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Chemical Speciation and Mobility of Heavy Metals (Cd, Pb, Zn) in Contaminated Soil Following Remediation with Nano-Zero-Valent Iron (nZVI)

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Abstract-

Heavy metal pollution in soil has become a major environmental issue across the world. It threatens the health of ecosystems, the productivity of farms, and the health of people. Cadmium (Cd), lead (Pb), and zinc (Zn) are three hazardous heavy metals that are especially bad because they stay in the environment for a long time, may build up in living things, and are found in many polluted areas. Chemical speciation, which is how metals are spread out among different geochemical forms, affects how easily they move through the environment, how available they are to living things, and how hazardous they might be. Total metal concentration is not enough to tell. Nano-zero-valent iron (nZVI) has garnered significant attention as a novel nanoremediation technique that may immobilize heavy metals via reduction, adsorption, and precipitation processes. This study paper investigates the efficacy of nZVI treatment in modifying the chemical speciation and diminishing the mobility of Cd, Pb, and Zn in contaminated soils. The core-shell structure of nZVI, which has a reactive zero-valent iron core and an iron oxide/hydroxide shell, gives it a unique dual role for cleaning up contaminants. Using successive extraction methods like the Tessier and BCR protocols, scientists may measure how metals move from mobile, bioavailable fractions (such exchangeable and acid-soluble) to more stable, residual fractions after nZVI therapy. Field and laboratory research show that using nZVI efficiently makes heavy metals less mobile by changing them into forms that are less bioavailable. However, how well it works depends on the soil's pH, organic matter content, moisture, nZVI dose, and weather circumstances. However, issues such as nanoparticle aggregation, quick oxidation, possible ecotoxicity, and cost-effectiveness compared to traditional iron-based remedies necessitate thorough evaluation. This thorough study brings together what we know about nZVI-mediated changes in chemical speciation, remediation mechanisms, evaluation methods, environmental effects, and future directions for sustainable soil remediation.

Introduction

Background and Significance

Heavy metals in soil are one of the most persistent environmental problems of the 21st century. They come mostly from human activities including mining, industrial production, metal smelting, farming, and throwing away trash in the wrong way. Heavy metals have a large atomic weight (>40 g/mol) and density (>5 g/cm³), which makes them quite different from organic contaminants. They don't break down and stay in the environment for an extended amount of time. Cadmium, lead, and zinc are some of the most common heavy metals found in polluted soils across the world. They come from places like metallurgical enterprises, battery manufacture, electroplating, phosphate fertilizers, and air deposition from car emissions.

Heavy metal pollution has a big and complicated effect on the environment and health. These metals easily get into food chains when plants take them up, build up in creatures, and become more toxic as they go up the food chain. They can cause serious health problems in humans, such as neurotoxicity, cancer, renal problems, reproductive problems, and developmental problems. Communities throughout the world that have been harmed by mining are at a higher risk of exposure. Studies show that almost 23 million people live on floodplains that are polluted by metal mining. Heavy metals may stay in soil for decades or even centuries, therefore we need effective and long-lasting ways to get rid of them.

Chemical Speciation: A Critical Determinant of Metal Behavior

The total concentration of heavy metals is essential, but it doesn't give enough information for a correct risk assessment. Chemical speciation, which is how metals are spread out across different physicochemical forms, is the most important factor in how they affect the environment, how they move about, how available they are to living things, and how dangerous they are to living things. Soil contains heavy metals in many different forms. These include dissolved free ions and complexed species, exchangeable cations that are attached to soil particles, metals that have precipitated with carbonates and oxides, metals that are attached to organic materials, and metals that are part of residual mineral lattices.

Sequential extraction methods, especially the Tessier and BCR (Community Bureau of Reference) protocols, make it possible to systematically separate heavy metals into operationally-defined groups that show varied binding strengths and mobilities. The Tessier technique usually separates five groups: exchangeable, bound to carbonates, bound to iron-manganese oxides, bound to organic materials, and residual. The BCR three-step process finds acid-extractable (exchangeable and carbonate-bound), reducible (iron-manganese oxide-bound), oxidizable (organic matter and sulfide-bound), and residual fractions. Metals in exchangeable and carbonate-bound fractions show strong mobility and bioavailability, which means they may quickly harm the environment. On the other hand, residual fractions show low mobility and biological absorption capacity.

Factors Influencing Heavy Metal Mobility and Bioavailability

Heavy metal speciation and mobility are controlled by several different soil characteristics. Soil pH is probably the most important component. Acidic circumstances ($pH < 6$) make metals more soluble by raising proton concentration and lowering adsorption capacity. Alkaline conditions, on the other hand, make metals less soluble by making metal hydroxides, carbonates, and phosphates. For cationic metals (Cd^{2+}, Pb^{2+}, Zn^{2+}), mobility often diminishes as pH increases, attributed to increased adsorption and precipitation.

Soil organic matter (SOM) has complicated, and sometimes opposite, impacts on how metals move about. SOM has a lot of functional groups (such carboxyl, phenolic, and hydroxyl) that can bind to metals and keep them from moving around. On the other hand, dissolved organic materials can make soluble metal-organic complexes, which could make it easier for metals to move about. Clay minerals and iron-manganese oxides provide significant adsorption sites, with elevated concentrations often associated with diminished metal mobility. Also, cation exchange capacity, redox potential, moisture content, and competing ions have a big effect on how species evolve.

Emergence of Nanoremediation with Zero-Valent Iron

Traditional methods for cleaning up soil, such digging it up and throwing it away, washing it, stabilizing it, solidifying it, using plants to clean it up, and using bacteria to clean it up, all have problems with cost, efficacy, ease of use, or environmental damage. Nanoremediation methods, especially those that use nanoscale zero-valent iron (nZVI), have become potential alternatives because they are very reactive, can be moved easily for in situ treatment, and can be used on many different types of contaminants.

Since the 1990s, permeable reactive barriers have used zero-valent iron at the macroscale to remediate groundwater. When iron particles are changed from microscale or bulk size to nanoscale size (usually 1–100 nm in diameter), the specific surface area goes up by a huge amount—often more than 90 m^2/g. This means that there are many more reactive sites than there were before. This increased reactivity makes it possible to effectively treat chlorinated organic compounds, heavy metals, metalloids, nitrates, and other hard-to-remove contaminants.

Methodology

Synthesis and Characterization of nZVI

The most common way to make nZVI is by chemical reduction, especially by utilizing sodium borohydride ($NaBH_4$) to reduce ferric or ferrous iron salts. The common reply goes like this:

$$4Fe^{3+}+3BH_4^{-}+9H_2O\rightarrow 4Fe^{0}+3H_2BO_3^{-}+12H^{+}+6H_2$$

Alternative green synthesis methods use plant extracts that have polyphenols, flavonoids, and other phytochemicals in them as natural reducing and stabilizing agents. This makes the production process better for the environment. Modified synthesis techniques include stabilizers such polymers (polyvinylpyrrolidone, carboxymethyl cellulose, chitosan), charcoal, clay minerals (bentonite, montmorillonite), or zeolites. These stabilizers help keep nanoparticles from clumping together and make them more stable, mobile, and reactive.

Comprehensive characterization employs multiple analytical techniques:

- **Transmission Electron Microscopy (TEM) and High-Resolution TEM (HR-TEM):** Visualize particle morphology, size distribution, and core-shell structure.
- **Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS):** Examine surface topography and elemental composition.
- **X-ray Diffraction (XRD):** Identify crystalline phases, particularly the characteristic Fe^0 peak at $2\theta \approx$ 44-45° and iron oxide phases.
- **X-ray Photoelectron Spectroscopy (XPS):** Determine surface chemical states and oxidation states of iron.
- **Fourier Transform Infrared Spectroscopy (FTIR):** Identify functional groups and surface chemistry.
- **Brunauer-Emmett-Teller (BET) Analysis:** Measure specific surface area and porosity.
- **Dynamic Light Scattering (DLS) and Zeta Potential Analysis:** Assess hydrodynamic diameter and colloidal stability.

Core-Shell Structure and Reaction Mechanisms

A fresh nZVI particle usually has a core-shell structure with a metallic Fe^0 core (2–50 nm in diameter) and a thin (2–4 nm) amorphous or crystalline iron oxide/hydroxide shell made of magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), goethite (α-FeOOH), or lepidocrocite (γ-FeOOH). This core-shell structure has several uses. The Fe^0 core has a significant reducing capacity (standard reduction potential $E^0 = -0.44$ V), while the oxide shell has plenty of hydroxyl groups and surface sites for adsorption, complexation, and catalytic processes.

Heavy metal removal by nZVI involves several synergistic mechanisms:

Reduction: Metals with reduction potentials more positive than Fe^0 (e.g., Cu^{2+}, Cr^{6+}, Hg^{2+}) undergo direct electron transfer reduction:

$$\boldsymbol{Fe^0 + M^{n+} \rightarrow Fe^{2+} + M^{(n-x)+}} \textbf{ or } \boldsymbol{M^0}$$

Adsorption: The oxide shell provides negatively charged hydroxyl groups that electrostatically attract and bind cationic heavy metals through surface complexation:

$$\boldsymbol{\equiv FeOH + M^{n+} \rightarrow \equiv FeO - M^{(n-1)+} + H^+}$$

Precipitation and Coprecipitation: Iron corrosion increases local pH and generates iron (hydr)oxides that promote metal precipitation as hydroxides, carbonates, or phosphates, and coprecipitation within iron oxide structures.

Statement of the Problem

Environmental and Health Risks of Heavy Metal Contamination

Heavy metal pollution still threatens the quality of the environment and human health across the world, even though governments have been trying to stop it for decades. Current estimates say that millions of hectares of farmland are polluted with heavy metals, especially in areas that are heavily industrialized or have a lot of mining. Cadmium, lead, and zinc are contaminants that should be dealt with first since they are common, poisonous, and tend to build up in food crops.

Cadmium (Cd): Cadmium is very poisonous, even in little amounts. It moves easily through soils (mobility factor 61–94%) and builds up quickly in plant tissues. People mostly become sick from eating crops that have been infected, which can hurt their kidneys, cause bone loss (Itai-itai sickness), and perhaps cause cancer.

Zinc (Zn): Zinc is a necessary micronutrient, but it may be harmful to plants and the environment when levels are too high. Mobility factors are between 19% and 62%, which means that the bioavailability is modest. Too much zinc messes up how plants work and is bad for soil microbes and animals.

Lead (Pb): Lead doesn't move about as much as cadmium does (mobility factor 2–46%), but it builds up near sources of contamination and is quite dangerous to the nervous system, especially for kids. Lead disrupts brain development, diminishes IQ, and induces behavioral abnormalities.

Limitations of Traditional Remediation Technologies

There are a lot of problems with traditional repair methods:

- Excavation and disposal: Very expensive ($200–500 per ton), disruptive, and just moves contaminants to places where it can be thrown away.
- Soil washing needs a lot of water, makes extra effluent, and might affect the structure of the soil.
- Chemical Stabilization: Regular changes like lime and phosphates don't always work and may not last long.
- Phytoremediation takes a long time (years to decades), is limited by how much plants can handle and how much they can take in, and only works on surface soils.
- Excavation Impracticality: For extensive or profound pollution, excavation is rendered commercially and technically unviable.

Specific Knowledge Gaps

Critical uncertainties persist regarding nZVI application for heavy metal remediation:

- Long-term Stability: The aging and changing of nZVI in soils over long periods of time (months to years) and how it affects the long-term immobilization of metals.
- Effects of Soil Heterogeneity: Different soil types, textures, and pollution situations might affect how well something works.

- Interactions between metals: how they compete with each other and how they bond to each other in soils that are polluted with more than one metal.
- Ecotoxicological Impacts: Possible harmful impacts on beneficial soil microbes, earthworms, and plant growth.
- Field-Scale Validation: Not much of a shift from lab accomplishments to full-scale field use.
- Cost-Benefit Analysis: Comparing the economic viability of microscale or bulk ZVI alternatives.

Solution: nZVI-Mediated Remediation and Metal Speciation Changes

Mechanisms of Heavy Metal Immobilization by nZVI

Nano-zero-valent iron binds heavy metals together through a combination of physical and chemical mechanisms that change the way metals are found in the environment, making them more stable.

Adsorption onto Iron Oxide Surfaces

The iron oxide/hydroxide shell of nZVI has amphoteric surface hydroxyl groups (≡FeOH) that may gain and lose protons depending on the pH:

$$\equiv FeOH2+ \leftrightarrow \equiv FeOH \leftrightarrow \equiv FeO-$$

At neutral to alkaline pH, negatively charged surface sites attract and bind cationic heavy metals through inner-sphere and outer-sphere complexation pathways. nZVI has a very large specific surface area (typically more than 30 m^2/g), which means it has a lot of places where heavy metals may stick to it. Reports say that nZVI can hold up to 165–200 mg/g of different heavy metals.

Precipitation and Coprecipitation

Iron oxidation during nZVI corrosion releases Fe^{2+} ions, which then oxidize to Fe^{3+} and form several iron (hydr)oxides, such as magnetite, maghemite, goethite, lepidocrocite, and ferrihydrite. This method makes it possible to trap heavy metals in many different ways:

- Increase in pH: Iron corrosion eats protons and raises the local pH, which causes metal hydroxides to form, especially for Pb and Zn:

$$M2++2OH- \rightarrow M(OH)2(s)$$

- Coprecipitation: Heavy metals take the place of iron in developing oxide or hydroxide precipitates or are trapped inside precipitate structures.
- Surface Precipitation: Supersaturation close to nZVI surfaces encourages heterogeneous nucleation and the development of several metal-bearing phases.

Reduction (Metal-Specific)

While Cd^{2+}, Pb^{2+}, and Zn^{2+} have less favorable reduction potentials than Fe^0 for direct reduction, localized reducing micro-environments may promote partial reduction or the generation of mixed-valence species, especially for metals near the oxide-metal interface.

Transformation of Metal Speciation: Evidence from Sequential Extraction

Numerous investigations utilizing consecutive extraction methodologies indicate substantial speciation alterations subsequent to nZVI therapy.

Awad et al. (2021) examined the effects of biochar and nZVI on multi-contaminated soil by BCR sequential extraction. The results indicated that the application of nZVI (0.5-1% w/w) effectively reduced the exchangeable and carbonate-bound fractions (F1) of Cd, Pb, and Zn by 25-45%, while concurrently augmenting the residual fraction by 30-60% following a 30-day incubation period. The reducible fraction (F2), linked to iron-manganese oxides, also rose, showing that metals were binding to iron oxides that had been formed via nZVI oxidation.

Research on soils impacted by mining indicated that nZVI treatment decreased the mobility factor of lead from 32% to 8%, zinc from 48% to 22%, and cadmium from 78% to 35% over a period of 60 days. The significant impact on cadmium, the most mobile metal, underscores nZVI's ability to immobilize even extremely labile species. XRD and XPS investigations verified the production of metal-iron oxide coprecipitates and surface complexes as the principal mechanisms of immobilization.

However, other study reports paradoxical conclusions. Research by researchers examining organic matter-amended soils observed that nZVI increased mobile fractions of certain metals under specific conditions, potentially due to complexation with dissolved organic carbon released during organic matter degradation or changes in redox conditions affecting metal speciation. This underscores the importance of considering soil-specific properties and amendment interactions.

Influence of Application Dosage and Contact Time

Dose-response studies show that there is a typically favorable link between the amount of nZVI used and the efficiency of metal immobilization, but this effect gets less at increasing concentrations. Research with nZVI at 100-1000 mg/kg shown best efficacy at intermediate dosages (500-1000 mg/kg), achieving metal removal rates of 80-95%. Conversely, large doses (>2000 mg/kg) occasionally diminished efficiency due to nanoparticle aggregation, which restricted reactive surface area.

Temporal dynamics show that the initial immobilization happens quickly (in hours to days), and then the metal binding happens more slowly and lasts for weeks to months. As nZVI ages, it goes through a process called progressive oxidation, which changes it from highly reactive magnetite/maghemite to more stable goethite/lepidocrocite phases. The Fe^0 core gets smaller and the oxide shell gets thicker. Even though aged nZVI is less reactive, it nevertheless holds onto metals through stable oxide phases. Studies have shown that less than 10% of metals are remobilized after 6 to 12 months.

Comparison with Modified nZVI Formulations

Enhanced nZVI formulations address limitations of bare nZVI, particularly aggregation and rapid oxidation:

Polymer-Stabilized nZVI: Coatings of carboxymethyl cellulose (CMC), polyvinylpyrrolidone (PVP), and chitosan give steric stabilization, which keeps particles from sticking together and makes them move more freely. CMC-nZVI was 2 to 3 times better at removing metals than bare nZVI because it spread out better and was reactive longer.

Biochar-Supported nZVI: Biochar has a porous support structure, its own functional groups that increase sorption capacity, and a buffering capacity that keeps the pH level stable. Research indicated that biochar-nZVI composites (5-10% biochar) attained 15-30% enhanced metal immobilization compared to nZVI alone, while simultaneously decreasing ecotoxicity.

Clay-Supported nZVI: Bentonite, montmorillonite, and other clay minerals spread out nZVI particles, stop them from clumping together, and add more places for cation exchange. Marine clay-supported nZVI showed a 15% improvement in its ability to adsorb, with particles that were well-dispersed and 30–60 nm in size keeping their core-shell structure.

Sulfidated nZVI (S-nZVI): Adding sulfur (0.25–5% S) makes it much more stable and last longer. After 60 days, 5% S-nZVI kept 78.6% Fe^0 content, while bare nZVI only kept 35.3%. Sulfidation encourages the creation of iron sulfide phases that have different reactivity profiles and may be better at picking out particular metals.

Soil Property Influences on Remediation Effectiveness

Soil physicochemical characteristics profoundly affect nZVI performance:

Effects of pH: Acidic soils (pH 4–6) speed up corrosion, which makes nZVI more reactive, but they may also stop metals from falling out of solution. Alkaline soils (pH 7–9) encourage the creation of metal hydroxides, but they can also make carbonate layers that protect nZVI surfaces. Most of the time, the best performance happens when the pH is close to neutral (6.5–7.5), which balances reactivity and precipitation.

Organic Matter Content: Moderate organic matter (2-5%) improves remediation by giving more places for sorption, buffering variations in pH, and stopping too much nZVI aggregation. But excessive levels of organic matter (>10%) can make metals more soluble or use up nZVI reactivity through competitive reactions.

Texture and Mineralogy: Soils with a lot of clay have a high cation exchange capacity, which helps keep metals in place, but they may make it harder for nZVI to move about and spread. Sandy soils allow nZVI to seep in more easily, but they have fewer natural sorption sites, which makes adding nZVI more important.

Moisture and Redox circumstances: When circumstances are saturated, nZVI oxidation and iron oxide precipitation happen faster. This makes short-term immobilization better, but it can make the material less stable over time. Unsaturated circumstances keep Fe^0 levels higher for longer, which keeps reactivity going.

Conclusion

Summary of Key Findings

This thorough analysis shows that nano-zero-valent iron is a potential and useful way to clean up soils that are polluted with cadmium, lead, and zinc by changing the way metals chemically interact with each other. The main results are:

- Speciation Transformation: Using nZVI always moves heavy metals from mobile, bioavailable fractions (exchangeable, carbonate-bound) to stable, immobile fractions (oxide-bound, residual). The amount of mobility decreases by 30% to 70%, depending on the type of metal, the properties of the soil, and the conditions of the treatment.
- Multi-Mechanism Action: The unique core-shell structure of nZVI allows for synergistic processes that immobilize metals, such as adsorption onto iron oxides with a large surface area, coprecipitation inside iron (hydr)oxide phases, surface complexation, and precipitation that is affected by pH.
- Responses to certain metals: Cadmium, which is the most mobile at first, displays huge drops in mobility (50–70%), however it may need greater dosages of nZVI. Lead reacts favorably at modest levels because it has a significant affinity for iron oxides. Zinc shows behavior that is in the middle, with mobility decreases of 40–60%.
- Changed Formulations Improve Performance: Stabilized (CMC, PVP), supported (biochar, clay), and sulfidated nZVI formulations solve problems with aggregation and quick oxidation, showing 20–40% better efficacy and a longer functional lifespan than bare nZVI.
- Soil Characteristics Modulate Effectiveness: pH (best between 6 and 7.5), organic matter content (moderate amounts are good), texture, and moisture levels all have a big impact on results; thus, each site needs to be optimized.

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