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SPECIALTY SECTION  
This article was submitted to Freshwater  
Science,  
a section of the journal  
Frontiers in Environmental Science

RECEIVED 14 June 2022  
ACCEPTED 08 August 2022  
PUBLISHED 06 September 2022

CITATION  
Li H and Liu Q (2022), Reaction medium  
for permeable reactive barrier  
remediation of groundwater polluted by  
heavy metals.  
*Front. Environ. Sci.* 10:968546.  
doi: 10.3389/fenvs.2022.968546

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# Reaction medium for permeable reactive barrier remediation of groundwater polluted by heavy metals

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Heavy metal pollution of groundwater has a serious impact on human health, which has become a key issue in the field of water resources and water environment. Permeable reactive barrier (PRB) is an *in-situ* remediation technology for passive groundwater pollution, with the advantages of economy and efficiency. The reaction material in the PRB wall is the key to the whole system, which can intercept or degrade heavy metals to achieve the removal of pollutants. Among a wide variety of reaction materials, PRB has been successfully used to remove various heavy metal contaminants. In this paper, reaction materials are classified into three broad categories, namely single material, mixed material, and composite material. On this basis, the action mechanism of various materials to remove heavy metal pollutants is analyzed, and the screening method of reaction medium is summarized. Finally, the deficiencies and development directions of PRB reaction medium materials in the removal of heavy metals in groundwater are pointed out, providing reference for the subsequent development and application of PRB reaction medium.

## KEYWORDS

reaction medium, permeable reactive barrier, heavy metals, removal mechanism, groundwater

## 1 Introduction

Approximately 2.5 billion people depend directly on groundwater for drinking water on a global scale (Li et al., 2021). In addition, more than half of agricultural irrigation water relies on groundwater (Famiglietti, 2014). In this case, the excessive consumption of groundwater makes it a research hotspot in this field (Jarvis, 2021). In general, heavy metals refer to metals and metalloids with a density greater than 5 g cm<sup>-3</sup> or an atomic number greater than 20 in the periodic table, including cadmium, mercury, copper, arsenic, chromium, etc., (Barceló and Poschenrieder, 1990). Sources of heavy metals in groundwater include natural and anthropogenic sources (Hashim et al., 2011). Heavy metals widely present in the earth's crust can dissolve in groundwater through natural weathering, erosion, or changes in soil pH value (Fedorocková et al., 2021). Moreover, landfill leachate, sewage, mine tailings leachate, deep well treatment liquid waste,

industrial waste seepage or industrial leakage may all cause elevated concentrations of heavy metals in groundwater (Ali et al., 2019). Since heavy metals cannot be degraded, their continuous accumulation poses a threat to drinking water safety and human and animal health (Mukherjee et al., 2020). Long-term direct or indirect exposure to heavy metal-contaminated groundwater may lead to the accumulation of heavy metals in various organs, leading to diseases such as osteoporosis, respiratory diseases, skin problems, cardiovascular, and cerebrovascular diseases, and reproductive diseases (Khan et al., 2013). For example, cadmium can cause symptoms such as acute respiratory failure in humans. cadmium, lead, and mercury can damage the kidneys of human body (Salman et al., 2011). As a hidden water source, the discovery of groundwater pollution is delayed (MacDonald and Kavanaugh, 1994).

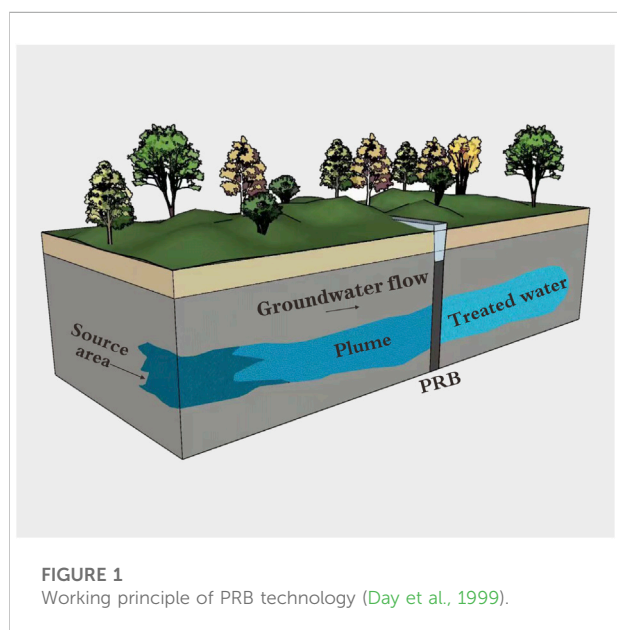
Groundwater treatment technology is mainly divided into *in-situ* treatment technology and *ex-situ* treatment technology. PRB technology and pump-treat technology are typical representatives of groundwater *in-situ* and *ex-situ* remediation technologies, respectively. Compared with traditional pump-treat technology, PRB technology relies on underground active reaction medium materials to remove dissolved pollutants in polluted water, which neither requires additional power systems nor damages natural environments such as soil and groundwater. Therefore, it has the advantages of simple operation, reasonable cost and ideal processing effect, which is considered as a promising processing technology (Obiri-Nyarko et al., 2014). However, PRB technology also has some disadvantages. For example, when the media material loses activity or becomes blocked due to precipitation, the media material should be replaced in time, which makes the cost difficult to quantify

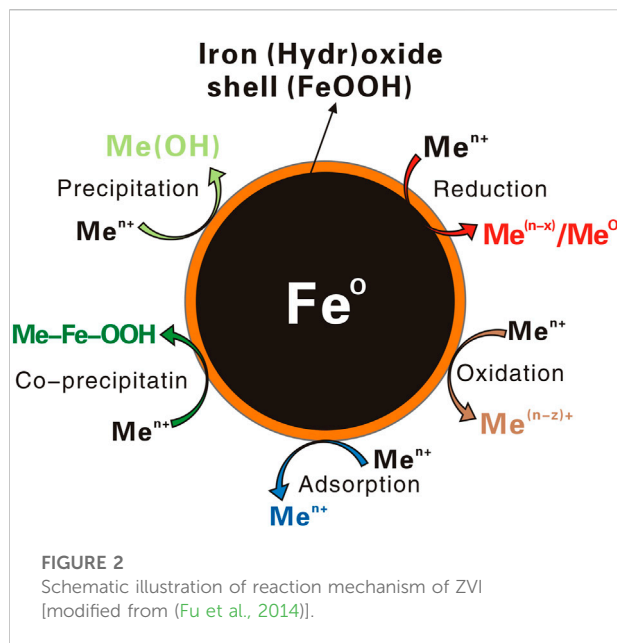
(Wilkin et al., 2009). During operation, treatment effects need to be closely monitored to ensure PRB effectiveness (Faisal et al., 2018). Moreover, PPR technology is greatly affected by geological conditions and site characteristics (Obiri-Nyarko et al., 2014). As shown in Figure 1, PRB technology is to build a reactive wall in the vertical direction of the groundwater pollution plume, and fill the wall with reactive substances. When the plume flows through the wall, the pollutants undergo a series of physical, chemical or biological reactions with the active reactive substance, thereby intercepting or converting the pollutants into non-toxic substances. According to reports, there have been more than 200 engineering application cases of PRB technology to deal with groundwater pollution around the world.

The key to PRB technology to deal with groundwater pollution is the active medium material filled in the wall. In more detail, the reactivity, cost, and lifetime of materials can have a direct impact on the stability, economy, and safety of PRB systems. The choice of reaction medium material mainly depends on the reaction mechanism between pollutants and medium material. In addition, it is also affected by hydrogeological conditions such as pH. Before 2000, the medium material was traditional zero-valent iron (ZVI). Since then, the research focus has turned to the development of new medium materials. According to the structural characteristics of medium material, there are three categories: single material, mixed material and composite material.

Under ideal conditions, the reaction medium should have the following characteristics. 1) The filling material should have stable structure and uniform particle size. In addition, the particle size should not be too small to ensure that the permeability coefficient is higher than the surrounding area. 2) The pollution component can fully react with the filler and be removed. 3) The filling material should be stable and active enough to ensure that the PRB system has a long-term stable treatment effect on pollutants (Asokbunyarat et al., 2017). 4) The product after the interaction between the reaction material and the pollution component should be non-toxic and free from secondary pollution (Jeen et al., 2011). 5) The reaction product is not easy to block the system (Blowes et al., 2000). 6) The filling material is cheap and readily available (Liu et al., 2020).

Scherer et al. (2000) summarized the types and properties of PRB reaction materials, and discussed the feasibility and long-term efficacy of PRB technology. However, some new materials have been developed and applied within the last 20 years (Obiri-Nyarko et al., 2014) reported the application of ZVI, zeolite, activated carbon, apatite and other materials in groundwater remediation, without introducing the application of mixed materials and composite materials (Wu et al., 2020) detailed the application of ZVI as a reactive material in the treatment of heavy metal pollution in groundwater (Song J. et al., 2021) reviewed the PRB technique for remediation of heavy metal-contaminated media materials, but did not indicate the process for





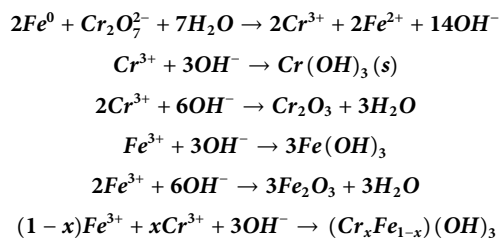
screening reactive materials. In this study, reaction materials are classified into three main categories, namely single material, mixed material, and composite material. The research status of various media materials in the treatment of heavy metal pollution in groundwater is summarized, including the types of heavy metals, experimental scale and removal effect. On this basis, the main mechanism of heavy metal removal by reaction materials is revealed and the experimental methods for screening dielectric materials are summarized. Finally, the development direction of reaction materials is pointed out.

## 2 Materials and methods

### 2.1 Single material

#### 2.1.1 Zero-valent iron

With strong electronegativity, high reactivity and fast reaction, ZVI has a good removal effect on heavy metals such as Cr, U, V, Ni, Pb, Cd, Hg, and Cu. ZVI has been used in many practical projects. ZVI easily reacts with oxygen to form FeO(OH) or Fe(OH)<sub>3</sub> solids, thus causing the clogging of the reaction medium. Usually, highly permeable substances (such as sand and gravel) are added to the reaction wall to increase the permeability and prolong the service life (Jeen et al., 2011). As shown in Figure 2, the main mechanism of ZVI removal of heavy metals lies in redox, precipitation, adsorption, etc. With the removal of Cr(VI) by ZVI as an example, the reaction equation is as follows (Dries et al., 2005; Lai and Lo, 2008; Soto et al., 2015):



ZVI may have bio-stimulatory effects on the PRB system and downstream microorganisms (Xu et al., 2017). According to (Wang et al., 2022), ZVI promotes the biological reduction of Cr(VI).

Compared with ZVI, nanoscale zero-valent iron (nZVI) has smaller particle size, larger specific surface area and surface energy, one to three orders of magnitude higher reactivity (Jiang et al., 2018), and stronger transport capacity in soil. nZVI can be directly injected into underground aquifers (Mystrioti et al., 2020), which has good application prospects. However, the high reactivity makes nZVI susceptible to oxidation, the magnetic properties make it easy to agglomerate and cause clogging. The modification of nZVI is an important research direction to develop new reaction medium.

#### 2.1.2 Carbonaceous material

A large number of hydroxyl, phenol and carboxyl groups are distributed on the surface of activated carbon (AC), and the internal pores are well developed (Li et al., 2010). Therefore, activated carbon has excellent adsorption and chemical stability (Dong et al., 2016), which is a commonly used material in the early stage of PRB. Moreover, it is widely used in the removal of heavy metals (Hornig et al., 2008). However, the heavy metal removal effect of activated carbon is easily affected by pH (Di Natale et al., 2007). The increase in pH would enhance the binding of water molecules to activated carbon and decrease the adsorption capacity of activated carbon (Obiri-Nyarko et al., 2014). The groundwater component affects the performance of activated carbon. For example, anions such as chloride and sulfate will compete with pollutants for reaction sites, thereby reducing the adsorption capacity of activated carbon (Namasivayam and Sangeetha, 2006).

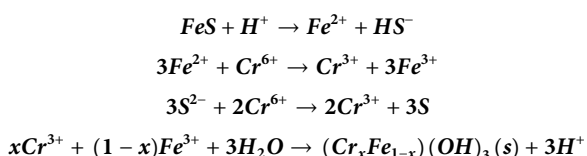
Another type of carbonaceous material is biochar (BC), with abundant internal pores and negative charges on the surface (Lou et al., 2016). This is prepared from various types of biowaste materials under low pyrolysis temperature and anoxic conditions (Liang et al., 2021). Compared with AC, BC is cheaper to produce and has a stronger affinity. However, the adsorption capacity of BC for Ni, Pb, Cr, and Cd is lower than that of modified AC (Wilson et al., 2006). By loading organic functional groups (Zhou et al., 2013), minerals (Han Y. et al., 2016) and nZVI (Zhou et al., 2014) or activated by acid and alkali solutions, the adsorption capacity of BC can be significantly improved. The heavy metal removal mechanisms include physical adsorption, ion exchange,

electrostatic interaction, etc. Typically, the entire removal process is a combination of different mechanisms (Shakoor et al., 2020). The materials used in the preparation of BC are of various types and sources, which have important application value in the restoration of heavy metals in groundwater.

### 2.1.3 Mineral material

#### 2.1.3.1 Iron-bearing mineral

Iron-bearing minerals have become a new type of reaction material for PRB systems, including iron sulfide mineral and iron oxide minerals (Aredes et al., 2012). The removal mechanism of heavy metal ions by natural iron oxide minerals is mainly (irreversible) chemisorption, and to a lesser extent (reversible) physisorption. As a good arsenic removal material, laterite can stably adsorb arsenic in water in the pH range of 4–11 (Aredes et al., 2012). Due to their abundant reserves, low price, and non-toxicity to the environment, iron sulfide mineral is usually used to remove heavy metals in polluted water (Abdul et al., 2019). The effect of groundwater composition on removal efficiency should be fully considered. When humic acid (HA) is contained in, for example, groundwater, HA competes with Cr(VI) for pyrite surface sites, resulting in the reduction of Cr(VI) removal (Kantar et al., 2017). In addition, the heat treatment method can also affect the removal effect of pyrite on heavy metal contaminants. The adsorption capacity of Hg(II) by natural pyrite is  $0.19 \text{ mg g}^{-1}$ , which could be increased to  $54.44 \text{ mg g}^{-1}$  by calcination under nitrogen atmosphere (Zhu et al., 2020). Under acidic conditions, the removal mechanism of Cr(VI) by pyrite is as follows (Gong et al., 2016):



#### 2.1.3.2 Channel/lamellar structural mineral

Minerals such as zeolite and apatite have channel or lamellar (chain lamellar) structure inside, with good adsorption performance and ion exchange performance, which can remove a variety of heavy metal ions (Kumara and Kawamoto, 2021). Zeolite is a hydrated framework-like aluminosilicate mineral composed of tetrahedra of  $\text{AlO}_4$  and  $\text{SiO}_4$  (Maharana and Sen, 2021), with abundant internal channels (Bailey et al., 1999), as well as catalytic ability and molecular sieving ability (Cerjan Stefanović et al., 2007). It has a negative surface charge (Abdelrahman et al., 2021), and a cation exchange capacity of 2–4 meq  $\text{g}^{-1}$  (Liu et al., 2020). With strong adsorption on Cu(II), Pb(II), Cd(II), Ni(II), and Zn(II), and low price, zeolite is considered to be an ideal material for heavy metals removal (Wang and Peng, 2010). At low pH values, an excess of protons can compete effectively with the heavy metal ions for binding sites on zeolite surface (Faisal and Hmood, 2015). The higher the

degree of groundwater mineralization, the better the removal efficiency of heavy metal ions by zeolite (Jarvis et al., 2006). Heavy metal cation contaminants can be adsorbed or exchanged into the internal channel structure of channel/lamellar (chain lamellar) structured minerals. Therefore, the voids between the medium material particles are not blocked, thereby maintaining high permeability and extending service life. This feature is of great significance in the practical application of PRB engineering.

Because of its wide source, non-toxic, cheap, and simple preparation process, apatite, a common phosphate material, is often used to remove divalent heavy metal ions. Dong et al. (2013), which is considered as a high-quality inorganic ion lattice adsorption and exchange material. When the environmental pH is neutral or weakly acidic, hydroxyl apatite (HAP) can remove heavy metal contaminants through surface adsorption and ion exchange. When the environmental pH is less than 4, apatite removes heavy metal pollutants through dissolution-precipitation reactions and other pathways (Oliva et al., 2010; Elkady et al., 2018; Nijhawan et al., 2018).

Due to the abundant channels, synthetic HAP is often used in the removal of target pollutants (Asri et al., 2010). HAP is the main inorganic component of animal bones, and the content can reach 70%. Therefore, HAP obtained from discarded animal bones has a cost advantage (Ngueagni et al., 2020). Studies have shown that HAP prepared from animal bones such as fish bones and bovine bones are mostly used for remediation of heavy metals in industrial wastewater and soil (Hernández-Cocolezzi et al., 2020; Wang et al., 2021). It is necessary to research biological HAP as PRB reaction materials. HAP can form stable minerals with metal cations, with high stability under oxidative or reducing conditions (Wellman et al., 2008). Without considering the coexistence of other anions and cations, the reaction between HAP and uranium has the following three main mechanisms: 1) Dissolution and precipitation. Under acidic conditions, hydroxyapatite dissolves part of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$ , and precipitate with  $\text{UO}_2^{2+}$ . New species are formed, such as  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot n\text{H}_2\text{O}$  and  $\text{H}_2[(\text{UO}_2)(\text{PO}_4)]_2 \cdot n\text{H}_2\text{O}$  (Kong et al., 2019). 2) Ion exchange. Divalent metal ions in solution are prone to ion exchange reaction with hydroxyapatite. Calcium sites on the surface of HAP can ion-exchange with uranium ions (Stötzel et al., 2009). 3) Adsorption.  $\text{UO}_2^{2+}$  achieves the adsorption of uranium by occupying surface active sites on hydroxyapatite (Simon et al., 2008).

Permeable concrete is a highly porous special concrete prepared from cement slurry and coarse aggregate (particle size greater than 4.75 mm) (Alighardashi, 2018; Wijeyawardana et al., 2022). The innovative development of mineral materials is to act as a reactive barrier to remove heavy metals and nitrates in groundwater (Shabalala et al., 2017; Alighardashi, 2018). The heavy metals removal mechanism of permeable concrete is mainly to generate metal hydroxide precipitation (Holmes et al., 2017). In addition, microbial action and adsorption also

facilitate the removal of heavy metals (Yousefi and Matavos-Aramyan, 2018).

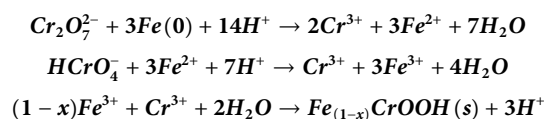
### 2.1.4 Ion exchange resin

Ion exchange resin has the characteristics of high adsorption capacity, long-lasting activity and fast reaction rate, which is often used for the removal of heavy metal ions in sewage (Vilensky et al., 2002; Ahmad and Sharma, 2019). Through continuous research on resin modification, selective adsorption and regeneration are significantly improved, which increases the possibility of application in groundwater remediation technology. As a promising PRB reaction medium, ion exchange resin is often used to treat uranium in groundwater, where the treatment process is not easily disturbed by groundwater components (Stucker et al., 2011; Zawierucha and Nowik-Zajac, 2019). With PHREEQE geochemical software (Barton et al., 2004), predicted the existence of uranium in groundwater under different pH conditions. On this basis, they proposed that  $H^+$  on the cation exchange resin can be replaced by cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) in groundwater, thereby reducing the pH of groundwater and promoting the formation of  $UO_2^{2+}$  and adsorption on the resin. However, the main removal mechanism of uranium by anion resins is electrostatic action. However, ion exchange resins are not suitable for treating wastewater with excessively high concentrations of pollutants. Expensive price is the main reason to limit its application. In this regard, the development of inexpensive ion exchange resins becomes an important research direction.

### 2.1.5 Solid waste

In recent years, solid waste have been used in the reaction medium, which plays a role in reducing the hazard of heavy metals in groundwater, as well as the cost of solid waste treatment and PRB operation. Solid waste such as waste sludge (Chien et al., 2021), fly ash (Yang et al., 2020), and recycled concrete (Indraratna et al., 2010) etc., has become a popular research object for the development of new reaction media. Solid waste in line with the concept of sustainable development is selected as the medium material. However, the composition of solid waste is complex, which may increase the risk of secondary pollution. For the development of solid waste reaction media, the removal capacity and removal mechanism of the material, and the stability of the generated product are important concerns (Faisal et al., 2018). Basic oxygen furnace sludge (BOFS) is rich in ZVI and iron oxides such as FeO and  $Fe_3O_4$  (Omran et al., 2020). BOFS has small particle size, large specific surface area, and positive charge on the surface, which is conducive to the adsorption of  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  in groundwater (Frade et al., 2018). In addition, co-precipitation can occur between  $Cr^{3+}$  and  $Fe^{3+}$  (Blowes et al., 2000). Therefore, the removal mechanisms of Cr(VI) in groundwater by BOFS are

mainly adsorption, reduction and co-precipitation. The possible reaction processes are as follows (Wilkin and Puls, 2003; Puls, 2006; Han C. et al., 2016):



For example, (Frade et al., 2018), found that steelmaking converter sludge is rich in iron oxides such as ZVI and FeO. At pH 5.5, its adsorption capacity for Cr (VI) is 0.213 mg g<sup>-1</sup>. Calcium content in BOFS is up to 13.9% (w/w). Calcium can promote the release of  $OH^-$  the increase of pH, and the precipitation of  $Cr(OH)_3$ . However, high pH is not conducive to the reduction of Cr(VI). In addition (Araujo et al., 2019), also confirmed that BOFS and ZVI have similar removal effects on high concentrations of arsenic in acidic wastewater.

The advantages and disadvantages of single reaction medium used within PRB have been summed up in Table 1.

## 2.2 Mixed material

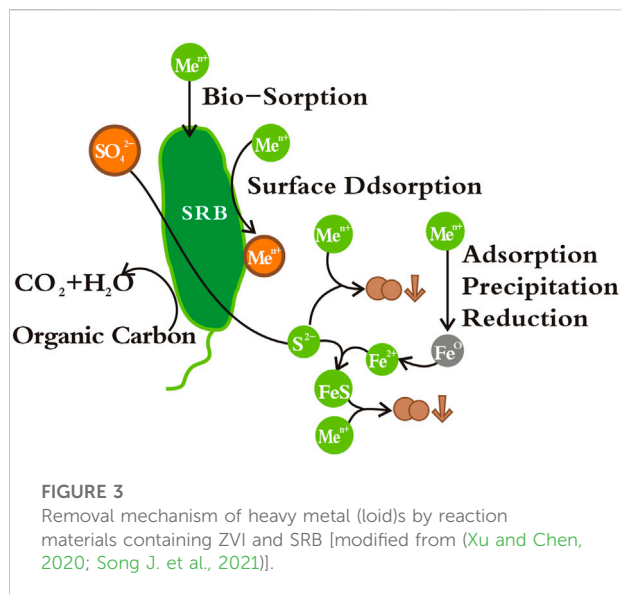
Although there are many types of single media and are widely used in groundwater heavy metal pollution control, it is difficult to meet complex environmental conditions. Two or more of ZVI, mineral material and carbonaceous material are mixed in a certain proportion to form the mixed material, which can enhance the penetration ability of the reaction medium, the type of removal mechanism, the removal rate and the service life.

### 2.2.1 Mixed material with zero-valent iron

#### 2.2.1.1 Zero-valent iron and mineral material

When ZVI is used as a single active substance, it is easy to cause passivation and blockage. The mixing of ZVI and mineral material can not only increase the permeability coefficient of the PRB system, but also effectively reduce the aggregation of ZVI. When ZVI is mixed with inert mineral materials such as sand and gravel, the permeability coefficient inside the PRB system is improved. In the study by (Wang et al., 2022), a mixed material consisting of ZVI (20%), gravel (20%), and sand (60%) was treated as a PRB filler for Cr(VI). At this time, the concentration of Cr(VI) can be reduced from 27.29–242.65 mg L<sup>-1</sup> to below 0.1 mg L<sup>-1</sup>. In addition, this study also found that ZVI could induce changes in the structure and composition of the downstream native microbial community, thereby promoting the biological reduction of Cr(VI).

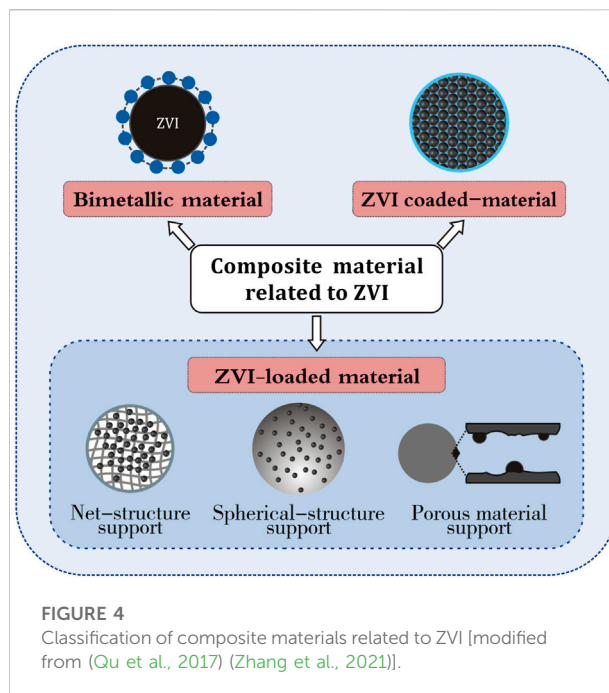
Pumice and trass have the advantages of abundant channels and large specific surface area, which are often used as adsorbents or filter media for sewage treatment.



The mixing of ZVI with porous minerals not only increases the permeability coefficient, but also solves the blocking problem of PRB walls. According to the study of (Faisal et al., 2020), when the initial concentration of nickel is  $8 \text{ mg L}^{-1}$ , the life expectancy of the PRB system with ZVI/pumice mixed material as the reaction medium is more than 26 months, while the life expectancy of the PRB system with only ZVI as the reaction medium is only 3.6 months. In addition, the pyrite/ZVI mixed material as a reaction medium can inhibit the increase of pH, promote the regeneration of Fe(II), and prolong the service life (Lü et al., 2018).

### 2.2.1.2 Zero-valent iron and compost

Subterranean environment is rich in microorganisms. Bioremediation is an important technology for remediation of soil and groundwater. Compost materials have attracted much attention due to their rich microbial species and high cation exchange capacity (Cancelo-González et al., 2017). Most heavy metal sulfides have low solubility. Sulfate reduction is often used to solve the problem of heavy metal pollution in mining wastewater. This provides a basis for the application of sulfate reducing bacteria (SRB) in PRB technology, and its removal mechanism of heavy metals is shown in Figure 3 (Wilopo et al., 2008) used ZVI, sheep manure, compost and sawdust as fillers to study the removal of arsenic and manganese by PRB. Inoculated SRB may promote the precipitation of part of arsenic in the form of Fe-As-S, but it is not conducive to the solidification of manganese. Inoculation with SRB increases the lifespan of PRB to 15.76 years, which is much higher than that of PRB without SRB (6.74 years). Appropriate pH is a



necessary condition for microbial growth. Good permeability is conducive to the normal operation of the PRB system (Gibert et al., 2013) constructed a field-scale PRB system with calcite, plant compost, ZVI, and sludge as fillers, with over 98% heavy metal removal. However, the complex media composition easily leads to the inhomogeneity of the filling material, which can produce clogging and preferential flow channel phenomena. The particle size distribution of the filling material is adjusted to improve this by adding inert materials such as sand and stones.

The growth of microorganisms requires a suitable growth environment. Therefore, suitable pH range and temperature and sufficient nutrients are beneficial to enhance the microbial action in the PRB system. Moreover, the toxic effects of the constituents of the pollutants on microorganisms need to be taken into account.

### 2.2.2 Mixed material without zero-valent iron

The cost of ZVI-containing fillers is relatively high. In order to improve the economics of PRB technology, solid wastes from agricultural or industrial production processes can be used as precursors to prepare PRB reaction medium (Faisal et al., 2020) mixed waste foundry sand (WFS) with a mass ratio of 82% and filter sand (FS) with a mass ratio of 18% as a reaction medium to treat wastewater containing lead and nickel. Among them, the removal mechanism of the former is mainly chemical adsorption, with the maximum adsorption capacities of  $13.966$  and  $4.227 \text{ mg g}^{-1}$ . In order to reduce the secondary pollution, more and more attention has been paid

TABLE 1 Analysis of the advantages and disadvantages of single reaction medium to remove heavy metals.

Mixed reaction media	Mechanism	Advantages	Disadvantages	References
ZVI/nZVI	(a) Adsorption (b) Reduction (c) Precipitation (d) Co-precipitation	(a) Strong reduction ability (b) A variety of heavy metals can be treated (c) Large specific surface area (d) Fast reaction rate	(a) Prone to passivation (b) Easy to cause clogging (c) Prone to agglomeration	Turner et al. (2005), Faisal et al. (2015), Pawluk et al. (2015)
carbonaceous material	Activated carbon	(a) Physical sorption (b) Ion-exchange	(a) Greatly affected by pH (b) High production cost	Li et al. (2010); Dong et al. (2016)
	Biochar	(c) Complexation (d) Precipitation (e) Electrostatic interaction	(a) Good adsorption properties (b) Steady chemical property (c) Low cost	Paranavithana et al. (2016); Xiang et al. (2021)
mineral material	Iron-bearing mineral	(a) Sorption	(a) Easy to passivate when pH increases (b) Low penetrability (c) Complex chemical composition (d) Potential secondary pollution	Aredes et al. (2012); Liu et al. (2015)
	Channel/lamellar structural mineral	(b) Ion exchange (c) Precipitation	(a) High permeability (b) High mechanical strength (c) Low cost (c) Difficult to recycle (d) Limited processing efficiency	Dong et al. (2013); Faisal and Abd Ali. (2016)
Ion exchange resin	Ion exchange	(a) Large exchange capacity (b) Strong selective (c) Fast reaction rate (d) Low risk of secondary pollution	(a) Not suitable for removal of high-concentration heavy metals (b) High cost	Barton et al. (2004), Flint et al. (2021)
Solid waste	(a) Sorption (b) Ion exchange (c) Precipitation	(a) Materials from a wide range of sources (b) Green development (c) Low cost	(a) Complex chemical composition (b) Limited processing efficiency (c) Potential secondary pollution	Faisal and Abd Ali. (2016), Araujo et al. (2019), Ali Alyaa and Abd Ali Ziad. (2020), Chien et al. (2021)

to the research and development of environmentally friendly materials (Fan et al., 2018) developed a new type of environmentally friendly filler, with corn straw, fly ash, synthetic zeolite, loess ferromanganese nodules and other mixed materials as active media. Its removal mechanism is mainly complexation and electrostatic attraction, with greater than 90% removal rate of Pb(II) and Cd(II).

In contrast, the preparation of mixed material is simpler than that of composite material. The key step in the preparation of mixed material lies in the selection and addition of a variety of single materials. As shown in Table 2, there are differences in the heavy metal treatment capacity and removal mechanism of the reaction medium composed of different types of materials. The selection of

active materials should fully consider the removal mechanism of target pollutants. In order to reasonably construct the reaction medium of the PRB, it is necessary to take into account the environmental conditions such as groundwater component and permeability of the surrounding soil.

## 2.3 Composite material

### 2.3.1 Composite material related to zero-valent iron

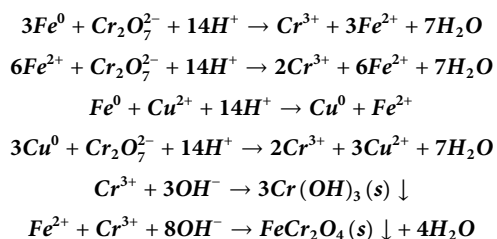
#### 2.3.1.1 Bimetallic material

The ZVI surface is plated with another metal with high reduction potential (such as copper, platinum, and nickel) to

TABLE 2 Application of mixed reaction medium in PRB treatment of groundwater heavy metals.

Mixed reaction media	Heavy metals	Type of experiment	Initial concentration (mg·L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg·g <sup>-1</sup> )	Mechanism	References
ZVI and sand	Cr(VI)	Field-scale	27.29–242.65	6 months	Close to 100%		Reduction; precipitation	Wang et al. (2022)
ZVI, pyrite and sand	Ni	Batch and column	20	120 min	>90%		Reduction; precipitation	Nicola et al. (2017)
ZVI and lapillus	Cu(II)	Column	500				Adsorption; co-precipitation	Bilardi et al. (2019)
	Ni(II)		50					
	Zn(II)		50					
ZVI, sheep manure etc.	As(III)	Batch and column	50	48 h	98.9	30.96	Reduction; adsorption; precipitation	Wilopo et al. (2008)
calcite, vegetal compost etc.	Al	Field-scale	15	3 years	>96		Reduction; adsorption; precipitation	Gibert et al. (2013)
	Zn		20		>95			
	Cu		1.2		>98			
BC and soil	Cd(II)	Batch	333	60 min	99.99	30.1	Adsorption	Paranavithana et al. (2016)
	Pb(II)		325		92.5	46.7		
WFS and FS	Pb(II)	Batch and column	50	60 min	>95	13.966	Adsorption; ion exchanges; precipitation	Faisal et al. (2020)
	Ni(II)		50			4.227		
AC and WFS	Zn(II)	Batch	155	3 h	>75		Adsorption	Naji et al. (2020)
Cement kiln dust and FS	Cu(II)	Column	100	99 days	98		Adsorption	Sulaymon et al. (2015)
	Zn(II)				99			
Corn straw, fly ash etc.	Pb(II)	Column	5	12 h	>90		Adsorption	Fan et al. (2018)
	Cd(II)		0.5					
leaf/yard compost, ZVI etc.	As	Pilot	206	30 months	>99		Adsorption; precipitation	Ludwig et al. (2009)
	Pb		2.02					
	Cd		0.324					
	Zn		1060					
	Ni		2.12					

form bimetallic material, which act as galvanic cells during the reaction to speed up the reaction rate. The bimetallic system composed of nZVI can reduce the agglomeration between nZVI and the activation energy during the reaction, thereby increasing the reduction rate (Maamoun et al., 2021). Shubair et al. (2018) demonstrated that the removal mechanism of cesium by nZVI and nZVI/Cu is mainly chemical adsorption, with a removal rate of more than 99%. In contrast, the reaction rate of nZVI/Cu is faster (Xie et al., 2021) synthesized nZVI/Pt bimetallic particles, which showed good removal of heavy metals and chlorophenols (Zhu et al., 2017) demonstrated that nZVI/Ni bimetallic material can reduce the effect of agglomeration, with 99% Cr(VI) removal rate. Copper can promote the electron transfer of Fe<sup>0</sup> and the generation of Fe<sup>2+</sup>, thereby accelerating Cr(VI) removal. With the remove of Cr(VI) by the bimetallic system composed of nZVI/Cu as an example, the chemical reaction formula is as follows (Maamoun et al., 2021):



Moreover, copper can inhibit the oxidation of Fe<sup>0</sup> and increase the electrons obtained by Cr(VI). As shown in Table 3, The research on removing heavy metals from groundwater with ZVI bimetal as reaction media is still in the laboratory stage. It has extensive removal of heavy metals, and its removal mechanism mainly consists of adsorption and reduction. Compared with ZVI and nZVI, bimetallic particles have a faster reaction rate and overcome the disadvantage of easy agglomeration. However, its preparation process is complicated. In addition, some metals are expensive (such as silver and platinum) or cause secondary pollution to the environment



TABLE 3 Application of bimetallic material in PRB treatment of heavy metals in groundwater.

Reaction media	Heavy metals	Type of experiment	Initial concentration (mg L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg g <sup>-1</sup> )	Mechanism	References
Cu/Fe	Cr(VI)	Batch and column	20	3 h	85	17.94	Reduction; precipitation	Maamoun et al. (2021)
Si/Fe	Ni(II)	Batch	150	60 min	65.90	55	Adsorption	Abdelrahman and Hegazey. (2019)
	Cu(II)				65.83	56		
	Zn(II)				62.53	53		
Fe/Al	Hg	Batch	32.5	90 min	99.74		Reduction; adsorption	Aghaei et al. (2021)
	As		9.3		99.80			
	Cu		53.4		98.20			
	Pb		91.4		95.50			
Cu/Fe	As(V)	Batch	50	4 h	55		Reduction; adsorption	Rajendran and Thangavelu. (2021)
Ce/Fe	As(V)	Batch and column	10	24 h	Nearly 100	164.94	Reduction; adsorption	Wen et al. (2018)
	Cr(VI)		10		>90	127.42		
Fe/Ni	Zn(II)	Batch	20	240 min	>90	149.25	adsorption	Abukhadra et al. (2018)
	Co(II)			240 min	106.4			
	Cu(II)			120 min	147.5			
Fe/Co.	Cr(VI)	Batch	8	12 h	99	1.6	Reduction; adsorption	Qin et al. (2016)
Fe/Al	U(VI)	Batch	100	24 h	99	575	Reduction; adsorption	Xiang et al. (2018)

(copper and nickel). These factors above limit the application of bimetallic materials.

### 2.3.1.2 ZVI-loaded material

In order to overcome the shortcoming of easy agglomeration in nZVI, a series of ZVI-loaded solid materials were developed. Reported loaded materials include pyrite (Lü et al., 2018), zeolite (Tasharofi et al., 2020), bentonite (Zhang et al., 2012), clay (Jia et al., 2011), montmorillonite (Jia and Wang, 2013), activated carbon (Wang M. et al., 2019), biochar (Liu Y. et al., 2019), and graphene (Xing et al., 2016). The application of ZVI-loaded material has been summed up in Table 4.

Magnetite and pyrite alone can be used as reaction medium for PRB system, or loaded material for ZVI. Magnetite is an octahedral crystal rich in Fe<sub>3</sub>O<sub>4</sub> and having strong magnetism. Magnetite can attach nZVI to its surface, thereby effectively preventing nZVI from agglomerating. The results of (Wu et al., 2009) showed that when Fe<sub>3</sub>O<sub>4</sub>:Fe<sup>0</sup> is 40:1, the reaction rate of composite material and Cr(VI) is the fastest. Furthermore, the reaction rate is related to the pH in the solution. Alkaline conditions are not conducive to the removal of Cr(VI). Pyrite is rich in FeS<sub>2</sub>, with strong electron transfer ability and reducibility (Min et al., 2021) prepared a ZVI-loaded pyrite composite material (ZVI/FeS<sub>2</sub>) using pyrite and ZVI as raw materials by ball milling, with over 99% Cr(VI) removal rate and long-term stability.

Silicon-containing minerals such as zeolite and clay are important heavy metal adsorbents for water. Natural zeolite

has high internal porosity and surface active sites, which is suitable as a loaded material for nZVI to eliminate aggregation of nZVI (Li et al., 2018). Clay minerals such as kaolinite, illite, pyrophyllite and montmorillonite can overcome the disadvantage of easy agglomeration in nZVI (Ezzatahmedi et al., 2017). (Bhowmick et al., 2014) prepared a nZVI-loaded montmorillonite, which has a maximum adsorption capacity of 59.9 and 45.5 mg L<sup>-1</sup> for As(III) and As(V) in a wide pH range (4–8). As(V) and As(III) form complexes on the surface of composites. As(III) is all oxidized to As(V), but As(V) is not reduced. NaOH solution (0.1 M) can be used for the regeneration of composites. After five cycles of test, the properties of composites don't change significantly. Therefore, it is considered an ideal reaction medium for handling arsenic containing groundwater.

BC and AC are porous organic carbonaceous materials with various functional groups on their surfaces. With their large heavy metal adsorption capacity, they are often used as remediation materials for heavy metal pollution in the environment. The ZVI-containing composite material with BC and AC as loaded materials has good removal effect on arsenic, strontium, chromium, and lead (Mandal et al., 2020) prepared nZVI-loaded green tea biochar. The stabilizing effect of Pb(II) is sorted as nZVI-loaded green tea biochar > pristine nZVI > green tea biochar. The load of ZVI to BC is greater than AC. ZVI affects the redox process of target heavy metals. With the removal of selenium as an example, the removal effect of ZVI-loaded BC on

TABLE 4 Application of ZVI-loaded materials in PRB treatment of heavy metals in groundwater.

Reaction media	Heavy metals	Type of experiment	Initial concentration (mg L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg g <sup>-1</sup> )	Mechanism	Reference
nZVI-loaded magnetite	As(III) As(V)	Batch	10	1 h	Nearly 100		Reduction; co-precipitation	Wu et al. (2009)
ZVI/FeS <sub>2</sub> -loaded natural pyrite	Cr(VI)	Batch	448.1 mg kg <sup>-1</sup> (soil)	7 d	99.5		Reduction; co-precipitation	Min et al. (2021)
ZVI-loaded pyrite (FeS <sub>2</sub> )	Sb(V)	Batch	100	180 min	99.18	248.1	Adsorption	He et al. (2020)
ZVI-loaded HAP	U(VI)	Batch	10	100 min	93.8	46.9	Adsorption; precipitation	Zeng et al. (2019)
nZVI-loaded modified zeolite	Cd(II)	Batch	50	90 min		20.6	Adsorption; precipitation; ion exchange	Tasharofi et al. (2020)
microscale ZVI-loaded zeolite	Pb (II) Cd(II)	Batch and column	50			154.61 63.14	Adsorption; precipitation; ion exchange	Kong et al. (2017)
nZVI-loaded attapulgite	Cr(VI)	Batch	40	12 h	90.6	266.65	Reduction; adsorption	Zhang et al. (2019)
nZVI-loaded AC	Pb(II)	Batch	10	5 min	95	59.35	Adsorption	Liu et al. (2019a)
nZVI-loaded BC	Cr(VI)	Batch	20	8 h	99	40.0	Reduction; adsorption	Qian et al. (2017)
nZVI-loaded exhausted coffee grounds	Pb(II) Cd(II) As(III) As(V)	Batch	10	1 h 24 h 1 h 1 h		164.1 112.5 23.5 9.3	Reduction; adsorption	Park et al. (2019)
nZVI-loaded GO	Cr(VI)	Batch	50	12 h		26.39	Adsorption; reduction; precipitation	Yang et al. (2021)

TABLE 5 Application of nZVI coated-material in PRB treatment of groundwater heavy metals.

Reaction media	Heavy metals	Type of experiment	Initial concentration (mg L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg g <sup>-1</sup> )	Mechanism	References
Double surfactant-modified nZVI	Cr(VI)	Batch	80	2 min	99	231.75	Adsorption; reduction; precipitation	Li et al. (2020)
CMC- wrapped nZVI	Cu(II) Ni(II)	Batch	100	2 min 5 min		99.7 84.7	Adsorption; precipitation	Lou et al. (2019)
APAM-modified nZVI	Ni(II)		100	2 h	>80		Adsorption; precipitation	Liu et al. (2016)
Chitosan nanospheres-encapsulated ZVI	As(III) As(V)	Batch	2	3 h		94 ± 1.5 119 ± 2.6	adsorption	Gupta et al. (2012)
CMC-wrapped nZVI	U(VI)	Batch and column	25	29.9 min	Nearly 100%		Adsorption; reduction; precipitation	Zhao et al. (2020)

Se(IV) and Se(VI) is higher than that of ZVI-loaded AC. In addition, pH significantly affected the removal of Se(IV) and Se(VI) by ZVI-loaded BC and ZVI-loaded AC (Tan et al., 2019).

Although the nZVI-loaded BC has an ideal removal effect of heavy metals, the preparation procedure is complicated (Zhang et al., 2022) prepared composite materials with biochar and nZVI

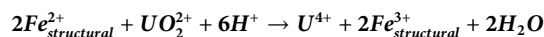
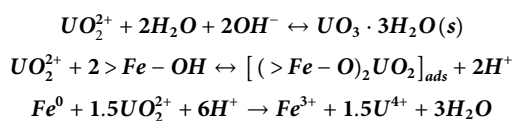
using a one-step pyrolysis method, enabling large-scale commercial applications. Furthermore, the activated carbon fiber (Qu et al., 2017) and graphene oxide (GO) (Yang et al., 2021) can also be used as the loaded material of ZVI.

With carbonaceous material as ZVI loading material, the ZVI-loaded BC and AC have more negative charges than the BC and AC surfaces, which has stronger adsorption capacity for cations. The main heavy metal removal mechanism is adsorption. As support material, GO can reduce ZVI aggregation. The abundant functional groups on its surface can well adsorb heavy metals. For Cr(VI) and As(V) in aqueous solution, the another main removal mechanism is reduction. With magnetite and pyrite as ZVI support materials, the main mechanisms for removing heavy metals are adsorption and reduction. HAP is rich in phosphate, and its main mechanism for heavy metal removal is adsorption and precipitation. When zeolite with abundant internal pores is used as ZVI support material, the main mechanisms of heavy metal removal are adsorption, precipitation and ion exchange.

### 2.3.1.3 Zero-valent iron coated-material

As shown in Table 5, ZVI can also be coated by other materials, which has a good removal effect on heavy metals in groundwater. Surfactants, natural or synthetic polymers can be used to coat the surface of nZVI, which can effectively overcome the agglomeration phenomenon by changing the surface charge of the particles (Reginatto et al., 2020). The nZVI coated by surfactant has good dispersion and transport, fast reaction rate, and wide application range. In addition to continuous reactive walls, injectable suspensions can be used to remediate groundwater (Truex et al., 2011). According to Li et al. (2020), two surfactants polyvinylpyrrolidone (PVP) and sodium oleate (NaOA) were used to coat nZVI. The two active materials exhibited a synergistic effect on Cr(VI) removal.

Surfactant and nZVI are easily desorbed in complex groundwater environments. Polyelectrolytes such as sodium carboxymethyl cellulose (CMC) (Yu et al., 2020), polyacrylic acid (PAA) (Jiemvarangkul et al., 2011), and polyacrylamide (APAM) (Liu et al., 2016) can exist stably for a long time (Zhao et al., 2020). prepared a CMC-wrapped ZVI composite material. When the initial concentration of U(VI) was 25 mg L<sup>-1</sup> and the pH was 6, the removal rate was close to 100%. According to the XPS spectra of uranium-loaded nanoparticles CMC-ZVI, U(IV) and U(VI) coexist on the surface of the composite material. The main removal mechanisms are reduction, adsorption and precipitation. Bicarbonate extraction is used to extract the precipitated and adsorbed U(VI). The removal mechanism of uranium by composite materials is as follows:



In summary, the classification of composite material related to ZVI is shown in Figure 4.

### 2.3.2 Mineral-related composite material

The removal effect of a single mineral medium on different pollutants has a huge difference. Many researchers have used nanoparticles-loaded mineral, surfactant modification, and polymer-encapsulated minerals to prepare composite materials to remove complex groundwater pollution (Zeng et al., 2020) made an environmentally friendly and economical SiO<sub>2</sub>/FeC<sub>2</sub>O<sub>4</sub> composite material using biotite as raw material by one-step synthesis. When the initial concentration was 20 mg L<sup>-1</sup>, the removal rate of Cr(VI) was close to 100% in the pH range of 2–10 (Wang et al., 2020) modified bentonite with cetyltrimethylammonium bromide (CTMAB), which increased the maximum adsorption capacity for Cr(VI) to 19-fold compared to before modification. In addition, the feasibility of its application in PRB was demonstrated by column experiments (Bambaero and Bazargan-Lari, 2021) prepared a HAP/chitosan composite material from shrimp shell, bovine bone and snail shell, which has good adsorption capacity for Zn(II) and Cu(II) (Vahdat et al., 2019) loaded Fe<sub>3</sub>O<sub>4</sub> on the surface of HAP prepared from chicken thigh bone, and successfully prepared a nano composite material, which has adsorption capacity on lead as high as 109.89 mg g<sup>-1</sup>. According to the desorption experiment, EDTA solution (0.001 M) is an ideal desorption reagent, and its adsorption capacity to composites only decreases by 19% after five cycles.

Microorganisms are abundant in nature. For example, both SRB and iron-reducing bacteria have been shown to have the ability to reduce Fe(III) to Fe(II) (Cao et al., 2010). Co-processing of heavy metal pollution in groundwater with mineral composite materials and microorganisms has become an important research direction. In the study of (Xu et al., 2022), SRB were used to synthesize biogenic FeS kaolin composite material, which has ideal adsorption effect on various heavy metals such as Pb(II), Sb(III), and Cd(II). The introduction of microorganisms can often save costs. During the operating life cycle of PRB, it is necessary to strengthen the control of environmental factors such as pH, redox potential and toxin substance.

As shown in Table 6, mineral-related composites can extensively remove heavy metal ions from groundwater. There are differences in the removal mechanisms of heavy metals by composites prepared from different substances and mineral materials. In general, clay has strong adsorption and ion exchange capacities. Zeolite has ideal adsorption, ion exchange and catalytic capabilities. Apatite can provide sufficient phosphate. Mineral materials can improve the comprehensive properties of materials while retaining the advantages of carrier materials, which can not only be embedded in polymers, but also

TABLE 6 Application of mineral-related composite materials in PRB treatment of groundwater heavy metals.

Reaction media	Heavy metals	Type of experiment	Initial concentration (mg L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg g <sup>-1</sup> )	Mechanism	References
FeS-loaded sand	As(III)	Batch	5	2 days		41.7	Precipitation; reduction; adsorption	Han et al. (2011)
Mackinawite-loaded sand	Cr(VI)	Batch	5	3 days	100	0.187	Reduction; precipitation; adsorption	Park et al. (2018)
Nano-FeC <sub>2</sub> O <sub>4</sub> -loaded SiO <sub>2</sub>	Cr(VI)	batch and column	20	90 min	95.45		Reduction; precipitation; complexation	Zeng et al. (2020)
Fe <sub>3</sub> O <sub>4</sub> -loaded HAP	Fe(II)		50	1 h	98	4.9	Adsorption; ion exchange	Vahdat et al. (2019)
	Mn(II)		50		95	4.8	precipitation;	
Chitosan-immobilized HAP	Zn(II)	Batch	3	95 min	60	25.78	Adsorption; precipitation	Bambaeero and Bazargan-Lari, (2021)
	Cu(II)		3	220 min	90	20.394		
Chitosan immobilized bentonite	Cu(II)	Column	500	24 h	85.57	14.92	Adsorption; ion exchange	Futalan et al. (2011)
CMC-stabilized FeS	Cr(VI)	Batch	50	150 min	92.5	1046.1	Adsorption; reduction; co-precipitation	Wang et al. (2019b)
CMC-stabilized FeS	U(VI)	batch	10	1 h	>90		Reduction; adsorption	Duan et al. (2020)
TMAB-modified bentonite	Cr(VI)	batch and column	100	40 min		7.227	Adsorption; ion exchange	Wang et al. (2020)
Biogenic FeS-loaded Kaolin	Cd	batch	250	360 min		71.71	Reduction; adsorption	Xu et al. (2022)
	Pb		250		133.54			
	Cu		250		51.90			
	Zn		250		54.41			
	As		250		38.71			
	Sb		250		96.38			

be used as support materials for nanoparticles such as FeC<sub>2</sub>O<sub>4</sub>, FeS, and Fe<sub>3</sub>O<sub>4</sub>.

### 2.3.3 Carbon-related composite material

Carbon composite material is another important medium material. The application of the carbon composite material have been summed up in Table 7. AC and BC have high porosity and large specific surface area, which are ideal loaded materials (Shapira and Zucker, 2022) loaded MoS<sub>2</sub> on AC, which achieved an adsorption capacity for mercury of 1280 mg g<sup>-1</sup>. In addition, this kind of composite material has a good recycling effect (Song X. et al., 2021) prepared biochar by microwave *in-situ* synthesis with reed as raw material and modified it by nanomagnetite. The maximum adsorption capacity of Cr(VI) by the modified composite material was 9.92 mg g<sup>-1</sup>, which was higher than that of unmodified biochar (8.03 mg g<sup>-1</sup>).

In general, polymers such as surfactant and polyelectrolyte are rich in functional groups. Such substances can be used to modify AC and BC (Inyang et al., 2016). Chen et al. (2022) loaded

chitosan on the surface of BC to synergize the hydroxyl groups of chitosan with the carbonyl groups of pristine BC, thereby enhancing the adsorption capacity for Sb(III). According to the research of (Yi et al., 2019), chitosan-coated AC has broad prospects in the treatment of groundwater and soil cadmium pollution remediation.

With large specific surface area, abundant functional groups, and strong hydrophilicity, GO can efficiently adsorb heavy metals. However, the characteristics of easy aggregation and difficult separation limit its scope of application. In addition to composite materials such as magnetic GO and ZVI-loaded GO, composite materials such as chitosan-coated GO (Yang et al., 2014), alginate-modified GO, silica-loaded GO (GO-SiO<sub>2</sub>), and thiol-modified GO have potential application value of removing heavy metals from groundwater (Zhang et al., 2020). Alginate is a hydrophilic biosorbent material rich in carboxylic acid groups. Despite its poor stability in the environment, it can be hydrogen-bonded with GO to prepare three-dimensional porous composite materials (Pan et al., 2018). The gel properties of alginate can

TABLE 7 Application of carbon-related composite materials in PRB treatment of groundwater heavy metals.

Reaction media	Heavy metals	Type of experiment	Initial concentration (mg·L <sup>-1</sup> )	Reaction time	Removal efficiency (%)	Adsorption capacity (mg·g <sup>-1</sup> )	Mechanism	References
nano-Fe <sub>3</sub> O <sub>4</sub> -loaded BC	Cr(VI)	Batch				9.92	Adsorption; reduction	Song et al. (2021b)
Fe <sub>3</sub> O <sub>4</sub> -loaded BC	As(V)	Batch and column	5	24 h	>90	7.41	Adsorption	Zhang et al. (2016)
Chitosan-loaded BC	Sb(III)	Batch	40	24 h		17.2	Adsorption	Chen et al. (2022)
Nano-zirconia-loaded BC	As(V)	Batch	10	12 h		7.867	Ion exchange; adsorption	Liu et al. (2021)
Ce-doped AC	Cd(II)	Batch	1.85	150 min	51.24	5.88	Adsorption	Kouotou et al. (2022)
4-vinylpyridine-coated AC	Cr(VI)	Batch	18.1	24 h		53.7	Adsorption; reduction; ion exchange	Fang et al. (2007)
Calcium alginate-coated GO	Pb(II)		310.8	40 min		368.2	Adsorption	Pan et al. (2018)
	Cu(II)		95.32			98.1		
	Cd(II)		168.8			183.6		
EDTA-modified GO	Pb(II)		100	20 min		479 ± 46	Adsorption	Madadrang et al. (2012)
NH <sub>2</sub> -functionalized GO-SiO <sub>2</sub>	Cu(II)	Batch	12.71–158.88	4 h		158.9	Adsorption	Yang et al. (2016)

ensure that the composite material is separated from the water environment, thereby avoiding secondary pollution of the water body (Pan et al., 2019). The composite of two novel materials, GO and SiO<sub>2</sub>, can complement each other's advantages (Yang et al., 2016) introduced amino groups into the GO-SiO<sub>2</sub>, which showed an adsorption capacity of up to 158.9 mg g<sup>-1</sup> for Cu(II) under the optimal adsorption conditions. On the one hand, the GO composite material has strong adsorption capacity for heavy metals. On the other hand, it has the disadvantages of complicated process and high cost. Therefore, it is necessary to develop new fabrication processes to reduce costs.

Carbonaceous material is light in weight and high in strength, and its large surface area can effectively disperse nanoparticles (such as MoS<sub>2</sub> and nano-magnetite). The surface properties and electron distribution of carbonaceous materials have positive effect on electron migration. In more detail, the electron transfer of heavy metal pollutants and their intermediates is effectively promoted during the adsorption process. Due to its environmental friendliness, it is considered as an ideal material for PRB reaction media.

In summary, there are differences in the removal mechanism and removal effect of heavy metals by different reaction media. Reasonable selection of medium materials should be based on actual conditions, such as groundwater quality and geological conditions. The advantages and disadvantages of the three types of reaction media are compared in Table 8.

### 3 Screening of reaction medium

The removal effect of PRB on heavy metals in groundwater mainly depends on the reaction medium filled inside. Under reaction medium adsorption, ion exchange, and chemical reaction, heavy metals can be converted into low-toxic substances or fixed in PRB, so as to achieve the purpose of reducing toxic effects. Thus, the key to PRB technology lies in the choice of reaction medium. The screening of reaction medium mainly has three stages, including static batch test, dynamic column test, and simulated slot test. The removal ability and principle, permeability, long-term effect and other properties of the reaction medium were studied.

#### 3.1 Batch test

The static batch test mainly explores the removal ability of the reaction medium to target pollutants through a series of condition control experiments, and obtains the preferred medium (Tasharofi et al., 2020) carried out batch tests for the removal of Cd(II) from native zeolite and different modified zeolites. According to the research results, sodium zeolite had the most ideal adsorption effect on Cd(II) with an initial concentration of 50 mg L<sup>-1</sup>, with a maximum adsorption capacity of 22 mg g<sup>-1</sup>, which was selected as the adsorbent for subsequent experiments.

TABLE 8 Comparison of advantages and disadvantages of three types of reaction media.

Reaction media	Advantages	Disadvantages
Single material	Simple reaction mechanism and high removal efficiency of characteristic pollutants	Limited effect on complex groundwater pollution control
Mixed materials	(a) Mechanical mixing of two or more materials, and simple preparation process (b) Good effect on complex groundwater pollution (c) Reasonable combination between different materials, and good hydraulic conditions	(a) Limited removal efficiency (b) Improper material particle size combination is prone to preferential flow or clogging (c) Multiple chemical reaction processes and poor controllability
Composite materials	(a) Cooperative work, and high removal efficiency (b) Good effect on complex groundwater pollution (c) Multiple reaction mechanism	(a) Complex preparation process, and high cost (b) Potential secondary pollution

After completing the preliminary screening, batch test can be used to determine the optimal reaction conditions and reaction principle, thus providing a basis for later dynamic experiments (Chattanathan et al., 2013) prepared HAP from catfish bone. The results of batch test showed that the medium was ideal for the removal of U(VI) when the pH was in the range of 5.5–7. In addition, the smaller the particle size and the larger the surface area, the higher the removal rate of U(VI) (Liu et al., 2014) conducted a batch test study of arsenic removal from ox bone spodium. The adsorption behavior fits the Langmuir isotherm, with an  $R^2$  of 0.97. Its main adsorption mechanism is monolayer chemisorption.

### 3.2 Column test

The dynamic column test mainly studies the effect of the medium on the removal of pollutants by the reaction medium under hydrodynamic conditions. Through a 9-months Column test, (Liu and Lo, 2011) found that HA could promote the removal of Cr(VI) in a PRB with ZVI as the reaction medium. In addition, calcium in the groundwater component affects the action of HA. Calcium in groundwater would cause precipitates to easily aggregate on the ZVI surface, thereby inhibiting electron transfer and affecting Cr(VI) removal. Second, column tests are often used to simulate the longevity of PRB when aquiclude runs. The long-term study of the reaction medium mainly involves the change of the activity of the reaction medium and the blockage of the medium pores during the service period of the PRB. According to the findings of (Kuma et al., 2016), in the PRB system with ZVI as the reaction medium, the reason that affects the long-term effect of PRB is the blockage of the medium pores caused by the precipitation of secondary minerals. In addition, the column test can study the long-term effect of the medium, as well as the influence of the initial concentration of heavy metals, hydraulic retention

time, flow rate, dissolved oxygen content, and organic matter content on the operation effect of PRB (Huang et al., 2020) carried out column tests with SGO/Fe-Mn as the reaction medium to study the removal ability and influencing factors of mercury. According to the research results, the higher initial concentration of mercury, the lower pore velocity, and the lower dissolved organic matter and dissolved oxygen content in the groundwater, the stronger removal ability. On the basis of column experiments, (Obiri-Nyarko et al., 2015) simulated the behavior of  $Pb^{2+}$  with the help of PHREEQC, which confirmed that zeolite is an effective media material for the removal of lead contamination in groundwater.

### 3.3 Pilot-scale test

According to the hydraulic characteristics, the column test simulates a 1D groundwater flow situation. The pilot-scale test can reflect the removal effect of the reaction medium on target pollutants under 3D water flow, with a more realistic simulation effect. Unlike batch and column experiments, the Pilot-scale test can reveal pollutant removal mechanisms in complex field environments, especially the effects of subsurface microorganisms (Beak and Wilkin, 2009). Therefore, pilot-scale test is necessary. Through Geochemist's Workbench and X-ray absorption spectroscopy, (Beak and Wilkin, 2009) found that the removal mechanism of arsenic by PRB with zero-valent iron as the reaction medium is more complicated than the results of previous laboratory simulation studies. Sulfate is reduced to sulfide under the action of microorganisms in the subterranean environment. The formation of FeS provides more mineral surface for arsenic removal (Rhee et al., 2010) conducted a pilot-scale test using ZVI-loaded zeolite as the reaction medium. According to the test results, ZVI-loaded zeolite can efficiently remove Cd(II) and Cr(VI), which is an ideal active

medium for processing complex groundwater polluted by heavy metals (Ludwig et al., 2009) conducted a 30-months experiment with leaf compost and ZVI as the active media for the PRB pilot-scale test to explore the removal effect of As, Pb, Cd, Zn, and Ni and other pollutants in groundwater. The test results show that the removal rate of each pollutant is more than 99%. The cycle of batch and column tests is too short to accurately predict the lifetime of the reaction medium and the long-term performance of the PRB.

The above three types of tests are widely used in the screening process of PRB reaction medium materials. The exploration of the reaction mechanism of the reaction medium and contaminants and the long-term performance of the reaction medium is advanced through the combination with numerical simulation.

## 4 Conclusion and outlook

PRB is a cost-effective remediation technology for heavy metal pollution in groundwater, in which the reaction medium is an important component. The development of cheap, efficient and environmentally friendly new reaction medium materials has far-reaching significance for the treatment of groundwater and soil heavy metal pollution. Despite extensive research on reaction medium materials, there are still some deficiencies, which hamper the application of PRB technology.

- (1) Most of the development of mixed material and composite material reaction medium for dealing with heavy metal pollution revolves around ZVI. The choice of reaction medium is relatively small. The development and research of a single new material is an important direction.
- (2) The types of active materials containing natural ore materials and industrial and agricultural solid waste are increasing. Despite good economics, the composition of such materials is complex. Besides the difficulty in controlling the reaction rate between active materials and heavy metals, there is unclear reaction mechanism as well as potential risk of environmental pollution.
- (3) The introduction of microbial action can enhance the long-term effect of PRB. The co-treatment of groundwater and soil heavy metal pollution with active materials and microorganisms is beneficial for cost savings. In addition, it is necessary to strengthen the control of pH, redox potential, toxin substance and other environmental factors.
- (4) For composite materials, the complex preparation process and high cost will limit the application of PRB technology. The development of composite materials with simple preparation process, strong adsorption capacity, good

chemical stability, and easy recycling will be the main development direction of reaction medium materials, especially nano-composite materials.

- (5) At present, the research on the treatment of heavy metal pollution in groundwater with reaction medium mainly relies on indoor batch test and column test. The pilot-scale test should be paid attention to, which can more accurately examine the removal effect of the reaction material on the target pollutant. In addition, geochemical numerical modelling is worth researchers' attention, which can more accurately analyze the removal mechanism, evaluate the service life and potential environmental risks of the reaction material, and determine the potential and limitations of use.

## Author contributions

HL and QL contributed to the writing of the manuscript. HL reviewed and edited the manuscript.

## Funding

This research was funded by Research Fund for high-level talents of Luzhou Vocational and Technical College (ZLYGCC202101).

## Acknowledgments

Wei Du of Luzhou Vocational and Technical College, was of great assistance during data collection.

## Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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