Perchlorate Contamination: Sources, Effects, and Technologies for Remediation

Rosa Acevedo-Barrios and Jesus Olivero-Verbel

Contents

Abstract Perchlorate is a persistent pollutant, generated via natural and anthropogenic processes, that possesses a high potential for endocrine disruption in humans and biota. It inhibits iodine fixation, a major reason for eliminating this pollutant from ecosystems. Remediation of perchlorate can be achieved with various physicochemical treatments, especially at low concentrations. However, microbiological approaches using microorganisms, such as those from the genera *Dechloromonas*, *Serratia*, *Propionivibrio*, *Wolinella*, and *Azospirillum*, are promising when perchlorate pollution is extensive. Perchlorate-reducing bacteria, isolated from harsh

R. Acevedo-Barrios
Environmental and Computational Chemistry Group, School of Pharmaceutical Sciences, University of Cartagena, Cartagena, Colombia

Grupo de Investigación en Estudios Químicos y Biológicos, Facultad de Ciencias Básicas, Universidad Tecnológica de Bolívar, Cartagena, Colombia
e-mail: racevedo@utb.edu.co

J. Olivero-Verbel (✉)
Environmental and Computational Chemistry Group, School of Pharmaceutical Sciences, University of Cartagena, Cartagena, Colombia
e-mail: joliverov@unicartagena.edu.co

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environments, for example saline soils, mine sediments, thermal waters, wastewater treatment plants, underground gas storage facilities, and remote areas, including the Antarctica, can provide removal yields from 20 to 100%. Perchlorate reduction, carried out by a series of enzymes, such as perchlorate reductase and superoxide chlorite, depends on pH, temperature, salt concentration, metabolic inhibitors, nutritional conditions, time of contact, and cellular concentration. Microbial degradation is cost-effective, simple to implement, and environmentally friendly, rendering it a viable method for alleviating perchlorate pollution in the environment.

Keywords Bacteria · Biological treatment · Environmental pollutant · Perchlorate-reducing · Toxicology

Highlights

- Perchlorate is a contaminant generated via natural and anthropogenic processes.
- It is persistent in the environment and exerts endocrine effects on humans and biota.
- Physicochemical processes are useful for treatment of low perchlorate concentrations.
- Bacteria-mediated remediation is suitable for treating perchlorate-polluted sites.
- *Dechloromonas*, *Serratia,* and *Propionivibrio* are promising perchlorate degradators.

1 Introduction

Perchlorate, a chemically stable anion, is a powerful oxidiser (Cao et al. 2019). It possesses a tetrahedral structure containing a chlorine atom surrounded by four oxygen atoms (Murray and Bolger 2014). Perchlorate salts are water soluble, being rapidly incorporated into aquatic ecosystems from polluted soils by runoff-related processes. Once in the water bodies, it bio-accumulates in leafy vegetables (Urbansky 2002). Animals, however, show lower perchlorate concentrations in their tissues, compared to those found in their environment, likely as a result of its hydrophilic nature (Lee et al. 2012) that allows its elimination by the urine.

Perchlorate has recently become a major inorganic contaminant in drinking water; therefore, the EPA has established an official reference dose (RfD) of 0.0007 mg/kg/day perchlorate (EPA 2005; Srinivasan and Sorial 2009).

Perchlorate is considered an endocrine disruptor that affects the thyroid function by inhibiting iodine uptake (Pleus and Corey 2018; Bardiya and Bae 2011). That is the main reason it is necessary to identify its sources, environmental and health effects, as well as to eliminate this pollutant from ecosystems (Kumarathilaka et al. 2016).

Because of the stable chemical structure of perchlorate, using reducing physico-chemical agents is effective especially in the treatment of low concentrations (Srinivasan and Sorial 2009), but it is ineffective for transforming it into less toxic

forms (Ghosh et al. 2014). Microbial perchlorate-reducing technologies may potentially aid in the reduction and degradation of this pollutant (Bardiya and Bae 2011; Wang et al. 2014).

This review provides an elaborate discussion of recent issues regarding perchlorate remediation, attempting to include different perspectives from recent research, in particular the origins and use of perchlorate, its environmental effects on human and biota health, and the various treatment technologies for the control of perchlorate contamination.

2 Origins and Utilisation of Perchlorate

The presence of perchlorate in the environment stems from human activities and natural sources. Drinking water is likely the greatest source of ClO_4^- exposure (Steinmaus 2016; Cao et al. 2019).

Perchlorate enters the body via trophic transfer because it is taken up into plants and crops from contaminated soils and irrigation waters. This is considered one of the most important routes of exposure. For these reasons, the presence of perchlorate in foods has been extensively studied and documented (Zhang et al. 2010; Lee et al. 2012). Perchlorate is present in certain crops such as lettuce, carrots, rice, spinach, and fruits (USFDA 2008; Calderón et al. 2017). Perchlorate is also detected in the milk of cattle, as well as in sausages, ham, instant noodles, fish, meat (Okeke et al. 2002; USFDA 2008; Lee et al. 2012; Maffini et al. 2016), tea, sodas, and tobacco plants and products (ATSDR 2008). Moreover, recent studies have detected perchlorate in breast milk (Wang et al. 2008a; Ye et al. 2012).

Other common routes of exposure include the ingestion and inhalation of domestic dust or atmospheric depositions can act as carriers of contaminants, affecting the health of children and adults. The daily ingested dose of perchlorate can reach 0.7 μg/kg/day for powdered perchlorate, 0.86 ng/mL for perchlorate in tap water, 1.03 ng/mL for perchlorate in bottled water, 536 ng/g for perchlorate in food, 160 ng/mL for inhaled perchlorate that is present in the atmosphere, and 0.03 ng/kg for dermal exposure (Gan et al. 2014; Wan et al. 2015; Kumarathilaka et al. 2016).

2.1 Natural Origin

Perchlorate formation can occur naturally in the environment. Recent findings indicate that perchlorate is continuously formed in the atmosphere by chlorine or sodium chloride reacting with ozone, likely via photochemical processes or electric activity during storms (USFDA 2008; Dasgupta et al. 2005). Other possible sources are volcano eruptions (Simonaitis and Heicklen 1975; Furdui et al. 2018). High

concentrations of perchlorate are found in arid (Murray and Bolger 2014) and/or hypersaline environments (Ryu et al. 2012; Acevedo-Barrios et al. 2019).

The most abundant perchlorate deposits are found in arid regions of South America, particularly in Chile, Peru, and Bolivia, especially in soils from arid and semi-arid regions, where it is usually mixed with calcium carbonate, gypsum, and sodium salts (Murray and Bolger 2014). Deposits containing perchlorate have also been found in Death Valley in the USA (Jackson et al. 2010). These are also rich in sodium and potassium nitrate, being extracted and exported worldwide for nearly 200 years, still generating increased interest (Murray and Bolger 2014).

Interestingly, perchlorate salts have also been found in kelp forests and the Antarctica (Jackson et al. 2010, 2015; Kounaves et al. 2010; Kumarathilaka et al. 2016). The perchlorate and chlorate detected in Antarctic lakes were determined to be of atmospheric origin, where perchlorate concentration is approximately 1,100 μg/kg.

It is known that perchlorate is a pollutant in mined nitrate salts that are used as fertilisers, being this a common pathway to reach soils used for agriculture purposes (Urbansky et al. 2001; Aziz et al. 2006; Sanchez et al. 2006). However, little is known about perchlorate levels in soils fertilised with nitrates and their impacts on agricultural systems and food security (Calderon et al. 2020).

2.2 Anthropogenic Origin

Most of the perchlorate distributed in environmental matrices results from anthropogenic activities. Perchlorate contamination has been increasingly generated by anthropogenic sources, with concentrations of 0.1–35.0 μg/L in drinking water (Blount et al. 2010), 0.1–22.1 μg/L in groundwater, 1.0–2,300 μg/L in surface water (Wu et al. 2010), and 1.0–13 μg/kg in soil (Jackson et al. 2010; Ye et al. 2013). In groundwater, perchlorate contamination may result from rainwater percolating through contaminated sand or soil (ATSDR 2008).

A substantial portion of perchlorate found in ground and surface water is associated with the military industry (Hubé and Urban 2013; Cao et al. 2019), aerospace industry, and manufacture of explosives (Murray and Bolger 2014; Kumarathilaka et al. 2016).

Fireworks, which contain chemicals such as potassium nitrate, potassium chloride, potassium or ammonium perchlorate, coal, sulphur, manganese, sodium, nitrate, strontium, aluminium, barium titanate, and powdered iron oxalate, are one of the main sources of perchlorate pollution in the environment (Wu et al. 2011; Vellanki et al. 2013; Ye et al. 2013).

Perchlorate is found in polyvinyl chloride (PVC) and in Li-ion batteries, in which it is used as dopant material (Interstate Technology Regulatory Council 2005); this indicates that residents and workers at electronic waste-recycling sites are likely exposed to this pollutant. Additionally, perchlorate is a strong oxidiser and is used as a cleaning agent during the production of LCD screens (Her et al. 2011).

Ammonium, lithium, magnesium, and potassium perchlorates are used during manufacture of herbicides and automotive airbag inflators. Potassium perchlorate has been used clinically in 1950–1960 to treat hyperthyroidism (Murray and Bolger 2014). Perchlorate is also utilised in the manufacture of matches, dyes, rubber, and lubricants (Interstate Technology Regulatory Council 2005). Other anthropogenic sources of perchlorate include foundries, road flares, drying and engraving agents, gunpowder, batteries (Wang et al. 2014), disinfectants, bleach, chlorine-based cleaners and chemicals for swimming pool chlorination, electronic tubes, paints, enamels, fertilisers, nuclear reactors, and other materials for commercial use (Interstate Technology Regulatory Council 2005; Agency for Toxic Substances and Disease Registry 2008; Kumarathilaka et al. 2016; Maffini et al. 2016). Additionally, perchlorate is a growth promoter and has been added to thyrostatic medication used for the fattening of livestock (Gholamian et al. 2011).

3 Environmental and Health Effects

3.1 Health Effects on Humans

Perchlorate affects the normal function of the thyroid gland (Murray and Bolger 2014). It inhibits iodine fixation, a process necessary for the production of thyroid hormones, leading to hypothyroidism (Ghosh et al. 2014; Murray and Bolger 2014; Cao et al. 2019). The thyroid gland, considered a major target for perchlorate, plays an important role in the regulation of metabolism and is essential for normal growth and development in children (Bruce et al. 1999; Agency for Toxic Substances and Disease Registry 2008; Bardiya and Bae 2011; Murray and Bolger 2014; Zhang et al. 2016).

Perchlorate can also induce damage to the nervous, reproductive, and immune systems (Gholamian et al. 2011), as well as induce teratogenesis in pregnant women, where it has been found in breast milk, saliva, and urine (Thrash et al. 2007; Zhang et al. 2010). Because it is found in breast milk, perchlorate is dangerous to nursing mothers and infants. Once ingested by the infant, it can impair thyroid function and cause physical and mental disabilities (Morreale de Escobar et al. 2000).

3.2 Effects on Biota

One study has shown that perchlorate is easily accumulated in plants (Andraski et al. 2014). Xie et al. (2014) showed that the rice plant *Oryza sativa* L. is easily contaminated by perchlorate and suggested that perchlorate may inhibit the growth of the plant. Perchlorate also affects chlorophyll content and root systems of *Acorus calamus, Canna indica, Thalia dealbata,* and *Eichhornia crassipes* (He et al. 2013). The study by Acevedo-Barrios et al. (2018) has shown that the survival of freshwater

algae *Pseudokirchneriella subcapitata* is considerably impaired by perchlorate (LC_{50} = 72 mM). However, the exact manner by which perchlorate damages the photosystem is unclear, and further studies are needed to understand its mechanisms of action (Xie et al. 2014).

Environmental perchlorate concentrations of 200–500 μg/L disrupt metamorphosis in amphibians (Goleman et al. 2002), and concentrations ≥500 μg/L cause diverse fish alterations (Schmidt et al. 2012). Perchlorate decreases the number of eggs spawned by the Japanese medaka (*Oryzias latipes*) (Lee et al. 2014), modifies sex ratio and decreases the growth rates of zebrafish (Liu et al. 2008; Schmidt et al. 2012), and causes functional hermaphroditism in *Gasterosteus aculeatus* females. These findings indicate that perchlorate exerts androgenic effects. Other effects of perchlorate on fish include abnormal development of the lateral plates, decreased swimming performance, slow growth rates, and reduced pigmentation (Bernhardt et al. 2011).

In *V. fischeri*, perchlorate-induced toxicity manifests as reduced bioluminescence, whereas in the crustaceans *D. magna* and *E. fetida,* perchlorate exposure disrupts endocrine function and can result in mortality (Acevedo-Barrios et al. 2019). In *E. fetida*, perchlorate can also induce avoidance behaviour, weight loss, decreased production of eggs and hatchlings, malformations, dwarfism, and necrosis. These findings demonstrate that perchlorate toxicity varies according to species (Acevedo-Barrios et al. 2018).

Exposure to perchlorate leads to embryonic hypothyroidism in bird species, such as the Japanese quail (Chen et al. 2008), and affects thyroid function in species such as *Colinus virginianus* and *Anas platyrhynchos* (McNabb 2003). Similarly, perchlorate affects reptiles and mammals such as lizards, mice, rats, and rabbits (USCHPPM 2007).

4 Technologies for Perchlorate Treatment

Perchlorate present in soils contaminates surface and groundwater (Kumarathilaka et al. 2016) and may threaten the ecosystem and human health. Some of the strategies used to remove perchlorate from environment are described below.

4.1 Physicochemical Methods

These reactions are divided into two types: sequestration and transformation. Sequestration reactions include different types of membrane-based separation, ion exchange, and precipitation and transformation reactions include chemical reduction, electrochemistry-based and activated carbon approaches (Coates and Jackson 2009; Ghosh et al. 2014).

Physicochemical methods are promising treatments, especially in the treatment of low concentrations of perchlorate (Coates and Jackson 2009).

4.1.1 Membrane-Based Technologies

Membrane filtration, via reverse osmosis, nanofiltration, and ultrafiltration, has been somewhat effective for perchlorate removal (Ye et al. 2012). Membrane-based techniques can be effective; however, membrane incrustations and high costs present drawbacks to these approaches (Srinivasan and Sorial 2009). Moreover, the rate of perchlorate diffusion decreases with increasing pH due to membrane surface charge becoming more negative (Yoon et al. 2005); and although membrane-based systems can remove various compounds, those can leave residues, requiring additional treatment (Coates and Jackson 2009).

In addition, water treated using this system has to be remineralised with sodium chloride, sodium bicarbonate, and other harmless salts to prevent degradation of the distribution system and render the water appealing to the consumer (Ghosh et al. 2014; Kumarathilaka et al. 2016).

4.1.2 Ion Exchange

Ion exchange is a promising technology for perchlorate elimination, offering a wide variety of strong anion exchange resins highly selective for perchlorate (Chen et al. 2012; Srinivasan and Sorial 2009; Batista et al. 2000). The perchlorate-laden spent resins require regeneration, which results in the production of concentrated brine (Bardiya and Bae 2011) that requires subsequent treatment (Srinivasan and Sorial 2009; Ghosh et al. 2011). The resins utilised in this approach are single-use, rendering this technology incomplete and economically unsustainable for perchlorate elimination (Ye et al. 2012).

The efficiency of this treatment primarily depends on the type of ion exchange matrix and concentration of other ions in the water (Coates and Jackson 2009). If concentration of other ions is higher than that of perchlorate, these other ions can compete for available sites on the resin, thereby reducing the capacity for perchlorate binding (Srinivasan and Sorial 2009).

During water treatment, this technology can produce salt resins in the presence of other anions, which constitutes a drawback. Therefore, for ion exchange, it is necessary to demineralise or remineralise the water being treated, depending on its anion content (Ghosh et al. 2014; Kumarathilaka et al. 2016).

4.1.3 Chemical Reduction

Chemical perchlorate reduction has been studied extensively because numerous metals can reduce perchlorate to chloride. For example, Hurley and Shapley

(2007) developed a bimetal Pd/Rh catalyst that exerts a rapid reduction of perchlorate in the presence of hydrogen, but it showed two limitations: the reaction occurred at a pH less than 3, and requires a pressure of 5 bars (Srinivasan and Sorial 2009). Similarly, Wang et al. (2008b) eliminated 90% of perchlorate ions over 3 days, using hydrogen gas and metallic Ti-TiO_2 catalysts in a pressurised reactor (Srinivasan and Sorial 2009). Despite high conversion yields, the use of this technology in environmental systems is not efficient due to the slow speed of the reaction process, costs, and technical factors (Coates and Jackson 2009; Ghosh et al. 2014; Kumarathilaka et al. 2016). Moreover, chemical reductions can be effective for decontamination of small systems, but cannot be scaled to real conditions in large water-treatment plants (Srinivasan and Sorial 2009).

4.1.4 Electrochemical Reduction

Electrochemical reduction is a promising removal technology because it completely destroys perchlorate without the use of catalysts; however, this approach can be implemented on a large scale (Srinivasan and Sorial 2009).

Historically, perchlorate has been used as an inert electrolyte in corrosion and electrochemical studies. Removing this pollutant through electrochemical approaches is a slow process (Srinivasan and Sorial 2009), rendering them ineffective for perchlorate reduction. Moreover, under environmental conditions, the reactions involved require large surfaces and can be affected by the presence of other reactive and non-reactive species. Although electrochemical processes are not suitable for *in situ* applications, those can be used to treat concentrated solutions (Coates and Jackson 2009; Kumarathilaka et al. 2016; Theis et al. 2002).

4.1.5 Activated Carbon

Granular activated carbon adsorption is simple to retrofit for targeting perchlorate in water and is, therefore, widely used for the treatment of drinking water (Srinivasan and Sorial 2009). This technique, however, is expensive because it has limited capacity for perchlorate adsorption and generates brines that can affect the effectiveness of the process (Na et al. 2002; Parette et al. 2005; Srinivasan and Sorial 2009).

4.2 Biological Treatment of Perchlorate

This technology implements biological systems (such as bacteria, algae, fungi, yeast, and plants) to remove or recover the pollutant from environmental matrices.

4.2.1 Types of Perchlorate-Reducing Bacteria

Perchlorate-reducing bacteria are phylogenetically diverse and include classes such as Alphaproteobacteria, Betaproteobacteria, Gammaproteobacteria, and Deltaproteobacteria, with Betaproteobacteria being the most commonly detected (Wallace et al. 1996; Coates et al. 1999; Bruce et al. 1999; Waller et al. 2004; Ye et al. 2012; Acevedo-Barrios et al. 2019). Although many details remain unknown, the enzymes perchlorate reductase and chlorite dismutase have been marked as critical for the reduction or elimination of perchlorate into Cl^- and O_2 (Youngblut et al. 2016; Xu and Logan 2003).

Table 1 illustrates the variety of currently known perchlorate-reducing species.

Table 1 Genera and species of currently known perchlorate-reducing bacteria

Bacterial genus and species	Percentage of reduction (%)	Environmental conditions and observations	Reference
Nesiotobacter sp.	25	FC, 37°C	Acevedo-Barrios et al. (2019)
Bacillus vallimostis	23	FC, 37°C	Acevedo-Barrios et al. (2019)
Salinivibrio costicola	25	FC, 37°C	Acevedo-Barrios et al. (2019)
Vibrio	14	FC, 37°C	Acevedo-Barrios et al. (2019)
Bacillus	12	FC, 37°C	Acevedo-Barrios et al. (2019)
Staphylococcus	10	FC, 37°C	Acevedo-Barrios et al. (2019)
Alteromonadaceae	30	ST, in presence of nitrate	Stepanov et al. (2014)
Azospirillum sp.	100	AN, 22°C	Waller et al. (2004)
Citrobacter sp.	32	30°C, pH 7, ST (0–5%)	Rikken et al. (1996); Okeke et al. (2002); Wang et al. (2008a)
Clostridium sp.	80	FC, 37°C	Chung et al. (2009)
Dechlorobacter hydrogenophilus	100	37°C, pH 6.5	Thrash et al. (2007)
Dechloromonas agitata	100	AN	Bruce et al. (1999); Sun et al. (2009); Vigliotta et al. (2010)
Dechloromarinus cepa NSS	30	37–42°C, pH 7.5, ST (2.5%)	Bardiya and Bae (2011)
Dechlorospirillum sp.	70	AN, 37°C	Coates et al. (1999); Vigliotta et al. (2010)
Escherichia coli K-12 cepa NAR gen G	90	AN, 37°C	Vigliotta et al. (2010)

(continued)

Table 1 (continued)

Bacterial genus and species	Percentage of reduction (%)	Environmental conditions and observations	Reference
Halomonas halodenitrificans	20	ST (5%)	Logan et al. (2001); Okeke et al. (2002)
Ideonella Dechloratans	90	AN 30°C	Bruce et al. (1999); Lindqvist et al. (2012)
Magnetospirillum magnetotacticum	70	AE, 37°C	Xu and Logan (2003)
Marinobacter sp.	7–11	ST (5%)	Ahn et al. (2009); Stepanov et al. (2014)
Propionivibrio militaris	100	AE, 30°C, ST (5%), pH 6.8	Gu and Brown (2006)
Proteus mirabilis	90	FC, AN, 30°C	Bruce et al. (1999)
Rhodobacter capsulatus	80	FC, 30°C	Bruce et al. (1999)
Serratia Marcescens	100	ST (>15%); pH 4.0 to 9.0	Vijaya Nadaraja et al. (2013); Sankar et al. (2014)
Vibrio dechloraticans	20	FC, AN. Degradation in concentrations of 1, 5, 25, 50, 75, 100, 125, 150, 175, 200 μg/L	Wang et al. (2008a)
Wolinella sp.	99.9	FC, AE, in presence of hydrogen	Rikken et al. (1996)

ST salt-tolerant (percentages of NaCl), *FC* facultative conditions, *AN* anaerobic conditions

4.2.2 Habitats of Perchlorate-Reducing Bacteria

Phenotypic characterisation studies have shown that perchlorate-reducing bacteria exhibit a wide range of metabolic capabilities and can thrive in diverse and extreme environments such as saline lakes, hot springs, and even hyperthermophilic and hypersaline soils (Rikken et al. 1996; Wallace et al. 1996; Coates et al. 1999; Bruce et al. 1999; Logan et al. 2001; Jackson et al. 2012; Matsubara et al. 2016; Acevedo-Barrios et al. 2019). In hypersaline soils, perchlorate is found at 25–2,700 mg/kg; these depositions are due to a shortage of rainfall. Marine soils usually contain bacteria species with biochemical versatility and ability to tolerate salt, being an interesting target for researchers due to the potential reduction of environmental perchlorate (Logan et al. 2001). The reason for selecting this type of environment is that degradation of perchlorate may be carried out using salt-tolerant bacteria (Okeke et al. 2002), although this perchlorate-reduction process could be impaired with increasing salinity (Vijaya Nadaraja et al. 2013; Matsubara et al. 2016).

Currently, no single technology can completely remove perchlorate from drinking water. However, combining the technologies described in this review may be a feasible approach (Srinivasan and Sorial 2009).

For example, combining physicochemical treatments and perchlorate-reducing halophilic bacteria may increase the efficiency of perchlorate reduction, allow the treatment of matrices with high salinity and perchlorate concentrations, and resolve the persistent issue of waste disposal (Xiao and Roberts 2013).

4.2.3 Environmental Requirements for Bacterial Degradation of Perchlorate

In biosorption, the capacity of perchlorate sorption by the microbial system is regulated by several factors. These include environmental factors, such as pH, temperature, salt concentration, presence of metabolic inhibitors or electron acceptors, nutritional conditions, and time of contact; and physiological factors, including type and physiological age of the microorganism, biomass condition, cellular concentration, and mutations in the bacteria being used for reduction (Coates et al. 1999; Logan et al. 2001; Ting et al. 2008). Perchlorate degradation is generally much slower in the pH range of 5.0–9.0 (Wang et al. 2008a; Wan et al. 2016; Zhu et al. 2016).

Reduction is generally inhibited by the presence of nitrate (Coates and Achenbach 2004; Wan et al. 2016) because some reducing microorganisms prefer other electron acceptors over perchlorate (Coates and Jackson 2009). To prevent this, donor species are added in excess to remove non-perchlorate electron acceptors before performing the reduction; this is done because non-perchlorate electron acceptors can activate bacteria that do not degrade perchlorate, which results in inefficient treatment. Oxygen is another inhibitor of microbial reduction of perchlorate because its presence can cause bacteria to utilise donors for oxygen consumption (Coates and Jackson 2009; Xu et al. 2015). Studies have shown that perchlorate reduction should ideally be performed under anaerobic facultative conditions (Shrout et al. 2005; Acevedo-Barrios et al. 2019).

Generally, perchlorate reduction occurs at a temperature range of 10–40°C, but an ideal condition requires temperatures between 28 and 37°C (Coates et al. 1999; Zhu et al. 2016; Acevedo-Barrios et al. 2019). A low salt content (<2% NaCl) in an environment can be a limiting factor. In contrast, reductions have been performed in matrices having salt concentrations higher than 11% (Logan et al. 2001; Okeke et al. 2002).

4.2.4 Biochemical Metabolism of Perchlorate-Reducing Bacteria

Perchlorate-reducing bacteria are omnipresent and easily obtainable from most environments (Coates et al. 1999). These organisms, which show a wide range of metabolic activities (Chaudhuri et al. 2002), contain proteins that can degrade contaminated matrices on-site; unlike other methods, this approach causes minimal physical disturbance around the treated area (Volesky 1999). For these reasons, perchlorate-degrading bacteria can be used for various applications, including

biotechnological processes (Wang et al. 2014), and represent a promising, effective, and economically viable solution for resolving perchlorate contamination (Logan et al. 2001; Acevedo-Barrios et al. 2016, 2019). Perchlorate-degrading bacteria utilise two key enzymes that reduce the activation energy required for perchlorate reduction and use perchlorate as an electron acceptor in their metabolic reactions (Coates et al. 2000; Jackson et al. 2015).

Enzymes, such as perchlorate reductase and superoxide chlorite, carry out the reduction or elimination of perchlorate. A reductase can reduce perchlorate to chlorate, and subsequently, to chlorite, whereas superoxide chlorite changes chlorite to chloride and molecular oxygen. Biological reduction of perchlorate using bacteria completely degrades perchlorate ions into Cl^- and O_2, as shown in Eq. 1 (Xu and Logan 2003; Matsubara et al. 2016; Acevedo-Barrios et al. 2019):

$$\begin{aligned}\left(ClO_4^-\right)\text{ (Perchlorate)} &\rightarrow \left(ClO_3^-\right)\text{ (Chlorate)} \rightarrow \left(ClO_2^-\right)\text{ (Chlorite)} \\ &\rightarrow Cl^-\text{(Chloride)} + O_2 \end{aligned} \quad (1)$$

Equation 1: Perchlorate-degradation pathway

Perchlorate-reducing bacteria are facultative anaerobes or microaerophilic because molecular oxygen is produced as an intermediate of the microbial perchlorate reduction (Rikken et al. 1996; Wallace et al. 1996; Bruce et al. 1999; Coates and Achenbach 2006; Jackson et al. 2015).

4.2.5 Application of Biological Reduction

Biotransformation is a method that contributes to environmental sanitation and involves the removal of perchlorate via microorganisms that selectively retain ions found in the solution. Consequently, these microorganisms either deteriorate these ions into less toxic forms or remove them completely (Logan et al. 2001).

This technology is used for bioremediation in and ex situ and for natural biodegradation. The ex-situ treatment process is suitable for waste that has high concentrations of perchlorate, such as water from facilities that manufacture ammunition. Bioremediation in situ is suitable for reducing concentrations of perchlorate in shallow (<15 m deep) or narrow zones such as groundwater. This technology is cost-effective with respect to transportation of materials, poses low risk for accidents, and does not require bioaugmentation. This approach, which can be used to treat unsaturated zones and soils, stimulates native microflora via the addition of carbon sources and electron donors (Bardiya and Bae 2011); these factors render this method less costly than ex-situ bioremediation (Ye et al. 2012). The use of heterotrophic and autotrophic system for perchlorate removal has also been proposed (Li et al. 2019), combining sulphuric-based autotrophic processes to increase performance and reduce high concentrations of perchlorate.

5 Conclusions

Perchlorate is a contaminant that is generated via natural and anthropogenic processes naturally formed in the atmosphere and likely released during volcanic eruptions (Simonaitis and Heicklen 1975). This compound is persistent in the environment and exerts endocrine effects on humans and biota, affecting thyroid function, growth, and reproduction (Gholamian et al. 2011; Acevedo-Barrios et al. 2018). Physicochemical methods are used to remove perchlorate, but these techniques can only separate this contaminant from matrices, producing residues in the process (Coates and Jackson 2009), but is effective especially in the treatment of low concentrations.

Because perchlorate is kinetically stable and inert at low concentrations, most traditional physicochemical processes are not applicable for the elimination and decomposition of perchlorate ion (Logan et al. 2001). These methods are also costly to maintain and operate, have high energy requirements, and generate excessive amount of brines and resins with high concentrations of the pollutant. Using bacteria that can reduce and eliminate perchlorate is an effective and economically feasible approach (Hatzinger 2005; Acevedo-Barrios et al. 2019).

Among such bacteria, organisms most common at perchlorate reduction belong to the genera *Dechloromonas*, *Serratia*, *Propionivibrio*, *Wolinella*, and *Azospirillum*. These organisms are mostly isolated from adverse environments and degrade 20–100% of perchlorate; their removal efficiency depends on pH, temperature, salt concentration, presence of metabolic inhibitors, nutritional conditions, time of contact, cellular concentration, and other factors, indicating that bacteria-mediated remediation of perchlorate is a suitable method for controlling this type of contamination.

Research is currently underway to find a novel technology to remediate perchlorate, and although microbial reduction and ion exchange technologies are used, a combination of several technologies is required to remove this pollutant from ecosystems (Srinivasan and Sorial 2009).

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