Journal of Environmental Management 392 (2025) 126665

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Review

Bio-augmented permeable reactive barriers for groundwater remediation: A comprehensive review

Hai Lin [a,b], Yuting Zhang [a], Yingbo Dong [a,b,*], Qi Jin [a]

[a] School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing, 100083, China
[b] Beijing Key Laboratory on Resource-oriented Treatment of Industrial Pollutants, Beijing, 100083, China

ARTICLE INFO

Keywords:
Groundwater
Permeable reactive barrier (PRB)
Heavy metals
Organic contaminants

ABSTRACT

Groundwater is an important component of water resources. Mixed contaminants comprising heavy metals and organic contaminants from industrial activities can contaminate groundwater, which pose direct threats to human health through the food chain or drinking water. Bio-augment permeable reactive barriers (Bio-PRB) remove contaminants through degradation, adsorption, precipitation, REDOX and other processes. This study provides original insights into the various active media and microbial carriers and the mechanisms of interaction among microorganisms, active media, and various contaminants. In addition, the possible solutions for prolonging the long-term performance as well as in addressing blockages of Bio-PRB are shown. Moreover, the presents insights into these methods are summarized. Finally, insights and outlooks were presented for Bio-PRB for complex groundwater contaminants. This review is expected to provide technical guidance and assistance for Bio-PRB of complex contaminated groundwater.

1. Introduction

Groundwater is one of the most important water sources for agricultural irrigation, industrial production and urban life (Liu et al., 2014). However, anthropogenic activities, mainly industrial and agricultural activities, threaten groundwater quality as many contaminants may reach the aquifer (Jurado et al., 2019). Organic contaminants such as chlorinated organic compounds, insecticides, herbicides, dyes, aromatic compounds (Liu et al., 2021; Tavakoli Dastjerdi et al., 2018) and inorganic contaminants such as heavy metals (Li et al., 2021, 2022a; Wang et al., 2020a), nitrate (Yu et al., 2024) and sulfate (Xiao et al., 2024) threaten groundwater resources. Many organic contaminants can be recalcitrant under natural conditions (Ahmad et al., 2012; Kim et al., 2022). The natural degradation of such contaminants to innocuous levels may take hundreds to thousands of years. Heavy metals widely present in the Earth's crust can be dissolved in groundwater through natural weathering, erosion, or changes in soil pH value (Ali et al., 2019; Fedoročková et al., 2021; Hashim et al., 2011). Cr (VI) is the most stable form of chromium, is highly toxic, mutagenic, and carcinogenic. Its high solubility and mobility facilitate environmental dispersion (Lu et al., 2020). Chronic exposure poses significant health risks, including organ damage and various diseases (Park, 2020; Wise et al., 2022). Cadmium is a cumulative toxin with a very long biological half-life about 30 years, which has harmful effects on the ecosystem (Tasharrofi et al., 2020). Lead exposure in humans causes anemia, weakness, and risk of high blood pressure (Hashim et al., 2011), while manganese is associated with Parkinson's disease, hallucinations, memory impairment, disorientation, and emotional instability (Casalini et al., 2020). Inorganic arsenic exhibits significant toxicity, leading to dermal, cardiovascular, neurological disorders, and cancer (Podgorski and Berg, 2020). Excessive vanadium (V) concentrations exhibit toxicity, detrimentally impairing plant growth and inducing renal and thyroid dysfunction in humans (Liu et al., 2022). Body-absorbed nitrate has negative effects on humans. The nitrate in drinking water is reduced to nitrite, and eventually to N-nitroso in body, which is a highly toxic and carcinogenic compound (Gibert et al., 2019). Therefore, it is vital to develop methods for the long-term remediation of contaminated groundwater.

Groundwater remediation techniques are mainly divided into in-situ remediation and ex-situ remediation. In-situ remediation technology has garnered significant attention due to its advantages, such as eliminating the need for groundwater extraction and minimizing site disturbance (Yuan et al., 2024b; Zhao et al., 2022). Permeable reactive barrier (PRB) technology appeared in the 1990s and is a typical representative of in-situ remediation technology for groundwater contaminants

* Corresponding author. School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing, 100083, China.
E-mail address: ybdong@ustb.edu.cn (Y. Dong).

https://doi.org/10.1016/j.jenvman.2025.126665
Received 29 May 2025; Received in revised form 8 July 2025; Accepted 16 July 2025
Available online 21 July 2025

(Upadhyay and Sinha, 2018). PRB is one of the effective in-situ groundwater remediation technologies due to its use of natural flow to bring contaminants into contact with reactive materials, without the need to install any above-ground facilities and energy inputs, low cost, simple operation and good removal effect (Gibert et al., 2019; Liu et al., 2021; Snape et al., 2001). However, traditional PRB technology faces challenges such as media saturation and declining long-term performance (Cao et al., 2020).

A solution to overcome these drawbacks is using bio-augmented permeable reactive barriers (Bio-PRBs). The Bio-PRB is a new type of PRB constructed from micro-activated or immobilized microorganisms with other media (iron-based materials, biochar, etc.), and is one of the innovative groundwater remediation technologies (Wang and Wu, 2019a; Xin et al., 2013a). The direct interaction between contaminants and reactive media reduces toxic effects of contaminants at high concentrations on microorganisms, and by-products provide more suitable living conditions for cells (Xu et al., 2017). Where nutrients are sufficient for growth, this can result in biofilm formation and generate a bio-reactive barrier. The roles of microorganisms in Bio-PRBs include providing electron donors (Sathishkumar et al., 2017), facilitating electron transfer (Zhou et al., 2022), and degrading contaminants (Fig. 1). Microorganisms utilize contaminants and/or reactive media as electron donors (Gibert et al., 2019), oxygen as a terminal electron acceptor under aerobic conditions, and alternative electron acceptors such as nitrate (Zhang et al., 2019), sulfate (Xu et al., 2024b) and contaminants (Wang et al., 2022a) as electron acceptors under anaerobic conditions to participate in and contribute to contaminant removal. As a result, the removal of contaminants can occur more effectively at the presence of microorganisms. This can promote a lower frequency of media replacement and disposal, resulting in reduced costs (Tiehm et al., 2008). Bio-PRBs have been shown to be efficient, economical and environmentally friendly when used to remove exogenous substances or single aromatic compounds from contaminated groundwater (Farhadian et al., 2008). Gholami et al. showed significant differences in removal efficiency between biological and non-biological PRB columns, illustrating the important role of microorganisms in groundwater Bio-PRB treatment (Gholami et al., 2019).

The objective of this study is to evaluate the research progress of Bio-PRB reactive media in the treatment of organic and inorganic contaminants in groundwater, and specifically analyze the applicable microbial agents and corresponding removal efficiency for different contaminant types. On this basis, the core mechanism of microbial enhancement removal of various contaminants was explored. Finally, this paper also points out the possible research gaps and future directions of Bio-PRB.

2. Reactive media

The key to Bio-PRB technology is the active medium material used in the treatment of groundwater contaminant. The principal considerations required for the selection of suitable reactive material are as follows: reaction with the contaminants (Amani et al., 2024), hydraulic performance (Yaman et al., 2021), availability and cost (Wang and Wu, 2019a), compatibility with the subsurface environment (Lawrinenko et al., 2023), suitability over long periods (Budania and Dangayach, 2023; Sakr et al., 2023) and microorganism loading capacity (Valdivia-Rivera et al., 2021).

Biochar, biomass and zeolite adapt to various hydraulic conditions, but due to their limited adsorption capacity, they are more suitable for groundwater environment with low contaminant concentration. Zero-valent iron (ZVI) provides a reductive environment, exhibiting optimal performance under neutral or slightly acidic groundwater conditions. In addition, many novel reactive media and microorganisms have been tested for optimizing Bio-PRBs with considerable effects on different types of contaminants and applications. In this portion of the review, we have considered widely used reactive materials biomass, biochar, zeolite, ZVI and novel composite materials in Bio-PRBs for various contaminants removal.

2.1. Biomass

Natural biomass materials have broad availability and cost-effectiveness, serving as an efficient carbon source for denitrification pathways after simple improvement. Corncob (Zhang et al., 2020), peanut shell (Wang et al., 2020b), wood chips (Sewwandi et al., 2012), etc. have been recognized as potential adsorbents in economical Bio-PRB systems due to their high performance in removing contaminants from wastewater. Natural biomass materials can become a suitable source of slow-release carbon through regulation, providing a long-term living conditions for Bio-PRB microorganisms and promoting microbial degradation of contaminants (Xie et al., 2017). Currently, sustainably released composite carbon source material developed with agricultural waste demonstrates stable carbon release rate, which is suitable for

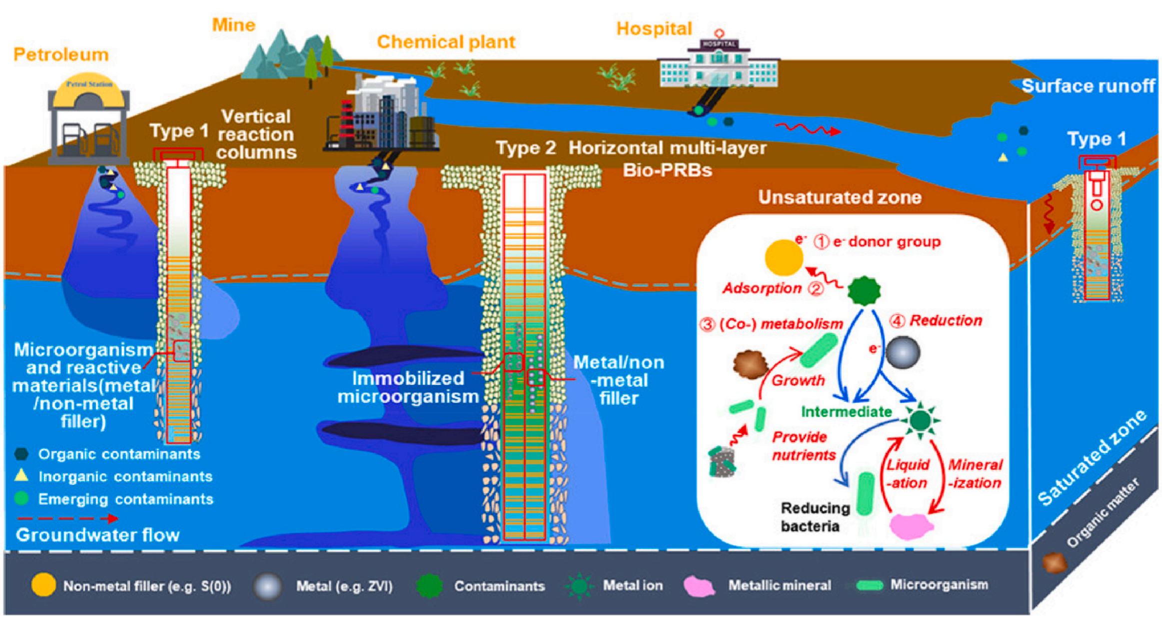

Fig. 1. Bio-PRB microbial-reactive media interaction mechanism (Wang et al., 2023b).

stimulating the condition with low microbial activity in groundwater (Fei et al., 2022; Pensky et al., 2023).

Wheat straw, corncob, wood chips and corn straw as active media in Bio-PRB system exhibit sustained carbon release capacity, which supplies optimal redox conditions for denitrification, enhances the proliferation and metabolic activity of denitrifying microbial communities, and achieves efficient nitrate removal (Zhang et al., 2020). Redwood chips and sandy soil are used as reactive media of horizontally configured Bio-PRB. The establishment of favorable growth conditions for denitrifying microorganisms through the provision of bio-available carbon substrates and the expansion of the saturation zone achieved nitrate removal efficiencies exceeding 98.68 %. When the permeation rate is relatively fast, the high porosity of wood chips helps to stimulate denitrification in sandy soil with lower permeation capacity. The redwood chips age over time, the amount of available carbon leached and permeability decreases, which will lead to a lower removal rate of nitrates (Beganskas et al., 2018). Natural biomass is highly competitive in the simultaneous remediation of nitrate and V(V) contaminants, with achieving nitrate reduction efficiency of corncob of 89.7 $\pm$ 5.5 % and V (V) removal rate of 16.59 mg/g (Wang et al., 2023a).

Biomass materials are environmentally friendly and cost-effective. However, the reaction efficiency and adsorption capacity of biomass are limited, and further optimization is necessary to augment stability and efficiency in practical applications.

2.2. Biochar

Biochar serves as a highly effective reactive media in Bio-PRBs, utilizing its powerful adsorption capabilities to remove diverse organic and inorganic contaminants (Liu et al., 2018; Lu et al., 2024a; Wang et al., 2020b, 2022b; Xie et al., 2017). Biochar can promote the chemical interaction between contaminants and microorganisms colonizing the biochar surface, achieving effective biodegradation (Fu et al., 2018; Patel et al., 2022). Furthermore, as a carrier for microorganisms, it enhances the adaptability of microorganisms to adverse environments in many bioremediation systems (Du et al., 2016; Shi et al., 2018; Zhao et al., 2020).

An immobilized biochar with slow-release characteristics was utilized for Cr (VI) removal, on which *M. morganii* subspecies was successfully immobilized and became the dominant microbial species during the Cr (VI) remediation process, achieving 100 % removal efficiency. In a study utilizing an immobilized biochar exhibiting slow-release properties for Cr (VI) removal, the *M. morganii* subspecies was successfully immobilized on the biochar. The immobilized strain became the dominant microbial species and achieved 100 % Cr (VI) removal efficiency (Xie et al., 2017). *Sporosarcina saromensis W5* and biochar were employed for Cr (VI) removal to determine the formation dynamics and colonization patterns of biofilms on filler surfaces. The results demonstrated that biochar exhibited optimal performance as a biofilm carrier (Huang et al., 2021). *K. Viariicola* H12-CMC-FeS bacteria and biochar were used as Bio-PRB reactive media to remove Cr (VI), achieving 94 % removal efficiency, which was significantly higher than bacteria or biochar alone (Man et al., 2023). A packed-column system incorporating herbal residue and spruce biochar achieved 99.7 % trichloroethylene (TCE) removal, with attached biofilms containing dechlorinating microorganisms including *Desulfitobacterium* spp., *Sulfurospirillum* spp. and *Desulfuromonas* spp. that partially transformed TCE to 1,2-dichloroethane (Siggins et al., 2021). However, the discovered species cannot completely degrade TCE to ethylene but produce intermediates, and further research should be done to avoid more toxic intermediates resulting from the removal of TCE by microbial coupling biochar.

Biochar-based Bio-PRBs demonstrate significant potential for groundwater remediation, offering advantages such as minimal byproduct generation and negligible secondary contamination, and obviation of the need for premature media replacement due to failure or clogging. However, their long-term efficacy may be constrained by adsorption capacity limitations, as progressive saturation of active sites can diminish contaminant removal efficiency.

2.3. Zeolite

Zeolite, a microporous crystalline hydrated aluminosilicate, is widely employed in environmental remediation studies due to its dual functionality as an effective adsorbent and cation exchanger (Nasief et al., 2021; Vocciante et al., 2018). It can efficiently treat groundwater contaminated by a variety of contaminants, such as heavy metals and ammonium. Therefore, it is considered as a promising Bio-PRB reactive medium for the remediation of groundwater (Kumara and Kawamoto, 2021; Tasharrofi et al., 2020; Yang et al., 2023). Heavy metal cations can be effectively adsorbed or exchanged within the internal channel structures of chain or layered minerals, maintaining high permeability and enhancing material longevity. The cation exchange property of zeolite makes it particularly valuable for applications in environmental remediation (Li and Liu, 2022). Zeolites can adsorb microbial cells, with some exhibiting selective adsorption for specific microorganisms (Kubota et al., 2008). They serve as effective carriers for microbial heavy metal removal systems (Yousefi and Matavos-Aramyan, 2018). In addition, the interaction between hydrocarbons and zeolites promotes microbial attachment and growth, enhancing the removal effect of petroleum hydrocarbons (Freidman et al., 2017a). Ahmadnezhad et al. demonstrated that natural zeolite combined with microbial strains significantly enhanced benzene, toluene, ethylbenzene and xylene (BTEX) removal, achieving 90 % adsorption and 80 % degradation efficiencies (Ahmadnezhad et al., 2021).

Despite zeolite has high initial removal efficiency for mixed contaminants, its long-term performance declines as surface pores and interstitial spaces become saturated, compromising barrier stability (Vaezihir et al., 2020). Therefore, zeolite is typically combined with other materials for Bio-PRB applications. Recent studies have prioritized the modification of natural materials to address these limitations.

2.4. ZVI

The main mechanism coupling between ZVI and microorganisms primarily involves the bio-stimulatory effects of Fe (II) or Fe (III) generated during contaminant degradation by ZVI, which enhance microbial growth (Xu et al., 2017). As summarized in Table 1, ZVI demonstrates effective application in groundwater heavy metal remediation. According to the study of Wang et al., ZVI enhances Cr (VI) biological reduction (Wang et al., 2022a).

The removal of heavy metals by ZVI is reduction and/or surface complexation, while the removal of heavy metals by S-ZVI is precipitation and/or surface complexation (Liang et al., 2021). The coupling of sulfate reducing bacteria (SRB) and ZVI has a good effect on the removal of Cr (VI) contaminant in groundwater. The SRB-ZVI coupling system demonstrates superior Cr (VI) removal efficiency compared to the chemically sulfidated NaS_2-ZVI system, exhibiting 1.8 times higher sulfidation efficiency and 2.2 times higher specific surface area with distinctive porous structures. The porous structure of sulfidated ZVI (S-ZVI) in the SRB-ZVI system is composed of FeS_x generated by the combination of Fe^{2+} and S^{2-}. The Cr (VI) in contact with S-ZVI is adsorbed and reduced by FeS_x and then precipitated, thus Cr (VI) is unable to contact and inactivate SRB (Xu et al., 2024b). This porous structure not only enhances contaminant removal but also provides microbial protection against Cr (VI) toxicity, enabling SRB colonization, environmental adaptation, and sustained in-situ sulfidation activity (Li et al., 2018; Xu et al., 2024b).

Due to excellent water treatment performance of ZVI, many studies have developed sulfidated microscale ZVI (S-mZVI) (Garcia et al., 2021). Studies demonstrate that S-mZVI not only effectively removes heavy metals but also protects groundwater microorganisms (Song et al., 2022;

Table 1
Different applications of ZVI for groundwater remediation.

Contaminant	Reactive Media PRB	Mechanism	Time	General Conclusion	Reference
As (V)	ZVI	Adsorption or coprecipitation	360 days	99.5 % removal for batch experiment. The removal rate decreased by 45 % in aerobic and by 39 % in anoxic conditions after 360 days for flow- through columns	Lee et al. (2009b)
As (V)	ZVI	Adsorption followed by coprecipitation	180 days	99 % removal in batch and column study	Abedin et al. (2011)
Cr (VI)	ZVI, gravel and sand mixture	Chemical reduction and bio-reduction	22–174 days	ZVI induced Cr (VI)-reducing bacteria competitive growth in PRB	(Q. Wang et al., 2022)
Ni (II)	Granular ZVI-pumice mixtures	Spontaneous electrochemical cementation or precipitation or coprecipitation	3240 h	74 % removal (50:50 ratio), 62 % removal (30:70), 40 % removal (10:90)	Calabrò et al. (2012)
Zn (II) and Cu (II)	Granular ZVI	Adsorption or coprecipitation, Cu^{2+} cementation, solution-based metal hydroxide formation	0, 21, and 42 freeze-thaw cycle	ZVI PRB could remediate heavy metal- contaminated cold regions	Statham et al. (2015)
Cu (II), Ni (II) and Zn (II)	ZVI and lapillus	Different removal mechanisms, adsorption for Ni and Zn	3000–5000 h	Heavy metals were effectively removed in efficiency sequence: Cu > Zn > Ni. The weight ratio of 50:50 mixture showed a higher removal rate	Bilardi et al. (2019)
Cr (VI)	S-ZVI	Adsorption	44 days	The system consumes only 14.65 % of ZVI after 11 cycles of removal and the system exhibits a significantly better Cr (VI) removal efficiency of 100.0 %.	Xu et al. (2024b)
As (III), Cu (II), Cr (VI) and Co (II)	ZVI and chitosan ZVI	Adsorption	30 days (continuous operation)	ZVI batch experiment removal reached 98 % in single-metal system. Chitosan ZVI continuous-flow column test reached 98.84 % for Cu (II), 88.28 % for Co (II), 95.65 % for Cr (VI) and 87.10 % for As (III)	Zhu et al. (2022)
Nitrate	ZVI modified raw wheat straw	Redox and bio-denitrification	22 days hydraulic retention time	The lab-scale results indicated nitrate removal rate was stable and reached 90 % with denitrifying bacteria up to 34.37 %	Guo et al. (2021)
Phosphorus	nZVI and iron-copper (nanoscale ZVI with bimetallic)	Corrosion of nZVI core by the release of iron oxides (Fe^{2+}/Fe^{3+}) then adsorption followed by co-precipitation	14 days	Anti-aggregation effect and enhanced removal by up to 2.2 times than nZVI alone and removal was improved by 22 % at a lower flow rate	Eljamal et al. (2020)
Chlorinated hydrocarbons	modified CS@ZVI	Adsorption, bio-stimulation and biodegradation	10 days	degradation rate reaching 100 % after 12 days	Chen et al. (2024)
2,4,6-TCP	ZVI@CA gel beads	Adsorption and biodegradation	96 h	reaction rate of 2,4,6-TCP increased by 175 %	Wang et al. (2022b)

Yang et al., 2024). The Bio-PRB systems were augmented with SRB-activated S-mZVI, SRB bio-reduction of Fe (III) enabled S-mZVI to achieved Cr (VI) removal capacity of 34.4 mg/g over four cycles, with 3.2 times enhancement (Yang et al., 2024). Optimal performance (S/Fe = 0.2) achieved 99.8 % of Cr (VI) removal and high removal efficiencies for Ni, Zn, and Al (Song et al., 2022).

Micron ZVI (mZVI) and bio-stimulation can be combined to achieve the efficient removal of hydrocarbons from contaminated groundwater sources (Puigserver et al., 2023; Summer et al., 2020; Wu et al., 2020). The combination of lactate and mZVI can achieve a removal rate of 96.3 % for tetrachloroethene (PCE). This process involves biological reduction dechlorination and abiotic reduction of mZVI, and coupling and interdependence occur between the biological and abiotic processes (Puigserver et al., 2023). In addition, the ZVI coupled with microorganisms also has a significant effect on the removal of total carbon (TC) in water. The ZVI products Fe (II) and Fe (III) through adsorption and reduction serve as essential nutrients for TC degrading microorganisms, further promoting contaminant degradation (Huang et al., 2017a).

The primary challenges of ZVI as reactive media involve declining remediation efficiency from active site depletion, reduced Bio-PRB permeability caused by particle agglomeration and byproduct accumulation and potential contaminant plume diversion (Fuller et al., 2013; Lawrinenko et al., 2023). Current mitigation strategies focus on composite media systems incorporating dispersants and the development of novel porous ZVI materials discussed in Chapter 4.

2.5. Composite material

Packing materials were encapsulated to form packing capsules. The encapsulation enhances the stability of the reactive media within Bio-PRB systems. It minimizes the negative impact of reactive media on the groundwater environment and creates more favorable conditions for microorganisms (Lemic et al., 2021; Vemmer and Patel, 2013).

The encapsulation of ZVI with calcium alginate and the encapsulation of biochar with immobilized microbial gel beads enhanced 2,4,6-trichlorophenol removal efficiency and reaction rates in Bio-PRB systems, while simultaneously increasing microbial richness and diversity (Wang et al., 2022b). For enhanced benzene removal efficiency from groundwater, an aerobic Bio-PRB system was developed utilizing sodium alginate encapsulated CaO_2 nanoparticles. This encapsulation strategy effectively buffered CaO_2 induced pH fluctuations in groundwater, thereby creating optimal conditions for microorganisms achieving a 50 % enhancement in benzene degradation efficiency (Mosmeri et al., 2017). Similarly, sodium alginate encapsulates MgO_2 nano-particles to minimize microbial inhibition caused by reactive media. This medium selectively promotes the growth of hydrocarbon degrading microorganisms (e.g., *Pseudomonas putida* and *Pseudomonas mendocina*) utilizing toluene and naphthalene as carbon sources, while effectively restoring microbial community diversity (Gholami et al., 2019).

The CaMgAl-layered double hydroxide (LDH) demonstrated remarkable denitrification performance, achieving 97.82 % nitrate removal efficiency through its distinctive two-dimensional layered structure. This structure enhanced enrichment of denitrifying bacteria and elevated activity of critical denitrification enzymes. The Ca in the reactive media reduces the surface charge of bacteria and makes them hydrophobic, promoting the formation of biofilm (Jiang et al., 2024).

The composite material reconciles the activity of reactive media and bio-adaptability, significantly enhancing the removal efficiency of Bio-PRB for the target contaminants. The core advantage lies in the optimization of the microbial microenvironment for efficient and stable synergistic remediation. However, the use of composite materials may be costly.

3. Bio-barriers

Bio-barriers can stimulate or enhance microbial activity for the degradation of contaminants (Diao and Yao, 2009; Tiehm et al., 2008). Table 2 summarizes the microorganism employed in Bio-PRBs for the remediation of various contaminants. The aerobic bacterium *Pseudomonas* demonstrates significant degradation efficiency to organic contaminants, including BTEX (Naeimi et al., 2021), polycyclic aromatic hydrocarbons (PAHs) (Freidman et al., 2017b), and Cr(VI) (Fei et al., 2022; Wang et al., 2022a). This process primarily relies on oxidation reactions catalyzed by oxidases (e.g., monooxygenase and dioxygenase) or the combination of extracellular polymeric substances (EPS) and contaminants. The anaerobic bacteria *Geobacter* and *Shewanella* are extensively utilized for reductive dechlorination processes, particularly in the remediation of chlorinated hydrocarbons (Lu et al., 2024a) (e.g., TCE). This degradation mechanism is primarily driven by reductive dehalogenase mediated electron transfer. In addition, SRB (Kumar et al., 2016) and denitrifying bacteria (Kong et al., 2015) are employed for the remediation of heavy metals and nitrate contaminants, achieving contaminant immobilization through sulfide precipitation and microbial denitrification, respectively. Microorganisms in Bio-PRBs perform critical functions such as serving as electron donors (Sathishkumar et al., 2017), mediating electron transfer processes (Zhou et al., 2022), and catalyzing contaminant degradation (Schostag et al., 2022).

Table 2
Microorganisms used in Bio-PRBs for removal of different kinds of contaminants.

Reactive media	Microoganisms type	Contaminants type	Mechanism	Optimal condition	Efficiency	References
Carbon-amended ZVI	*Desulfitobacterium* and *Dehalococcoides*	1,1,2-trichloroethane (1,1,2-TCA)	Biodegradation and redox reaction	–	Half-life reduced by a factor of 5	Patterson et al. (2016)
ZVI, sheep manure, compost and woodchips	*Desulfitobacterium hafniense Y-51*, *Geobactermetallireducens*	As (III) and Mn (II)	Adsorption,co-precipitation and biodegradation	–	80 %	Wilopo et al. (2008)
ZVI	Heterotrophic bacteria	Nitro benzene	Adsorption and/or co-precipitation biodegradation	pH values were 7.2 ± 0.1and ORP were 180 ± 10 mV	Increase by 50 %	Yin et al. (2015)
ZVI	*Microthrixaceae*、*Chitinophagaceae*、*Comamonadaceae* and *Oxalobacteraceae*	TC	Adsorption, reduction and biodegradation	Hydraulic retention time 7.2 h, ambient temperature from 25 to 30 °C	50 %	Huang et al. (2017b)
ZVI	SRB	As (V)	Biodegradation and reduction	20 °C	47 %	Kumar et al. (2016)
ZVI	SRB	Zn (II)	Biodegradation and precipitate	16 ± 2 °C and avoid direct sunlight	–	Kumar et al. (2015)
Rice straw biochar	*Pseudomonas putida*	Nitro benzene	Biodegradation	–		Liu et al. (2018)
Spruce biochar	*Dehalococcoides mccartyi* and *Clostridium butyricum*	TCE	Biodegradation reduction	Keep the temperature at 4 °C	99.7 %	Lu et al. (2024a) Lu et al. (2024b)
Carboxymethylcellulose -FeS @ biochar	*Klebsiella variicola* H12	Cr (VI)	Adsorption and biological reduction	optimal solid-liquid ratio 30:1	94 %	Man et al. (2023)
Slow released nutrient-immobilized biochar	*M. morganii*	Cr (VI)	Adsorption, reduction and biodegradation	30 °C	100 %	Hu et al. (2019a)
Woodchips	Dechloromonas, Chris tensenellaceae, and Chthioniobacteraceae Deferri bacteraceae、*Magnetospirillum* and *Novosphingobium*,SRB	inorganic mercury and nitrate	Mercury methylation and demethylation are coupled, denitrification	–	–	Hiller-Bittrolff et al. (2018)
Woodchip	Heterotrophic *Geobacter*	V (V)	Biodegradation	22 °C ± 2 °C	68.5 %–98.2 %	Li and Zhang (2020)
Woodchips and BOF slag	Denitrifying bacteria	nitrate and PO_4^{3-}	Adsorption and biodegradation	Strict pH requirements	Average removal 0.64 ± 0.23 mmol/(L·d)	Buyanjargal et al. (2021)
Woodchip-elemental sulfur mixture	*Geobacteraceae* and *Pseudomonas*	Cr (VI)	Biodegradation and reduction	Anaerobic and dark environment	87.2 ± 2.09 %	Fei et al. (2022)
Immobilized bead	*Mycobacterium* sp. *CHXY119 and Pseudomonas* sp. *YATO411*	BTEX	Biodegradation	25 °C	91.98 %	Xin et al. (2013b)
(BC&Cell@CA) gel beads	*Desulfitobacterium*	2, 4, 6-trichlorophenol	Chemical reduction and biological reduction	–	84 %	(Wang et al., 2020b, 2022a)
Clay composite adsorbent	–	PhACs (tenolol, ciprofloxacin and gemfibrozil)	Adsorption and biodegradation	–	80 %, 90 % and 75 %	Vijayanandan et al. (2018)
Vermiculite clay	*Pseudomonas putida*	Cu and Zn	Adsorption and biodegradation	26 °C	Increase by 34.4 % and 22.8 %	Ferronato et al. (2016)
Bioelectrode	*Anaerobic sludge Dechlorosoma*	*p*-chloronitrobenzene (*p*-CNB)	Bioelectrocatalytic reduction	30 ± 2 °C	94.76 %	Li et al. (2024)
Geotextile fabric specimens and gravel mixture	*Alcanivorax*	Toluene	Biodegradation	–	90.8 %–99.3 %	Yaman et al. (2021)
Luffa sponge	Aerobic bacteria and/or fungi	nitrate	Heterotrophic nitrification and aerobic or anoxic denitrification	Avoid light in hypoxic conditions	98 %	Özkaraova et al. (2022)

3.1. Heavy metal

The modified biochar composite *K. variicola* H12-CMC-FeS@biochar demonstrated effective Cr (VI) removal from groundwater with the removal rate of 94 %. Studies indicate that the biofilm formation by *K. variicola* on the biochar surface significantly promoted Cr (VI) adsorption capacity (Man et al., 2023). Furthermore, the presence of ZVI induced the competitive reproduction of Cr (VI) reducing bacterial populations within the Bio-PRB. Specifically, ZVI led to decrease relative abundances of *Pseudomonas, Hydrogenophaga*, *Exiguobacterium*, and *Rhodobacter* and significantly enrich *Rivibacter* and *Candidatus_Desulforudis* species (Wang et al., 2022a). ZVI (ZVI-PRBs), Activated carbon (AC-PRBs), ZVI-immobilized *S. saromensis* W5 (ZVI Bio-PRBs) and AC-immobilized *S. saromensis* W5 (AC Bio-PRBs) were utilized to establish four Bio-PRB columns for Cr (VI) remediation in simulated groundwater systems. The Bio-PRB demonstrated significantly enhanced Cr (VI) removal efficiency compared to the abiotic PRB. AC Bio-PRBs achieved a 64 % removal rate, representing a 498 % improvement over the 10.7 % removal achieved by AC-PRBs. Similarly, ZVI Bio-PRBs exhibited 90 % Cr (VI) removal, representing a 466 % increase over the 15.9 % removal achieved by ZVI-PRBs. The synergistic interaction between microorganisms and ZVI in ZVI Bio-PRBs substantially reduced the redox potential, establishing a reductive condition favorable for microbial activity. The iron-reducing bacteria reduced Fe (III) to Fe (II), generating additional electrons that enhance Cr (VI) reduction (Huang et al., 2021). *Klebsiella variicola* H12-CMC-FeS@biochar was employed as the reactive medium in Bio-PRB for chromium remediation in simulated groundwater. The Cr (VI) removal rate was 94 %, representing a significant enhancement compared to PRB utilizing either *Klebsiella variicola* H12 or biochar alone (Man et al., 2023).

PRBs were constructed using vermiculite clay mixed with sediment (vermiculite PRBs) or vermiculite-immobilized *P. putida* combined with fresh sediment (*Pseudomonas* Bio-PRBs) to remediate simulated Cu (II) and Zn (II) contaminated groundwater. Compared to vermiculite PRBs, the Bio-PRBs exhibited significantly enhanced removal efficiencies, with Cu (II) and Zn (II) removal rates increasing by 34.4 % and 22.8 %, respectively. The improved performance was attributed to the catalytic role of *P. putida*, which secreted exopolysaccharides (EPS) that enhanced electrostatic interactions between vermiculite and the metal ions, thus facilitating adsorption (Ferronato et al., 2016). Furthermore, the formation of microbial biofilms on the vermiculite surface contributed to the higher removal capacity of the Bio-PRB (Ferronato et al., 2016).

A woodchip-sulfur packed Bio-PRB was developed for efficient V(V) biodetoxification, achieving removal efficiencies of 68.5 %–98.2 %. Heterotrophic *Geobacter* played a dominant role in reducing soluble V (V) to insoluble V (IV), utilizing organic carbon derived from woodchip hydrolysis, while autotrophic bacteria (e.g., *Sulfuricurvum* and *Thiobacillus*) contributed through sulfur anabolism (Li and Zhang, 2020). Moreover, a Bio-PRB column containing an anaerobic microbial consortium, elemental sulfur (S^0) and quartz sand was designed for V (V) contaminated groundwater treatment. S^0 served as electron donor, while quartz sand optimized the permeability. V (V) removal rate was enhanced by 10 %–159 % in Bio-PRB, with insoluble V (IV) precipitation effectively reducing mobility and toxicity (Fig. 2). Microbial analysis revealed that the reduction and oxidation of functional microorganisms (*Bacteroidetes vadin* HA17 and *Geobacter*) accelerated the transformation of contaminants (Shi et al., 2020).

SRB, as a common group of anaerobic microorganisms, have demonstrated exceptional efficiency in remediating various heavy metal contaminants. Notably, the synergistic combination of SRB, ZVI, sheep manure, compost, and woodchips has achieved high removal efficiencies reaching 80 % for both As (III) and Mn (II) through biodegradation, metal co-precipitation, and reductive precipitation (Wilopo et al., 2008). SRB bioprecipitation can efficiently remove Pb (II) and Cd (II) via the formation of insoluble metal sulfides PbS and CdS. In a continuous fixed-bed column reactor, a mixture consisting of 6 % leaves, 9 % compost, 3 % ZVI, 30 % perlite, 30 % silica sand and 22 % limestone was inoculated with SRB for wastewater treatment containing Cd(II). The system achieved excellent removal efficiency through combined mechanisms of adsorption and bioprecipitation (Ludwig et al., 2009).

Bio-PRBs demonstrate significant advantages for As contaminated groundwater remediation, particularly in simultaneous removing As (III) and As (V). The core mechanism relies on SRB metabolic activity, which continuously produces reduced sulfides (e.g., H_2S) by dissimilatory sulfate reduction in organic-rich sediments. H_2S promotes As (V) immobilization through multiple pathways, including chemisorption onto pyrite surfaces, reduction of As (V) to low-mobility As (0) or As (III), and formation of As-Fe-S co-precipitates with sulfides. Bio-PRBs composed of silica sand, organic carbon and organic-rich sediments, and ZVI were used to construct for As (V) contaminated groundwater remediation. Compared to PRBs, the Bio-PRB system enhanced As (V) removal efficiency by 2650 %. As(V) was reduced through electron transfer, forming As (III), As (II), and As (I), which precipitated as As_2S_3,

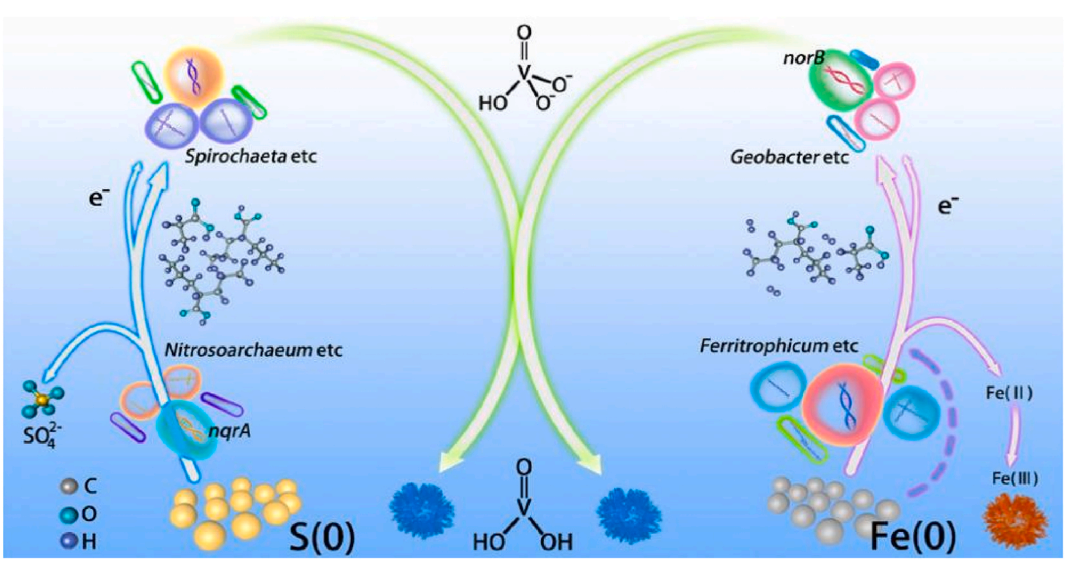

Fig. 2. Removal performance and reaction mechanism of V(V) in Bio-PRBs constructed of wood chips, S^0, shell immobilized with an anaerobic consortium, and quartz sand (Zhang et al., 2018).

AsS, and FeAsS, respectively. ZVI facilitated As (V) reduction, while ferric hydroxide or iron oxide contributed to adsorptive removal. Fe (III) served as an electron acceptor for SRB, promoting precipitate formation (Angai et al., 2022). Two Bio-PRB columns were constructed using nonsterilized sheep manure or sterilized sheep manure, wood chips, compost and glass beads with ZVI for As (III) remediation. The non-sterilized system exhibited a 50 % higher As (III) removal rate than the sterilized control. As (III) was adsorbed onto ZVI and compost, as well as co-precipitation with iron-bearing minerals (Wilopo et al., 2008).

Researchers have identified fungi as another group of microorganisms with significant bioremediation potential, due to their ability to degrade diverse contaminants through aerobic co-metabolic pathways. Notably, white-rot fungi exhibit remarkable capabilities in degrading various xenobiotic compounds. These fungal species have been successfully employed as biological reactive media for groundwater remediation (Folch et al., 2013). An innovative adsorbent composed of carbonized fungi loaded nano ZVI (nZVI) demonstrated high reactivity toward U (VI) in neutral to alkaline conditions, achieving nearly complete removal of 0.25 mmol/L U (VI) in 30 min (Ding et al., 2018).

Microbial coupling to electron donor groups enhances heavy metal reduction to less toxic states, enabling efficient removal via sulfide or hydroxide precipitation and adsorption fixation. Current studies mainly address single or multiple heavy metal pollutants, whereas the intricate interactions in heavy metal and organic co-contamination systems and their synergistic interference mechanisms remain profoundly underexplored. Therefore, the combined pollution of heavy metals and organic contaminants and its mechanism should be addressed in future research.

3.2. Anionic contaminants

The reactive media in Bio-PRBs serves as electron donors, while contaminants (e.g., nitrate, sulfate etc.) act as electron acceptors for microbial metabolism (Pensky et al., 2023). Treatment relies primarily on the inoculation of microorganisms (Liu et al., 2020; Yu et al., 2024) and in-situ microbial communities (Buyanjargal et al., 2021). ZVI provides an external electron donor Fe (II) for denitrifying microorganisms through corrosion dissolution (Zhao et al., 2022). Nitrate was completely removed in the presence of ZVI for 80 h, and the nitrate reduction rate was 30 % faster than that without ZVI (Zhang et al., 2019). The electron source for denitrifying bacteria also includes organic carbon (such as pine bark, wood chips) (Lawrinenko et al., 2025). The reactive medium of Bio-PRB consisted of gravel and mulch, providing a carbon source for denitrifying bacteria. The system achieved more than 97 % nitrate removal rate from groundwater at inlet concentrations up to 280 mg/L. Bio-PRBs can simultaneously remove multiple contaminants that may act as nutrients. Nitrate is reduced by denitrification in sawdust layers, while phosphate is immobilized through mineral precipitation (e.g., hydroxyapatite) in converter slag layers (Buyanjargal et al., 2021). Spongy iron removed oxygen, and pine bark supplied organic carbon for heterotrophic denitrification. Nitrate concentration declined from 14 to below 5 mg N/L by iron-driven chemical reduction and microbial denitrification (Kong et al., 2015).

Bio-PRBs demonstrate high nitrate removal efficiency under optimal conditions, particularly when amended with organic carbon sources (Li et al., 2022b). Their passive operation reduces energy consumption, while their modular design allows for adaptability to various hydrogeological conditions (Ghaeminia and Mokhtarani, 2018; Guan et al., 2019). However, limitations include susceptibility to environmental factors (e.g., temperature, pH, redox potential) inhibiting microbial activity (Law et al., 2018; Liu et al., 2020; Luo et al., 2018), potential secondary contamination (Liu et al., 2020), and long-term efficacy decline from substrate depletion (Feyereisen et al., 2016; Hu et al., 2019b; Zhao et al., 2018). Research indicates that denitrification rates using cotton and newspapers as carbon sources are reduced by 50 %–67 % at 14 °C compared to 32 °C (Liu et al., 2020). The nitrate removal rate with wood chips decreases when the temperature is below 10 °C (Law et al., 2018). Incomplete denitrification can produce nitrous oxide (N_2O), a potent greenhouse gas (Feyereisen et al., 2016). The aging of the media wood chips will reduce the overall nitrate removal rate in the Bio-PRB columns (Halaburka et al., 2017).

3.3. Hydrocarbon organic contaminants

The surface functional groups (including carboxyl and hydroxyl groups) of biochar enable organic contaminant adsorption while enhancing bioavailability and stimulating aerobic microbial degradation (Shi et al., 2018; Zhu et al., 2020). Bio-PRBs incorporating coconut shell biochar pellets with diatomite, attapulgite and CaO_2 demonstrated 169 % greater PAHs adsorption capacity (0.035 mg/g) versus wheat straw pellet Bio-PRB (0.013 mg/g) (Liu et al., 2019). Bio-PRB filling *Mycobacterium* sp. *CHXY119* and *Pseudomonas* sp. *YATO411* immobilized microbeads achieved substantial removal efficiency improvements: 37.8 % for *p*-benzene, 14.2 % for *p*-toluene, and 9.4 % for *p*-xylene (Xin et al., 2013a). Novel Bio-PRBs incorporating biochar-immobilized microorganisms with ZVI gel beads were developed for 2, 4, 6-trichlorophenol (2, 4, 6-TCP) contaminated groundwater treatment (Ahmadnezhad et al., 2021). The systems demonstrated 175 % higher removal efficiency compared to ZVI-PRBs (Wang et al., 2022b) (Fig. 3). Silva et al. achieved a 55.7 % increase in Cr (VI) adsorption capacity (24.6 mg/g *vs.* 15.8 mg/g) and a 24.9 % increase for Cu (II) (34.1 mg/g *vs.* 27.3 mg/g) compared to sepiolite PRBs. Furthermore, the biofilm reduced Mg (II) leaching from the sepiolite structure by 67.8 % (124 mg/L for Bio-PRB *vs.* 385 mg/L for PRB) (Silva et al., 2021).

The genus *desulfit* plays a critical role in anaerobic bioremediation by facilitating the reductive dechlorination of organochlorine contaminants. Bradley et al. treated the 1,1,2-trichloroethane (1,1,2-TCA) contaminated groundwater and demonstrated 5 times reduction in the half-life of 1,1,2-TCA degradation compared to abiotic processes. This enhancement was attributed to the synergistic activity of a microbial consortium comprising *Desulfitobacterium* and *Dehalococcoides*, which mediated the biodegradation of 1,1,2-TCA to ethene (Patterson et al., 2016).

Bio-PRB for organic contaminant removal still faces considerable limitations. Laboratory studies often examine single contaminants or idealized hydraulic conditions, and real-world applications involve complex environmental matrices (e.g., co-existing contaminants, salinity or pH variations), whose effects on microbial activity and reactive media functionality remain poorly understood. Notably, incomplete degradation in Bio-PRBs may generate more toxic intermediates (e.g., chlorinated or nitro derivatives), yet current research lacks comprehensive secondary pollution risk assessments. Future investigations should integrate metagenomic and metabolomic approaches to elucidate links between functional gene expression and toxicity evolution, facilitating the transition from bench-scale studies to field-scale implementation.

3.4. Emerging contaminants

Four Bio-PRBs were established for pesticide removal, utilizing porous media to support microbial biofilm colonization. The systems demonstrated high insecticide removal rates and efficiencies under unaerated conditions. In aerobic configurations, *Micractinium* sp. primarily facilitated pyrethroid bioaccumulation, confirming biosorption as a critical removal mechanism in aerobic Bio-PRBs (Contreras-Blancas et al., 2020). A sand-packed Bio-PRB demonstrated effective removal of pharmaceutical active compounds (PhACs), achieving significant removal efficiencies of 80 %, 90 %, and 75 % for atenolol, ciprofloxacin, and gemfibrozil, respectively (Vijayanandan et al., 2018). Furthermore, Bio-PRBs incorporating anaerobically activated sludge and ZVI were employed for tetracycline (TC) contaminated groundwater remediation (Fig. 4). Bio-PRBs exhibited significantly enhanced TC removal

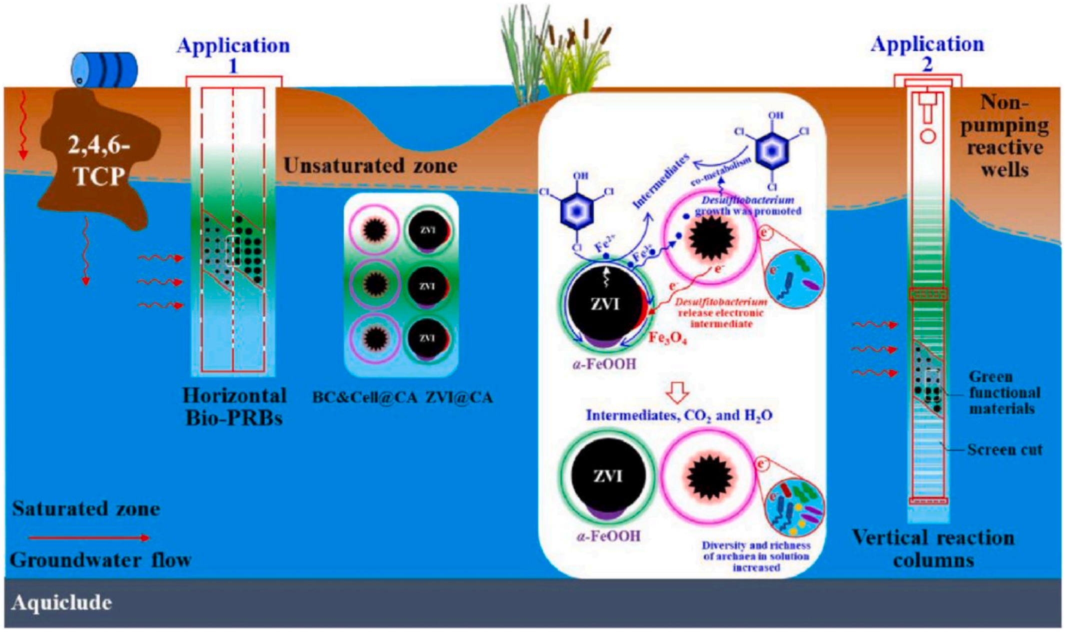

Fig. 3. Degradation mechanism of 2, 4, 6-trichlorophenol in Bio-PRB (Wang et al., 2022b).

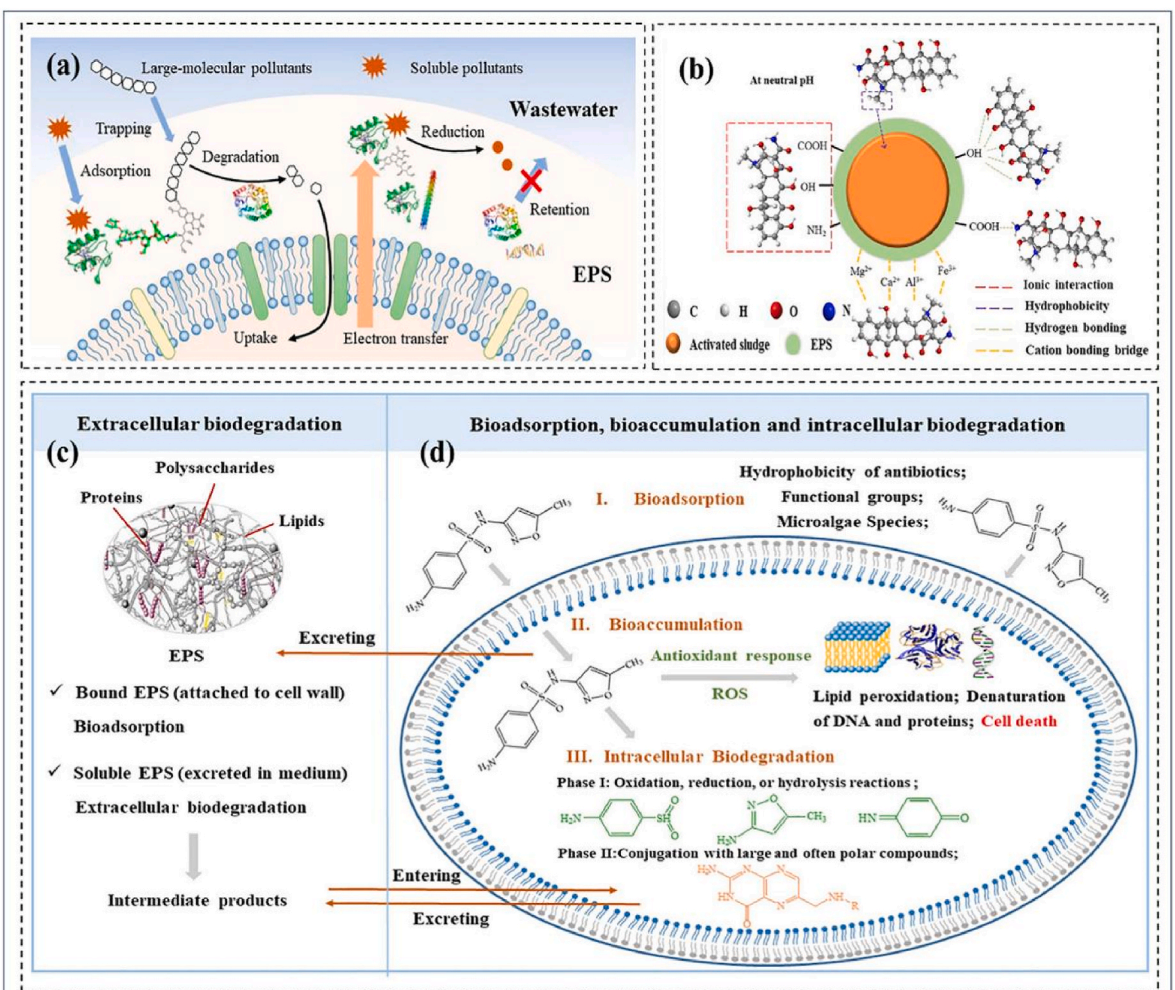

Fig. 4. Microbial biological mechanisms (Zhao et al., 2024a). (a) Diagram of the interaction between water contaminants and EPS molecules (Yu, 2020). (b) Biosorption mechanism of activated sludge on TC (Liao et al., 2016). (c) Extracellular biodegradable components (Xiong et al., 2021). (d) Antibiotic removal mechanism: bio-adsorption, bioaccumulation, biodegradation (Xiong et al., 2021).

performance compared to ZVI-PRBs and microorganism only PRBs, with removal rates improved by 25–400 % (reaching 50 % in Bio-PRB) (Huang et al., 2017a).

Microorganisms mineralized TC and PhACs intermediates to H_2O and CO_2. Simultaneously, the reactive medium synergistically immobilized contaminants through adsorption and complexation. Moreover, limited studies have investigated microplastic in Bio-PRBs, making their application for emerging microplastic co-contaminants a significant research frontier.

4. Enhance permeability and long-term effectiveness of Bio-PRB

The sustainable operation of Bio-PRB is restricted by the clogging and failure of the medium, which reduces its permeability, biological activity and the removal rate of the target contaminant. The use of mixed materials, the optimization of Bio-PRB structure and grain size gradation can alleviate these problems.

4.1. Combination of different kinds of reactive media

Bio-PRBs constructed with a single reactive medium are prone to clogging, material inactivation, and corrosion. To mitigate these issues while reducing costs and extending service life, composite materials can be formulated by mixing components at optimized ratios. This approach enhances Bio-PRB permeability and improves treatment performance for both individual and mixed contaminants through synergistic removal mechanisms (Pawluk and Fronczyk, 2015; Połoński et al., 2017).

The Bio-PRB was constructed by combining sand, cement, S^0, and scallop shells in a 1:1:1.5:2 ratio. This composite medium achieved an average NO_3^- removal efficiency of 97.75 %. Its porous structure facilitated the colonization and growth of *Thiomonas* and *Thiobacillus* species and enabled efficient transport of reaction products and microbial metabolites within the system (Farhadian et al., 2008). ZVI has been extensively employed as a conventional reactive material in PRBs. However, ZVI readily undergoes oxidation reactions with oxygen, forming insoluble FeO(OH) or Fe(OH) that precipitate and cause pore clogging. Such pore blockage predominantly occurs at the influent interface of Bio-PRBs, compromising hydraulic performance and potentially enabling contaminant migration to bypass the treatment zone (Lawrinenko et al., 2023). To enhance permeability and service life, highly porous materials including silica sand and gravel have been incorporated into reactive media (Moraci and Calabrò, 2010; Jeen et al., 2011). Composite materials combining ZVI with zeolites have demonstrated effectiveness in addressing common limitations of ZVI-PRB systems, including hydraulic inefficiency (Tasharrofi et al., 2020), treatment performance decline, and pH fluctuations. These improvements stem from exceptional ion-exchange capacity, selective adsorption properties, and robust chemical and mechanical stability of zeolites. An innovative approach involving the sequential integration of immobilized microorganisms with ZVI, using high-density velour sponge (HDLS) as the PRB reactive medium, has shown mitigating biological and chemical clogging. The metabolic activity of immobilized microbial colonies in upper layers significantly reduces inorganic ion concentrations, thus preventing substantial amounts of 1,1,1-trichloroethane (1,1,1-TCA) and ionic species from reaching downstream ZVI-PRB sections. This configuration consequently reduces the operational burden on ZVI-PRBs while minimizing permeability impairment caused by planktonic microbial cells and inorganic precipitates (Wang and Wu, 2019b).

4.2. Grain size gradation of reactive media

The particle size gradation of reactive media significantly influences the permeability, treatment efficiency, and long-term performance of Bio-PRBs. Generally, smaller particle sizes with higher specific surface areas enhance contaminant adsorption capacity by providing more active surface sites and improving contact efficiency between contaminants and reactive materials (Zafar et al., 2021). However, excessively fine particles can compromise Bio-PRB permeability, potentially causing contaminant plume bypass or clogging of both the Bio-PRB and adjacent aquifer systems. Conversely, larger particles reduce hydraulic retention times (HRTs) and may fail to achieve target remediation outcomes (Yuan et al., 2024b). Therefore, optimized gradation design of reactive media is critical to ensure adequate interaction between contaminants and reactive media while preventing system clogging and short-circuiting.

Gradation design includes two approaches: uniform gradation or continuous gradation (Zhao et al., 2024b). Uniformly graded media exhibit high porosity, enabling superior hydraulic conductivity, but may result in inadequate contact time between contaminant and media. In contrast, continuously graded media integrate particles of varying sizes to enhance pore structure configuration and prolong hydraulic retention time, thus optimizing reaction efficiency (Mackenzie et al., 1999). The incorporation of finer particles enhances the specific surface area, improving contaminant removal efficiency. However, excessive small particles may induce pore clogging. Strategically positioning larger ZVI particles at the Bio-PRB inlet mitigates mineral precipitation and scaling while increasing average hydraulic residence time, enhancing long-term performance. Large particle materials improve system permeability, but may significantly reduce treatment efficiency (Li and Benson, 2010). Therefore, investigating the optimal balance between long-term effectiveness and permeability is essential. A multi-layered reactive medium composed of ZVI and lapillus particles, a volcanic material serving as a dispersant for ZVI particles, demonstrates enhanced performance. The improved dispersion of ZVI particles not only sustains permeability but also extends PRB service life by 68 % (Bilardi et al., 2023). Additionally, incorporating highly permeable materials (e.g., sand and gravel) into the reactive media enhances permeability while prolonging operational longevity (Jeen et al., 2011).

Furthermore, the chain kinetic reaction model has been employed to simulate contaminant transport and degradation processes, describing the kinetic reaction mechanisms of contaminants within porous media. This modeling approach provides theoretical guidance for the design and optimization of Bio-PRBs, offering potential solutions to mitigate biological clogging issues encountered in practical engineering applications (Wang and Wu, 2018; Yuan et al., 2024a).

4.3. Structural design optimization of Bio-PRB

The construction costs of PRBs may increase substantially due to the requirement for greater barrier thickness to ensure adequate hydraulic retention time under conditions of elevated groundwater flow velocity. Implementing a multi-layered PRB configuration or incorporating a pretreatment zone can significantly enhance the long-term performance of PRB systems (Kenneke and McCutcheon, 2003). A study of this configuration is at Monticello, Utah, USA, where a pre-treatment zone consisting of 13 % ZVI and 87 % gravel is placed upstream of the reaction zone, and a diversion zone consisting of 100 % coarse sand is placed downstream, which has been shown to extend the life of Bio-PRB. Furthermore, a sequential two-layer Bio-PRB system has been successfully implemented for the remediation of methyl tert-butyl ether (MTBE) contaminated groundwater. The system configuration comprised two functional layers: an upstream oxygen releasing barrier containing CaO_2, KH_2PO_4 and $(NH_4)_2SO_4$, followed by a downstream biodegradation barrier utilizing granular expanded perlite as the bio-barrier. The primary barrier demonstrated effective oxygen release capacity (reaching 21 mg/L) while simultaneously supplying essential nutrients, thus ensuring stable microbial metabolic activity in the secondary biodegradation layer (Liu et al., 2006). To address performance degradation in Bio-PRBs, an innovative in-situ regeneration method was developed, integrating gas injection with oxidant oxidation. This dual approach simultaneously enhances system permeability and reactivates microbial metabolic functions in failed Bio-PRBs. A CO_2 enhanced media flushing technique, adapted from well washing technique, was implemented to restore system permeability (Xu et al., 2024a). The bioremediation system adopts a dual-barrier configuration, consisting of a ZVI barrier and an anaerobic municipal sludge bio-barrier. Operational data collected after 470 days of continuous column operation demonstrated significant changes in wastewater chemistry. The pH increased from 4 to 7 and the oxidation reduction potential decreased to −180 mV. Removal of TCE, heavy metals and nitrate contaminants was achieved (Lee et al., 2009a). Sequential PRB systems consisting of woodchips and basic oxygen furnace slag can be effective for removal of nitrate and phosphate in groundwater (Buyanjargal et al., 2021). The sequential PRB system, comprising recycled concrete aggregates and limestone aggregates, demonstrates effective long-term pH neutralization, thereby decreasing frequent maintenance or material replacement (Medawela et al., 2022).

The combination of microorganisms with other reactive media can enhance the reaction rate and contaminant removal efficiency. Bio-PRBs demonstrate superior economy compared to inorganic media PRBs due to their enhanced performance, reduced media replacement frequency, and lower disposal requirements (Bertolini et al., 2021). However, microbial activity may decrease effluent pH (Padhi and Gokhale, 2017). Microbial degradation converts organic contaminants into small molecules (e.g., CO_2, H_2O, etc.), thus partially mitigating media clogging and preserving permeability (Bertolini et al., 2021). Nevertheless, prolonged operation leads to biological clogging of granular materials within the system (Aiello et al., 2016). Severe biological blockage caused by rapid proliferation of aerobic microorganisms near the inlet decreases the hydraulic stability of the media, including key parameters such as hydrodynamic dispersion, permeability coefficient, and porosity (Zhong et al., 2013), ultimately diminishing wastewater treatment efficiency.

The combination of SRB with ZVI as reactive media of Bio-PRB significantly improved the long-term performance, maintaining a consistently high removal efficiency of 100 %. This combined system demonstrated effective Cr (VI) elimination over 11 operational cycles, with only 14.65 % ZVI consumption, thereby substantially enhancing long-term utilization efficiency of ZVI (Xu et al., 2024b). Furthermore, in-situ reactivation and reuse of sulfidated nZVI (S-nZVI) in Bio-PRBs through SRB-rich cultures enabled the development of bio-renewable S-nZVI. After four activation cycles, the Cr (VI) removal capacity of S-nZVI reached 34.4 mg/g, representing a 3.2 times enhancement compared to non-recycled systems. This finding significantly reduces chemical consumption and maintenance costs associated with frequent ZVI material replacement (Yang et al., 2024). The sulfonic acid-based tri-component hydrogen-bonded covalent organic aerogel demonstrates excellent potential as a Bio-PRB reactive material. It maintains approximately 90 % removal efficiency for fluoroquinolone antibiotics over 72 h while exhibiting self-assembly capability, environmental adaptability, high swelling capacity, and favorable permeability (Jia et al., 2024).

5. Prospection

Bio-PRBs represent a promising in-situ technology for groundwater remediation, effectively addressing contaminants such as heavy metals and organic compounds. However, some matters need attention. Despite extensive research, there are still unresolved and urgent issues regarding the investigation of reactive media within PRBs, which have slightly affected their removal efficiency, acceptability, and full-scale implementation.

(1) To enhance the removal efficiency of Bio-PRBs, novel filler materials capable of increasing microorganism activity need to be further explored, and the relation between filler material composition and the long-term operational stability of Bio-PRBs should be evaluated.
(2) The interaction between microorganisms and the reactive media remains a major challenge in optimizing microbial–chemical remediation for Bio-PRBs, especially the interaction between microorganisms and other environmental factors in groundwater.
(3) The long-term stability and performance of Bio-PRBs under varying hydrogeological conditions, such as fluctuating groundwater flow rates and contaminant concentrations, require comprehensive evaluation. Understanding the adaptive mechanisms of microbial communities to these dynamic conditions is crucial for optimizing the design and operation of Bio-PRBs in diverse environmental settings.
(4) The integration of advanced monitoring and modeling techniques is essential to predict and assess the performance of Bio-PRBs over extended periods. Developing real-time monitoring systems and predictive models that account for microbial activity, contaminant degradation kinetics, and geochemical changes will enhance the reliability and scalability of Bio-PRB technology for large-scale groundwater remediation projects (Połoński et al., 2017; Xu et al., 2012).

CRediT authorship contribution statement

Hai Lin: Writing – original draft, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Yuting Zhang:** Writing – original draft, Validation, Formal analysis, Data curation. **Yingbo Dong:** Writing – original draft. **Qi Jin:** Writing – original draft.

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.

Acknowledgements

This work was financially supported by National Key Research and Development Program of China [2023YFC3207303]

Data availability

Data will be made available on request.

References

Abedin, M.A., Katsumi, T., Inui, T., Kamon, M., 2011. Arsenic removal from contaminated groundwater by zero valent iron: a mechanistic and long-term performance study. Soils Found. 51, 369–377. https://doi.org/10.3208/sandf.51.369.
Ahmad, M., Lee, S.S., Dou, X., Mohan, D., Sung, J.-K., Yang, J.E., Ok, Y.S., 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. Bioresour. Technol. 118, 536–544. https://doi.org/10.1016/j.biortech.2012.05.042.
Ahmadnezhad, Z., Vaezihir, A., Schüth, C., Zarrini, G., 2021. Combination of zeolite barrier and bio sparging techniques to enhance efficiency of organic hydrocarbon remediation in a model of shallow groundwater. Chemosphere 273, 128555. https://doi.org/10.1016/j.chemosphere.2020.128555.
Aiello, R., Bagarello, V., Barbagallo, S., Iovino, M., Marzo, A., Toscano, A., 2016. Evaluation of clogging in full-scale subsurface flow constructed wetlands. Ecol. Eng. 95, 505–513. https://doi.org/10.1016/j.ecoleng.2016.06.113.
Ali, H., Khan, E., Ilahi, I., 2019. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. J. Chem., 6730305 https://doi.org/10.1155/2019/6730305.
Amani, S., Akbari, Z., Ghiassi, R., Ehsani, S., Rezaeishirazi, M., 2024. Nitrate and ammonium removals from groundwater by permeable reactive barrier method (PRB): column experiments. Water Air Soil Pollut. 235, 136. https://doi.org/10.1007/s11270-024-06936-6.
Angai, J.U., Ptacek, C.J., Pakostova, E., Bain, J.G., Verbuyst, B.R., Blowes, D.W., 2022. Removal of arsenic and metals from groundwater impacted by mine waste using zero-valent iron and organic carbon: laboratory column experiments. J. Hazard. Mater. 424, 127295. https://doi.org/10.1016/j.jhazmat.2021.127295.
Beganskas, S., Gorski, G., Weathers, T., Fisher, A.T., Schmidt, C., Saltikov, C., Redford, K., Stoneburner, B., Harmon, R., Weir, W., 2018. A horizontal permeable

reactive barrier stimulates nitrate removal and shifts microbial ecology during rapid infiltration for managed recharge. Water Res. 144, 274–284. https://doi.org/10.1016/j.watres.2018.07.039.

Bertolini, M., Zecchin, S., Beretta, G.P., De Nisi, P., Ferrari, L., Cavalca, L., 2021. Effectiveness of permeable reactive bio-barriers for bioremediation of an organohalide-polluted aquifer by natural-occurring microbial community. Water 13, 2442. https://doi.org/10.3390/w13172442.

Bilardi, S., Calabrò, P.S., Moraci, N., 2019. The removal efficiency and long-term hydraulic behaviour of zero valent iron/lapillus mixtures for the simultaneous removal of Cu^{2+}, Ni^{2+} and Zn^{2+}. Sci. Total Environ. 675, 490–500. https://doi.org/10.1016/j.scitotenv.2019.04.260.

Bilardi, S., Simonetti, S., Calabrò, P.S., Moraci, N., 2023. Behavior of multi-layer permeable reactive barriers for groundwater remediation. Soils Found. 63, 101398. https://doi.org/10.1016/j.sandf.2023.101398.

Budania, R., Dangayach, S., 2023. A comprehensive review on permeable reactive barrier for the remediation of groundwater contamination. J. Environ. Manag. 332, 117343. https://doi.org/10.1016/j.jenvman.2023.117343.

Buyanjargal, A., Kang, J., Sleep, B.E., Jeen, S.-W., 2021. Sequential treatment of nitrate and phosphate in groundwater using a permeable reactive barrier system. J. Environ. Manag. 300, 113699. https://doi.org/10.1016/j.jenvman.2021.113699.

Calabrò, P.S., Moraci, N., Suraci, P., 2012. Estimate of the optimum weight ratio in zero-valent iron/pumice granular mixtures used in permeable reactive barriers for the remediation of nickel contaminated groundwater. J. Hazard. Mater., Selected papers presented at the 2nd International Conference CRETE 2010, October 2010. Industrial and Hazardous Waste Management 207–208, 111–116. https://doi.org/10.1016/j.jhazmat.2011.06.094.

Cao, V., Yang, H., Ndé-Tchoupé, A.I., Hu, R., Gwenzi, W., Noubactep, C., 2020. Tracing the scientific history of Fe^0-Based environmental remediation prior to the advent of permeable reactive barriers. Processes 8, 977. https://doi.org/10.3390/pr8080977.

Casalini, L.C., Vidoz, M., Piazza, A., Labanca, C., Pacini, V.A., Ottado, J., Gottig, N., 2020. Optimization of bacterial bioaugmentation for groundwater Mn removal using a waste-based culture medium and lyophilization. Environ. Sci.: Water Res. Technol. 6, 3255–3261. https://doi.org/10.1039/D0EW00777C.

Chen, Z., Cao, W., Li, Y., Song, J., Liu, Y., Liu, J., Zhang, R., Su, R., Bai, H., 2024. Enhancing the removal of chlorinated hydrocarbons from groundwater using a new BL5 microorganism with functional CS@ZVI materials. J. Water Proc. Eng. 57, 104699. https://doi.org/10.1016/j.jwpe.2023.104699.

Contreras-Blancas, E., Ruiz-Ordaz, N., Galíndez-Mayer, J., Torres-Gómez, R.E., Arias, R. A., Juárez-Ramírez, C., 2020. Permeable reactive surface-biobarriers. Testing and evaluation of an ecotechnology for the removal of agrotoxic compounds carried by agricultural runoffs. J. Environ. Health Sci. Eng. 18, 559–571. https://doi.org/10.1007/s40201-020-00482-z.

Diao, M., Yao, M., 2009. Use of zero-valent iron nanoparticles in inactivating microbes. Water Res. 43, 5243–5251. https://doi.org/10.1016/j.watres.2009.08.051.

Ding, C., Cheng, W., Nie, X., Yi, F., Xiang, S., Asiri, A.M., Marwani, H.M., 2018. Reactivity of carbonized fungi supported nanoscale zero-valent iron toward U(VI) influenced by naturally occurring ions. J. Ind. Eng. Chem. 61, 236–243. https://doi.org/10.1016/j.jiec.2017.12.021.

Du, J., Sun, P., Feng, Z., Zhang, X., Zhao, Y., 2016. The biosorption capacity of biochar for 4-bromodiphengl ether: study of its kinetics, mechanism, and use as a carrier for immobilized bacteria. Environ. Sci. Pollut. Res. 23, 3770–3780. https://doi.org/10.1007/s11356-015-5619-8.

Eljamal, O., Thompson, I.P., Maamoun, I., Shubair, T., Eljamal, K., Lueangwattanapong, K., Sugihara, Y., 2020. Investigating the design parameters for a permeable reactive barrier consisting of nanoscale zero-valent iron and bimetallic iron/copper for phosphate removal. J. Mol. Liq. 299, 112144. https://doi.org/10.1016/j.molliq.2019.112144.

Farhadian, M., Vachelard, C., Duchez, D., Larroche, C., 2008. In situ bioremediation of monoaromatic pollutants in groundwater: a review. Bioresour. Technol. 99, 5296–5308. https://doi.org/10.1016/j.biortech.2007.10.025.

Fedoročková, A., Raschman, P., Sučik, G., Švandová, M., Doráková, A., 2021. Reactive, sparingly soluble calcined magnesia, tailor-made as the reactive material for heavy metal removal from contaminated groundwater using permeable reactive barrier. Minerals 11, 1153. https://doi.org/10.3390/min11111153.

Fei, Y., Chen, S., Wang, Z., Chen, T., Zhang, B., 2022. Woodchip-sulfur based mixotrophic biotechnology for hexavalent chromium detoxification in the groundwater. J. Environ. Manag. 324, 116298. https://doi.org/10.1016/j.jenvman.2022.116298.

Ferronato, C., Silva, B., Costa, F., Tavares, T., 2016. Vermiculite bio-barriers for Cu and Zn remediation: an eco-friendly approach for freshwater and sediments protection. Int. J. Environ. Sci. Technol. 13, 1219–1228. https://doi.org/10.1007/s13762-016-0957-8.

Feyereisen, G.W., Moorman, T.B., Christianson, L.E., Venterea, R.T., Coulter, J.A., Tschirner, U.W., 2016. Performance of agricultural residue media in laboratory denitrifying bioreactors at low temperatures. J. Environ. Qual. 45, 779–787. https://doi.org/10.2134/jeq2015.07.0407.

Folch, A., Vilaplana, M., Amado, L., Vicent, T., Caminal, G., 2013. Fungal permeable reactive barrier to remediate groundwater in an artificial aquifer. J. Hazard. Mater. 262, 554–560. https://doi.org/10.1016/j.jhazmat.2013.09.004.

Freidman, B.L., Gras, S.L., Snape, I., Stevens, G.W., Mumford, K.A., 2017a. A bio-reactive barrier sequence for petroleum hydrocarbon capture and degradation in low nutrient environments. Int. Biodeterior. Biodegrad. 116, 26–37. https://doi.org/10.1016/j.ibiod.2016.09.025.

Freidman, Benjamin L., Speirs, L.B.M., Churchill, J., Gras, S.L., Tucci, J., Snape, I., Stevens, G.W., Mumford, K.A., 2017b. Biofilm communities and biodegradation within permeable reactive barriers at fuel spill sites in Antarctica. Int. Biodeterior. Biodegrad. 125, 45–53. https://doi.org/10.1016/j.ibiod.2017.08.008.

Fu, D., Singh, R.P., Yang, X., Ojha, C.S.P., Surampalli, R.Y., Kumar, A.J., 2018. Sediment in-situ bioremediation by immobilized microbial activated beads: pilot-scale study. J. Environ. Manag. 226, 62–69. https://doi.org/10.1016/j.jenvman.2018.08.021.

Fuller, S.J., Stewart, D.I., Burke, I.T., 2013. Chromate reduction in highly alkaline groundwater by zerovalent iron: implications for its use in a permeable reactive barrier. Ind. Eng. Chem. Res. 52, 4704–4714. https://doi.org/10.1021/ie302914b.

Garcia, A.N., Zhang, Y., Ghoshal, S., He, F., O'Carroll, D.M., 2021. Recent advances in sulfidated zerovalent iron for contaminant transformation. Environ. Sci. Technol. 55, 8464–8483. https://doi.org/10.1021/acs.est.1c01251.

Ghaeminia, M., Mokhtarani, N., 2018. Remediation of nitrate-contaminated groundwater by PRB-electrokinetic integrated process. J. Environ. Manag. 222, 234–241. https://doi.org/10.1016/j.jenvman.2018.05.078.

Gholami, F., Mosmeri, H., Shavandi, M., Dastgheib, S.M.M., Amoozegar, M.A., 2019. Application of encapsulated magnesium peroxide (MgO_2) nanoparticles in permeable reactive barrier (PRB) for naphthalene and toluene bioremediation from groundwater. Sci. Total Environ. 655, 633–640. https://doi.org/10.1016/j.scitotenv.2018.11.253.

Gibert, O., Assal, A., Devlin, H., Elliot, T., Kalin, R.M., 2019. Performance of a field-scale biological permeable reactive barrier for in-situ remediation of nitrate-contaminated groundwater. Sci. Total Environ. 659, 211–220. https://doi.org/10.1016/j.scitotenv.2018.12.340.

Guan, Q., Li, F., Chen, X., Tian, C., Liu, C., Liu, D., 2019. Assessment of the use of a zero-valent iron permeable reactive barrier for nitrate removal from groundwater in the alluvial plain of the Dagu river, China. Environ. Earth Sci. 78, 244. https://doi.org/10.1007/s12665-019-8247-7.

Guo, C., Qi, L., Bai, Y., Yin, L., Li, L., Zhang, W., 2021. Geochemical stability of zero-valent iron modified raw wheat straw innovatively applicated to in situ permeable reactive barrier: N_2 selectivity and long-term denitrification. Ecotoxicol. Environ. Saf. 224, 112649. https://doi.org/10.1016/j.ecoenv.2021.112649.

Halaburka, B.J., LeFevre, G.H., Luthy, R.G., 2017. Evaluation of mechanistic models for nitrate removal in woodchip bioreactors. Environ. Sci. Technol. 51, 5156–5164. https://doi.org/10.1021/acs.est.7b01025.

Hashim, M.A., Mukhopadhyay, S., Sahu, J.N., Sengupta, B., 2011. Remediation technologies for heavy metal contaminated groundwater. J. Environ. Manag. 92, 2355–2388. https://doi.org/10.1016/j.jenvman.2011.06.009.

Hiller-Bittrolff, K., Foreman, K., Bulseco-McKim, A.N., Benoit, J., Bowen, J.L., 2018. Effects of mercury addition on microbial community composition and nitrate removal inside permeable reactive barriers. Environ. Pollut. 242, 797–806. https://doi.org/10.1016/j.envpol.2018.07.017.

Hu, B., Song, Y., Wu, S., Zhu, Y., Sheng, G., 2019a. Slow released nutrient-immobilized biochar: a novel permeable reactive barrier filler for Cr(VI) removal. J. Mol. Liq. 286, 110876. https://doi.org/10.1016/j.molliq.2019.04.153.

Hu, R., Zheng, X., Zheng, T., Xin, J., Wang, H., Sun, Q., 2019b. Effects of carbon availability in a woody carbon source on its nitrate removal behavior in solid-phase denitrification. J. Environ. Manag. 246, 832–839. https://doi.org/10.1016/j.jenvman.2019.06.057.

Huang, L., Liu, G., Dong, G., Wu, X., Wang, C., Liu, Y., 2017a. Reaction mechanism of zero-valent iron coupling with microbe to degrade tetracycline in permeable reactive barrier (PRB). Chem. Eng. J. 316, 525–533. https://doi.org/10.1016/j.cej.2017.01.096.

Huang, L., Liu, G., Dong, G., Wu, X., Wang, C., Liu, Y., 2017b. Reaction mechanism of zero-valent iron coupling with microbe to degrade tetracycline in permeable reactive barrier (PRB). Chem. Eng. J. 316, 525–533. https://doi.org/10.1016/j.cej.2017.01.096.

Huang, Y., Zeng, Q., Hu, L., Xiong, D., Zhong, H., He, Z., 2021. Column study of enhanced Cr(VI) removal and removal mechanisms by *Sporosarcina saromensis* W5 assisted bio-permeable reactive barrier. J. Hazard. Mater. 405, 124115. https://doi.org/10.1016/j.jhazmat.2020.124115.

Jeen, S.-W., Gillham, R.W., Przepiora, A., 2011. Predictions of long-term performance of granular iron permeable reactive barriers: field-scale evaluation. J. Contam. Hydrol. 123, 50–64. https://doi.org/10.1016/j.jconhyd.2010.12.006.

Jia, A., Zhang, F., Zhao, Y., Liu, Z., Xin, L., Hong, M., Li, Y., 2024. Facile fabrication of shapeable three-component hydrogen-bonded covalent-organic aerogel as permeable reactive barrier material for efficient in-situ fluoroquinolone contaminated groundwater remediation. Sep. Purif. Technol. 334, 126037. https://doi.org/10.1016/j.seppur.2023.126037.

Jiang, Z., Liu, R., Wang, Y., Cheng, W., Chen, Y., Yu, H., Pei, Y., 2024. Synergistic effect of LDHs/loofah composites for in-situ remediation of nitrate in contaminated groundwater. Sep. Purif. Technol. 336, 126306. https://doi.org/10.1016/j.seppur.2024.126306.

Jurado, A., Walther, M., Díaz-Cruz, M.S., 2019. Occurrence, fate and environmental risk assessment of the organic microcontaminants included in the watch lists set by EU decisions 2015/495 and 2018/840 in the groundwater of Spain. Sci. Total Environ. 663, 285–296. https://doi.org/10.1016/j.scitotenv.2019.01.270.

Kenneke, J.F., McCutcheon, S.C., 2003. Use of pretreatment zones and zero-valent iron for the remediation of chloroalkenes in an oxic aquifer. Environ. Sci. Technol. 37, 2829–2835. https://doi.org/10.1021/es0207302.

Kim, H., Voutchkova, D.D., Johnsen, A.R., Albers, C.N., Thorling, L., Hansen, B., 2022. National assessment of long-term groundwater response to pesticide regulation. Environ. Sci. Technol. 56, 14387–14396. https://doi.org/10.1021/acs.est.2c02261.

Kong, X., Bi, E., Liu, F., Huang, G., Ma, J., 2015. Laboratory column study for evaluating a multimedia permeable reactive barrier for the remediation of ammonium contaminated groundwater. Environ. Technol. 36, 1433–1440. https://doi.org/10.1080/09593330.2014.992482.

Kubota, M., Nakabayashi, T., Matsumoto, Y., Shiomi, T., Yamada, Y., Ino, K., Yamanokuchi, H., Matsui, M., Tsunoda, T., Mizukami, F., Sakaguchi, K., 2008. Selective adsorption of bacterial cells onto zeolites. Colloids Surf. B Biointerfaces 64, 88–97. https://doi.org/10.1016/j.colsurfb.2008.01.012.

Kumar, N., Chaurand, P., Rose, J., Diels, L., Bastiaens, L., 2015. Synergistic effects of sulfate reducing bacteria and zero valent iron on zinc removal and stability in aquifer sediment. Chem. Eng. J. 260, 83–89. https://doi.org/10.1016/j.cej.2014.08.091.

Kumar, N., Couture, R.-M., Millot, R., Battaglia-Brunet, F., Rose, J., 2016. Microbial sulfate reduction enhances arsenic mobility downstream of zerovalent-iron-based permeable reactive barrier. Environ. Sci. Technol. 50, 7610–7617. https://doi.org/10.1021/acs.est.6b00128.

Kumara, G.M.P., Kawamoto, K., 2021. Use of natural zeolite and its mixtures to refine high-concentrated heavy metal-contaminated wastewater: an investigation of simultaneous removal of Cd (II) and Pb (II) by batch adsorption method. Water Air Soil Pollut. 232, 463. https://doi.org/10.1007/s11270-021-05420-9.

Law, J.Y., Soupir, M.L., Raman, D.R., Moorman, T.B., Ong, S.K., 2018. Electrical stimulation for enhanced denitrification in woodchip bioreactors: opportunities and challenges. Ecol. Eng. 110, 38–47. https://doi.org/10.1016/j.ecoleng.2017.10.002.

Lawrinenko, M., Kurwadkar, S., Wilkin, R.T., 2023. Long-term performance evaluation of zero-valent iron amended permeable reactive barriers for groundwater remediation – a mechanistic approach. Geosci. Front. 14, 101494. https://doi.org/10.1016/j.gsf.2022.101494.

Lawrinenko, M., Rhea, L., Forshay, K.J., Lee, T.R., White, M., Wilkin, R.T., 2025. Long-term field study of nitrate and ammonium remediation using a permeable reactive barrier at a livestock feeding operation. J. Environ. Manag. 380, 124962. https://doi.org/10.1016/j.jenvman.2025.124962.

Lee, J.-Y., Lee, K.-J., Youm, S.Y., Lee, M.-R., Kamala-Kannan, S., Oh, B.-T., 2009a. Stability of multi-permeable reactive barriers for long term removal of mixed contaminants. Bull. Environ. Contam. Toxicol. 84, 250–254. https://doi.org/10.1007/s00128-009-9918-y.

Lee, K., Lee, Y., Yoon, J., Kamala-Kannan, S., Park, S., Oh, B., 2009b. Assessment of zero-valent iron as a permeable reactive barrier for long-term removal of arsenic compounds from synthetic water. Environ. Technol. 30, 1425–1434. https://doi.org/10.1080/09593330903186240.

Lemic, D., Orešković, M., Mikac, K.M., Marijan, M., Jurić, S., Vlahoviček-Kahlina, K., Vinceković, M., 2021. Sustainable pest management using biodegradable apitoxin-loaded calcium-alginate microspheres. Sustainability 13, 6167. https://doi.org/10.3390/su13116167.

Li, D., Li, G., He, Y., Zhao, Y., Miao, Q., Zhang, H., Yuan, Y., Zhang, D., 2022a. Key Cr species controlling Cr stability in contaminated soils before and chemical stabilization at a remediation engineering site. J. Hazard. Mater. 424, 127532. https://doi.org/10.1016/j.jhazmat.2021.127532.

Li, H., Liu, Q., 2022. Reaction medium for permeable reactive barrier remediation of groundwater polluted by heavy metals. Front. Environ. Sci. 10. https://doi.org/10.3389/fenvs.2022.968546.

Li, J., Zhang, B., 2020. Woodchip-sulfur packed biological permeable reactive barrier for mixotrophic vanadium (V) detoxification in groundwater. Sci. China Technol. Sci. 63, 2283–2291. https://doi.org/10.1007/s11431-020-1655-6.

Li, J., Zhang, X., Liu, M., Pan, B., Zhang, W., Shi, Z., Guan, X., 2018. Enhanced reactivity and electron selectivity of sulfidated zerovalent iron toward chromate under aerobic conditions. Environ. Sci. Technol. 52, 2988–2997. https://doi.org/10.1021/acs.est.7b06502.

Li, L., Benson, C.H., 2010. Evaluation of five strategies to limit the impact of fouling in permeable reactive barriers. J. Hazard. Mater. 181, 170–180. https://doi.org/10.1016/j.jhazmat.2010.04.113.

Li, P., Jin, a., Liang, Y., Zhang, Y., Ding, D., Xiang, H., Ding, Y., Qiu, X., Han, W., Ye, F., Feng, H., 2024. Biocathode-anode cascade system in PRB: efficient degradation of *p*-chloronitrobenzene in groundwater. Water Res., 122359. https://doi.org/10.1016/j.watres.2024.122359.

Li, S., Wu, Y., Nie, F., Tu, W., Li, X., Luo, X., Luo, Y., Fan, H., Song, T., 2022b. Remediation of nitrate contaminated groundwater using a simulated PRB system with an La–CTAC–modified biochar filler. Front. Environ. Sci. 10. https://doi.org/10.3389/fenvs.2022.986866.

Li, Y., Huang, Y., Wu, W., Yan, M., Xie, Y., 2021. Research and application of arsenic-contaminated groundwater remediation by manganese ore permeable reactive barrier. Environ. Technol. 42, 2009–2020. https://doi.org/10.1080/09593330.2019.1687587.

Liang, L., Li, X., Guo, Y., Lin, Z., Su, X., Liu, B., 2021. The removal of heavy metal cations by sulfidated nanoscale zero-valent iron (S-nZVI): the reaction mechanisms and the role of sulfur. J. Hazard. Mater. 404, 124057. https://doi.org/10.1016/j.jhazmat.2020.124057.

Liao, X., Li, B., Zou, R., Xie, S., Yuan, B., 2016. Antibiotic sulfanilamide biodegradation by acclimated microbial populations. Appl. Microbiol. Biotechnol. 100, 2439–2447. https://doi.org/10.1007/s00253-015-7133-9.

Liu, B., Li, G., You, H., Sui, M., Wang, S., 2014. Evaluation of dynamic groundwater quality simulation based on Cloud-GIS: a case study in Harbin urban area. China. Water Sci. Technol.: Water Supply 14, 1095–1104. https://doi.org/10.2166/ws.2014.070.

Liu, C., Chen, X., Banwart, S.A., Du, W., Yin, Y., Guo, H., 2021. A novel permeable reactive biobarrier for *ortho*-nitrochlorobenzene pollution control in groundwater: experimental evaluation and kinetic modelling. J. Hazard. Mater. 420, 126563. https://doi.org/10.1016/j.jhazmat.2021.126563.

Liu, C., Chen, X., Mack, E.E., Wang, S., Du, W., Yin, Y., Banwart, S.A., Guo, H., 2019. Evaluating a novel permeable reactive bio-barrier to remediate PAH-contaminated groundwater. J. Hazard. Mater. 368, 444–451. https://doi.org/10.1016/j.jhazmat.2019.01.069.

Liu, H., Chen, S., Lu, J., Li, Q., Li, J., Zhang, B., 2022. Pentavalent vanadium and hexavalent uranium removal from groundwater by woodchip-sulfur based mixotrophic biotechnology. Chem. Eng. J. 437, 135313. https://doi.org/10.1016/j.cej.2022.135313.

Liu, N., Zhang, Y., An, Y., Wang, L., 2018. Preparation of integrative cubes as a novel biological permeable reactive barrier medium for the enhancement of in situ aerobic bioremediation of nitrobenzene-contaminated groundwater. Environ. Earth Sci. 77, 707. https://doi.org/10.1007/s12665-018-7890-8.

Liu, S.-J., Jiang, B., Huang, G.-Q., Li, X.-G., 2006. Laboratory column study for remediation of MTBE-contaminated groundwater using a biological two-layer permeable barrier. Water Res. 40, 3401–3408. https://doi.org/10.1016/j.watres.2006.07.015.

Liu, Yong, Liu, Yajing, Ma, L., Gong, Y., Qian, J., 2020. Corncob PRB for on-site nitrate removal in groundwater. Arabian J. Geosci. 13, 1084. https://doi.org/10.1007/s12517-020-06089-w.

Lu, C.-W., Lo, K.-H., Wang, S.-C., Kao, C.-M., Chen, S.-C., 2024a. An innovative permeable reactive bio-barrier to remediate trichloroethene-contaminated groundwater: a field study. Sci. Total Environ. 920, 170885. https://doi.org/10.1016/j.scitotenv.2024.170885.

Lu, C.-W., Lo, K.-H., Wang, S.-C., Kao, C.-M., Chen, S.-C., 2024b. An innovative permeable reactive bio-barrier to remediate trichloroethene-contaminated groundwater: a field study. Sci. Total Environ. 920, 170885. https://doi.org/10.1016/j.scitotenv.2024.170885.

Lu, J., Zhang, B., He, C., Borthwick, A.G.L., 2020. The role of natural Fe (II)-bearing minerals in chemoautotrophic chromium (VI) bio-reduction in groundwater. J. Hazard. Mater. 389, 121911. https://doi.org/10.1016/j.jhazmat.2019.121911.

Ludwig, R.D., Smyth, D.J.A., Blowes, D.W., Spink, L.E., Wilkin, R.T., Jewett, D.G., Weisener, C.J., 2009. Treatment of arsenic, heavy metals, and acidity using a mixed ZVI-compost PRB. Environ. Sci. Technol. 43, 1970–1976. https://doi.org/10.1021/es802394p.

Luo, J.-H., Chen, H., Yuan, Z., Guo, J., 2018. Methane-supported nitrate removal from groundwater in a membrane biofilm reactor. Water Res. 132, 71–78. https://doi.org/10.1016/j.watres.2017.12.064.

Mackenzie, P.D., Horney, D.P., Sivavec, T.M., 1999. Mineral precipitation and porosity losses in granular iron columns. J. Hazard. Mater. 68, 1–17. https://doi.org/10.1016/S0304-3894(99)00029-1.

Man, M., Yu, R., Jiang, X., Liu, Z., Zeng, W., 2023. Cr(VI) removal and mechanism from simulated polluted groundwater by *Klebsiella variicola* H12-CMC-FeS@biochar assisted permeable reactive barrier. J. Water Proc. Eng. 55, 104115. https://doi.org/10.1016/j.jwpe.2023.104115.

Medawela, S., Indraratna, B., Athuraliya, S., Lugg, G., Nghiem, L.D., 2022. Monitoring the performance of permeable reactive barriers constructed in acid sulfate soils. Eng. Geol. 296, 106465. https://doi.org/10.1016/j.enggeo.2021.106465.

Moraci, N., Calabrò, P.S., 2010. Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers. J. Environ. Manag. 91, 2336–2341. https://doi.org/10.1016/j.jenvman.2010.06.019.

Mosmeri, H., Alaie, E., Shavandi, M., Dastgheib, S.M.M., Tasharrofi, S., 2017. Bioremediation of benzene from groundwater by calcium peroxide (CaO_2) nanoparticles encapsulated in sodium alginate. J. Taiwan Inst. Chem. Eng. 78, 299–306. https://doi.org/10.1016/j.jtice.2017.06.020.

Naeimi, M., Shavandi, M., Alaie, E., 2021. Determining the impact of biofilm in the bioaugmentation process of benzene-contaminated resources. J. Environ. Chem. Eng. 9, 104976. https://doi.org/10.1016/j.jece.2020.104976.

Nasief, FadyaM., Shaban, M., Alamry, K.A., Khadra, M.R.A., Khan, A.A.P., Asiri, A.M., El-Salam, H.M.A., 2021. Hydrothermal synthesis and mechanically activated zeolite material for utilizing the removal of Ca/Mg from aqueous and raw groundwater. J. Environ. Chem. Eng. 9, 105834. https://doi.org/10.1016/j.jece.2021.105834.

Özkaraova, E.B., Aydın, S., Gemechu, A.U., 2022. Screening of organic substrates for a permeable biobarrier to remediate nitrate contaminated groundwater. Water Environ. J. 36, 43–55. https://doi.org/10.1111/wej.12755.

Padhi, S.K., Gokhale, S., 2017. Benzene biodegradation by indigenous mixed microbial culture: kinetic modeling and process optimization. Int. Biodeterior. Biodegrad. 119, 511–519. https://doi.org/10.1016/j.ibiod.2016.10.011.

Park, J.H., 2020. Contrasting effects of Cr(III) and Cr(VI) on lettuce grown in hydroponics and soil: chromium and manganese speciation. Environ. Pollut. 266. https://doi.org/10.1016/j.envpol.2020.115073.

Patel, A.K., Singhania, R.R., Pal, A., Chen, C.-W., Pandey, A., Dong, C.-D., 2022. Advances on tailored biochar for bioremediation of antibiotics, pesticides and polycyclic aromatic hydrocarbon pollutants from aqueous and solid phases. Sci. Total Environ. 817, 153054. https://doi.org/10.1016/j.scitotenv.2022.153054.

Patterson, B.M., Lee, M., Bastow, T.P., Wilson, J.T., Donn, M.J., Furness, A., Goodwin, B., Manefield, M., 2016. Concentration effects on biotic and abiotic processes in the removal of 1,1,2-trichloroethane and vinyl chloride using carbon-amended ZVI. J. Contam. Hydrol. 188, 1–11. https://doi.org/10.1016/j.jconhyd.2016.02.004.

Pawluk, K., Fronczyk, J., 2015. Evaluation of single and multilayered reactive zones for heavy metals removal from stormwater. Environ. Technol. 36, 1576–1583. https://doi.org/10.1080/09593330.2014.997299.

Pensky, J., Fisher, A.T., Gorski, G., Schrad, N., Bautista, V., Saltikov, C., 2023. Linking nitrate removal, carbon cycling, and mobilization of geogenic trace metals during infiltration for managed recharge. Water Res. 239, 120045. https://doi.org/10.1016/j.watres.2023.120045.

Podgorski, J., Berg, M., 2020. Global threat of arsenic in groundwater. Sci 368, 845–850. https://doi.org/10.1126/science.aba1510.

Połoński, M., Pawluk, K., Rybka, I., 2017. Optimization model for the design of multi-layered permeable reactive barriers. IOP Conf. Ser. Mater. Sci. Eng. 245, 072017. https://doi.org/10.1088/1757-899X/245/7/072017.

Puigserver, D., Herrero, J., Carmona, J.M., 2023. Mobilization pilot test of PCE sources in the transition zone to aquitards by combining mZVI and biostimulation with lactic acid. Sci. Total Environ. 877, 162751. https://doi.org/10.1016/j.scitotenv.2023.162751.

Sakr, M., El Agamawi, H., Klammler, H., Mohamed, M.M., 2023. A review on the use of permeable reactive barriers as an effective technique for groundwater remediation. Groundw. Sustain. Dev. 21, 100914. https://doi.org/10.1016/j.gsd.2023.100914.

Sathishkumar, K., Murugan, K., Benelli, G., Higuchi, A., Rajasekar, A., 2017. Bioreduction of hexavalent chromium by *Pseudomonas stutzeri* L1 and *Acinetobacter baumannii* L2. Ann. Microbiol. 67, 91–98. https://doi.org/10.1007/s13213-016-1240-4.

Schostag, M.D., Gobbi, A., Fini, M.N., Ellegaard-Jensen, L., Aamand, J., Hansen, L.H., Muff, J., Albers, C.N., 2022. Combining reverse osmosis and microbial degradation for remediation of drinking water contaminated with recalcitrant pesticide residue. Water Res. 216, 118352. https://doi.org/10.1016/j.watres.2022.118352.

Sewwandi, B.G.N., Vithanage, M., Wijesekara, S.S.R.M.D.H.R., Rajapaksha, A.U., Jayarathna, D.G.L.M., Mowjood, M.I.M., 2012. Characterization of aqueous Pb(II) and Cd(II) biosorption on native and chemically modified Alstonia macrophylla saw dust. Bio J. 16, 113–124. https://doi.org/10.1080/10889868.2012.665963.

Shi, C., Cui, Y., Lu, J., Zhang, B., 2020. Sulfur-based autotrophic biosystem for efficient vanadium (V) and chromium (VI) reductions in groundwater. Chem. Eng. J. 395, 124972. https://doi.org/10.1016/j.cej.2020.124972.

Shi, X., Zhou, G., Liao, S., Shan, S., Wang, G., Guo, Z., 2018. Immobilization of cadmium by immobilized *Alishewanella* sp. WH16-1 with alginate-lotus seed pods in pot experiments of Cd-contaminated paddy soil. J. Hazard. Mater. 357, 431–439. https://doi.org/10.1016/j.jhazmat.2018.06.027.

Siggins, A., Thorn, C., Healy, M.G., Abram, F., 2021. Simultaneous adsorption and biodegradation of trichloroethylene occurs in a biochar packed column treating contaminated landfill leachate. J. Hazard. Mater. 403, 123676. https://doi.org/10.1016/j.jhazmat.2020.123676.

Silva, B., Rocha, V., Lago, A., Costa, F., Tavares, T., 2021. Rehabilitation of a complex industrial wastewater containing heavy metals and organic solvents using low cost permeable bio-barriers – from lab-scale to pilot-scale. Sep. Purif. Technol. 263, 118381. https://doi.org/10.1016/j.seppur.2021.118381.

Snape, I., Morris, C.E., Cole, C.M., 2001. The use of permeable reactive barriers to control contaminant dispersal during site remediation in Antarctica. Cold Reg. Sci. Technol. 32, 157–174. https://doi.org/10.1016/S0165-232X(01)00027-1.

Song, I., Kang, Y., Kim, J., Yoon, H., Um, W.Y., Chang, Y., 2022. Assessment of sulfidated nanoscale zerovalent iron for in-situ remediation of cadmium-contaminated acidic groundwater at a zinc smelter, 2023. J. Hazard. Mater. 441, 129915. https://doi.org/10.1016/j.jhazmat.2022.129915.

Statham, T.M., Mumford, K.A., Rayner, J.L., Stevens, G.W., 2015. Removal of copper and zinc from ground water by granular zero-valent iron: a dynamic freeze–thaw permeable reactive barrier laboratory experiment. CCold Reg. Sci. Technol. 110, 120–128. https://doi.org/10.1016/j.coldregions.2014.12.001.

Summer, D., Schöftner, P., Watzinger, A., Reichenauer, T.G., 2020. Inhibition and stimulation of two perchloroethene degrading bacterial cultures by nano- and micro-scaled zero-valent iron particles. Sci. Total Environ. 722, 137802. https://doi.org/10.1016/j.scitotenv.2020.137802.

Tasharrofi, S., Rouzitalab, Z., Maklavany, D.M., Esmaeili, A., Rabieezadeh, M., Askarieh, M., Rashidi, A., Taghdisian, H., 2020. Adsorption of cadmium using modified zeolite-supported nanoscale zero-valent iron composites as a reactive material for PRBs. Sci. Total Environ. 736, 139570. https://doi.org/10.1016/j.scitotenv.2020.139570.

Tavakoli Dastjerdi, M.H., Habibagahi, G., Ghahramani, A., Karimi-Jashni, A., Zeinali, S., 2018. Removal of dissolved toluene in underground water with nanowires of manganese oxide. Adsorpt. Sci. Technol. 36, 393–407. https://doi.org/10.1177/0263617417698469.

Tiehm, A., Müller, A., Alt, S., Jacob, H., Schad, H., Weingran, C., 2008. Development of a groundwater biobarrier for the removal of polycyclic aromatic hydrocarbons, BTEX, and heterocyclic hydrocarbons. Water Sci. Technol. 58, 1349–1355. https://doi.org/10.2166/wst.2008.730.

Upadhyay, S., Sinha, A., 2018. Role of microorganisms in permeable reactive bio-barriers (PRBBs) for environmental clean-up: a review. Global NEST J. 20, 269–280. https://doi.org/10.30955/gnj.002525.

Vaezihir, A., Bayanlou, M.B., Ahmadnezhad, Z., Barzegari, G., 2020. Remediation of BTEX plume in a continuous flow model using zeolite-PRB. J. Contam. Hydrol. 230, 103604. https://doi.org/10.1016/j.jconhyd.2020.103604.

Valdivia-Rivera, S., Ayora-Talavera, T., Lizardi-Jiménez, M.A., García-Cruz, U., Cuevas-Bernardino, J.C., Pacheco, N., 2021. Encapsulation of microorganisms for bioremediation: techniques and carriers. Rev. Environ. Sci. Biotechnol. 20, 815–838. https://doi.org/10.1007/s11157-021-09577-x.

Vemmer, M., Patel, A.V., 2013. Review of encapsulation methods suitable for microbial biological control agents. Biol. Control 67, 380–389. https://doi.org/10.1016/j.biocontrol.2013.09.003.

Vijayanandan, A., Philip, L., Bhallamudi, S.M., 2018. Enhanced removal of PhACs in RBF supplemented with biofilm coated adsorbent barrier: experimental and model studies. Chem. Eng. J. 338, 341–357. https://doi.org/10.1016/j.cej.2017.12.099.

Vocciante, M., De Folly D'Auris, A., Finocchi, A., Tagliabue, M., Bellettato, M., Ferrucci, A., Reverberi, A.P., Ferro, S., 2018. Adsorption of ammonium on clinoptilolite in presence of competing cations: investigation on groundwater remediation. J. Clean. Prod. 198, 480–487. https://doi.org/10.1016/j.jclepro.2018.07.025.

Wang, H., Chen, N., Feng, C., 2023a. Multiple interactions of coupled denitrification, V (V) reduction, and natural organics oxidation in a permeable reactive barrier-a neglected behavior of pentavalent vanadium re-release. J. Clean. Prod. 418, 138063. https://doi.org/10.1016/j.jclepro.2023.138063.

Wang, J., Jiang, Y., Wang, H., Huang, Q., Deng, H., 2020a. Groundwater irrigation and management in northern China: status, trends, and challenges. Int. J. Water Resour. Dev. 36, 670–696. https://doi.org/10.1080/07900627.2019.1584094.

Wang, Q., Song, X., Wei, C., Jin, P., Chen, X., Tang, Z., Li, K., Ding, X., Fu, H., 2022a. In situ remediation of Cr(VI) contaminated groundwater by ZVI-PRB and the corresponding indigenous microbial community responses: a field-scale study. Sci. Total Environ. 805, 150260. https://doi.org/10.1016/j.scitotenv.2021.150260.

Wang, W., Gong, T., Li, H., Liu, Y., Dong, Q., Zan, R., Wu, Y., 2022b. The multi-process reaction model and underlying mechanisms of 2,4,6-trichlorophenol removal in lab-scale biochar-microorganism augmented ZVI PRBs and field-scale PRBs performance. Water Res. 217, 118422. https://doi.org/10.1016/j.watres.2022.118422.

Wang, W., Wu, Y., 2019a. A multi-path chain kinetic reaction model to predict the evolution of 1,1,1-trichloroethane and its daughter products contaminant-plume in permeable reactive bio-barriers. Environ. Pollut. 253, 1021–1029. https://doi.org/10.1016/j.envpol.2019.07.103.

Wang, W., Wu, Y., 2019b. Sequential coupling of bio-augmented permeable reactive barriers for remediation of 1,1,1-trichloroethane contaminated groundwater. Environ. Sci. Pollut. Res. 26, 12042–12054. https://doi.org/10.1007/s11356-019-04676-3.

Wang, W., Wu, Y., 2018. Effects of biological clogging on 1,1,1-TCA and its intermediates distribution and fate in heterogeneous saturated bio-augmented permeable reactive barriers. Environ. Sci. Pollut. Res. 25, 28628–28641. https://doi.org/10.1007/s11356-018-2908-z.

Wang, W., Zhang, M., Qiu, H., Gong, T., Xiang, M., Li, H., 2023b. Microbe–mineral interaction-induced microorganism-augmented permeable reactive barriers for remediation of contaminated soil and groundwater: a review. ACS EST Water. 3, 2024–2040. https://doi.org/10.1021/acsestwater.3c00188.

Wang, W., Zhao, L., Cao, X., 2020b. The microorganism and biochar-augmented bioreactive top-layer soil for degradation removal of 2,4-dichlorophenol from surface runoff. Sci. Total Environ. 733, 139244. https://doi.org/10.1016/j.scitotenv.2020.139244.

Wilopo, W., Sasaki, K., Hirajima, T., Yamanaka, T., 2008. Immobilization of arsenic and manganese in contaminated groundwater by permeable reactive barriers using zero valent iron and sheep manure. Mater. Trans. 49, 2265–2274. https://doi.org/10.2320/matertrans.M-MRA2008827.

Wise, J.P., Young, J.L., Cai, J., Cai, L., 2022. Current understanding of hexavalent chromium [Cr(VI)] neurotoxicity and new perspectives. Environ. Int. 158, 106877. https://doi.org/10.1016/j.envint.2021.106877.

Wu, N., Zhang, W., Wei, W., Yang, S., Wang, H., Sun, Z., Song, Y., Li, P., Yang, Y., 2020. Field study of chlorinated aliphatic hydrocarbon degradation in contaminated groundwater via micron zero-valent iron coupled with biostimulation. Chem. Eng. J. 384, 123349. https://doi.org/10.1016/j.cej.2019.123349.

Xiao, C., Qu, S., Ren, Z.J., Chen, Y., Zou, X., Chen, G., Zhang, Z., 2024. Understanding the global distribution of groundwater sulfate and assessing population at risk. Environ. Sci. Technol. 58, 21002–21014. https://doi.org/10.1021/acs.est.4c10318.

Xie, Y., Zhang, D., Lou, S., He, F., Yin, L., 2017. Slowly released carbon source from composite materials system for removing nitrate pollution in groundwater. RSC Adv. 7, 10215–10220. https://doi.org/10.1039/C6RA27639C.

Xin, B.-P., Wu, Chih-Hung, Wu, Cheng-Han, Lin, C.-W., 2013a. Bioaugmented remediation of high concentration BTEX-contaminated groundwater by permeable reactive barrier with immobilized bead. J. Hazard. Mater. 244–245, 765–772. https://doi.org/10.1016/j.jhazmat.2012.11.007.

Xin, B.-P., Wu, Chih-Hung, Wu, Cheng-Han, Lin, C.-W., 2013b. Bioaugmented remediation of high concentration BTEX-contaminated groundwater by permeable reactive barrier with immobilized bead. J. Hazard. Mater. 244–245, 765–772. https://doi.org/10.1016/j.jhazmat.2012.11.007.

Xiong, Q., Hu, L.-X., Liu, Y.-S., Zhao, J.-L., He, L.-Y., Ying, G.-G., 2021. Microalgae-based technology for antibiotics removal: from mechanisms to application of innovational hybrid systems. Environ. Int. 155, 106594. https://doi.org/10.1016/j.envint.2021.106594.

Xu, F., Luo, X., Huang, J., Dong, Y., Zheng, K., Liu, Y., Liu, Y., Wang, H., 2024a. Using CO_2 and oxidants for in situ regeneration of permeable reactive barriers for leachate–contaminated groundwater. J. Environ. Sci. 145, 152–163. https://doi.org/10.1016/j.jes.2023.08.002.

Xu, H., Qin, C., Zhang, H., Zhao, Y., 2024b. New insights into long-lasting Cr(VI) removal from groundwater using in situ biosulfidated zero-valent iron with sulfate-reducing bacteria. J. Environ. Manag. 355, 120488. https://doi.org/10.1016/j.jenvman.2024.120488.

Xu, Y., Wang, C., Hou, J., Wang, P., You, G., Miao, L., Lv, B., Yang, Y., Zhang, F., 2017. Application of zero valent iron coupling with biological process for wastewater treatment: a review. Rev. Environ. Sci. Biotechnol. 16, 667–693. https://doi.org/10.1007/s11157-017-9445-y.

Xu, Z., Wu, Y., Yu, F., 2012. A three-dimensional flow and transport modeling of an aquifer contaminated by perchloroethylene subject to multi-PRB remediation. Transport Porous Media 91, 319–337. https://doi.org/10.1007/s11242-011-9847-1.

Yaman, C., Anil, I., Alagha, O., Blaisi, N.I., Yaman, A.B., Qureshi, A., Cevik, E., Rehman, S., Gunday, S.T., Barghouthi, M., 2021. Toluene bioremediation by using geotextile-layered permeable reactive barriers (PRBs). Processes 9, 906. https://doi.org/10.3390/pr9060906.

Yang, Y., Zhan, C., Li, Y., Zeng, J., Lin, K., Sun, J., Jiang, F., 2024. *In-situ* reactivation and reuse of micronsized sulfidated zero-valent iron using SRB-enriched culture: a sustainable PRB technology. Water Res. 253, 121270. https://doi.org/10.1016/j.watres.2024.121270.

Yang, Y.-X., Chen, J.-K., Zhao, L., You, Y.-Q., Chen, Z.-J., Cao, J.-N., Liu, F., Zhang, S., Zhan, L.-T., Chen, Y.-M., Bate, B., 2023. A kinetic-based zeolite PRB design method for remediating groundwater polluted by high NH_4^+ MSW leachate considering spatio-temporal concentration evolutions. Environ. Technol. Innovation. 29, 103020. https://doi.org/10.1016/j.eti.2023.103020.

Yin, W., Wu, J., Huang, W., Wei, C., 2015. Enhanced nitrobenzene removal and column longevity by coupled abiotic and biotic processes in zero-valent iron column. Chem. Eng. J. 259, 417–423. https://doi.org/10.1016/j.cej.2014.08.040.

Yousefi, A., Matavos-Aramyan, S., 2018. Mix design optimization of silica fume-based pervious concrete for removal of heavy metals from wastewaters. Silicon 10, 1737–1744. https://doi.org/10.1007/s12633-017-9663-5.

Yu, H.-Q., 2020. Molecular insights into extracellular polymeric dubstances in sctivated sludge. Environ. Sci. Technol. 54, 7742–7750. https://doi.org/10.1021/acs.est.0c00850.

Yu, W., Zheng, T., Guo, B., Tao, Y., Liu, L., Yan, N., Zheng, X., 2024. Coupling of polyhydroxybutyrate and zero-valent iron for enhanced treatment of nitrate pollution within the permeable reactive barrier and its downgradient aquifer. Water Res. 250, 121060. https://doi.org/10.1016/j.watres.2023.121060.

Yuan, L., Li, J., Wang, X., Zhao, Q., Li, L., Wang, K., Wang, G., 2024a. Preparation of iron composite filler for PRB technology and its application in the removal of toxic metals (loids) from groundwater. J. Environ. Chem. Eng. 12, 112570. https://doi.org/10.1016/j.jece.2024.112570.

Yuan, L., Wang, K., Zhao, Q., Yang, L., Wang, G., Jiang, M., Li, L., 2024b. An overview of in situ remediation for groundwater co-contaminated with heavy metals and petroleum hydrocarbons. J. Environ. Manag. 349, 119342. https://doi.org/10.1016/j.jenvman.2023.119342.

Zafar, A.M., Javed, M.A., Hassan, A.A., Mohamed, M.M., 2021. Groundwater remediation using zero-valent iron nanoparticles (nZVI). Groundw. Sustain. Dev. 15, 100694. https://doi.org/10.1016/j.gsd.2021.100694.

Zhang, B., Qiu, R., Lu, L., Chen, X., He, C., Lu, J., Ren, Z.J., 2018. Autotrophic vanadium (V) bioreduction in groundwater by elemental sulfur and zerovalent iron. Environ. Sci. Technol. 52, 7434–7442. https://doi.org/10.1021/acs.est.8b01317.

Zhang, W., Shan, N., Bai, Y., Yin, L., 2020. The innovative application of agriculture straw in *in situ* field permeable reactive barrier for remediating nitrate-contaminated groundwater in grain-production areas. Biochem. Eng. J. 164, 107755. https://doi.org/10.1016/j.bej.2020.107755.

Zhang, Y., Douglas, G.B., Kaksonen, A.H., Cui, L., Ye, Z., 2019. Microbial reduction of nitrate in the presence of zero-valent iron. Sci. Total Environ. 646, 1195–1203. https://doi.org/10.1016/j.scitotenv.2018.07.112.

Zhao, B., Sun, Z., Liu, Y., 2022. An overview of in-situ remediation for nitrate in groundwater. Sci. Total Environ. 804, 149981. https://doi.org/10.1016/j.scitotenv.2021.149981.

Zhao, J., Feng, C., Tong, S., Chen, N., Dong, S., Peng, T., Jin, S., 2018. Denitrification behavior and microbial community spatial distribution inside woodchip-based solid-phase denitrification (W-SPD) bioreactor for nitrate-contaminated water treatment. Bioresour. Technol. 249, 869–879. https://doi.org/10.1016/j.biortech.2017.11.011.

Zhao, K., Si, T., Liu, S., Liu, G., Li, D., Li, F., 2024a. Co-metabolism of microorganisms: a study revealing the mechanism of antibiotic removal, progress of biodegradation transformation pathways. Sci. Total Environ. 954, 176561. https://doi.org/10.1016/j.scitotenv.2024.176561.

Zhao, L., Xiao, D., Liu, Y., Xu, H., Nan, H., Li, D., Kan, Y., Cao, X., 2020. Biochar as simultaneous shelter, adsorbent, pH buffer, and substrate of *Pseudomonas citronellolis* to promote biodegradation of high concentrations of phenol in wastewater. Water Res. 172, 115494. https://doi.org/10.1016/j.watres.2020.115494.

Zhao, L., Xue, L., Wang, L., Liu, C., Li, Y., 2022. Simultaneous heterotrophic and FeS_2-based ferrous autotrophic denitrification process for low-C/N ratio wastewater treatment: nitrate removal performance and microbial community analysis. Sci. Total Environ. 829, 154682. https://doi.org/10.1016/j.scitotenv.2022.154682.

Zhao, P., Liu, S., Wu, K., 2024b. Study on macro and micro shear strength of continuously graded and gap-graded sand. Particuology 86, 101–116. https://doi.org/10.1016/j.partic.2023.05.002.

Zhong, X., Wu, Y., Xu, Z., 2013. Bioclogging in porous media under discontinuous flow condition. Water Air Soil Pollut. 224, 1543. https://doi.org/10.1007/s11270-013-1543-z.

Zhou, S., Song, D., Gu, J.-D., Yang, Y., Xu, M., 2022. Perspectives on microbial electron transfer networks for environmental biotechnology. Front. Microbiol. 13. https://doi.org/10.3389/fmicb.2022.845796.

Zhu, F., Tan, X., Zhao, W., Feng, L., He, S., Wei, L., Yang, L., Wang, K., Zhao, Q., 2022. Efficiency assessment of ZVI-based media as fillers in permeable reactive barrier for multiple heavy metal-contaminated groundwater remediation. J. Hazard. Mater. 424, 127605. https://doi.org/10.1016/j.jhazmat.2021.127605.

Zhu, S., Wang, S., Yang, X., Tufail, S., Chen, C., Wang, X., Shang, J., 2020. Green sustainable and highly efficient hematite nanoparticles modified biochar-clay granular composite for Cr(VI) removal and related mechanism. J. Clean. Prod. 276, 123009. https://doi.org/10.1016/j.jclepro.2020.123009.