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A new method to produce nanoscale iron for nitrate removal

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Key words: zero-valent iron, nanoscale, nitrate, stabilizer, ESCA, first-order reaction, electroplating

Abstract

This article proposes a novel technology combining electrochemical and ultrasonic methods to produce nanoscale zero valent iron (NZVI). With platinum placed in the cathode and the presence of the dispersion agent, 0.2 g/l cetylpyridinium chloride (CPC), a cation surfactant, in the solution, the nanoscale iron particle was successfully produced with diameter of 1–20 nm and specific surface area of 25.4 m^2/g. The produced NZVI was tested in batch experiments for nitrate removal. The results showed that the nitrate reduction was affected by pH. Al low pH, nitrate was shown faster decline and more reduction in term of g NO_3^-–N/g NZVI. The reaction was first order and kinetic coefficients for the four pHs were directly related to pH with $R^2 > 0.95$. Comparing with microscale zero-valent iron (45 μm, 0.183 m^2/g), microscale zero-valent iron converted nitrate to ammonia completely, but NZVI converted nitrate to ammonia partially from 36.2 to 45.3% dependent on pH. For mass balance of iron species, since the dissolved iron in the solution was very low (< 1 mg/l), Electron Spectroscopy for Chemical Analysis (ESCA) was used for identification of oxidation state of the surface species on the NZVI and Fe_2O_3 was recognized. Thus the reaction mechanisms can be determined.

Introduction

Treatment of nitrate contaminants by zero-valent iron (ZVI) represents one of the latest innovative technologies for environmental remediation. This research uses nanoscale ZVI for transformation of nitrate for their advantages of higher surface area and reactivity. Reductions of nitrate by ZVI have been appeared in many researches (Agrawal and Tratnyek, 1996; Siantar et al., 1996; Cheng et al., 1997; Chew and Zhang, 1998; Chew et al., 1998; Huang et al., 1998; Zawaideh and Zhang, 1998; Choe et al., 2000; Huang and Zhang, 2002; Huang et al., 2003; Westerhoff, 2003; Huang and Zhang, 2004). The metallic particles are useful in environmental applications. For example, ZVI could be injected directly into contaminated soil, sediment and aquifer for in situ remediation or served as an above ground treatment for nitrate removal. NZVI has been studied for their advantages of higher surface area and reactivity (Wang and Zhang, 1997; Lien and Zhang, 1999; Choe et al., 2000; Lien and Zhang, 2001; Zhang, 2003). Nitrate was converted to ammonia stoichiometrically by microscale ZVI, but was converted to nitrogen gas by NZVI (Choe et al., 2000). NZVI is not available in the market and is needed to be produced in the laboratory. A traditional method reported in many literatures is to use strong reducing agent $NaBH_4$ to reduce ferric ion to NZVI, as shown in Equation (1) (Wang and Zhang, 1997; Lien and Zhang, 1999; Ponder et al., 2000; Lien and Zhang, 2001; Zhang, 2003).

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 \downarrow + 3B(OH)_3 + 10.5H_2 \quad (1)$$

However, in this method, in addition to the strong reducing agent is needed, other salt such as sodium and boron are being added to water. Boron is not acceptable in the drinking water in many countries, in Taiwan for example. In this article, an electrochemical method is proposed. This method combines electrochemical and ultrasonic techniques with platinum in the cathode to produce NZVI by electroplating iron particle in the cathode but remove the nanoscale iron particle into the solution instantaneously. Transmission Electron Microscope (TEM) was used for identification of nanoscale iron particle size and Electron Spectroscopy for Chemical Analysis (ESCA) was used for identification of the oxidation state of surface species on the nanoscale iron.

The produced nanoscale particle tends to cluster together. Without the use of stabilizers, the nanoparticle could coalesce to increase their size and to reduce their reactivity (Wilcoxon and Provencio, 1999). But these effects were not well discussed. Tekaia-Elhsissen (1999) indicated polyvinyl pyrrolidine (PVP) could be used as a dispersing agent to disperse out some metal particles such as iron. Surfactant micelles using cationic surfactant were reported to prevent the iron nanoparticle clustering (Wilcoxon and Provencio, 1999). Thus, this research utilized PVP and a cationic surfactant CPC (Cetylpyridinium Chloride) as stabilizers to study the potential of iron nanoparticle coalescing.

Nitrate was reported to completely convert to nitrogen gas using NZVI (Choe et al., 2000), although mass balance data was not shown in their research. Consequently, the purposes of this research are aimed to: (1) characterize the NZVI synthesized in the laboratory; (2) assess the stability of the synthesized NZVI; (3) study the mechanisms of the nitrate removal by the synthesized NZVI.

Theories

The reaction between ZVI and nitrate is a redox reaction. Oxidative dissolution of ZVI occurs and results in the formation of metal ions. For example of iron, the following reaction takes place: $Fe^o \rightarrow Fe^{2+} + 2_e{}^-$. This makes Fe^o (ZVI) a reducing agent for many redox labile substances. Nitrite, nitrogen gas and ammonia are all possible generated species for nitrate reduction. Combining the theoretical aspects and discussions form literatures, generally, there are several pathways to categorize the possible reactions between ZVI and nitrate. Equations (2)–(4) indicate that ammonia, nitrite and nitrogen gas are all possible generated species for nitrate reduction by ZVI, where ZVI was converted to ferrous ion. Huang and Zhang (2002) reported the mechanism as shown in Eq. (5), where ZVI reacted with ferrous ion to produce Fe_3O_4 on the ZVI surface.

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O \quad (2)$$

$$Fe^0 + NO_3^- + 2H^+ \rightarrow NO_2^- + Fe^{2+} + H_2O \quad (3)$$

$$5Fe^0 + 2NO_3^- + 12H^+ \rightarrow N_2(g) + 5Fe^{2+} + 6H_2O \quad (4)$$

$$NO_3^- + 2.82Fe^o + 0.75Fe^{+2} + 2.25H_2O \rightarrow NH_4^+ + 1.19Fe_3O_4 + 0.50OH^- \quad (5)$$

Experimental methods

The electrochemical method of producing NZVI

This method is a novel technology combining electrochemical and ultrasonic methods to produce NZVI by electroplating iron particle but remove the nanoscale iron particle into the solution instantaneously. The iron particle was plated on the cathode by putting ferric chloride in the solution to reduce the ferric ion to iron particle according to the following equation.

$$\text{Cathode}: Fe^{+3} + 3e^- + \text{stabilizer} \rightarrow Fe_{\text{nano particle}} \quad (6)$$

In this experiment, 1 M $FeCl_3$ was used for the solution. An inert metal has to place in the cathode so no reaction occurred between produced iron and inert metal used in the cathode. Platinum was used in this study. Therefore, according to

Faraday's theory, iron atoms were gradually formed on the cathode. Since an iron atom is less than nanoscale, the iron particle produced on the cathode was also in the nanoscale range if these particles can be removed from cathode into solution on time before clustering. Therefore, ultrasonic vibrators with 20 kHz were used simultaneously during the reaction to provide physical energy to remove the iron particle from the cathode. The schematic diagram for the experiment is shown in Figure 1. From Figure 1, it is recognized that iron particle was produced in the cathode during the experiment while chlorine gas was formed in the anode. Direct current power supply (with voltage and ampere meters) with output voltage 0–30 V and output current 0–10 A was utilized. Ultrasonic vibrator (Enshine UC-300, 20 kHz), manufactured by Enshine Inc. Taiwan., was used. Platinum was used for both electrodes with size of 6 cm × 4 cm. Five mm thickness acrylic plastic with size 16 cm(L) × 10 cm(W) × 5 cm(H) was used for the reactor. During the experiment, 400 ml was used. 1 M $FeCl_3$ solution was used for ferric source and also for electrolytes to increase the conductivity in the system.

The detailed experimental procedures are listed in the following: In 400 ml deionized water, placing electrode in the solution, the power supply was connected the electrode and the electrolyte was added into the solution. The whole reactor was then put inside the ultrasonic vibrator (with water inside), then turned on the power of the ultrasonic vibrator. Either dispersing agent or surfactant was added into the solution to test their dispersing abilities. The precipitation on the bottom of the reactor, which is the produced nanoscale iron, was collected under oxygen free water. The produced nanoscale iron was immediately used for test for nitrate removal test.

The amount of NZVI generated was determined either by the ferric ion in the solution, dry weight of the produced iron or by the Faraday's law as shown in Equation (7), where I is the current in ampere, T is the time to pass through the solution in second, M is the molecular weight, n is charge of the metal ion and F is Faraday's constant.

$$w = \frac{ITM}{nF} \tag{7}$$

In this experiment, output voltage is 20 V with current 0.4 A. With current efficiency about 70%, the weight of generated ZVI can be determined. Furthermore, since nanoscale particle tends to coalescence to become bigger particle, a stabilizer has to be used for stored solution. In this research, a dispersion agent, polyvinyl pyrrolidine (PVP), and a cationic surfactant, cetylpyridinium chloride (CPC), both purchased from SHOWA chemicals Co., Japan, were chosen to test. Since NZVI is a very strong reducing agent, for characterizing

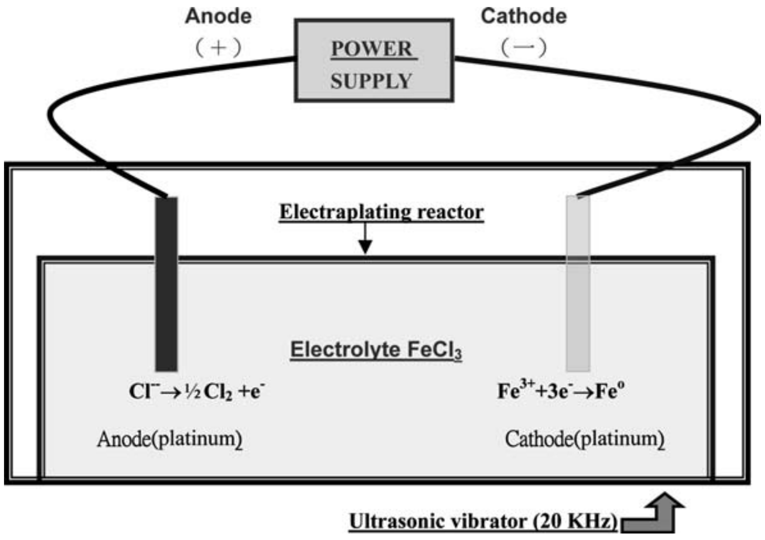

Figure 1. Schematic diagram to produce nanoscale iron by electrochemical method.

particle size by TEM, the storage solution has to be oxygen free and argon gas was used to pass through the storage solution to reduce the oxygen. For nitrate removal test, the produced NZVI was used on site immediately.

Batch experiments and analytical methods

Batch experiments were conducted in 250 ml glass bottles. Each bottle was filled with synthesized NZVI particles and nitrate solution of 20 mg/l as N. These bottles were rotated for adequate time for nitrate reduction at about 200 rpm to ensure complete mixing. pH was controlled using buffered solution of 0.2 M acetic acid (for pH 4 and 5) and 0.1 M phosphoric acid (for pH 6 and 7). Parallel experiments were also performed with laboratory grade iron powders (40 mesh, about 45 μm in diameter, purchased from RDH chemicals, Inc) to operate at pH 5. Nitrate, nitrite, ammonia and dissolved iron were measured for their residuals in water. Nitrate and nitrite were measured by a HACH Model DR-4000 spectrophotometer according to the 20th edition Standard Method (1998). Ammonium ion was measured by an ammonium ion selective electrode connected to a digital ion-analyzer pH meter. Dissolved iron was measured by GBC 932 atomic absorption. The total dissolved iron concentration was taken to be the same as the Fe^{2+} concentration since dissolved Fe^{3+} is thermodynamically unstable under nitrate reduction conditions in presence of ZVI (Huang et al., 1998). Surface areas were determined by a nitrogen sorption BET test using Micromeritics ASAP 2020 Accelerated Surface Area Analyzer. TEM (Hitachi, type H710) was used to characterize the particle size of the nanoscale iron particle. Surface characteristics and oxidation state of the ZVI species were analyzed by ESCA from Omicron Nanotechnology GmbH, Germany.

Results and discussion

Characteristics of nanoscale iron particles by electrochemical method

Based on the experimental methods, comparative studies were conducted to test the production of nanoscale iron particle and possible clustering effect with and without the addition of stabilizers. TEM was used to determine their particle sizes of the produced irons. Figure 2(a) presents TEM image of nanoscale iron particles produced by electrochemical method without stabilizers added. Comparing to the 50 nm scale shown in this Figure, without adding dispersion agent or surfactant, these iron particles tend to coalescence to become large particles and exceed the nanoscale range (1–100 nm). A dispersion agent, 0.1 g/l polyvinyl pyrrolidine (PVP), was added in the solution and the TEM image of nanoscale iron particles is shown in Figure 2(b). PVP was ineffective since there is no dispersing effect on the nanoscale ZVI. A cation surfactant, 0.1 g/l cetylpridinium chloride (CPC), was also added and the TEM image of nanoscale iron particles is shown in Figure 2(c). The dispersing effect was observed although there is still some ZVI coalesced. CPC was then increased to 0.2 g/l and the TEM image is shown in Figure 2(d). The result was more successful since all the iron particles were in the size range of 1–20 nm TEM image. Therefore, the optimum concentration 0.2 g/l CPC dose was determined.

The solution containing NZVI in Figure 2(d) was measured for the specific surface area using BET method and compared with microscale laboratory grade ZVI powders (40 mesh, about 45 μm in diameter). Table 1 present the size and surface area of nano and microscale ZVI. The size is much smaller for the NZVI and the specific surface area is 139 times than that of the microscale iron.

Mechanisms of nitrate removal by nanoscale ZVI

The produced NZVI were used in batches for kinetic study at dosage of 0.5 g/l (12.7 m^2/l), NO_3^-–N = 20 mg/l for pH 4–7. Figure 3 presents the nitrate removal *versus* time for the four pHs. Nitrate was successfully reduced by the synthesized NZVI. Nitrate was declined fast in the beginning but no more reduction after 4 h and the nitrate removals were from 60 to 78% for different pHs in this dosage. Kinetically speaking, operated at lower pH had faster nitrate decline. Figure 4 presents the determination of the kinetic coefficients for the four pHs. First order reactions were seen for these results with R^2 all greater than 0.94. Plotting the kinetic coefficients (K_{obs}) versus pH in Figure 5, K_{obs} for the four pHs are directly related with pH with $R^2 > 0.98$. A similar result was also

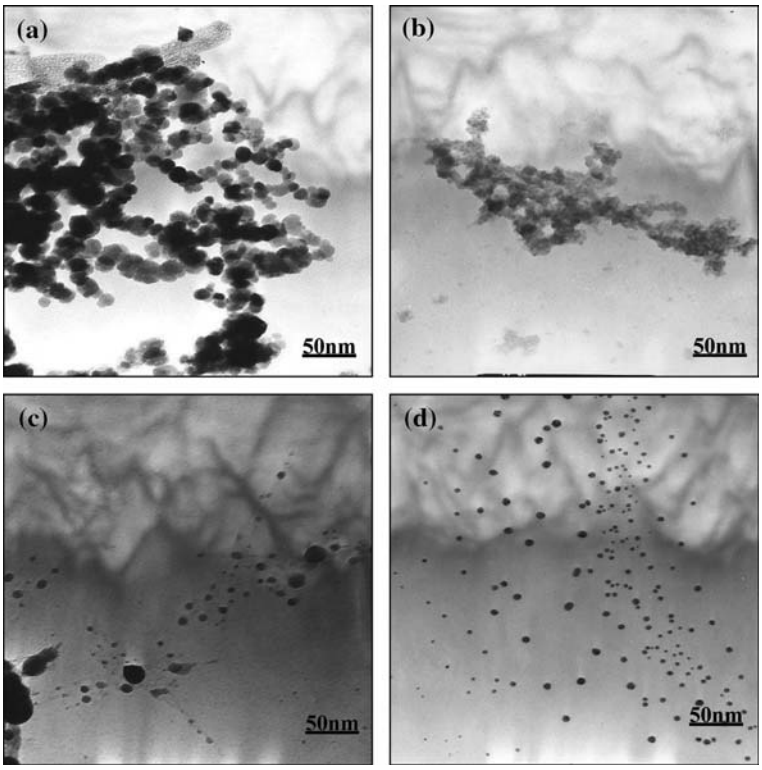

Figure 2. (a) TEM image of nanoscale iron particles without PVP or CPC added, (b) TEM image of nanoscale iron particles for 0.1 g/l PVP, (c) TEM image of nanoscale iron particles for 0.1 g/l CPC, (d) TEM image of nanoscale iron particles for 0.2 g/l CPC.

Table 1. Size and specific surface area of nano and microscale irons

Type	Particle size	Specific surface area(m^2/g)
Nanoscale	$>$ 20 nm	25.4
Microscale	45 μm	0.183

reported that first order kinetic coefficients were related with pHs for the microscale ZVI (Alowitz and Scherer, 2002).

Table 2 summarizes NZVI usage per mass of nitrate removed (mg NO_3^-–N/g NZVI). Al low pH, nitrate was reduced more in term of g NO_3^-–N/g NZVI. Assuming Eq. (2) is followed, at least 64 mg/g NZVI can be achieved. However, only from 23.78 to 31.14 mg NO_3^-–N/g NZVI or around 37–49% of NZVI were actually used. Stoichiometrically, dosage of 0.5 g/l is sufficiently to remove nitrate in these batch solutions. Since nitrate was not completely removed and only partial NZVI was used, NZVI was deactivated before they were completely used up. Formation

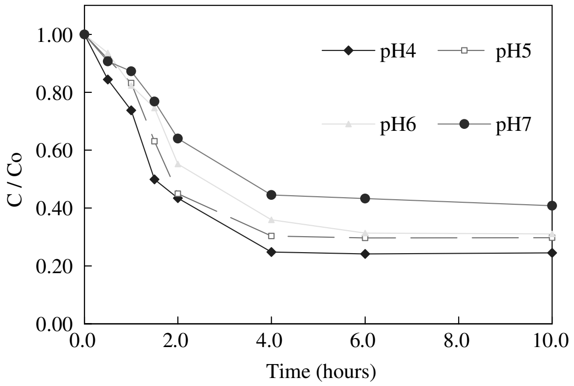

Figure 3. Nitrate reductions for the experimental results for ZVI dosage of 0.5 g/l, initial NO_3^-–N = 20 mg/l.

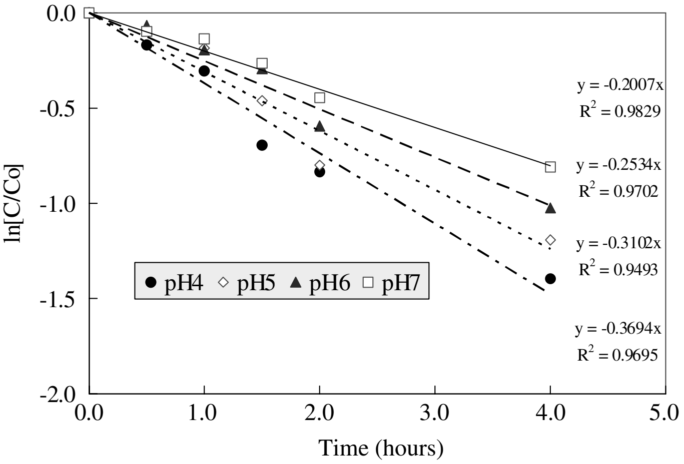

Figure 4. Determination of kinetic coefficients for different pH.

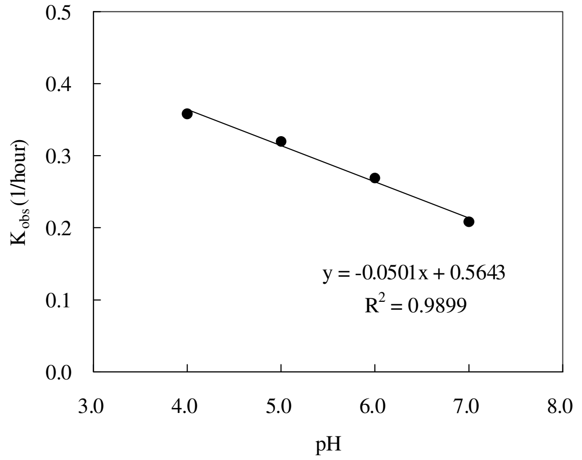

Figure 5. kinetic coefficients for nanoscale ZVI versus pH.

Table 2. The NZVI usage for different pH

pH	mg NO_3^-–N/g NZVI	mg NO_3^-–N/m^2 NZVI	*Percentage of iron usage (%)
4	31.14	1.23	48.6
5	28.28	1.11	44.2
6	27.62	1.09	43.2
7	23.78	0.94	37.2

*Based on stoichiometry in Eq. (2).

of iron oxide film was the possible reason to deactivate the NZVI, but surface characteristics of NZVI needed to be identified and is discussed in the next section.

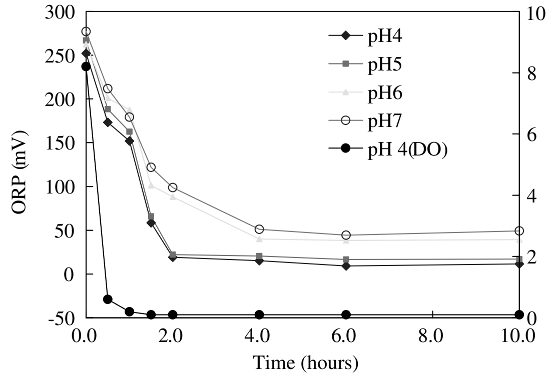

Figure 6. ORP and DO (for pH 4 only) for the experimental results for ZVI dosage of 0.5 g/l, initial NO_3^-–N= 20 mg/l.

ORPs (oxidation–reduction potentials) *versus* time for the four pHs were shown in Figure 6. ORP is an indicator where higher ORP indicated that oxidized species tend to lose electrons. From Figure 6, the ORP dropped around 250 mV when the pH was controlled. The ORP dropped more for pH 4 since more nitrates were converted to ammonia, which is more stable in reducing environment (lower ORP). Measurements of dissolved oxygen (DO) at pH 4 were also shown in Figure 6. Oxygen dropped very fast and faster than nitrate comparing with Figure 3, since the most oxidizing species in this system is oxygen from fundamental theory (Sawyer et al., 2003). Therefore, oxygen

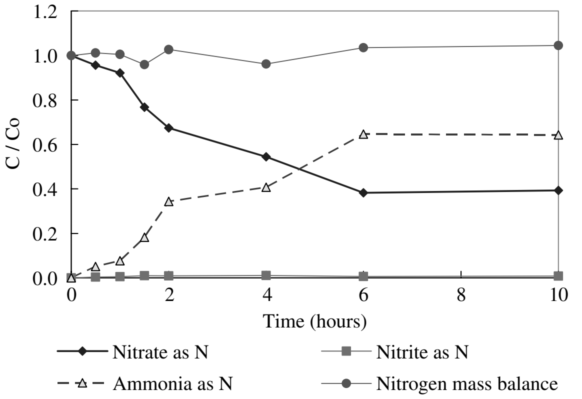

Figure 7. Mass balances for microscale iron (45 μm) at pH 5 for ZVI dosage of 0.5 g/l (0.09 m^2/l), NO_3^-–N = 20 mg/l.

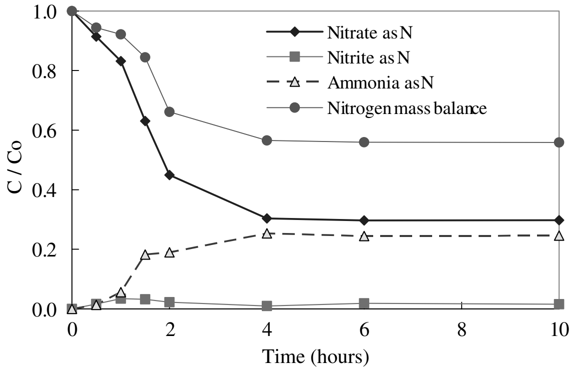

Figure 8. Mass balance for nanoscale ZVI at pH 5 for ZVI dosage of 0.5 g/l (12.7 m^2/l), NO_3^-–N = 20 mg/l.

will be removed first and the system was anoxic except in the very beginning.

Mass balance of the nitrogen and iron species

Figures 7 and 8 compare the mass balance of nitrogenous species during the reactions for the microscale ZVI and NZVI, and pHs were controlled at 5 for simultaneous comparisons for both figures. For the microscale ZVI at pH 5 in Figure 7, all the reduced nitrate were converted to ammonia. Nitrite was almost not detected. Since the percentage of ammonia + nitrite + remaining nitrate ≈ 100%, there is no other nitrogenous species generated in the system. However, for nanoscale ZVI at pH 5 in Figure 8, mass balance of the nitrogen species for ammonia + nitrite + remaining nitrate was only around 60%. It appeared that some of the nitrate was converted to other species, such as nitrogen gas as specified in Choe et al. (2000). Therefore, the mechanisms are different where part of the nitrate converted to ammonia for NZVI but all the nitrate was converted to ammonia for microscale iron. Table 3 presents the percentage of ammonia generated for different pH using NZVI. NZVI converted nitrate to ammonia partially from 36.2 to 45.3% for different pH. The most probable species for the rest is nitrogen gas, but nitrogen gas was not analyzed since head spaces of the bottles will have air, too.

Table 3. Percentage of ammonia generated from nitrate removal for different pH by NZVI

pH	NH_4^+ (%)	N_2 or other gas (%)
4	45.3	54.7
5	36.2	63.8
6	37.3	62.7
7	36.2	63.8

Dissolved iron (Fe^{2+} + Fe^{3+}) was less than 1 mg/l in the effluent solution for both Figures 7 and 8. If Eq. (2) is followed, the iron concentration should be 320 mg/l if 20 mg/l NO_3^-–N was removed. Therefore, these NZVIs were possibly converted to solid iron species instead of in dissolved form. ESCA analysis is used for identifying the solid species. The theory for ESCA is the measurement of the chemical binding state of the surface molecules determined by the chemical shift of the electronic states of the atoms involved in the reaction based their binding energy on the surface material. Figure 9 shows ESCA chromatograph and Table 4 is the result for the surface analysis of the binding energy for different orbital. From Figure 9, the binding energy is clearly important around 700 eV. O_{1s} around 530 eV would not be significant since it is in the inside shell of the iron oxide species. Hence, from Table 4, the binding energy from 719 to 704 eV with center binding energy 713 eV in Fe_{2p3} is important and identified as Fe_2O_3 according the Handbook of X-ray Photoelectron Spectroscopy(Moulder et al., 1995). Since only around 36–45% nitrate was converted into ammonia, one of the chemical equations

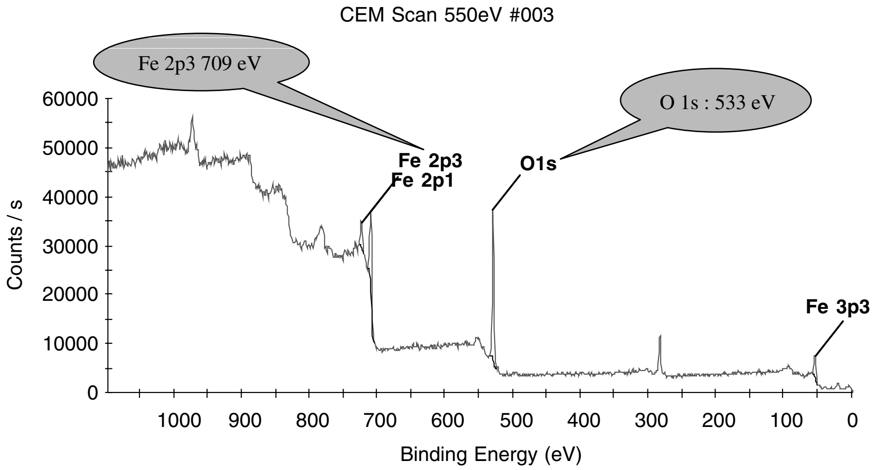

Figure 9. ESCA chromatograph for nanoscale iron surface species.

Table 4. ESCA analysis for ZVIR surface of binding energy for different orbital

Name	Start BE	Center BE	End BE	Height Counts
O 2s	31	26	21	515.01
O 1s	540	534	523	23681.1
Fe 2p3	719	713	709.23	2451.57
Fe 2p1	733	726	723	925.5

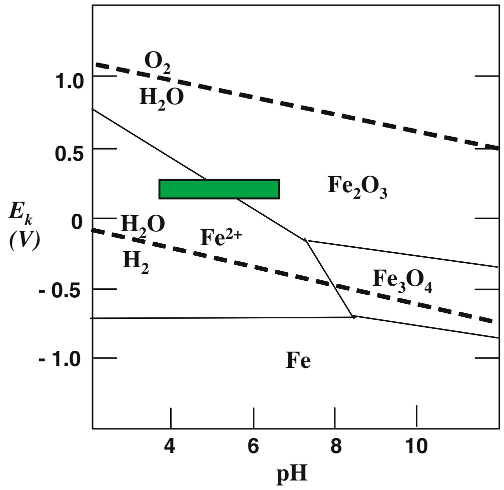

Figure 10. Pourbaix diagram based on solid species of Fe^o, Fe_2O_3 and Fe_3O_4 Source: Montgomery (1985).

between nitrate and NZVI can be proposed by the findings and shown in the followings:

$$8Fe^o + 3NO_3^- + 9H_2O = 4Fe_2O_3 + 3NH_4^+ + 6OH^- \quad (8)$$

A pE–pH predominance area diagram based on thermodynamical theory for the solid of Fe, Fe_2O_3 and Fe_3O_4 was shown in Figure 10. Fe^{2+} occurs on lower pH and ORP and Fe_2O_3 occurs on higher pH and ORP, but both species could co-exist around the Fe^{2+}/Fe_2O_3 boundary line. The shaded area in Figure 10 is the area of pH and ORP fallen on for this study. The most dominant iron specie was Fe_2O_3 when Fe^{2+} was not detected in the solution, and the results were theoretically confirmed by ESCA. Huang and Zhang (2002) reported that magnetite (Fe_3O_4) was the resulting species on the ZVI surface after reacting with nitrate, but probably due to their high resulting pH since their pH was not buffered during the reaction causing high pH and low ORP in the end of the reaction.

Conclusions

A new technology combining electrochemistry and ultrasonic vibration to produce nanoscale zero valent iron (NZVI) is proposed. With platinum placed in the cathode and the presence of the dispersion agent, 0.2 g/l cetylpyridinium chloride (CPC), a cation surfactant, in the solution, the nanoscale iron particle was successfully produced with diameter of 1–20 nm and specific surface area of 25.4 m^2/g. The produced NZVI was tested in batch experiments for nitrate removal. The results showed that the nitrate reduction was affected by pH. Al low pH, nitrate was shown faster decline and more reduction in term of g NO_3^-–N/g NZVI. The reaction was first order and kinetic coefficients for the four pHs were directly related to pH with $R^2 > 0.95$. Comparing with microscale zero-valent iron (45 μm, 0.183 m^2/g), microscale zero-valent iron converted nitrate to ammonia completely, but NZVI converted nitrate to ammonia partially from 36.2 to 45.3% dependent on pH. For mass balance of iron species, since the dissolved iron in the solution was very low (lower than 1 mg/l), ESCA were used for identification of oxidation state of the surface species on the NZVI and Fe_2O_3 was recognized. A pE–pH predominance area diagram based on thermodynamical theory can also theoretical prove the presence of Fe_2O_3 species.

Acknowledgements

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