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Laboratory study on sequenced permeable reactive barrier remediation for landfill leachate-contaminated groundwater

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ABSTRACT

Permeable reactive barrier (PRB) was a promising technology for groundwater remediation. Landfill leachate-polluted groundwater riches in various hazardous contaminants. Two lab-scale reactors (reactors A and B) were designed for studying the feasibility of PRB to remedy the landfill leachate-polluted groundwater. Zero valent iron (ZVI) and the mixture of ZVI and zeolites constitute the first section of the reactors A and B, respectively; the second section of two reactors consists of oxygen releasing compounds (ORCs). Experimental results indicated that BOD₅/COD increased from initial 0.32 up to average 0.61 and 0.6 through reactors A and B, respectively. Removal efficiency of mixed media for pollutants was higher than that of single media (ZVI only). Zeolites exhibited selective removal of Zn, Mn, Mg, Cd, Sr, and NH₄⁺, and removal efficiency was 97.2%, 99.6%, 95.9%, 90.5% and 97.4%, respectively. The maximum DO concentration of reactors A and B were 7.64 and 6.78 mg/L, respectively, while the water flowed through the ORC. Therefore, sequenced PRB system was effective and was proposed as an alternative method to remedy polluted groundwater by landfill leachate.

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1. Introduction

Permeable reactive barrier (PRB) is an effective alternative to conventional remediation methods (such as pump-and-treat, physical-chemical, etc.) for groundwater remediation. It has gained popular because of its efficient removal of pollutants and low operating and maintenance costs. To date, PRB has been studied in laboratory and used in pilot-scale or full scale sites. An important step in constructing PRB is choosing effective fillings. Granular zero valent iron (ZVI) is the most common PRB fillings. ZVI-PRB has been developed and demonstrated to be effective for the treatment of chlorinated hydrocarbon [1-4], petroleum hydrocarbon [5], sulphates [2], nitrates [2,6], and heavy metals [7–11]. Other media that can be used in PRB include zeolites and activated carbon. which sorb and entrap contaminants on the barrier surface, and limestone, which neutralizes acidic, lead-contaminated groundwater and traps lead in the barrier [12-16]. Pollution arising from organic compounds like BTEX and compounds, which cannot be easily degraded by reduction like vinyl chloride, can be treated with oxygen releasing compounds (ORCs) [17]. Heavy metals and ammonium in the water were removed successfully by natural and modified zeolites [12–16]. Bentonite-amended natural zeolite is

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used as earthen liners to reduce the hazards associated with liquid wastes including landfill leachate [13]. A batch study conducted by Pratt et al. showed that different reactive mixture compositions, such as calcite, quartz sand, and pyrite, in the reactors may introduce different precipitates and alter the morphology on the ZVI surface [18].

Landfill leachate is a kind of highly concentrated waste water rich in various contaminants including dissolved organic matter (such as CH₄, volatile fatty acids, humic, fulvic compounds, etc.); inorganic macrocomponents (such as Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻, HCO₃⁻, etc.); heavy metals (such as Cd, Cr, Cu, Ni, Pb, Zn, Cu, etc.); xenobiotic organic compounds including halogenated hydrocarbons, aromatic hydrocarbons, phenols, chlorinated aliphatics, etc. [19–22]. In the past decades, landfill leachate has led to serious groundwater pollution due to improper management. In landfill leachate-polluted groundwater, the concentrations of ammonium, heavy metals and organic contaminants were very high. Therefore, cleaning up landfill leachate-contaminated groundwater is desirable.

Although significant degradation efficiencies towards a wide range of contaminants, ZVI corrosion [1,23,38], mineral precipitation [24,25], and gas production [26] may limit barrier longevity by reducing porosity, conductivity and iron reactivity [27]. Even if overall hydraulic conductivity is not significantly reduced, filling of pore spaces can increase heterogeneity within the barrier, leading to preferential flow [28,29], increased fluid velocities and signif-



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Table 1
Configurations of first section of reactors A and B

Reactor	Components	Diameter (mm)	Percentage (%)
Reactor A	Quartz	0.25–0.5	40
	Fe ⁰	<0.25	60
Reactor B	Quartz	0.25-0.5	34.78
	Fe ⁰	<0.25	43.48
	Zeolites	0.5-1.0	21.74

Table 2

Configurations of the ORC section

Components	Quartz	MgO ₂	Mg(OH) ₂	MgO
Diameter (mm)	0.25-0.5	<0.15	<0.25	<0.25
Percentage (%)	75	8.33	8.33	8.33

icant decrease in reactant contact time within the PRB. Previous researches have demonstrated that PRB is effective for treatment of heavy metals, acid-mine drainage, chlorinated solvents, etc. polluted groundwater [1–17,30–37]. However, using PRB to treat landfill leachate-polluted groundwater is still lacking. The objective of this paper is to investigate the feasibility of treating landfill leachate-polluted groundwater by PRB. Considering the high concentrations of ammonium, heavy metals and organic contaminants in landfill leachate-polluted groundwater, single-reactor-PRB may not effective, so a sequenced PRB was developed in this paper.

2. Material and methods

Two experimental reactors (reactors A and B) were performed in two Plexiglas columns (Fig. 1). Total length of the column is 90 cm and inner diameter is 15 cm. Where I is 6 cm thick quartz; II and IV are simulated aquifer with thickness of 12 cm and 9 cm, respectively; III is the first section of the reactor which with 8cm thickness, and their configurations are illustrated in Table 1 in detail. Zeolites, ZVI and mixture of them were chosen as reactive media for this section to remove or break down organics, ammonia and heavy metals, which may inhibit or reduce the effectiveness of



Fig. 1. Diagram of experiment equipment.



Fig. 2. Plots of COD concentration vs. PVN.



Fig. 3. Plots of BOD₅/COD vs. PVN.



Fig. 4. Plots of ammonium ion concentration vs. PVN.



Fig. 5. Plots of N concentration vs. PVN.

biodegradation of organic contaminants; V is the second section of the reactor with 10-cm thickness, that is ORC section. The configurations of the ORC section are demonstrated in Table 2. ORC was used as reactive media for this section to remove organics by chemical or biological process. The polluted water used in the experiment was taken from Shibailing Landfill in Changchun, China. Chemical constituents of the water are shown in Table 3.

Table 3

Chemical constituents of the polluted water used in the test

Components	Concentration (mg/I			
COD	1027.1			
BOD ₅	328.7			
NH4 ⁺	60.4			
NO ₃ ⁻	5.3			
NO ₂ -	15.1			
PO4 ³⁻	2.1			
SO4 ²⁻	571.6			
Zn	82.8			
ΣCr	0.2			
Cd	0.04			
ΣMn	13.8			
Pb	0.3			
Ca	555.9			
Mg	186.4			
Ni	0.1			
Cu	0.6			
Eh	20			
рН	6.9			



Fig. 6. Plots of Cd concentration vs. PVN.







Fig. 8. Plots of hardness vs. PVN.



Fig. 9. Plots of iron concentration vs. PVN.



Fig. 10. Plots of pH vs. PVN.



Fig. 11. Plots of sulphate concentration vs. PVN.



Fig. 12. Plots of DO concentration vs. time.

3. Results and discussion

The results of the experiment illustrated in Figs. 1–12. In these figures pore volume number (PVN) represents the ratio of the accumulated water volume with time to the pore volume of the reactive media. A1, A2, A3 represent the samples taken from the port1, port 2, port 3 of the reactor A, respectively. B1, B2, B3 represent the samples taken from the port1, port 2, port 3 of the reactor B, respectively.

3.1. Availability of the first section of the sequenced PRB

3.1.1. Organics removal

Organic compounds found in leachate-polluted groundwater are typically volatile fatty acids, humic, fulvic compounds, and toxic halogenated hydrocarbons. In the reactors, difficult-biodegradable or non-biodegradable complex organics compounds, such as halogenated hydrocarbons, humic, fulvic, etc. were broken down to simple and biodegradable organics by ZVI, and these organics can be degraded by microbes on the other site of the aquifer [21]. For example, chemical reactions happened between the chlorinated hydrocarbons and ZVI, chlorine ions are substituted by hydrogen ions to produce hydrocarbons and chlorine. Dechlorination is achieved via the following reaction:

$$2Fe^{0} + 3H_{2}O + X - CI \rightarrow 2Fe^{2+} + X - H + 0.5Cl_{2}$$
(1)

In the dehalogenation process, ZVI dechlorinates chlorinated hydrocarbons in aqueous media by releasing electrons while water molecules dissociate to yield hydrogen and hydroxyl ions, the reaction expressed as follows:

$$H_2 O \rightarrow H^+ + O H^-$$
⁽²⁾

Fig. 2 indicates that COD concentration of reactors A and B decreased from initial 1027.1 mg/L down to an average of 341.3 and 200.9 mg/L, respectively, when polluted water flowed through the first section of the reactors, the concentration of COD decreases drastically; the removal efficiency of COD for the reactor B is 80.5%, and it is much better than that is 66.8% for the reactor A. There are mainly two reasons rendered as following: firstly, VZI could decompose difficult-biodegradable or non-biodegradable organics and produce volatile fatty acids and other simple organics which could be removed by biological processes. Secondly, some of COD could be adsorbed by soil, zeolites and powdered ZVI when polluted water flows through aguifer and the reactor. The first section of reactor B, which consists of ZVI and zeolites, is more effective on removal of COD than that of reactor A, which comprises ZVI only; this may be resulted from the differences of the reactive media. Zeolites have strong adsorption ability and could enhance removal of COD. Therefore, zeolites have positive impacts on the removal of COD

BOD₅/COD is another important indicator used to appraise the biodegradability of the organics. When polluted water passed through the first section of the reactors, BOD₅/COD is increased from initial 0.32 up to average 0.613 and 0.6 in reactors A and B, respectively (Fig. 3), which gives a strong evidence that part of the difficult-biodegradable or non-biodegradable organics have been transformed to simple biodegradable organics. ZVI might break down the carbon chains of the complex organics, which lead to some of difficult-biodegradable or non-biodegradable organics converted to biodegradable organics. After some time, BOD₅/COD decrease steadily, this is likely due to the reactions between reactive media and the contaminants, the contaminants might impair the reactor's efficiency by coating or clogging through precipitates.

3.1.2. Nitrogen removal

Nitrogen is another kind of harmful pollutant in landfill leachate. Nitrogen usually exists as ammonia, ammonium, nitrate, and nitrite, and these forms may originate from organic compounds, such as urea and proteins or their degradation products [39]. Figs. 4 and 5 illustrate the changes of ammonium and N (*N* represents of the sum of the ammonium, nitrate, and nitrite nitrogen) concentration through the first section of reactors. Results indicate that the two reactors showed high removal capacity for NH₄⁺ ions and N. The concentration of ammonium and N of reactor A decreased from 60.374 and 52.731 mg/L down to minimum 4.072 and 7.768 mg/L, respectively, and the removal efficiency averaged 73% and 74.6%. There are four processes might control nitrogen concentration in liquid: oxidation-reduction reactions, anaerobic ammonium oxidation (anammox), denitrification and sorption.

ZVI act as a reducing agent which convert nitrate to nitrogen gas or ammonium. The possible pathway described as follows [40–42]:

$$2NO_3^- + 5Fe + 6H_2O \rightarrow 5Fe^{2+} + N_2 + 12OH^-$$
(3)

$$NO_{3}^{-} + 4Fe + 7H_{2}O \rightarrow 4Fe^{2+} + NH_{4}^{+} + 10OH^{-}$$
(4)

$$NO_3^- + Fe + H_2O \rightarrow Fe^{2+} + NO_2^- + 2OH^-$$
 (5)

Compared with reactor B, reactor A is not effective for longevity, after a short time, the concentration of the ammonium and N increased gradually, which indicated that ZVI could remove ammonium and N effectively, in turn ammonium and N could accelerate corrosion of the ZVI.

Anammox processes may occur under anoxic condition, ammonium was converted to nitrogen gas, nitrite as the electron acceptor in biological process [43,44], which is summarized by the equation:

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O$$
(6)

Denitrification is a biochemical conversion of nitrate to nitrogen gas. In the absence of the oxygen, the denitrifiers such as *Pseudomonas*, *Micrococcus*, *Archromobacter*, *Bacillus*, etc. use nitrate as the final electron acceptor [39]. In the reactors, the low redox potential of the reactive iron media gives rise to anaerobic corrosion in the anoxic environment, i.e. the breakdown of water to form H₂. Denitrification bacteria would use H₂ establishing themselves to convert nitrate to N₂ or N₂O directly. Therefore, ZVI is a continuous source of hydrogen to support biological denitrification. The reaction can be written as follows:

$$Fe^{0} + 2H^{+} \rightarrow H_{2} + 2Fe^{2+}$$
 (7)

Sorption includes absorption, adsorption, surface complexation, and ion exchange. Figs. 4 and 5 illustrate that reactor B is more effective than reactor A on removal of ammonium and N, the concentration of ammonium and N declined to 0.873–2.14 and 1.305–2.717 mg/L, respectively, removal ratio averaged 97.4% and 96.0%, which indicated that the mixture of zeolites and ZVI might be more feasible than ZVI only to remedy nitrogen contaminated ground water. Zeolites have cage-like structure, a large specific surface area and high concentrations exchangeable cations, so zeolites exhibit high sorbent potentials and high cation exchange capacity for contaminants. Ammonium can be exchanged by cations [45]:

$$Z^{-}M^{+} + NH_{4}^{+} \rightarrow Z^{-}NH_{4}^{+} + M^{+}$$
 (8)

3.1.3. Heavy metals removal

Heavy metals mainly include, but are not limited to, Cr, Ni, Pb, Mn, Se, Co, Cu, Cd, Zn etc., which are typical pollutants existing widely in the landfill leachate. Table 4 and Figs. 6–9 illustrate the changes of some of the heavy metals and hardness. Table 4 shows

	Zn	Mn	Ca	Mg	Cd	Cr	Sr	Al
Initial concentration (mg/L)	82.8	13.8	555.9	186.4	0.08	0.2	1.2	16.2
Reactor A Final concentration (mg/L) Removal efficiency (%)	5.6 93.2	1.4 90.2	125.9 77.4	88.3 52.6	0.01 88.0	0.07 67.4	0.4 62.9	8.6 46.7
Reactor B Final concentration (mg/L) Removal efficiency (%)	2.3 97.2	0.06 99.6	101.9 81.7	7.7 95.9	0.004 95.2	0.06 70.7	0.1 90.5	6.7 58.7

 Table 4

 Removal of the heavy metals by reactor A and B

the removal efficiency of Zn, Mn, Ca, Mg, Cd, Cr, Sr, and Al of reactors A and B, it ranges from 46.7% to 93.2% for reactor A, and 58.7% to 99.6% for reactor B. In general, reactor B is more effective than reactor A, which might also due to the sorption of the zeolites. Figs. 6–9 show that the concentration of heavy metals are decreased steeply in the beginning and then remain steadily except iron. Fig. 9 shows that the concentration of iron increased from initial 1.7 mg/L to a maximum of 3.6 and 3.5 mg/L in reactors A and B, respectively, which may be caused by the oxidizing of ZVI to Fe²⁺ and Fe³⁺, with the accumulation of the precipitates, which weakened the efficiency of the ZVI, Fe concentration decreased gradually. Fig. 10 indicated that pH value of the reactors A and B increased from 6.9 to maximum of 8.2 and 10.4, respectively. A satisfactory explanation of reaction chemistry should consider significant changes that occurred in pH and major ion concentrations. Some diagnostic changes include increased pH, increased concentrations of Fe, decreased concentrations of Ca, Mg, S, etc., These changes in fluid chemistry are consistent with the effects of Fe⁰ corrosion. Concentrations of dissolved heavy metals, such as Ca, Mg, Mn, etc., decreased because of their precipitation, which was triggered by the increased pH value. When the contaminated water flows through the PRB system, there are three possible ways by which heavy metals precipitate. Firstly, ZVI interactions with the contaminant plume raise the water's pH by producing hydroxyl (OH⁻). An increase concentration of OH- would favorable to form hydroxide precipitates with heavy metals, just as $Mg(OH)_2$, $Fe(OH)_2$, $Fe(OH)_3$, etc., the reaction can been described as follows:

$$Me^{n+} + OH^- \rightarrow Me(OH)_n$$
 (9)

Some heavy metals occurred as an oxyanions, and exist in the oxidation states in natural waters, as hexavalent chromium usually exists in the form of CrO_4^- or as $Cr_2O_7^{2-}$. Reduction of chromate with elemental iron has been intensively studied [38,46,47]. The overall reaction can be written as

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O$$
 (10)

In a further step, iron and chromium are precipitated as oxyhydroxides [46]:

$$(1-x)Fe_3^+ + xCr_3^+ + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH + 3H^+$$
 (11)

Secondly, carbonate (CO_3^{2-}) exhibits acid base behavior, reactions would occur relevant to pH, the process can be described as follows:

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O \tag{12}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$
 (13)

An increase in CO_3^{2-} and OH^- can result in precipitates with Fe, Ca, Mg and other heavy metals. By this way, some toxic metals removed from the groundwater. Several metal contaminants can form solid precipitates with CO_3^{2-} and OH^- . More HCO_3^- is in the reaction zone in the form of di-valent iron carbonate.

As heavy metal precipitates, the release of H⁺ helped maintain a low pH value, take Ca as an example as follows:

$$Ca^{2+} + HCO_3^{-} \rightarrow CaCO_3(s) + H^+$$
(14)

Thirdly, some heavy metals maybe precipitate as metal sulphide. Fig. 11 exhibits the concentration of the sulphate. Results indicated that concentration of the sulphate declined from 571.6 mg/L to the average of 97.4 and 125.2 mg/L for reactors A and B, respectively, which would attribute to redox reaction. Electrons donated to the system by ZVI dissolution caused the oxidation state to decrease, polluted water flowed into the PRB system, Eh decreased abruptly, and the sulphate was initially bound in the Fe⁰ reactor in the form of di-valent Fe or tri-valent Fe-mixed sulphate and adsorbed on the reactor material [48]. After a certain time under anaerobic conditions, sulphate-reducing bacteria established themselves and used the hydrogen from anaerobic corrosion as an electron donor to reduce sulphate with the associated release of hydrogen sulphide. Sugars or organic acids can stimulate microorganisms to reduce SO₄²⁻ to S²⁻ by the following reaction [49]:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^{-}$$
 (15)

The consumption of elemental hydrogen by microorganisms may enhance anaerobic corrosion within the reaction zone [50,51], leading to increasing corrosion and thus the enhanced generation of H₂. More reaction progress was indicated by large decrease in Ca concentrations, large increase in pH values and lower concentration of dissolved Fe in the effluent. The S^{2–} likely interacted with contaminant metals (Me²⁺), like Cd, etc., to form insoluble precipitate as follows:

$$Me^{2+} + S^{2-} \to MeS \tag{16}$$

Removal efficiency of the reactor A was higher than that of reactor B, which was probably due to the difference percentage of the ZVI, reactor A have higher percentage of the ZVI than that of reactor B.

From Figs. 6 to 9 we can find that reactor B is more effective for removal of Cd and hardness, this is because zeolites have stronger sorption impact on Cd and hardness, which exhibits selectivity for heavy metal removal.

3.2. Availability of ORC barrier (the second section of the sequenced PRB)

When polluted water flows through the first section of the reactors, most of the difficult-biodegradable or non-biodegradable organics converted to simple biodegradable organics. In order to further remove the organic contaminants, ORC barrier can be used. ORC is a source of oxygen, which attempts to either oxidize contaminants directly or stimulate indigenous aerobic microbes to flourish in the presence of the long-lasting oxygen source, thus accelerating natural attenuation of organics. In this experiment, magnesium peroxide is used as ORC, which is insoluble and releases its oxygen



Fig. 13. Plots of COD concentration vs. PVN.

Table 5

Average concentration of NH_4^+ , NO_3^- , and N in liquid from different port of reactor A (mg/L)

Components	A1	A2	A3
NH4 ⁺	15.01	15.96	2.98
NO ₃ -	6.74	4.90	5.04
N	13.43	13.63	3.59

when hydrated is finally converted to ordinary insoluble magnesium hydroxide, in accordance with the following reaction [41]:

$$MgO_2 + H_2O \rightarrow 1/2O_2 + Mg(OH)_2$$
 (17)

Both magnesium peroxide and magnesium hydroxide are environmentally benign and actually safe enough to ingest. In the process of the reaction, phosphates permeate into the crystalline structure of magnesium peroxide. This inhibits transmission of water into the structure, which creates the extended oxygen release. Phosphate intercalation also prevents "oxygen lock-up". As water reacts with un-intercalated magnesium peroxide, a cementlike coating of magnesium hydroxide forms, which prevents water from penetrating deeper into the crystal to release all of the available oxygen. ORC's phosphate intercalation keeps the crystal "open" and prevents this problem. ORC is thus a Time-Release Electron Acceptor, meaning that oxygen is an electron acceptor, which can catch or accept the "spent" electrons from contaminant molecules that are being degraded by microbes for energy and raw materials.

Fig. 12 shows that the maximum DO concentration of reactors A and B are 7.64 and 6.78 mg/L, respectively. DO decline steadily with time, and ORC lost its effectiveness entirely after 60 days. Fig. 13 indicates that most COD values from the port 2 of reactors A and B, on passing through the ORC barrier, COD decreased to the range from 42–112 to 68–135 mg/L and removal efficiency averaged 75.85% and 51.37%, respectively. Removal efficiency declined with deterioration of the ORC. DO deplete steadily with the increasing distance. Organics degraded by the microbes or oxidized by DO directly, and after flowing 10 cm distances, most COD values decreased to less than 52 and 64 mg/L, respectively. In reactors A and B, about 2 mg/L DO was consumed approximately during this course. From these experiments we can draw a conclusion that ORC can remove organics effectively.

Table 5 shows the average concentration of NH_4^+ , NO_3^- and N in liquid taken from the different ports of reactor A. The table indicates NH_4^+ , NO_3^- and N concentration changed from 15.0, 6.74 and 13.43 mg/L to 15.96, 4.90 and 13.63 mg/L, respectively. When the water flowed through the ORC barrier, the extent of change was not very large, which might be due to the transformation of the different kinds of nitrogen each other, and the oxygen oxidized some of

Table 6

		-	-		
Heavy metals	Mn	Zn	Cd	Al	Cu
Final concentration	0	1	0	0	0
(mg/L)	.062	.872	.004	.737	.366
Removal efficiency (%)	95	57	64	54	30
	.4	.3	.3	.0	.8

the contaminants. NH_4^+ , NO_3^- and N concentration changed from 15.96, 4.90 and 13.63 mg/L to 2.98, 5.04 and 3.59 mg/L, respectively, when the water flowed through 10 cm length of simulated aquifer, the extent of change was large, which might be caused by biological activity.

Table 6 illustrates the concentrations and removal efficiencies of some heavy metals after the polluted water passing through the ORC reactor. Experimental results indicate that final concentration of Mn, Zn, Cd, Al, and Cu is 0.062, 1.872, 0.004, 0.737, and 0.366 mg/L, respectively, and removal efficiency is 95.4%, 57.3%, 64.3%, 54.0%, and 30.8%. The concentration of the heavy metals is inversely proportional to the K_{sp} (solubility product) of the metal hydroxide, i.e. the lower a certain metal's K_{sp} , the easier metals precipitate.

4. Conclusions and suggestions

ZVI can decompose difficult-biodegradable or nonbiodegradable complex or toxic organics to simple biodegradable organics compounds, which result in a rise of the BOD₅/COD. ZVI used in a PRB acts as a reducing agent and generates ferrous ion by undergoing oxidation. ZVI impacts chemical alteration on metals, which are sensitive to redox reactions, these redox sensitive metals are thus rendered immobile by co-precipitation with iron hydroxides, carbonates, sulfides, hydroxides, etc.

Zeolites exhibit high sorbent potentials and high cation exchange capacity for contaminants. Zeolites exhibit a ion selectivity for heavy metals such as Pb, Cd, Sr, as well as NH₄⁺, i.e. they have a tendency to exchange inherent cations for other cations on basis of ion selectivity; ORC as long-lasting oxygen source, not only to accelerate natural attenuation of organics, but also has positive impact on some of heavy metals removal; mixture media, namely ZVI and zeolites is more effective than ZVI only on remedying contaminants.

Problems such as pore space filling and reaction sites blocking resulted from precipitation, permeability losing caused by the hydrogen gas which produced by breakdown of water, and bioblock and bio-fouling needed further study.

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