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# **Decomposition of refractory organics in wastewater by electrocatalytic reduction: Mechanism, challenges and future perspectives**

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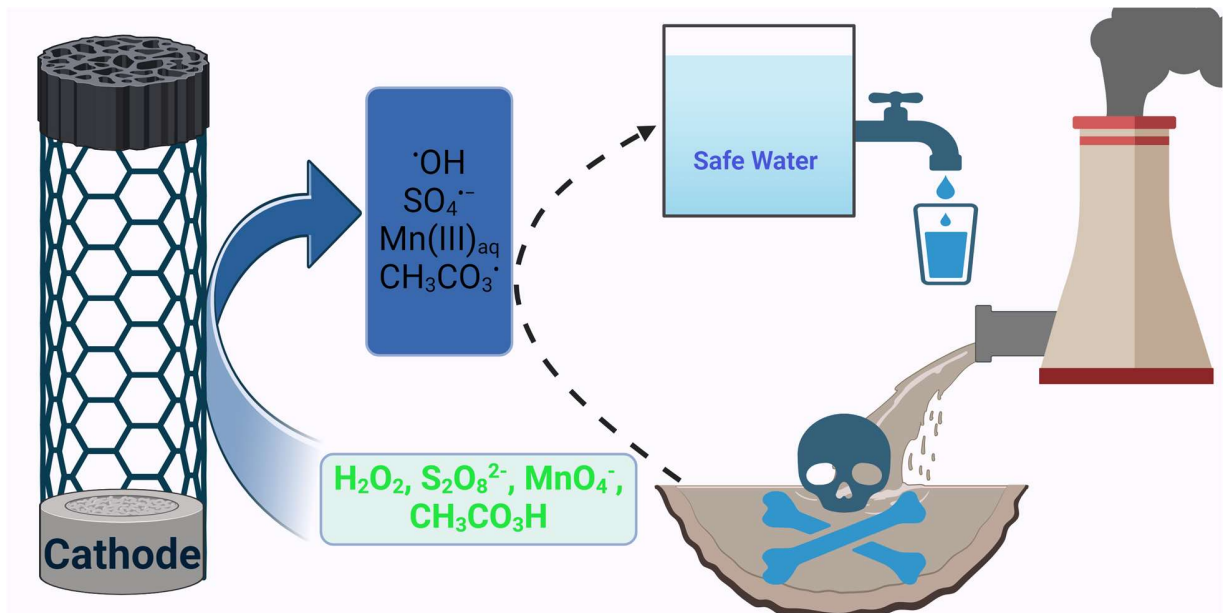
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## **Abstract**

This review provides a brief overview of the electrocatalytic reduction of refractory organic contaminants in water. The electrocatalytic reduction mechanism and principle is thoroughly discussed. The role of various oxidants like ozone (O<sub>3</sub>), persulfate (PS), permanganate (PM), peracetic acid (PAA), and mixed oxidants on the electrocatalytic reduction of refractory organic contaminants was deeply explored. The impact of various operational parameters such as current density, initial concentration of oxidants, solution pH, and water matrices on the electrocatalytic degradation of refractory organic compounds has been investigated in detail. Moreover, the role of electrode materials and electrocatalytic reactor design in the electrocatalytic reduction of refractory organic contaminants in water was also discussed. Finally, the challenges and future perspectives were highlighted for practical implementation of electrocatalytic reduction processes for water treatment.

**Keywords:** cathodic reduction, electrocatalysis, oxidants, reactive oxygen species, water treatment

## Graphical Abstract



## 1. Introduction

Nowadays, water pollution is one of the major concerns that the world is facing due to increased industrialization and discharge of untreated waters to the fresh aquatic bodies. Wastewater coming from various industries such as paper mill [1], textile [2], pharmaceuticals and personal care products [3], as well as landfill leachate [4] contain different types of refractory organic compounds and its highly concentrated debris coming from membrane filtration [5]. It has been reported that the traditional treatment techniques are not very much helpful to deal with such wastewater due to the presence of high levels of toxicity, organics and salinity [6].

Electrochemical processes have gain interests in the last years for their flexibility/modularity, lower footprint as well as their heterogeneous catalytic behavior that could allow avoiding additions of chemicals [7, 8]. Most of the works performed on the electrochemical degradation of refractory organic contaminants in wastewater have been involving anodic oxidation [9]. However, recently the cathodic reduction of refractory contaminants have gained increasing attention [10] due to higher efficiency for some of the highly oxidized pollutants, being also more eco-friendly and economical in certain conditions [10]. Notably, this approach favors many advantages such as no secondary pollution, mild operation conditions and controlled and effective reduction of refractory contaminants [10]. Moreover, in case of regular electro-oxidation of refractory organic contaminants, the formation of toxic halogenated inorganic and organic byproduct formation is a concern [11]. In this regard, the electrocatalytic advanced reduction processes (EARPs) have shown tremendous performance in terms of degradation and mineralization of such refractory compounds via indirect cathodic production of reactive oxygen species (ROS) [12]. There are several advantages of treating refractory organic compounds by EARPs such as convenience in operation and management, environmental friendly, less possibility to get potentially toxic by-products and is therefore, one of the most encouraging and assuring ARPs in the future [12]. Moreover, electrocatalytic reactors are easy to operate and adjustable in small space and this makes EARPs an ideal treatment process to deal with refractory organics at the site of source. It is also pertinent to mention that the thermodynamic potential can be controlled in EARPs, which is helpful in the production of high potential electrons and thus the desired byproduct could be potentially obtained more easily compared to non-electrochemical technologies [12].

Recently, research has been conducted on the EARPs for the treatment of refractory contaminants by direct reduction at cathode as well as via indirect reduction by involving the

reduction of oxygen ( $O_2$ ), ozone ( $O_3$ ), peroxymonosulfate (PMS), persulfate (PS) and permanganate (PM) at cathode, leading then to indirect oxidation of pollutants [13]. These oxidants ( $O_2$ ,  $O_3$ , PMS, PS and PM) can be activated by electrocatalytic methods resulting in the formation of stronger oxidants such as hydroxyl radicals ( $\cdot OH$ ), sulfate radicals ( $SO_4^{\cdot -}$ ) and/or reactive manganese species, that are mainly responsible for the degradation and mineralization of organic compounds.

A recent review presented the electrochemical reduction of hazardous inorganic species such as oxyanions (e.g.,  $NO_3^-$ ,  $ClO_3^-$ ,  $ClO_4^-$ ) that are initially present in wastewater or generated as unwanted by-products during oxidation treatments [14]. However, to the best of author's knowledge there is no recent review that deals with advanced reduction of organic pollutants in wastewater. Therefore, we have decided in this review to focus on the mechanism involved in the EARPs and their associated combinations for organic pollutant removal, as well as on the key process parameters that can affect the EARPs efficiency.

## **2. Principle of most recent EARPs and associated mechanisms**

Currently, research has been more focused towards direct cathodic reduction of refractory contaminants as well as via indirect reduction by oxidants assisted electrocatalytic technologies. In case of oxidants assisted indirect cathodic reduction technologies, the electrons, playing the role of activators are received by the adsorbed oxidants on the surface of cathode and results in the appearance of ROS which then attack the target refractory organic contaminants causing their degradation on the cathode and/or in the aqueous media [15]. In the following sections, mechanisms of these cathodic reduction technologies have been explained.

### **2.1. Direct cathodic reduction**

In the case of direct cathodic reduction, the electrons from the cathode pass through Helmholtz layer of the solution and attack the specific bonds of the target refractory contaminant. For example, Wang and co-workers [16], investigated the direct defluorination of perfluoroalkyl substances (PFAS) over quaternary ammonium surfactant modified cathode. The results of their research showed ca. 99% of PFAS and defluorination was achieved of 79% under low cathodic potential of  $-1.6$  V (vs Ag/AgCl) at the cathode modified by octadecyltrimethylammonium bromide (OTAB). The C-F bond breakage with direct electron transfer via modified cathode played a crucial role in the degradation of PFAS. Similarly, dehalogenation of halogenated

refractory organics has been well documented by direct electron transfer via cathodic reduction [12].

## 2.2. Indirect cathodic reduction by oxidant assisted technologies

This section is focused on the indirect cathodic reduction by emerging and frequently used oxidants like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), persulfate (PS), permanganate and peracetic acid. The detailed description is provided in the corresponding sections below.

### 2.2.1. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

H<sub>2</sub>O<sub>2</sub> is considered as one of the green/environmentally friendly and strong oxidants that decomposes into H<sub>2</sub> and O<sub>2</sub> without producing any toxic side products. Due to these advantages, it is widely used for drinking water disinfection and wastewater treatment [17]. Its production at the surface of cathode occurs via 2-electron oxygen reduction reaction (ORR) (Eq.(1)) [18].



The 2-electron ORR can be attained via two 1-electron reactions as shown by Eqs. 2 and 3.

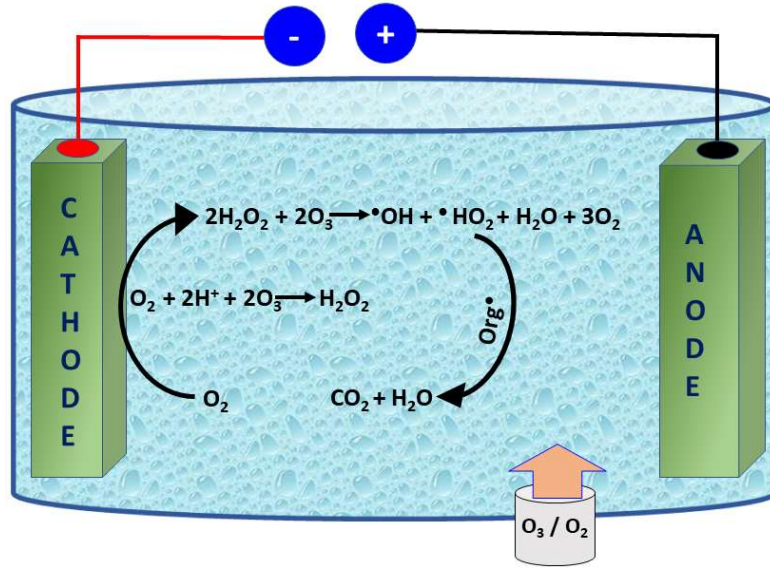


Consequently, by changing the adsorption energy of  $\bullet\text{OOH}$  and lowering the probability of O-O bond breakage, the selective generation of H<sub>2</sub>O<sub>2</sub> can be made possible [19].

Similarly, Ozone (O<sub>3</sub>) is a powerful oxidant and is frequently used for treatment of wastewater [20]. The main advantage of O<sub>3</sub> is its high selectivity towards functional groups having double bonds, amines and aromatic rings [20]. Sometimes O<sub>3</sub> is combined with H<sub>2</sub>O<sub>2</sub> for the treatment of wastewater. The H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> mixture is called peroxone. During wastewater treatment by peroxone, H<sub>2</sub>O<sub>2</sub> can decompose O<sub>3</sub>, resulting in the formation of  $\bullet\text{OH}$ , and  $\bullet\text{HO}_2$  (Eq. 4), which then attack the target contaminant causing its mineralization [21].



Recently, a more novel technology known as electro-peroxone process generates H<sub>2</sub>O<sub>2</sub> electrochemically at cathode [21]. The carbon-based cathode reduces the O<sub>2</sub> and generates *in-situ* H<sub>2</sub>O<sub>2</sub> which then reacts with the dissolved O<sub>3</sub>, resulting in the formation of  $\bullet\text{OH}$  for the destruction of refractory organic contaminants [21]. The schematic sketch of electro-peroxone process is shown in **Figure 1**.



**Figure 1.** Scheme of the electro-peroxone process for the degradation of refractory organics.  
(Reproduced with permission from [21]. Copyright 2023, Elsevier).

### 2.2.2. Persulfate (PS)

The electrocatalytic activation of PS, called electro-persulfate (E-PS) process, has been introduced recently [22]. This novel method produces less sludge and thereby reducing the reactor volume and thus the expenditure cost [23]. In E-PS process as shown in **Figure 2**,  $\text{SO}_4^{\cdot-}$  can be generated at cathode and is known as cathodic activation of PS (Eq. 5). In addition, PS can be regenerated back at anode, as shown by Eq. (6).

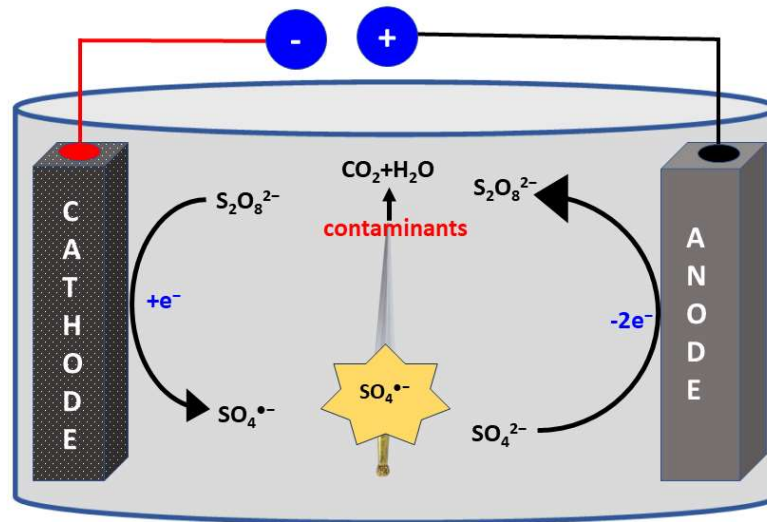


The E-PS process can thus generate  $\text{SO}_4^{\cdot-}$  and  $\text{SO}_4^{2-}$  that causes degradation of the persistent refractory organic contaminants [24]. In literature, both cathode and anode have been documented to trigger PS and are also referred to as radical and non-radical activation in Eqs. (7) (at cathode) and (8) (at anode), respectively [25].



In Eq. (8), CNT corresponds to carbon nanotube, while “\*” represents non-radical activation.

The mechanism and effective activation of PS is greatly associated with the nature of electrode and the operating conditions, which is deeply discussed in the later section.

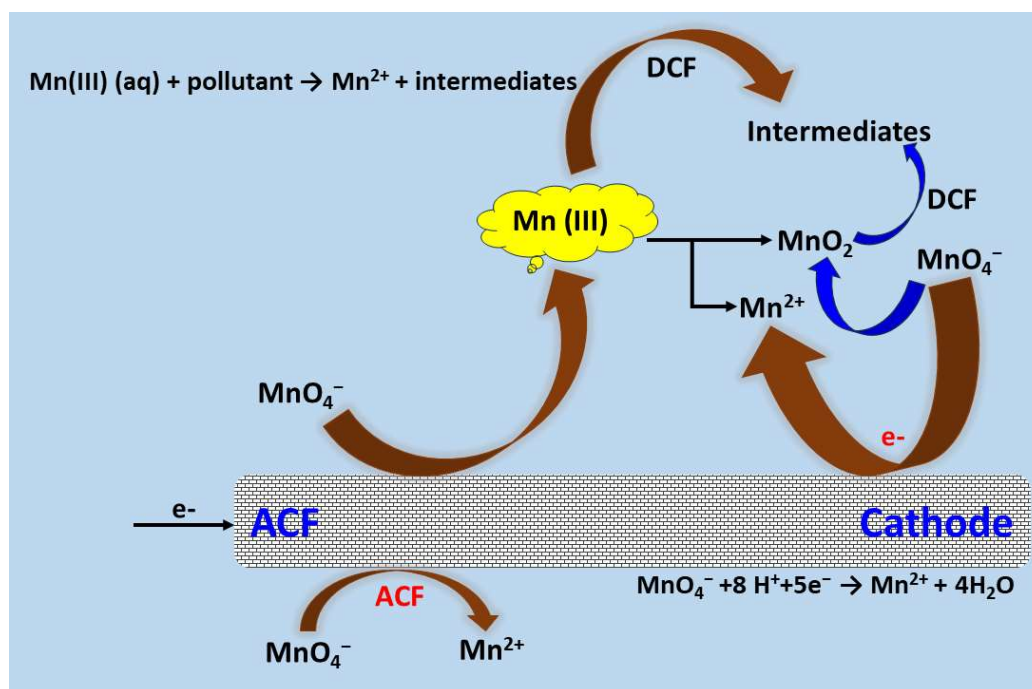


**Figure 2.** Scheme of the E-PS process for the degradation of refractory contaminants (Reproduced with permission from [24]. Copyright 2023, Elsevier).

### 2.2.3. Permanganate

PM is an extensively applied oxidant for the treatment of wastewater owing to its comparatively low cost, easy and safe storage, advantageous transport, and no known resulting unwanted disinfection byproducts after the treatment [26]. However, only a few studies have been performed about the electrocatalytic activation of PM for the degradation of refractory contaminants. Zhu et al. [27] performed the degradation of diclofenac (DCF) by electrocatalytically activated PM using an activated carbon fiber (ACF) as cathode (E-ACF-PM). As depicted in **Figure 3**, the degradation mechanism of DCF by E-ACF-PM involved the following steps: (i) PM was initially reduced by both ACF and electrons to produce  $Mn^{2+}$ , (ii) afterwards, the free electrons from ACF cathode resulted in the formation of  $Mn(III)_{aq}$ , (iii) then  $Mn(III)_{aq}$  attacked the DCF, causing its degradation and also to the partially dissociated  $Mn^{2+}$  by disproportionation reaction or by reaction with electrons. Moreover, their study also showed that  $Mn(III)$  was constantly produced in E-ACF-PM process for the degradation of DCF [27]. In

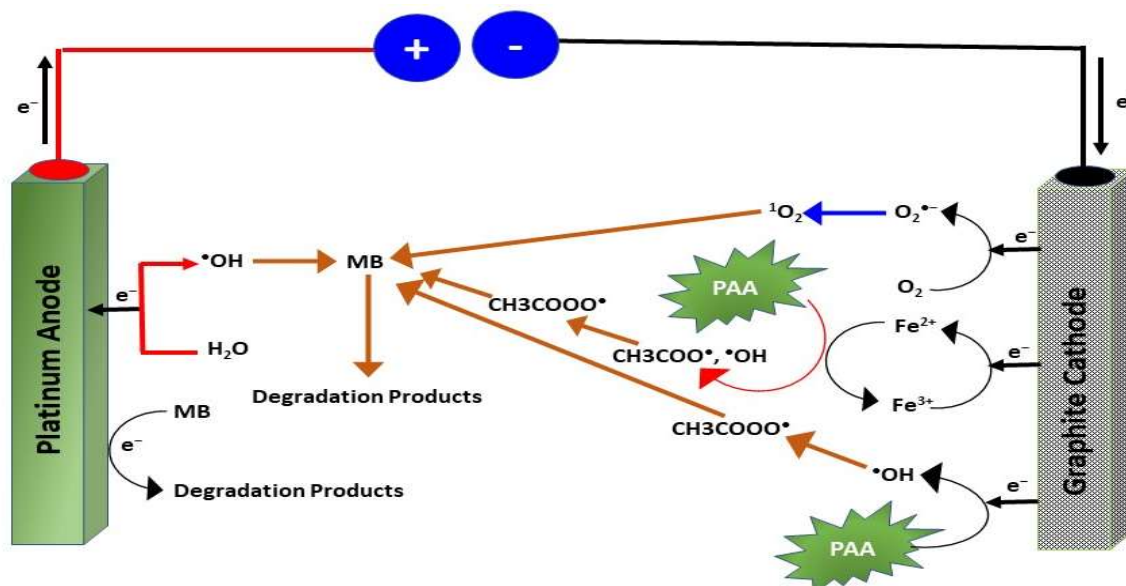
conclusion, the reactive manganese species (e.g.,  $\text{Mn}^{2+}$ ,  $\text{Mn(III)}_{\text{aq}}$ ) are accountable for the enhanced degradation of DCF. Moreover, it has been proven that the operating conditions like the initial concentration of  $\text{Mn}^{2+}$ , PM, applied current density, initial solution pH, and the initial amount of contaminant can affect the degradation performance of E-PM- $\text{Mn}^{2+}$  process [28]. It is noteworthy to mention here that E-PM- $\text{Mn}^{2+}$  process can be applied at scalable levels [28] and  $\text{Mn}^{2+}$  can be recycled in the system [28]. Similarly, Zhang and co-workers [29] performed the degradation of DCF via cathodic reduction of Mn (VII) to  $\text{MnO}_2$ . The proposed mechanism involved first, the reduction of Mn(VII) to Mn(III) at cathode. Afterwards, Mn(III) disproportionated to form Mn(II) and  $\text{MnO}_2$ . Meanwhile,  $\text{O}_2$  is reduced at cathode via a two-electron transfer giving  $\text{H}_2\text{O}_2$ , which helps in the formation of  $\text{MnO}_2$  by reduction of Mn(VII). Additionally, the resulted Mn(II) can also cause reduction of Mn(VII) to Mn(IV). Therefore, the cycle of Mn(VII),  $\text{MnO}_2$  and Mn(II) is continuous as long as there is enough residual Mn(VII).



**Figure 3.** Mechanism of electrocatalytic degradation of DCF by Mn(III)aq produced in E-ACF-PM process (Reproduced with permission from [27]. Copyright 2019, Elsevier).

#### 2.2.4. Peracetic acid

PAA is widely used for water disinfection due to its high oxidation capability (1.96 V vs. standard hydrogen electrode), less toxic by-products formation, handy operation/storage and low cost [30]. It has been proven that PAA alone is less effective in degradation of refractory organic contaminants due to its selectivity towards organic compound oxidation [31], therefore it is of utmost importance to investigate the activation of PAA for the generation of reactive oxidizing species to achieve excellent degradation of refractory organic contaminants. Recently, Yuan et al. [32] activated PAA by electro-Fenton process using graphite plate as cathode according to the mechanism detailed in **Figure 4**. The results of their study showed that PAA could be activated via electrocatalytic electron transfer from cathode producing  $\cdot\text{OH}$ ,  $\text{CH}_3\text{CO}_2\cdot$  and  $\text{CH}_3\text{CO}_3\cdot$ . Secondly,  $\text{Fe}^{2+}$  performs a synergistic role in the activation of PAA and can also generate  $\cdot\text{OH}$ ,  $\text{CH}_3\text{CO}_2\cdot$  and  $\text{CH}_3\text{CO}_3\cdot$ . At the same time,  $\text{Fe}^{2+}$  is regenerated via cathodic reaction and performs a beneficial role in the continuous activation of PAA. Furthermore, the dissolved oxygen is also converted to singlet oxygen ( $^1\text{O}_2$ ) via cathodic reduction. The target contaminant, methylene blue (MB), could also be degraded via anodic oxidation. In conclusion, radical and non-radical pathways are responsible for the electrocatalytic degradation of MB by  $\text{Fe}^{2+}$ /PAA synergistic system.



**Figure 4.** Mechanism of electrocatalytic activation of PAA by graphitic cathode (Reproduced with permission from [32]. Copyright 2022, mdpi).

### 2.2.5. Mixed oxidants

More recently, research has also been performed on the electrocatalytic activation of mixed oxidants by cathodic reduction to enhance the degradation of refractory organic contaminants. Zhu et al. [33] combined electrolysis (E) with both persulfate (PS) and PM to investigate their co-activation roles on cathode and anode. It is noteworthy to mention that in contrary to E-PDS (20%) and E-PM (36%), E-PS-PM successfully degraded ca. 70% of DCF at a reaction time of 180 min. The results showed that electricity meaningfully improved the activation of PS and *in-situ* generation of amorphous MnO<sub>2</sub> via non-radical pathways (<sup>1</sup>O<sub>2</sub> and electron transfer). Moreover, the activated PS helped Mn(II)<sub>aq</sub> to create reactive Mn(III)<sub>aq</sub> and MnO<sub>2</sub>. In another study by Song et al. [34], reactive manganese species and <sup>•</sup>OH were generated by combined E-PM and low additive O<sub>3</sub>. The combined results showed synergistic effects on the degradation of diclofenac, sulfamethoxazole and carbamazepine. It was indicated that slight addition of O<sub>3</sub> (1 mg L<sup>-1</sup> @ 60 mL min<sup>-1</sup>) remarkably enhanced the degradation and mineralization of the target refractory contaminants due to the creation of more reactive manganese species and <sup>•</sup>OH. Mechanistic studies revealed that <sup>•</sup>OH formation in E-PM with low additive ozone occurs via reduction of O<sub>3</sub> at cathode, homogenous manganese catalysis and via heterogenous manganese catalysis. Moreover, the reactive manganese species were generated by direct cathodic reduction of high valent manganese, oxidation of Mn species by O<sub>3</sub> and/or <sup>•</sup>OH. It is also noteworthy to mention that the *in-situ* generated Mn(IV)s played an important role in producing <sup>•</sup>OH and reactive manganese species. Thus, electrolysis with PM and small amount of O<sub>3</sub> could be considered as more sustainable, practical and economically efficient for the scalable remedy of refractory organic contaminants [34].

## 3. Influence of main operational parameters

This section reports the various operational parameters that can influence the electrocatalytic cathodic reduction of refractory organic contaminants.

### 3.1. Current density and initial concentration of oxidants

The current density is considered to be one of the most critical factors in the electrochemical/electrocatalytic reactions as it can easily be controlled [35]. It has been proven that when the electrochemical reactions are not kinetically controlled by the mass transfer of the

target contaminants on the surfaces of electrodes, the reaction rate can be made faster by improving the current density [35]. However, the increase in current density on the other hand facilitates the formation of some side reactions which afterwards affects the energy cost and significantly decreases the current efficiency [35]. Therefore, it is of utmost importance that both the current efficiency and degradation rate should be factored before setting the required current density [36]. Moreover, with the increase of current density, the rate of formation of ROS also increases, which promotes the degradation of target contaminants. More precisely, the current density can also influence the oxidants (PS, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and PM) activation efficiency of electrodes to optimize the rate of formation of various ROS.

Furthermore, it has been documented that the electrocatalytic degradation of refractory organics usually increases with increase in the initial concentration of the oxidant [37]. In this regard, different researchers reported that cathodic activation of oxidants like PS [38], PM [39] and PAA [40] synergistically improved the degradation percentage of target refractory contaminants due to boost in the concentration of ROS and this increase in degradation percentage is directly related with the initial concentration of the applied oxidant dosage. In addition, the decrease of initial concentration led to the increase of mass transfer limitation at a given current density, which therefore decreases the kinetics.

### **3.2. Solution pH**

The pH of electrocatalytic solution greatly influences the degradation of refractory organic contaminants by impacting on the contaminant species structure as well as on the formation of various ROS [41]. For example, Zhao et al. [42] investigated the degradation of ciprofloxacin (CIP) via electrochemical activation of PS using iron incorporated-carbon membrane as cathodic material. The outcomes of their study suggested that the degradation of CIP was more promising at acidic pH than alkaline one. The reason for high degradation at low pH (pH = 3.0) was due to the fact that at low pH, CIP bears positive charge (CIP<sup>+</sup>) and thus has high electrostatic attraction with the electrocatalytically produced SO<sub>4</sub><sup>•-</sup>. However, at high pH values, the conversion of Fe<sup>2+</sup> to Fe<sup>2+</sup> complex and Fe<sup>3+</sup> oxyhydroxides delays the interaction between Fe<sup>2+</sup> and PS to form SO<sub>4</sub><sup>•-</sup> [42]. This results in a decrease in degradation of CIP. Similarly, Wang et al. [43] conducted degradation of phenol by heterogenous electro-Fenton process using cobalt and nitrogen co-doped graphene (Co/N-GO)-modified cathode. The results of their study indicated that degradation

percentage of phenol at pH= 2.0, 4.5, 6.9, 9.0, 11.0, and 12.5 were 100 %, 97.5 %, 97.0 %, 78.0 %, 56.4 %, and 39.5 % within 4 h, respectively. The authors concluded that the electrocatalytic degradation of phenol is favored at acidic conditions because the increased  $H^+$  helps in the intensified formation of  $H_2O_2$  [43].

### 3.3. Water Matrices

Electrocatalytic degradation of refractory organic contaminants are significantly influenced by water matrices due to the presence of varied concentration of organic matters and interfering ionic species [44]. The findings of Peng and co-workers [45] showed that cathodic degradation of p-nitrophenol was greatly influenced by co-existing anions ( $Cl^-$ ,  $HCO_3^-$ , and  $CO_3^{2-}$ ) and organic substances (humic acid (HA)). It is noteworthy to mention that these anions compete with the electrocatalytic reactions and thus inhibit the degradation of p-nitrophenol. Moreover, HA forms electrolyte-HA complex and thereby promotes the cathodic degradation of p-nitrophenol. Nearly identical results were observed by Yuan and co-workers [32], the cathodic degradation of MB via PAA activation with electro-Fenton was greatly suppressed in the presence of  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  and HA as co-existing ions.

## 4. Electrode Materials

The electrode material is of significant importance in the electrocatalytic reduction/oxidation processes. In the case of assisted technologies such as  $H_2O_2$ ,  $O_3$ , PS, PM, PAA and mixed oxidants activated by cathodic reduction, the types of material for both anode and cathode are significant for the electrocatalytic degradation of refractory organic contaminants. The carbonaceous materials have been applied as anode and cathode in the electrochemical system due to their high surface area, excellent electrical conductivity, good stability, resistance to acids/bases and relatively low price [46]. Additionally, carbon-based materials as cathodes are potential substitutes due to their non-toxicity, fewer side reactions and effectiveness in the *in situ*  $H_2O_2$  production via  $2e^-$  ORR [45]. Table 1 reports the most recent research conducted regarding carbon-based cathodes for the electrocatalytic removal of refractory contaminants.

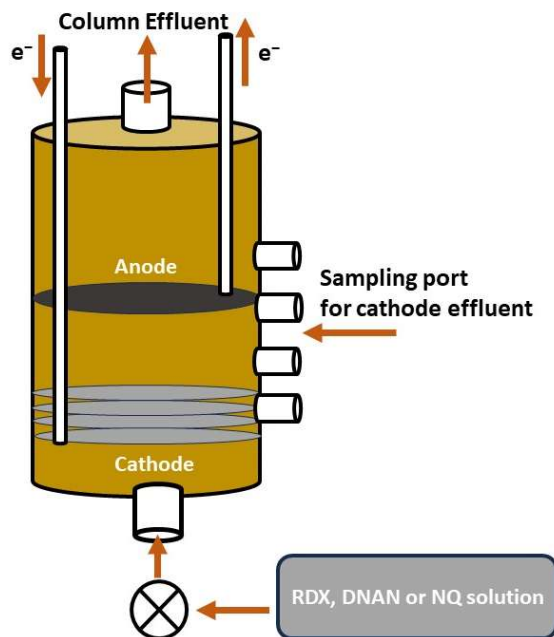
**Table 1.** Electrocatalytic reduction of refractory contaminants by various cathodes.

Cathode	Modifiers	Pollutant/s	Anode	Best % removal of pollutant	Reference
Carbon felt (CF)	Fe-N-C catalyst coated.	levofloxacin, sulfamethoxazole, meropenem and tetracycline	Raw CF	levofloxacin (96.1 within 40 min), sulfamethoxazole (99.7 within 40 min), meropenem (98.8%) and tetracycline (95.5 within 40 min)	[47]
Carbon felt (CF)	Cu <sub>x</sub> O-loaded	iohexol	Ti/Pt	100 within 25 min	[25]
Graphite felt (GF)	modified with CuFe <sub>2</sub> O <sub>4</sub> /Cu <sub>2</sub> O/Cu catalyst	sulfamethoxazole	Pt	100 within 60 min	[48]
GF gas diffusion cathode	modified with acetylene black/PTFE	norfloxacin	Pt	92.2 within 120 min	[49]

## 5. Electrocatalytic reactor design

For a successful electrocatalytic reduction of refractory organic contaminants at the industrial scale, the reactor design is of utmost importance. For example, the reactor design plays a crucial role in the enhanced production of H<sub>2</sub>O<sub>2</sub> by accelerating the mass transport of dissolved O<sub>2</sub> to the surface of cathode [13]. It has been observed that the conventional stirred tank reactors with occupied carbonaceous cathodes results in comparatively low H<sub>2</sub>O<sub>2</sub> concentration due to limited transport [13]. To improve this process, the addition of turbulence promoters in this type of reactor or in flow cells is suggested. In a study by Dehkordi [50], cathodic reduction of highly explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitroanisole (DNAN) and nitroguanidine (NQ) was performed using stainless steel (SS) cathode and downstream titanium/mixed metal oxide (Ti/MMO) as anode in an electrochemical flow-through reactor. The plug flow reactor was composed of all electrodes installed in a vertical acrylic column reactor (208 mL), direct current (DC) source and a peristaltic pump for providing the constant flow rate as shown in **Figure 5**. For convenience, several cathode disks were assembled together. The cathode and anode plates were attached to the DC power supply using titanium rods within Teflon jacket to avoid the cathode-anode junction. The results of their study indicated that contrary to traditional stirred batch reactors with more homogenous environment, the separation of cathode and anode provided the benefit of

local conditions for the effective reductive degradation. It particularly helped facilitating alkaline hydrolysis at the cathode. Furthermore, the results also indicated that the solution flow rate affected the percentage of degradation of the target contaminants.



**Figure 5.** Schematic sketch of the electrochemical flow-through reactor with an upstream cathode and upstream anode. The corresponding electrodes were connected to the titanium rods at one end and to a DC power supply on the other end (Reproduced with permission from [50]. Copyright 2022, Elsevier).

Similarly, in another study, the research group of Scialdone proposed microfluidic reactors for the electrocatalytic reduction of organic halides [13]. The proposed device showed more efficient performance compared to conventional macroreactor by 2-electron ORR at a graphite cathode in a continuous flow mode [13]. These results are of practical significance because graphite is cheaper and of higher stability compared to other carbon electrodes. In another study, the efficient degradation of Acid Orange 7 azo dye was performed by several microreactors connected in series by *in-situ* generating  $H_2O_2$  in continuous mode [13].

## 6. Conclusions, challenges, and future perspectives

This review has thoroughly discussed the principles and electrocatalytic mechanisms for the degradation of refractory organic contaminants. Moreover, the indirect oxidation of refractory organic contaminants by combination of oxidants such as H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, PS, PM, PAA and mixed oxidants with the relevant cathode have also been discussed in detail. In addition, the impact of various operational conditions such as electrode material, current density, pH, initial concentration of oxidants and water matrices that can influence the performance of electrocatalytic reduction of refractory organic contaminants have also been discussed deeply. However, despite so much progress in the electrocatalytic reduction of refractory organic contaminants, there are still some issues that need to be paid more attention:

1) Selection of most appropriate material:

- **Type of reactive species:** it is very important to have adequate knowledge about the type of contaminant to be electrocatalytically treated and the essential reactive species for that contaminant's degradation. For example, it has been documented that PS/CNT system mainly proceeds via non-radical oxidation process induced by surface bounded PS and prefers degradation of phenolic compounds [51]; however, PMS/CNT system is obliged to degrade more refractory contaminants having electron-rich moieties [51]. Therefore, it is of utmost importance that the selection of reactive species is to be made in accordance with the nature of the target contaminant and the resulting byproducts should also be critically examined considering their ecotoxicity.
- **Cost:** the actual expense on electrode material, operation, and oxidant type/chemical needs to be strictly considered for practical implication of any treatment system. Among which chemical cost is of primary importance. For example, the cost of PS is \$ 0.74 per kilogram which is much lower than the cost of PMS (\$ 2.2 per kilogram) and therefore, PS is recommended for scalable applications [51]. Moreover, the electrode material and the synthesis procedure for electrode also play crucial roles in selecting the cost of any electrocatalytic treatment. Generally, it has been considered that carbon-based materials are efficient and cheaper materials for electrode synthesis [52], which could be an advantage over advanced electro-oxidation with boron-doped diamond.

2) Electrode stability needs to be upgraded: it has been reported that metal oxide-based electrodes have problems associated with dissolution of surface-active element and oxidation of

surface oxide layer. Therefore, the long-term stability of the electrode material needs to be improved and more frequently tested. Furthermore, it is also advised to design a new three-dimensional (3D) electrode system that can provide a better contact area for the target contaminant on the electrode surface and thus better mineralization performance.

3) Cathodic electrocatalytic activation mechanism of oxidants should be explored and improved: it is important to significantly improve and further explore the mechanism for the cathodic electrocatalytic activation of oxidants (i.e., O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, PS, PM, PAA and mixed oxidants). For instance, PMS is mainly activated via radical and non-radical pathways for water purification / wastewater treatment. It is documented that transition metals mainly activates PMS to produce free radicals while carbonaceous materials mainly activate PMS via non radical pathway. However, recently, some studies have disclosed contradictory results. For examples, Fe-Mn oxides were documented to activate PMS for the formation of singlet oxygen (<sup>1</sup>O<sub>2</sub>) as non-radical reactive oxygen species (ROS) [53]. Some other studies also reported nearly identical results for other metal oxides such as MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and SnO<sub>2</sub> [53]. Therefore, it is crucial to further explore the mechanism and improve the catalytic/electrocatalytic activation of oxidants.

4) Scaling up of cathode materials: The scaling up of the cathode material is one of the main challenges in widespread applications of electrochemical techniques for the cathodic reduction of refractory contaminants. Generally, in case of wastewater treatment the scale layer on cathode causes decrease of active cathode surface area and thus obstruct the electrocatalytic and mass transfer reactions which leads to decrease in its degradation performance. Furthermore, the scale layer also causes resistance of the cathode and thus redundant energy dissipation. Therefore, some essential improvements in cathode synthesis methods are needed so that the cathode has large surface area, require low voltages and show higher degradation performance.

5) Reactor designs at different scales: It is of high importance to investigate the results at a larger scale and to validate them with the investigations acquired at small scale in addition to recognize the major hindrances that causes the barrier for full scale deployment. To date, larger reactors to treat up to 10 L in batch to recirculation operation mode are scarce but they can provide more decisive information such as reliability of industrial scale implementation as well as more accurate technico-economic study.

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