

# Characterization of zero valent iron used for nitrate removal in drinking water

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## Introduction

Nitrogen is one of the important pollutants present in drinking water are runoff from fertilizer use; leaking from septic tanks, sewage; and erosion of natural deposits. When nitrate is absorbed in to blood hemoglobin is converted to methemoglobin. Methemoglobin does not carry oxygen efficiently. This results in reduced oxygen supply to vital tissues such as the brain. Severe methemoglobinemia (blue baby syndrome) can result in brain damage and death. In recent years, considerable efforts have been made to remove nitrate in water. The use of zero valent iron to remove nitrate from water represents one of the latest innovative methods in the reducing process. The major reduction product was ammonia. Zero valent iron in contrast with iron powder have some advantages of specific surface area, high active surface, which lead to a increased denitrification rate of nitrate.

## Materials and Methods

### Surface titrations

Surface titration was carried out as a function of the concentration of NaCl to determine  $pH_{zpc}$  (Point of Zero net proton Charge). Prior to commencement of a titration 10.0g/l zero valent iron was equilibrated at a desired ionic (0.100, 0.010, 0.001 mol dm<sup>-3</sup> NaNO<sub>3</sub>) strength. The initial pH value is around 10.0 after equilibration by adding 0.101 mol dm<sup>-3</sup> NaOH. Then, surface titration was started from pH 10.0 to 3.0 while bubbling with N<sub>2</sub> gas to prevent any interference from atmospheric CO<sub>2</sub>. All titrations were carried out in thermostatic bath at 25.0 °C. At each titration point the data versus titrant volume (0.05 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl) were measured by an auto titrator. A reverse base titration with 0.101 mol dm<sup>-3</sup> NaOH was performed to return the suspension to the original starting pH under same experimental conditions. This titration was repeated for three different ionic strength (0.10, 0.01, 0.001 mol dm<sup>-3</sup> NaCl). However, only the acid titration data were considered for the analysis. These data unit for surface charge density was calculated.

### Oxide layer thickness by the chemical oxidation of iron with copper

The aqueous Cu<sup>2+</sup> solutions were prepared from cupric chloride salt. The solution was purged with nitrogen for 10 min period to addition of Zero valent iron (ZVI) particles to strip away any dissolved oxygen from the water. A set of experiment were conducted at various initial concentrations of Cu<sup>2+</sup> with the iron particles concentration fixed at 0.1g/l. The bottles were capped, tape sealed, and agitated for 1h. After the reaction, the solutions were filtered, and the concentration of Cu<sup>2+</sup> remaining in the aqueous phase were analyzed by atomic adsorption spectrometer.

Characterization of ZVI was done to identify morphology, particle size and the structure.. X-ray diffraction (XRD), scanning electron microscopy(SEM),and Fourier Transformation Infrared spectroscopy(FT-IR) were also used to further characterize the synthesized ZVI.

## Results and discussion

Figure 01 presents SEM images of the iron particles. A single median particle size is around 150 $\mu\text{m}$  as shown in figure 01(b).

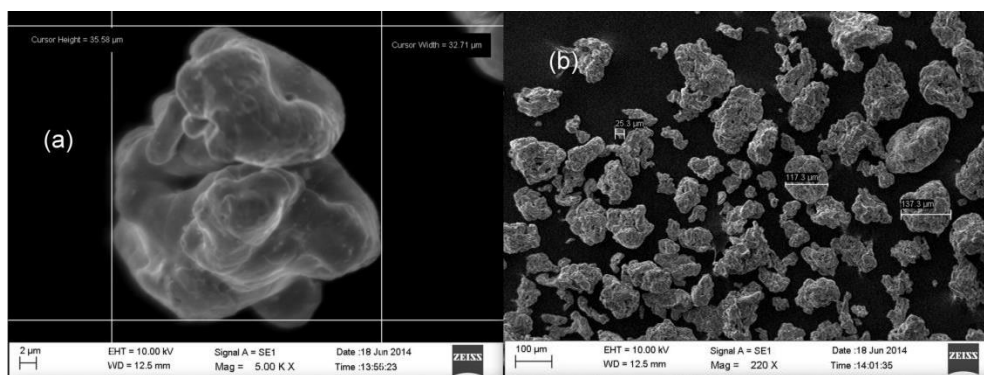


Figure 01: SEM images of (a) a single particle and (b) aggregates of iron particles

The ZVI powder having the smaller particle sizes and lower crystal structure shows a relatively broad peak. The diffraction patterns of the ZVI show that all the Fe(0) particles were single-phase cubic closest-packed structure.

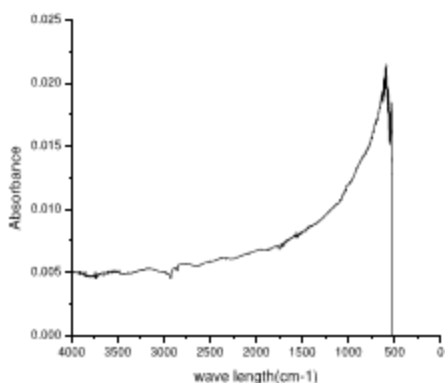


Figure 02: XRD pattern of ZVI

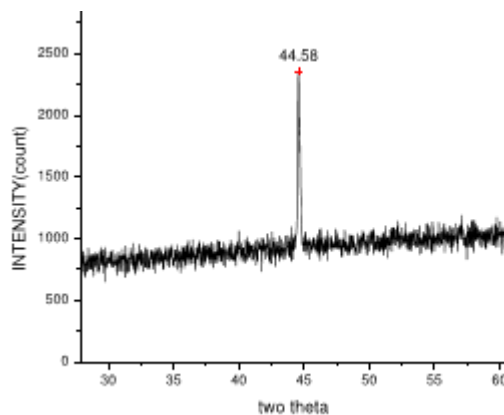


Figure 03: FTIR spectrum of synthesized ZVI

The XRD pattern in figure 02 shows that the Fe(0) standard characteristic peak of  $2\theta = 44.58$  which indicates that the crystallization of the ZVI powder.

Figure 03 shows FT-IR analysis results of all ZVI samples taken after their synthesis. Physically there was no change in colour which indicated that no oxidation or negligible oxidation of outer surface of ZVI occurred.

There was no existence of any functional group corresponding to any chelating agent used during the synthesis of ZVI.

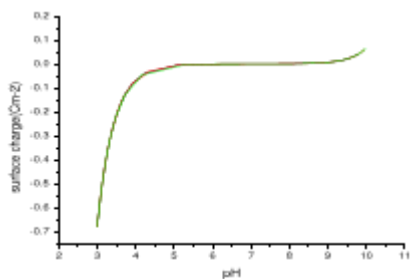


Figure 04: Zero point charge of prepared iron

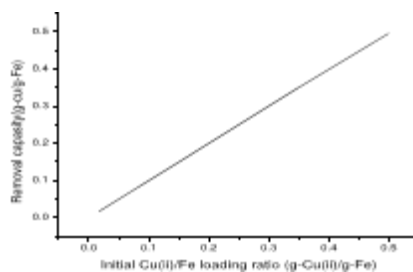


Figure 05: Removal capacity of ZVI particles at different NaCl ionic strengths at room temperature (0.001,0.01,0.1 mol $\text{dm}^{-3}$ )

Figure 4 shows the zero point charge of synthesized zero valent iron particles. The point of zero charge was obtained at approximately pH 7.31. The iron surface is negatively charged up to pH 7 but positively charged from pH 8. The surface is positive under acidic conditions but negative in basic condition. The negative surface charge density did not appear to decrease significantly with the increase of pH. Such measurements show that the effect of salt on the surface charge value is negligible.

The figure 05 shows the removal of iron particles at different Cu<sup>2+</sup>-to-Fe ratios. The shape of the curve indicates that at low initial Cu<sup>2+</sup> concentration, the Cu<sup>2+</sup> being removed per gram of iron particles increases with the initial copper concentration. The line which represents the complete removal of the Cu<sup>2+</sup>. The maximum reduction capacity can thus be estimated.

The total reduction is approximately 0.9945g of Cu<sup>2+</sup>/g of iron particles. One mole of Fe is consumed for every mole of Cu<sup>2+</sup>. Using median particles diameter of 150 $\mu\text{m}$  and the bulk densities of Fe (7.87g/cm<sup>3</sup>), FeOOH (4.28g/cm<sup>3</sup>), the thickness of the oxide shell was estimated to be 0.312 $\mu\text{m}$ .

## Conclusion

The synthesized zero valent iron was characterized with the techniques of XRD, SEM, FTIR. The average particle size of the particle is approximately 150 $\mu\text{m}$ . Point of zero charge is in the range of pH 6.83-7.31. Microscale iron particles have a core of zero-valent iron and a shell of mainly iron oxides (FeO). These dual properties of iron particles may prove to be useful for the separation of many contaminants specially nitrate from the drinking water.

## References

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