

Integration of microbial reductive dehalogenation with persulfate activation and oxidation (Bio-RD-PAO) for complete attenuation of organohalides

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HIGHLIGHTS

- Bio-RD-PAO can effectively and extensively remove organohalides.
- Bio-RD alone effectively dehalogenate the highly-halogenated organohalides.
- PAO alone is efficient in degrading the lowly-halogenated organohalides.
- The impacts of PAO on organohalide-respiring microbial communities remain elusive.
- Bio-RD-PAO provides a promising solution for remediation of organohalide pollution.

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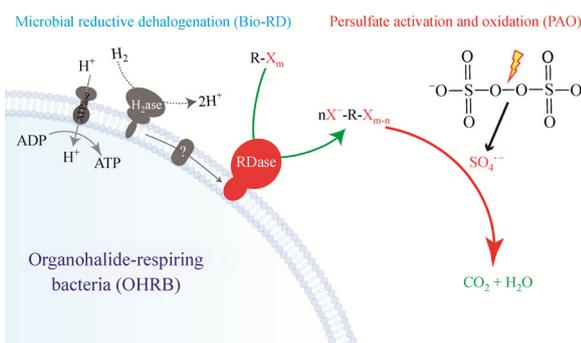
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GRAPHIC ABSTRACT



ABSTRACT

Due to the toxicity of bioaccumulative organohalides to human beings and ecosystems, a variety of biotic and abiotic remediation methods have been developed to remove organohalides from contaminated environments. Bioremediation employing organohalide-respiring bacteria (OHRB)-mediated microbial reductive dehalogenation (Bio-RD) represents a cost-effective and environmentally friendly approach to attenuate highly-halogenated organohalides, specifically organohalides in soil, sediment and other anoxic environments. Nonetheless, many factors severely restrict the implications of OHRB-based bioremediation, including incomplete dehalogenation, low abundance of OHRB and consequent low dechlorination activity. Recently, the development of in situ chemical oxidation (ISCO) based on sulfate radicals ($\text{SO}_4^{\cdot-}$) via the persulfate activation and oxidation (PAO) process has attracted tremendous research interest for the remediation of lowly-halogenated organohalides due to its following advantages, e.g., complete attenuation, high reactivity and no selectivity to organohalides. Therefore, integration of OHRB-mediated Bio-RD and subsequent PAO (Bio-RD-PAO) may provide a promising solution to the remediation of organohalides. In this review, we first provide an overview of current progress in Bio-RD and PAO and compare their limitations and advantages. We then critically discuss the integration of Bio-RD and PAO (Bio-RD-PAO) for complete attenuation of organohalides and its prospects for future remediation applications. Overall, Bio-RD-PAO opens up opportunities for complete attenuation and consequent effective in situ remediation of persistent organohalide pollution.

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1 Introduction

Organohalides refer to an extensive range of organic

compounds containing one or more substituted halogen atoms, including tetrachloroethylene (PCE), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (Jugder et al., 2015). The massive use of these compounds in industry and agriculture, coupled with their natural

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formation results in their environmental prevalence (Fiedler, 2007; Sadowsky et al., 2013; Maucourt et al., 2020). Owing to their strong chemical stability, recalcitrance to degradation, global transfer and bioaccumulation and bioaugmentation via food webs, organohalides are raising concerns about their side effects on public health and ecosystems (Johnson-Restrepo B et al., 2005; Xu et al., 2006; Lu et al., 2019). For example, Japanese rice bran oil contaminated with PCBs and PCDFs in 1968 caused the death of 400,000 birds and 500 people (Uenotsuchi et al., 2005). In addition, the reproductive and immune function of more than half of the population of killer whales (*Orcinus orca*) are affected by PCBs, even though PCBs have been banned for more than 40 years (Desforges et al., 2018).

To remove organohalides from contaminated environments, many different remediation strategies have been developed, including both biotic and abiotic remediation methods: (1) physical strategies, e.g., high temperature and pressure, air sparging, electroremediation, active carbon adsorption and filtration (Ranck et al., 2005; Yang et al., 2005); (2) chemical methods, e.g., photocatalysis, metal catalysis, electrochemical catalysis and persulfate activation and oxidation (PAO) (Mascolo et al., 2008; Cai et al., 2020); and (3) biological techniques, e.g., phytoremediation and bioremediation (Wallace and Kadlec, 2005; Martinez et al., 2007). Almost all of the above-mentioned remediation methods can be conducted in situ and *ex situ* (pump-and-treat). In particular, in situ bioremediation employing a diverse range of organohalide-respiring bacteria (OHRB) is a comparatively effective, economical and eco-friendly way to remove organohalides from anaerobic/anoxic contaminated environmental matrices, including soil, sediment and groundwater (Heavner et al., 2019). At these anaerobic/anoxic bioremediation sites, organohalides are generally highly oxidized and electrophilic, which support OHRB-mediated organohalide respiration as electron acceptors (Wang et al., 2018; Willemin et al., 2020). Thus far, many lineages of OHRB have been identified to employ different reductive dehalogenases (RDases) to remove halogens from a variety of anthropogenic organohalides, including chloroethene, chlorophenols, chlorobenzenes, PCBs, PBDEs, PCDD/Fs and PFOCs (Fincker and Spormann, 2017; Maillard and Willemin, 2019). In their organohalide-respiring electron transport chains, OHRB employs hydrogen or organics as electron donor and organohalides as electron acceptor to harvest energy for cell growth (Atashgahi et al., 2018). Nonetheless, dehalogenation-generated organohalides become reduced and nucleophilic, which may no longer support organohalide respiration of OHRB as electron acceptors and result in accumulation of lowly-halogenated organohalides (Chen and He, 2018; Dam et al., 2019). Taking microbial reductive dechlorination of PCBs as an example, *Dehalococcoides mccartyi* strains (e.g., CG1,

CG4, CG5, JNA, CBDB1 and 195) as obligate OHRB dechlorinate hexa- and hepta-CBs in PCB commercial mixtures (e.g., Aroclor 1260) to di-, tri- and tetra-CBs (Adrian et al., 2009; Wang and He, 2013; LaRoe et al., 2014; Wang et al., 2014; Zhen et al., 2014), and their further dechlorination to biphenyl was seldom observed.

Chemical oxidation based on advanced oxidation processes (AOPs) with highly reactive free radicals (OH^\cdot , 1.9–2.7 V_{NHE} ; $\text{SO}_4^{\cdot-}$, 2.6–3.1 V_{NHE}) has been extensively applied to degrade various types of recalcitrant contaminants into innocuous CO_2 and H_2O (Oh et al., 2016; Guvenc et al., 2021). OH^\cdot is a short-lived free radical (with a half-life time of $<1 \mu\text{s}$), which is generally produced in situ during ozone- and UV-activation of H_2O_2 or other precursors (Bokare and Choi, 2014). By contrast, the highly reactive ($V_{\text{SO}_4^{\cdot-}} = 2.6\text{--}3.1 V_{\text{NHE}}$ vs $V_{\text{OH}^\cdot} = 1.9\text{--}2.7 V_{\text{NHE}}$) and long lived (with a half-life time of 4 s) sulfate radicals are produced in situ by cleaving the peroxide bond of persulfate molecules via energy or electron transfer reactions (Waclawek et al., 2017; Ike et al., 2018). Moreover, persulfate-AOP has the following advantages over H_2O_2 -AOP: (1) a higher radical formation rate (Anipsitakis and Dionysiou, 2004; Zhiyong et al., 2013); (2) more flexible activation methods (Duan et al., 2018; Zhu et al., 2019a; Li et al., 2021); (3) less dependence on operational parameters, including pH and initial loading concentration (Luo et al., 2015; Lutze et al., 2015); and (4) a lower cost of persulfate production, storage and transportation, e.g., peroxydisulfate (PS) costs \$0.74/kg in contrast to \$2.2/kg peroxymonosulfate (PMS) and \$1.5/kg H_2O_2 (Zhang et al., 2014). In addition, PMS has two “dead” sulfate salts in its structure that cannot be activated, yet persulfate is stable and soluble in water, enabling wide application of persulfate (Zhang et al., 2015; Ike et al., 2018). Consequently, the comparatively longer lifetime, higher reactivity and lower cost of persulfate-AOP relative to H_2O_2 -AOP enable the former method to be an optimal option for the remediation of lowly-halogenated organohalides at in situ remediation sites. Consequently, PAO may complement the OHRB-mediated microbial reductive dehalogenation (Bio-RD) process for extensive cleanup of pollutants (Nam et al., 2001; Hrapovic et al., 2005; Kulik et al., 2006; Ndjou'ou et al., 2006; Sahl and Munakata-Marr, 2006; Lu et al., 2010; Venny et al., 2012; Sutton et al., 2014a; Sutton et al., 2014b; Nemeček et al., 2019; Xia et al., 2020). Nonetheless, these studies employed in situ chemical oxidation (ISCO) as a pretreatment process to enhance the bioavailability and biodegradability of pollutants. In this review, we propose the consequent integration of Bio-RD and PAO (Bio-RD-PAO) for complete mineralization of organohalides, and summarize recent research progress of Bio-RD and PAO, as well as their pros and cons. We also discuss the feasibility and challenges of applying Bio-RD-PAO and its prospects for future remediation applications.

2 Microbial reductive dehalogenation (Bio-RD)

2.1 Organohalide-respiring bacteria and their organohalide respiration

Phylogenetically diverse organohalide-respiring bacteria (OHRB) employ organohalides as electron acceptors to conserve cell growth energy (Adrian and Löffler, 2016). After isolation of the first organohalide-respiring bacterium, *Desulfomonile tiedjei* (DeWeerd et al., 1990), extensive studies on the isolation and characterization of OHRB for their potential and limitations in the bioremediation of organohalides have resulted in a long list of well-characterized OHRB, which can be classified as obligate and non-obligate OHRB based on their metabolic flexibility (Hug et al., 2013; Maillard and Willemin, 2019). The obligate OHRB, including *Dehalococcoides* and *Dehalogenimonas* of Chloroflexi, are restricted to using H₂ as electron donors and organohalides as electron acceptors in their respiratory electron transport chains. In contrast, non-obligate OHRB of Proteobacteria (e.g., *Geobacter*, *Desulfuromonas*, *Anaeromyxobacter* and *Sulfurospirillum*) and Firmicutes (e.g., *Desulfitobacterium*) are versatile in their metabolism and utilize a wide range of electron donors (e.g., hydrogen, formate and lactate) and electron acceptors (e.g., sulfate, nitrate and organohalides) for their respiration (Fincker and Spormann, 2017).

The key enzyme in OHRB to catalyze halogen removal from organohalides is reductive dehalogenase (RDase). A typical RDase homolog (*rdh*) gene cluster contains *rdhA* and *rdhB* genes encoding the catalytic subunit and a membrane-anchoring protein, respectively, as well as other regulatory genes (Türkowsky et al., 2018). For organohalide respiration, OHRB employ several sets of functional enzymes to derive and transfer electrons from H₂ or other organics (e.g., dehydrogenases) to organohalides (e.g., RDases). Nonetheless, specific organohalide-respiratory electron transport chains for electron transfer from electron donors to acceptors can be grouped into quinone-independent populations (e.g., *Dehalococcoides* relying on menaquinones as electron shuttles) and quinone-dependent populations (e.g., non-obligate OHRB of Proteobacteria and Firmicutes) (Kublik et al., 2016; Schubert et al., 2018).

2.2 Bio-RD of organohalides

OHRB have multiple RDase-encoding genes and are consequently capable of removing halogens from various aliphatic and aromatic organohalides (Table 1). Chloroethenes have been widely used as industrial solvents and result in environmental contamination, of which trichloroethene (TCE) and vinyl chloride (VC) are ranked #16 and #4, respectively, on the Substance Priority List (SPL) (Mayer-Blackwell et al., 2017). Although phylogenetically

diverse microorganisms dechlorinate chloroethenes, *Dehalococcoides* and *Dehalogenimonas* are the only isolated and characterized lineages for the complete dechlorination of chloroethenes to benign ethene (Löffler et al., 2013; Wang and He, 2013; Mao et al., 2017; Yang et al., 2017b; Marcet et al., 2018; Zhao and He, 2019). At contaminated sites, co-existing pollutants or natural matter can affect the extent of OHRB-mediated dechlorination. For example, nitrous oxide (N₂O), a common pollutant in groundwater, can decrease dechlorination rates and result in incomplete dechlorination of chloroethenes (Yin et al., 2019). In addition, sulfate reduction products, as well as sulfur oxyanions (e.g., S₂O₃²⁻ and SO₃²⁻), may inhibit microbial reductive dehalogenation (Townsend and Suffita, 1997; Heimann et al., 2005; Aulenta et al., 2007; Berggren et al., 2013). Notably, if provided with enough electron donors with prolonged incubation time, complete dechlorination of TCE can be achieved in the presence of high concentrations of sulfate (Antonioni et al., 2019). In contrast, the addition of NH₄⁺ accelerates DCE-to-ethene dechlorination rates and increases the abundance of OHRB (Kaya et al., 2019). Other chlorinated aliphatic compounds, including chloroethanes, chloropropanes and chlorocyclohexane (i.e., $\alpha/\beta/\gamma/\delta$ -HCH), can also be completely dechlorinated by OHRB (Table 1) (Qiao et al., 2020). Their dechlorination extent largely depend on the growth conditions of the OHRB. Under harsh conditions, environmental parameters (e.g., temperature, pH and co-existing heavy metals) affect the dechlorination activities of OHRB and of other functional populations (Yang et al., 2017a; Marcet et al., 2018; Puentes Jácome et al., 2019; Gushgari-Doyle and Alvarez-Cohen, 2020).

Compared with microbial reductive dehalogenation of aliphatic compounds, complete dechlorination of aromatic organohalides is more challenging, particularly for persistent organohalides, including PCBs, deca-BDE and PCDD/Fs (Bedard, 2008; Rodenburg et al., 2015; Zhu et al., 2019b). Taking the reductive dechlorination of PCBs as an example, several lineages of OHRB (e.g., *Dehalococcoides*, *Dehalogenimonas* and *Dehalobacter*) have been identified to couple their growth with PCB dechlorination (Fricker et al., 2014; Wang et al., 2014; Wang et al., 2015; Wang et al., 2019). These OHRB preferentially attack *meta*- and/or *para*-chlorines in PCBs, leaving *ortho*-chlorinated PCBs as dechlorination products (Wu et al., 2002; Fennell et al., 2004; Adrian et al., 2009; Wang and He, 2013; LaRoe et al., 2014; Wang et al., 2014; Zhen et al., 2014; Wang et al., 2019). Thus far, several *ortho*-chlorine-removing microcosms have been established, e.g., *o*-17 culture (Cutter et al., 2001; Xu et al., 2018). However, the *ortho*-chlorine attacking OHRB have continued to elude enrichment and isolation. The characterized OHRB can only remove chlorines from highly-chlorinated PCBs (e.g., penta- to nona-CBs in commercial PCB mixtures) to lowly-chlorinated PCBs (e.g., di- to tetra-CBs), seldom to benign biphenyl (Table 1).

Table 1 Dechlorination of typical organohalides and their associated OHRB and RDases

Parent compounds	Daughter products	Strain	RDase	Reference
PCE, TCE, DCE	Ethene	<i>Dehalococcoides</i>	PceA, VcrA, BvcA, TeeA	Wang and He, 2013; Marcet et al., 2018; Zhao and He, 2019
TCE, DCE	Ethene	<i>Dehalogenimonas</i>	prokka_00862, prokka_02004	Yang et al., 2017b
(α , β , γ , δ)-HCH	Benzene	<i>Dehalococcoides</i>	ND	Bashir et al., 2018
Trichloroethane	Ethene	<i>Desulfitobacterium</i>	CtrA	Zhao et al., 2015
Dichloroethane	Ethene	<i>Dehalococcoides</i>	BvcA, VcrA	Tang et al., 2013; Parthasarathy et al., 2015
		<i>Dehalogenimonas</i>	ND	Key et al., 2017
Dichloropropane	Propene	<i>Dehalogenimonas</i>	DcpA	Martin-Gonzalez et al., 2015
Trichloromethane	Dichloromethane	<i>Dehalobacter</i>	CfrA, TmrA	Heckel et al., 2019
Hepta-, Octa-, Nona-CB, Aroclor 1260	Penta-, Tetra-, Tri-CB, Di-CB	<i>Dehalococcoides</i>	PcbA1, PcbA4, PcbA5, JNA_RD8, JNA_RD11	Wang and He, 2013; Wang et al., 2015; Chen and He, 2018; Yu et al., 2018; Wang et al., 2019
PeCDD	DiCDD	<i>Dehalococcoides</i>	ND	Bunge et al., 2003
TeCDD	MoCDD	<i>Dehalococcoides</i>	CbrA	Bunge et al., 2003; Pöritz et al., 2015
TrCDD	DD	<i>Dehalococcoides</i>	CbrA	Pöritz et al., 2015
HeCDF	TeCDF	<i>Dehalococcoides</i>	ND	Liu and Fennell, 2008
TeCDF	TrCDF	<i>Dehalococcoides</i>	ND	Fennell et al., 2004
Penta-BDE, Tetra-BDE	Diphenyl ether	<i>Dehalococcoides</i>	PbrA1, PbrA2, PbrA3	Ding et al., 2017
Pentachlorophenol	Monochlorophenol	<i>Desulfitobacterium</i>	CprA3	Bisaillon et al., 2010
Trichlorophenol	Monochlorophenol	<i>Dehalobacter</i>	ND	Li et al., 2013; Wang and He, 2013
Hexachlorobenzene	Monochlorobenzene	<i>Dehalobacter</i>	ND	Nelson et al., 2014
Pentachlorobenzene	Benzene	<i>Dehalobacter</i>	ND	Nelson et al., 2014
TBBPA	Bisphenol A	<i>Dehalococcoides</i>	CbdbA80, CbdbA1092, CbrA, CbdbA1503,	Yang et al., 2015
Bromophenol blue	Phenol red	<i>Dehalogenimonas</i>	ND	Rosell et al., 2019

Notes: Abbreviations: ND, not determined; Penta-CB, pentachlorinated biphenyls; Tetra-CB, tetrachlorinated biphenyls; Octa-BDE, octabrominated diphenyl ethers; Tetra-BDE, tetrabrominated diphenyl ethers; TCE, trichloroethene; DCE, dichloroethene; VC, vinyl chloride; PeCDD, pentachlorodibenzo-p-dioxin; TeCDD, tetrachlorodibenzo-p-dioxin; TrCDD, trichlorodibenzo-p-dioxin; DiCDD, dichlorodibenzo-p-dioxin; MoCDD, monochlorodibenzo-p-dioxin; DD, dibenzo-p-dioxin; HeCDF, hexachlorodibenzofuran; TeCDF, tetrachlorodibenzofuran; TBBPA, tetrabromobisphenol A; HCH, hexachlorocyclohexane.

PCDD/Fs are a group of the most notorious environmental pollutants, particularly the extremely toxic and carcinogenic congeners with lateral 2-, 3-, 7- and 8-chlorine substitutions (Bunge et al., 2003). The OHRB-mediated reductive dechlorination of PCDDs typically generates less toxic or nontoxic daughter compounds, which could be further subjected to oxidation via aromatic ring cleavage (Dam et al., 2019). Several *D. mccartyi* strains have been identified to dechlorinate PCDD/Fs, including strains 195, CBDB1, and DCMB5 (Fig. 1). Strain 195 dechlorinates 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HeCDF by exclusively attacking lateral chlorines, resulting in accumulation of tri- and tetra-CDD/Fs (Liu and Fennell, 2008; Zhen et al., 2014). Strain CBDB1

dechlorinates 1,2,3,7,8-PeCDD to less toxic 2,7-/2,8-DiCDD via toxic 2,3,7,8-TeCDD as an intermediate (Bunge et al., 2003). When amended with 1,2,3,4-TeCDD, strain CBDB1 dechlorinates it to 1,2,4-TrCDD, 1,3-DiCDD and 2-MoCDD (Bunge et al., 2003). The dechlorination pathways of strain DCMB5 resembled those of strain CBDB1, particularly the removal of peripheral chlorines (positions 1 and 4), leaving the 2,3-DiCDD as dechlorination product of 1,2,3,4-TeCDD and 1,2,3-TrCDD (Pöritz et al., 2015). Interestingly, trace amounts of MoCDD and non-chlorinated dibenzo-p-dioxin (DD) were observed as products of 1,2,4-TrCDD dechlorination (Pöritz et al., 2015). Strain DCMB5 was the first and only reported OHRB that can completely

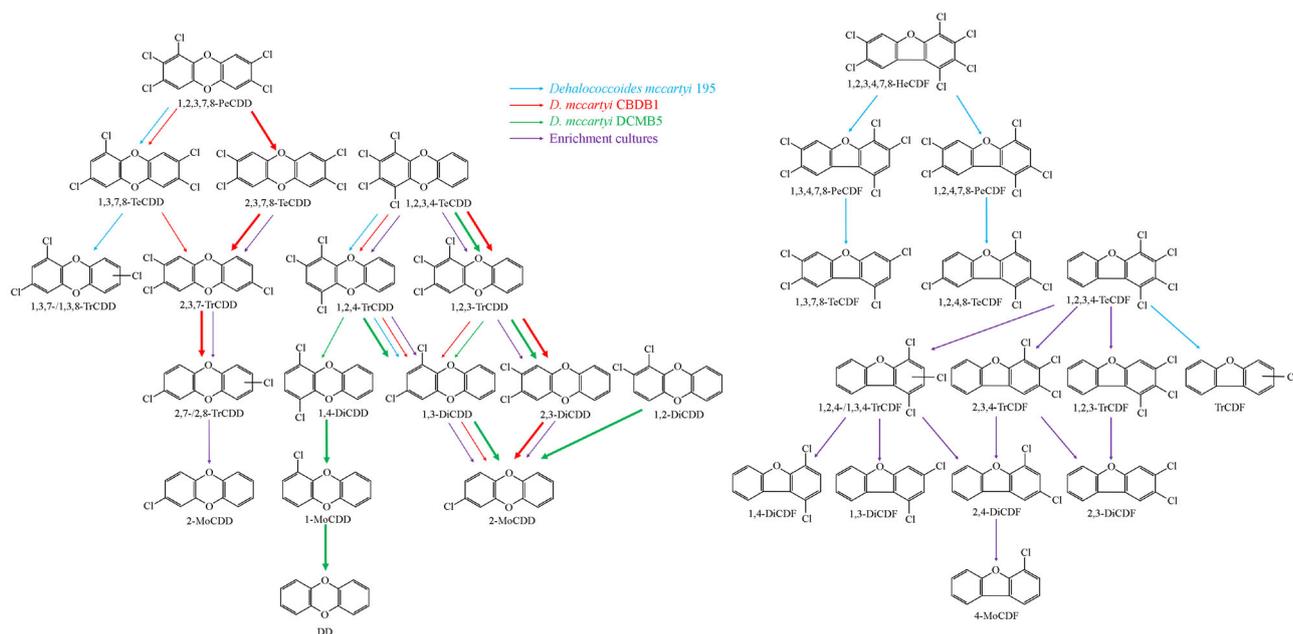


Fig. 1 Observed pathways for PCDD/Fs dechlorination in *Dehalococcoides mccartyi* strains and enrichment cultures. Major and minor dechlorination pathways are marked with thick and thin arrows, respectively.

dechlorinate PCDD. There are enrichment cultures showing dechlorination activities of PCDD/Fs in similar pathways with those of reported pure cultures (Liu et al., 2014a; Dam et al., 2017; Dean et al., 2020). Incomplete dechlorination of PCDD/Fs may generate highly toxic intermediates, warranting further integration of other methods to complement Bio-RD for complete dechlorination or degradation. In contrast to incomplete dechlorination of PCBs and PCDD/Fs, several other halogenated aromatic compounds could be completely dehalogenated by OHRB, including penta-BDEs to diphenyl ether (Ding et al., 2017) and pentachlorobenzene to benzene (Nelson et al., 2014). Nonetheless, these complete dehalogenation activities are limited to specific PBDEs and chlorobenzene congeners.

2.3 Challenges in Bio-RD

Despite the economical and eco-friendly advantages of OHRB-mediated reductive dehalogenation for the bioremediation of organohalides, its application is hindered by many challenges. OHRB may compete with indigenous populations for carbon sources, electron donors, nutrients and other growth-supporting compounds at bioremediation sites. The phase-out of fastidious OHRB could result from their long generation time and extremely narrow metabolic range (Ritalahti et al., 2005; Löffler et al., 2013; Bommer et al., 2014). The restricted metabolism of obligate OHRB has been verified by their small genomes (Siddaramappa et al., 2012; Richardson, 2013). The OHRB in *Dehalococcoidia* cannot synthesize corrinoid *de novo* as a key

cofactor of RDases and they require external acetate and hydrogen to support organohalide respiration (Fincker and Spormann, 2017). Consequently, OHRB need to work closely with fermenters and acetogens to acquire essential carbon sources, electron donors, cofactors and other nutrients to support cell growth. In addition, the low bioavailability of persistent organohalides (e.g., PCBs and PCDD/Fs) further restricts the cell growth of OHRB. Moreover, uncertainties and complexities in biological and geochemical parameters (e.g., pH, redox potential, temperature, salinity and co-existing pollutants) may severely inhibit OHRB activity (Lee et al., 2016). Therefore, many biostimulation and bioaugmentation strategies have been devised to guarantee dechlorination activities of OHRB at bioremediation sites (Löffler and Edwards, 2006; Sowers and May, 2013; Cervantes-Gonzalez et al., 2019), including the addition of biosurfactants, slow-releasing carbon/nutrients and cofactors.

Nonetheless, incomplete dehalogenation is a great challenge in the OHRB-mediated bioremediation of persistent organohalides. Possible reasons for the incomplete dehalogenation include the following: (1) due to the high selectivity of RDases, OHRB attack halogens of a particular position and leave the lowly-halogenated compounds as dechlorination products (Sowers and May, 2013; Kunze et al., 2017); (2) when removing chlorines from PCBs, dechlorination compounds become more nucleophilic relative to their parent PCB substrates (Jugder et al., 2016; Williams et al., 2020); and (3) accumulation of dehalogenation intermediates may have inhibitive or other side effects on subsequent dechlorination steps (Moe et al.,

2018). The incomplete dehalogenation of organohalides results in the generation of lowly-halogenated compounds, which are nucleophilic and may be effectively degraded through oxidative processes.

3 Persulfate activation and oxidation (PAO) for extensive degradation of organohalides

3.1 Principles of PAO

PAO is an effective way to remove a variety of organic contaminants from soil, groundwater and sediment, of which persulfate activation is a crucial step. Thus far, many methods have been devised to activate persulfate, which have been extensively studied and identified with their pros and cons (Vakili et al., 2021). Compared with persulfate activation by alkali, transition metals and radiation, thermal activation and iron-/carbon-based activation are more environmentally friendly and cost-effective, being promising for field applications (Li et al., 2020; Ma et al., 2021). The detailed activation methods have been comprehensively reviewed very recently (Matzek and Carter, 2016; Pang et al., 2019; Zhi et al., 2020; Karim et al., 2021; Tan et al., 2021).

Persulfate activation refers to the reaction of persulfate with an activator to form $\text{SO}_4^{\cdot-}$ radicals ($E^0 = 2.5\text{--}3.1$ V, depending on pH; Eq. (1)) and subsequent generation of other radicals. Generally, persulfate can be activated by energy input in the form of photons (e.g., UV photolysis) and heat (e.g., thermolysis) (Fig. 2), or by direct electron transfer (e.g., metal-based and activated carbon/biochar-based electron shuttles) (Zhu et al., 2018c; Chen et al., 2019; Yao et al., 2019). Then, the newly-born $\text{SO}_4^{\cdot-}$ radical can trigger the propagation of more $\text{SO}_4^{\cdot-}$ radical through a series of chain reactions, and OH^{\cdot} will be generated upon the reaction between $\text{SO}_4^{\cdot-}$ and $\text{H}_2\text{O}/\text{OH}^-$ (Eq. (2)). For in situ soil remediation, soil organic matter (SOM) contain various phenolic moieties as persulfate activators (Ahmad et al., 2013) and play an important role in persulfate activation (Ahmad et al., 2010). Two mechanisms have been proposed for the soil phenoxide activation of persulfate, i.e., direct electron transfer from phenoxide to persulfate (Eq. (3)) (Behrman, 2006), and nucleophilic attack of persulfate by phenoxide to generate HO_2^- (Eq. (4)) and subsequent electron transfer from HO_2^- to persulfate (Eq. (5)) (Watson and Serban., 1995; Behrman, 2006). The formation of free radicals usually involves three steps: initiation, propagation and termination (Petri et al., 2011). The initiation step generally includes persulfate activation with activators for the formation of $\text{SO}_4^{\cdot-}$ and other reactive radicals by radical chain reactions (Devi et al., 2016). The propagation step contains the chain reactions in which radicals extensively react with organic pollutants (Huang et al., 2002). The termination step

includes removing radicals by reaction scavengers and intermediates, or by self-destruction mechanisms.

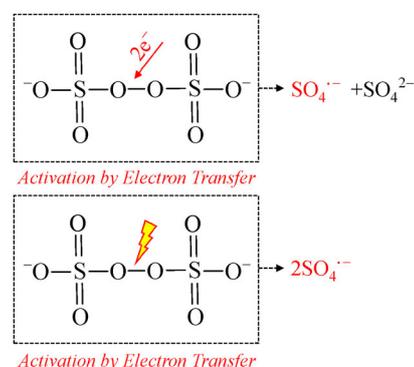
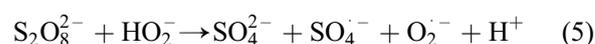
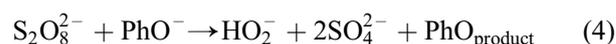
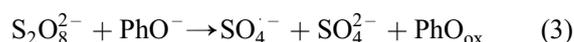
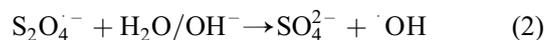
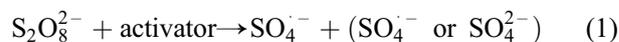


Fig. 2 Persulfate activation through electron- or energy-transfer (modified from Lee et al., 2020a).

Electron transfer in redox reactions mainly occurs by bridging mechanisms or outer-sphere mechanisms. The outer-sphere mode has a faster electron transfer rate than the bridged mechanism, due to the transient bond formation during the bridging process (Rastogi et al., 2009). In particular, electron transfer for $\text{SO}_4^{\cdot-}$ -mediated organohalide degradation mainly involves the outer-sphere mechanism, while OH^{\cdot} -mediated organohalide degradation involves the bridged mechanism (Monteagudo et al., 2016). In contrast to the OH^{\cdot} oxidization of organic matter by hydrogen abstraction or addition, $\text{SO}_4^{\cdot-}$ prefers direct electron transfers and consequently more easily reacts with aromatic molecules by providing electron substituents (Mandal et al., 2018).

3.2 PAO for organohalide degradation: pros and cons

3.2.1 PAO for organohalide degradation

PAO has been applied to organohalide degradation and remediation in different environmental matrices (Table 2), including soil, sediment, surface water and groundwater, in which $\text{SO}_4^{\cdot-}$ and OH^{\cdot} coexist as major reactive groups for efficient degradation of lowly-halogenated organohalides

(Pan et al., 2018). However, highly-halogenated contaminants are recalcitrant to SO_4^{2-} -based degradation (Huang et al., 2005), including polybrominated diphenyl ethers (PBDEs), hexachloroethane (HCA), polychlorinated biphenyls (PCBs) and perfluorooctanoic acids (Teel et al., 2011; Rybnikova et al., 2016; Zhu et al., 2018b). For example, the perfluorooctanoic acids with a high oxidation state are resistance to oxidation (Wardman, 1989; Liu et al., 2012). In a previous study investigating the degradability of 51 groups of volatile organic compounds (VOCs) by Fe (II)-activated PAO, VOCs were classified into three classes based on their degradation efficiencies, suggesting the lower degradation rates of the higher halogenated compounds (Zhu et al., 2016a). For example, the PAO reaction rates of p-chlorotoluene, 1,2-dichlorobenzene and 1,2,3-trichlorobenzene are 0.0024, 0.00017, and 0.00006 L/ $\mu\text{g}/\text{h}$, respectively (Zhu et al., 2016a). By contrast, the aforementioned OHRB-mediated Bio-RD mainly removes halogens from highly-halogenated organohalides. Therefore, PAO can complement Bio-RD and other strategies for extensive conversion of organohalides. Thus far, PAO has been widely employed to degrade a diverse range of organohalides (Table 2):

1) Aliphatic organohalides. PAO has emerged as an effective and efficient technique for removing chlorinated aliphatic hydrocarbons, particularly chlorinated olefins and chlorinated alkanes. For example, thermal activation of persulfate has been identified as an effective technique to remediate organohalide-contaminated groundwater, in which chlorinated olefins (e.g., PCE or TCE) and brominated alkanes (e.g., HBCD) can be degraded entirely (Waldemer et al., 2007; Yuan et al., 2014; Wu et al., 2015; Dong et al., 2019; Li et al., 2019).

2) Polychlorinated biphenyls (PCBs). The lowly-chlorinated PCBs (e.g., PCB1, PCB3, PCB7, PCB8 and PCB28) can be completely mineralized to CO_2 and H_2O in aqueous solution at near ambient temperature (Fang et al., 2013). Nonetheless, under the same conditions, the removal efficiency of PCB30 only reached 78%. Moreover, PAO-based degradation of PCB31, PCB44 and PCB153 in soil has been reported to range from 67.2% to 97.2% after several days of incubation (Yukselen-Aksoy and Reddy, 2012; Tang et al., 2015). Therefore, PAO-based PCBs degradation largely depends on both environmental matrices (e.g., water and soil) and chlorine numbers, the specific contributions of which await clarification.

3) Polybrominated diphenyl ethers (PBDEs). At an e-waste contaminated soil site with 53.8 ± 0.5 mg/kg PBDEs (from tri- to deca-BDEs), PAO has been identified to be capable of degrading PBDEs with an efficiency of 49.5% under optimal conditions (Ma et al., 2020). In another study, 53.8% of deca-BDE (BDE-209) in soil was observed to be degraded to short-chain acids, CO_2 and H_2O after thermal-based PAO treatment for 360 min (Peng

et al., 2016). Interestingly, Huang and colleagues (Huang et al., 2016) reported nearly 100% degradation and mineralization of powdery deca-BDE by employing a mechanochemical (ball milling) activation of persulfate, involving stepwise debromination, cleavage of ether bonds and collapse of benzene rings. The strong oxidation capacity is due to the mechanochemical enhancement of persulfate activation for the production of sulfate radicals. This method provides a promising way to remove solid and highly-halogenated organohalides.

4) Dichlorodiphenyltrichloroethane (DDT). DDT, as a toxic pesticide, was included in the first batch of the 12 most hazardous and long-lasting organic compounds defined by the Stockholm Convention on Persistent Organic Pollutants (POPs) (Sharma et al., 2014; Asaoka et al., 2019). Iron-based PAO can achieve 87.9% DDT degradation, and free radicals (i.e., $\text{SO}_4^{\cdot-}$ and OH^{\cdot}) mediate DDT degradation via stepwise hydrodechlorination, dehydrochlorination, ring-opening and final mineralization (Zhu et al., 2016b).

5) Atrazine. Atrazine is one of the most widely used pesticides in agriculture. Luo and colleagues (Luo et al., 2015) investigated atrazine degradation by using UV-based activation and oxidation of three types of oxidants (i.e., H_2O_2 , peroxymonosulfate and persulfate), providing a full understanding of the role of Cl^- , natural organic matter (NOM) and $\text{CO}_3^{2-}/\text{HCO}_3^-$ on free radicals. The results showed that Cl^- (0.5–10 mmol/L), NOM and $\text{CO}_3^{2-}/\text{HCO}_3^-$ significantly scavenged free radicals. In addition, the underlying mechanism of SO_4^{2-} -based degradation of chlorotriazine has been identified to be similar to that of OH^{\cdot} -based oxidation (dealkylation) (Lutze et al., 2015). The high reactivity of chlorotriazine is primarily due to the ethyl and isopropyl groups, but the dealkylated products of chlorotriazine degradation have poor reactivity to $\text{SO}_4^{\cdot-}$. Based on experiments, atrazine oxidation by free radicals has been proposed to have three transformation pathways, i.e., dealkylation, alkyl chain oxidation and dechlorination-hydroxylation (Ji et al., 2015). It is important to note that some of the products (e.g., di-isopropylatrazine and diethylatrazine) converted from atrazine by $\text{SO}_4^{\cdot-}$ or OH^{\cdot} have similar levels of toxicity to atrazine (Whalen et al., 2003).

6) Hexachlorocyclohexane (HCH). HCH, as a pesticide includes many isomers, of which γ -HCH (lindane) is the most toxic and hazardous. Experiments show that Fe^{2+} -based PAO can altogether remove and mineralize lindane within 12 h (Cao et al., 2008). Further kinetic studies show that lindane degradation follows second-order degradation with a rate constant of $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Khan et al., 2016).

7) Chloroaniline. Highly toxic and carcinogenic p-chloroaniline is a critical intermediate in the synthesis of pesticides, medicines and dyes. Investigations on the PAO degradation of p-chloroaniline showed its complete

Table 2 Persulfate activation and oxidation for degradation of organohalides

Compound	Concentration (mmol/L)	PS Concentration (mmol/L)	Degradation efficiency	Final products	Activator	Run time (min)	Reference
TCE	1.0	5	90.68%	ND	nZVI	30	Dong et al., 2019
	0.4	5	>99%	short chain acids, CO ₂	Fe ²⁺	20	Yuan et al., 2014
	0.15	2.25	>99%	ND	Fe ²⁺	30	Wu et al., 2015
	0.15	4.5	99.4%	ND	biochar supported nZVI	5	Yan et al., 2015
Hexabromocyclododecane	0.04	4	100%	Carboxylic acids, CO ₂	UV/TiO ₂	180	Li et al., 2019
Perfluorooctanesulfonate	0.15	4.5	>99%	PFOA	hydrothermal	5	Yang et al., 2013
	0.01	4.2	>99%	ND	ultrasound	360	Lei et al., 2020
Perfluorooctanoic acid	0.01	4.2	100%	CO ₂ , HF	ultrasound	360	Lei et al., 2020
	0.12	12	61.7%	CO ₂ , F ⁻	iron/activated carbon	600	Lee et al., 2020b
	0.15	15	85.6%	short chain acids	UV	480	Qian et al., 2016
6:2 FTS	0.01	4.2	87%	ND	ultrasound	360	Lei et al., 2020
	0.0025	50	100%	short chain acids	heat	60	Bruton and Sedlak, 2017
PCB1	0.0019	16.8	100%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB3	0.0019	16.8	100%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB7	0.0019	16.8	100%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB8	0.0019	16.8	100%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB28	0.0019	5	88%	CO ₂ , H ₂ O	iron	240	Rodriguez et al., 2017
	0.0039	2	82%	CO ₂ , H ₂ O	vanadium species	240	Fang et al., 2017b
	0.0039	2	100%	ND	vanadium species	1440	Fang et al., 2017a
	0.0039	8	100%	ND	biochar	240	Fang et al., 2015
	0.0019	16.8	100%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB30	0.0025	2	100%	ND	iron	240	Rodriguez et al., 2017
	0.0019	16.8	78%	CO ₂ , H ₂ O	heat	480	Fang et al., 2013
PCB31 (in soil)	0.006	500	67.2%	ND	iron	3 Days	Tang et al., 2015
PCB44 (in soil)	0.171	ND	97.4%	ND	electricity	7 Days	Yukseleir-Aksoy and Reddy, 2012

(Continued)

Compound	Concentration (mmol/L)	PS Concentration (mmol/L)	Degradation efficiency	Final products	Activator	Run time (min)	Reference
PCB153 (in soil)	0.005	500	67.7%	ND	iron	3Days	Tang et al., 2015
BDE47	0.0031	71.4	75%	ND	nZVI	2 Days	Wang et al., 2017
BDE209	0.021	500	53.8%	short chain acids, CO ₂ , H ₂ O, Br ⁻	heat	360	Peng et al., 2016
Monochlorobenzene	0.3	15	>90%	CO ₂ , H ₂ O	Fe ²⁺	180	Jiang et al., 2020
DDTs	0.00138	10	87.9%	CO ₂ , H ₂ O	ZVI	30	Zhu et al., 2016b
Atrazine	0.05	1	100%	DEIA, HAIT, DEIHA	heat	120	Ji et al., 2015
	0.025	1	63%	DIA, DEA	heat	35	Lutze et al., 2015
Pentachlorophenol	50	0.115	75%	CO ₂ , H ₂ O	electrochemical	60	Govindan et al., 2014
2,4-Dichlorophenol	0.184	12.5	98%	CO ₂ , H ₂ O	iron-based nanoparticles	180	Li et al., 2015
	0.034	0.5	82.7%	CO ₂ , H ₂ O	ZVC/nZVC	120	Zhou et al., 2018
	0.1	1	100%	ND	heat/Fe ²⁺	45	Kuśmirek et al., 2016
Tetrabromobisphenol A	0.018	3.6	94.8%	CO ₂ , H ₂ O, Br ⁻	Iron-based MOFs	120	Huang et al., 2020
Triclosan	0.17	9.4	80%	ND	heat	360	Chen et al., 2019
p-chloroaniline	0.5	2.5	98.03%	CO ₂ , H ₂ O	activated carbon	120	Yao et al., 2019
	0.2	4	>99%	CO ₂ , H ₂ O	FeS	150	Yuan et al., 2015

Notes: Abbreviations: ND, not determined; PCB, polychlorinated biphenyls; BDE209, decabromodiphenyl ether; TCE, trichloroethene; DDTs, dichlorodiphenyltrichloroethane; 6,2-FTS, 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid; DEIA, deethyldeisopropylatrazine; HAIT, 2-hydroxy-4-acetamido-6-isopropylamino-1,3,5-triazine; DIA, deisopropylatrazine; DEA, deethylatrazine; DEIHA, deethyldeisopropylhydroxyatrazine; nZVI, nanoscale zero-valent iron; UV, ultraviolet; ZVC, zero-valent copper; MOF, metal organic frameworks.

degradation and mineralization in waste streams containing p-chloroaniline (Yuan et al., 2015; Yao et al., 2019).

8) Chlorophenols. Toxic chlorophenols (e.g., pentachlorophenol or PCP) are massively produced and utilized as fungicides and antiseptics. Investigations on the degradation of PCP by $\text{SO}_4^{\cdot-}$ and OH^{\cdot} radicals have shown that approximately 75% of PCP degradation and mineralization were achieved within 60 min under optimal conditions (Govindan et al., 2014). By contrast, almost complete degradation and mineralization of 2,4-dichlorophenol and tetrabromobisphenol A were achieved with PAO (Kuśmierek et al., 2016; Li et al., 2015; Zhou et al., 2018; Huang and Zhang, 2019).

Compared with the OHRB-mediated removal of highly-halogenated organohalides, PAO is relatively more effective in the degradation and mineralization of lowly-halogenated organohalides. Therefore, PAO may complement Bio-RD for the extensive and complete degradation and mineralization of a wide range of organohalides, particularly the highly-halogenated organohalides. Nonetheless, radicals and their intermediates play pivotal roles in PAO-based degradation of organohalides, of which radical scavenging and nonproductive reactions largely determine the overall remediation efficiency of PAO-based organohalide degradation (Crincoli et al., 2020). Consequently, future extensive studies are necessary to reveal the critical parameters affecting the reactive radicals in PAO. In addition, efforts should also go toward the prevention of hazardous byproduct formation in PAO.

3.2.2 Advantages of PAO for organohalide degradation

The $\text{SO}_4^{\cdot-}$ -based advanced oxidation process (AOP) is a promising technology for the remediation of organohalide contamination. Compared with other AOPs, PAO has the following advantages: (1) high stability; compared with other oxidants, e.g., O_3 and H_2O_2 , persulfate is relatively more stable in various environmental matrices; (2) high solubility; persulfate is highly soluble and can be used for remediation of groundwater polluted by dense nonaqueous phase liquids (DNAPLs); (3) wide pH range; persulfate-derived $\text{SO}_4^{\cdot-}$ is less sensitive to pH, and can mediate organohalide degradation in a wide range of pH conditions; (4) long lifetime; the comparatively much longer lifetime of $\text{SO}_4^{\cdot-}$ relative to OH^{\cdot} significantly prolongs the exposure of $\text{SO}_4^{\cdot-}$ to organohalides and enhances their remediation efficiency; (5) low cost and environmental impacts; PAO is a cost-effective and environmentally friendly technique for in situ remediation of organohalides.

Compared with Bio-RD, PAO has the following advantages: (1) PAO is an efficient chemical reaction process with high reactivity, which is much faster than Bio-RD; (2) persulfate-derived $\text{SO}_4^{\cdot-}$ with a high redox

potential of 2.5–3.1 V is nonselective to pollutants and can degrade a wide range of lowly-halogenated organohalides; and (3) PAO is easy to be operated and managed at remediation sites.

3.2.3 Limitations of PAO for organohalide degradation

Although PAO is very promising in the remediation of organohalides, there are several significant limitations in practical PAO applications:

1) Persulfate itself has very low reactivity toward organohalides, and its activation is critical for improving the degradation efficiency. Nonetheless, thermal and chemical activation methods consume much energy and chemicals, respectively (Zhang et al., 2014). The high chemical dose and energy input, as well as the long contact time (usually in days), largely hinder field applications of PAO (Zhang et al., 2014). Consequently, it is necessary to develop novel, efficient and cost-effective activation methods for PAO.

2) $\text{SO}_4^{\cdot-}$ as a strong oxidant can non-selectively oxidize a wide range of organic/inorganic components, which may generate toxic byproducts (Hori et al., 2005). For example, ubiquitous chlorine ions are widespread in natural environments, and they can be oxidized to chlorine-free radicals ($\text{Cl}_2^{\cdot-}$) by $\text{SO}_4^{\cdot-}$, which not only reduces the degradation rate but also leads to the formation of harmful chlorinated products (Zhang et al., 2013). Similar problems exist for bromide as well (Fang and Shang, 2012). Consequently, preventing the generation of harmful byproducts has become a concern in applying PAO in the field remediation of organohalides.

3) The PAO process reduces the pH of contaminated aquifers and soil in the range of 2.8–6.0 (Liang et al., 2004; Tsitonaki et al., 2008). In addition, PAO produces a large amount of sulfate, resulting in the salinization of soil and groundwater. Therefore, improving the activation efficiency of persulfate and precisely controlling the addition amount of persulfate is of great significance in alleviating soil acidification and salinization.

4) PAO-based remediation may change the microbial community composition and function and biomass abundance at contaminated sites. For example, PAO remediation was observed to result in biomass decline and a consequent decrease in organohalide biodegradation efficiency (Tsitonaki et al., 2010). To alleviate the negative impacts of PAO on microbial communities, many different biostimulation and bioaugmentation methods have been developed and employed to stimulate biodegradation activities (Sutton et al., 2011), which represent a challenge. For example, neither OHRB (e.g., *Dehalococcoides*) nor *rdhA* genes have been observed after the biostimulation of the OHRB community at PAO-treated sites (Sutton et al., 2015), suggesting the disruption of natural attenuation capacities after PAO remediation.

4 Integration of Bio-RD and PAO (Bio-RD-PAO) for extensive attenuation of organohalides

4.1 Bio-RD-PAO for complete removal of organohalides

Both anthropogenic and natural sources of organohalides result in the wide distribution of massive amounts of organohalides in different environmental matrices (Xu et al., 2006; Maucourt et al., 2020). Particularly in anoxic subsurface environments, highly-halogenated organohalides (e.g., PCBs in commercial PCB mixture Aroclor 1260) need to be reduced first before their subsequent complete degradation via oxidative processes. Consequently, an ideal bioremediation process for the in situ removal of organohalides would integrate reductive dehalogenation with subsequent oxidative degradation/mineralization. At OHRB-based bioremediation sites, lowly-halogenated pollutants (e.g., mono- to tetra-CBs and vinyl chloride) may accumulate as intermediates await further extensive degradation. In contrast, sulfate radicals have difficulty in breaking down highly-halogenated contaminants, but they can efficiently and extensively degrade lowly-halogenated organohalides (Huang et al., 2005; Zhu et al., 2016a). Taking PCBs as an example, OHRB of different lineages have been identified to remove chlorine atoms from highly-chlorinated PCBs and generate di- to tetra-CBs, which can be effectively mineralized to CO₂ and H₂O by PAO (Yukselen-Aksoy and Reddy, 2012; Fang et al., 2013; Fang et al., 2017a). Therefore, integration of Bio-RD with PAO (Bio-RD-PAO) may provide a feasible process for the efficient in situ remediation of organohalides at contaminated sites.

Nonetheless, the co-existence of aggressive chemical oxidants and fastidious OHRB may have many yet-to-understand interactions (Sutton et al., 2011; Zhang et al., 2020), hindering Bio-RD-PAO for in situ remediation applications. Previous studies have investigated the impacts of chemical oxidation as a pretreatment method to enhance both the degradability and availability of organohalides for subsequent biological conversion processes (Nam et al., 2001; Hrapovic et al., 2005; Kulik et al., 2006; Ndjou'ou et al., 2006; Sahl and Munakata-Marr, 2006; Lu et al., 2010; Venny et al., 2012; Sutton et al., 2014a). Results have shown that aggressive oxidation and deleterious effects of chemical oxidants significantly decrease the amount of biomass and change the composition of the microbial community (Sutton et al., 2014b; Nemeček et al., 2019; Xia et al., 2020). Consequently, chemical pretreatments with oxidants may not improve the overall remediation efficiency. For example, the low abundance of OHRB rather than bioavailability have ultimately determined the low-rate and incomplete reaction of dehalogenation (Lombard et al., 2014). In addition, although regeneration of the microbial communities

occurred after six months of chemical oxidation pretreatment, neither *D. mccartyi* strains as key OHRB nor any *rdhA* genes were observed (Sutton et al., 2015). These results suggest that consequent treatment of organohalides with Bio-RD and PAO, rather than PAO pretreatment and then Bio-RD, may be feasible to combine the strengths of Bio-RD and PAO and to prevent shortages, as well as their side effects simultaneously. In Bio-RD-PAO, various biostimulation and bioaugmentation strategies can be employed to enhance OHRB-mediated halogen removal from the highly-halogenated organohalides (Tyagi et al., 2011; Roy et al., 2018; Xu et al., 2019). For example, bioaugmentation with anaerobic microorganisms has been employed to enhance the conversion of highly-chlorinated PCBs to lowly-chlorinated PCBs. In addition, after completion of Bio-RD-PAO remediation at contamination sites, microbial communities may be regenerated by biostimulation and bioaugmentation (Dogan-Subasi et al., 2013; Martínez-Pascual et al., 2015).

4.2 Challenges in Bio-RD-PAO for in situ remediation of organohalides

Bio-RD-PAO may synergistically combine advantages of Bio-RD and PAO for extensive remediation of a wide range of organohalides, particularly highly-halogenated organohalides that cannot be effectively remediated by Bio-RD or PAO alone. Nonetheless, there are several major challenges for remediation applications of Bio-RD-PAO:

- 1) Substrate addition in biostimulation may affect the subsequent PAO process. The fastidious growth requirements and long generation time of OHRB, and complicated microbial interactions result in difficulties in maintaining efficient organohalide respiration. To enhance the microbial reductive dehalogenation efficiency, many biostimulation strategies have been devised and employed, including the addition of vegetable oils as slow-releasing organic carbons and electron donors to support organohalide respiration of OHRB (Herrero et al., 2019). These biostimulation materials are left or transferred into other organic matter as intermediates, which may consume sulfate radicals and decrease the efficiency of subsequent PAO in organohalide remediation (Ouyang et al., 2017; Fang et al., 2018). In addition, a variety of minerals, ions and organic matter in soil and subsurface environments also consume persulfate-derived sulfate radicals, which has been comprehensively reviewed by Lee and colleagues (Lee et al., 2020a). The authors suggested to establish field-proven operating procedures to minimize the side impact of by-products and associated reactions on PAO (Lee et al., 2020a). Both experimental and computational evidences suggested that minerals containing iron/manganese-oxides decompose persulfate and produce active free radicals to accelerate persulfate decomposition upon contaminant's exposure (Liu et al., 2014b; Pari et al.,

2017). It is the distance between contaminants and persulfate that may affect the diffusion rate of active free radicals and the pollutant removal efficiency. Therefore, the effects of biostimulation substrates-derived matter on subsequent PAO are different under varied environmental conditions, on which the detailed information remain elusive.

2) Mechanisms underlying the oxidative PAO process in aerobic and anaerobic environments may be different from each other, which remain elusive. Persulfate activation is generally performed under aerobic conditions, and there are limited reports of persulfate activation in anaerobic environments. Recently, both reductive dechlorination and consequent oxidation of hexachloroethane were observed during the PAO process under anaerobic conditions (Zhu et al., 2018b), in which persulfate radicals ($S_2O_8^{\cdot-}$) were identified to play a significant role in hexachloroethane degradation. Interestingly, in another study on PAO under anaerobic conditions, persulfate-derived alcohol radicals (ARs) with low redox potential were proposed to reductively dechlorinate trichloroacetic acid (TCA) and carbon tetrachloride (CCl_4) (Zhu et al., 2018a). Other oxidative radicals (e.g., $SO_4^{\cdot-}$ and OH^{\cdot}) were generated in the subsequent radical chain reactions, which further reacted with lowly-chlorinated intermediates and converted them into CO_2 and chloride ions (Zhu et al., 2018a; Zhu et al., 2018b). Therefore, under anaerobic conditions, persulfate can be activated to generate both reductive radicals and oxidative radicals through radical chain reactions, which warrants more experimental and mechanistic investigations.

3) A third challenge is that of the effective integration of Bio-RD and PAO for complete degradation of organohalides. Theoretically, Bio-RD can remove halogens from highly-halogenated organohalides, and then PAO can effectively and extensively degrade the dehalogenation products. Nonetheless, during Bio-RD, various parameters work together to determine the number of removed chlorine compounds, particularly the OHRB and their growth conditions, resulting in the varied extent of dehalogenation (Nijenhuis and Kuntze, 2016; Wang et al., 2018). For example, recently isolated and characterized *D. mccartyi* CG1 and CG5 could dechlorinate PCB180 (2345-245-CB) to hexa-CB (245-245-CB) and tetra-CB (24-24-CB), respectively (Wang et al., 2014). Subsequent PAO-based degradation of the generated hexa- and tetra-CBs has different efficiencies, and PAO is more effective in degrading the lowly-chlorinated PCBs (Rybnikova et al., 2016).

4) The hydrophobic properties of organohalides severely restrict their bioavailability and in situ chemical oxidation efficiencies. The hydrophobicity of organohalides results in their low availability, which leads to the low and incomplete degradation of organohalides by Bio-RD-PAO. Particularly in organohalide-contaminated subsurface environments, the organohalides may be adsorbed to soil

organic matter. To enhance the desorption and dissolution of organohalides, soil heating strategies were investigated to improve microbial reductive dehalogenation and subsequent activation of persulfate (Peng et al., 2016). The heating temperature is a critical parameter, and high temperature may inactivate the OHRB and result in persulfate decomposition. Nonetheless, soil heating is an energy-intensive process. Recent studies showed that biostimulation with nutrients and surfactants promoted cell growth of OHRB by increasing the bioavailability of hydrophobic organohalides (Jasmine and Mukherji, 2014), which may be a feasible way to enhance the efficiency of Bio-RD-PAO in organohalide remediation.

5) The integrated Bio-RD-PAO process may affect the abundance of biomass, microbial community composition and physiochemical properties of remediated soil by increasing redox potential and decreasing pH (Sutton et al., 2014b; Sutton et al., 2015). Although the regeneration of microbial communities can be achieved through biostimulation and bioaugmentation, unpredictable side effects may occur at remediation sites (Sutton et al., 2011; Cycoń et al., 2017). For example, microbial activities have been changed even after microbial community regeneration (Sutton et al., 2015). Therefore, it is challenging to alleviate the side impacts of persulfate oxidation on microbial communities and their activities. Although it has been reported that the impacts of persulfate activation on bioremediation are reduced by optimizing the molar ratio of persulfate and pollutants, as well as of persulfate and activators (Xia et al., 2020), the specific mechanism is still unclear.

5 Conclusions and future perspectives

Bio-RD and PAO are two efficient techniques for in situ remediation of highly-halogenated and lowly-halogenated organohalides, respectively. Bio-RD-PAO via sequential integration of Bio-RD and PAO can provide a solution for remediation of a wide range of organohalides, which is not only feasible but extensive, efficient and cost-effective, if properly implemented, compared with Bio-RD and PAO treatment alone. To enhance the efficiency of Bio-RD-PAO in remediation of organohalide pollution, the following perspectives are proposed for future studies:

1) Novel surfactants should be developed to improve the availability of hydrophobic organohalides for Bio-RD-PAO. Hydrophobic organohalides may bond to soil organic matter, which severely decreases their availability and results in low dechlorination efficiency. Surfactants can enhance the organohalide removal by improving the organohalides' bioavailability and the interaction between cell surface and reactants (Mulligan and Gibbs, 2004; Liu et al., 2021). A variety of surfactants (e.g., anionic, cationic, zwitterionic and nonionic surfactants) have been developed and applied in soil remediation (Fountain et al.,

1996; Mao et al., 2015), including bioremediation (Pacwa-Plociniczak et al., 2011), phytoremediation (Aioub et al., 2019) and electrokinetic remediation (Fardin et al., 2021; Chen et al., 2021). To develop novel surfactants for enhanced remediation of organohalide-contaminated soil, especially for the Bio-RD-PAO process, the following properties of the surfactants should be considered:

(a) The surfactants cannot inhibit the microbial activity. Although surfactant-amended bioremediation has been widely applied, the impact of surfactants on the organohalide degradation have been controversial in the past years, and little is known about the effect of emulsifiers on the biodegradation of complex hydrocarbon mixtures. To clarify the effect of surfactant addition on microbial activity and pollutant removal efficiency, Liu et al. (2016) compared the effects of three surfactants (Tween80, TritonX-100 and Brij30) and found that Tween80 promoted the growth and activity of microorganisms (*Sphingomonas* sp. GY2B), and improved the pollutant degradation efficiency. By contrast, slight and severe inhibitions were observed in cultures amended with TritonX-100 and Brij30, respectively (Liu et al., 2016).

(b) There is a good compatibility of surfactants with the microorganisms and oxidants. Several studies testing the chemical compatibility between surfactants and pollutants suggested that alcohol-based surfactants were more likely to react with pollutants and not conducive to use with the oxidants (Zhai et al., 2006).

(c) The surfactants should not quench the persulfate-derived free radicals. Previous studies showed that removal of organohalides were improved by combining nonionic surfactants (e.g., TX-100, Brij-35 and E-Mulse 3®) and oxidants (Mulligan and Eftekhari, 2003; Villa et al., 2010; Rios et al., 2013; Dominguez et al., 2019). Interestingly, a recent study comparing the effect of three nonionic surfactants (E-Mulse 3®, Tween80 and a mixture of Tween80-Span80) and an anion surfactant (sodium dodecyl sulfate, SDS) on PAO degradation of organohalides demonstrated that combining SDS and Emulse-3® consumed less persulfate, but was more efficient, relative to SDS (García-Cervilla et al., 2021).

Therefore, interactions among surfactants, oxidants and organohalides are complicated, and the selection of optimum surfactants for ISCO treatment is challenging. The compatibility of surfactants with oxidants, the solubility of surfactants, and the oxidation rate of organohalides in aqueous surfactant emulsion warrant future investigation.

2) Multifunctional materials and techniques can be devised for simultaneous stimulation of Bio-RD and persulfate activation. For example, glucose was recently utilized to activate persulfate and, at the same time, provide a carbon source for indigenous microorganisms, which work together to effectively degrade nitrobenzene and chloroethane (Watts et al., 2018). Moreover, surfactant foam could be an effective carrier for OHRB and persulfate

in the vadose zone, which has been successfully employed to enhance remediation of contaminated soil (Zhang et al., 2012; Bajagain et al., 2018; Bouzid et al., 2019; Bajagain et al., 2020). Consequently, new materials with multiple similar functions should be developed specifically to enhance the organohalide remediation efficiency of Bio-RD-PAO.

3) Strategies should be developed to alleviate the side effects of Bio-RD and PAO, which include capsulation of OHRB and their growth-requiring nutrients and substrates for Bio-RD-PAO-based in situ remediation. The OHRB-dwelling and nutrient-slow-releasing capsules can alleviate the strong-oxidative damaging effects of PAO on the OHRB by preventing direct contact of the OHRB with persulfate-derived oxidative species. Many other novel materials have been developed to protect anaerobic bacteria from exposure to oxygen and other oxidative species. For example, Ji and colleagues (Ji et al., 2018) recently developed a cytoprotective metal-organic frameworks (MOFs) material to wrap anaerobes and to decompose reactive oxygen species, which decreased anaerobic cell damage by 5-fold upon oxygen exposure.

4) To completely mineralize highly-halogenated organohalides, it is crucial that the OHRB can effectively remove halogens from highly-halogenated substrates. For a specific organohalide pollutant, the proper organohalide-respiring bacterial candidate may be different. Of the currently-characterized OHRB, *Dehalococcoides* represents a unique lineage for reductive dechlorination of a wide range of organohalides, and is an optimal candidate for applying the Bio-RD-PAO process. For example, *Dehalococcoides* is one of the only two organohalide-respiring genera able to dechlorinate hexachlorocyclohexane (HCH) (Doesburg et al., 2005; Maphosa et al., 2012; Bashir et al., 2018). *Dehalococcoides* transforms (α , β , γ , δ)-HCH to monochlorobenzene and benzene (Bashir et al., 2018), which enables their efficient and complete degradation via subsequent PAO. For reductive dichlorination of PCBs, *Dehalococcoides*, *Dehalogenimonas* and *Dehalobacter* can remove flanked *meta*-/*para*-chlorines from PCBs with different specificities and generate a variety of lowly-chlorinated PCBs for subsequent degradation using PAO. Therefore, the overall efficiency of degrading PCBs and other organohalides in the Bio-RD-PAO process may be optimized by screening and selection of proper OHRB based on extensive cultivation studies.

5) For the complete degradation of highly-halogenated organohalides, dehalogenation products of Bio-RD may be further degraded by aerobic microorganisms (Rieger et al., 2002), which has been observed in natural environments for attenuation of organohalide pollutants (Abramowicz, 1995). The stepwise anaerobic-aerobic coupled process has been employed for the removal of a variety of organohalides, including chloroethenes (Yoshikawa et al., 2017), HCB (Kengara et al., 2013), TBBPA (Ronen and Abeliovich, 2000), PCBs (Tsuneta et al., 2008; Pathiraja

et al., 2019), and PBDEs (Pan et al., 2019). For example, approximately 70% of Aroclors can be effectively degraded by coupling an anaerobic PCB-dechlorinating culture with an aerobic culture containing *Burkholderia xenovorans* LB400 (Evans et al., 1996; Master et al., 2002). Nonetheless, compared with Bio-RD-PAO, the sequential anaerobic-aerobic coupled process may have disadvantages, including a long remediation time (Liu et al., 2013) and high substrate selectivity (Sowers and May, 2013). For example, PCB dechlorinating products with *ortho*-chlorines are recalcitrant to aerobic degradation, but can be easily degraded by PAO. Compared with the sequential anaerobic-aerobic coupled process and the detailed pros and cons, as well as how to prevent its drawbacks, in-depth studies are needed to further investigate Bio-RD-PAO.

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