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Synthesis and characterization of Nano particles of zero-valent iron for environmental remediation

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Abstract
Nanoparticles of ZVI are the first field application of free released nanoparticles for environmental remediation. Nanoparticles of zerovalent iron have larger surface area and reactivity than normal zerovalent iron particles. A laboratory experiment was conduct to synthesize of nanoparticles of zerovalent iron. The 0.1M FeSO4 and 0.05M EDTA was mixed in a two necked flask by using propeller mixing. The 0.75M $NaBH_4$ was added drop wise into the mixture solution. Slowly the solution turned to black colour. FTIR, TEM, SEM, DLS, DLS zeta, XRD and BET techniques were used to characterization of nanoparticles of zerovalen iron. In present study we synthesized nZVI with <100nm size, zeta potential -9.9mv, Surface area 20.96 m^2/g. The safely ability of iron to act as an electron donor or reducing agent.

Keywords: Nanotechnology, Environment, Iron

1. Introduction
Nanoparticles of Zero Valant Iron are the first field application of free released nanoparticles for environmental remediation. The application of macro scale Zero Valant Iron in subsurface permeable reactive barrier (PRBs) is a good established technology for the reduction of toxic metals in contaminated soil and water. The chemistry of nanoparticle ZVI is same, but has advantage of having large surface area and the rheological ability of nanoparticles to flow in the subsurface. ZVI nanoparticles can be able to achieve the remediation to mixed contaminants, such as higher valence toxic metals and chlorinated compounds. Application of nanoparticles of zero valent iron to remediate contaminated soil and groundwater since last decade, primarily due to its potential for higher reactivity, broader application and cost effectiveness compared to conventional zero-valent iron and other in situ methods. nZVI have larger surface area and reactivity than $Fe^{(0)}$ particles [1] and has been found effective for the detoxification of organic contaminants such as polychlorinated biphenyls (PCB), or trichloroethene (TCE) [2, 3]. It is reported that the surface area normalized rate constant for degradation of PCBs by nZVI is 10-100 times higher than those commercially available iron particles. Using nZVI to reduce TCE essentially eliminates all the undesirable byproducts such as dichloroethylenes and vinyl chloride [4].
The ability of iron to act as an electron donor or reducing agent is utilized in technique known as Fenton treatment techniques, whereby Fe^{2+} or Fe^0 are used to reduce hydrogen peroxide and generate the highly reactive OH radical, e.g. for Fe^{2+} [5]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \bullet OH + OH^-$$
$$Fe^0 \longrightarrow Fe^{2+} + 2e^-$$

2. Material and Methods
Nanoscale Fe^0 particles were produced by adding 1.6 M $NaBH_4$ aqueous solution drop wise to a 1.0 M $FeCl_3.6H_2O$ aqueous solution at ambient temperature with magnetic stirring. Slowly the solution turned to black colour. The black coloured particles were washed two times with absolute ethanol and finally filtered and dried. In our previous experiment we followed the procedure of Wang and Zhang 1997 [13]. But the main drawback of the procedure (nZVI) is not stable (colour change from black to yellow). So we followed the procedure Murad *et al.,* 2010 [9] and the procedure mentioned below.

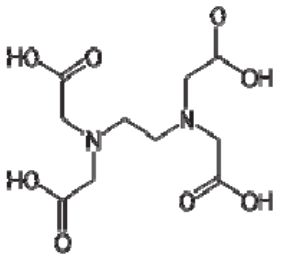
The 0.1M $FeSO_4$ in 150mL of de-ionized water (4.1703 g) and 0.05M EDTA in 100 mL de-ionized water (3.7224 g) were mixed in a three necked round bottomed flask by using propeller mixing. The 0.75M $NaBH_4$ in 100 mL de-ionized water (2.837 g) was added drop wise into the mixture solution. Slowly the solution turned to black colour. The black coloured particles were washed trice with absolute ethanol and finally filtered, dried and pulverized.

Scheme

Step-1 $FeSO_4 + EDTA \longrightarrow Fe(EDTA) + SO^{2-}_4$

Step-2 $SO^{2-}_4 + NaBH_4 \longrightarrow BH^{4-} + NaSO_4$

Step-3 $4Fe^{2+}_{(aq)}(EDTA) + 3BH^-_4 + 12H_2O \longrightarrow [4Fe^0_{(s)}(EDTA)]\downarrow + 3H_2BO_4 + 14H^+_{(aq)} + 8H_{2(g)}\uparrow$



EDTA

Metal EDTA

FTIR, TEM, SEM, Zetapotential, Size (DLS), XRD and BET techniques were used to characterization of nanoparticles of zerovalen iron.

Results and Discussion

Fourier Transforms Infrared Spectroscopy (FTIR)

The FTIR spectra of the EDTA stabilized Nano Zero Valent Iron were recorded in the transmission mode at room temperature using KBr pellet technique (1:20). SpectrumTH 100 Optica Perkin Elmer USA infrared spectrophotometer was used to determine the spectra of the sample which was mixed with spectrally pure KBr and pressed to form thin plate, then were subjected to IR spectroscopic analysis in the spectral range 600 and 4000 cm^{-1} (Figure 1). Gyliene *et al.*, (2007) [2] also observed the use of characterization iron along with nickel through FTIR.

Transmission Electron Microscopy (TEM)

TEM images of nZVI were taken with JEOL, 100 CX, Japan TEM instrument, operated at200 kV. Samples were prepared by depositing a few droplets of dilute Nano Zero Valent Iron particles Suspension on to a carbon film. The particles are spherical with the size ranging from 10 to 100 nm in diameter. The average size was found <100 nm (Figure 2). TEM images also show that most particles formed chain-like aggregates. Similar observation also showed by Wang *et al.*, (2007) [14].

Scanning Electron Microscopy (SEM)

The FE-SEM micrograph (Figure 3) revealed the structural and topology of nZVI. The micrographs of Nano Zero Valent Iron particles studied and the changes in particle shapes and sizes were distinctly visible. It is also observed by Kuen *et al.*, (2008) [8].

Zeta potential

Zeta potential measurements were carried out with a DLS (HORIBA SZ-100) instrument equipped with a universal zeta dip cell. Stability behavior of the colloid is highly dependent upon the zeta potential value. In our study the zeta potential values of nZVI were recorded -9.9 mv (Figure 4). This was farther described by many researchers (Hunter, 1988) [5].

Size (DLS)

The mean hydrodynamic diameter of nZVI was determined by particle size analyzer (HORIBA SZ-100). The samples (15 ppm) were sonicated for 20 min before analysis. The mean hydrodynamic diameter was around 100 nm (Figure 5). It have been also observed by Nurmi *et al.*, (2005) [10], they found that the size of particles between 100-110nm.

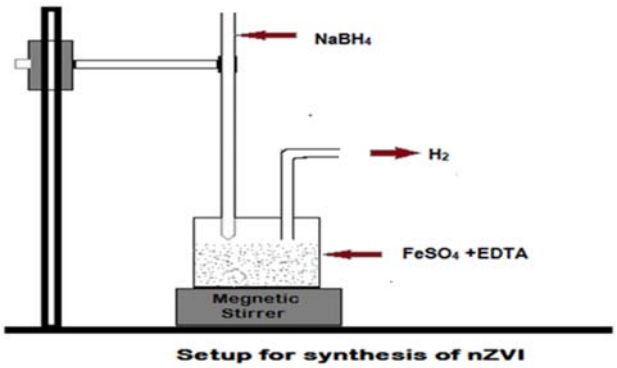
X-ray Diffraction (XRD)

Powder of nZVI was placed in glass holder and scanned from 20^0 to100^0 Scanning rate was 2.5 min^{-1}. Figure 6 shows that powder XRD pattern of nZVI samples under ambient conditions. The broad peak reveals the existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45º indicates that the zero valent iron is predominantly present in the sample. Yuan *et al.*, (2006) [15] also used XRD for these determinations of particle size and characterization of nZVI.

BET-Surface area analyzer

BET-Surface area analyzer was used to measure the specific surface area of the nZVI. It was observed that nZVI has a specific surface area of 20.96 m^2/g. Hence it was evident that the higher specific surface area of nZVI was effective to decontaminate the nickel contaminated soil and water. This has been also studied by Yuvakkumar *et al.*, (2011) [16].

The synthesized nanoparticles of zero valant iron can be use for environmental remediation.



Schematic Diagram of Synthesis of nZVI

Plate 1: Photos during preparation of nZVI

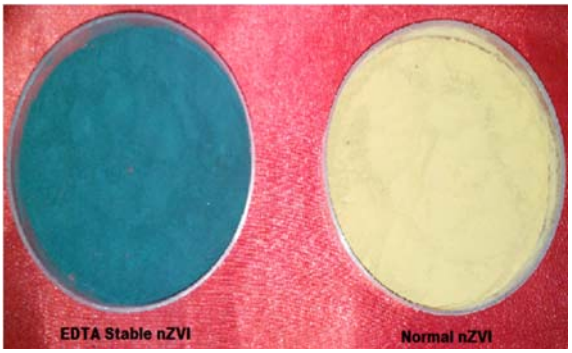


Plate 2: Photo of EDTA stable and normal nZVI

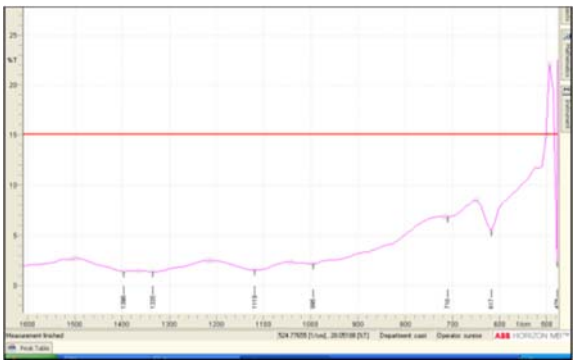


Fig 1: FTIR of nZVI powder

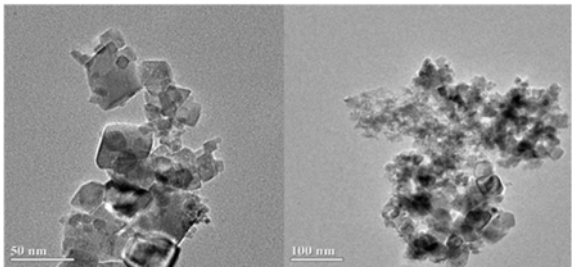


Fig 2: TEM micrograph of nZVI

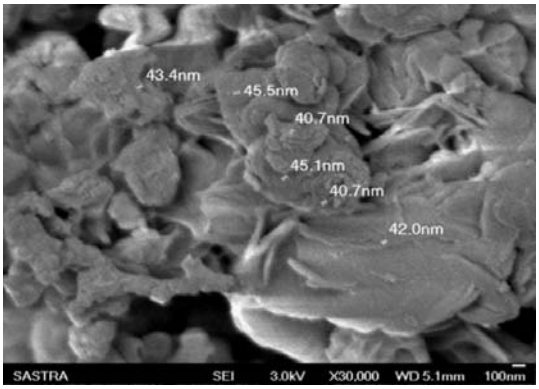


Fig 3: SEM micrograph of nZVI powder

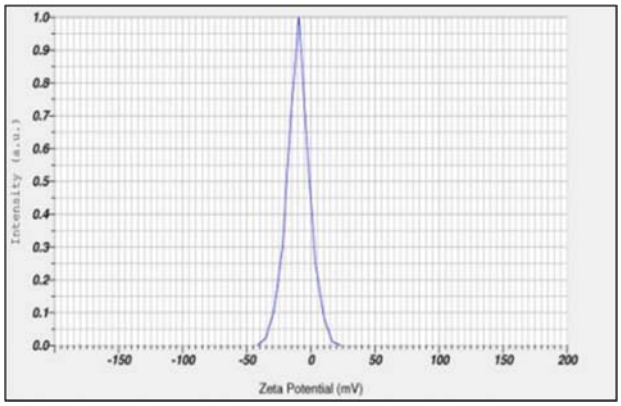


Fig 4: Zeta potential of nZVI powder

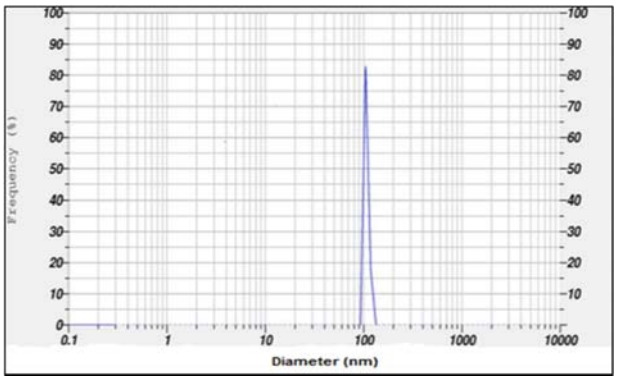


Fig 5: Size (DLS) of nZVI powder

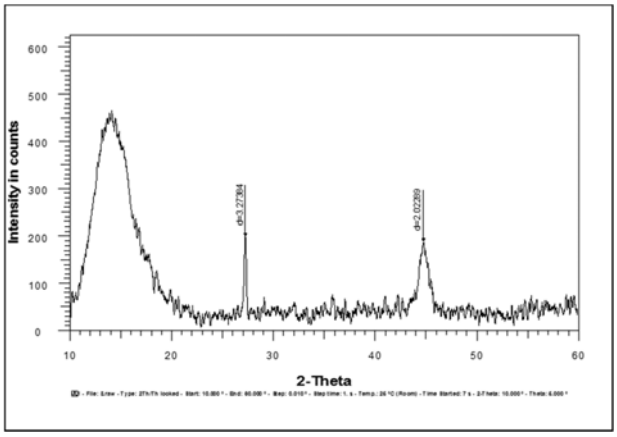


Fig 6: XRD of nZVI powder

Conclusion

In this study nZVI was synthesized and characterized. Stable nZVI were successfully synthesized in the laboratory using iron sulphate, EDTA and sodium borohydride. The size, zeta potential, morphology, surface area and shape of synthesized nZVI were characterized using DLS, XRD, FTIR TEM, BET and SEM respectively. In present study we synthesized nZVI with <100nm size, zeta potential -9.9mv, XRD analysis 2θ value of 45° indicates the formation of nZVI in zero valent state, TEM images also show that most particles formed chain-like aggregates with <100nm size, Surface area 20.96 m^2/g, SEM micrographs of nZVI powder studied and the changes in particle shapes and sizes were distinctly visible. The characterization results clearly show that the present synthesis method would be useful to synthesize and could solve long pending stability issue of nZVI for its adaptable applications in environmental remediation. The nZVI has

quite a lot of advantages such as low cost, easy preparation and high reactivity compared to other nanoparticles.

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