

SYNTHESIS OF NANO-SIZED IRON FOR REDUCTIVE DECHLORINATION.

2. Effects of Synthesis Conditions on Iron Reactivities

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(received February 2005, accepted July 2005)

Abstract : Nano-sized iron was synthesized using borohydride reduction of Fe^{3+} in aqueous solution. A wide range of synthesis conditions including varying concentrations of reagents, reagent feeding rate, and solution pH was applied in an aqueous system under anaerobic condition. The reactivity of nano-sized iron from each synthesis was evaluated by reacting the iron with TCE in batch systems. Evidence obtained from this study suggests the reactivity of iron is strongly dependent on the synthesis solution pH. The iron reactivity increased as solution pH decreased. More rapid TCE reduction was observed for iron samples synthesized from higher initial Fe^{3+} concentration, which resulted in lower solution pH during the synthesis reaction. Faster feeding of BH_4^- solution to the Fe^{3+} solution resulted in lower synthesis solution pH and the resultant iron samples gave higher TCE reduction rate. Lowering the pH of the solution after completion of the synthesis reaction significantly increased reactivity of iron. It is presumed that the increase in the reactivity of iron synthesized at lower pH is due to less precipitation of iron (hydr)oxides or less surface passivation of iron.

Key Words : zero-valent metals, nano-particle, pH, borate injection rate, reduction, dechlorination

INTRODUCTION

As a chemical reactant, nano-sized metals exhibit high reactivity due to increased surface area and high mobility due to small size. These characteristics led environmental scientists to explore the possibility of producing nano-sized iron for use in treating environmental organic contaminants. For example, Wang and Zhang synthesized nano-sized iron and bimetallic nano-sized iron (Pd/Fe^0) by borohydride (NaBH_4) reduction of a iron salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in an

aqueous phase, and used them as reductants for trichloroethylene (TCE) and a polychlorinated biphenyl (PCB) mixture (Aroclor 1254).¹⁾ It was quickly recognized that nano-sized iron displays significantly greater reactivity than commercial grade micro-sized iron and has practical implication of development into a viable remedial option, with the growing awareness of the limitations of conventional permeable reactive barrier (PRB) technology.

Interests in PRB technology have intensified over the past few years, and many reports have appeared on the use of nano-sized iron to treat various types of contaminants including chlorinated ethylenes,²⁻⁴⁾ chlorinated methanes,^{5,6)} chlorinated benzenes,^{2,7)} chromium,^{8,9)} lead,^{8,9)} and

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nitrate.¹⁰⁾ These studies demonstrated that this new approach not only substantially improved contaminant degradation, but also curtailed production of undesirable byproducts from the reduction, especially for chlorinated ethylenes, of which reduction of PCE and TCE by commercial grade iron has been observed to produce *cis*-DCE and vinyl chloride.

However, most studies to date in this area emphasized bimetallic nano-sized iron (e.g. Pd/Fe⁰, Ni/Fe⁰), and it is not certain whether the enhancement in the reaction rate is due to the increased surface area of iron or to the catalytic effect of the secondary metals, or both. In fact, doping of iron with secondary metals has been observed to increase the rate of degradation of many organic compounds with commercial micro-sized iron.¹¹⁻¹³⁾ Further, no study has dealt with aspects of variable iron synthesis conditions and their possible impacts on the reactivity of produced nano-sized iron. As nano-sized metals with different size, composition, and structure were obtained from different synthesis conditions in previous studies involving the same approach of nano-sized iron synthesis as in most studies mentioned above, the reactivity of nano-sized iron is highly variable depending on the synthesis conditions.¹⁴⁻¹⁶⁾

Current study is focusing on the improvement of the activity of the metal surfaces which is usually achieved by bimetallic combination in previous studies.¹⁷⁾

The objective of this study was to identify reaction conditions that can be used to synthesize nano-sized iron with high reactivity. A wide range of synthesis conditions including reagent concentrations, reagent feeding rate and solution pH was investigated. The reactivity of nano-sized iron from each synthesis was compared by running parallel batch experiments in which the iron samples from each synthesis were reacted with a model compound, TCE.

MATERIALS AND METHODS

Materials

The same chemicals as described in the preceding paper were used in this study.

Synthesis of Nano-sized Iron

The method for synthesis of nano-sized iron was described in the preceding paper. In this study, all the procedures for iron synthesis were carried out in anaerobic condition to produce more reactive iron as evinced in the preceding paper. Details of the iron synthesis method are as follows. In an anaerobic chamber (5% H₂: 95% N₂, Coy laboratory), a Fe³⁺ solution was prepared in a filter flask by dissolving FeCl₃ · 6H₂O in water. The reductant solution was also prepared in the anaerobic chamber. After the preparation, the solutions were removed from the chamber and set up for reaction. NaBH₄ solution was added dropwise to the ferric solution by a Manostat cassette[®] pump while the solution was vigorously mixed by magnetic stirring under N₂. pH change during the reaction was monitored. As the reaction continued, a black precipitate started to form and pH steadily increased as a result of reduction of water by BH₄⁻ that generates OH⁻. Upon the completion of delivering all the NaBH₄ solution, the reaction vessel was transferred to the chamber and filtered on a Microfiber filter paper (Whatman) to retrieve the iron, and iron was washed with water three times (1L H₂O/1g Fe⁰), followed by acetone washing to expedite drying of the particles. The iron was dried under N₂ atmosphere at 120°C for 4 hrs, transferred to the chamber, retrieved, pulverized with a spatula, and stored in a vial.

Batch Experiment and Analytical Method

All experiments were carried out in 125 mL amber glass bottles (VWR), sealed with Teflon[®]-lined septa (VWR) and Mininert[®] caps (VICI). The preparation and use of reactors and controls (without iron) in 125 mL bottles was described in the preceding paper. Unless otherwise stated, all reactors and controls were prepared in duplicate. The method for analyses of TCE was also described in the preceding paper.

RESULTS AND DISCUSSION

Effect of Fe^{3+} Concentration

A series of nano-sized iron synthesis experiments was carried out with varying Fe^{3+} concentration. Different amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water to yield Fe^{3+} concentration from 0.2 to 1.2 M. NaBH_4 solutions with exactly 3 times of stoichiometric concentration for each Fe^{3+} solution were prepared. The delivery rate of BH_4^- solution was constant.

For each iron synthesis, the initial pH of the Fe^{3+} solution before adding the reductant solution (BH_4^-) and the final pH after the completion of the BH_4^- solution delivery were monitored (Table 1). The observed pseudo-first order rate constants for TCE reduction by 0.05 g nano-sized iron synthesized from different Fe^{3+} concentrations are also listed. Figure 1 shows the timecourse study of TCE reduction experiment. More rapid TCE reduction was observed for iron samples synthesized with higher Fe^{3+} concentration, giving approximately one order of magnitude difference in the reaction rate between the most and the least reactive iron samples. This significant difference in the reactivity of iron appears to be related to the solution pH under which iron is produced. The final solution pH values after the completion of the BH_4^- solution delivery are inversely proportional to the reaction rate constants obtained for each iron sample. Such an effect of solution pH on reaction rate may be evaluated in conjunction

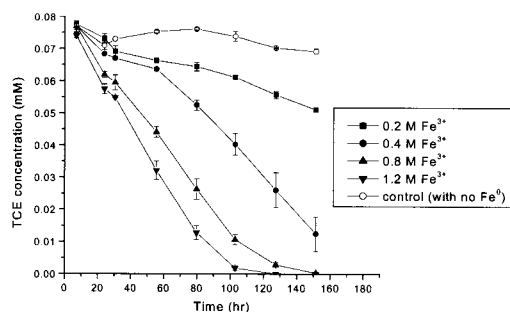


Figure 1. Effect of initial Fe^{3+} concentration on the reactivity of synthesized nano-sized iron. An iron dose of 0.05g was used for reaction with TCE. Symbols represent average value of duplicate sample concentrations and error bars represent the corresponding concentration ranges.

with the possibility of the formation of minerals other than iron. The addition of BH_4^- solution to Fe^{3+} solution induces not only the formation of iron but also other iron-bearing minerals (mostly iron (hydr)oxides) as solution pH increases due to concurrent reduction of water by BH_4^- , thereby raising the solution pH. The formation of iron (hydr)oxides depends on the solubility product (K_{sp}) of each mineral, and K_{sp} is a function of pH in a way that precipitation becomes more thermodynamically favorable with increasing pH. Therefore, the reduced reactivity of iron synthesized from low Fe^{3+} concentration is probably due to the increased formation of such minerals during the synthesis. In addition, increased solution pH might have also contributed to the decrease in iron reactivity by

Table 1. Observed pseudo first order rate constants (k_{obs}) for TCE reacted with nano-sized iron synthesized under different Fe^{3+} concentrations

Fe^{3+} (M)	BH_4^- (M)	Initial pH	Final pH	k_{obs} (hr^{-1}) ^a
0.2	0.6	1.62	9.26	2.59×10^{-3} ($\pm 4.60 \times 10^{-4}$)
0.4	1.2	1.28	8.28	8.2×10^{-3} ($\pm 3.24 \times 10^{-3}$)
0.8	2.4	1.13	7.35	1.69×10^{-2} ($\pm 5.39 \times 10^{-3}$)
1.2	3.6	0.98	4.95	2.19×10^{-2} ($\pm 7.14 \times 10^{-3}$)

^a Reported uncertainties represent 95% confidence intervals assuming the data follow the normal distribution.

inducing instantaneous passivation of iron during the synthesis at elevated pH.

Effect of NaBH_4 Concentration

The effect of NaBH_4 concentration on the reactivity of nano-sized iron was investigated by synthesizing iron using two different concentrations of NaBH_4 , and carrying out kinetics experiments with TCE. Given the same concentration of Fe^{3+} (1.2 M), NaBH_4 solutions of exact stoichiometric (3.6 M) and two times of stoichiometric (7.2 M) amounts were prepared. Similar to the iron synthesis trials with varying Fe^{3+} concentration, NaBH_4 solution was delivered at constant rate. The experimental conditions, initial and final pH, and the observed pseudo-first order rate constants for TCE reduction by 0.05 g nano-sized iron synthesized from different NaBH_4 concentrations are given in Table 2. The results of TCE reduction kine-

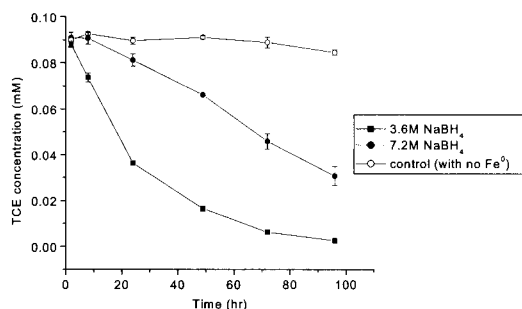


Figure 2. Effect of initial NaBH_4 concentration on the reactivity of synthesized nano-sized iron. An iron dose of 0.05g was used for reaction with TCE. Symbols represent average value of duplicate sample concentrations and error bars represent the corresponding concentration ranges.

tics with iron prepared under different NaBH_4 concentrations are shown in Figure 2. The reduction of TCE proceeded faster for iron synthesized with exact stoichiometric amount of NaBH_4 , giving about 4-fold increase in observed rate constant. As observed in the kinetics of TCE reduction by iron samples synthesized with different Fe^{3+} , it appears that the increased reactivity of iron produced with smaller amount of NaBH_4 is due to the lower solution pH maintained during the synthesis.

Effect of NaBH_4 Solution Feeding Rate

Since reduction of Fe^{3+} ($E^0 = 0.33 \text{ V}$) to Fe^0 is expected to be faster than that of water ($E^0 = -0.83 \text{ V}$) to H_2 and OH^- if the kinetics of both reduction reactions are under thermodynamic control,¹⁴⁾ one may speculate that the faster feeding rate of BH_4^- solution to Fe^{3+} solution may result in less increase in solution pH, thereby reducing the formation of other mineral phases. This hypothesis was tested by synthesizing iron with varying feeding rate of BH_4^- solution, while fixing other synthesis conditions to be the same for all trials. Also run in parallel with other reduction experiments involving iron samples synthesized with varying rate of BH_4^- solution feeding conducted in a batch reactor that contained iron synthesized using a typical method (no expedited feeding of BH_4^- solution). However the solution pH during the synthesis was kept below 5 by adding acid as necessary.

Iron synthesis conditions and calculated rate constants for TCE reduction by 0.05 g iron samples from each synthesis trial are shown in Table 3, and the timecourse is present in Figure 3. As the figure and table reveal, the faster

Table 2. Observed rate constants (k_{obs}) for TCE reacted with nano-sized iron synthesized under different NaBH_4 concentrations

Fe^{3+} (M)	BH_4^- (M)	Initial pH	Final pH	k_{obs} (hr^{-1}) ^a
1.2	3.6	0.94	4.70	3.79×10^{-2} ($\pm 4.99 \times 10^{-3}$)
1.2	7.2	0.97	8.95	1.01×10^{-2} ($\pm 3.50 \times 10^{-3}$)

^a Reported uncertainties represent 95 % confidence limits.

Table 3. Observed rate constants (k_{obs}) for TCE reacted with nano-sized iron synthesized with different addition rate of BH_4^- solution

Fe^{3+} (M)	BH_4^- (M)	BH_4^- delivery time (min)	Initial pH	Final pH	k_{obs} (hr^{-1}) ^a
0.4	1.2	5	1.20	5.50	2.70×10^{-2} ($\pm 1.24 \times 10^{-2}$)
0.4	1.2	10	1.32	6.46	1.46×10^{-2} ($\pm 6.40 \times 10^{-3}$)
0.4	1.2	40	1.13	8.35	3.87×10^{-3} ($\pm 1.17 \times 10^{-3}$)
0.4	1.2	40b	1.19	4.95	6.52×10^{-2} ($\pm 2.14 \times 10^{-2}$)

^a Reported uncertainties represent 95% confidence limits.

^b Solution pH was kept below 5 during the synthesis by adding 1 M HCl.

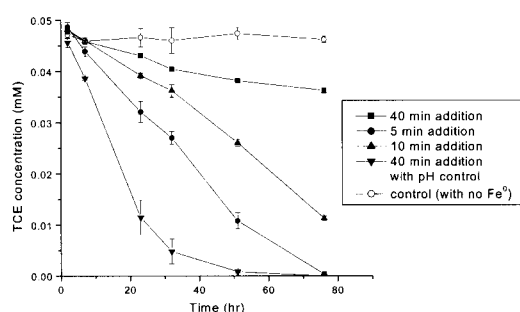


Figure 3. Effect of BH_4^- solution feeding rate on the reactivity of synthesized nano-sized iron. An iron dose of 0.05 g was used for reaction with TCE. Symbols represent average value of duplicate sample concentrations and error bars represent the corresponding concentration ranges.

feeding of BH_4^- solution to Fe^{3+} solution resulted in lower final solution pH and the resultant iron samples gave higher TCE reduction rate.

Of note in the reaction rates for different iron samples is that the iron synthesized with the typical feeding rate of BH_4^- solution (40 min for complete delivery of BH_4^- solution), while maintaining solution pH under 5, gave an even faster reaction rate than other iron samples. As shown in Table 3, the final solution pH for this iron synthesis was lower than that for other syntheses in which pH was not controlled. This result suggests that more reactive iron may be synthesized by proper control of solution pH during or after the formation of iron. Iron synthesis under solution pH control is further

discussed below.

Effect of Solution pH

Since evidence indicated the reactivity of iron is strongly dependent upon the iron synthesis solution pH, the effect of pH was further investigated by synthesizing iron with active pH control. For this, the reaction of Fe^{3+} and BH_4^- was allowed to occur under the typical feeding rate of BH_4^- solution until the complete delivery of 1.2 M BH_4^- solution into 0.4 M Fe^{3+} solution. Solution pH was, then, adjusted to the desired pH by adding acid solution. The synthesis conditions and rate constants obtained from the reduction experiments that involved reaction of 0.05 g iron samples for each synthesis with TCE are presented in Table 4, and the time-course is given in Figure 4. Higher reaction rates were obtained for iron samples retrieved from solution with lower final pH. Assuming each synthesis batch had the same amount and composition of solids (iron + other precipitates) before the addition of acid solution, the increased reactivity of iron from solution to which acid was added indicates that acid dissolved away non-reactive precipitated solids (possibly iron, too). As more acid is added, more dissolution of precipitates might have occurred, which, in turn, also reduced the amount of iron that can be retrieved. Acid washing is a commonly used method for pretreatment of

Table 4. Observed rate constants (k_{obs}) for TCE reacted with nano-sized iron synthesized under pH control

Fe^{3+} (M)	BH_4^- (M)	Initial pH	Final pH	k_{obs} (hr^{-1}) ^a
0.4	1.2	1.03	2.99	6.40×10^{-2} ($\pm 1.21 \times 10^{-2}$)
0.4	1.2	1.24	4.89	4.05×10^{-2} ($\pm 7.50 \times 10^{-3}$)
0.4	1.2	1.13	7.12	2.90×10^{-2} ($\pm 1.02 \times 10^{-2}$)
0.4	1.2	1.28	8.24	2.69×10^{-3} ^b ($\pm 2.14 \times 10^{-3}$)

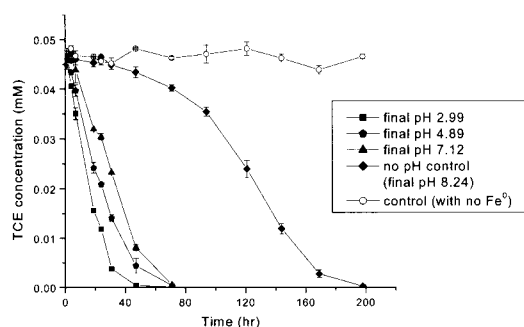
^a Reported uncertainties represent 95% confidence limits.^b Rate constant was obtained for the data up to 70hr reaction.

Figure 4. Effect of solution pH on the reactivity of synthesized nano-sized iron. An iron dose of 0.05g was used for reaction with TCE. Symbols represent average value of duplicate sample concentrations and error bars represent the corresponding concentration ranges.

commercial grade iron to remove surface oxides.¹⁸⁾ In Figure 4, comparison of the TCE reduction profile by iron from synthesis pH of 8.24 and 7.12 indicate that only a small change in pH that resulted from acid addition increased reaction rate constant by almost one order of magnitude. Therefore, acid treatment after synthesis of iron has an important role in enhancing the reactivity of iron.

CONCLUSION

A widely different synthesis conditions including reagent concentration, reductant feeding rate, and solution pH were examined in an effort to develop optimum iron synthesis protocol, and to produce highly reactive iron useful

for reductive dechlorination of chlorinated solvents.

- 1) Higher initial concentration of Fe^{3+} resulted in lower final solution pH after the formation of iron and produced more reactive nano-sized iron particles.
- 2) Lower concentration of NaBH_4 resulted in iron with higher reactivity to TCE.
- 3) Faster feeding of BH_4^- to the Fe^{3+} solution resulted in lower final solution pH and the resultant iron particles gave higher reaction rate of TCE reduction.
- 4) The final solution pH was an important factor in determining the reactivity of the nano-sized iron, showing the trend of increasing reactivity of iron with decreasing final pH.

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