

Optimization of Iron-Based Nanoparticles for Enhanced Degradation of Persistent Organochlorine Pesticides

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Abstract: *Persistent organochlorine pesticides such as dichlorodiphenyltrichloroethane, lindane (γ -HCH), aldrin, dieldrin and related chlorinated compounds remain important environmental contaminants because of their persistence, hydrophobicity, resistance to biological degradation and tendency to accumulate in soil, sediments and aquatic systems. Conventional remediation methods are frequently limited by incomplete degradation, high operational requirements or transfer of contaminants between environmental compartments. Iron-based nanoparticles, particularly nanoscale zero-valent iron, have attracted considerable attention because their high specific surface area, strong reducing capacity and tunable surface chemistry can promote reductive dechlorination of persistent chlorinated pollutants.*

Keywords: Iron nanoparticles, nanoscale zero-valent iron, environmental remediation, pesticide degradation

I. INTRODUCTION

Organochlorine pesticides constitute an important group of persistent environmental contaminants because of their chemical stability and resistance to natural degradation processes. Compounds such as DDT, lindane and aldrin were extensively used for agricultural pest control and disease-vector management, but their persistence has resulted in long-term contamination of soils, sediments and water resources. Their hydrophobic nature enables them to partition into organic matter and sediments, while their chemical stability allows residues to remain in environmental systems for extended periods. A review of nanoparticle-based treatment strategies identified organochlorine pesticides as particularly hazardous persistent contaminants and highlighted zero-valent iron nanoparticles as promising materials for their removal and degradation.

The development of nanotechnology has provided new possibilities for addressing persistent contaminants. Nanoscale zero-valent iron possesses a large reactive surface area compared with conventional iron particles and can participate in electron-transfer reactions with chlorinated organic molecules. During treatment, Fe^0 can act as an electron donor, while chlorine-containing organic molecules can undergo reductive dechlorination, resulting in the replacement of chlorine atoms by hydrogen or the formation of less chlorinated intermediates. The environmental application of nZVI has consequently expanded from laboratory studies toward soil and groundwater remediation. However, the high reactivity of nanoparticles can simultaneously promote oxidation, aggregation and loss of mobility, creating an important optimization challenge.

Experimental evidence specifically involving OCPs provides a useful basis for optimization. Shoiful et al. (2016) investigated Fe-based materials containing zero-valent iron and magnetite for the degradation of DDT, lindane and aldrin in water. At an initial pesticide concentration of 0.001 mg L^{-1} , the reported degradation after 12 h was 100% for γ -HCH, 81% for p,p'-DDT and 79% for aldrin. The researchers also found that increasing the quantity of Fe-based

material increased degradation rates, whereas increasing the initial OCP concentration reduced the degradation rate. Increased free chloride during the reaction provided evidence of dechlorination.

NEED FOR OPTIMIZATION OF IRON-BASED NANOPARTICLES

Although iron nanoparticles demonstrate substantial potential, maximum degradation cannot be assumed simply by increasing nanoparticle concentration. Particle aggregation can reduce the effective reactive surface area, while oxidation of Fe^0 can decrease electron-transfer capacity. Similarly, environmental factors such as pH, dissolved oxygen, competing ions, natural organic matter and contaminant concentration may strongly influence nanoparticle performance. A review of nZVI soil remediation reported that chemical modifications, including transition-metal doping, stabilization with polymers or surfactants and sulfidation, have been investigated to reduce undesirable oxidation and aggregation and to improve electron utilization.

Optimization is therefore a multidimensional process involving nanoparticle composition, particle size, surface properties, dosage, contaminant concentration, pH and reaction time. Bimetallic nanoparticles are particularly interesting because a second metal can provide catalytic sites and facilitate hydrogen generation or electron-transfer reactions. Studies of bimetallic nZVI have shown that Fe/Pd and Fe/Ni can outperform pristine nZVI for several chlorinated organic compounds. In one 2022 comparative study, Fe/Pd and Fe/Ni nanoparticles achieved complete degradation of several tested chlorinated volatile organic compounds within 24 h, whereas pristine nZVI showed substantially lower removal for some compounds.

IRON-BASED NANOPARTICLES FOR ORGANOCHLORINE PESTICIDE DEGRADATION

Iron-based nanoparticles can be divided into several functional categories, including pristine nZVI, stabilized nZVI, bimetallic Fe nanoparticles, iron-oxide-based nanomaterials and supported iron nanoparticles. Among these, nZVI has received considerable attention because Fe^0 provides a reducing environment capable of transferring electrons to chlorinated contaminants. Iron oxides such as magnetite can also contribute to adsorption and surface-mediated reactions. The combination of Fe^0 and iron oxides may therefore produce complementary treatment mechanisms.

Table 1. Major Iron-Based Nanoparticles Used for Environmental Remediation

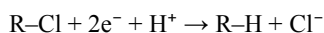
Iron-based nanoparticle	Major characteristic	Potential role in OCP degradation	Main limitation
nZVI (Fe^0)	Strong reducing ability	Reductive dechlorination	Aggregation and oxidation
Fe_3O_4 nanoparticles	Magnetic and surface-active	Adsorption and catalytic support	Lower direct reducing capacity than Fe^0
Fe/Pd	Bimetallic catalytic system	Enhanced hydrogenation/dechlorination	Higher material cost
Fe/Ni	Bimetallic catalytic system	Enhanced reduction of chlorinated compounds	Potential metal release
Stabilized nZVI	Surface-modified Fe^0	Improved dispersion and longevity	Stabilizer may affect reactivity
Supported nZVI	Fe^0 deposited on a carrier	Improved dispersion and accessibility	Carrier preparation required
Sulfidated nZVI	Modified Fe surface	Improved electron utilization and stability	More complex synthesis

MECHANISM OF ORGANOCHLORINE PESTICIDE DEGRADATION

The primary mechanism associated with Fe^0 nanoparticles is reductive dechlorination. In simplified terms, metallic iron undergoes oxidation while the chlorinated organic compound receives electrons. The resulting reaction can be represented conceptually as:



The released electrons participate in the reduction of carbon–chlorine bonds. A simplified representation of reductive dechlorination is:



The actual degradation process is more complex because contaminant adsorption, iron corrosion, hydrogen production, surface oxidation and intermediate formation can occur simultaneously. The release of chloride ions is an important indicator that chlorine atoms have been removed from the original molecule. In the experimental study of DDT, lindane and aldrin, increasing free chloride over time supported the occurrence of dechlorination and formation of lower molecular-weight degradation products.

Surface adsorption is another important component. Hydrophobic OCP molecules can interact with nanoparticle surfaces, increasing their local concentration near reactive iron sites. This concentration effect can facilitate electron transfer. However, excessive adsorption without subsequent transformation may result in temporary sequestration rather than true degradation; therefore, successful optimization should evaluate both disappearance of the parent pesticide and formation and toxicity of transformation products.

COMPARATIVE DEGRADATION OF SELECTED ORGANOCHLORINE PESTICIDES

Published evidence demonstrates that different OCPs do not respond identically to Fe-based treatment. Molecular structure, number and position of chlorine atoms, hydrophobicity and accessibility of reactive bonds can affect degradation. In the Fe-based study by Shoiful et al., γ -HCH exhibited the highest degradation, followed by p,p'-DDT and aldrin under the investigated conditions. After 12 h, degradation reached 100%, 81% and 79%, respectively, at the reported initial concentration of 0.001 mg L^{-1} .

Table 3. Reported Degradation of Selected OCPs by Fe-Based Materials

Pesticide	Iron-based treatment	Initial concentration reported	Reaction period	Reported degradation
γ -HCH (lindane)	Fe-based material containing $\text{Fe}^0/\text{Fe}_3\text{O}_4$	0.001 mg L^{-1}	12 h	100%
p,p'-DDT	Fe-based material containing $\text{Fe}^0/\text{Fe}_3\text{O}_4$	0.001 mg L^{-1}	12 h	81%
Aldrin	Fe-based material containing $\text{Fe}^0/\text{Fe}_3\text{O}_4$	0.001 mg L^{-1}	12 h	79%

ROLE OF BIMETALLIC IRON NANOPARTICLES

Bimetallic iron nanoparticles represent an important optimization strategy because combining Fe^0 with another metal can alter the surface reaction pathway. Palladium and nickel have been particularly investigated for chlorinated contaminants. The secondary metal can function as a catalyst, while Fe^0 serves as an electron donor. This combination can improve the conversion of chlorinated compounds compared with unmodified nZVI. Reviews of nZVI remediation identify Fe/Pd, Fe/Ni and other bimetallic systems as important approaches for treating halogenated organic compounds.

Venkateshaiah et al. (2022) compared pristine nZVI with Fe/Pd, Fe/Ni, Fe/Ag and Fe/Cu nanoparticles for several chlorinated volatile organic compounds. Their results showed that Fe/Pd and Fe/Ni had substantially higher degradation performance than pristine nZVI under the experimental conditions, with complete degradation reported for the tested contaminants within 24 h in several cases. Although these compounds were chlorinated solvents rather than OCPs, the

findings are relevant to optimization because they demonstrate how bimetallic modification can enhance reductive treatment of chlorinated organic molecules.

Table 4. Optimization Strategies for Iron-Based Nanoparticles

Strategy	Mechanistic purpose	Expected benefit	Potential concern
Particle-size control	Increase accessible Fe ⁰ surface	Faster reaction	Aggregation
Polymer stabilization	Improve dispersion	Greater contact with OCPs	Surface blocking
Surfactant stabilization	Improve suspension	Increased mobility	Secondary environmental effects
Fe/Pd modification	Catalytic enhancement	Strong dechlorination activity	Cost of Pd
Fe/Ni modification	Catalytic enhancement	Improved chlorinated-compound degradation	Ni release
Sulfidation	Modify surface reactivity	Improved electron utilization	Additional synthesis step
Carbon support	Disperse Fe nanoparticles	Improved accessibility	Support preparation
Magnetic recovery	Enable post-treatment separation	Easier recovery	Additional processing
Combined biological treatment	Complement chemical reduction	Potentially improved complete degradation	Process complexity

PROPOSED OPTIMIZATION FRAMEWORK

An effective optimization framework should begin with the synthesis and characterization of the iron nanoparticle. Particle size, morphology, surface area, crystallinity, oxidation state and surface chemistry should be determined before degradation experiments. The nanoparticles should then be evaluated against representative OCPs such as DDT, lindane and aldrin. Batch experiments can initially be used to optimize Fe dosage, pH, reaction time and contaminant concentration. The response variables should include percentage degradation, degradation rate constant, chloride release and concentration of transformation products.

A second optimization stage should compare pristine nZVI with stabilized and bimetallic variants. The objective should not simply be maximum disappearance of the parent pesticide because apparent removal can result from adsorption rather than chemical degradation. Therefore, optimized treatment should demonstrate parent-compound degradation together with appropriate identification or monitoring of transformation products. The environmental literature emphasizes that nZVI performance depends on particle characteristics, soil or water chemistry and modification strategies, indicating that laboratory optimization should eventually be validated under realistic environmental conditions.

Table 5. Suggested Experimental Design for Optimization

Experimental variable	Suggested levels/categories	Response variable
Nanoparticle type	nZVI, stabilized nZVI, Fe/Pd, Fe/Ni	Degradation %
Fe dosage	Low, medium, high	Rate constant
pH	Acidic, neutral, mildly alkaline	Degradation %
Reaction time	0–24 h or longer	Kinetic constant
OCP concentration	Low, medium, high	Removal and kinetics
Particle size	Nano-size ranges	Specific activity
Temperature	Ambient and elevated	Reaction rate
Dissolved oxygen	Controlled conditions	Fe stability
Water matrix	Deionized water, groundwater, wastewater	Real-matrix efficiency
Reuse cycles	Multiple cycles	Activity retention

ENVIRONMENTAL AND PRACTICAL CONSIDERATIONS

Despite the promising laboratory performance of iron nanoparticles, environmental application requires consideration of nanoparticle mobility, persistence, aggregation and possible release of secondary metals. The advantages of nZVI include high reactivity and applicability to soil and groundwater remediation, but reviews also emphasize the gap between laboratory investigations and large-scale field implementation.

Another important consideration is the distinction between contaminant removal and degradation. Adsorption can temporarily reduce the concentration of an OCP in water without destroying its molecular structure. Consequently, optimized treatment should monitor parent compounds, chloride release and transformation products. For DDT and related compounds, identifying potentially persistent intermediates is particularly important because incomplete dechlorination could produce compounds that remain environmentally relevant.

The cost of bimetallic nanoparticles must also be considered. Palladium-containing materials can provide strong catalytic performance but are more expensive than unmodified iron. Nickel-based systems may provide an alternative, although possible metal release must be evaluated. Thus, the optimum nanoparticle is not necessarily the material with the highest laboratory degradation percentage; rather, optimization should consider degradation efficiency, material cost, stability, recoverability, toxicity and performance in realistic environmental matrices.

II. CONCLUSION

Iron-based nanoparticles, particularly nanoscale zero-valent iron, provide a promising platform for the degradation of persistent organochlorine pesticides because of their high reactive surface area and reducing capability. Published experimental evidence has demonstrated degradation of important OCPs including lindane, DDT and aldrin using Fe-based materials, with reported degradation after 12 h of 100%, 81% and 79%, respectively, under specific experimental conditions. Optimization of the treatment process depends on controlling particle size, iron dosage, pH, reaction time, contaminant concentration, nanoparticle stability and surface chemistry. Stabilization can reduce aggregation and premature oxidation, while bimetallic modification with catalytic metals such as Pd or Ni can substantially improve reductive treatment of chlorinated organic compounds. Future research should move beyond simple measurement of pesticide disappearance and evaluate complete degradation pathways, transformation products, toxicity, nanoparticle recovery and performance in realistic soil and groundwater systems. A combined optimization approach involving material engineering, kinetic modeling and environmental risk assessment can contribute to the development of safer and more efficient nanotechnology-based remediation systems for persistent OCP contamination.

REFERENCES

1. Application and development of zero-valent iron (ZVI) for groundwater and wastewater treatment. (2022). *International Journal of Environmental Science and Technology*.
2. Iron-based nanoparticles in wastewater treatment: A review on synthesis methods, applications, and removal mechanisms. (2021). *Journal of Saudi Chemical Society*.
3. Potential environmental implications of nanoscale zero-valent iron particles for environmental remediation. (2014). *Environmental Science and Pollution Research*.
4. Recent strategies for removal and degradation of persistent and toxic organochlorine pesticides using nanoparticles: A review. (2017). *Journal of Environmental Management*, 190, 208–222.
5. Remediation of soil contaminated with organic compounds by nanoscale zero-valent iron: A review. (2021). *Science of the Total Environment*, 760, 143413.
6. Zero-valent iron nanoparticles for soil and groundwater remediation. (2020). *Nanomaterials*.
7. Shoiful, A., Ueda, Y., Nugroho, R., & Honda, K. (2016). Degradation of organochlorine pesticides (OCPs) in water by iron (Fe)-based materials. *Journal of Water Process Engineering*, 11, 110–117.
8. Venkateshaiah, A., Silvestri, D., Waławek, S., Ramakrishnan, R. K., Krawczyk, K., Saravanan, P., Pawlyta, M., Padil, V. V. T., Černík, M., & Dionysiou, D. D. (2022). A comparative study of the degradation efficiency

of chlorinated organic compounds by bimetallic zero-valent iron nanoparticles. *Environmental Science: Water Research & Technology*, 8, 162–172.

9. Wu, Y., Guan, C.-Y., Griswold, N., Hou, L.-Y., Fang, X., Hu, A., Hu, Z.-Q., & Yu, C.-P. (2020). Zero-valent iron-based technologies for removal of heavy metal(loid)s and organic pollutants from the aquatic environment: Recent advances and perspectives. *Journal of Cleaner Production*, 277, 123478.