Comparative study on iron removal using chemically and greenly synthesised zero-valent iron nanoparticles

Antony Jismy, V Meera and P Raphael Vinod

1Department of Civil Engineering, Government Engineering College Thrissur, Kerala, India
2Department of Chemistry, Government Engineering College Thrissur, Kerala, India
3APJ Abdul Kalam Technical University, Kerala, India
4Email: jismykannappilly@gmail.com

Abstract. As an adsorbent, the nano zero-valent iron (nZVI) has gained attention among researchers for the removal of pollutants like metallic ions from water. The high surface area and resulting high reactivity of nZVI make it a promising material for water/wastewater treatment. The uptake behaviour of iron on nZVI has not been investigated so far. The aim of the study is to compare greenly synthesised (GnZVI) and chemically synthesised (CnZVI) nano zero-valent iron in terms of size, functional groups and stability and to explore the feasibility of utilizing it for iron removal from water. In this study, the liquid-phase reduction technique was used to synthesis nZVI. Sodium borohydride as well as Amaranthus Dubius leaf extract were used as the reductants in this process. Characterization study of nZVI was performed using UV, FTIR, XRD and TEM. The peaks obtained at 312 nm and 316 nm in UV-Vis spectrum for chemically and greenly synthesised particles respectively, confirmed the formation of nanoparticles. The FTIR spectrum revealed the presence of C=O, C-O stretching and –CH bending vibrations of bonds. It was found that the CnZVI nanoparticles were largely spherical with size ranging from 80 nm-99 nm whereas GnZVI nanoparticles were in the range of 1nm-3nm. For an influent total iron concentration of 0.5ppm with Fe²⁺/Fe³⁺ ratio as 2.5:0.5, total iron removal efficiencies of 54.00% and 35.19% were achieved by CnZVI and GnZVI respectively, at pH of 6.85 and contact time of 3 hours.

1. Introduction
Nowadays, the heavy metal iron is a major concern in environmental and industrial research. The pollution from iron and steel industries, mining and metal corrosion causes the increasing rate of iron concentration in surface water. Similarly, leaching from iron bearing rocks and minerals are the main reasons for the presence of iron in groundwater [1]. The presence and persistence of iron in the tissues cause conjunctivitis, choroiditis, and retinitis. The excess amount destroys progenitor cells and microenvironment for hematopoiesis and in turn leads to hematopoiesis[2]. The higher concentration of iron in water should be treated unless it can cause hemochromatosis, a condition that adversely affects the internal organs of human body. The World Health Organization (WHO) has set 0.3 ppm as permissible concentration for iron in drinking water. The increasing rate of iron contamination and its stringent standard for drinking water creates an urge for the development of iron removal techniques. Adsorption is an advanced and effective technique used to remove heavy metal contaminants from water [3, 4]. Various adsorbents like fly ash, clay, zeolites, biomass, biopolymers, micro-organisms and activated carbon were used for removing iron. Nowadays, nano zero-valent iron treatment has
emerged out to be a latest technique to effectively remove metal ions from water (Cr$^{6+}$, Cu$^{2+}$, Ag$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Ba$^{2+}$, As$^{3+}$, As$^{5+}$ and Co$^{2+}$)[5-7]. Nano iron particles have significant surface area to weight ratio which results in greater density of reactive sites and efficient removal of heavy metals. Heavy metals are removed either by reduction (e.g., Cu$^{2+}$, Ag$^{2+}$) or adsorption (e.g., Zn$^{2+}$, Cd$^{2+}$) at the nZVI surface [8]. The standard reduction potential of the contaminant heavy metal is the controlling mechanism for removal.

Synthesis of nano zero-valent iron can be achieved by a variety of chemical and biosynthesis methods. Simplicity of chemical reduction makes it as the most frequently used method for nZVI synthesis. Nanoparticles can also be biosynthesised using plant extracts due to its reducing ability. Green synthesis is not only environment-friendly, but also inexpensive [9]. Various photo chemicals present in leaves of amaranth species like amaranthine, iso-amaranthine, phenols, flavanoids, and lysine can act as reducing agents and thereby used for synthesis of nanoparticles. This study mainly aims to compare the properties of nZVI, synthesised using sodium borohydride reduction, as well as by green synthesis from Amaranthusdubius (A. dubius) leaf extract. The study was also investigated the adsorption capability of nZVI towards contaminant iron in aqueous solution.

2. Materials and Methods

2.1 Materials

The chemicals ferrous sulphate heptahydrate (FeSO$_4$.7H$_2$O), ammonium ferrous sulphate ((NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O), ammonium ferric sulphate (NH$_4$FeSO$_4$), ethylene diaminetetraacetic acid (EDTA), sodium borohydride (NaBH$_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH), hydroxylamine hydrochloride (NH$_2$OH.HCl), ammonium acetate (NH$_4$C$_2$H$_3$O$_2$), acetic acid (CH$_3$COOH) and 1,10-phenanthroline monohydrate (C$_{12}$H$_8$N$_2$·H$_2$O) were purchased from Merck Millipore and supplied by chemik, Thrissur, Kerala.

2.2. Chemical and green synthesis of zero-valent iron nano particles

The chemical reduction method for synthesising nZVI was carried out as follows: 0.1 M FeSO$_4$.7H$_2$O (150 mL) and 0.05 M EDTA (100 mL) was mixed in a round bottomed flask. The reducing agent (0.75 M NaBH$_4$, 100 mL) was added drop wise into the mixture solution[10]. Black particles were immediately formed after the first drop of NaBH$_4$ addition and afterward the excess sodium borohydride was added totally to accelerate the reduction reaction. Slowly the solution turned to black colour.

$$\text{FeSO}_4 + \text{EDTA} \rightarrow \text{Fe}^{2+}(\text{EDTA}) + \text{SO}_4^{2-} \quad (1)$$

$$\text{SO}_4^{2-} + 2\text{NaBH}_4 \rightarrow 2\text{BH}_4^- + \text{Na}_2\text{SO}_4 \quad (2)$$

$$2\text{Fe}^{2+}(\text{EDTA}) + 4\text{BH}_4^- + 16\text{H}_2\text{O} \rightarrow 2\text{Fe}^{0}\text{(EDTA)} + 4\text{H}_2\text{BO}_4^- + 20\text{H}_2 \quad (3)$$

The leaf extract for the green synthesis of nZVI was prepared as follows: fresh leaves were collected from A. dubius plant. It is thoroughly washed with deionised water. About 20 gm of finely chopped leaves was made to get heated with 100 mL distilled water at 50$^0$C for a period of 45 minutes. The Whatmann filter paper grade 1 was used to filter the supernatant. The leaf extract was preserved at 4°C for later use. The pH level of leaf extract was adjusted to 6 with the addition of 0.1N NaOH and 0.1N HCl. About 40 mL of leaf extract was added as droplets to a mixture of 0.1 M FeSO$_4$.7H$_2$O(75 mL) and 0.05 M EDTA (25 mL) accompanied by continuous stirring on magnetic stirrer for a time span of 90 minutes. The yellow coloured mixture solution was turned to blackish green colour, upon addition of leaf extract. A black precipitation was noticed at the bottom which indicates the presence of green synthesised nano zero-valent iron (GnZVI) [10-13].

Both precipitates of CnZVIs and GnZVIs were collected by centrifugation at 3000 rpm for 10 minutes and quickly washed thrice with ethanol. Prepared particles were dried in an oven at 50 °C and were stored in sealed bottles under dry conditions.
2.3 Characterization studies

UV-Vis spectrophotometer (Systronics 2202) was employed to analyse spectrum of nanoparticle solution before and after synthesis in the range 200-900 nm to ensure the formation of zero-valent iron nanoparticles.

The TEM analysis of freshly prepared nZVI was done with Jeol/JEM 2100 instrument at 200 kV acceleration voltages to inspect the morphology and surface characteristics. The XRD patterns were recorded with a Bruker D8 Advance diffractometer which contains a high-power CuKα (\(\lambda = 1.54 \text{ Å} \)) source working at 40 kV/40 mA. The characteristics of functional groups were detected from the FTIR spectrum by using Thermo Nicolet Avtar 370 model spectrometer in the range 400–4000 cm\(^{-1}\).

2.4 Batch study for iron removal from aqueous solution

Batch experiments were carried out using both CnZVI and GnZVI under the same set of conditions to compare iron removal efficiency from aqueous solution containing Fe\(^{2+}\) and Fe\(^{3+}\) ions. Blank experiments (without addition of nanoparticles) were considered as parallel control. On an average, the ratio of Fe\(^{2+}/Fe^{3+}\) in surface water was found to be 2.5:0.5, even though it shows wide seasonal variations [14]. Therefore, this ratio was fixed as 2.5:0.5 in aqueous solution for the batch study. 1000 ppm stock solutions of Fe(II) and Fe(III) ions were prepared by dissolving 7.02 gms of ammonium ferrous sulphate and 4.72 gms of ammonium ferric sulphate in 500 mL of distilled water, respectively. 0.42 ppm ferrous iron solution and 0.08 ppm ferric iron solution was prepared from stock solutions and mixed to obtain a sample having 0.5 ppm total iron concentration (Fe\(^{2+}/Fe^{3+}\)=2.5:0.5). The pH of this solution was found to be 6.85. 200 mL of 0.5 ppm miron solution was taken and 1 g/L of nanoparticle (either CnZVI or GnZVI) was added. These samples were kept in an orbital shaker and given continuous stirring at 100 rpm for 1 h, 2 h, 3 h, 6 h, 12 h and 24 h. After the fixed time intervals, 50 mL of samples were taken and allowed for settling of 20 minutes. The supernatant was collected; centrifuged and finally magnetic stirring was given for the separation of nanoparticles from the treated sample. The concentration of iron in the control and clear extract solution were determined by using UV-Vis spectrophotometer based on the Phenanthroline method.

3. Results and discussion

3.1 Characterization studies

The formation of nano zero-valent iron particles was ensured by measuring UV-Vis spectrum in the wavelength ranges from 200-900 nm. As shown in the Figure 1(a), 1(b) and 1(c), a shift in the absorption peaks was observed from 425 nm to 312 nm and 316 nm for chemically and greenly synthesised particles respectively, which confirmed the formation of nanoparticles[11-12, 14].

![Figure 1. UV-Vis spectrum of (a) Fe\(^{2+}\)-EDTA solution before reduction (b) Solution containing CnZVI (c) Solution containing GnZVI](image)

The morphological features and surface characteristics of the greenly and chemically synthesised nanoparticles were obtained from Transmission Electron Microscopy (TEM). The chemically prepared
zero-valent iron nanoparticles were largely spherical with size ranging from 80 nm–99 nm and greenly synthesised particles were in the range 1nm-3nm. The nanoparticles appeared agglomerated, forming chain-like formations due to its high surface energy, strong dipole-dipole magnetic interactions and Van der Waals forces, as expected [15, 16] (Figure 2 and Figure 3). The conceptual structure of the nZVI can be seen from the Figure 2 as the dense core of a single particle surrounded by a thin shell, which shows notably less contrast than the interior iron core [17-19]. It is seen that the connected nanoparticle chains have a continuous shell, but, a thinner interfacial layer separates the individual iron cores from one another [20].

![Figure 2. TEM images of freshly prepared CnZVI](image1)

![Figure 3. TEM images of freshly prepared GnZVI](image2)
The XRD patterns of freshly prepared CnZVI and GnZVI are depicted in Figure 4(a) and 4(b). The diffraction peak at 2θ=44.6° in Fig. 4(a) indicates that the prepared CnZVI exists in zero-valent state and is persistent without corrosion [21]. In Figure 4(b), the 2θ peaks at 44.84 and 53.4 corresponds to zero-valent Iron (ZVI) and iron- oxohydroxide (FeOOH), respectively. However, an additional peak at 26.8 in GnZVI is possibly due to interaction of biomolecules with iron nanoparticles [11].

FTIR spectrum of CnZVI and GnZVI are shown in Figure 5(a) and 5(b) respectively. The peaks located at 1630 cm\(^{-1}\) and 1625 cm\(^{-1}\) reveal the presence of strong C=O stretching vibrations and peaks at 1107 cm\(^{-1}\) and 1112 cm\(^{-1}\) are associated with C-H bending vibrations. Weak signals observed at 617 cm\(^{-1}\) and 613 cm\(^{-1}\) are assigned to C-O stretching and –CH bending vibrations respectively [16, 22-24]. The absorption peak at 3485 cm\(^{-1}\) in CnZVI can be ascribed to O-H stretching vibration of carboxylic groups. As shown in Figure 5(b), the peak observed at 3251 cm\(^{-1}\) in GnZVI can be assigned to the stretching vibrations of –NH or –OH groups of amaranthine pigment and phenolic compounds present in the A. dubius leaf extract [11]. Moreover, abundant oxygen functional groups seen in the FTIR spectrum of freshly prepared nZVI could serve as accessible sites for adsorption.

![Figure 4. XRD pattern of (a) CnZVI (b) GnZVI](image)

![Figure 5. FTIR spectrum of (a) CnZVI (b) GnZVI](image)

### 3.2 Batch study for iron removal from aqueous solution

The percentage removal of iron species with contact time is presented in Figure 6. It can be observed that iron is adsorbed rapidly during the first 3 hours, beyond which, there is no significant change with time. The number of active sites on the nZVI surface is more and iron concentration is high at initial
stage. Therefore, these active sites are rapidly interacting with contaminant iron. The CnZVI and GnZVI achieved a total iron removal efficiency of 54.00% and 35.19 % respectively after 3 hour contact time. After 3 hours, the adsorbed amount reached equilibrium due to the slow diffusion of Fe^{2+}/Fe^{3+} ions to the nanoparticles. Treatment with CnZVI resulted in an effluent iron concentration of 0.24 ppm which is within the drinking water standards.

In light of the previous literatures, the reactivity of the nano zero-valent iron particles can be related with the standard reduction potential (SRP) of iron. The structure of the nano zero-valent iron, as suggested by Yan et al., 2010 [25], comprises of metallic iron core and surrounding oxide shell. The SRP of iron core was reported as -440 mV and is good reductant in water [5,8]. According to Li and Zhang, 2007[8], the metals having SRP more negative or very close to that of zero-valent iron, reduction doesn’t occur for the contaminant metal ions and the ions are removed by pure sorption or complex formation. Therefore, it is recommended that contaminant iron is fixed by iron oxo-hydroxide layer on nZVI surface through surface complexation and/or electrostatic interactions. Furthermore, the oxide layer consists of boron (mostly in +3 oxidation state) in addition to iron oxide and it was reported that this boron can enhance its resistance against oxidation. [26]. This boron is formed from the sodium borohydride in CnZVI and is absent in GnZVI. The biomolecules such as flavonoids, iso-amaranthine and phenolic compounds present in leaf extract even though take part in reduction of Fe^{3+} to Fe^{0} and yield smaller particles, their presence in the surface may reduce the adsorption sites and in turn resulted in lower removal efficiency.

![Graph](image.png)

**Figure 6. Iron removal efficiency with contact time**

4. Conclusions

In this study, zero-valent iron nanoparticles were prepared by both chemical reduction and green synthesis, and further evaluated for their potential in removing contaminant iron from aqueous solutions. The XRD pattern and UV−Vis spectrum confirmed the formation of nanoparticles. FTIR spectrum of CnZVI and GnZVI showed the presence of C=O, C-O stretching and –CH bending vibrations of bonds present in EDTA. FTIR analysis of GnZVI further revealed the presence of main reducing agents in the leaf extract such as flavonoids, isomaranthine and phenolic compounds. The batch study conducted with influent iron concentration of 0.5mg/l at near neutral pH, indicated that CnZVI has good removal efficiency and could bring the effluent iron concentration to the desirable limit of potability. Thus CnZVI can be an effective and versatile material for the contaminant iron removal. Removal efficiency could be further enhanced with optimization of reaction parameters as well as surface modifications of nZVI.
Acknowledgement
This research was funded by AICTE through the NDF-RPS scheme for the NDF research scholars. The authors would like to thank the Sophisticated Test and Instrumentation Centre (STIC, CUSAT), CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram and Centre for Materials for Electronics Technology (C-MET), Thrissur for providing facilities for characterisation studies.

References
[1] Khatri N., Tyagi S. and Rawtani D., 2017, Recent strategies for the removal of iron from water: A review, J. Water Process Eng. 19, 291–304
[2] Alimohammadi V., Sedighi M. and Jabbari E., 2017, Experimental study on efficient removal of total iron from wastewater using magnetic-modified multi-walled carbon nanotubes, Ecol. Eng. 102, 90–97
[3] Gangadhar G., Maheshwari U. and Gupta S., 2013, Application of nanomaterials for the removal of pollutants from effluent streams, Nanosci. & Nanotechnology-Asia 2, 140–150
[4] Boparai H. K., Joseph M. and Carroll D. M. O., 2011, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, J. Hazard. Mater. 186, 458–465
[5] Yan W., Herzing A. A., Kiely C. J. and Zhang W. X., 2010, Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water, J. Contam. Hydrol. 118, 96–104
[6] Ji B., Shu Y., Li Y., Wang J., Shi Y. and Chen W., 2018, Chromium (VI) removal from water using starch coated nanoscale zerovalent iron particles supported on activated carbon, Chem. Eng. Commun. 0, 1–8
[7] Li X., Lei L., Yang C. and Zhang W. X., 2010, Reduction of Cr(VI) by nanoscale zero valent iron (nZVI): The reaction kinetics, 4th International Conference on Bioinformatics and Biomedical Engineering, iCBBE
[8] Li X. Q. and Zhang W. X., 2007, Sequestration of metal cations with zerovalent iron nanoparticles - A study with high resolution x-ray photoelectron spectroscopy (HR-XPS), J. Phys. Chem. C 111, 6939–6946
[9] Stefaniuk M., Oleszczuk P. and Ok Y. S. 2016, Review on nano zerovalent iron (nZVI): From synthesis to environmental applications, Chem. Eng. J. 287, 618–632
[10] Agents D. C., 2010, Preparation of stable zero valent iron nanoparticles using different chelating agents, J. Chem. Pharm. 2, 67–74
[11] Harshini M., Iswarya C. N. and Matheswaran M., 2015, Biogenic synthesis of iron nanoparticles using Amaranthus dubius leaf extract as a reducing agent, Powder Technol. 286, 744–749
[12] Pattanayak M. and Nayak P. L., 2013, Green synthesis and characterization of zero valent iron nanoparticles from the leaf extract of azadirachta indica (neem), World J. Nano Sci. Technol. 2, 6–9
[13] Journal A. and Studies M. 2015, Green synthesis of zero valent iron nano particles from coriandrum sativum (coriander) and its application in reduction chemical oxygen demand and biological oxygen demand in waste water, South-Asian Journal of Multidisciplinary Studies 5, 132–139
[14] Subin M. P., Anitha C. T. and Sidhimol P. D., 2011, The study of water quality of tripunithura, a city suburb of ernakulam district in Kerala, India, Nature Environment and Pollution Technology 10, 583-588
[15] Bao T, Damtie M. M, Hosseinzadeh A. and Frost R. L., 2020, Catalytic degradation of P-chlorophenol by muscovite-supported nano zero valent iron composite: Synthesis, characterization, and mechanism studies. Appl Clay Sci., 195, 23-34
[16] Zhang Q, Wang Y, Wang Z, Zhang Z, Wang X and Yang Z., 2021, Active biochar support nano zero-valent iron for efficient removal of U(VI) from sewage water. J Alloys Compd., 852, 993-1001.
[17] Kanel S. R., Nepal D., Manning B. and Choi H., 2007, Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation, *J. Nanoparticle Res.* **9**, 725–735

[18] Desalegn B., Megharaj M and Chen Z. and Naidu R., 2019, Green synthesis of zero valent iron nanoparticle using mango peel extract and surface characterization using XPS and GC-MS, *Heliyon* **5**, 175-184

[19] Zhang X, Shi D, Li X, Zhang Y, Wang J and Fan J. 2019, Nanoscale dispersing of zero-valent iron on CaCO₃ and their significant synergistic effect in high performance removal of lead. *Chemosphere*. **224**, 390-397

[20] CelebiO., Uzum C., ShahwanT. and ErtenH. N., 2007, A radiotracer study of the adsorption behavior of aqueous Ba²⁺ ions on nanoparticles of zero-valent iron, *J. Hazard. Mater.* **148**, 761–767

[21] CirtiuC. M., RaychoudhuryT., Ghoshal S. and MooresA., 2011, Systematic comparison of the size, surface characteristics and colloidal stability of zero valent iron nanoparticles pre- and post-grafted with common polymers, *Colloids Surfaces A Physicochem. Eng. Asp.* **390**, 95–104

[22] ShiL. na, ZhangX. and liang ChenZ., 2011, Removal of Chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron, *Water Res.* **45**, 886–892

[23] RathorG., ChopraN., Tapan Adhikari I., Gopal RathorC. and AdhikariT., 2017, Synthesis and characterization of Nano particles of zero-valent iron for environmental remediation, *Int. J. Chem. Stud.* **5**, 282–285

[24] Li J.H., Yang L. X. and Li J.Q,2019, Anchoring nZVI on metal-organic framework for removal of uranium(VI) from aqueous solution. *J Solid State Chem.* **269**, 16-23

[25] Yan W, Herzing A.A, Kiely C. J. and Zhang W.X., 2010, Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water. *J Contam Hydrol.* **118**, 96-104

[26] YangF., ZhangS., SunY., Cheng K., Li J. and TsangD. C. W., 2018, Fabrication and characterization of hydrophilic corn stalk biochar-supported nanoscale zero-valent iron composites for efficient metal removal, *Bioresour. Technol.* **265**, 490–497