Bioremediation of organohalide pollutants: progress, microbial ecology, and emerging computational tools

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Abstract

Organohalide chemicals such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and poly-fluoroalkyl substances (PFASs) are prevalent contaminants in the environment. Recent findings that certain microbes could attenuate these pollutants suggest the potential to develop bioremediation technologies using functional microorganisms to combat this pollution crisis. A timely review on bioremediation progress and emerging tools that can be used to facilitate bioremediation design is needed. Thus far, bioremediation of PCBs and PBDEs is at the developing stage from laboratory investigation to field application, whereas exploring potent microbes remains the central task for PFASs. Successful bioremediation is underpinned by a collection of interactive microbes; however, relevant microbial ecology questions affecting bioremediation performance are underexplored. Machine learning, quantum chemistry, and biomolecular modeling are prospective tools to optimize system operation, predict environmental fate of chemicals, and explore functional enzymes, but their application in bioremediation only emerged recently. This review summarizes recently discovered microbes and genes involved in biodegradation of organohalide pollutants, highlights practical and ecological questions, and discusses potential application of computational tools in bioremediation of organohalide pollutants.

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Introduction

A variety of halogenated organic compounds (termed as organohalides) are manufactured for industrial and agricultural applications. However, many organohalides have been proven harmful to human and wildlife and prohibited for commercial use. For example, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are carcinogenic and endocrine disruptive, respectively [1], while certain polyfluoroalkyl substances (PFASs) were also reported to cause reproductive toxicity, cardiovascular damage, hepatic toxicity as well as negative immune and neurological effects [2]. Unfortunately, emission of most organohalide pollutants to the environment will continue in the foreseeing decades due to massive amounts of in-use and waste consumer products containing these compounds. Thus far, most commercialized organohalides have been detected in diverse ecosystems, for example, PFASs were detected in air, water, soils, wildlife, and human from the globe [3]. This pollution crisis is threatening public and ecosystem health. To tackle this crisis, researchers are searching for efficient and affordable remediation approaches. Bioremediation is one of such approaches that effectively eliminates organohalide pollutants in contaminated environments [3]. In the past few years, diverse microorganisms have been credited with the capability of biotransforming organohalide pollutants [4–8], some of which were further tested in bioremediation [9–13]. Emerging tools including machine learning, quantum computation, and biomolecular modeling, are attracting attentions owing to their demonstrated ability to solve complex environmental problems (e.g., source appointment of air pollution and waste treatment system management) [6,14].

Here, we concisely summarized progress in bioremediation of organohalide pollutants including newly discovered microorganisms and bioremediation practices, with a particular focus on the notorious organohalides (PCBs, PBDEs, and PFASs). Bioremediation progress of these pollutants was compared with the bioremediation history of the well-studied chlorinated solvents to demonstrate the foreseen future of achieving successful field bioremediation of PCBs, PBDEs, and PFASs. Additionally, critical microbial ecology questions that may determine the outcomes of bioremediation was

highlighted and discussed. Lastly, potential application of emerging tools (i.e., machine learning, quantum chemistry, and biomolecular modeling) in bioremediation was proposed.

Expanded diversity of microorganisms metabolizing organohalide pollutants

Microbial reductive dehalogenation and oxidative degradation are predominant pathways to attenuate organohalides in anaerobic and aerobic environments, respectively. The former pathway is initiated by reductive dehalogenases (RDases) synthesized by organohalide-respiring bacteria (OHRB) [7]. Recent studies have yielded new insights into *in-situ* dehalogenation activity of PCBs and PBDEs as well as diversity of OHRB [6,7,15—19]. Multiple-line-of-evidence indicated widespread onset of PCB dechlorination but incidental debromination of highly brominated PBDEs *in-situ* [16,17], which were further collaborated by laboratory microcosm tests [7,15]. A new genetic marker revealed coexistence of numerous *Dehalococcoides* populations in environmental samples [7,20], suggesting underexplored diversity of OHRB capable of dehalogenating PCBs and PBDEs. Correspondingly, several novel *Dehalococcoides* strains (TZ50, MB, CG1, CG4, and 11a5) were recently credited with the capability of reductively debrominating PBDEs [5—7]; more evidence was also obtained to support the involvement of *Dehalogenimonas* in PCB dechlorination (Table 1) [21,22]. Recent studies also suggest that multifunctionality is not an incidental phenomenon for RDases in OHRB; more OHRB were found to employ a single RDase to dehalogenate multiple organohalides [6,7,15,18], benefiting bioremediation of sites co-contaminated with multiple pollutants. Phylogenetically diverse aerobic microbes have also been isolated with the capability of degrading PCBs (e.g., *Bacillus*, *Comamonas*, *Pseudomonas*, *Paraburkholderia*, *Ralstonia*, and *Rhodococcus*) [23—27] and PBDEs (e.g., *Bacillus*, *Pseudomonas*, *Rhodococcus*, and *Stenotrophomonas*; Table 1) [4,28,29]. The functional enzymes catalyzing aerobic mineralization of PCBs include biphenyl dioxygenase, dihydrodiol dehydrogenase, 2,3-dihydroxybiphenyl dioxygenase, and hydrolases [23,24], whereas haloacid dehalogenase, biphenyl dioxygenase, and hydrolase collaboratively converted PBDEs to CO_2 [4]. However, these aerobic enzymes are only efficient in degrading lowly halogenated compounds with 1—4 halogens [24]; therefore, complete mineralization of higher PCB and PBDE congeners usually requires collaboration between anaerobic OHRB and aerobic degraders [30].

Exciting progress has also been made for biodegradation of polyfluorinated pollutants. Several studies reported aerobic biodegradation of perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and other fluorinated compounds (Table 1) [31—36]. *Pseudomonas* stands out as the most potent aerobic bacterium degrading polyfluorinated pollutants owing to its tolerance to fluoride inhibition, versatile metabolic activity, and ability to grow on fluorinated compounds [37]. Anaerobic biodegradation of polyfluorinated pollutants was discovered very recently. A well-known dechlorinating consortium transformed C_6 per- and polyfluorinated compounds via reductive defluorination and hydrogenation, proving the feasibility of anaerobic microbes to breakdown polyfluorinated pollutants although the pollutant degraders remain unidentified [38]. Later, Yu et al. [39] reported anaerobic defluorination of fluorinated carboxylic acids and found that α, β-unsaturation is crucial for reductive defluorination and/or hydrogenation. Jin and colleagues also showed that Cl substitutions resulted in more extensive and complete defluorination [40]. These studies provided unprecedented insights into the relationship between structure and biodegradability of fluorinated contaminants. Biodegradation of 8:2 fluorotelomer alcohol was compared under different reducing conditions, with faster biodegradation under nitrate-reducing condition than that under sulfate- and iron-reducing conditions [41]; additionally, the biodegradation pathways varied under different reducing conditions. Despite these exciting findings, it should be noted that biodegradation of polyfluorinated pollutants usually proceeded slowly and removed limited fluorine under either aerobic or anaerobic conditions [38—40]. Continuous efforts are needed to obtain microbes capable of efficiently degrading and detoxifying polyfluorinated pollutants.

New findings about biodegradation of other emerging organohalides have also been achieved although with limited information. Triclosan, diclofenac, and tetrabromobisphenol A were metabolically dehalogenated by *Dehalococcoides* or *Dehalogenimonas* under anaerobic conditions [8,42,43]. Contrarily, hexachloro-1,3-butadiene was co-metabolically dechlorinated by *Dehalococcoides* due to inhibition of parent compounds on ATPase [44]. *Burkholderiales* and *Rhizobiales* were potentially responsible for hydrolytic dechlorination and oxidation of tris(2-chloroethyl) phosphate in an aerobic sediment microcosm, which were identified to harbor genes associated with those pathways via metagenomic analyses [45]. However, microbes that could efficiently degrade several massively used organohalides such as decabromodiphenyl ethane, short-chain chlorinated paraffins, and 1,2-bis-(2,4,6-tribromophenoxy) ethane remain unknown.

Advances and obstacles in bioremediation of organohalide pollutants

The journey from recognition of pollution to establishment of mature bioremediation technologies is always tortuous and long, as demonstrated by the bioremediation history of chloroethenes. Pioneering field

Table 1

Representative microbes and their functional enzymes degrading the selected organohalide pollutants.

Pollutants	Microbes	Redox condition	Representative pathways	Functional enzymes	References
PCBs	*Dehalococcoides*	Anaerobic	Reductive dehalogenation	Reductive dehalogenases (PcbA1, PcbA4, PcbA5, and MbrA)	[6,46]
	Dehalobium			–	[47]
	Dehalogenimonas			–	[21,22]
	Bacillus	Aerobic	Aerobic dehalogenation and mineralization	Dioxygenase, dehydrogenase, and hydrolases	[24]
	Comamonas				[23]
	Paraburkholderia				[48]
	Pseudomonas				[25]
	Ralstonia				[27]
	Rhodococcus				[49]
PBDEs	*Acetobacterium*	Anaerobic	Reductive dehalogenation	–	[50]
	Dehalococcoides			Reductive dehalogenases (PbrA1, PbrA2, PbrA3, PcbA4, PteA, TceA, BdeA, and MbrA)	[5−7,51]
	Dehalobacter			–	[52]
	Sulfurospirillum			–	[53]
	Bacillus	Aerobic	Aerobic debromination, hydroxylation, and ring-opening reactions	Haloacid dehalogenase and dioxygenase	[28]
	Pseudomonas				[29]
	Rhodococcus				[54]
	Stenotrophomonas				[4]
PFOA	*Acidimicrobium*	Iron-reducing	Aerobic defluorination, desulfonation, and decarbonization	–	[13,55]
	Delftia	Aerobic	Aerobic defluorination	Haloacid dehalogenases	[56]
PFOS	*Acidimicrobium*	Iron-reducing	Aerobic defluorination, desulfonation, and decarbonization	–	[13,55]
	Pseudomonas	Aerobic		–	[31]
6:2 Fluorotelomer sulfonamidoalkyl betaine/sulfonate	*Gordonia*	Aerobic	Aerobic defluorination, desulfonation, and C-N bond cleavage	–	[32]
Nonadecafluorodecanoic acid	*Pseudomonas*	Aerobic	–	–	[57]
Mono-difluorinated alkanes (C7-C10)	*Pseudomonas*	Aerobic	Aerobic defluorination and oxidation	–	[33,35]
2,2-Difluoro-1,3-Benzodioxole	*Pseudomonas*	Aerobic	Aerobic defluorination	Dioxygenase	[34]
6:2 Fluorotelomer sulfonic acid	*Rhodococcus*	Aerobic	Aerobic defluorination, desulfonatio, and decarbonization	Haloacid dehalogenase, monooxygenase, and cytochrome P450	[36]
4-Hydroxy-chlorothalonil	*Dehalogenimonas*	Anaerobic	Reductive dechlorination	–	[58]
Diclofenac	*Dehalogenimonas*	Anaerobic	Reductive dechlorination	–	[43]
Triclosan	*Dehalococcoides*	Anaerobic	Reductive dechlorination	Reductive dehalogenase (PcbA1)	[42]
Tetrabromobisphenol A	*Dehalococcoides*	Anaerobic	Reductive debromination	Reductive dehalogenase (PcbA1)	[8]
Tris(2-chloroethyl) Phosphate	*Burkholderiales and Rhizobiales*	Aerobic	Hydrolysis and oxidation	Phosphatase	[45]
Hexachloro-1,3-butadiene	*Dehalococcoides*	Anaerobic	Reductive dechlorination	–	[44]

monitoring revealed widespread contamination of underground water with chlorinated solvents in the 1970s, followed by laboratory validation of bioremediation during the 1980s–2000s, initial field-scale application in the 2000s, and establishment of mature bioremediation technologies (e.g., biostimulation and bioaugmentation) thereafter. A breakthrough in bioremediation of chloroethenes is the discovery of microorganisms that could completely detoxify chloroethenes to non-toxic product in a growth-supporting manner [59]. It stands to reason that bioremediation technologies of PCBs, PBDEs, PFASs, and other emerging organohalides will evolve similarly. Microbes capable of metabolizing PCBs and PBDEs have been obtained since the 1990s [7,46,51], but they were only applied in bioremediation very recently [11,12,30,31,47]. In 2008, bioaugmentation using Candidatus "*Dehalobium chlorocoercia*" DF1 enhanced PCB dechlorination by approximately 50% in a laboratory study [47]. Granular-activated carbon was identified as suitable carrier to grow and deliver bioinoculants to soil [47]. Later, it was found that combined bioaugmentation of anaerobic *D. chlorocoercia* DF1 with aerobic *Paraburkholderia xenovorans* LB400 more efficiently mineralized PCBs [30], owing to the capability of *P. xenovorans* LB400 to further degrade lower PCB congeners produced by *D. chlorocoercia* DF1 [26]. The first *in-situ* pilot-scale bioremediation of PCBs using *D. chlorocoercia* DF-1 and *P. xenovorans* LB400 was reported in 2019, decreasing PCB concentration by 52% and 95% in sediments and porewater, respectively, after 409 days [11]. Despite that diverse *Dehalococcoides* strains and aerobic microbes have been isolated to dechlorinate/degrade PCBs [6,24,46,48,60], studies evaluating their efficacy in bioremediation remain sparse. More recently, sewage sludge was supplemented as both bioinoculant and organic substrates to remediate PCBs in sediment microcosms [9,10]; this economical approach may circumvent difficulties in cultivating fastidious PCB-dechlorinating consortia. Thus far, only one study reported laboratory bioremediation of PBDEs in sediments by bioaugmentation with *Dehalococcoides* [12]; nonetheless, similar bioremediation performance of PBDEs is expected using other PBDE-degrading microbes such as *Bacillus*, *Pseudomonas*, and other *Dehalococcoides* strains [5,7]. The abovementioned progress is important to promote bioremediation of PCBs and PBDEs from laboratory studies to field application.

Bioremediation studies of fluorinated pollutants are still rare. Chetverikov et al. reported 75% depletion of PFOS in soil after 3-month bioaugmentation with *Pseudomonas plecoglossicida* 2.4-D [31]. Similarly, bioaugmentation with *Acidimicrobium* sp. strain A6 resulted in 30–60% removal of PFOA in biosolids [13]. However, it should be noted that the fraction of fluorine removed from fluorinated pollutants was low (<5%) in previous laboratory bioremediation due to the low defluorination capability of bioinoculants [13,31]. Therefore,

exploration of microbes that could extensively defluorinate and mineralize polyfluorinated compounds is still the central task for developing relevant bioremediation technologies. Additionally, the influence of organic and inorganic co-contaminants [12], environmental factors (e.g., pH, temperature, and redox potential) determining the survival of bioinoculants [61], and long-term effectiveness of bioremediation approaches need to be considered during bioremediation of organohalide pollutants.

Underexplored microbial ecology affecting bioremediation

Successful bioremediation relies on collaboration of diverse microbes; therefore, in-depth knowledge about their microbial ecology is needed to manipulate the microbiota for better bioremediation performance. There are several important ecology questions affecting bioremediation that remain to be addressed (Figure 1). Microbial diversity is a crucial factor determining ecosystem functioning. Biodegradation of organohalides was stimulated by introducing partner microbes into axenically cultivated cultures [60,62,63]. However, the exact relationship between microbial diversity and degradation of organohalides awaits further exploration (Figure 1a). Another question is how interactions between microbes themselves and their surrounding environments affect pollutant biodegradation (Figure 1b). Previous studies suggested that certain microbial interactions benefited dehalogenation of organohalide pollutants by transferring cofactors and substrates [60,62], relieving autotoxicity of metabolites [63], and collaboratively degrading intermediate products [64] in defined cultures. Additionally, microbe–environment interactions can substantially affect biotransformation of organohalide pollutants. For example, porous materials (e.g., activated carbon) could provide favorable surfaces for proliferation of functional microbes and shield sensitive microbes from environmental stress [11,61], whereas some electron-shuttling compounds (e.g., humic acid) changed pollutant degradation by regulating interspecies and intracellular electron transfer [65]. Currently, introduction of potential partner microbes and amendment of beneficial compounds are the main approaches to regulate these interactions [11,62]. However, it should be noted that the same microbes and materials sometimes could exhibit both beneficial and detrimental effects on organohalide-degrading microbes, depending on the conditions [60]. Thus far, it is still challenging to decipher these interactions and assess their collective consequences on pollutants degradation at real contamination sites with high heterogeneity and countless microbial species. Evaluating the potential of native microbes to degrade organohalide pollutants is fundamental to select suitable bioremediation strategies. Laboratory treatability tests are usually unaffordable in terms of time [12]. Multiomics tools seem to be prospective and timely to evaluate pollutant

Figure 1
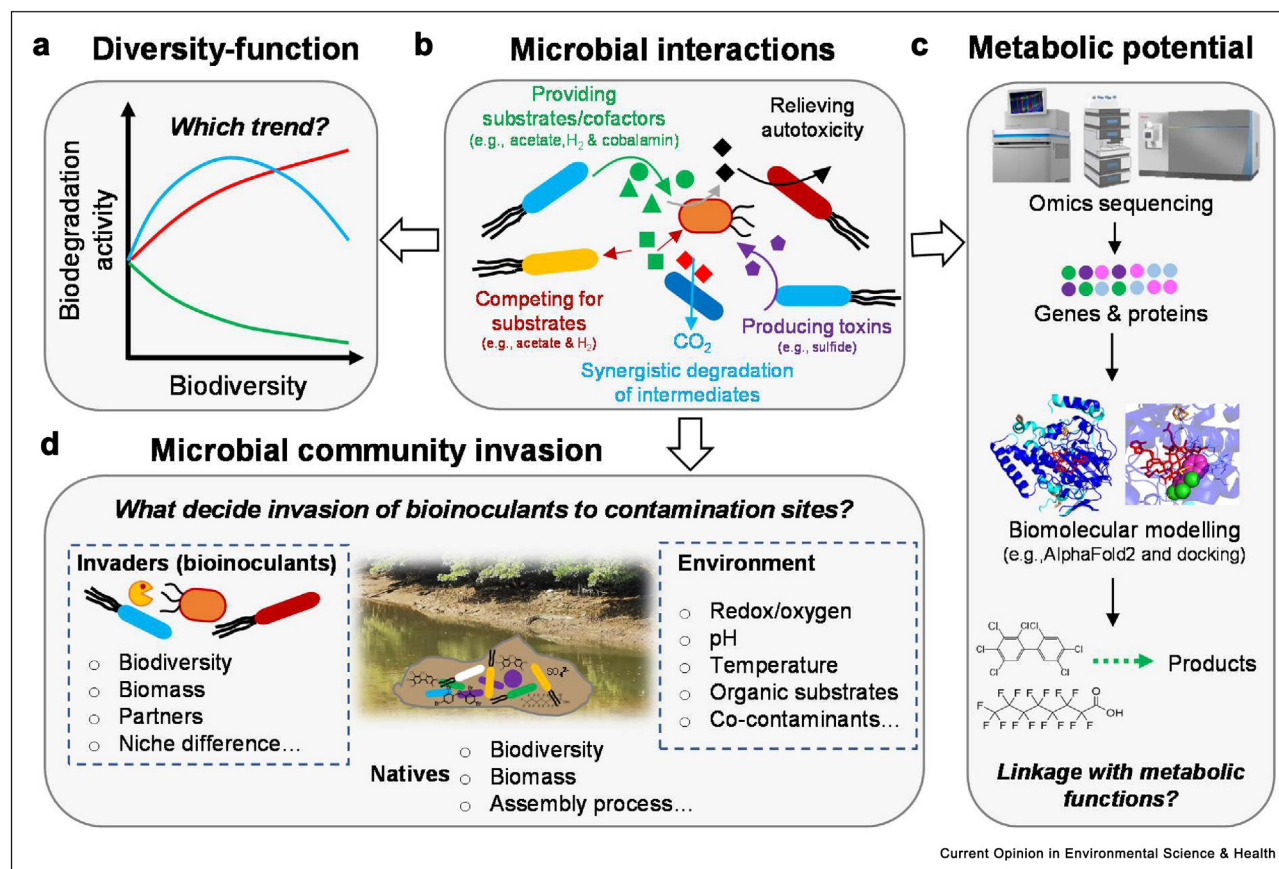
Microbial ecology associated with bioremediation of organohalide pollutants. (**a**) The potential relationship between microbial diversity and biotransformation of organohalide pollutants. (**b**) Interspecies interactions that may accelerate or inhibit pollutant removal. (**c**) Abiotic and biotic factors affecting the establishment and functioning of bioinoculants after bioaugmentation. (**d**) Exploration of the linkages between genetic information of microbes and metabolic activity via multiomics sequencing techniques.

degradation potential by native microbiota (Figure 1c). But this requires a dataset of functional genes and enzymes linked to biodegradation of organohalide pollutants and their metabolites.

Survival and well-functioning of augmented microbes in recipient environments are the prerequisite for successful bioremediation. However, cases where augmented microbes were phased out after bioaugmentation are not uncommon [9,66]. Identifying environmental and biological factors that determine survival and functioning of bioinoculants at contamination sites is imperative (Figure 1d). The influence of environmental factors such as organic substrates, redox condition, and co-contaminants on bioaugmentation has been investigated in previous studies [67]. Contrarily, it remains unknown how the properties of bioinoculant and resident microbiota would affect bioremediation. Bioaugmentation could be regarded as an "invasion" event (the establishment of an alien microbial

population in a resident community), and niche difference and cell density of the invasion community could determine the outcome of invasion events [66,68,69]. Increasing difference in niches between the invaders and natives could improve invasion success owing to reduced competitive interactions [69]. Higher biomass of invaders also benefited invasion events [70]. However, repeated long-term cultivation of bacteria in monoculture could lead to the loss of their ability to coexist with another, potentially hampering their establishment in recipient environments [68]. Properties of resident microbial communities also matter to invasion events. Generally, survival of the invader was negatively correlated with diversity of native communities [71]. The abovementioned invasion knowledge provides insights to better design bioremediation strategy. For example, the quantity and timing of substrate injection could be optimized to avoid overproliferation of native microbes before augmentation of bioinoculants; cultivating functional bacteria like OHRB in

consortia containing potential partners may also improve establishment of bioinoculants in resident microbial communities. It deserves more efforts to test these interpretations in future laboratory and field investigation.

Potential application of machine learning, quantum chemistry, and biomolecular modeling in bioremediation

Bioremediation performance is influenced by a variety of biological and geochemical factors, challenging the selection of optimal bioremediation strategies. Trial-and-error tests are conventionally used to select bioremediation approach, which rely on empirical judgment rather than quantitative analyses. In contrast, machine learning emerges as a promising tool to aid the selection and optimization of bioremediation approaches, mitigating subjective biases. For example, monitoring data including dechlorination potential of chloroethenes as well as geochemical and biological parameters were collected from 35 wells at five contamination sites to develop machine learning models using the classification and regression tree algorithm; the developed models predicted dechlorination potential of chloroethenes with 69.5% sensitivity and elucidated the overwhelming roles of nitrate, nitrite, and ferrous iron in determining dechlorination of chloroethenes [72]. This finding indicates that biostimulation (e.g., injection of electron donors) rather than bioaugmentation is more likely to accelerate bioremediation of these sites. The contribution of machine learning models also extends to optimizing microbial compositions of bioinoculants [73]. However, efforts are needed to improve data availability, model development and interpretation, and applicability analysis before we could really harness the power of machine learning to promote bioremediation [14].

Organohalide pollutants such as PCBs, PBDEs, and PFASs contain dozens to hundreds of congeners, the physicochemical properties of which vary considerably, making it important to understand their environmental fate during bioremediation. Quantum chemistry is an attractive tool to achieve this goal (Figure 2). The electron density of halogens obtained from quantum computation successfully rationalized microbial dehalogenation pathways of various organohalides [44,74]. For example, chlorine substituents with the lowest electron density were prone to be removed from polychlorinated dibenzo-p-dioxins, and this successfully predicted 90% dechlorination pathways [74]. The efficiency and accuracy of quantum chemistry in predicting pollutants degradation pathway could be further improved by machine learning [14]. This strategy predicted complex metabolic reactions of tris(1,3-dichloro-2-propyl) phosphate catalyzed by human CYP450 enzymes [75]. However, developing

Figure 2
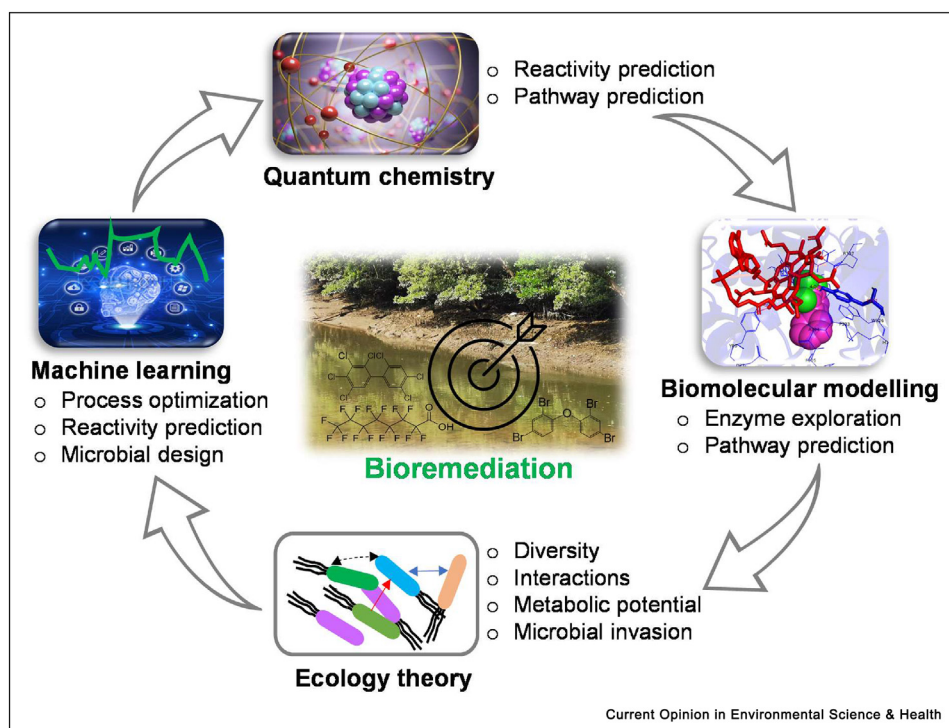
A conceptual framework of bioremediation technology development incorporating machine learning, quantum chemical methods, biomolecular modeling, and ecology theories.

high-resolution analytical methods (e.g., liquid/gas chromatography-mass spectrometry) remains indispensable to verify and quantify the predicted degradation products [76,77].

The crystal structures of most enzymes involved in organohalide pollutants degradation are not available, which prevents mechanistic insights into pollutant degradation. The invention of computational three-dimensional structure modeling of proteins powered by machine learning (e.g., AlphaFold2) is a giant leap; it enables researchers to predict reliable structures of proteins timely with minimal cost [78]. Recently, the structure of RDase MbrA was predicted and docked with different organohalides, with different active sites identified for dehalogenation of aliphatic and aromatic organohalides [6]. With the aid of machine learning, biomolecular docking analysis between the predicted structures of enzymes and organohalide pollutants may help to identify the key features of enzymes (e.g., conserved 3D structure regions) linked to pollutant degradation and to explore novel enzymes degrading organohalide pollutants (Figure 2).

Concluding remarks

The diversity of microorganisms that could metabolize organohalide pollutants such as PCBs, PBDEs, and PFAS has been expanded over recent years. Preliminary attempts to employ these microbes in bioremediation were also made, providing valuable information in promoting the development of bioremediation technologies. However, it should be noted that exploring more potent microbes remains a central task for bioremediation of polyfluorinated pollutants as well as other emerging pollutants. Microbial ecology associated with bioremediation is a relatively untapped field despite the well-accepted notion that a collection of interactive microbes catalyze biodegradation of pollutants. More research efforts in microbial ecology could facilitate researchers and practitioners to better understand and manipulate the microbial world for predictable and desirable bioremediation performance. Machine learning, quantum chemistry, and biomolecular modeling are prospective tools to explore novel pollutant-degrading microbes, optimize bioremediation strategy, and predict environmental fate of pollutants, yet we are at the nascent stage to apply them in bioremediation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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