APPLICATION OF NANOSCALE ZERO-VALENCE IRON (nZVI) FOR CONTAMINATED SOIL REMEDIATION – A REVIEW

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ABSTRACT

Industrial development in global scenario has an impact on environmental degradation. The contaminants discharged from various industrial activities have effect on soil environment and in turn on the health of living organisms. The treatment processes involved in contaminated soil remediation include physical, chemical and biological methods. Nanoscience and nanotechnology, a rapidly developing field in research and development have gained importance in the area of contaminated soil remediation (nanoremediation). Nanoremediation is a very effective in-situ remediation method due to its worthy rate of treatment, easy and higher mobilization of particles in to the contaminated soil system. Nanomaterials can chemically reduce the pollutants and also can act as a catalyst to mitigate the reaction. This review presents the application of nanoscale zero-valent iron (nZVI), one of the most effective and widely used nanoparticles, for contaminated site remediation. nZVI has the property of both adsorption and reduction. Further, the advantage of nZVI particles are (i) it can be directly injected into the contaminated sites and (ii) it can remove the contaminants completely from soil. nZVI can also be modified to enhance its properties for better performance. Physical and chemical methods are used for the synthesis of nZVI. Physical methods used for synthesis are inert gas condensation; severe plastic deformation, high energy ball milling, and ultra sound shot peening and chemical methods used are reverse micelle, controlled chemical coprecipitation, chemical vapour condensation, pulse electrode position, liquid flame spray, liquid-phase reduction, and gas-phase reduction. Liquid and gas phase reduction methods are preferred mostly. nZVI is synthesized by wet chemical precipitation of FeCl₃·6H₂O and NaBH₄ solution. Gas reduction method is done by either of the three methods (i) precipitation of acicular goethite ((FeO)OH) from oxygenated FeSO₄ solution (ii) acicular goethite is reduced to α-Fe grains in a heated hydrogen gas atmosphere at high temperature (350-600°C) (iii) wet-milling of α-Fe grains to convert its surface to magnetite. Understanding the transport of nZVI into the soil is important as the proper dispersion of particles depends on it. The electrokinetic experiments have been carried out on bare nZVI, modified nZVI, bare nZVI aided with surfactants and cosolvents, and nZVI aided with dispersing agents (aluminium lactate), by the researchers to understand the transport of particles into the soil. The electrokinetic experiments on nZVI aided with dispersing agents improve the transport of particles. The application of nZVI in soil remediation includes degradation of 1,1- dichloroethane, 1,1dichloroethene, 1,1,1-trichloroethane, 1,2-dichloroethane, trichloroethane and removal of heavy metals, dyes and organic pollutants. The efficiency of nZVI for soil remediation depends on the type of contaminant to be removed and nature of soil. Although the application of nZVI for soil remediation is advantageous, its environmental effects at later stage are still unknown. In addition, not much information is available on the effect of nZVI on the food chain, animal life and microbial life, and the cost analysis for
The nanoremediation process. The various factors to be considered for the cost analysis includes site conditions, type of contaminant to be treated and the duration of the remediation process. However, the additional factors that may influence the cost analysis are cost of synthesizing nanoparticle, injection of nanoparticle to the contaminated site, operation of equipments at site and administrative cost.

Keywords: Nanoscale zero-valent iron, Soil remediation, Application.

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ABSTRACT: Nanoremediation is one of the most effective and widely used methods for decontamination of soil, water and aqueous medium. It is being used for the remediation of pollutants like dyes, pesticides, fertilizers, heavy metals and organic matter. The larger surface area is the reason for its high efficiency in decontamination. Another main advantage of nanoparticle is its detoxification of contaminants. Wet chemical precipitation is the most widely used laboratory method for the synthesis of Nano Zero-Valent Iron (nZVI). nZVI is being effectively used for soil remediation process. The small size initiates easy transport of the particles into the soil. To improve the efficiency of transport of nanoparticle modifiers, cosolvents and dispersing agents are being used. Electro kinetic techniques are being used to enhance the transport of nanoparticles. nZVI has the capability for both adsorption and reduction. Nanoscale iron particles can be modified by using catalysts such as palladium (Pd), polyelectrolyte or triblock polymer coating or by emulsified vegetable oil droplets to enhance transport of nanoparticles. Studies have shown that nZVI presence in soil has harmful effects on soil microbes and earthworms present in soil. In order to overcome this, synthesis of nanoparticles from green leaves have been developed and researches are carried out to know its efficiency and environmental effects.

INTRODUCTION
Rapid industrialization and population growth has led to the increase in pollution. The level of organic and inorganic pollution is increasing in soil, air and water. Some inorganic pollutants take decades to degrade and hence its effect on the ecosystem is very high. The major sources of pollutants are municipal waste, waste from agricultural sectors, industries and pollution from vehicles.

Various remediation works are being done by researchers for the pollutants like dyes, heavy metals, pesticides, fertilizers, organic matter. Some of the remediation works done are reverse osmosis, coagulation, flocculation, incineration, ion exchange, membrane filtration, photoelectrochemistry, electrochemistry, advanced oxidation process, adsorption and biological methods [1].

Recently nanoparticles are being used for site remediation and water purification. Nanoparticles are being used because they have a greater treatment rate. The treatment rate of nanoparticle is greater than that of micron-scale treatment media. Another advantage of nanoparticle is that since their size is very small they are easily mobile in aquifer system and can be directly injected into the subsurface to treat contaminated zones [2].

NANOREMEDIATION
Nanoremediation has a great importance in the area of research due to its great scope of improving the environment by using nanomaterials. Nanomaterials have the capability of detoxification of pollutants from the environment. Main property of nanomaterial is its novel surface coating which enables in wider distribution of particles compared to larger sized particles [3]. Materials used for nanoremediation has the capability to enable both
chemical reduction and to act as a catalyst to mitigate the pollutants. Using nanoremediation, contaminants level can be even reduced to zero. The main advantage of nanoremediation is it requires less time and it is less expensive, because there is no need to pump the waste out and treat it. Nanoparticles and electrokinetics has to be combined for the effective removal of contaminants from soil[4]. Nanoremediation has been proved to be a very effective method, but its risk and after effects are yet to be studied and understood[5].

**NANO SCALE ZERO-VALENT IRON (nZVI)**

Carbon nanotubes, metal oxides, nanoscale zeolites, noble metals, titanium oxides are some of the nanomaterial which are being used for nanoremediation. The important and widely used nano material is nanoscale zero-valent iron (nZVI) which is used for the remediation of water and soil[3].

Iron nanoparticles are highly efficient in nanoremediation. nZVI are preferred for nanoremediation because of large surface area and large number of reactive sites. nZVI also possess dual property that is both adsorption and reduction. nZVI can also be modified based on the contaminants present[3]. Particles of nano iron range from 10 to 100 nanometers in diameter or slightly larger. They exhibit a core shell structure. The core consists of zero-valent or metallic iron, the mixed valent [Fe(II) and Fe(III)] oxide is formed due to the oxidation of metallic iron [3].

The performance of nano iron particle (NIP) is found to be more than micro scale particle, dechlorination of trichloroethane (TCE) was found to be 95% with NIP which is more than the percentage removal by micro scale iron particle (86%). Nano iron particle has high attractive force because of high van der Waals attraction, high Haymaker constant and high magnetic property due to which nanoparticles agglomerates and settles [6]. Nanoscale iron particles can be modified by using catalysts such as palladium(Pd), polyelectrolyte or triblock polymer coating or can be enhanced in emulsified vegetable oil droplets. Modification of nanoparticles helps in reducing agglomeration of nanoparticles[7].

The reaction of nano iron particles with soil depends on the concentration of nanoparticles, concentration of contaminant, type of contaminant and reaction time of the nanoparticle. Some of the other factors on which reaction depends on are pH, temperature, aerobic and anaerobic conditions and reaction rate.

**SYNTHESIS OF NANOSCALE IRON PARTICLES**

Various methods are available for the synthesis of nZVI. It is synthesized by both physical and chemical method. Physical method consists of inert gas condensation, severe plastic deformation, high energy ball milling, and ultra sound shot peening. The chemical methods that rare used for the synthesis are reverse micelle, controlled chemical co-precipitation, chemical vapor condensation, pulse electro deposition, liquid flame spray, liquid-phase reduction, and gas-phase reduction[6].

Wet-chemical precipitation process for the synthesis of nanoscale iron is done by adding FeCl$_2$.6H$_2$O solution to a solution of NaBH$_4$ due to which sedimentation of iron Fe$^0$ occurs. The iron obtained is then freeze and dried out. The synthesized nano zero-valent iron is then preserved in nitrogen[8].

Gas phase reduction synthesis method is done by precipitation of acicular goethite (FeO)OH from oxygenated FeSO$_4$ solution or acicular goethite is reduced to elemental iron core ($\alpha$-Fe) grains in a heated hydrogen gas atmosphere at high temperature (350-600°C) or by wet-milling of $\alpha$ -Fe grains to convert its surface to magnetite[6].

**TRANSPORT OF NANOSCALE IRON PARTICLE**

Methods traditionally used for predicting the behavior of chemicals in the environment are mainly based on the principles of chemistry such as molarity, partition, fungacity etc. The transport of nanomaterials in the environment can be analyzed by including environmental and material properties such as viscosity, steric force, Hakman force, buoyancy, surface area and charge accumulation[2]. Methods that are used for injection of nanoparticles include direct push, liquid atomization injection, pneumatic fracturing, hydraulic fracturing, pressure pulse technology,
and rig technology[7]. Soils with high clay content show greater dispersal of nZVI. Anionic clay particles present in soil act as a natural stabilizer and helps in effective transport of nanoparticles. Increased mobility would result in migration of nanomaterials from contaminated site to drinking water aquifers.

The efficiency of nano iron particles (NIP) used for in-situ remediation depends on the distribution of particles in soil. The barriers for effective transport of nanoparticles in soil are agglomeration, settling and low permeability in soil. Electrokinetics helps in effective transport of nanoparticles. Electrokinetics is the application of low electric potential across the soil due to which the particles gets transported into the electrode by electro osmosis, electromigration and electrophoresis process[9]. Researchers studied the electrokinetic experiments in laboratory using kaolin soil spiked with Pentachlorophenol (PCP). It was reported that the total iron in the soil increases at cathode electrode which indicates the transport of NIP anode to the cathode. Further, it was reported that the transport of NIPs in the soil was reduced due to the aggregation and settling of NIPs in the anode. The PCPs were not fully degraded due to the low solubility and low pH conditions induced near the anode due to low electro osmotic flow[10].

K. R. Reddy [9] studied the improvement in transport efficiency by using Modified reactive nanoscale iron particles (MRNIP) by conducting the experiments with different level of pressure conditions, oxygen free conditions and polymer to reactive nanoscale iron particle (RNIP) ratio. It was reported that the transport of particles also depends upon the surface conditions and the surface modifications of the RNIP[9].

Electrokinetic delivery of nano iron particles aided with cosolvent and surfactant to understand the transport and removal efficiency was studied by Reddy and Karri [11]. It was reported that the utilization of surfactant helps in transport of NIP and not in the degradation of contaminants.

Furthermore, Reddy and Darko [12] studied the application of aluminum lactate as a dispersing agent for transport of NIP and reported that the aluminum lactate enhances the transport of NIP in soil under gravity and pressurized conditions. In addition, it helps in uniform distribution of NIP in the soil.

APPLICATONS
The small particle size and high surface area to mass ratio make iron nanoparticle highly used for remedial purpose. Nanoparticles are highly reactive and extremely versatile in nature. Some of the contaminants remediated using iron nanoparticle are Carbon Tetrachloride, Tropaeolin, cis-dischloroethene, trans-dichloroethene, Dichloromethane, Hexachlorobenzene, Chloromethane, Pentachlorobenzene, Pentachlorophenol, Trichloroethene, Tetrachloroethene, Chlorobenzene, Dichromate, Arsenic, Perchlorite, Nitrate, dioxins, NDMA, TNT, Silver, Cadmium, Bromoform, VinyChloride, Acid red, Mercury, Nickel, Chloroform, Acid orange, DDT, Lindane[13]. Nano iron is also being used for the removal of 1,1-dichloroethene, 1,1,1-trichloroethene, 1,2 – dichloroethane and trichloroethane[6].

LIMITATIONS OF USING NANOPARTICLE
Information about the toxicological effects of nano iron particle is unknown because very little study or research has been done. The impact of accumulation of nanoparticles on environmental relevant species are yet unknown. The effect on the microbial community has also not yet been understood[7]. Modifiers are being used to improve the efficiency of nanoparticles and also to increase the mobility. Due to high mobility there is possibility of nanoparticle to migrate from the plume area and enter the ground water. The health effects of nanoparticles are also unknown when inhaled or absorbed through skin[3].

Under standard environmental conditions with pH 5 to 9, Fe$^{2+}$ readily oxidizes to Fe$^{3+}$. The precipitates thus formed are iron oxides and oxy-hydroxide which are insoluble in water[3]. The impact of nanoparticles on specific and immediate environmental media has to be studied.
has to be done to study the impact of nanoparticles on the food chain and also on animal life[13]. Also, site conditions such as site location, geological conditions and concentration of constituents may limit the effectiveness of nanoparticles. Majorly nZVI particles had been experimented on laboratory scale hence its toxicity effect on soil could not be understood [1]. Researchers even suggest numerical simulations and mathematical models have to be prepared to analyze the effect of nZVI on soil [14]. Site studies have to be done to know the infiltration of nanoparticle after injected into the soil. Distribution of nanoparticle in the subsurface is very less compared to below subsurface due to soil properties of the soil[13]. The main challenge in nanoparticles being used is pumping of the viscous polymer solution into the subsurface and the assessment of time required for the nanometals that has been injected to reach the target contaminated zone. As the travel time increases the nanoparticles should also have sufficient stability[2]. Some of the other limitations of using iron nanoparticles are

(i) After a certain time period, zero valent iron particle gets oxidized easily forming a coating over its surface thus reducing its reactivity
(ii) nZVI from different origin has different reactions with the pollutants
(iii) When nZVI comes in contact with its surface reactivity decreases
(iv) Easily oxidizing nature of nZVI make it difficult to maintain the surface reactivity.

Due to these factors in-situ remediation process using nZVI becomes difficult. Considering these constraints it would be better to inject the nZVI particles

Information regarding the cost analysis for nanoremediation is also limited. Hence a comparison of nanoremediation with other treatment process in the basis of cost analysis cannot be done. The parameters that has to be considered while analyzing the cost are site conditions, contaminants to be removed, and the duration required for remediation[7].

CONCLUSIONS
The aim of the review paper is to give a perspective about nano zero-valent iron particle. Nanoremediation is an effective method for site remediation, even though ex-situ method is not much preferred. The capability of NIP in soil remediation, its transport and reactivity with soil is also discussed. nZVI effects the microorganisms present in soil.Modifiers are used to increase the mobility of nanoparticles in soil and also to reduce the effect on microorganisms in soil. NIP has to be carefully considered for remediation since it’s after effects are unknown.

REFERENCES
5. Todd Kuiken (2009), Cleaning up Contaminated Waste site: Is nanotechnology the answer?, NanoToday 5, 6-8.


