



Review

Catalytic and electrocatalytic reduction of perchlorate in water
– A review

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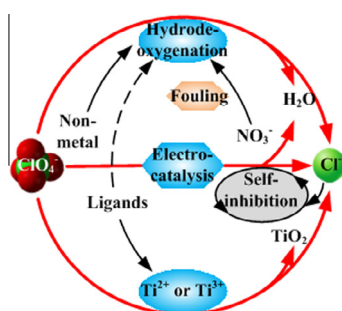
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HIGHLIGHTS

- The mechanisms of catalytic/electrocatalytic reduction of ClO_4^- were elucidated.
- The approaches for improving the removal efficiency were summarized.
- The inhibition and fouling of catalyst and electrode were discussed.
- The advantages and barriers of catalytic/electrocatalytic reduction were prospected.

GRAPHICAL ABSTRACT



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ABSTRACT

Although perchlorate (ClO_4^-) is a trace of emerging contaminant in ground and surface water system, it has a detrimental effect on human health. Catalytic/electrocatalytic reduction has attracted increasing attention to remove ClO_4^- from water because of the fast and permanent conversion of ClO_4^- into innocuous chloride (Cl^-). However, there are also many problems that hinder its implementation, i.e., the lower removal efficiency and catalytic activity to ClO_4^- , the poorer selectivity toward desired reduction products (Cl^-), the easier deactivation of catalysts or electrodes. This paper critically reviews the state of knowledge in the field of catalytic/electrocatalytic reduction of ClO_4^- so as to find better methods to overcome these weaknesses. Specifically, the review summarizes the reported researches related to (1) proposed reaction mechanisms, (2) approaches to improve catalytic/electrocatalytic reduction of ClO_4^- , (3) inhibition and fouling of catalyst and electrode, (4) prospecting the advantages and barriers of this technology. This review will significantly improve the understanding of the detail processes and mechanisms of ClO_4^- reduction by catalysis/electrocatalysis and provide fundamental and useful information and data to scientific research and actual practice.

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1. Introduction

Perchlorate (ClO_4^-), an emerging trace contaminant in drinking water, has been widely detected in the surface and ground water around the world due to its kinetic inertness, high water solubility, and low adsorption to natural substance [1]. ClO_4^- and its salts are the important national strategic chemicals, which are generally used in the manufacturing of rocket propellants and explosives for the defense industries and also in the manufacturing of electronics [2–5]. Researchers had demonstrated that the health risk of ClO_4^- is to disrupt the iodine uptake by thyroid gland, which is very critical to synthesize the thyroid hormones. For human, thyroid hormones play an essential role for growth, metabolism, and the development of central nervous system, particularly for pregnant and fetuses [6,7]. Therefore, ClO_4^- has been listed on the drinking water contaminant candidate lists by U.S. EPA [8].

Various technologies have been developed to remove ClO_4^- from water. These technologies can be grouped into three general categories: (1) biological remediation, (2) physical adsorption, and (3) chemical reduction [9–11]. In the biological remediation, ClO_4^- can be reduced by enzymatic reduction function of microorganisms in the presence of organic or inorganic reducing agents (e.g., hydrogen [12], ethanol [13], lactate [14], methane [15] or acetate [16]). Biological remediation is a cost-effective method for the poor-quality water containing high concentrations of ClO_4^- . However, when the concentration of ClO_4^- is very low in the wastewater, biological remediation is very expensive because a highly reducing environment is required [17]. In addition, the key challenge of biological remediation is the lack of public acceptance for the introduction of microorganisms into drinking water systems. Hence, subsequent treatment processes are required to remove the potential pathogens and nutrients supplied in the biological treatment process [18].

In the physical adsorption methods, activated carbon (AC) and anion exchange resin (IX) are the most common adsorbents for ClO_4^- removal [19,20]. Although AC can effectively remove ClO_4^- , its adsorption capacity and ion selectivity is relatively smaller and weaker in neutral conditions. Therefore, surface modification methods have been widely studied to enhance ClO_4^- adsorption capacity of AC such as pre-adsorption of cationic surfactants [21–23], oxidation [24] and ammonia-tailor [25,26]. Fang et al. [24] reported that the oxidized double-walled carbon nanotubes (DWCNTs) possessed the perfect adsorption capacity for ClO_4^- since numerous of O-containing functional groups were introduced, which served as additional adsorption sites for ClO_4^- adsorption. It had been validated that the adsorption capacity, ion selectivity, and thermodynamic properties of IX are superior to AC for ClO_4^- removal [27]. However, the regeneration of IX is particular difficult and costly. Gu et al. [28] demonstrated that the ClO_4^- adsorbed on IX could be effectively desorbed by the concentrated FeCl_3 -HCl solution. They also found that the desorbed ClO_4^- in the regeneration solution could be reduced to Cl^- using Fe^{2+} as a

reducing agent at 443 K [29]. In general, physical adsorption provides cost-effective and fast method for ClO_4^- removal, but the economy, environment-friendly, and high-efficiency regeneration and disposal technologies should be developed to deal with the ClO_4^- -saturated adsorbents.

Chemical reduction has emerged as a promising treatment technology for ClO_4^- removal. The biggest advantage of this technology is the permanent reduction of ClO_4^- to non-toxic Cl^- species. Based on the thermodynamic point of view, the chemical reduction of ClO_4^- is kinetically hampered because of its high activation energy (120 kJ/mol) [30]. However, the application of catalysts can surmount this energy barrier and effectively realize the reduction of ClO_4^- to Cl^- . The supported-metal-based (e.g., Pd [31], Pt [32], and Pd-Re [33]) catalysts or electrodes can catalyze the formation of adsorbed hydrogen atoms (H_{ads}) and then reduce ClO_4^- on the surface of catalytic metal [33]:



The electrochemical reduction and the catalytic hydrogenation can simultaneously happen in the electrocatalytic hydrogenation (ECH) system. Therefore, the catalytic hydrodeoxygenation can be successfully performed in the ECH system based on the essential similarity of catalytic and electrocatalytic reaction process [34]. Catalyst and electrode plays an important role in the catalytic and electrocatalytic process, respectively. Many catalysts and catalytic electrodes were explored (e.g., poly-electrode [35], Re-based homogeneous catalyst [33], and Pt-Ni [36]). Rusanova et al. [36] found that a trace of Pt deposited on the pure Ni electrode as the cathode could easily reduce ClO_4^- in the region of high negative potentials. Hurley et al. [33] confirmed that ClO_4^- could be rapidly reduced by Re/Pd-C through an oxygen transfer reaction. However, there are also a large number of shortcomings for these methods. The biggest challenges of catalytic and electrocatalytic reduction of ClO_4^- are to improve the adsorption capacity, catalytic activity, selectivity toward desired reduction products (Cl^-), resistant to fouling, and the reusability and stability of the catalysts and electrodes.

This paper focuses on published reports in the area of catalytic/electrocatalytic reduction of ClO_4^- and summarizes the state of knowledge related to (1) proposed reaction mechanisms, (2) approaches to improve catalytic/electrocatalytic reduction of ClO_4^- , (3) inhibition and fouling of catalyst and electrode, (4) prospecting the advantages and barriers of this technology.

2. Proposed reaction mechanisms

Proposed reaction mechanisms or pathways for catalytic reduction and electrochemical treatment of ClO_4^- by several catalysts or electrodes are summarized in Table 1. The reactions can be divided into three categories: (1) hydrodeoxygenation, (2) electrocatalysis, and (3) multivalent titanium ions reduction. Catalyst/electrode and H/electron donor are fundamental substances for all three reaction

Table 1Proposed reaction mechanisms or pathways for catalytic and electrocatalytic reduction of ClO_4^- in water.

Mechanisms	Catalysts or electrodes	Illustration of proposed reaction pathways	Ref.
Hydrodeoxygenation	Re-Pd/C or IX, Pd/N-AC, and Pd/IX (e.g., Re-Pd/C and Pd/N-AC)	$\text{ClO}_4^- \xrightarrow[\text{H}_2]{\text{Re-Pd/C}} \text{ClO}_3^- \xrightarrow[\text{H}_2]{\text{Re-Pd/C}} \text{ClO}_2^- \xrightarrow[\text{H}_2]{\text{Re-Pd/C}} \text{ClO}^- \xrightarrow[\text{H}_2]{\text{Re-Pd/C}} \text{Cl}^-$	[33]
			[55]
Electrocatalysis	Pt-Ti, Zn, and Pt-Ni (e.g., Zn)		[61]
Multivalent titanium ions reduction	Ti^{2+} and Ti^{3+} (e.g., Ti^{2+})	$\text{ClO}_4^- \xrightarrow{\text{Ti}^{2+}} \text{ClO}_3^- \xrightarrow{\text{Ti}^{2+}} \text{ClO}_2^- \xrightarrow{\text{Ti}^{2+}} \text{ClO}^- \xrightarrow{\text{Ti}^{2+}} \text{Cl}^-$	[42]

categories. Monometallic catalysts have been generally used for reducing some oxyanions (e.g., BrO_3^- [37], NO_3^- [38], and NO_2^- [39]), whereas ClO_4^- reduction always requires a secondary promoter metal. Common promoter metal in ClO_4^- reduction is Re [33]. Choe et al. [40] reported that the reduction rates of ClO_4^- by Re/Pd catalyst linearly depended on the Re content from 0 to 6 wt%. In the electrocatalytic reduction of ClO_4^- process, the adsorbed ClO_4^- on the electrode can be reduced by the adsorbed hydrogen atoms (H_{ads}), which are formed through catalytic reduction of the adsorbed H_2O when a constant cathodic current is imposed on the cathode [41]. Both Ti^{3+} and Ti^{2+} species are strong reducing agents, which can directly react with many oxyanions such as NO_3^- [42] and BrO_3^- [43]. It had also been demonstrated that Ti^{2+} and Ti^{3+} could act as reductants and electron donors for ClO_4^- reduction [44]. In addition, for all reactions, reaction intermediate products including ClO_3^- , ClO_2^- , and ClO^- anions are kinetically much less stable than ClO_4^- and they are completely reduced to Cl^- once they produced from the reduction of ClO_4^- [45,46].

To enhance the adsorption capacity, metal dispersion, facilitate handling, and phase separation, catalytic metals are often loaded onto support materials. Common supports for ClO_4^- reduction are AC [47] and IX [48] because of the often-cited advantages, including large surface area, low cost, good adsorption ability, and catalytic activity for a series of redox reactions.

The accurate characterization of catalysts and electrodes is crucial to understand the reaction pathways and mechanisms of catalytic and electrocatalytic reduction of ClO_4^- . Characterization tools include X-ray diffraction (XRD) for submicrometer particles and crystallinity, dynamic light scattering for the particles of micrometer, X-ray photoelectron spectroscopy (XPS) for the elements type and oxidation state, energy dispersive X-ray spectroscopy (EDX) for the composition of catalyst, scanning electron microscopy (SEM) for physical morphology, and transmission electron microscopy (TEM) for morphology and size of catalysts and electrodes supported nanoparticles [49,50]. High energy X-ray adsorption methods are used for local catalysts or electrodes geometric and/or electronic structure study [51]. Voltammetry, chronoamperometry, and impedance spectroscopy techniques are generally used in analysing electrochemical properties and reaction mechanism of electrocatalysis [41,52,53]. In this review, we

mainly discuss their application in the investigation of reaction mechanisms, catalyst deactivation, modification methods, and reaction rates in catalytic and electrocatalytic reduction of ClO_4^- .

2.1. Hydrodeoxygenation

H_2 is commonly a colorless and odorless gas and it can be activated by metallic catalysts and then serves as a good reducing agent for ClO_4^- reduction. Wang et al. [54] studied 78 catalytic systems to remove ClO_4^- from dilute solutions using H_2 as reducing agent. It was found that ClO_4^- could be reduced to Cl^- by H_2 assisted with metallic catalysts and the Ti-TiO₂ was the most efficient catalytic system. These results clearly indicate that catalytic reduction using H_2 is a potential approach to remove ClO_4^- from water. In addition, an adsorption/catalysis bifunctional material (Pd/N-AC) had been developed to remove ClO_4^- [55]. As shown in Fig. 1, this reaction pathway includes two stage, being adsorption and catalytic reduction. During the adsorption part, the ClO_4^- adsorption capacity of Pd/N-AC is enhanced due to the presence of the positively charged N-functional groups, which provide increased number of adsorption sites for ClO_4^- adsorption. Subsequently, the ClO_4^- adsorbed on carbon surface can be effectively reduced to Cl^- by the supported Pd clusters in H_2 atmosphere.

H_2 is also widely used in ClO_4^- reduction by heterogeneous catalysis. This reaction mechanism is characterized by the sequential oxygen atoms removal from ClO_4^- through hydrogenation to H_2O . Oxygen atom transfer (OAT) from ClO_4^- to the catalytic metal lowers the redox state of the chloro-oxyanions. The roles of catalytic metals in monometallic and bimetallic catalysts are to (1) dissociate H_2 to form activated H and (2) facilitate H_2O formation from the abstracted oxygen atoms. For instance, the Re-Pd bimetallic heterogeneous catalyst had been broadly investigated for ClO_4^- reduction with H_2 in the controlled aqueous environments [33,40,56–59]. The proposed mechanism is illustrated in Fig. 2. The Fig. 2 reveals that the Re-Pd/C + H_2 catalytic reaction is a cyclic process. The Pd presents as nano-crystallites dispersed over the carbon surface and the varying amounts of oxo-rhenium species are deposited on the carbon surface [59]. The function of Pd is to bind and dissociate the adsorbed H_2 , forming Pd-adsorbed atomic hydrogen (Pd- H_{ads}), which can then spill over to the higher

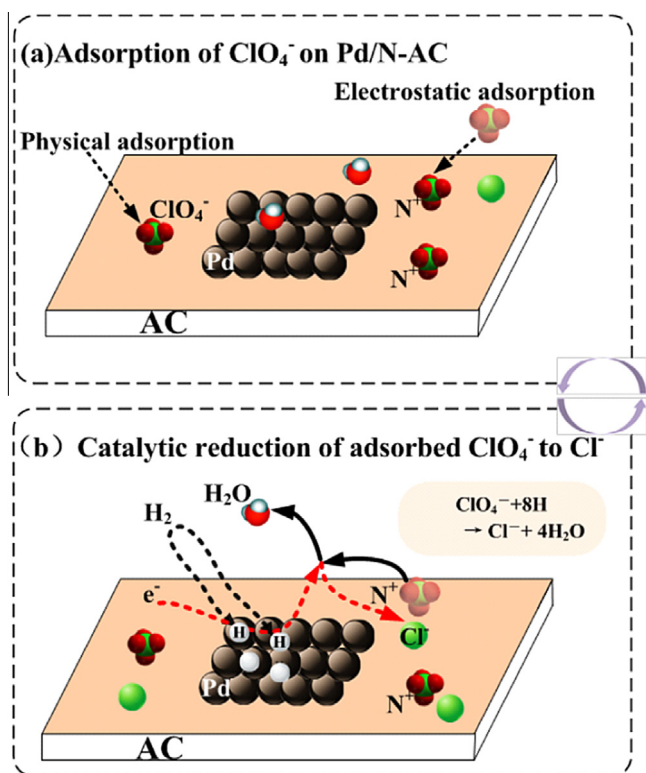


Fig. 1. The reaction pathway of ClO_4^- reduction on Pd/N-AC. Adapted from Ref. [55].

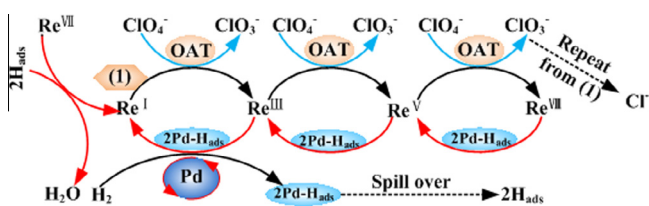


Fig. 2. The proposed mechanism of ClO_4^- reduction on Re-Pd/C. Adapted from Ref. [59].

oxidation state Re species [33]. When the higher oxidation state Re reacts with $2\text{Pd-H}_{\text{ads}}$, it will be reduced to lower oxidation state and then dissociate H_2O , which provides an open site on the Re center to combine ClO_4^- [33]. XPS data indicates that the Re cycles between the highest oxidation state (Re^{VII}) and lower oxidation states (Re^{V} , Re^{III} , and Re^{I} et al.) [40]. The catalytic cycle process will finally complete as the lower oxidation state Re species successively abstract an oxygen atom from ClO_x^- ($x = 1, 2, 3, 4$), yielding a reduced Cl^- product and an oxidized Re species. Hurley and his co-worker [33] found that the reduction rate of ClO_4^- induced by Re/Pd-C catalyst was dependent on the pH. They thought that the proton assisted in the complexation and activation of ClO_4^- and the hydrogen-bonding interaction with one of the ancillary ClO_4^- oxygen atoms would be help to stabilize the intermediate by providing enzyme-like binding site.

In addition, Choe et al. [59] demonstrated that Re^{I} monomeric species were more reactive with ClO_4^- than the species of Re^{V} cluster. This result can be explained as the followings. 1) The OAT reaction between ClO_4^- and Re^{I} OH is faster than those between ClO_4^- and $\text{Re}^{\text{V}}\text{O}_5$. 2) The re-reduction of Re from the higher oxidation state to the species of Re^{I} monomer is faster than to the species of Re^{V} cluster because the Re^{I} monomeric species are closer to the Pd surface during the catalytic cycle reaction process. The rate of ClO_4^- reduction can be greatly influenced by the Re because the Re centers are

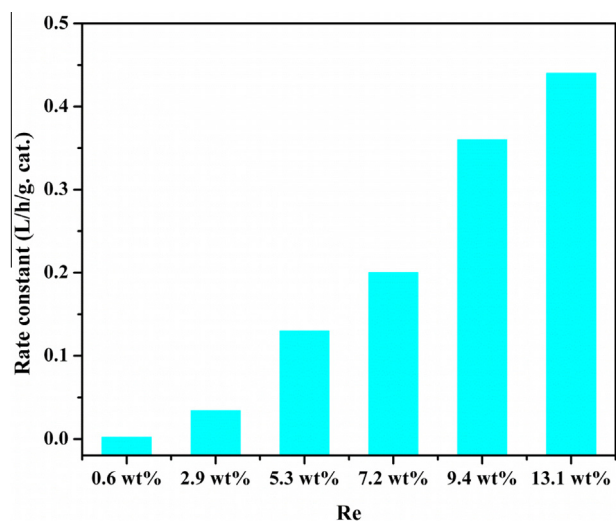


Fig. 3. Calculated pseudo-first-order rate constants for ClO_4^- reduction as a function of the weight percent of Re in the catalyst. Data cited from Ref. [33].

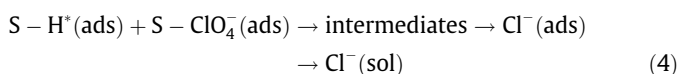
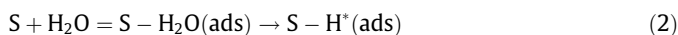
the key determinants of the ClO_4^- reduction process. Choe et al. [40] reported that the positive electronic environment of Re centers (metal active sites) might promote the reaction rate by enhancing the rate-determining OAT step in the catalytic cycle reaction system. Hurley et al. [33] found that the reduction rate constants of ClO_4^- increased when the content of Re in the catalyst increased from 0.6 to 13.0 wt% (Fig. 3).

2.2. Electrocatalysis

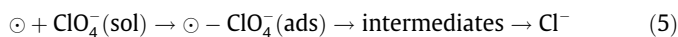
HClO_4 and its salts, particularly NH_4ClO_4 , are always used as supporting electrolytes in various electrochemical studies in the past decades since they have a wealth of merits, being inert, stable, and resistant to reduction. However, according to previous reports, it can be found that ClO_4^- can be subject to reductive attacks induced by Rh [41], Ti [42], Zn [60], and Pt [36] electrodes. Electrocatalytic reduction of ClO_4^- has drawn more attention because of the permanent reduction of ClO_4^- to non-toxic Cl^- in a clean way.

This reaction mechanism can be explained by two fundamental types of possible categories: (I) involving protons and/or hydrogen, (II) involving free-metal site.

The pathway of mechanism (I):



The pathway of mechanism (II):



where sol refers to the components in the solution phase, while ads denotes that the species is adsorbed. S stands for the active site of the catalyst surface. \odot represents a free active site. The intermediates include ClO_3^- , ClO_2^- , and ClO^- anions.

According to mechanism (I), it should be assumed that the reactions start with the adsorption of H_2O (Eq. (2)) and ClO_4^- (Eq. (3)) onto the electrode and quickly reach dynamic equilibrium [61]. When a constant cathodic current is applied on the electrode, the

adsorbed H_2O can be reduced to the adsorbed hydrogen atoms ($\text{S-H}_{\text{ads}}^*$). The reaction between the $\text{S-H}_{\text{ads}}^*$ and an adsorbed ClO_4^- (S-ClO_4^- (ads)) has been recognized as the rate-limiting step in the complicated stepwise reduction process [41]. As a consequence, H^* plays a primary role in the whole process of electrocatalytic reduction of ClO_4^- [62,63]. Meanwhile, it should be noticed that the electrocatalytic reduction of ClO_4^- can be realized without the production of any stable intermediates or side products (Eq. (4)). The electrocatalytic reduction rate of ClO_4^- is dependent on the type of catalytic metal and its density [61]. Wang et al. [61] investigated the electrocatalytic reduction of ClO_4^- by 18 metals supported on the stainless steel mesh in the electro-dialytically assisted catalytic reduction system. It was found that the ClO_4^- reduction rate followed the order: $\text{Cd} > \text{Pt} > \text{Cr} > \text{Mo} > \text{Sc} \gg \text{Rh} > \text{Ru} \sim \text{Sn} > \text{Pd} > \text{V} \sim \text{Ti} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Zr} > \text{Co} > \text{Cu} > \text{Pb}$. The electrocatalytic reduction of ClO_4^- by metal loaded on the stainless steel mesh is a typical of surface reaction. So increasing the amount of catalyst density on the stainless steel mesh can promote the reduction rate of ClO_4^- because of the specific catalyst surface area increased. However, further enhancing the catalyst density will make metallic element partially convert to metal oxide, which hinders the reduction reaction.

However, some researchers found that although the reduction rate of ClO_4^- on metal electrode kept a measurable level at potentials, the concentration of H^* on the electrode surface was very low, which suggests that H^* may unlikely play an important role [41]. Hence, they supposed that the rate-key step of reaction should be the reduction of the adsorbed ClO_4^- with the participation of a free adsorption site in its neighborhood [41]. As depicted in mechanism (II), the adsorption of ClO_4^- is an elementary step in the overall reduction. The reduction process begins with decomposition of the adsorbed ClO_4^- if a free active site (\odot) is in its neighborhood and the reduction of intermediates can be neglected (Eq. (5)). Many researchers observed the reduction of ClO_4^- and ClO_3^- under the same experimental system using voltammetry, chronoamperometry, and impedance spectroscopy. They confirmed that the reduction rate of ClO_3^- was much higher than that of ClO_4^- . Therefore, it can be concluded that the ClO_4^- to ClO_3^- transformation is the rate-determining step of the reduction ClO_4^- [36,41]. On the other hand, it also can be speculated that the concentration of active sites on the electrode is determined by Eq. (6).

2.3. Multivalent titanium ions reduction

Ti can exist in the form of several redox states. Metallic titanium (Ti^0) is not an effective reductant due to the formation of a tight oxide film on the surface [64]. However, Ti^{2+} and Ti^{3+} are sufficient strong reductants, which have the thermodynamic ability to reduce ClO_4^- [65]. This reaction pathway is illustrated in Fig. 4. The reaction pathway includes three steps. The first step is the adsorption of ClO_4^- on the surface of Ti electrode. It is well-known that the adsorption capacity of the un-polarized Ti electrode for ClO_4^- is low. However, Wang et al. [42] demonstrated that if the Ti electrode was polarized through imparting Ti surface anodic current, its adsorption capacity for ClO_4^- could be enhanced

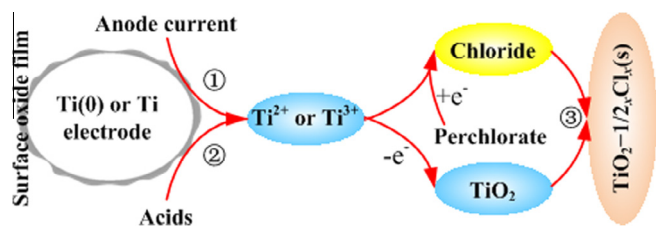


Fig. 4. ClO_4^- reduction on multivalent titanium ions: ① pitting corrosion of the titanium electrode; ② dissolving metallic titanium; ③ forming $\text{TiO}_2-1/2_x\text{Cl}_x(\text{s})$ complexes.

due to the presence of the highly positively charge on the electrode surface. Several publications had reported the adsorption of ClO_4^- on the electrode surface. Fawcett et al. [66] confirmed that ClO_4^- could be adsorbed on the polarized Hg electrode. Jusys et al. [67] speculated that the double layer region on the Au electrode surface contained almost 8% of the adsorbed ClO_4^- .

The reducing agents of multivalent Ti ions (Ti^{2+} and Ti^{3+}) can be readily prepared by pitting corrosion of the titanium electrode [42,68] and dissolving metallic titanium (Ti^0) [69]. For the pitting corrosion of the titanium electrode, there is a traditional point of view that the current and pitting corrosion will increase with increasing of applied potential. However, Lee et al. [65] found that the average current significantly decreased as potential increased. The research results presented that the different thicknesses of surface oxide films were formed on the titanium electrode surface, resulting in lower pitting corrosion and current [70]. For the dissolving metallic titanium (Ti^0), low pH must be maintained and the amount of Ti^{2+} produced is dependent on the type of the used acidic and the amount of Ti^0 . Park et al. [69] reported that the amount of Ti^{2+} produced using HCl and H_2SO_4 increased as the amount of Ti^0 increased. When the same initial dosage of Ti^0 was used, HCl produced more Ti^{2+} than H_2SO_4 .

As displayed in Fig. 4, the reaction of ClO_4^- with Ti^{2+} and Ti^{3+} species is a complex process. The Ti^{2+} and Ti^{3+} can directly react with ClO_4^- , leading to produce a series of intermediate chloroxyanions and ultimately Cl^- [42]. Simultaneously, Ti^{2+} and Ti^{3+} will be oxidized, forming TiO_2 on the Ti electrode surface. Park et al. [71] investigated the effects of titanium type, ionic strength, and metal and solid catalysts on ClO_4^- degradation using aqueous multivalent titanium. The results indicated that the ClO_4^- - Ti^{3+} reaction rate was not enhanced in the presence of high ionic strength, but improved with the increase of acid concentration. Amadei et al. [72] found that the formation of complexes between Ti ions and ClO_4^- was prior to ClO_4^- reduction, which accelerated the electron transfer for the ClO_4^- reduction. Wang et al. [42] proposed that Cl^- was the mainly end product but the chlorine mass was imbalance in this process. The XPS results suggested that $\text{TiO}_2-1/2_x\text{Cl}_x(\text{s})$ complexes were formed on the surface of Ti electrode, which could be attributed to some chlorine doped into the TiO_2 structure.

3. Approaches to improve catalytic/electrocatalytic reduction of ClO_4^-

How to enhance the removal efficiency of ClO_4^- and improve the catalytic activity of catalysts and electrodes is the main focus of the recent research. Several approaches have been proposed: electro-dialytically assisted catalytic reduction (EDACR), non-metal doped with catalyst surface, complex with ligands. The mechanisms of each method and their merits and drawbacks are listed in Table 2 and discussed in detail in the followings.

3.1. Electro-dialytically assisted catalytic reduction

Over the past decades, electro-dialysis (ED) has been widely used for wastewater cleanup as a separation method [73,74]. ED is an electro-membrane technique based on the transport of the objective ions through selective ion-exchange membranes (anion or cation exchange membranes) at different potential. It had been validated that ClO_4^- could be successfully removed by electro-dialysis reversal (EDR) and electro-dialytically assisted catalytic reduction (EDACR) system [75,76]. Wang et al. [76] found that the electro-dialytically assisted catalytic reduction (EDACR) system could reduce ClO_4^- to Cl^- at initial ClO_4^- concentrations of 10–100 ppm under ambient conditions. This method superimposes an electro-dialysis process with a catalytic medium that serves as a

Table 2
The approaches to improve catalytic/electrocatalytic reduction of ClO_4^- .

Methods	Improvements/mechanisms	Drawbacks	Ref.
Electrodiallytically assisted catalytic reduction	<ul style="list-style-type: none"> Reducing the activation barrier Enhancing adsorption of ClO_4^- at the vicinity of catalytic medium (CM) 	<ul style="list-style-type: none"> Costly Handling in extreme low concentration is difficult The imposed potential and catalytic electrode could be significant factors in influencing the treatment 	[76]
Non-metal doped with catalyst surface	<ul style="list-style-type: none"> Forming H_{ads} for ClO_4^- reduction Enhancing adsorption of ClO_4^- Improving the stability of catalysts and electrodes Reducing the activation barrier Serving as catalytic active site 	<ul style="list-style-type: none"> Heavy cost High temperature for preparation and the procedures are complicated Producing by products in the preparation process 	[55,78,79]
Complex with ligands	<ul style="list-style-type: none"> Enhancing the activity and stability of catalysts and electrodes Donating electron density Facilitating the electron change of ClO_4^- Increasing the solution of titanium ions Forming dinuclear complex 	<ul style="list-style-type: none"> The type and the dosage level of ligands were important factors for ClO_4^- reduction The common and simple ligands should be investigated to improve ClO_4^- reduction Introducing new contaminants 	[58,72,82–85]

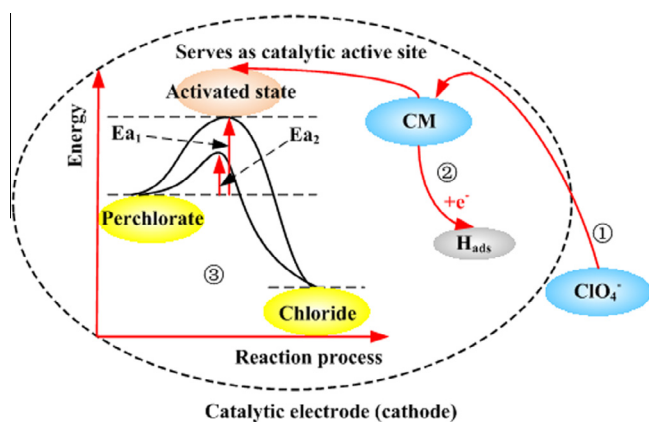


Fig. 5. Mechanisms of electro-diallytically assisted catalytic reduction (EDACR): ① enhancing adsorption of ClO_4^- at the vicinity of catalytic medium (CM) surface; ② forming H_{ads} for ClO_4^- reduction; ③ reducing the activation barrier (E_{a1} : pure catalytic electrode; E_{a2} : EDACR system) for ClO_4^- reduction.

cathode. The reduction of ClO_4^- in EDACR system can be explained by a multiple-step reaction process, including the transfer, the accumulation, and the reduction of ClO_4^- . As shown in Fig. 5, the EDACR system can reduce the activation barrier (E_{a1} to E_{a2}) for ClO_4^- reduction due to the presence of catalytic metal. An additional benefit of EDACR system is that the adsorption of ClO_4^- is enhanced at the vicinity of catalytic medium (CM) (Fig. 5). Therefore, the ClO_4^- adsorbed on the surface of CM can be easily reduced by hydrogen atoms following a step-by-step process to Cl^- ultimately.

The performance of EDACR system could be influenced by the type of catalysts. Wang et al. [76] found that the end products of ClO_4^- reduction were dependent on the type of catalytic metal supported on the electrode. For example, the predominant end product was Cl^- with the Co-Ru electrode. Instead, for the Co-Cr and Co-Rh electrode, the predominant end product becomes ClO_2^- . However, additional applied voltage for electro-dialysis was necessary in EDACR reaction system, which required more energy consumption. In addition, although this system could reduce low concentration of ClO_4^- in the synthetic solutions containing ClO_4^- and NO_3^- , the reaction was apparently limited by the ClO_4^- concentration on the surface of CM, especially when the ClO_4^- concentration was extremely under ultra-low concentrations (<1 ppm).

3.2. Non-metal doped with catalyst surface

In the recent studies, non-metal dopants, such as C, N, and B, doped on catalysts to strengthen the catalytic activity has attracted

more attention [55,77]. Among all non-metal dopants, N-dopant may be more appropriate to enhance the catalytic activity of catalysts or electrodes for ClO_4^- reduction.

Until now, much effort has been aimed to develop the N-doped AC. There are a large number of publications about the preparation of N-doped AC by physical or chemical methods, including thermal treatment with ammonia, oxido-amination, and redox-amination-methylate [78,79]. However, the states of nitrogen doped into the catalyst surface were similar, which mainly were the positively charged N-functional groups such as pyridinic nitrogen, pyrrolic nitrogen, and pyridinic oxide [80]. For example, Byrne et al. [79] published a three-step method to prepare the positively charged N-functional groups modified granular activated carbon (GAC). 1) Introducing oxygen groups onto the GAC treated by nitric acid; 2) incorporating nitrogen groups by thermal treatment in NH_3 flow to replace O with N; 3) quaternizing pyridine-like groups to create positively charged pyridinium-like groups. CV and XPS analysis results indicated that those N-functional groups had electro-chemical activity, so that the modified GAC media could adsorb ClO_4^- and desorb the adsorbed ClO_4^- when they were oxidized and reduced, respectively. The effect of N-dopant on the catalytic efficiency is complex. As presented in Fig. 6, the activation barrier for ClO_4^- reduction can be reduced (E_{a1} to E_{a2}) because of the presence of positively charged N-functional groups. Kim et al. [55] reported that the N-dopant in the Pd/N-AC could cooperate with the adsorbed H_2O synergistically to thoroughly reduce the activation barrier for ClO_4^- reduction. Other benefits of N-dopant

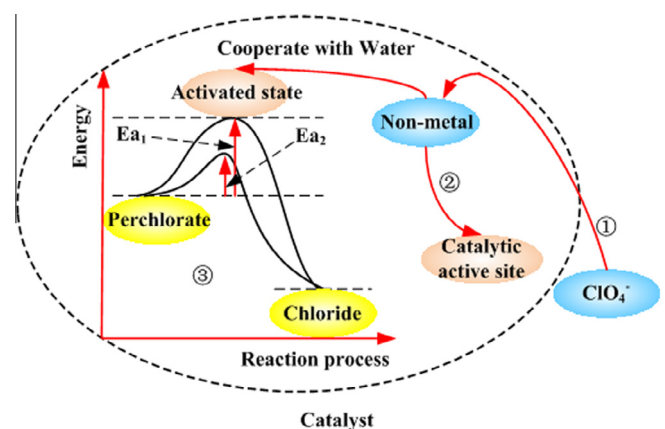


Fig. 6. Mechanisms of non-metal doped with catalytic surface: ① enhancing adsorption of ClO_4^- on the catalyst surface; ② serving as catalytic active sites for ClO_4^- reduction; ③ reducing the activation barrier (E_{a1} : pure catalyst; E_{a2} : non-metal doped catalyst) for ClO_4^- reduction.

include enhancing the adsorption of ClO_4^- and serving as the catalytic active sites for ClO_4^- reduction.

In spite of its benefits for ClO_4^- reduction, there are many weaknesses for N-dopant doped catalysts. N doped into the catalyst surface usually was carried out by heat NH_3 treatment under high temperature and even needed further treatment with methyl iodide, which is highly flammable and harmful to human. These processes may be unfavorable in energy and safety. In addition, the preparation procedures are somewhat tedious and waste gas byproducts are usually produced in the preparation process. Therefore, these modification or preparation methods are difficultly applied in practice due to their severe conditions and heavy cost [78].

3.3. Complex with ligands

More recently, surface modification of catalysts with ligands has attracted considerable interest and also opens an avenue to develop sustainable materials for ClO_4^- removal. Compared with non-modified materials, these modified materials have been demonstrated to have dramatically improved activity and stability [81–83]. The effect of complex with ligands on the catalytic and electrocatalytic reduction of ClO_4^- is showed in Fig. 7. For example, the modification of pyridine ligand for AC powder supported with Re-Pd shows positive effect, which significantly enhances the catalytic degradation rate of ClO_4^- in acid solution [58]. It was proposed that pyridine ligand serves as a resonant ligand, speeding up the reaction process, which not only stabilizes the developing positive character for ClO_4^- reduction via donating electron density to the Re center (Fig. 7), but also minimizes the prospect of deactivating release of perchlorate into solution upon oxidation (Fig. 7). Zhuo et al. [82] investigated the catalytic effects of two Ni^{2+} complexes bearing pyrrolide-imine ligand on thermal decomposition of NH_4ClO_4 . It was found that the Ni^{2+} complex $[[(\text{Fc-NCH})\text{C}_4\text{H}_3\text{N}_2\text{Ni}(\text{2b})$ bearing ferrocene-based pyrrolide-imine N,N-chelate ligand exhibited an excellent catalytic efficiency on the thermal decomposition of ClO_4^- . Amadei et al. [72] studied the effects of some macrocyclic ligands on the reduction rate of ClO_4^- by Ti^{3+} . It was confirmed that the ligands formed dinuclear complexes with Ti^{3+} , which facilitated a 2-electron change (ClO_4^- to ClO_3^-) even though Ti^{3+} is a 1-electron reductant (Fig. 7). The ligand of cyclam is known to form dinuclear complexes if involving bivalent cations [84]. In addition, some relatively common and simple ligands (i.e., β -alanine, oxalate acid, and malonic acid) have been reported to

greatly promote the reduction rate of ClO_4^- by Ti^{3+} . The ligand increases the dissolution of Ti^{3+} due to the formation of complexes between ligands and Ti^{3+} [85].

However, the catalytic activity was often influenced by the type and the dosage level of ligand. Hurley et al. [58] reported that the reduction rate constants of ClO_4^- markedly depended on the pyridine ligand substituent. As summarized in Table 3, for different ligands, the reduction rates increased due to the increasing donor character ($\text{H} < \text{Me} < \text{OMe} < \text{NMe}_2$). Amadei et al. [72] found that a cyclam modified with pendant amine and p-aminobenzyl functional groups (6-amino-6-(4-aminobenzyl)-1,4, 8,11-tetraazacyclotetradecane) showed more effective in ClO_4^- reduction than the pristine cyclam (1,4,8,11-tetraazacyclotetradecane) itself (observed rate constants increased 16 times compared to non-modified cyclam). Wang et al. [85] confirmed that the reduction rate of ClO_4^- by Ti^{3+} was greatly enhanced at M (β -alanine): M (Ti^{3+}) = 3: 1 even in near neutral pH. It should be attributed to the formation of complexes between β -alanine and Ti^{3+} , thus the total soluble Ti^{3+} was significantly improved in the pH 3.5–6. However, the modification with ligands also showed some drawbacks. For example, the new contaminants would be introduced in the wastewater treatment system. In addition, further lab or pilot scale experiments should be employed to investigate the effects of common and simple ligands and coexistence ions such as nitrate, organic and sulfate for practical application.

The reuse and stability of catalysts or electrodes is another main purpose in this studied area. Unfortunately, only a few publications have been reported on the section of reuse and stability of the catalysts. You et al. [55] evaluated the performance of N doped Pd-AC in ClO_4^- degradation through five adsorption-catalytic decomposition cycle experiments. After five repeated experiments, the Pd/N-AC retained high adsorption capacity and selectivity to ClO_4^- . They also found [86] that the ClO_4^- adsorption capacity and selectivity of Pd-IX didn't obviously lose after five adsorption/catalytic decomposition cycle experiments. Nowadays, there are only a few reports on the performance improvement and composition of the modified material after a long time reaction. So it is worthwhile to study the stability and reuse of catalysts and electrodes in view of practical application.

4. Inhibition and fouling of catalyst and electrode

Numerous researches report deactivation and/or fouling of catalysts and electrodes by natural water constituents, including sulfide [87], nitrogenous compounds [57], Cl^- [41], and microbial biomass [88]. Sulfide and other reduced sulfur species (e.g., HS^- and SO_3^{2-}) are the main low molecular weight inorganic anions in natural water, which can deactivate catalysts by forming stable complexes with the catalytic metals and then poison the catalytic active sites [88,89], particularly for Pd based catalysts. In order to understand the deactivation of trace reduced sulfur species for the Re-Pd/C catalyst, Liu et al. [57] used a strong oxidant (NaClO) to pretreat the reduced sulfur species, which can rapidly react with reduced sulfur species [90]. The XPS analysis of the catalyst after treating waste brine indicated no PdS on the catalyst surface. The results directly suggest that reduced sulfur species have no significant effect on catalytic reduction rates of ClO_4^- and unlikely deactivate the catalyst (Re-Pd/C). On the other hand, they also mentioned that the ClO_4^- reduction activity of the Re-Pd/C was severely inhibited by NO_3^- or one of its transient reduction intermediates (e.g., NO and N_2O) [57]. Although the specific mechanism responsible for catalyst deactivation was not explained in detail in their paper, they implied that it should involve the immobilized Re component change in the catalyst rather than the Pd or support material.

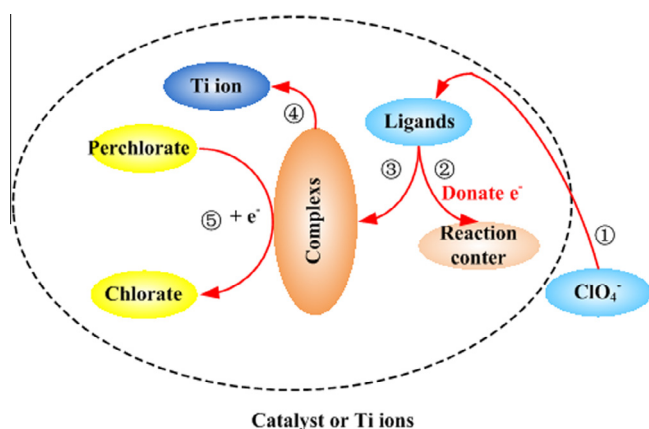


Fig. 7. Mechanisms of complex with ligands: ① enhancing adsorption of ClO_4^- on the catalyst surface; ② donating electron density to speed up the reaction rate; ③ forming dinuclear complexes; ④ increasing titanium ions concentration; ⑤ facilitating electron change (ClO_4^- to ClO_3^-).

Table 3
Comparison of ClO_4^- reduction in different catalytic system.

Reaction style	Catalyst or electrode ^a	pH	Current (mA)	$C_0(\text{ClO}_4^-)$ (mg/L)	$k(\text{obsd})^b$ (h^{-1})	First order rate constant (L/h/g cat.)	Ref.
Catalysis	5.0 wt% Pd-0.6 wt% Re	2.7	–	200	0.0029	0.0015	[33]
	5.0 wt% Pd-2.9 wt% Re	2.7	–	200	0.068	0.034	[33]
	5.0 wt% Pd-5.3 wt% Re	2.7	–	200	0.25	0.13	[33]
	5.0 wt% Pd-7.2 wt% Re	2.7	–	200	0.24	0.20	[33]
	5.0 wt% Pd-9.4 wt% Re	2.7	–	200	0.60	0.30	[33]
	5.0 wt% Pd-13.1 wt% Re	2.7	–	200	0.88	0.44	[33]
	Pd-ReO ₂ (py-X) ₄ /C; X = H	2.7	–	200	0.35	0.20	[58]
	Pd-ReO ₂ (py-X) ₄ /C; X = 4-Me	2.7	–	200	0.34	0.23	[58]
	Pd-ReO ₂ (py-X) ₄ /C; X = 4-OMe	2.7	–	200	0.45	0.45	[58]
	Pd-ReO ₂ (py-X) ₄ /C; X = 4-NMe ₂	2.7	–	200	0.73	0.84	[58]
	5.0 wt% Pd-5.0 wt% Re/C	2.9	–	100	–	0.155	[57]
	5.0 wt% Pd-1.0 wt% In/Al ₂ O ₃ + 5.0 wt% Pd-5.0 wt% Re/C ^c	2.9	–	100	–	0.158	[57]
	Electrocatalysis	Cathode: tin membrane	5.0	20	2.2	0.24	–
Cathode: tin membrane		5.0	20	6.8	0.12	–	[61]
Cathode: tin membrane		5.0	20	100	0.072	–	[61]
Anode: Ti		4.6	20	20	0.036	–	[42]
Cathode: SS mesh coated with Pt-Ti ^d		5.6	10	2.3	0.16	–	[76]
Ti ions reduction	Ti ²⁺ (112 mM)	HCl (4.7 M)	–	467	0.16	–	[69]
	Ti ³⁺ (40 mM)+beta-alanine (120 mM) ^e	2.0	–	100	1.08	–	[85]
Iron reduction	Nano-iron	8.0	–	200	0.0016	8E–05	[92]
	ZVI + microbes	8.5	–	0.5	0.06	6E–04	[94]
	ZVI + microbes	7.0	–	65	0.007	5E–05	[95]

–, Not shown.

^a All reaction temperature with room temperature.

^b The observed rate constants of ClO_4^- reduction.

^c Sequential treatment of waste IX brine (containing 2360 mg/L NO_3^- and 100 mg/L ClO_4^-) with Pd-In and Pd-Re catalysts.

^d Anionic-electrodiallytically assisted catalytic reduction (A-EDACR) system.

^e Reaction temperature: 50 °C.

The Cl^- shows different effects on catalytic and electrocatalytic reduction process. Hurley et al. [33] found that ClO_4^- reduction by Re-Pd/C catalyst was not affected even in the presence of 1000 ppm Cl^- . However, the self-inhibition induced by Cl^- existed in the electrocatalytic reaction process [41]. The adverse effect can be attributed to the relatively strong adsorption capacity of Cl^- ions on the electrode, which results in the self-inhibition of Cl^- . Láng et al. [56] investigated the effect of Cl^- or intermediates (i.e., ClO_3^- and ClO_2^-) on the electrocatalytic reduction ClO_4^- anions by voltammetric experiments and demonstrated that these anions competed with the adsorption sites or occupied the active sites for ClO_4^- reduction. Lee et al. [65] studied ClO_4^- reduction during electrochemically inducing pitting corrosion of zero-valent titanium (ZVT). It was found that Cl^- had both beneficial and detrimental effects on ClO_4^- removal. This conclusion can be explained from two aspects. At the pitting corrosion part, Cl^- can help to induce pitting corrosion of ZVT, which improves the ClO_4^- reduction. However, the presence of Cl^- will hinder the adsorption and reduction of ClO_4^- on the electrode surface.

The deactivation of catalyst or electrode by microbial biomass has not been observed in the most bench-scale studies so far because of the relatively short operation time. While in the long-term lab and pilot natural water treatment tests, microbial biomass fouling has been shown to affect catalyst performance [45]. A series of autotrophic bacteria are able to grow utilizing CO_2 as the carbon source, H_2 as electron donor, and either ClO_4^- or SO_4^{2-} as the terminal electron acceptor under anaerobic conditions [91]. Meanwhile, the SO_4^{2-} in water can be bio-reduced to the product of HS^- , which has strong toxicity to the catalysts. So how to prevent the deactivation of catalysts and catalytic electrodes by microbial growth and microbial metabolic products should be the promising direction in catalytic field.

5. Prospecting the advantages and barriers to implementation

In order to compare the advantages and disadvantages of different reactions, the representative data from recent studies on ClO_4^- reduction are summarized in Table 3, involving the area of catalysis, electrocatalysis, Ti ions reduction and zero-valent iron (ZVI) reduction or it assisted with microbes. ZVI is a stoichiometric reagent that can be directly used for ClO_4^- destruction [92,93]. It may also serve as an electron donor for the microbial reduction of ClO_4^- [94–96]. However, on the first order rate constants basis, the best rate coefficients $k(\text{obsd})$ presented by ZVI systems (0.06 h^{-1}) are several times and even more less than that of other reaction systems. In addition, compared with all reaction systems, Re-Pd/C shows remarkable and reasonable higher reduction rate. It can be concluded that catalysis, electrocatalysis, and Ti ions reduction for ClO_4^- removal have remarkable advantages in terms of removal rate, especially for the catalytic reaction system.

However, ClO_4^- degradation rates for different reaction system have approximate 2 orders of magnitude difference. This phenomenon can be explained by the different reaction conditions such as pH, initial concentration of ClO_4^- , and type of catalysts or electrodes. Besides, in order to gain reasonable ClO_4^- reduction rate, the extreme acidic or high temperature must be maintained. Therefore, they make it difficult to apply these technologies in practical water treatment. To overcome these shortcomings, a double-chamber reaction system separated by Ti membrane hybrid (TMH) had been developed [97]. The membrane adsorbed anions (ClO_4^-) and then transported them to the degradation zone where the presence of Ti^{3+} led a rapid reduction of ClO_4^- . In addition, the inhibition and fouling of catalysts and electrodes have been generally recognized as the primary challenges in the practical application. Future studies should focus on developing

anti-fouling catalysts and designing strategies to mitigate catalyst inhibition. A 2-stage catalytic treatment reaction system had been proved to be a successful strategy to eliminate catalyst deactivation by NO_3^- . Two research groups [98,99] demonstrated that NO_3^- could be stably and effectively reduced by In-Pd/ Al_2O_3 catalyst and finally produced the desired product N_2 . Liu et al. [57] used the In-Pd/ Al_2O_3 to pretreat NO_3^- and avoid the influence of excess NO_3^- on ClO_4^- reduction by Re-Pd/C. The ClO_4^- reduction rate in the NO_3^- -pretreated brine was nearly equal to that observed in the synthetic brine (only NaCl and ClO_4^-) as listed in Table 3.

Finally, from the economics and environmental impacts point of view, any pilot and field scale studies should further incorporate a full assessment of capital and operating costs, which can provide more basic information and data, facilitating the real applications of these technologies. Choe et al. [100] assessed the environmental implications of various technologies for ClO_4^- treatment using life cycle assessments (LCA). Compared with the conventional treatment process, catalytic reduction shows comparable implications and even higher environmental impacts in terms of human health, eco-toxicity, and acidification. Therefore, it is urgent to explore the effective strategy to lower both economic consumables and environmental implications of catalysis/electrocatalysis technology, which would broaden its field of application in practice.

6. Conclusions

Catalytic/electrocatalytic reduction of ClO_4^- has attracted increasing attention during the past decades due to their undisputed advantages such as easy operation and without secondary pollution. This review summarized the proposed reaction mechanisms or pathways in the field of catalytic/electrocatalytic reduction of ClO_4^- , including hydrodeoxygenation by H_2 , electrocatalytic reduction, and multivalent titanium ions reduction. Several approaches to improve catalytic/electrocatalytic reduction of ClO_4^- have been discussed, being electro-dialytically assisted with catalysis, non-metal doped catalyst surface, and complex with ligands. However, these technologies still suffer some technical (e.g., inhibition of catalyst/electrode and extreme reaction conditions), economic, and environmental (e.g., ecotoxicity and acidification) barriers that hamper their application in practice. Further research and development in this field should be focused on how to overcome these shortcomings and barriers and extend the application scope of catalytic/ electrocatalytic reduction.

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