

## PREPARATION AND CHARACTERIZATION OF ZERO VALENT IRON NANOPARTICLES

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In the present work, nano scaled zero valent irons (nZVI) were synthesized in ethanol medium by the method of ferric iron reduction using sodium borohydride as a reducing agent under atmospheric conditions. The obtained iron nanoparticles are mainly in zero valent oxidation state and remain without significant oxidation for weeks. A systematic characterization of nZVI was performed using UV, XRD, SEM, TEM, PSA and BET studies. The obtained iron nanoparticles consist of a zero valent core surrounding a rest oxide shell. The diameter of iron nanoparticles was predominantly within the range 50-100 nm.

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### 1. Introduction

Nanotechnology is the engineering and art of manipulating matter at the nano scale (1–100 nm) [1–3]. The iron nanoparticle technology has received considerable attention for its potential application in groundwater treatment and site remediation. Recent studies have demonstrated the effect of zero valent iron nanoparticles for the transformation of halogenated organic contaminants and heavy metals. In addition, several studies demonstrated that zero valent iron is effective at stabilization or destruction of a host of pollutants by its highly reducing character. From these aspects, zero valent iron (ZVI) is proposed as one of the best reactive materials in permeable reactive barrier (PRB) technology [4]. At nanoscales, the specific surface area of zero valent iron increases dramatically and hence the surface reactivity of nanoscaled iron particles is enhanced 30 times higher remediation rate than compared to 325 mesh iron powder [5]. Over the last few years, extensive laboratory studies have demonstrated that nanoscaled zero valent iron (nZVI) was used to destruct or stabilize halogenated hydrocarbons [6], carbon tetrachloride [7] and polychlorinated biphenyls (PCBs) [8] etc. In addition, nanoscale iron particles are effective for the transformation of a wide array of common environmental contaminants like chlorinated organic solvents [9], organochlorine pesticides [10], organic dyes [11], various inorganic compounds [12] and metal ions. Several field tests have demonstrated the promising prospective for in situ remediation [13].

Over the last few years, various synthetic methods have been developed to produce iron nanoparticles, modify the nanoparticle surface properties and enhance its efficiency for field delivery and reactions [14-15]. The most widely used method for environmental purposes is the borohydrate reduction of Fe(II) or Fe(III) ions in aqueous media. In the above studies, the synthesis of nZVI was performed in inert conditions to keep iron in its zero valent form. However, the synthesized zero valent iron is unstable in atmospheric conditions and it tends to form oxides/hydroxides in the forms of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and FeOOH [16]. Over the last few years many

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research papers have been published to synthesis the iron nanoparticles in aqueous medium, while synthesis of iron nanoparticles in ethanol medium is still limited in a peer reviewed journals and has not been well documented. Hence, the objective of this present investigation is to synthesis zero valent iron nanoparticles in open air in presence of ethanol to prevent massive oxidation and to characterize the synthesized materials in terms of its size and surface properties.

## 2. Experimental methods

The iron nanoparticles were synthesis in a flask reactor in ethanol medium with three open necks as illustrated in Fig. 1. The following is the reaction,

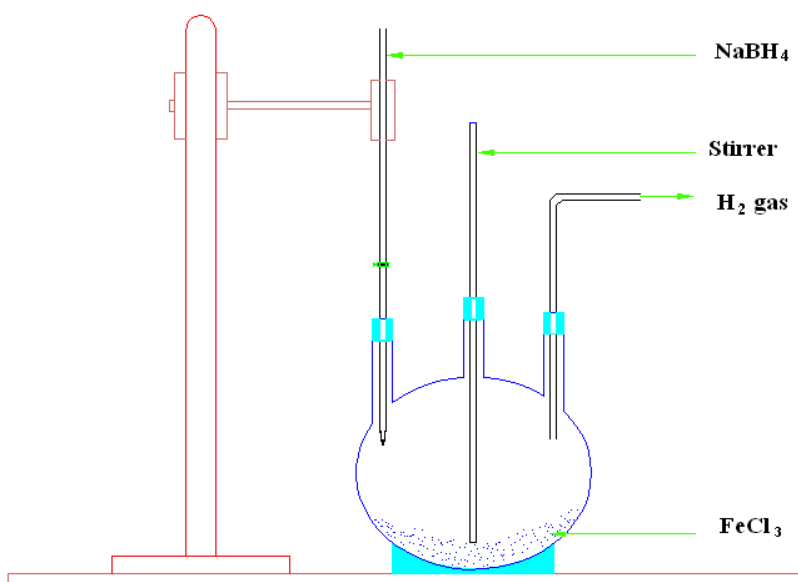


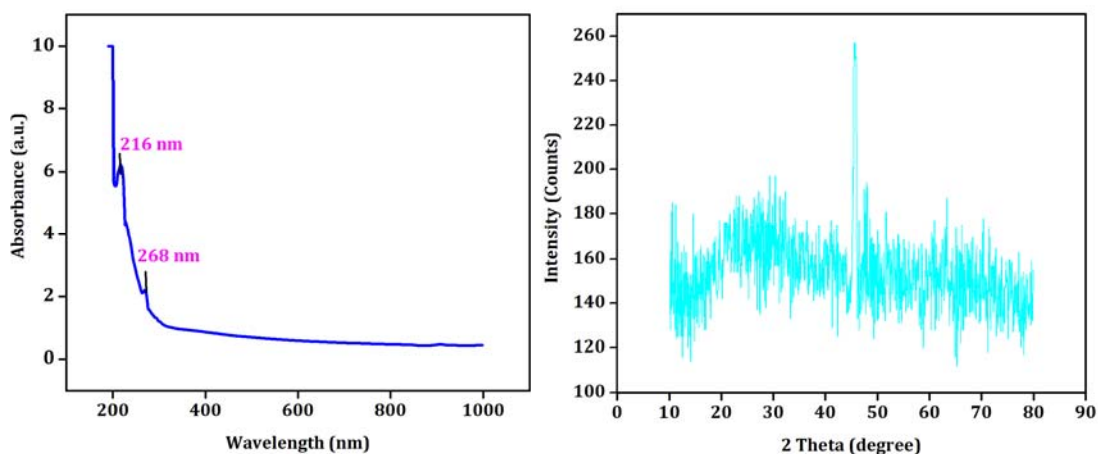
Fig. 1. Schematic diagram for synthesis of iron nanoparticles

For the synthesis of nanoscale Zero Valent Iron (nZVI); 0.5406 g FeCl<sub>3</sub>.6H<sub>2</sub>O was dissolved in a 4/1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water) and stirred well. On the other hand, 0.1 M sodium borohydride solution was prepared i.e., 0.3783 g NaBH<sub>4</sub> was dissolved in 100 ml of deionized water; since for better growth of iron nanoparticles excess borohydride is needed. The borohydride solution is poured in a burette and added drop by drop (1 drop per 2 seconds) into iron chloride solution with vigorous hand stirring. After the first drop of sodium borohydride solution, black solid particles immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction. The mixture was left for another 10 minutes of stirring after adding the whole borohydride solution. The vacuum filtration technique was used to separate the black iron nanoparticles from the liquid phase. Two sheets of Whatman filter papers were used in filtration. The solid particles were washed three times with 25 ml portions of absolute ethanol to remove all of the water. This washing process is probably the key step of synthesis since it prevents the rapid oxidation of zero valent iron nanoparticles. The synthesized nanoparticles were finally dried in oven at 323 K overnight. For storage, a thin layer of ethanol was added to preserve the nano iron particles from oxidation.

### 3. Results and discussion

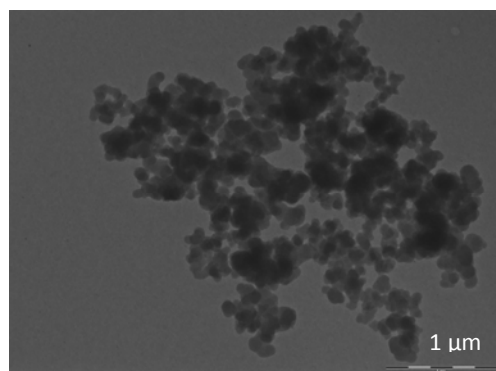
In the present work, nanoscaled (50-100 nm) zero valent irons (nZVI) have been synthesised in ethanol medium by the method of ferric iron reduction using sodium borohydride as a reducing agent under atmospheric condition. The iron nanoparticles are mainly in zero valent oxidation state and remain without significant oxidation for weeks. A systematic characterisation of nZVI has been performed using UV, XRD, SEM, TEM, PSA and BET studies. The UV Visible spectrum of nano iron particle is shown in Fig. 2a. The two absorption peaks at wavelengths of 216 nm and 268 nm indicates the formation of nano iron particles. Fig. 2b shows the 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  $2\theta$  of  $45^\circ$  indicates that the zero valent iron is predominantly present in the sample.

Fig. 2c shows the SEM image of freshly synthesized iron nanoparticles. It can be observed that the iron particles are in the form of nanospheres, which exist in contact with each other and form chains having diameters of 50-100 nm. This linear orientation is nearly due to the magnetic properties of iron species [17].

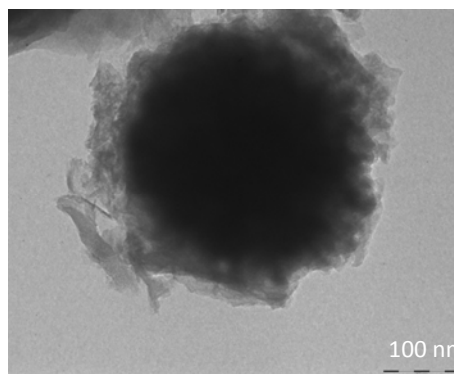


a) UV images of iron

b) XRD pattern of iron



c) SEM images of iron



d) TEM images of iron

Fig. 2. UV, XRD, SEM and TEM images of iron nanoparticles.

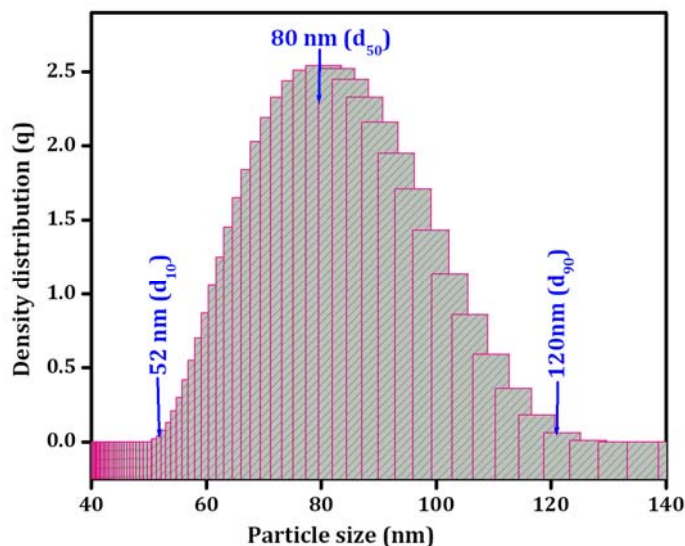


Fig. 3. Particle size distribution of iron nanoparticles

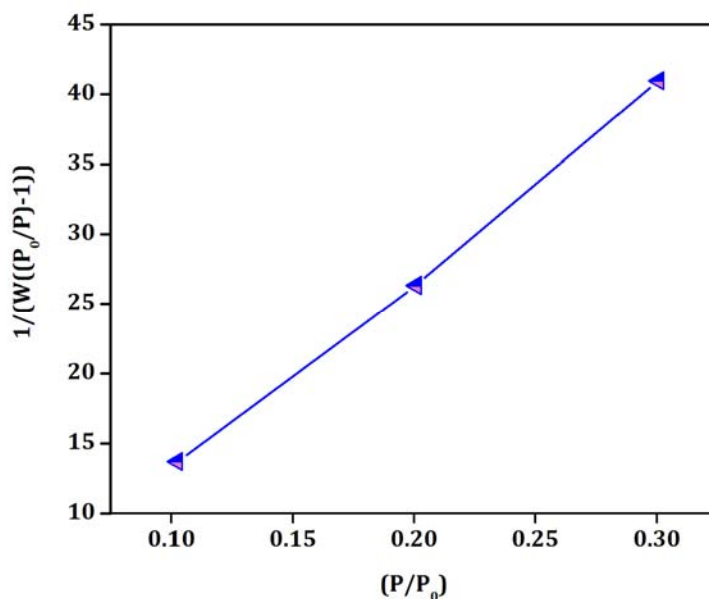


Fig. 4. BET surface area plot of iron nanoparticles

Transmission Electron Microscopy image of iron nanoparticles is shown in Fig. 2d. The spheres having diameters of around 100 nm can be distinguished from each other and is in agreement with SEM results. With closer inspection, the metallic iron and iron oxide phases can be distinguished from the corresponding color contrast in TEM images. The lighter regions are mainly on the surface of the particle and the dark regions are concentrated in the center of the particle (Fig. 2d). One can know that a TEM instrument is designed so that the elements with higher atomic numbers seem darker than the ones with lower atomic numbers. One can conclude with the above point in mind that the average atomic number of central elements is higher than the average atomic number of the surface elements. The core is formed of metallic iron and the surface (shell) is formed of iron oxides. In addition, the particle size distribution of nano iron is also measured using Nanophox particle size analyser. The particle size distribution (PSD) of iron nanoparticles are presented in Fig. 3. The iron particles have a mean diameter of 80 nm

(designated as  $d_{10}=52$ ,  $d_{50}=80$  and  $d_{90}=120$  nm). The above results indicate that the iron nanoparticles are entirely within the nanoscale domain. The particle size obtained from particle size analyser has been exactly correlated with the manual measurements of particle size from TEM images. The difference in particle size measurement from TEM and particle size analyser is very less.

*Table 1 Nitrogen physisorption data of nano iron.*

$P/P_0$	Surface area $\text{m}^2 \text{g}^{-1}$	Total pore volume $\times 10^3 \text{cc g}^{-1}$	Average pore diameter $\text{\AA}$
0.1	26.00	10.32	16.21
0.2	26.58	11.85	18.62
0.3	25.55	13.02	20.16

The BET surface area values were determined as  $25 \text{ m}^2 \text{ g}^{-1}$  for nZVI as shown in Fig. 3. Some of the BET surface area values reported in literature are  $14.5 \text{ m}^2 \text{ g}^{-1}$  [14],  $33.5 \text{ m}^2 \text{ g}^{-1}$  [18] and  $36.5 \text{ m}^2 \text{ g}^{-1}$  [19]. In comparison, commercially available Fe powder ( $<10 \mu\text{m}$ ) has a specific surface area of just  $0.9 \text{ m}^2 \text{ g}^{-1}$  [18]. The increase in specific surface area means an increase in the total amount of iron on the surfaces. The nitrogen physisorption data of nano iron is shown in Table 1. Therefore, it is evident that nanoscaled zero valent irons (nZVI) (50-100 nm) with good properties are synthesised in ethanol medium by sodium borohydride reduction method under atmospheric condition.

#### 4. Conclusions

Nanoscaled zero valent iron (nZVI) (50-100 nm) was synthesized in ethanol medium by borohydride reduction method under atmospheric conditions. It was observed that iron nanoparticles are mainly in zero valent oxidation state and that no significant oxidation took place for weeks of storage under atmospheric conditions. The characterization of the nZVI was performed using UV, XRD, SEM, TEM, BET studies and indicated partial dispersion of the chainlike structure of iron nanoparticles. From the results of TEM, it was observed that iron nanoparticles consist of a zero valent core and surrounding an oxide shell. The iron nanoparticles tend to form chain like structures with a particle size in the range 50-100 nm. BET surface area of pure nZVI was determined as  $25 \text{ m}^2 \text{ g}^{-1}$ . The nanoparticles have strong tendency to form microscale aggregates likely due to the weak surface charges.

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