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Investigation on Nanoscale Zero Valent Iron interactions in aqueous solution

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Abstract: *Nanoscale Zero Valent Iron (NZVI) is a waste water treatment approach that is currently gaining attention due to its high efficiency on removal of various water contaminants. To understand its chemical reaction mechanisms, NZVI interactions in aqueous solution free from contaminants were investigated in this study. Several batch experiments were conducted to determine the effect of pH, temperature and dissolved oxygen on ferrous and ferric concentrations. Results showed that the elution of iron ion occurred fast in the first 10 minutes followed by an obvious depletion in concentration due to iron precipitation, and then remained constant. The concentration of ferric was higher than that of ferrous in both oxic and anoxic conditions. Acidic condition enhanced the amount of iron elution because it provided H⁺ to promote the iron elution reaction forward. The highest temperature of 90 °C condition gave highest iron concentration. However, among lower temperatures, relatively lower temperature gave higher iron concentration. These results are useful for the NZVI application on water treatment in a large scale.*

Keywords: Nanoscale Zero Valent Iron (NZVI), aqueous solution, chemical reaction mechanisms

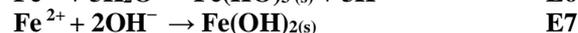
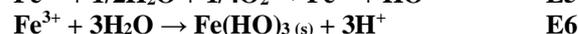
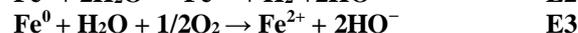
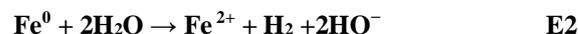
1. INTRODUCTION

Nanoscale Zero Valent Iron (NZVI) has been used as a remedy for water contamination due to its potential to treat a broad range of contaminants because of its; (i) environmental friendliness, (ii) high reactivity and (iii) cost effectiveness [1]. The outstanding characteristic of NZVI is its particle size which is at the nano scale (one-billionth or 10⁻⁹ meter). In comparison to the micro-particles, the iron nano-particles are useful owing to their greater efficiency in reduction reactions, high reactivity due to the high surface area, mobility and filtration efficiency when used in technologies for remedying a certain contaminant. The particles being in nano-size remain in suspension for a long period of time, thereby facilitating the various known applications such as water and wastewater treatment [2]. Additionally, as the particle size decreases, the proportion of atoms at the surface increases therefore raising its tendency to adsorb, interact, and react with other atoms, molecules, and complexes to achieve charge stabilization [3].

Structurally, NZVI particles are composed of a core providing the reducing power for reactions and the shell consisting of iron oxides and hydroxides which offer sites for adsorption and chemical complex formation [4]. Most of the mechanisms for contaminant sequestration by NZVI that have been studied are attributed to surface reduction and complexation. However, the structural transformation of NZVI can also affect the removal process [5]. The nano-particles naturally oxidize upon reaction with water and oxygen (i.e corrosion) [6] therefore the practical applicability of NZVI is based on the fact that it easily gets oxidized to +2 and +3 oxidation states thus reducing other organic and inorganic contaminants in the oxidation process [3]. In its interactions, metallic iron easily acts as an electron donor and it provides electrons for the reduction of pollutants:



The most relevant processes associated with the NZVI interactions in aqueous solution are displayed in equations E2-E7 [7, 8].



The first three equations are the Fe²⁺ and Fe³⁺ production reactions whereas the last three equations are consumption reactions since Fe²⁺ and Fe³⁺ are consumed to give other reaction products. It is mainly the formation of iron oxides and hydroxides that enhances the removal of contaminants through sorption and precipitation [4]. In as much as the iron oxide/hydroxide layer is formed in both oxic and anoxic conditions, the presence of dissolved oxygen (DO) may enhance the formation of the oxidation layer thus DO may be consumed in large amounts. The kinetics of Fe⁰ oxidation as well as the sorption properties of iron corrosion products can be strongly affected by the operating conditions, and some aspects concerning the relative contribution of E2-E7 to the mechanism of NZVI corrosion have not been completely clarified [7].

The intention of this current study is to explore in detail the NZVI interactions in aqueous solution counter influenced by the main variables being; pH, temperature as well as the abundant and limited oxygen supply. By conducting this research, we will have a better

understanding of the underlying mechanisms affecting NZVI which will help give a clearer and broader picture of NZVI application in real life environments. The implication of successful water treatment is the enhancement of clean water accessibility globally.

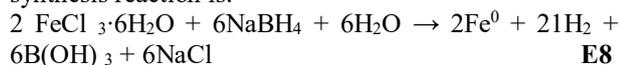
2. MATERIALS AND METHODS

2.1 Chemical and Reagents

Deoxygenated deionized (DI) water, Sodium borohydride (NaBH_4), ferric chloride (FeCl_3) and Nitrogen gas. HCl (0.1M), NaOH (0.1M), FerroVer iron reagent, Ferrous iron reagent.

2.2 NZVI synthesis and Experimental setup

NZVI was chemically synthesized by the reduction of ferric chloride with sodium borohydride. The overall synthesis reaction is:



With reference to Fig. 1, sodium borohydride solution was added dropwise (pump speed 10 RPM – 16 ml/min) to ferric chloride solution under vigorous string 250 RPM and anaerobic condition inside a 500ml round bottom 4 neck glass flask immersed in a water bath with 25 °C temperature. After stirring at 250 RMP for 20 minutes (aging time), NZVI was filtrated using vacuum filtration with a filter paper of 0.45 micrometer diameter and washed with deoxygenated DI water to remove the residual reagents. The filtration process was continued for 30 minutes with nitrogen injection to avoid oxidation of the synthesized NZVI.

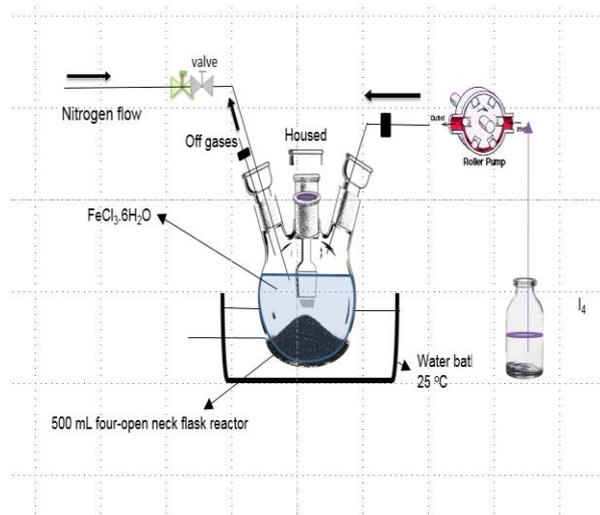


Fig. 1. Schematic diagram for NZVI synthesis.

For each set of the batch experiments, freshly synthesized NZVI was used following the synthesis procedure. The batch experiments were conducted inside the 300 ml conical flasks under continuous magnetic bar stirring and the overall time of the experiment was 168 hours (7 days). The initial conditions were: pH; 7, temperature; 23.3 °C, NZVI; 0.2g, DI water volume; 200ml. The variables were; (1) pH; 3,7,9,12, (2) oxic condition; (continuous and limited oxygen supply) whereby for the limited air supply the air was only injected into the system for 20-30 minutes and (3) temperature; 5, 20, 50, 90 °C for batch experiments 1 to 3 respectively, unless specified, the initial conditions were kept similar.

2.3 NZVI characterization and analysis

The synthesized nanoparticles were analysed and characterized by the X-ray diffraction (XRD) as well as the Transmission Electron Microscopy (TEM).

Before starting the reaction in each batch experiment, the initial pH of the aqueous solution was adjusted to the preferred value using 0.1M HCl or NaOH. Since the overall time of the experiment was 7 days, the samples were taken within the accumulative time of 10, 30, 60, 90, 120, 150 and 180 minutes during the first three hours in each batch experiment. For the next 7 days, the time interval of sampling was increased to 24 hours.

For measurement and analysis, 3ml of each sample was withdrawn by a syringe connected to a plastic tube then filtered using 0.45 μm syringe filters then the analysis was done immediately after filtered samples were obtained. Before the analysis, the analysed solution was diluted 10 times. However, the dilution in some of the batch experiments was 5, 20 and 50 times such that the values that were displayed were within the analysis instrument range. The pH was adjusted to 3-5 to suit the analysis equipment requirements. FerroVer and Ferrous iron reagents were added to the diluted samples to determine the concentration of total iron and ferrous present in each sample respectively, using the spectrometer (Hach DR 3900). USEPA FerroVer iron method was used to analyse the total iron whereas 1,10-phenanthroline method was used for ferrous analysis. The concentration of ferric was calculated by the formula: $(\text{Fe}^{3+} = \text{Fe}_{\text{total}} - \text{Fe}^{2+}) \text{ mg/L}$.

3. RESULTS AND DISCUSSION

3.1 dissolution of iron in acidic condition

Fig. 2 and Fig. 3 show the profile of iron dissolution under anoxic condition in first 3 hours and 7 days, respectively. The experiments were performed at the NZVI dosage of 1g/L and the solution pH of 3.

As shown in Fig. 2, the concentration of total iron and Fe^{2+} increased rapidly during initial time. After reaching the maximum point of 25 mg/L at 10 minutes, the concentration of total iron decreased gradually and maintained constant at 15 mg/L after 1 hour time. For Fe^{2+} , the maximum concentration was 15 mg/L and constant concentration was 5 mg/L. In terms of Fe^{3+} , the concentration of Fe^{3+} also increased dramatically to during first 10 minutes but followed by a lower increasing rate from 10 to 15 minutes. Then after a slight depletion, the concentration of Fe^{3+} stayed constant at about 10 mg/L throughout the reaction period.

It can be seen from Fig. 1 that the curve for total iron and Fe^{2+} have the same trend. This implies that the depletion of Fe^{2+} after maximum concentration is the main contribution to the depletion in total iron. After NZVI is added into water, dissolution and precipitation occur simultaneously, their occurrence coexists and they compete with each other. In the first 10 minutes, initial rapid growth is controlled by E2 in which zero valent iron reacts with water to produce Fe^{2+} and hydrogen [7]. Since NZVI is of high reactivity, the reaction speed is very high. In this period, dissolution is the dominant process.

After the concentration of Fe²⁺ reaches maximum point, the curve shows an inverse behavior and this could be due to the ferrous precipitation reaction, E7, being the dominant reaction [8]. After about 1 hour, the rate of dissolution and precipitation became equal and the concentration maintained at a constant value. However, for Fe³⁺, the precipitation process was weaker than dissolution process. Therefore the concentration curve only showed a slight depletion.

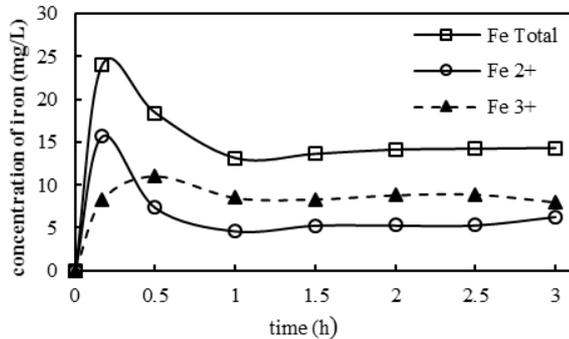


Fig. 2. Iron concentration in first three hours (NZVI dosage = 1g/L, pH = 3, anoxic condition)

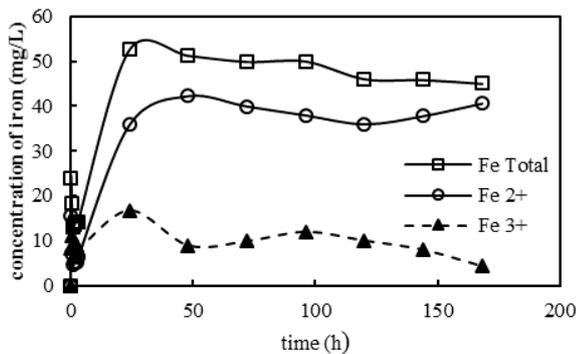


Fig. 3. Iron concentration in 7 days (NZVI dosage = 1g/L, pH = 3, anoxic condition)

In the 7-days' time scale, the concentration of total iron and Fe²⁺ increased quickly during first 24 hours, and then remained at a constant value of about 50 and 40 mg/L respectively. In terms of Fe³⁺, the concentration did not change so much during the whole reaction time. It can be observed that the concentration of Fe²⁺ is considerably higher than that of Fe³⁺ and E2 explains this observation.

3.2 Effect of controlled solution pH

The solution pH influences the concentration of iron significantly because H⁺ participates in a number of reactions. In this research, experiments were performed in the solution pH of 3, 7 and 12 to explore the effect of pH on iron concentration.

As seen in Fig. 3, the concentration of total iron decreased with the increasing pH. The dissolution of iron is considerably high in acidic pH which is about 25mg/L in maximum and 15 mg/L in the equilibrium state. However, not much difference was observed between pH 7 and pH 12, both of these two batches' constant concentration was below 5 mg/L. In Fig. 5 which is of 7-day timescale, it also shows the similar trend that the concentration of total iron in pH 3 is much higher than that of pH 7 and 12. This is because the increasing concentration of Fe²⁺ is contributed by E2 which generates OH⁻. In the presence of H⁺, E2 is enhanced to

the products side as OH⁻ is consumed by neutralizing with H⁺.

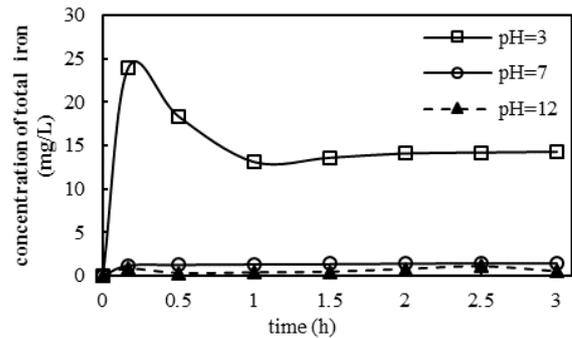


Fig. 4. Effect of pH in first 3 hours (NZVI dosage = 1g/L, anoxic condition)

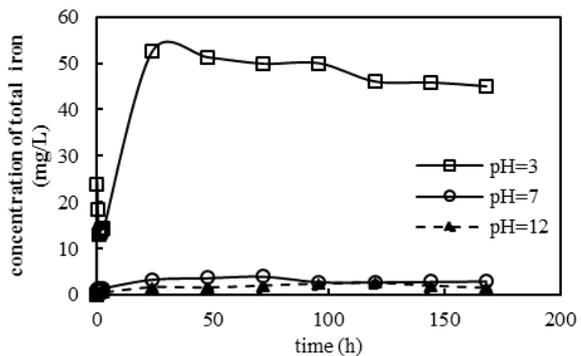


Fig. 5. Effect of pH in 7 days (NZVI dosage = 1g/L, anoxic condition)

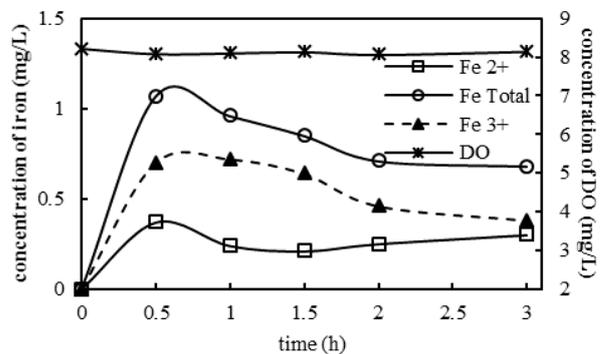


Fig.6. Effect of oxygen (NZVI dosage = 1 g/L, oxalic condition, pH = 7)

3.3 Effect of oxygen

Similar batch experiments were performed under oxalic condition by continuous injection of oxygen during the whole reaction time. As shown in Fig. 6, rapid dissolution at initial phase was obtained. The concentration of total iron, Fe²⁺ and Fe³⁺ increased from 0 to about 1.1, 0.7 and 0.4 mg/L respectively. Subsequently, the concentration had a slight decreasing trend due to precipitation and remained constant throughout the reaction period. The observed trend of Fe³⁺ being larger than Fe²⁺ in terms of concentration is in agreement with Juan et al [7] results. The explanation of the behavior is that Fe²⁺ is oxidized to Fe³⁺ and the formation of Fe³⁺ species from NZVI involves two consecutive processes whereby during the first stage, metallic iron is oxidized to Fe²⁺ iron by heterogeneous reactions while on the second stage Fe²⁺ ions get oxidized to Fe³⁺ ions (E5), and this can be both homogeneous and heterogeneous [7].

3.4 Effect of temperature

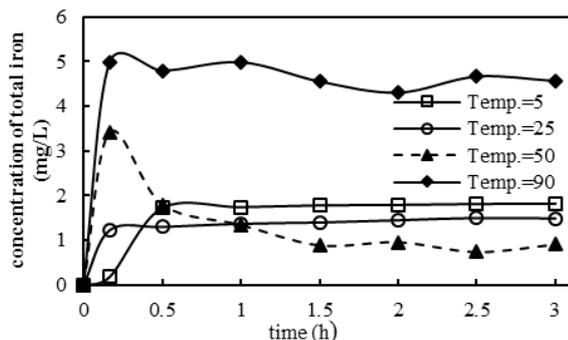


Fig. 7. Effect of temperature (NZVI dosage = 1 g/L, anoxic condition, pH = 7)

The solution temperature also has a significant influence on the dissolution of iron. Fig. 7 shows the iron dissolution in first 3 hours of four different temperatures. From the initial growth phase, larger increasing slope was obtained at higher temperature, which means higher the temperature may lead to a higher reaction rate during first few minutes after reaction started. From the general concentration amount, it is obvious that the batch under 90 °C had the highest concentration. This is because when temperature is high, the space between two iron atoms increases, therefore water molecules will easily occupy the larger space and react with iron, subsequently the dissolution amount increase. However, it shows an opposite trend in terms of lower temperatures. The final constant total iron amount of batches at temperature of 5, 25 and 50 °C are about 1.8, 1.5 and 0.9 mg/L, which means iron dissolution shows a reverse proportion to temperature. It should be mentioned that for temperature 50 °C, iron concentration reached a maximum point of 3.4 mg/L at 10 minutes, and then dropped to 1.5 mg/L gradually due to iron dissolution, while that of other temperatures didn't show this trend.

4. CONCLUSION

When NZVI reacts with water, the concentration of Fe^{2+} increased rapidly in the initial period due to intensive dissolution of iron followed by a depletion due to iron precipitation. In the case of Fe^{3+} , the precipitation process was much weaker and the concentration only showed a slight depletion. The constant concentration of Fe^{2+} after 1 hour was lower than that of Fe^{3+} . The iron concentration in the process of NZVI interacting with water is effected by pH, oxygen condition and temperature. In terms of pH, lower pH enhanced the dissolution of iron by accelerating E2. In the presence of oxygen, the precipitation rate of iron after reaching maximum point is lower compared with anoxic condition. The highest temperature of 90 °C condition gave highest iron concentration. However, for the temperature case, relatively lower temperature gave higher iron concentration.

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