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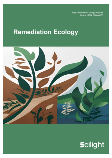

Review

Mechanistic and Engineering Perspectives on Coupled Nanoscale Zero-Valent Iron-Organohalide-Respiring Bacteria Remediation of Trichloroethylene-Contaminated Groundwater

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Abstract: *Dehalococcoides* (TCE) frequently persists in groundwater due to the inherent limitations of both abiotic and biotic remediation approaches. Nanoscale zero-valent iron (nZVI) enables rapid contaminant removal but is constrained by inefficient electron utilization, parasitic hydrogen evolution, and short reactive lifetimes. In contrast, organohalide-respiring bacteria, particularly *Dehalococcoides mccartyi*, can achieve complete detoxification to ethene, yet are limited by strict redox conditions and electron donor availability. Recent evidence suggests that nZVI–microbial systems function as a controllable "peak shaving–detoxification relay", in which nZVI regulates electron flux and subsurface conditions, while microbial reductive dechlorination removes toxic intermediates such as cis-DCE and vinyl chloride. This review synthesizes advances in (i) electron transfer and allocation mechanisms; (ii) material design strategies for hydrogen regulation and electron selectivity; (iii) microbial interactions under nZVI-induced conditions; and (iv) engineering implementation from laboratory to field scale. Emphasis is placed on hydrogen management, system compatibility, and stability constraints. Overall, effective coupling relies on balancing electron flux and maintaining a sustainable reductive microenvironment rather than maximizing material reactivity. Future work should focus on defining operational windows and developing engineering control strategies for predictable groundwater remediation

Keywords: nanoscale zero-valent iron; *Dehalococcoides mccartyi*; trichloroethylene; coupled remediation; groundwater

1. Introduction

Chlorinated aliphatic hydrocarbons (CAHs) represent one of the most prevalent and technically challenging classes of organic contaminants in groundwater systems. Among them, trichloroethene (TCE) is subject to priority regulation in many countries due to its high toxicity, environmental persistence, and potential carcinogenicity [1]. TCE has been extensively used in metal degreasing, dry cleaning, and chemical manufacturing. Improper disposal and legacy leaks have resulted in widespread groundwater contamination worldwide. Owing to aquifer heterogeneity, constrained reactant transport, and irreversible perturbations induced during remediation, TCE-contaminated sites are typically characterized by long remediation timelines, high costs, and persistent residual risks. These constraints have made TCE remediation a central challenge in groundwater pollution control [2]. Notably, the key scientific and engineering challenge is not whether TCE can be transformed, but rather how peak shaving and complete detoxification of terminal products can be simultaneously achieved under complex subsurface conditions.

To address groundwater TCE contamination, a range of remediation approaches has been developed, including physical separation, chemical oxidation/reduction, and biodegradation (Table 1). Among these, anaerobic microbial reductive dechlorination is considered one of the most promising strategies due to its suitability for deep anoxic aquifers and its potential for sustained in situ operation. However, this process typically proceeds through stepwise transformation of TCE to cis-1,2-dichloroethylene (cis-DCE) and vinyl chloride (VC). VC exhibits higher toxicity and mobility than its parent compounds, and inhibition of complete dechlorination can substantially amplify secondary contamination risks. Current evidence indicates that microorganisms capable of complete dechlorination of TCE to non-toxic ethene are extremely limited, primarily within the genera *Dehalococcoides* and *Dehalogenimonas* [3]. These strictly anaerobic organohalide-respiring bacteria are highly sensitive to electron donor availability, redox conditions, and nutrient supply. As a result, complete dechlorination is often kinetically constrained [4] and difficult to initiate and sustain at highly contaminated sites, which significantly limits the engineering applicability of these bacteria.

In contrast, chemical reduction technologies represented by nanoscale zero-valent iron (nZVI) have attracted considerable attention due to their peak shaving reaction kinetics and operational flexibility. Owing to its high specific surface area and abundant reactive sites, nZVI can achieve TCE peak shaving over relatively short time scales [5]. However, under field-relevant groundwater conditions, nZVI suffers from short reactive lifetimes, oxidative passivation, and low electron utilization efficiency. In some cases, it can still generate toxic intermediates such as VC [6]. Further studies have shown that, in chemically complex aquifers, electrons released from nZVI corrosion are preferentially consumed by hydrogen evolution or scavenged by competing electron acceptors such as nitrate and sulfate. Consequently, the effective electron flux available for reductive dechlorination of target contaminants is often substantially lower than theoretical predictions. These limitations indicate that neither purely chemical nor purely biological approaches can independently satisfy engineering requirements for efficiency, safety, and long-term stability.

Against this backdrop, an emerging strategy involves constructing coupled systems that integrate zero-valent iron (particularly nZVI) with anaerobic dechlorinating microorganisms to leverage complementary functions of abiotic reduction and biotic dechlorination. Although hydrogen (H_2) generated during nZVI corrosion can reduce the efficiency of direct abiotic TCE reduction, it serves as an ideal electron donor for organohalide-respiring bacteria, thereby alleviating electron donor limitation commonly observed on microbial systems. Concurrent microbial consumption of H_2 can also reduce its local accumulation on nZVI surfaces, potentially delaying passivation and enabling partial coupling between chemical reduction and biological dechlorination processes [7].

Beyond electron donor interactions, nZVI-*D. mccartyi* coupling can further restructure the groundwater reaction microenvironment through multiple pathways. nZVI addition rapidly consumes dissolved oxygen, lowers redox potential (Eh), and modulates pH, thereby creating more favorable conditions for strictly anaerobic dechlorination. Peak shaving of high TCE concentrations can mitigate acute toxic stress on microorganisms, while microbial activity may in turn help sustain nZVI reactivity and system stability, forming a potential positive feedback loop [8]. Importantly, the advantage of this coupled system lies not in a simple additive effect on degradation rates, but in the redistribution of electron fluxes and regulation of the reaction microenvironment to establish a new balance between chemical peak shaving and complete detoxification.

Although several reviews have summarized the mechanistic interactions between nZVI and microorganisms and their impacts on chlorinated hydrocarbon degradation [9,10], a systematic assessment of the applicability boundaries, engineering constraints, and potential failure modes of nZVI-*D. mccartyi* coupled systems at contaminated groundwater sites remains lacking. To address this gap, the present review is structured around engineering demands of in situ groundwater remediation and focuses on three key aspects: (1) the dominant mechanisms governing TCE degradation in nZVI-*D. mccartyi* coupled systems; (2) research progress across laboratory to field-relevant scales; and (3) critical challenges and mitigation strategies for engineering implementation. This analysis aims to provide a more operationally relevant framework and methodological reference for efficient and sustainable remediation of TCE-contaminated groundwater.

Table 1. Representative technologies for TCE removal in groundwater.

Strategy (Process-Dominated)	Primary Function	Strength	Core Trade-Off/Constraint	Ref.
Physical phase transfer (adsorption, air stripping)	Mass removal without transformation	peak shaving; mature technologies	Contaminant transfer rather than destruction; secondary waste or emissions	[11]
Abiotic chemical reduction (ZVI/nZVI)	Electron-driven dechlorination	Fast kinetics; effective peak shaving	Limited electron efficiency; passivation; intermediate accumulation	[12]
Chemical oxidation (ISCO)	Direct oxidative destruction	Rapid reaction rates	Byproduct formation; high cost; poor persistence	[13]
Electro-/photo-chemical processes	Controlled redox transformation	High process controllability	Energy demand; scale and subsurface applicability limits	[14]
Aerobic cometabolism	Enzymatic transformation	Potential mineralization	Requires oxygen and cosubstrates; low robustness	[15]
Anaerobic reductive dechlorination	Microbial detoxification	Complete dechlorination to ethene	Slow kinetics; stringent redox and donor requirements	[16]
nZVI-dechlorinating bacteria coupling	Electron flux redistribution	Integrates peak shaving with complete detoxification	Process controllability and site-specific constraints	[17]

2. Mechanisms of TCE Remediation in nZVI-*D. mccartyi* Coupled Systems

2.1. Chemical Reductive Dechlorination by nZVI

Zero-valent iron (ZVI) has long been applied in the chemical remediation of chlorinated hydrocarbon-contaminated groundwater due to its strong reducing capacity [18]. In 1997, Wang and Zhang first demonstrated the technical feasibility of TCE reductive dechlorination by ZVI under controlled laboratory conditions [19]. With progressive size reduction, ZVI has evolved from microscale zero-valent iron (mZVI) to nanoscale zero-valent iron (nZVI). When particle size decreases from the micrometer to nanometer scale, the specific surface area increases from approximately 1 m^2 g^{-1} to 20–40 m^2 g^{-1}, accompanied by a 10–1000-fold enhancement in apparent reactivity [20].

Structurally, nZVI typically exhibits a core-shell architecture consisting of a Fe^0 core surrounded by an oxide shell composed of Fe^{3+}, Fe^{2+}, and oxygen-containing species. The shell governs contaminant adsorption and surface complexation, while the metallic core serves as the primary electron source for reductive reactions. In comparison, mZVI shows lower hydrogen evolution rates during corrosion and reduced biotoxicity toward *D. mccartyi*, but its reactivity toward TCE is substantially lower [21]. Although the relatively low hydrogen release and reduced toxicity of mZVI may favor coupling with organohalide-respiring bacteria (OHRB), its slow reaction kinetics limit practical applicability. In contrast, appropriately modified nZVI can retain high Fe^0 reactivity while mitigating biotoxic effects and tuning hydrogen release rates to better match OHRB metabolic demands. As a result, modified nZVI has emerged as a focal material for recent studies and is increasingly regarded as a more suitable partner for microbial coupling systems [22].

Importantly, the value of nZVI in coupled systems does not solely derive from faster apparent reaction rates. Rather, its engineering relevance lies in whether it can provide a bioavailable and sustainable electron and hydrogen flux that simultaneously supports contaminant mass peak shaving and complete detoxification of terminal products.

Despite its high surface area and reactivity, nZVI exhibits pronounced limitations and side effects in groundwater systems. Under field conditions, nZVI commonly undergoes rapid corrosion, hydrogen evolution reaction (HER), electron diversion to non-target acceptors (e.g., dissolved oxygen, nitrate, bicarbonate), particle aggregation and sedimentation, and surface passivation. These processes not only reduce effective electron utilization efficiency but may also induce sharp local increases in pH and transient accumulation of reactive iron species, thereby exacerbating stress on strictly anaerobic OHRB and hindering complete dechlorination [23]. Moreover, excessive short-term release of H_2 and iron ions from highly reactive nZVI can impose redox stress or interfacial toxicity on microorganisms, suppressing OHRB activity and slowing complete dechlorination of TCE.

High reactivity should therefore be redefined beyond rapid initial kinetics. In coupled nZVI-OHRB systems, reactivity is meaningful only when it contributes to efficient and selective dechlorination while remaining compatible with microbial activity and sustainable under realistic groundwater conditions. In this context, material performance should be evaluated using a broader framework that incorporates effective electron utilization efficiency, hydrogen selectivity (or suppression of hydrogen evolution reaction, HER), intermediate accumulation, ethene selectivity, microbial compatibility window, and resistance to matrix interference.

From a semi-quantitative perspective, electron allocation in nZVI-based systems is often highly uneven under groundwater conditions. Previous studies have reported that electron utilization efficiency is typically low (often <10–20%), as a substantial fraction of electrons released from Fe^0 corrosion is consumed by hydrogen evolution rather than target contaminant reduction [24,25]. Hydrogen evolution is widely recognized as a dominant competing pathway that diverts electrons from dechlorination reactions. Reported H_2 levels in Fe^0/nZVI systems can vary substantially, typically spanning from μM to mM levels depending on corrosion rate, material properties, and groundwater chemistry [26,27]. In addition, competing electron acceptors such as nitrate, sulfate, and dissolved oxygen can consume a significant proportion of reactive electrons; for example, nitrate alone may account for nearly 30% of Fe^0 oxidation-related electron consumption under groundwater conditions [28]. Hydrogen generation and availability further regulate microbial processes: excessive hydrogen accumulation may promote methanogenesis and suppress dechlorinating bacteria, whereas insufficient hydrogen limits organohalide respiration. Accordingly, product distribution (e.g., accumulation of cis-DCE and vinyl chloride versus formation of ethene) together with hydrogen levels can serve as practical indicators of electron selectivity and system performance [29].

These observations collectively indicate that system performance is governed not only by intrinsic material reactivity, but more fundamentally by how electron flux is partitioned among competing pathways. Such variability across studies highlights the need for standardized metrics for comparing electron utilization efficiency in nZVI-based systems [26,30]. This conceptual shift highlights that a material with a high apparent reaction rate may still perform poorly if electrons are predominantly lost to corrosion, toxic intermediates accumulate, or microbial reductive dechlorination is inhibited. Therefore, semi-quantitative indicators such as electron utilization efficiency, hydrogen availability, and product selectivity provide a more informative and system-relevant basis for evaluating and optimizing coupled TCE remediation systems.

To address these constraints, various modification strategies have been proposed, among which sulfidation represents a prominent example. Introducing sulfide phases (e.g., FeS_x) onto the nZVI surface can regulate interfacial electron transfer and adsorption behavior, effectively suppressing HER, reducing non-target electron consumption, and enhancing selectivity toward chlorinated hydrocarbons [29]. Unlike certain bimetallic systems (e.g., Fe-Cu, Fe-Ag) that may inadvertently promote HER and electron diversion, sulfidized nZVI (S-nZVI) generally exhibits higher effective electron utilization, greater resistance to matrix interference, and a reaction microenvironment more compatible with OHRB [31].

Notably, the performance of S-nZVI does not increase monotonically with sulfidation degree. Its reactivity and durability are jointly governed by structural parameters such as sulfide layer thickness, Fe/S ratio, continuity, and crystallinity. Insufficient sulfidation fails to effectively suppress HER and competing reactions, whereas excessive sulfidation may reduce surface accessibility or hinder electron transfer. This results in inherent trade-offs among reaction rate, selectivity, and resistance to aging [24,29]. Although optimal Fe/S ratios vary with synthesis conditions and groundwater chemistry, moderate sulfidation levels are generally more effective in balancing reactivity, selectivity, and long-term stability than either insufficient or excessive sulfidation [30]. Under chemically complex conditions that more closely resemble real groundwater plumes and multicomponent chlorinated hydrocarbon systems, optimization of the sulfidized shell structure becomes increasingly critical. Such optimization provides an engineering basis for reducing electron loss, delaying material deactivation, and maintaining a stable, low-stress microenvironment for microbial activity [25,30]. In essence, sulfidation aims to identify a sustainable operational window that balances HER suppression, targeted electron allocation, material longevity, and microbial compatibility, rather than simply maximizing sulfidation degree or initial reactivity.

Beyond sulfidation, composite stabilization strategies—including coupling with carbon materials [32] and polymer-based dispersants [6,33]—have also been employed to mitigate aggregation, transport limitations, and surface passivation of nZVI. These approaches further enable regulation of interfacial microenvironments to optimize hydrogen evolution behavior and biocompatibility. In terms of product pathway control, S-nZVI and other modified nZVI materials often shift TCE transformation toward less toxic products, characterized by reduced DCE and VC accumulation and increased proportions of ethene or acetylene. These trends are typically supported by converging evidence from H_2 release profiles, kinetic parameters, and product distributions. Controlled H_2 release, enhanced target compound transformation rates, and suppressed intermediate peaks collectively indicate improved electron selectivity and more predictable reductive pathways, while simultaneously providing OHRB with a stable, moderate hydrogen supply and a low-stress microenvironment. For example, Li Tielong et al. [34] demonstrated that phosphorus-doped mZVI could regulate TCE dechlorination pathways, favoring ethene formation over acetylene. Overall, research on modified nZVI has evolved from simply enhancing intrinsic material reactivity toward optimizing electron allocation, interfacial reactions, and product pathways under complex groundwater conditions. These advances establish a mechanistic foundation for efficient coupling between nZVI and microorganisms such as OHRB (Table 2). Overall, these studies indicate that modified nZVI systems generally exhibit higher removal efficiency, improved electron utilization, and better pathway control compared to unmodified systems [26,30,35]. More critically, material design directly determines whether microorganisms in coupled systems can access a stable, moderate hydrogen supply and a low-stress reaction environment, thereby enabling progression of the dechlorination chain to the terminal, non-toxic step of "VC to ethene".

Table 2. Performance comparison of modified nZVI-*D. mccartyi* coupled systems for TCE degradation.

Iron Type/Modification	Coupled Microbial System	Application Scenario	Key Outcomes Relative to Single Systems	Ref.
Bare ZVI	Mixed anaerobic consortium	Laboratory	Addition of TCE did not alter product distribution; indicates limited microbial contribution within the Fe^0 system and highlights the need to monitor intermediates.	[36]
Bare ZVI (FeS-coated)	Autotrophic bacteria (with SRB)	Reactor/batch	Dechlorination rate constant increased to 3.2× that of ZVI alone, indicating effective coupling between abiotic reduction and biological dechlorination.	[37]
Bare nZVI	*Dehalococcoides* spp.	Laboratory batch	Achieved complete dechlorination with ethene as the terminal product, supporting nZVI-driven electron/H_2 supply enabling complete dechlorination.	[17]
Bare mZVI	Autotrophic hydrogen-oxidizing bacteria (AHB)	Laboratory batch	TCE removal reached 92.4% ($k = 0.117\ d^{-1}$), outperforming mZVI-alone and AHB-alone systems, confirming enhanced performance of the coupled system.	[8]
Co-immobilized ZVI	Autotrophic bacteria	Reactor	Removal rate increased to 3.5× that of ZVI alone and 5× that of microbes alone; attributed to co-localization-enhanced mass transfer and electron/H_2 coupling.	[38]
FeS nanoparticles (iron sulfide phase)	*Dehalococcoides mccartyi* strain 195	Laboratory	Enhanced TCE dechlorination rate and increased *tceA* gene abundance, indicating Fe-S-mediated facilitation of electron transfer to reductive dehalogenases.	[39]
S-ZVI@biochar (BC)	*Dehalococcoides* spp. (DB) + *Shewanella* MR-1	Laboratory	Time to complete TCE removal significantly shortened relative to bare systems, attributed to directed electron transfer and sustained Fe redox cycling.	[35]
CMC-stabilized nZVI (Pd-doped)	Indigenous groundwater microorganisms	Field	Exhibited a “abiotic-first, biotic-enhanced” remediation pattern; stabilization improved mobility and supported subsequent biological dechlorination.	[40]
CMC-stabilized nZVI	Indigenous system; *Dhc* abundance contribution partitioning	Field	Quantified abiotic vs biotic contributions and observed increased Dhc abundance, providing field-scale evidence for coupling.	[28]
Encapsulated/coated nZVI	*D. mccartyi* (BAV1)	Laboratory	Enhanced TCE removal and reduced direct contact stress; spatial confinement improved coupling stability.	[41]
Microemulsion-encapsulated ZVI	Indigenous *Dehalococcoides* spp.	Field (2.5 years)	Reduced TCE mass flux (>85%) with concomitant ethene increase, indicating transition from abiotic peak removal to biological detoxification.	[42]
Encapsulated/emulsified LECS (nZVI + long-acting substrates)	Indigenous dechlorinating consortium	Laboratory microcosm	Sustained long-term removal (~99% over 130 d), attributed to slow electron/carbon release and maintenance of reducing conditions.	[43]
Non-metallic regulation: spatiotemporal decoupling of Fe^0 and bioaugmentation	Bio-enhanced dechlorinating system	Column experiment	Achieved complete TCE-to-ethene dechlorination while reducing direct Fe^0-microbe stress and improving engineering controllability.	[27]

2.2. Biological Reductive Dechlorination by Dehalococcoides

Biological reductive dechlorination refers to a microbial energy-conserving process in which chlorinated organic compounds such as TCE serve as terminal electron acceptors, while H_2 or formate functions as the electron donor. Microorganisms capable of this metabolism are collectively termed organohalide-respiring bacteria (OHRB) [44]. Based on metabolic specificity, OHRB can be classified as obligate or facultative. Obligate OHRB, represented by *Dehalococcoides*, rely on reductive dehalogenases (RDases) to catalyze C-Cl bond cleavage and can sequentially reduce TCE to ethene [45]. To date, obligate chloroethene-degrading bacteria are primarily confined to the genera *Dehalococcoides* and *Dehalogenimonas* within the phylum *Chloroflexi*. The former strictly uses H_2 as the electron donor, whereas the latter can utilize H_2 or formate [16]. Both genera are capable of complete dechlorination of TCE to non-toxic ethene [3]. From a risk-closure perspective, the critical contribution of OHRB lies not in lowering TCE concentrations per se, but in determining whether the system can traverse the DCE/VC stages and achieve terminal ethene formation, thereby avoiding engineering accumulation of highly toxic intermediates.

The capacity for complete dechlorination in *Dehalococcoides* and *Dehalogenimonas* is tightly linked to their RDase gene repertoire. Commonly reported RDase genes include *tceA*, *vcrA*, *bvcA*, and *cerA*, whose encoded enzymes exhibit distinct substrate preferences and catalytic specificities toward TCE, cis-DCE, and VC [46,47]. Among these steps, the reduction of VC to ethene is widely regarded as the principal rate-limiting bottleneck. Certain strains exhibit a strict requirement for exogenous vitamin B_{12}, underscoring its role as an essential cofactor in energy metabolism and growth [48]. Accordingly, evaluation of coupled systems should prioritize evidence of ethene formation and detection of terminal RDase markers (e.g., *vcrA*, *bvcA*), rather than relying solely on parent compound removal as an indicator of remediation completion. These gene expression patterns are closely associated with enhanced dechlorination rates and improved ethene formation, linking microbial function to system performance [26,35].

Regarding respect to cultivation and environmental tolerance, *Dehalococcoides* typically uses H_2 as the sole direct electron donor, acetate as the carbon source, and requires vitamin B_{12} supplementation to maintain activity [48]. Optimal growth generally occurs at pH 6.0–7.2 and temperatures between 22 and 38 °C. In groundwater systems, however, dissolved oxygen intrusion, elevated salinity, co-contaminants, heavy metal stress, and competing electron acceptors such as NO_3^- and SO_4^{2-} can inhibit growth and dechlorination activity [49]. These constraints indicate that the success of coupled systems depends not merely on the presence of *Dehalococcoides*, but rather on the ability to sustain a reaction window characterized by low redox potential (Eh), a moderate and continuous H_2 supply, and minimal competition from alternative electron acceptors, thereby enabling persistent terminal ethene formation.

In nZVI-*D. mccartyi* coupled systems, iron materials contribute not only by lowering Eh and serving as potential hydrogen sources, but also by influencing process stability through iron redox cycling. nZVI readily undergoes aging, forming Fe(III) oxide or hydroxide corrosion layers, whereas reductive transformations in Fe^0 systems are often mediated by Fe(II) species and associated surface processes. This interplay provides a mechanistic basis for microbially driven Fe(III)/Fe(II) cycling to mitigate passivation and extend material functionality. Dissimilatory iron-reducing bacteria (IRB/DIRB) can reduce Fe(III) to Fe(II), alter corrosion layer morphology, and enhance the reactivity of aged iron materials. Available evidence further suggests that iron reduction can improve electron transfer efficiency and maintain a reducing microenvironment, thereby synergizing with OHRB to stabilize and enhance complete dechlorination. It should be emphasized that, under in situ conditions, this effect primarily manifests as regeneration and transformation of Fe(III)/Fe(II) phases. Its engineering significance thus lies in maintaining low Eh, sustaining Fe(II) cycling, and slowing material deactivation while providing *D. mccartyi* with a more stable energy supply, rather than implying direct microbial regeneration of Fe^0 itself [50]. These findings indicate that effective nZVI–microbial coupling is achieved only within a constrained operational window defined by appropriate nZVI dosage, strongly reducing conditions (low Eh and DO), and a sustained but balanced hydrogen supply.

In summary, under chemically and physically complex groundwater conditions, a single microbial genus is unlikely to withstand multiple stressors and electron acceptor competition simultaneously. Coupled systems integrating modified nZVI with multispecies microbial consortia enhance resilience and long-term dechlorination performance through functional complementarity, iron redox cycling, and regulation of the reducing microenvironment. Notably, this enhanced performance is underpinned by nZVI-induced hydrogen availability and redox regulation, which govern microbial reductive dechlorination processes. Such integrated approaches are therefore more compatible with field-scale remediation demands.

2.3. Coupling Mechanisms in nZVI-D. mccartyi Remediation Systems

As early as the mid-1990s, Gillham and co-workers [18] observed a critical phenomenon during field trials of zero-valent iron permeable reactive barriers (ZVI-PRBs) in Canada: chlorinated hydrocarbon degradation persisted downstream of the ZVI barrier, accompanied by detection of dechlorinating microorganisms and fully dechlorinated products such as ethene. This observation provided the first indication that, beyond direct abiotic reduction, hydrogen generated during ZVI corrosion could fuel downstream anaerobic microbial dechlorination, giving rise to a coupled chemical-biological process. Subsequent work by Scherer et al. [51] systematically demonstrated that ZVI can consume dissolved oxygen, lower redox potential, and continuously generate H_2, thereby creating favorable habitats for anaerobic OHRB such as *Dehalococcoides*. In turn, microbial activity can remove intermediates that are difficult for nZVI to completely degrade (e.g., VC), enabling full contaminant transformation. In China, Xiu et al. [17] provided early experimental evidence that nZVI-*D. mccartyi* coupled systems outperform single abiotic or biotic systems in both TCE removal rate and completeness of dechlorination. Since then, the concept of coupling chemical and biological reduction has been extended to a broader range of contaminants.

The core advantage of nZVI-*D. mccartyi* systems lies in their dual regulation of groundwater physicochemical conditions and energy fluxes (Figure 1). Importantly, the benefit of this approach does not stem from simply adding two faster processes together, but from using nZVI to establish a reducing microenvironment and controlled hydrogen supply, while OHRB perform terminal cleanup. This coupling establishes a new balance between contaminant mass peak shaving and complete detoxification.

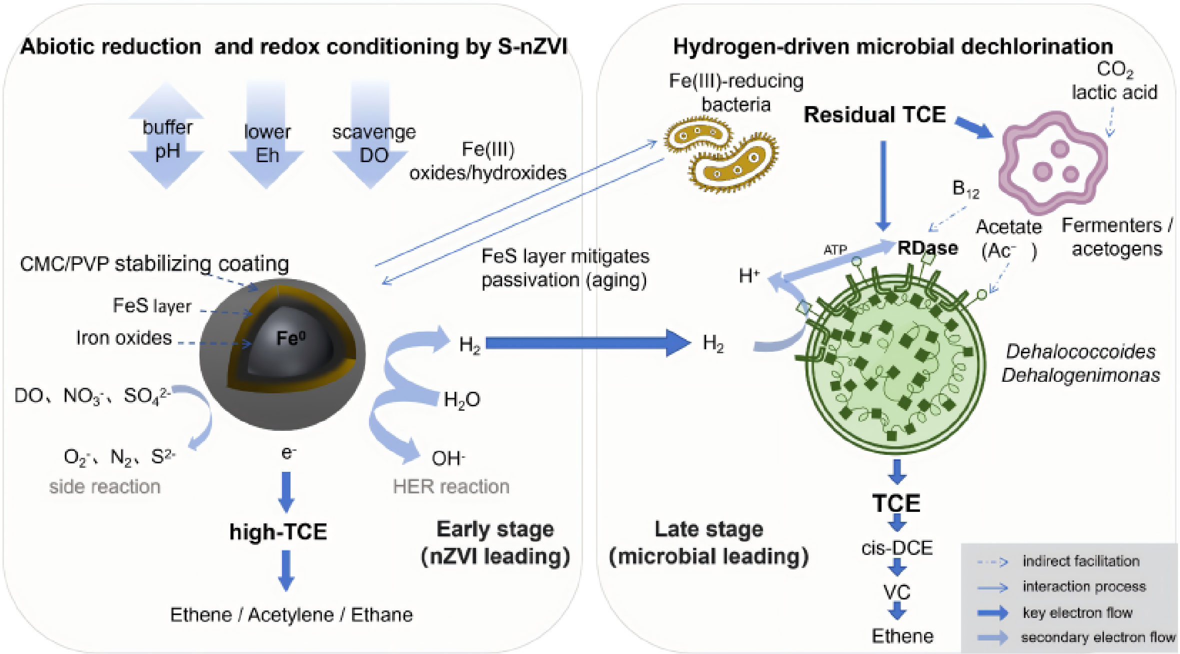

Figure 1. Conceptual framework of the peak shaving-complete detoxification relay in nZVI-*Dehalococcoides mccartyi* coupled remediation systems.

(1) Microenvironment and community restructuring

nZVI alters groundwater geochemistry to favor *D. mccartyi* growth and metabolism [52], while also promoting interspecies electron transfer and enhancing microbial community diversity and stability. Dissolved oxygen (DO) poses a severe constraint for obligate anaerobes such as *D. mccartyi*; nZVI rapidly scavenges DO, thereby establishing anaerobic conditions suitable for organohalide respiration [53]. Ri et al. [54] showed that ball-milled Fe^0/FeS_2 promoted direct interspecies electron transfer (DIET) involving *Methanosarcina*, thereby enhancing anaerobic dehalogenation efficiency. Fe^{2+} and Fe^{3+} released during nZVI corrosion can serve as nutrients for specific microorganisms, while the presence of nZVI can stimulate growth of companion populations (e.g., fermenters and acidogens) that supply essential growth factors such as vitamin B_{12} and suitable carbon sources to *D. mccartyi* [55]. Mechanistically, this represents a process of microenvironment and community network reconfiguration, whereby rapid oxygen consumption and Eh reduction push the system into an operable window for OHRB, while iron nutrition and companion microbes indirectly sustain complete dechlorination capacity.

(2) Toxicity mitigation through abiotic mass peak shaving.

The strong reducing power of nZVI enables rapid peak shaving of high TCE concentrations, thereby alleviating acute toxicity to *D. mccartyi*. At heavily contaminated sites, neither nZVI alone nor microbial dechlorination alone is typically sufficient to achieve complete remediation. In contrast, nZVI-*D. mccartyi* coupled systems can substantially improve overall performance. From an engineering perspective, strategies that temporally decouple concentration abatement from terminal detoxification are often more feasible and controllable: nZVI is first introduced to rapidly remove bulk TCE and reduce toxicity, followed by inoculation with high-activity dechlorinating cultures to eliminate residual intermediates or low-level TCE, thereby achieving faster and more complete remediation [56]. Viewed as a process unit operation, this strategy functions as a "peak shaving-loop closure" relay, in which nZVI lowers contaminant loading and creates a startup window, while microorganisms remove high-risk intermediates such as VC and complete terminal detoxification.

(3) Hydrogen-mediated electron donor coupling.

Hydrogen generated during nZVI corrosion can directly serve as an electron donor for *D. mccartyi* [17]. Compared with nZVI, mZVI produces H_2 more slowly, supplying low-partial-pressure hydrogen that is less prone to competition from methanogens [21]. In contrast, nZVI corrosion generates H_2 rapidly, particularly during early reaction stages, where H_2 evolution competes with direct abiotic TCE reduction. However, corrosion extent and rate can be regulated through particle size control and surface modification. He et al. [12,26] compared bimetallic and sulfidized nZVI under simulated source-zone conditions and found that bimetallic modification enhanced H_2 production, whereas sulfidation suppressed it. In S-nZVI, highly conductive FeS surfaces act as primary reaction sites for TCE reduction, while poorly conductive iron oxide surfaces dominate hydrogen evolution. As a result, slower and more controlled H_2 release better supports sustained electron donation to *D. mccartyi*. Wang [26] further showed that, under H_2-limited conditions, S-nZVI maintained TCE degradation efficiency comparable to nZVI while significantly reducing Fe^0 consumption. Importantly, H_2 flux also shapes microbial community structure: excessive hydrogen favors methanogens while inhibiting *D. mccartyi*, whereas insufficient hydrogen constrains organohalide respiration [8]. Thus, sulfidized nZVI offers improved control over hydrogen release rate and magnitude, providing a clearer advantage for sustained electron delivery to *D. mccartyi*. This mechanism defines a critical boundary of coupled systems: hydrogen under-supply limits dechlorination flux, whereas over-supply induces methanogenic competition and suppresses OHRB. Accordingly, controllability of the hydrogen release profile is a key determinant of long-term system stability.

(4) Microbially mediated extension of nZVI lifetime.

Microorganisms can prolong the functional lifetime of nZVI by mitigating passivation processes. Certain microbes remove or transform Fe(III) oxide layers formed during nZVI corrosion, thereby preventing accumulation that could otherwise impede electron transfer between nZVI and contaminants. Dissimilatory iron-reducing bacteria can reduce Fe(III) to Fe(II), sustaining iron redox cycling and regenerating reactive iron phases. This process enhances electron availability and creates favorable chemical and biogeochemical conditions for reductive dechlorination of chlorinated organics. Under specific conditions, Fe(II) generated by microbial activity may further participate in iron-mediated Fenton-like reactions or related oxidative pathways, producing reactive species that promote contaminant transformation [57]. In addition, organic acids produced during microbial metabolism can buffer pH increases caused by nZVI-derived OH^-, facilitating dissolution of surface oxide films and alleviating passivation. Some microorganisms can also alter the mineralogy of nZVI corrosion products, inducing formation of highly reactive phases (e.g., green rust, ferrihydrite, magnetite) that adsorb and transform contaminants [58]. From a system-level perspective, the engineering significance of these processes lies in extending the low-Eh reaction window and maintaining interfacial electron transfer capacity, thereby shifting nZVI from a short-lived pulse material toward a more sustainable in situ reactive unit.

3. Progress in nZVI-*D. mccartyi* Coupled Remediation Systems

Building on the mechanistic insights discussed above, this section synthesizes recent advances in nZVI-*D. mccartyi* coupled remediation across system configuration, material modification, and microbial coordination. Emphasis is placed on how these factors regulate electron flux partitioning, redox microenvironment stability, and the controllability of terminal ethene formation, with particular attention to evidence at the field scale. Collectively, the literature indicates that coupling nZVI with organohalide-respiring bacteria (OHRB), represented by *Dehalococcoides*, can simultaneously enhance TCE removal rates and ensure terminal detoxification.

Early studies reported that the coexistence of nZVI with mixed anaerobic consortia accelerated TCE dechlorination and altered product distributions, suggesting a substantive biological contribution to nZVI-based systems [36].

Subsequent batch and reactor studies formalized a “hydrogen donor-acceptor” framework, demonstrating that H_2 generated during nZVI corrosion can directly fuel OHRB-mediated reductive dechlorination [37]. Research focus has since shifted toward a more engineering-oriented paradigm, in which nZVI (or modified nZVI) provides chemical peak shaving abatement of high TCE loads and reshapes redox conditions, while OHRB complete the removal of toxic intermediates such as vinyl chloride (VC), thereby achieving sustained ethene-oriented endpoints [40,59]. The central advance lies in reconfiguring electron and hydrogen fluxes via nZVI to open and stabilize the reaction window for complete dechlorination, enabling a “peak shaving-closed-loop” risk management pathway.

From a system compatibility perspective, the performance of nZVI-*D. mccartyi* coupling is not governed by iron-to-biomass ratios alone, but by the integrated effects of configuration, material electron efficiency, microbial functional partitioning, and site-specific boundary conditions. At the configuration level, simultaneous injection and staged (spatial or temporal) coupling exhibit distinct engineering attributes. Simultaneous injection colocates strong reductants, electron donors, and biomass, allowing rapid startup and peak shaving of high TCE concentrations, but it is highly sensitive to dosage and hydrochemical conditions. Excessive or unmodified nZVI can induce particle stress, sharp pH or ORP fluctuations, and amplification of competing electron sinks, thereby constraining OHRB activity [60]. This promotion-inhibition boundary is supported at the functional level: Xiu et al. observed significant downregulation of *tceA* and *vcrA* transcription after 72 h exposure to 1 g L^{-1} bare nZVI, whereas surface-modified nZVI reversed this trend, identifying nZVI dosage and surface state as key determinants of synergistic versus inhibitory outcomes [61].

By contrast, staged coupling strategies treat upstream nZVI zones as abiotic peak shaving units that remove dissolved oxygen, lower Eh, and reduce high TCE loads, followed by downstream biostimulation to achieve complete dechlorination. Such decoupling improves reproducibility and resistance to perturbation at the engineering scale. Column studies by Rangan et al. [27] demonstrated that spatially separated nZVI and bioactive zones enabled complete conversion of high TCE concentrations to ethene and maintained stability under oxidative disturbances, directly supporting the role of staged coupling in enhancing process controllability. In essence, configuration functions as a boundary-condition management tool, mitigating transient stress and competitive amplification to translate mechanistic synergy into engineering robustness.

At the material level, research has progressed from bare nZVI toward sulfidated and supported composites designed to enhance electron selectivity and suppress parasitic reactions. In groundwater systems, rapid hydrogen evolution often limits electron utilization efficiency; accordingly, optimization targets have shifted from maximizing instantaneous reactivity to improving electron efficiency (ε_e), resistance to aging, and pathway control [60]. For example, Xu et al. [62] showed that combined CMC stabilization and sulfidation suppressed H_2 evolution and preserved Fe^0, extending reactive lifespan and improving electron utilization toward TCE dechlorination. Cai et al. [63] further compared sulfidation routes and identified aqueous S^0 sulfidation as a controllable approach suitable for scale-up. Phosphidated mZVI was reported to redirect dechlorination pathways toward ethene rather than acetylene, reducing accumulation of toxic intermediates [64]. Collectively, these material strategies aim to convert high intrinsic reactivity into effective, directed electron flux while minimizing diversion to hydrogen evolution, thereby lowering DCE/VC accumulation risks and improving compatibility with downstream complete detoxification.

At the microbial level, coupling strategies have evolved from single *D. mccartyi* cultures toward functionally integrated consortia that reinforce electron delivery and iron cycling. While *D. mccartyi* governs terminal detoxification, its persistence depends on auxiliary organisms and optimized electron channels. Li et al. [65] reported that inclusion of *Shewanella oneidensis* MR-1 shortened complete dechlorination times and enhanced functional gene expression, accompanied by shifts in corrinoid availability, indicating dual roles in electron transfer and cofactor supply. Interactions with iron sulfide phases further highlight the feedbacks between materials and microbes: FeS nanoparticles increased TCE dechlorination rates and *tceA* abundance in *D. mccartyi* strain 195, suggesting that iron-sulfur phases modulate both electron pathways and functional expression [39]. More integrated systems combining sulfidated ZVI-biochar composites with MR-1 and *D. mccartyi* achieved improved directional electron transfer and stabilized iron cycling [35], while sulfate-reducing bacteria have also been leveraged to promote sulfidation and improve redox conditions for biological dechlorination [66]. These advances underscore that functional partitioning, coupled with engineered electron channels, is critical for sustaining low-Eh conditions and stable hydrogen supply.

Finally, the evidentiary basis for evaluating coupled systems has expanded from concentration reduction to multi-line indicators, including ethene formation, functional gene responses, and long-term field performance. Field-scale studies provide decisive tests of sustainability. He et al. [40] observed early TCE peak shaving following CMC-Fe-Pd injection, followed by declining chemical reductive capacity but continued decreases in total chlorinated ethenes attributable to enhanced biological activity. Long-term monitoring at sites treated with CMC-nZVI further linked increases in *Dehalococcoides* abundance with sustained dechlorination and community succession [28,59]. A 2.5-year evaluation of EZVI showed significant declines in cis-DCE and concurrent ethene accumulation, consistent with a prolonged chemical-biological relay [42]. Boundary-condition analyses indicate that inorganic species such as phosphate can inhibit nZVI reactivity, yet sediment-associated microbes may partially offset passivation by maintaining Fe(II) pools and active sites [67]. Together, these studies signal a shift in evaluation criteria from short-term removal rates toward terminal products, functional biomarkers, and long-term compliance.

In summary, current evidence suggests that faster is not inherently better. Rather, engineering-relevant performance emerges when (i) staged or spatially separated coupling reduces contact stress and improves controllability; (ii) sulfidation or composite design enhances electron selectivity and durability; and (iii) functional consortia and iron cycling stabilize electron supply and complete detoxification [27,39,60]. For field applications, optimal strategies should therefore be framed as a tunable control logic: configuration governs boundary conditions, materials regulate electron flux, and microbial consortia secure terminal detoxification. Only through the coordinated control of all three factors can the nZVI-*D. mccartyi* system achieve sustainable, verifiable remediation outcomes.

4. Engineering Considerations and Challenges for nZVI-*D. mccartyi* Coupled Remediation

4.1. Engineering Considerations

For in-situ groundwater remediation, the primary engineering advantage of nZVI-*D. mccartyi* coupling does not lie in single, high-dose nZVI injection aimed at maximizing instantaneous removal rates. Instead, it resides in organizing chemical peak shaving and biological terminal polishing into a staged, zone-based process chain that can be sustained over time. This distinction reflects the intrinsic mismatch in process longevity: nZVI rapidly loses reactivity in aquifers due to hydration corrosion and consumption by dissolved oxygen, nitrate, bicarbonate, and other competing sinks, whereas *D. mccartyi*, once established under favorable Eh/pH and supplied with continuous electron donors, can maintain reductive dechlorination over extended periods. Accordingly, engineering design should prioritize maintenance of reducing conditions and controllable electron fluxes rather than maximizing short-term material reactivity (Figure 2). From an engineering perspective, the objective is not speed per se, but the conversion of short-lived chemical reducing capacity into a biologically amplified, long-term remediation function.

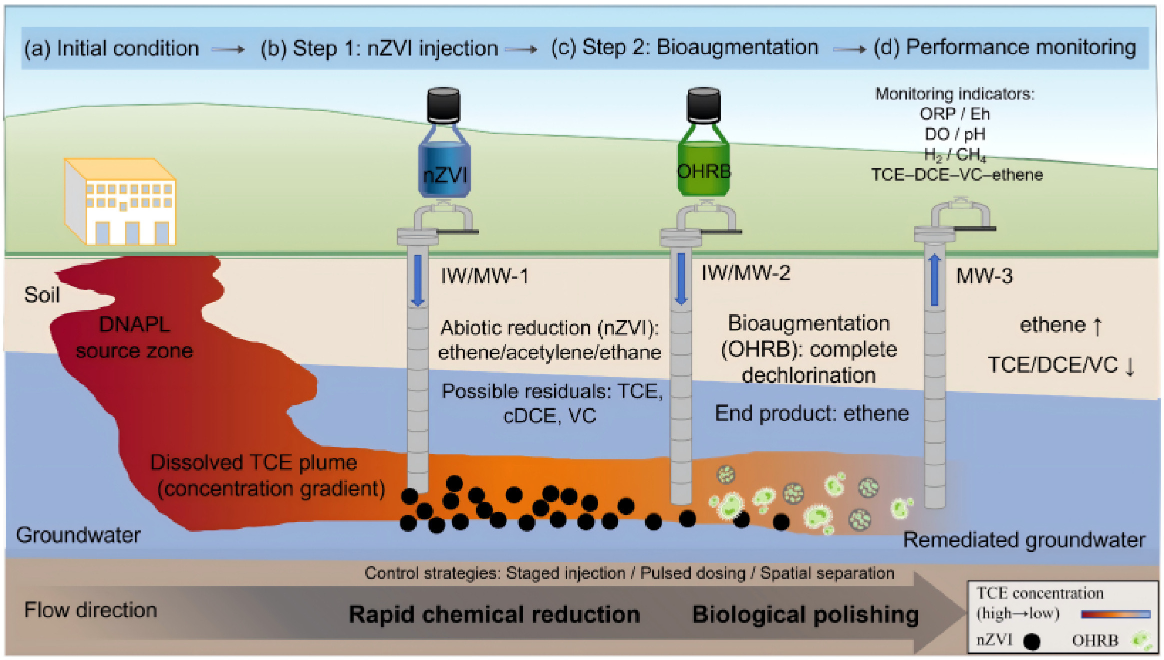

Figure 2. Staged and spatially decoupled implementation of peak shaving and complete detoxification in groundwater remediation.

At the implementation level, nZVI-OHRB systems dominated by *Dehalococcoides* are better suited to staged or spatially separated coupling than to one-time, high-dose simultaneous injection [28,40,42]. Stage 1 focuses on chemical peak shaving of high TCE concentrations. Low-to-moderate doses of stabilized or modified nZVI are applied in source zones to rapidly consume dissolved oxygen, depress Eh, and weaken competing electron acceptors such as nitrate, thereby establishing a redox window compatible with OHRB activity. The engineering aim at this stage is to alleviate toxicity stress on OHRB rather than to achieve complete TCE removal in a single step. Because simultaneous injection exhibits a narrow promotion-inhibition boundary—particularly under conditions of fresh, highly reactive, or excessive nZVI—nanoparticle stress, abrupt pH/Eh excursions, and hydrogen competition can suppress dechlorination gene expression. Consequently, iron dosage and iron-to-biomass ratios should be bounded by contaminant electron equivalents and background competitive demand, while biological thresholds are better defined by functional gene or biomass indicators. Temporal staggering of injections is therefore recommended to reduce direct stress [60,61,68]. Success at this stage is defined not by full TCE removal, but by successful establishment of a stable reducing microenvironment that provides viable electron flux for OHRB.

Stage 2 shifts control of long-term electron flux to biological processes through biostimulation or bioaugmentation once hydrochemical conditions have stabilized. This stage targets robust conversion of residual TCE and intermediates to ethene, minimizing DCE/VC accumulation risks [27,42,59]. Spatially, a more resilient paradigm is temporal or zonal separation of functions: upstream nZVI zones regulate DO, Eh, and competitive acceptors, while downstream biological zones drive terminal detoxification. Such decoupling improves process resilience and reproducibility under fluctuating influent conditions [27]. Conceptually, this design separates peak shaving from closure, reducing system sensitivity to transient disturbances and enhancing long-term stability.

Practical deployment must also address nZVI aggregation, sedimentation, and aquifer heterogeneity, which often lead to overexposure near injection wells and underdelivery to distal zones. Engineering controls should integrate stabilization strategies, injection rate and pressure management, well spacing, segmented injection, and permeability contrasts, while explicitly evaluating risks of pore clogging and irreversible permeability loss caused by iron corrosion products and biofilm growth [32,69,70]. Thus, spatial control of nZVI distribution and the evolution of pore structure represent critical engineering boundary conditions for coupled system performance.

Monitoring strategies should be elevated from concentration-based metrics to process-criteria-driven feedback control. Key indicators include ORP/Eh, DO, pH, Fe(II)/total iron, dissolved gases (H_2/CH_4), competing electron acceptors (NO_3^-/SO_4^{2-}), and product distributions (TCE-DCE-VC-ethene/ethane). Where feasible, functional genes (e.g., tceA, vcrA, bvcA) or *Dehalococcoides* abundance provide direct evidence of biological relay establishment [61,71,72]. Such process-oriented monitoring enables adaptive triggering of subsequent injection or maintenance pulses and is essential for achieving a tunable, maintainable remediation system.

Operationally, initiation of Stage 2 bioaugmentation is recommended when DO is largely depleted, ORP/Eh remains in a sustained reducing range, Fe(II) is detectable, and TCE shows substantial peak reduction with residual DCE/VC but without methane dominance. Conversely, recovery pulses of low-dose nZVI may be applied when ORP/Eh rebounds, competing acceptors reappear, or ethene formation declines alongside intermediate accumulation [27]. This criterion-triggered, pulse-maintenance logic reflects a shift from one-off amendment toward long-term process management.

These observations highlight that groundwater chemistry not only controls competing reactions and material aging, but also defines the operational constraints and design considerations for field-scale coupled remediation systems.

4.2. Challenges

Despite strong performance at laboratory and pilot scales, field outcomes of coupled systems are highly site-dependent. Aquifer permeability governs residence time and spatial distribution of amendments: high-permeability media favor advective loss, whereas low-permeability zones are limited by mass transfer constraints [59,73]. Seasonal fluctuations in recharge and temperature further increase operational uncertainty, as most *D. mccartyi* strains exhibit optimal activity within a relatively narrow temperature range (approximately 22–38 °C). These physical constraints limit direct extrapolation of laboratory synergy to field conditions and necessitate explicit incorporation of hydrodynamic and seasonal variability into engineering design. In particular, groundwater constituents such as nitrate, sulfate, and bicarbonate play a critical role in regulating electron competition and redox dynamics, thereby directly affecting the efficiency and stability of coupled systems.

Geochemical complexity imposes additional constraints. Natural organic matter can accelerate nZVI passivation [74,75], while nitrate and sulfate act as strong competing electron acceptors that suppress reductive dechlorination [76]. Under co-contaminant scenarios, laboratory-derived efficiencies are therefore prone to overestimation. Simultaneously, the strict dependence of *D. mccartyi* on strongly reducing conditions (ORP < -387 mV), sustained electron donor supply, and corrinoid availability complicates long-term stability in-situ [77–79]. Together, these factors define a finite applicability window for coupled systems, beyond which synergistic benefits rapidly diminish.

From an engineering standpoint, the rapid aging of nZVI concentrates its chemical contribution in early phases, leaving long-term performance increasingly dependent on sustained biological activity. Excessive hydrogen production and Fe^{2+} release may restructure microbial communities, favor methanogens, and elevate risks of intermediate accumulation [76,80,81]. Aquifer heterogeneity further undermines direct scaling of laboratory kinetics, underscoring the need for pilot testing and model calibration [28,82]. For example, permeability contrasts can lead to orders-of-magnitude differences in amendment distribution and residence time, thereby affecting contact efficiency and long-term remediation performance [27,83]. Designs that overemphasize material reactivity while neglecting biological stability are therefore unlikely to support durable compliance.

At the management level, amendment dosage, injection strategy, and long-term monitoring must balance remediation efficiency against impacts on aquifer permeability and ecological safety. Although molecular biological and isotopic tools provide powerful diagnostic capabilities [59,84], their high cost limits routine field application [85]. Regulatory compliance and public acceptance related to nanoparticle use and exogenous microbial introduction must also be addressed during project planning [75,76]. These non-technical constraints reinforce that nZVI-*D. mccartyi* coupling should be treated as a system-level engineering solution rather than a simple scale-up of individual technologies.

5. Conclusions and Perspectives

Zero-valent iron (ZVI), particularly surface-modified nanoscale ZVI (nZVI), drives chemical reduction, while *Dehalococcoides mccartyi* mediates biological reductive dechlorination. Together, these processes represent two core pathways in chlorinated solvent groundwater remediation: contaminant peak shaving and terminal detoxification, respectively. However, each single technology exhibits inherent engineering limitations in terms of reaction selectivity, long-term stability, and adaptability to heterogeneous aquifers. The nZVI-*D. mccartyi* coupled system integrates the high reaction rates of chemical reduction with the complete dechlorination capacity of microbial dechlorination within a single remediation framework, providing complementary advantages in high-concentration TCE removal, toxicity mitigation via peak shaving, terminal ethene formation, and community structure regulation. Consequently, it is regarded as one of the most promising coupled remediation strategies.

Systematic analysis indicates, however, that the observed synergy is not a simple additive effect of the material and the microorganism. Instead, it is constrained by interfacial electron flux distribution, hydrochemical conditions, and microbial ecological responses, representing a conditionally governed synergy. Mechanistically, nZVI in the coupled system functions beyond a mere electron donor and chemical reductant; it modulates groundwater microenvironments and electron flow as an interfacial regulator. Similarly, the functional expression of *D. mccartyi* depends not merely on its presence but on a sustainable electron supply, low competition, and a stable reductive ecological window. The core synergy arises from coordinating nZVI reactivity and electron selectivity such that the chemical peak shaving phase can be effectively “handed off” to biological processes, converting the finite reactive lifetime of the material into a durable dechlorination function.

Future research should shift from verifying the mere existence of synergy toward engineering-focused studies on how conditions enabling effective coupling can be established and maintained. Key directions include: (1) system-level interrogation of electron transfer pathways, competitive partitioning, and regulatory mechanisms in nZVI-microbial interfaces, linking electron fluxes to community succession; (2) material strategies such as sulfidation or supported composites, combined with spatial or temporal dosing, to enhance electron utilization, reduce biological toxicity, and expand operational windows for synergy; and (3) integration of reactive-transport models with pilot- and field-scale validation to quantify the applicable boundaries of coupled systems under variable hydrochemical and aquifer conditions. Only when the synergistic mechanisms are mechanistically interpretable, operational windows definable, and process behavior predictable can nZVI-*D. mccartyi* systems transition from laboratory concepts to controllable, sustainable groundwater remediation technologies.

Author Contributions

A.G.: conceptualization, writing—original draft; H.Y.: formal analysis, visualization, writing—original draft; T.L.: supervision; writing—review & editing; Y.Y.: supervision; writing—review & editing; Q.L.: investigation, writing—review & editing, project administration; Z.X.: methodology, funding acquisition, resources, project administration. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used ChatGPT for language polishing and partial content reduction. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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