

Synthesis, Characterization, and Environmental Application of Iron-Based Nanoparticles for the Degradation of Organochlorine Pesticides

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Abstract: *Organochlorine compounds constitute an important class of persistent environmental contaminants because of their chemical stability, hydrophobicity, toxicity, and resistance to conventional biological degradation. Important organochlorine pollutants include trichloroethylene, perchloroethylene, dichloroethylene, vinyl chloride, polychlorinated biphenyls, and other chlorinated solvents and pesticides. During the period 2010-2022, iron-based nanomaterials, particularly nanoscale zero-valent iron and iron oxide nanoparticles, received considerable attention as remediation agents because of their high surface area, redox activity, adsorption capacity, and potential for in-situ treatment of contaminated soil and groundwater. nZVI primarily promotes reductive dechlorination by donating electrons to carbon-chlorine bonds, whereas iron oxide phases such as magnetite and maghemite can provide adsorption sites, participate in electron transfer, and influence the reactivity and stability of Fe⁰-based particles.*

Keywords: Iron oxide nanoparticles, dechlorination, groundwater remediation, nanoremediation

I. INTRODUCTION

Organochlorine compounds are a major group of persistent environmental pollutants associated with industrial activities, solvent use, electrical equipment, pesticides, waste disposal, and accidental releases. Chlorinated volatile organic compounds such as TCE, PCE, DCE, and VC are particularly important groundwater contaminants because they can migrate through soil and persist for long periods. PCBs and other highly chlorinated compounds are also environmentally significant because of their persistence and tendency to accumulate in sediments and biological systems. Conventional remediation methods, including excavation, pump-and-treat treatment, air stripping, thermal processes, and biological treatment, can be effective under appropriate conditions but may require substantial time, energy, infrastructure, or operational control. Consequently, nanotechnology-based remediation has attracted increasing interest as a means of accelerating contaminant transformation and improving treatment in difficult subsurface environments. Among nanomaterials, nanoscale zero-valent iron (nZVI) has been extensively investigated because Fe⁰ possesses strong reducing capability and nanoparticles provide a high reactive surface area. Reviews published during this period describe nZVI as a promising material for soil and groundwater remediation, particularly for chlorinated organic compounds.

Nature and Environmental Significance of Organochlorine Pollutants

Organochlorines contain one or more carbon-chlorine bonds and include a diverse range of industrial chemicals, solvents, pesticides, and persistent organic pollutants. The strength of carbon-chlorine bonds and the hydrophobic character of many organochlorines contribute to their persistence and resistance to natural degradation. TCE and PCE are among the most widely studied chlorinated solvents because they can contaminate groundwater and subsurface

environments. Their reductive transformation may proceed through sequential removal of chlorine atoms, potentially producing DCE and VC before conversion to less chlorinated products. The accumulation of intermediates is an important consideration because incomplete dechlorination can produce compounds that remain environmentally problematic.

PCBs represent another important group of organochlorines. Their highly chlorinated structures make them resistant to degradation, while hydrophobicity promotes strong association with soil and sediment organic matter. Research on NZVI has consequently examined not only dissolved chlorinated compounds but also sorbed contaminants. Studies have shown that contaminant sorption, particle size, and nanoparticle coatings can affect the rate and extent of degradation of both TCE and PCBs.

Table 1. Major organochlorine contaminants relevant to iron-based nanoremediation

Pollutant group	Representative compounds	Major environmental medium	Main remediation challenge
Chlorinated solvents	TCE, PCE	Groundwater and soil	Persistence and subsurface transport
Dichloroethylenes	cis-DCE, trans-DCE	Groundwater	Intermediate formation during dechlorination
Vinyl chloride	VC	Groundwater	Toxicity and incomplete dechlorination
PCBs	Aroclors and PCB congeners	Soil and sediment	Strong sorption and persistence
Chlorinated pesticides	DDT and related compounds	Soil and sediment	Hydrophobicity and persistence
Other chlorinated organics	Chlorinated hydrocarbons	Soil/water	Variable reactivity and transport

Iron-Based Nanoparticles for Remediation

Iron is particularly attractive for environmental applications because it is relatively abundant and can participate in oxidation reduction reactions. Conventional ZVI has been used for environmental treatment for decades, while nZVI offers increased specific surface area and generally faster reaction rates. The smaller dimensions of nanoparticles provide more reactive surface sites and can facilitate contact with contaminants. The development of stabilized nZVI has further addressed the tendency of nanoparticles to aggregate, thereby improving their mobility and interaction with contaminants in subsurface systems. A major review of stabilized nZVI reported that surface modifiers and stabilizers can improve particle deliverability and reactivity during in-situ remediation.

Iron oxide nanoparticles, including magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and other iron oxyhydroxide phases, have different chemical properties from Fe^0 . Their environmental importance arises from their surface reactivity, adsorption properties, magnetic behavior, and ability to participate in electron-transfer processes. In many nZVI systems, iron oxide is naturally generated on the Fe^0 surface during aging.

Application of NZVI to TCE and Other Chlorinated Solvents

TCE has served as one of the principal model contaminants for evaluating nZVI. Research during 2010-2022 examined free nanoparticles, stabilized nanoparticles, supported particles, bimetallic systems, sulfidated nZVI, and combinations with other remediation technologies. An early study using immobilized nZVI and Fe/Pd nanoparticles demonstrated very high TCE removal in an alginate-supported system, while also reducing concerns about nanoparticle mobility.

Research on soil-sorbed TCE demonstrated that remediation performance is more complex in soil than in simple aqueous systems. He et al. (2011) reported that CMC-stabilized Fe/Pd nanoparticles could degrade soil-sorbed TCE, but contaminant desorption, soil organic matter, nanoparticle aggregation, and surfactant concentration affected the

observed reaction rate. This finding is important because laboratory experiments conducted in pure water may overestimate performance under field conditions.

Table 2. Selected studies on nZVI and organochlorine remediation, 2010 2022

Year	Material/system	Target contaminant	Major observation
2010	nZVI/Fe-Pd immobilized in alginate	TCE	Supported nanoparticles achieved very high TCE removal and reduced particle-release concerns
2011	CMC-stabilized Fe-Pd nanoparticles	Soil-sorbed TCE	Soil sorption, organic matter and surfactants influenced degradation
2012	nZVI with different particle sizes/coatings	TCE and PCBs	Particle size and sorption/coating interactions influenced degradation
2016	Stabilized nZVI	Chlorinated organic contaminants	Stabilizers improved particle stability, transport and applicability
2017	Fe ⁰ /iron oxide core shell nZVI	Organic contaminants	Iron oxide shell strongly influenced nZVI environmental properties
2018	nZVI and enhanced nZVI	Chlorinated organic compounds	Soil chemistry, pH, organic matter and particle properties influenced performance
2020	Sulfidated Fe/FeS nanoparticles	TCE	Sulfidation was investigated to improve selectivity and reduce corrosion
2021	Sulfidated ZVI	TCE	Fe ₃ O ₄ formation and groundwater conditions influenced performance
2022	Modified nZVI + electrokinetic treatment	TCE	Combined treatment improved dechlorination and addressed limitations of conventional nZVI
2022	Bimetallic nZVI	VC, DCE, TCE, PCE	Pd- and Ni-modified nZVI showed substantially higher degradation than pristine nZVI

IRON OXIDE NANOPARTICLES AND THEIR ROLE IN REMEDIATION

Iron oxide nanoparticles can contribute to remediation through adsorption, surface complexation, electron transfer, catalytic activity, and interaction with microorganisms. Magnetite is particularly interesting because it contains both Fe(II) and Fe(III), enabling redox cycling under appropriate conditions. The conductive characteristics of magnetite can also influence electron-transfer processes. Although the direct reductive dechlorination capability of pure iron oxides is generally different from that of Fe⁰, iron oxide phases can form important components of composite remediation materials.

In practical nZVI applications, iron oxide is especially relevant because Fe⁰ particles naturally develop oxide shells. These shells may protect the core from rapid corrosion to some extent while simultaneously controlling the movement of electrons and contaminants across the interface. Consequently, the performance of nZVI depends on both the Fe⁰ core and the surface oxide layer.

EFFECT OF PARTICLE SIZE

Particle size is a critical parameter governing the performance of iron-based nanoparticles. Reduction in particle size increases the surface-area-to-volume ratio and can provide a greater number of reactive sites per unit mass. This characteristic is one of the major reasons why nZVI is generally more reactive than larger iron particles. However, nanoparticles also possess strong tendencies toward aggregation, which can reduce the effective surface area and mobility.

Research comparing particle sizes and surface coatings for TCE and PCBs showed that both physical dimensions and interactions between contaminants and polymer coatings influence degradation. Thus, the smallest possible particle is

not necessarily the optimal field material. A balance must be achieved among reactivity, mobility, stability, aggregation resistance, and environmental compatibility.

STABILIZATION AND SURFACE MODIFICATION

Aggregation is one of the major limitations associated with nZVI. Nanoparticles can rapidly aggregate because of magnetic and surface forces, reducing mobility in soil and groundwater. Stabilizers such as carboxymethyl cellulose and other polymers have therefore been employed to modify surface properties. Stabilized nZVI can remain dispersed for longer periods and may move more effectively through porous media.

The 2016 review of stabilized ZVI nanoparticles emphasized that stabilizers can improve soil deliverability and reactivity, while also identifying remaining limitations concerning field transport and environmental behavior. Similarly, research on TCE-contaminated soils showed that CMC stabilization enabled effective degradation while the interaction of surfactants, dissolved organic matter, and soil particles remained important.

BIMETALLIC IRON NANOPARTICLES

One important strategy for increasing nZVI reactivity is the addition of a second metal such as palladium, nickel, copper, or silver. Bimetallic nanoparticles can facilitate hydrogen activation and electron transfer and may increase the rate of dechlorination. Among these systems, Fe/Pd has received substantial attention because palladium can act as a catalytic surface for hydrogen-related reactions.

A 2022 comparative study examined Pd-, Ni-, Ag-, and Cu-modified nZVI against VC, DCE, TCE, and PCE. In spiked water, pristine nZVI degraded only part of the tested contaminants, whereas nZVI/Pd and nZVI/Ni achieved complete degradation of the tested compounds within 24 hours under the reported experimental conditions. These findings demonstrate the potential of bimetallic modification, although the cost, environmental behavior, durability, and large-scale feasibility of secondary metals must be considered.

SULFIDATED ZERO-VALENT IRON

Sulfidated nZVI emerged as an important development during the later part of the 2010-2022 period. The basic objective of sulfidation is to modify the particle surface so that electron transfer toward target contaminants becomes more selective and unwanted corrosion reactions are reduced. A major challenge of conventional nZVI is that Fe⁰ electrons can be consumed by water, oxygen, nitrate, and other natural electron acceptors rather than chlorinated contaminants.

Research on Fe/FeS core shell nanoparticles demonstrated that sulfidation can create an FeS-containing shell while maintaining an Fe⁰-dominated core. Studies published in 2022 further investigated sulfidated nZVI for TCE removal and identified the importance of particle composition and reaction pathways.

II. CONCLUSION

Iron oxide and zero-valent iron nanoparticles have emerged as important materials for the remediation of organochlorine-contaminated soil, sediment, and groundwater. The literature published between 2010 and 2022 demonstrates that nZVI can promote reductive dechlorination of important chlorinated contaminants such as TCE, PCE, DCE, VC, and PCBs. Its effectiveness arises primarily from the electron-donating capability of Fe⁰, while iron oxide shells and nanoparticles contribute through adsorption, surface reactions, electron-transfer processes, and control of particle stability.

Research during this period established that particle size, aggregation, soil sorption, natural organic matter, pH, dissolved oxygen, aging, and oxide formation strongly influence remediation performance. Stabilized, supported, bimetallic, and sulfidated nZVI systems have been developed to overcome limitations of conventional nZVI. In particular, studies have shown that modified nanoparticles can improve contaminant degradation compared with pristine particles under specific experimental conditions.

However, laboratory efficiency alone is insufficient for determining field suitability. Nanoparticle transport, electron efficiency, passivation, contaminant rebound, transformation products, ecological effects, material cost, and long-term stability must be considered. Overall, the 2010 2022 literature indicates that the future development of iron-based nanoremediation lies in controlled surface engineering, improved electron selectivity, environmentally compatible stabilization, integration with biological and electrokinetic methods, and rigorous field-scale assessment.

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