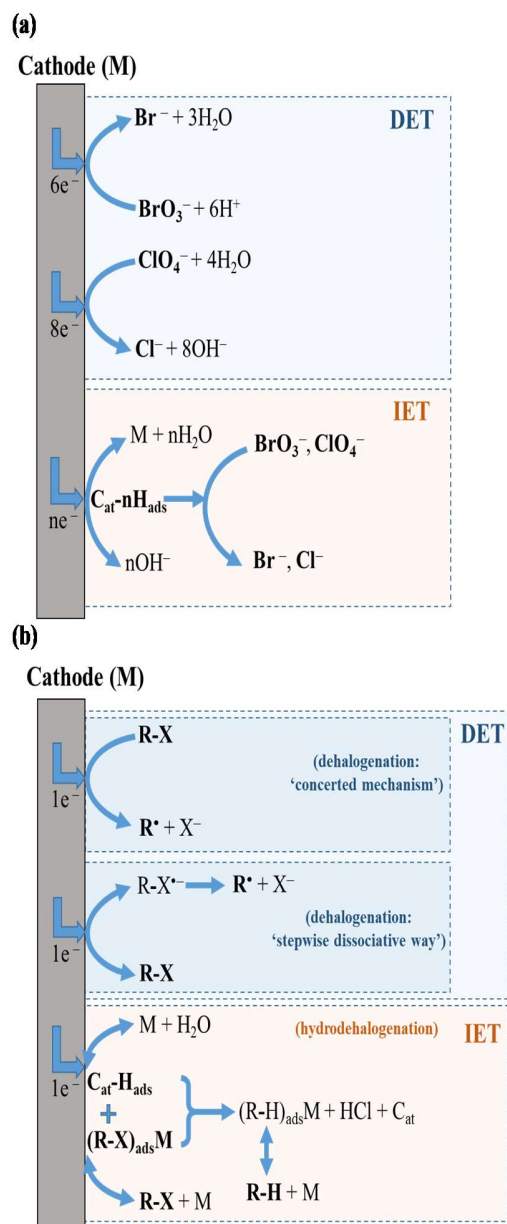
## Introduction

There are several emerging organic and inorganic contaminants in drinking water and wastewater that fall under a broad classification termed oxidized contaminants. These include, but are not limited to, oxyanions (e.g., nitrate), halogenated compounds (e.g., trichloroethylene), and nitrogenous compounds (e.g., nitrosamines). While physical treatment processes such as reverse osmosis or ion exchange can separate the contaminant from the source water, they generate a highly concentrated brine waste that must still be treated. This leads to unnecessary costs and hazards. Chemical or biological treatment methods are more promising because they convert the contaminant, but due to the recalcitrant nature of many oxidized contaminants, even these may be insufficient. Biological processes (e.g., activated sludge) are typically used for wastewater treatment, but they are not efficient at treating bio-recalcitrant contaminants such as per- and polyfluoroalkyl substances (PFAS). Instead, the treatment of oxidized contaminants requires more sophisticated reduction processes that generate high energy electrons or reactive species.

Electrochemical reduction processes (ERPs) are an emerging treatment approach for oxidized contaminants. ERPs have many advantages over conventional reduction processes (e.g., chemical reduction using iron). ERPs can be operated at ambient temperature and pressure and there is no chemical addition required or waste production [1]. The reactors are easily customizable and a small footprint area can be maintained, which makes them the ideal for point-of-use treatment or to retrofit treatment plants constrained by size. Additionally, because the applied potential (i.e., thermodynamics and reactivity) can be controlled, high potential electrons can be generated, and the desired byproduct can often be selected.

In ERPs, electrons are transferred to the oxidized contaminant through a direct or indirect pathway. In a direct electron transfer (DET), electrons are transferred from the cathode to the oxidized contaminant that is adsorbed at the electrode-electrolyte interface. In an indirect electron transfer (IET), the electrons are transferred to the oxidized contaminant through an electron-shuttling mediator such as a catalyst or other adsorbed species. Wherein, the electrons are first transferred to the mediator, which then reacts with the contaminant and thus reduces the contaminant and oxidizes the mediator back to its original state. The processes can occur indefinitely, and the contaminant does not have to be bound to the electrode for reduction to occur.

In this review, we discuss the recent literature for the use of ERPs to treat oxidized contaminants present in drinking water and wastewater. As an advanced oxidation processes, electrochemical treatment processes have been one of the most studied [2,3]. By comparison, there has been a significantly smaller body of knowledge for ERPs. Reviews exist on the electrochemical reduction of specific oxidized contaminants such as organic halogenated compounds [4], nitrate [5], or perchlorate [6]. Instead, this review intends to provide a critical recent overview on prevalent compounds, either organic or inorganic, that align with current and emerging drinking water regulations (e.g., non-metal oxyanions, halogenated organics). There is a large body of work on the treatment of nitrate (and nitrite) oxyanions using ERPs [5], unlike the electro-reduction of bromate and perchlorate and its reduction byproducts (e.g. chlorate and chlorite). In parallel, the removal of organic halides (R-X) contaminants has been often considered by electro-reduction (e.g. 2,4-dichlorophenoxyacetic acid (2,4-D) [7,8], 2,4-dichlorobenzoic acid (2,4-DCBA) [9], hexachlorocyclohexane [10], chloropicolinic acids [11], chloroacetic acid [12], trichloroethylene [13], 1,1,2,2-tetrachloroethane [14], PFAS [15], fluoroaromatic compounds [16]), due to their molecular structure that contains reducible groups (C-Cl, C-F). Therefore, this short review is focused on bromate, perchlorate, R-Cl, and R-F electro-reduction. Their main mechanisms of electro-reduction by either DET or IET are depicted in Fig. 1, based on literature (oxyanions: [17–21], organic halides: [7,8,11,13,16,22]).



**Fig. 1.** Schematic detailing the main electro-reduction mechanisms by either DET or IET of (a) oxyanions ( $\text{BrO}_3^-$  and  $\text{ClO}_4^-$ ) and (b) organic halides ( $\text{R-X}$ ) compounds. M refers to the cathode material (i.e., the catalyst ( $\text{C}_{\text{at}}$ ) or the support of catalyst), while  $\text{C}_{\text{at}}-\text{H}_{\text{ads}}$ ,  $(\text{R-X})_{\text{ads}}\text{M}$ , and  $(\text{R-H})_{\text{ads}}\text{M}$  are the hydrogen atom,  $\text{R-X}$ , and  $\text{R-H}$  compounds, respectively, adsorbed on the cathode material.

### Major Parameters Influencing the Electrochemical Reduction Efficiency

The catalyst loading is crucial for the electrocatalytic efficiency. Generally, an increase in the catalyst loading results in increased activity until a limiting amount is reached, at which point the activity either steadies or decreases (i.e., volcano plot). When the catalyst loading is too high the substrate will contain multiple catalyst layers and the effective number of active sites does not increase and electron transfer

distance to/from the electrode is increased [8]. In the case of nano-sized catalysts such as Pd, the particles will aggregate at higher loading, which results in excessive local H<sub>2</sub> evolution [20]. The accumulation of H<sub>2</sub> bubbles then restricts the diffusion and the access of the contaminant (e.g., bromate) towards the catalyst and substrate [20].

The thermodynamics and kinetics of an electroreduction reaction are controlled by the cathodic potential value. This potential is directly related to the current (i.e., Butler-Volmer). Generally, a reaction will have an optimal cathodic potential or current density. If the current density is too high, then an abundance of hydrogen bubbles from the hydrogen evolution reaction (HER) could retard the ability for oxidized contaminants to adsorb on the electrode due to mass transport limitation in the vicinity of the cathode [23–25]. In this scenario, mass transport becomes the rate-limiting step.

The water quality characteristics of the source are critical to the reduction efficiency and lifetime of the electrode. Generally, lower pH results leads to increased adsorb hydrogen atom (H<sub>ads</sub>) formation from the electro(catalytic) reduction of H<sub>2</sub>O at the cathode surface [26]. This increases the efficiency of electro-reduction reactions following an H<sub>ads</sub>-based mechanism [17,25]. Moreover, the pH also influences the molecular structure of R-X (e.g., pK<sub>a</sub> of functional groups, length of C-X bonds) and therefore their adsorption behavior due to modification of surface adsorption geometry and electrostatic attraction/repulsion [11]. The presence of certain ions and the ionic strength can also impact performance. An increased ionic strength will decrease the electric double layer at the cathode, making adsorption to the electrode easier. Further, ion adsorption to the cathode can modify the potential and the current at the electrode surface, which depends on the cathode properties [27]. For example, nitrate has been shown to drastically decrease the reduction rate of R-X, while the role of carbonate and chloride ions were negligible [28]. Additionally, reduced sulfur compounds can poison the Pd electrocatalyst through the formation of Pd sulfide, which impedes H<sub>ads</sub> adsorption [28]. The presence of dissolved organic matter can also inhibit electro-reduction, as observed for bromate [20].

### Importance of Electrode Selection on the Electro-Reduction Mechanism

The electrode material (i.e., the substrate with or without a catalyst) plays a major role in the electro(catalytic) reduction mechanism. When using a catalyst, its support material may influence the electrochemical efficiency since it may change the electronic structure of the catalyst or influence the adsorption behavior of reducible compounds [11]. Table 1 shows the major electrode materials tested for electro-reduction of bromate, perchlorate, and organic halides. It is interesting to note that (bi)metallic-based, carbon-based, and metal/carbon-based materials have been tested for the electro-reduction of all these contaminants.

Metallic catalysts have been widely tested in ERPs. A good catalyst allows high bonding strength on the surface, which is related to the number of d-electrons of the metal [29]. Numerous monometallic metal catalysts have been tested for perchlorate reduction and the following order of perchlorate reduction rate has been observed: Cd>Pt>Cr>Mo>Sc>>Rh>Ru~Sn>Pd>V~Ti >Zn >Mn >Ni >Zr >Co >Cu >Pb) [29]. The best catalytic activity for perchlorate reduction was given with Group VIII of transition metals over Groups I, IIB, and IV to VII from periodic table [29]. Numerous noble metals have been also tested for electrocatalytic hydrodechlorination such as Pd, Pt, Ru, and Rh, while Pd gave the best performance for its superior ability to adsorb atomic H<sub>ads</sub> for subsequent reduction [8]. Considering the dechlorination mechanism, it has been shown that among Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag cathode materials, Ag had the highest electrocatalytic activity for the electro-reduction of organic halides [30].

Bimetallic catalysts have shown synergistic effects compared to monometallic materials (e.g., increased efficiency, reduced poisoning [31,32]. Adding In to a Pd catalyst improved the reduction of bromate, depending on their respective proportion [33]. This enhancement was presumably due to the increase in zeta potential of the Pd-In catalyst, which facilitated the adsorption of bromate before its reduction. Between Rh, Pt, Ir, Ru, and Pd catalysts loaded onto different cathode metallic supports (Ni foam, Cu foam, Ag mesh), Rh/Ni foam gave the best performance for hydrodefluorination, which could be due to the small  $Rh^{n+}/Rh^0$  ratio value of 0.66 [16]. The modification of bimetallic materials may also enhance the electrocatalytic efficiency. Adding nano-sized titanium nitride (nTiN) on Pd/Ni foam increased the HER and therefore increased the amount of electrogenerated  $H_{ads}$ , while the nanostructure provided an increase in the number of active sites [8]. The introduction of anchored  $Ni(OH)_2$  catalyst on a Pd/Ni structure increased the  $H_{ads}$  production and thus enhanced the dechlorination rate at low Pd loadings [7]. The low cost and abundance of  $Ni(OH)_2$  and its superior ability to produce  $H_{ads}$  makes it an attractive alternative over noble metals such as Pd [7]. The same trend could be observed with the intercalation of  $MnO_2$  between an Ni foam substrate and Pd nanoparticles [9].  $MnO_2$  enhanced  $H_{ads}$  production, while Pd enhanced  $H_{ads}$  adsorption [9]. The synergetic effect increased the electrocatalytic activity while minimizing the required Pd loading [9].

An alternative to expensive metallic materials is the development of carbon-based materials to enhance the electrocatalytic activity. Bromate was reduced using polyaniline (PANI) coated on a glassy carbon material through a reaction that involved the loss of electrons from nitrogen atoms of the PANI chains [34]. Alternatively, nanostructured copolymer poly(aniline-co-o-aminophenol) (PANOA) coated on glassy carbon selectively adsorbed perchlorate when PANOA was polarized, which enhanced the subsequent perchlorate reduction through an anion-exchange mechanism [35]. The glassy carbon material itself can potentially electro-reduce organic halides, especially alkyl halides, which was partly due to its surface properties [22]. However, modified carbon materials such as boron-doped diamond (BDD) have a negligible activity for reducing organic halides compared to metallic materials [30]. Another way to improve the catalytic activity of carbon materials is to combine a carbon nanostructure with metallic and carbon/metallic electrodes. Reduced graphene oxide (rGO) sheets enhanced the electron transfer for a Pd catalyst, which accelerated the  $H_{ads}$  formation and led to a faster indirect bromate reduction by  $H_{ads}$  [20]. The same trend was observed for Pd/rGO coated on carbon fiber paper [25].

Thus, numerous efforts have been made to develop advanced electrode materials to enhance the electrocatalytic reduction. In this context, the stability and long-term use of the materials are important to be assessed for practical applications. For example, after five successive cycles using a nTiN/Pd/Ni foam electrode, the metallic catalyst was enriched by hydrogen, resulting in swelling and pulverization of the metal-hydrogen system [28]. The interaction between materials in advanced composite materials must be maximized to increase the life span of electrode materials. For a Pd/rGO/CFP composite electrode, the stability was enhanced through strong interaction between surface oxides of rGO and Pd, resulting in a constant reduction efficiency over ten cycles; however, the efficiency decreased after 20 cycles [25].

**Table 1.** Main electrode materials tested for electro-reduction of bromate, perchlorate and organic halides.

Electrode materials tested	Bromate	Perchlorate	Organic halides
<b>Monometallic</b>			
Pt		X ([36])	X ([30])
Zn		X ([18])	X ([30])
Sn		X ([37])	X ([30])
Bi			X ([30])

Pb		X ([29])	X ([30])
Au			X ([30])
Cu		X ([29])	X ([30])
Ag			X ([10], [12], [14], [30])
Cd		X ([29])	
Cr		X ([29])	
Co		X ([29])	
Mo		X ([29])	
Mn		X ([29])	
Sc		X ([29])	
Pd		X ([29])	
V		X ([29])	
Zr		X ([29])	
Ni		X ([38])	
Ti		X ([39], [40])	
Ir		X ([41])	
Rh		X ([42], [43])	
Ru		X ([44])	
Re		X ([45])	
<b>Bimetallic</b>			
Pd/In	X ([33])		
Rh/Cu		X ([46])	
Rh/Ru		X ([46])	
Ag/Cu			X ([13])
Rh/Ni foam			X ([16])
Pt/Ni (foam)		X ([38])	X ([16])
Pd/Ni foam			X ([8], [9], [11], [16])
<b>Modified bimetallic</b>			
Pd-anchored Ni(OH) <sub>2</sub> /Ni			X ([7])
Pd/MnO <sub>2</sub> /Ni foam			X ([9])
nTiN-Pd/Ni foam			X ([8])
<b>Metal/metal oxide-carbon composites</b>			
WC		X ([47])	
Pd/rGO/CFP	X ([25])		
graphene-modified Pd/C	X ([20])		
Pd/GAC particles	X ([20])		
Nanoscale zero valent Fe (nZVI)/activated carbon fiber	X ([17])		
<b>Carbon</b>			
Glassy carbon			X ([30], [22])
Compact graphite			X ([12])
<b>Modified carbon</b>			
Surfactant/carbon nanotubes (CNT)			X ([15])
nanostructured PANOA/glassy carbon		X ([35])	
PANI/glassy carbon	X ([34])		
<b>Metalloid/carbon</b>			
BDD			X ([30])



## **Emerging process combinations for enhancement of removal efficiency**

Some promising combinations between ERPs and other treatment processes have been suggested to further improve the removal efficiency.

The recent synergistic combination of ultraviolet (UV) light with electro-reduction by DET showed promising removal efficiency of PFAS, while minimizing the energy requirement [15]. The hypothesis was that the DET increased the PFAS adsorption efficiency on the surfactant modified-carbon nanotubes (CNT) cathode and lowered the activation energy of the C-F bond under low potential conditions, while the UV produced hydrated electrons that cleaved the C-F bond [15].

The combination of ERPs with advanced electro-oxidation involving high overvoltage O<sub>2</sub> evolution using a BDD anode has been proposed in undivided cells. BDD permits the electro-generation of hydroxyl radicals (<sup>•</sup>OH) that have a high oxidation power [48]. The removal of 1,1,2,2-tetrachloroethane [14] and chloroacetic acid [12] in this hybrid reactor showed considerable enhancement. The ability of oxidized contaminant elimination by electro-oxidation has been highlighted in a recent paper that evidence the oxidation mechanism involving <sup>•</sup>OH with perhalogenocarbon compounds (e.g., CCl<sub>4</sub>) having very high oxidation state [49]. This oxidation pathway was supplemental to the indirect reduction of such compounds by superoxide ion (O<sub>2</sub><sup>•-</sup>). It further emphasized the possible degradation of PFAS by <sup>•</sup>OH. However, such a combination needs to avoid the re-oxidation of reduced oxyanions or reduced organohalogenated byproducts, otherwise the oxidation state will remain the same and there will be no elimination.

Another interesting feature is the combination of electro-reduction with biological processes. A late study proposed the removal of adsorbable organic halogens (AOX) by combining dehalogenating bacteria using AOX as terminal electron acceptors in their metabolism with electrolysis in a hybrid bioelectrochemical process [50]. The electrochemically-assisted bioprocess improved the organohalogenated compounds removal while the decrease of cathodic potential was favorable for methane production. Still, improvements are needed to increase the coulombic efficiency and the scalability.

## **Conclusions and Future Outlook**

This brief review depicts the potential of ERPs to treat primary and emerging oxidized contaminants in water. There are still some challenges to overcome to commercialize these technologies and bring them to full scale, including reducing the cost of electrodes, increasing the stability of modified electrodes, reducing the formation of unwanted byproducts, increasing the process efficiency in real waters, reducing the energy requirements, and increasing the treatment capacity.

The price of electrodes is usually high in the overall cost of ERPs since noble metals are often used to increase the selectivity and activity; however, some studies have shown that cheaper materials such as carbon or nickel could also be efficient. Further progress is needed to improve the cathode surface properties of cheap supports and catalyst materials. Moreover, the electro-reduction efficiency and the possible formation of intermediates must be assessed in real matrices, since many existing studies focus only on ultrapure systems. Other constituents in the water are likely to reduce efficiencies and induce fouling and poisoning of the electrodes. The energy consumption could be minimized by implementing thin film electrochemical reactors with micro-distances between electrodes as previously suggested [12]. However, the treatment capacity in such a configuration is lower than in macro-reactors. Thus, improvements in overall electrochemical reactor design and modeling is needed for scale-up.

Another treatment strategy is the possible valorization of the so-called “pollutants” by making them a source of formation of highly added-value compounds (i.e., waste-to-value). The combination of electro-reduction with electro-synthesis would be promising for treating the wastewater while upgrading the effluent content for subsequent promotion. The electrochemical dehalogenation of cyclopropane derivative for drug

214 synthesis has primary shown interesting opportunities [\[51,52\]](#) and could be adapted for the valorization of  
215 water content.

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389 **Annotations regarding references with special interest (\*) or outstanding interest (\*\*):**

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391 \*[5] →A complete review covering the electrochemical reduction of nitrate, including reaction  
392 mechanisms and pathways, nano-enabled electrodes, combined technologies, and future directions  
393 and scale-up.

394 \*[7] →This research paper proposes the use of a bifunctional cathode using nickel hydroxide that  
395 reduces the need for expensive noble metal catalysts like Pd.

396 \*\*[15] →This research paper describes one of the first successful electro-reduction (i.e.  
397 defluorination) strategies for perfluorooctanesulfonic acid. Electrochemistry is combined with  
398 direct photolysis and adsorption (to carbon nanotubes) for energy efficient reduction to shorter-  
399 chain perfluoroalkyl acids.

400 \*[17] →This research paper proposes a new electrode for bromate electro-reduction using earth  
401 abundant elements, iron and carbon.

402 \*[49] →This research article propose a new mechanism of action for perhalogenocarbon oxidation  
403 by OH radicals in parallel to their reduction by superoxide ion. This novel feature enlarges the  
404 possible treatment of PFAS by both ERPs and electro-oxidation processes.