Vol. 5 Issue- 3, November 2024 (e-ISSN: 2582-8223)

JUST AGRICULTURE
multidisciplinary e-Newsletter

# Potential of Nano Scale Zero Valent Iron in Remediating Heavy Metals Contaminated Soil

**Varalakshmi. V[1], Ambruthavarshini[2] and Shivakumar Mirji[3]**
[1]Ph.D Scholar, Dept. of Soil Science, College of Agriculture, V.C. Farm, Mandya-571405.
[2]Ph.D Scholar, Dept. of Soil Science, College of Agriculture, V.C. Farm, Mandya-571405.
[3]M.Sc. (Agri.), Dept. of Soil Science, College of Agriculture, V.C. Farm, Mandya-571405.

**ARTICLE ID: 32**

**Nano Remediation:** is the use of nanoparticles for environmental remediation. It is being explored to treat ground water, wastewater, soil, sediment, or other contaminated environmental materials.


## Nano zero valent iron

In the last years and decades, the development of nanosized materials has facilitated the application of remediation technologies based on highly efficient and versatile nanomaterials. Among the possible nanoparticulate systems successfully used on a laboratory scale for soil decontamination, zero-valent iron nanoparticles (NZVI) have achieved very interesting and promising results. Zero-valent iron nanoparticle are type of nanomaterial that have been proposed for use in environmental remediation of metal pollutions in soil and waterbodies. Due to their low toxicity and decent activity, nZVI and its corrosion products have shown huge potential for the removal of heavy metal from soil and water. The properties like strong reducing capacity, good adsorption capacity, rheological ability to move subsurface of the soil,

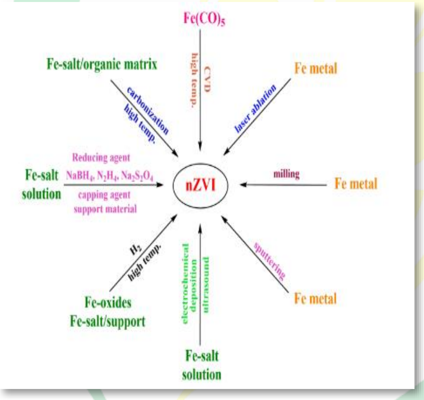
JUST AGRICULTURE
multidisciplinary e-Newsletter

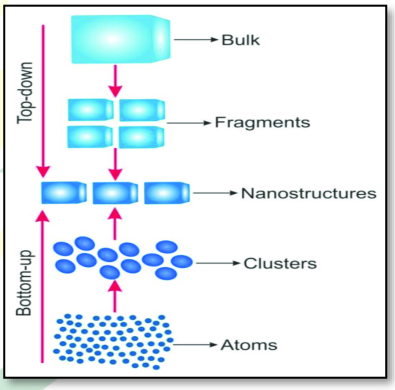
and its cost effectiveness make nZVI as a potential remediating agent. Not only heavy metal, but also it can remediate organochlorides, organic dyes, antibiotics and toxic radionuclides in soil.

- It is having Size range:1-100nm
- Strong reducing agent
- Strong sorption capacity
- High reactivity
- Rapid action
- Versatality

**Synthesis of nano zero-valent iron**

nZVI, in general, can be produced using physical or chemical methods either by reducing the size of bulk iron to nanoscale (top-down approach) or building up nano iron from atoms generated from ions or molecules (bottom-up approach) (El-shafei *et al.*, 2018).



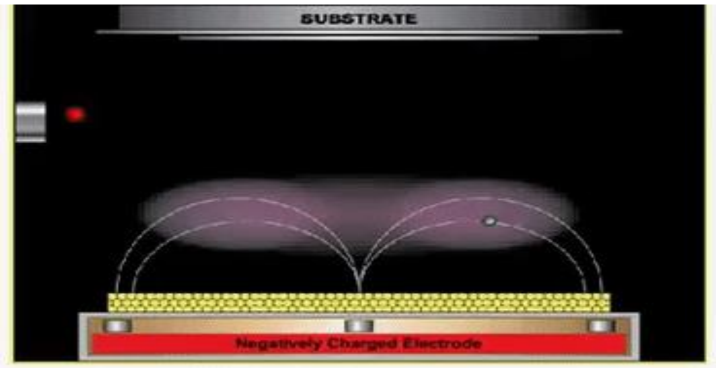

**1. Top-Down Synthesis**

Top-down methods for nZVI production are the milling processes, pulsed laser ablation, and noble gas sputtering.

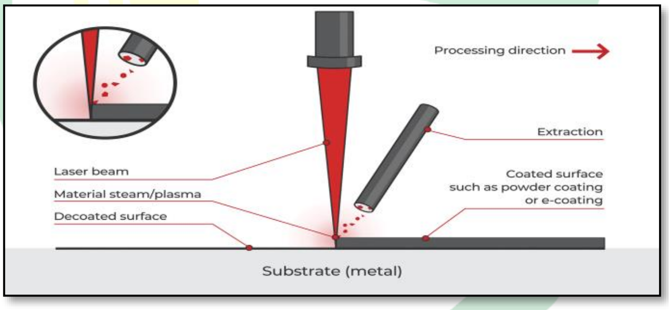
- **Milling process:** The most frequently used top-down method is the milling process. It starts from micro meter- to milli meter-sized iron filings (e.g., carbonyl iron, sponge iron, cast iron, and iron powder), which are milled (using ball-mills, vibrating mills, and stirred ball mills) to fine, nanosized particles. One of the advantages of this method is that it is easy to scale-up. Another advantage is that the method does not require the use of expensive and toxic chemicals (compare, e.g., to the borohydride solution used in reduction method).
- **Noble gas sputtering**: is a less frequently used method for nZVI synthesis and mainly

JUST AGRICULTURE
multidisciplinary e-Newsletter

used in specialized laboratories. If iron is used as the sputtering target, a supersaturated iron vapor forms in the sputtering process, which can be condensed into solid clusters by cooling. Kuhn *et al.* prepared core–shell iron–iron oxide (γ-Fe2O3/Fe3O4) nanoparticles by using an iron hollow cylinder as the cathode and argon as the sputtering gas in a high-vacuum chamber, and oxidizing iron NPs in a consecutive step by exposing them to an increasing pressure of oxygen.




- **Pulsed Laser ablation**: is another method to synthesize Fe NPs on a small scale. Irradiation of an iron metal target with a laser pulse locally melts and vaporizes the metal. Hot metal atoms are cooled by the surrounding medium and form metal NPs.



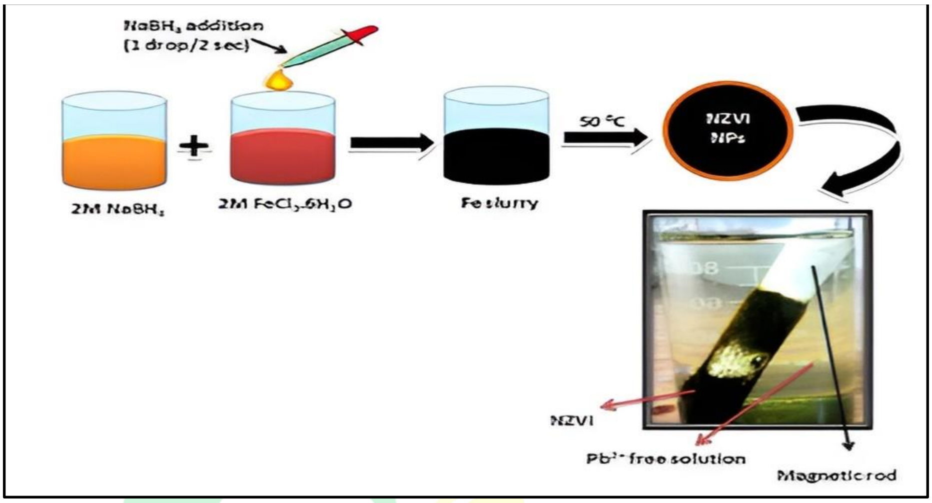

## 2. Bottom-Up Synthesis

Bottom-up approaches to build nZVI start from either dissolved iron salts, nanosized iron oxides, or iron-containing molecules.

### a) Solution Based Processes

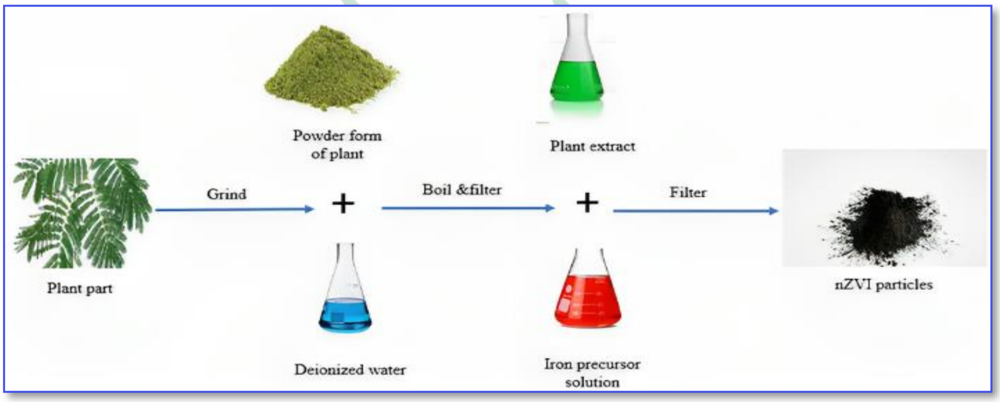
- **Reduction of ionic iron with NaBH4:**

The most frequently used method for nZVI synthesis in laboratories is the borohydride route, where iron salts, typically chlorides, are reduced in aqueous environment under inert atmosphere with sodium borohydride. nZVI can be synthesized by reduction of ferric and ferrous source of iron using sodium borohydride solution.




**b) Green synthesis of nZVI:**

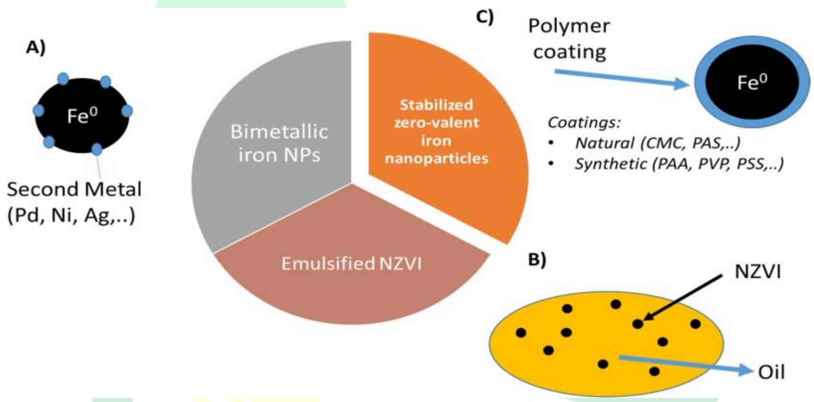
Green methods for producing nZVI are becoming more important due to safety and environmental concerns. In this respect the replacement of borohydride with green alternatives is the key issue. The green production method uses extracts from natural products such as tree leaves, fruits, etc. having high antioxidant capacities, therefore components that react with iron ions in solution to produce nZVI particles. The advantages of this method are the use of non-toxic reducing agent, the natural capping of the NPs by the extract matrix, and valorisation of natural products. Due to capping they have less tendency to agglomerate and have prolonged reactivity. A wide range of natural products or their extract have been used to date such as oak leaves extract, apple, apricot, avocado, cherry, eucalyptus, kiwi, lemon, mandarin, medlar, mulberry, oak, olive, orange, passion fruit, peach, pear, pine, pomegranate, plum, quince, raspberry, strawberry, tea-black, tea-green, vine, and walnut leaf extracts.



### 3. Stabilization of nZVI

Stabilization of nano Zero-Valent Iron with any polyelectrolyte or polymer or surfactant is important because nZVI is more versatile for oxidation due to its high reactivity and aggregation due to its magnetic nature in its bare and pure form. Particles coated with certain polymer like Carboxy Methyl cellulose [CMC], polystyrene sulfonate [PSS], alginate, starch, cellulose acetate, polyacrylic acid, etc. can remain more mobile for long time and can flow towards subsurface. These additives effectively control the shape and size of nanoparticles, enhance nanoparticles stability and mobility, and thereby increase the nanoparticle efficiency.

### 4. Different kinds of nZVI

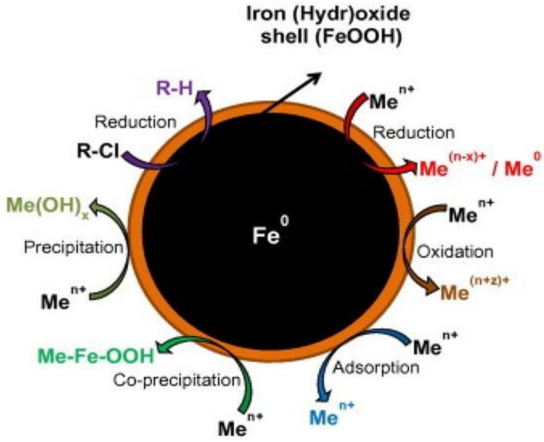



Bimetallic particles are composed of iron (or zinc) and a noble metal such as palladium (Pd), platinum (Pt), nickel (Ni), silver (Ag), or copper (Cu), being the main role of these noble metals the catalysis of the reduction reaction, thus facilitating contaminant degradation. The facile access to palladium BNPs since they are commercial have spread their use among the BNPs developed. The use of BNPs for the remediation of common halogenated contaminants and metals has been demonstrated.

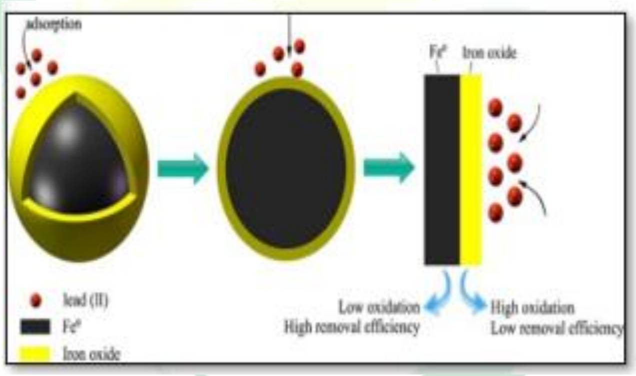
Emulsified zero-valent iron (EZVI) [103]. The aim of this kind of systems is to deliver NZVI in an oil–water emulsion, which eases the transportation into the contaminated zones and reduces the NZVI's degradation [104]. EZVI is a surfactant-stabilized, biodegradable emulsion that forms emulsion droplets consisting of an oil–liquid membrane surrounding zero-valent iron (ZVI) particles in water.

### 5. Inttion mechanism of nZVI with heavy metals

The main interaction mechanisms between nZVI and heavy metals assisted in the literature are adsorption (Ni, Cd, Pb), reduction (Ni, Cu, Pb) oxidation/reduction (U, As, Pb, Se) and precipitation (Cd, Pb, Cu) (Alazaiza *et al.*,2022).




**a. Adsorption**: nZVI's large active sites and functional groups make it an effective adsorbent for heavy metal removal. Iron oxides or hydroxides formed on its surface enhance adsorption, making iron-based materials cost-effective and non-toxic. Adsorption is the dominant removal mechanism, influenced by the metal's standard redox potential ($E_0$). Metals like Cd and Zn, with similar or more negative $E_0$ values, are adsorbed, while metals like Pb and Ni, with more positive $E_0$, are reduced and precipitated. Metals such as Cr, Cu, and As undergo both adsorption and reduction in the $Fe^0$-$H_2O$ system.




**b. Reduction:** Reduction reactions are key in nZVI's interaction with heavy metals, altering their properties and valence. nZVI's reduction capacity, where $Fe^0$ donates electrons, is crucial for removing multivalent heavy metals from solutions. Two different mechanisms controlled the reduction reaction of nZVI with heavy metals:

- direct reduction with $Fe^0$ as the electron donor
- the gradual reduction of heavy metals by $Fe^{2+}$ after the primary adsorption through electrostatic interaction and surface complexation to nZVI core-shell. For $Cr^{2+}$ and $Cr^{6+}$, the reduction is the main removal mechanism by nZVI.

### c. Oxidation/reoxidation

Oxidation of heavy metals by nZVI occurs in specific environments, often in the presence of oxygen via the Fenton reaction. $Fe^0$ derivatives can oxidize metals, leading to their separation. In the Fe-$H_2O$ system, $Fe^0$ oxidizes to Fe(II) and Fe(III), while Cr(VI) reduces to Cr(III). nZVI may also reduce $As^{5+}$ to less toxic $As^{3+}$.

### d. Precipitation

Heavy metal removal by nZVI involves adsorption, reduction, and co-precipitation. For Cr(VI), Fe oxidation and Cr reduction occur before, during, or after co-precipitation. Cu is adsorbed at pH 4–6 and precipitates as $Cu(OH)_2$ at higher pH. U(VI) remediation involves reduction and precipitation in alkaline conditions. $Pb^{2+}$ is adsorbed and reduced on nZVI. Ni(II) and Zn(II) removal occurs via adsorption, electrostatic attraction, and co-precipitation with iron products and hydroxides.To sum up, the removal mechanism of heavy metals by nZVI is as a synergistic process where adsorption, oxidation/ reduction and precipitation take place simultaneously or in series. Nevertheless, the main removal mechanism could be attributed to one or two interactions.

## Conclusion:

Nano-remediation with nZVI transforms and detoxifies heavy metals. To enhance its effectiveness in complex soils, modifications like polymer coating, biochar embedding, or green synthesis are used. nZVI removes metals through synergistic mechanisms: adsorption, reduction, co-precipitation, and oxidation, occurring simultaneously or sequentially.

## References:

Alazaiza, M.Y., Albahnasawi, A., Copty, N.K., Bashir, M.J., Nassani, D.E., Al Maskari, T., Abu Amr, S.S. And Abujazar, M.S.S., 2022, Nanoscale zero-valent iron application for the treatment of soil, wastewater and groundwater contaminated with heavy metals: a review. *Desalin.*, 253:194-210.

El-Shafei, M. M., Hamdy, A. And Hefny, M. M., 2018, Zero-valent iron nanostructures: synthesis, characterization and application. *J. Environ. Biotechnol.*, *7*:1-10.

Fitz, W. J., Wenzel, W. W., Zhang, H., Nurmi, J., Stipek, K., Fischerova, Z., Schweiger, P., Kollensperger, G., Ma, L.Q. And Stingeder, G., 2003, Rhizosphere characteristics of the arsenic hyperaccumulator *Pteris vittata L.* and monitoring of phytoremoval efficiency. *Environ. Sci. Technol, 37*(21): 5008-5014.

Kuhn, L. T.; Bojesen, A.; Timmermann, L.; Nielsen, M. M.; Morup, S., 2002, Structural and magnetic properties of core–shell iron–iron oxide nanoparticles. *J. Phys. Condens. Matter*., 14: 13551–13567.