INTERACTION BETWEEN NATURAL ORGANIC MATTER (NOM) FRACTIONS AND NANO-ZERO VALENT IRON (NZVI)

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ปฏิสัมพันธ์ระหว่างกลุ่มของสารอินทรีย์ธรรมชาติและอนุภาคนาโนของเหล็กประจุศูนย์

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สารอินทรีย์ธรรมชาติ (NOM) ในน้ำใต้ดินมีบทบาทสำคัญต่อประสิทธิภาพการกำจัดสารปนเปื้อนด้วยอนุภาคนาโนของเหล็กประจุศูนย์ (NZVI) NOM มีโครงสร้างที่หลากหลายและสามารถแบ่งตามความมีขั้วและประจุได้เป็น 6 กลุ่ม คือ ไฮโดรโฟบิกที่เป็นกรด (HPOA) ไฮโดรโฟบิกที่เป็นด่าง (HPOB) ไฮโดรโฟบิกที่เป็นกลาง (HPON) ไฮโดรฟิลิกที่เป็นกรด (HPIA) ไฮโดรฟิลิกที่เป็นด่าง (HPIB) และไฮโดรฟิลิกที่เป็นกลาง (HPIN) งานวิจัยนี้มีวัตถุประสงค์ที่จะศึกษาปฏิสัมพันธ์ระหว่างกลุ่มของสารอินทรีย์ธรรมชาติ (NOM fractions) กับ NZVI โดยใช้ตัวแทนสารอินทรีย์ธรรมชาติ (NOM surrogates) กลุ่มสารอินทรีย์ธรรมชาติที่ถูกสกัด (NOM fraction isolated) และสารอินทรีย์ธรรมชาติ (Bulk NOM) จากตัวอย่างน้ำ 2 แหล่ง คือ น้ำใต้ดิน (GWNOM) จากจังหวัดขอนแก่น ประเทศไทย และน้ำผิวดินจากแม่น้ำสุวรรณี (SRNOM) ประเทศสหรัฐอเมริกา จากการศึกษาพบว่า NOM surrogate ที่ทำปฏิกิริยากับ NZVI ได้สูงที่สุด คือ กรดฮิวมิก (HPOA) ซึ่งเป็นปฏิกิริยาที่มีการเปลี่ยนแปลงของปริมาณคาร์บอนที่ละลายน้ำ (DOC) มากที่สุด ในขณะที่ NOM surrogates ตัวอื่นๆได้แก่ แอลทริปโตฟาน (HPON) อะนิลีน (HPOB) กรดออกซาลิก (HPIA) แอลแอสพาราจีน (HPIB) และ ดีไซโลส (HPIN) มีการเปลี่ยนแปลงของ DOC น้อยมาก อาจเนื่องจากการดูดซับของ NOM บนพื้นผิว NZVI โดยพบว่าไอโซเทอมของการดูดซับแบบฟรุนดลิช (Freundlich adsorption isotherm) เหมาะสำหรับการดูดซับของตัวแทนกลุ่ม HPOA และ HPIA จากการศึกษาผลของค่าพีเอชที่ 5 7 และ 9 พบว่า NOM fractions จากตัวอย่างน้ำทั้ง 2 แหล่งทำปฏิกิริยากับ NZVI ได้ดีที่ค่าพีเอช 5 ซึ่งสัมพันธ์กับค่า DOC และค่าการดูดกลืนแสงยูวีที่ความยาวคลื่น 254 นาโนเมตร (UV_{254}) NOM fractions ของตัวอย่างน้ำ GWNOM ที่มีค่าการดูดซับบนพื้นผิวของ NZVI มากที่สุดและน้อยที่สุดที่ pH 5 คือ HPOA (6.95 มก./ก.) และ HPIN (1.42 มก./ก.) ตามลำดับ ในขณะที่ตัวอย่างน้ำ SRNOM พบว่า HPIA มีความสามารถในการดูดซับมากที่สุดที่ค่าพีเอช 5 (18.66 มก./ก.) และ HPIN มีความสามารถในการดูดซับน้อยที่สุดที่ค่าพีเอช 7 (1.45 มก./ก.) นอกจากนี้ยังพบว่า HPOA ของตัวอย่างน้ำ GWNOM มีการแข่งขันการทำปฏิกิริยากับ HPON ในขณะที่ตัวอย่างน้ำ SRNOM พบว่า HPOA เป็นกลุ่มที่ทำปฏิกิริยาหลัก กับ NZVI จากผลการศึกษาแสดงให้เห็นว่าองค์ประกอบของ NOM ที่แตกต่างกันมีผลต่อปฏิสัมพันธ์ระหว่าง NOM กับ NZVI โดยกลุ่ม NOM ที่เป็นกรดสามารถทำปฏิกิริยากับ NZVI ได้ดีกว่ากลุ่มอื่นๆ ดังนั้น ในการประยุกต์ใช้ NZVI เพื่อบำบัดสารปนเปื้อนในน้ำใต้ดินจึงควรพิจารณาถึงองค์ประกอบของ NOM ที่อยู่ในแหล่งน้ำนั้นด้วย

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KATIKA INTARASUWAN: INTERACTION BETWEEN NATURAL ORGANIC MATTER (NOM) FRACTIONS AND NANO-ZERO VALENT IRON (NZVI). ADVISOR: THUNYALUX RATPUKDI, Ph.D., CO-ADVISOR: PROF. EAKALAK KHAN, Ph.D., 71 pp.

The presence of natural organic matter (NOM) in groundwater could play an important role on removal of contaminants by nano-zero valent iron (NZVI). NOM has heterogeneous structure and could be divided into 6 fractions based on polarity and charges including hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). This study investigated the interaction between NOM fractions and NZVI using NOM surrogates. The reactivity between NZVI and NOM fractions isolated and bulk NOM from two sources including groundwater (GWNOM), Khon Kaen, Thailand and Suwannee River NOM (SRNOM), USA was also examined. The results showed that for NOM surrogates, humic acid (HPOA) had the highest interaction with NZVI while other NOM surrogates ((L-tryptophan, HPON), (aniline, HPOB), (oxalic acid, HPIA), (L-asparagine, HPIB), (D-xylose, HPIN)) had limited interactions. The Freundlich adsorption isotherm was found to fit the adsorption of HPOA and HPIA surrogates on NZVI. The results of fractionated NOM under various pH (5, 7, and 9) revealed that NOM fractions had more interaction with NZVI at pH 5 for both GWNOM and SRNOM. HPOA of GWNOM had the highest adsorption capacity (q_e) of 6.95 mg/g while HPIN yielded the lowest q_e (1.42 mg/g) at pH 5. For SRNOM, HPIA has the highest q_e of 18.66 mg/g at pH 5 whereas the lowest q_e of 1.45 mg/g was obtained from HPIN at pH 7. In addition, the effect of competitive interaction of NOM fractions was studied. HPOA was found to compete with HPON for GWNOM while HPOA remained the main fraction which reacted with NZVI for SRNOM. The findings of this study suggest that different components of NOM had different interactions with NZVI. Acid fractions tend to have more interaction than the other fractions. To apply NZVI for groundwater remediation, the composition of NOM should be considered to project the performance of NZVI for contaminant removals.

Field of Study:	Environmental Management	Student's Signature	....
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		Co-Advisor's Signature	....

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CHAPTER I

INTRODUCTION

1.1 Motivations

Nowadays, nanotechnology becomes a popular technology in many industries such as cosmetic, electronic parts, and environmental remediation. Nano-zero valent iron (NZVI) is engineered material that has been applied for groundwater remediation. Due to its size, NZVI has more specific surface areas and reactivity with groundwater contaminants than macro-zero valent iron, which was previously used. Other advantages of groundwater remediation by NZVI include easy operation and that it can be performed in situ.

NZVI is reactive against variety organic and inorganic contaminants. Organic contaminants that can be degraded by NZVI are chlorinated hydrocarbons such as hexachlorobenzene and trichloroethylene (TCE). For inorganic contaminants, cadmium (Cd), arsenic (As), and lead (Pb), perchlorate (ClO_4^-) and nitrate (NO_3^-) are removable by NZVI (Zhang, 2003; Li et al., 2006a). NZVI has been applied to contaminated sites in several countries including the U.S., Canada, Germany, Italy, and Czech Republic by injecting it through wells into contaminated areas (Li et al., 200b; Mueller et al., 2012).

Groundwater contamination has become a serious problem in recent years. Both natural and anthropogenic sources contribute to groundwater contamination. For natural sources, heavy metals in subsurface layers and rocks such as arsenic, iron, and manganese can undergo dissolution and permeate into soil and groundwater. Nitrate

(NO_3^-) in fertilizers, pesticides, and gasoline and TCE from leaky underground storage tanks are examples of contaminants from human activities (USEPA, 2009 : online)

Groundwater contains many kinds of non-contaminant substances such as bicarbonate, sulfate, and natural organic matter (NOM) that influence its characteristics including alkalinity, hardness and pH. Effect of these non-contaminant substances particularly NOM on NZVI reactivity has been studied (Hwang et al., 2011; Wang et al., 2011; Kim et al., 2012; Lv et al., 2013). The effect of NOM on NZVI reactivity has been examined using humic acid (HA) or humic substance that acts as a representative of NOM. Many studies reported that contaminant degradation by NZVI was enhanced in the presence of HA. For example, 4-chlorobiphenyl (4-ClBP) degradation (Wang et al., 2011) and nitrate reduction rate (Kim et al., 2012; Kim et al., 2013) by NZVI are promoted or inhibited depending on the NOM concentration.

Based on previous studies reviewed above, the effects of bulk NOM on NZVI reactivity are evident. However, NOM is heterogeneous in nature consisting of a variety of chemicals that can be categorized into different fractions including hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB), and hydrophilic neutral (HPIN). Reactivity of these NOM fractions with NZVI is not known. Understanding how NOM fractions interact with NZVI would be beneficial when applying NZVI to groundwater sources that have different NOM constituents. This study focuses on the interactions between different NOM fractions and NZVI. Model compounds (surrogates) representing NOM fractions and NOM fractions obtained from the groundwater, Khon Kaen Province, Thailand, and the Suwannee River, USA are examined. Six NOM surrogates including humic acid (HPOA), aniline (HPOB), L-tryptophan (HPON), oxalic acid (HPIA), L-asparagine (HPIB), D-xylose (HPIN) were studied. The effect of solution pH on the reactivity was investigated for NOM fractions. For comparison, bulk NOM from the two natural sources were also experimented. Bulk NOMs were fractionated before and after NZVI reaction to determine competition among NOM fractions.

1.2 Objectives

The main objective of this study is to investigate the interactions of NOM fractions with NZVI. The specific objectives are:

1. To determine the reactivity between NOM surrogates and NZVI,
2. To investigate the reactivity between NOM fractions from natural water sources and NZVI different solution pHs, and
3. To compare the reactivity between bulk NOM and NZVI versus that of fractionated NOM and NZVI

1.3 Scopes of the Study

1. Selected NOM surrogates and bulk NOMs from the groundwater, Khon Kaen Province, Thailand, and the Suwannee River, USA were used in this study.
2. All experiments were conducted at laboratory scales under anaerobic condition.
3. Dissolved organic carbon (DOC) is used as parameter to measure NOM concentration. UV absorbance at 254 nm (UV_{254}) is used for detecting unsaturated carbon content of NOM.

1.4 Hypotheses

1. NOM fractions have different reactivity toward NZVI. HPOA and HPIA fractions will be more reactive than other fractions.

2. Solution pH influences the reactivity between NOM fractions and NZVI. NOM fraction will be more reactive to NZVI at acidic pH than neutral and basic pH.

3. The reactivity of individual NOM fraction with NZVI and reactivity of NOM fraction in bulk solution will be different because there is competition among NOM fractions in bulk solution.

CHAPTER II

LITERATURE REVIEW

2.1 Nano-Zero Valent Iron (NZVI)

2.1.1 Nano-zero valent iron background

Zero-valent iron (ZVI, Fe^0) was first applied for water remediation to remove halogenated organic compounds in 1992 (Gillham and O'Hannesin, 1992). The ZVI was reported to have higher degradation rates of aqueous halogenated compounds than biological degradation process (Lo et al., 2006). In the past, ZVI was used as small powder called micro-scale zero valent iron (MZVI) (> 1 µm) for treating contaminated groundwater and soil. The MZVI was applied in either pump-and-treat systems or permeable reactive barriers (PRB). Over the last few decades, nano-zero valent iron (NZVI) has received attention as an environmental remediation technology and a replacement of MZVI. The superior treatment efficiency of contaminant by NZVI over MZVI was due to its smaller size (1-100 nm) compared to MZVI (> 1 µm). Thus, NZVI has more reactive sites to react with contaminants and more appropriate for in situ and ex situ applications (Zhang, 2013). Besides, a cost of using NZVI is less than MZVI based on their efficiencies (Karn et al., 2009).

2.1.2 Characteristics of NZVI

Nanoparticles including NZVI are typically defined as a material that has a dimension ranging between 1 and 100 nm. NZVI particle typically has a spherical shape that consists of core and shell (Figure 2.1). The core of NZVI is where the reduction of target contaminant occurs while the shell of NZVI is composed of iron oxides or hydroxides form due to oxidation reaction (Li et al., 2006a; Li et al., 2006b). Table 2.1 lists the characteristics of NZVI.

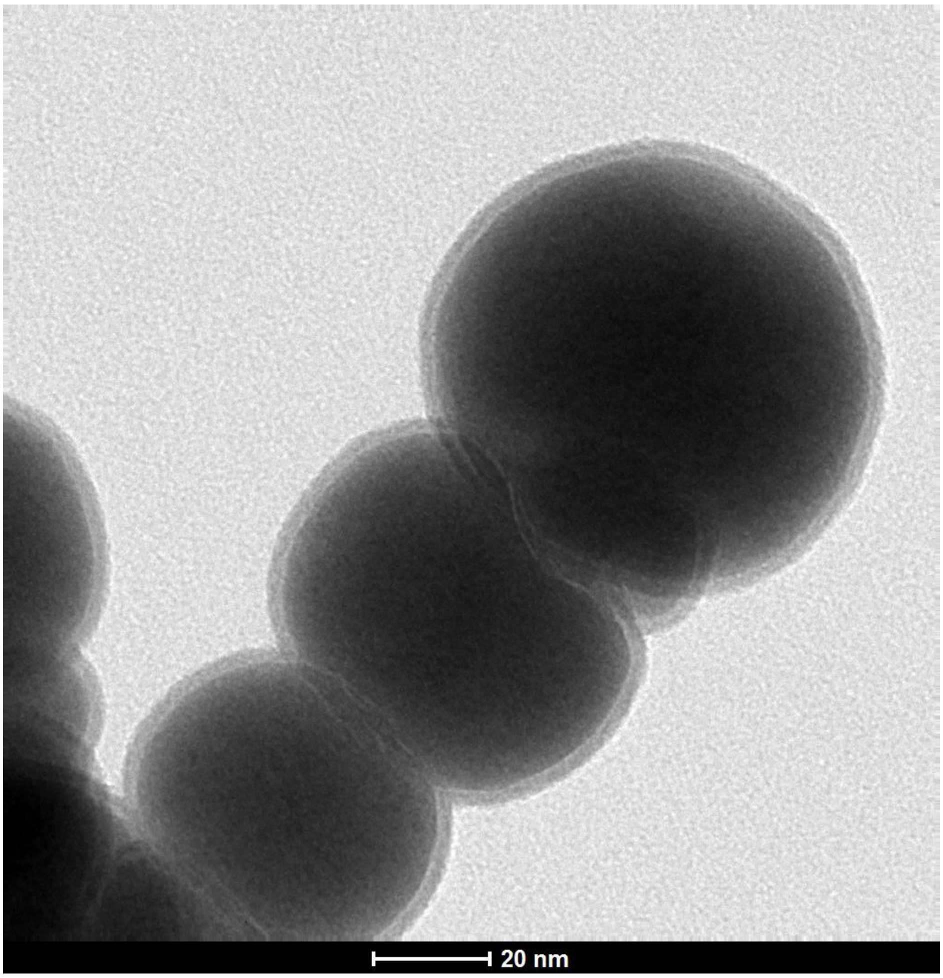


Figure 2.1 Transmission electron microscope (TEM) image of NZVI particles (285000X)

Table 2.1 NZVI properties

Properties	**Value**	**Reference**
Range of NZVI size (nm)	1-100	Li, et al., 2006
Specific surface area (m^2/g)	12.4-46.27	Zhang, 2003; Liu et al., 2005; Giasuddin et al., 2007; Zhang et al., 2010; Hwang et al., 2011; Shih et al, 2011 Kim et al., 2013;
pH_{pzc}	7.7-7.8	Giasuddin et al., 2007; Tanboonchuy et al., 2011

2.1.3 Removal mechanism of contaminant by NZVI

NZVI serves as an electron donor when reacting with contaminants as shown in Eq. 2.1.

$$Fe^0_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad (2.1)$$

Fryxell and Cao (2007) described NZVI reaction in the environment under aerobic and anaerobic conditions. Aerobic condition refers to the contaminated area that oxygen can penetrate and dissolve into; for example, shallow groundwater (oxygenated groundwater), and oxygenated soil. Under the presence of dissolved oxygen (DO) and acidic condition, NZVI (Fe^0) loses electrons to a molecule of oxygen as shown in Eq. 2.2.

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad (2.2)$$

In 2009, Kang et al. (2009) reported enhanced removal of 4-chlorophenol by zero-valent iron (ZVI) in the presence of humic acid (HA) and fulvic acid (FA). The results showed that HA and FA serving as electron shuttle to mediate electron transfer from ZVI surface to O_2 (Eq. 2.3). The products of this reaction are ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2). Under a pH range of 2-4, the Fenton’s reaction occurred. The ferrous ion (Fe^{2+}) in solution would react with hydrogen peroxide (H_2O_2)

to produce hydroxyl radical (•OH) which was more reactive for pollutant degradation as shown in Eq. 2.4.

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (2.3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2.4)$$

Moreover, Wu et al. (2014) also reported that there were two reactions involved with the reaction between humic acid and iron-iron (III) oxide ($Fe@Fe_2O_3$) core-shell nanowires under aerobic condition. The results showed that under oxic condition, the interaction involved with adsorption and subsequent oxidation of humic acid. This is because the oxygen molecule could help $Fe@Fe_2O_3$ core-shell nanowires to produce reactive oxygen species (•OH) which could oxidize humic acids. On the other hand, anaerobic condition typically occurs in most groundwater in deeper aquifers where the amount of DO is near zero or absent (Fryxell and Cao, 2007). Abundant of contaminants such as chlorinated compounds, which heavier than water, are at the bottom of aquifer. The reaction between NZVI and water is shown in Eq. 2.5.

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + H_2 + 2OH^-_{(aq)} \qquad (2.5)$$

Under anaerobic condition, the contaminants can be reduced by NZVI through oxidation-reduction reactions shown in Eq. 2.6-2.9 (Zhang et al., 2010; Wang et al., 2011).

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \qquad (2.6)$$

$$Fe^0 + Ni^{2+} \rightarrow Fe^{2+} + Ni^0 \qquad (2.7)$$

$$Fe^0 + Co^{2+} \rightarrow Fe^{2+} + Co^0 \qquad (2.8)$$

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ \; 3H_2O \qquad (2.9)$$

These aerobic and anaerobic conditions could result in different removal of contaminants. Tanboonchuy et al. (2011) revealed that the presence of DO promoted the iron corrosion rate, and enhanced arsenic adsorption onto NZVI surface. Their work showed after 10 min of reaction, As (III) was removed greater than 80%, and 52% under oxygenated, and deoxygenated conditions, respectively, while As (V) was removed 99%, and 76% after 7 min of reaction under oxic and deoxygenated conditions, respectively.

NZVI has been used to remediate several environmental contaminants. Chlorinated organic solvents and pesticides such as trichloroethane, TCE, 2,4-dichlorophenol, butachlor and alachlor were dechlorinated through reaction with NZVI (Zhang, 2003; Kim et al., 2006; Liu et al., 2007; Thompson et al., 2010; Xu et al., 2013). Heavy metals (chromium, lead, cadmium, and arsenic) and inorganic anions (NO_3^- and ClO_4^-) are from human activities (industrial disposal and mining) and natural sources (biochemical process in nature, corrosion from soil and rock). Applications of NZVI were found to successfully remove these contaminants to become less toxic (Ponder et al., 2000; Lo et al., 2006a; Liu et al., 2011). The examples of contaminants degraded by NZVI are summarized in Table 2.2.

2.1.4 Application of NZVI to environmental remediation

Based on high efficiency of NZVI for contaminant removal, NZVI has been widely applied for site remediation in Europe (Mueller et al., 2012), and in the U.S. (Karn et al., 2009). Currently, there were more than 18 sites that use NZVI to clean up soil and groundwater. For example, in Bornheim, Germany, NZVI was applied to treat tetrachloroethylene contamination at a full-scale level (Mueller et al., 2012). The Naval Air Station, Jacksonville, Florida, USA was one of the contaminated sites that used NZVI to remove TCE from groundwater (Karn et al., 2009). NZVI can be applied as in situ remediation. Due to relatively small size of NZVI, it cannot be used in PRB in the same manner as MZVI (granular iron). Alternatively, NZVI was injected directly into contaminated zone (Figure 2.2). It is noted that more than single injection well may be needed to cover the entire contaminant plume.

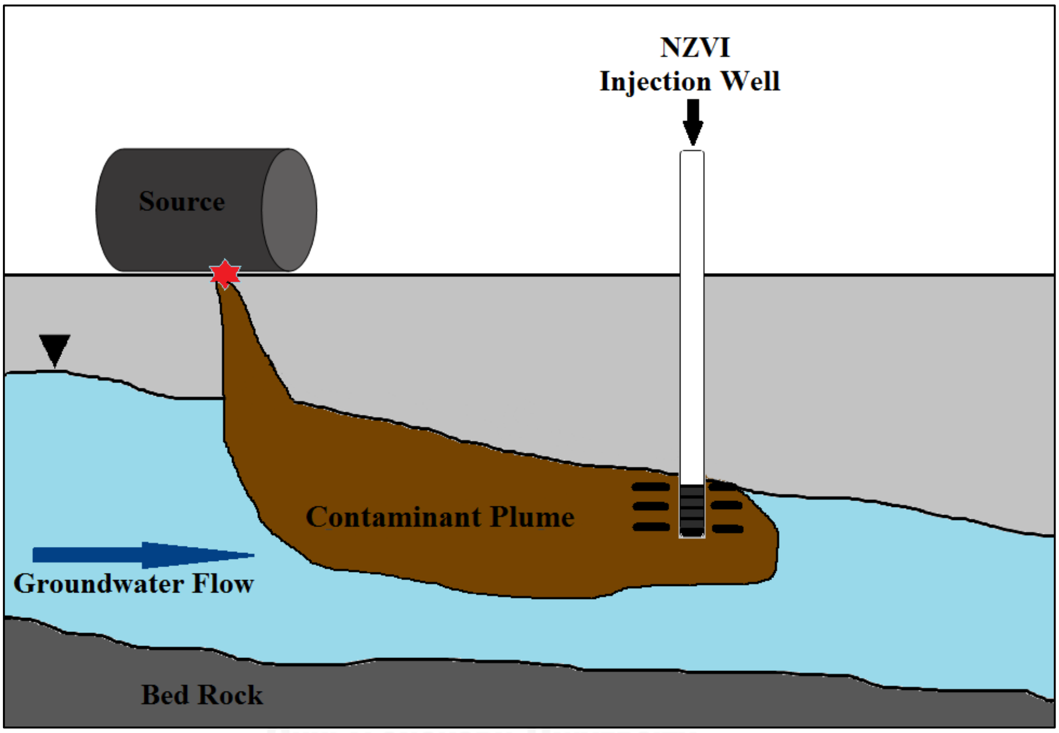
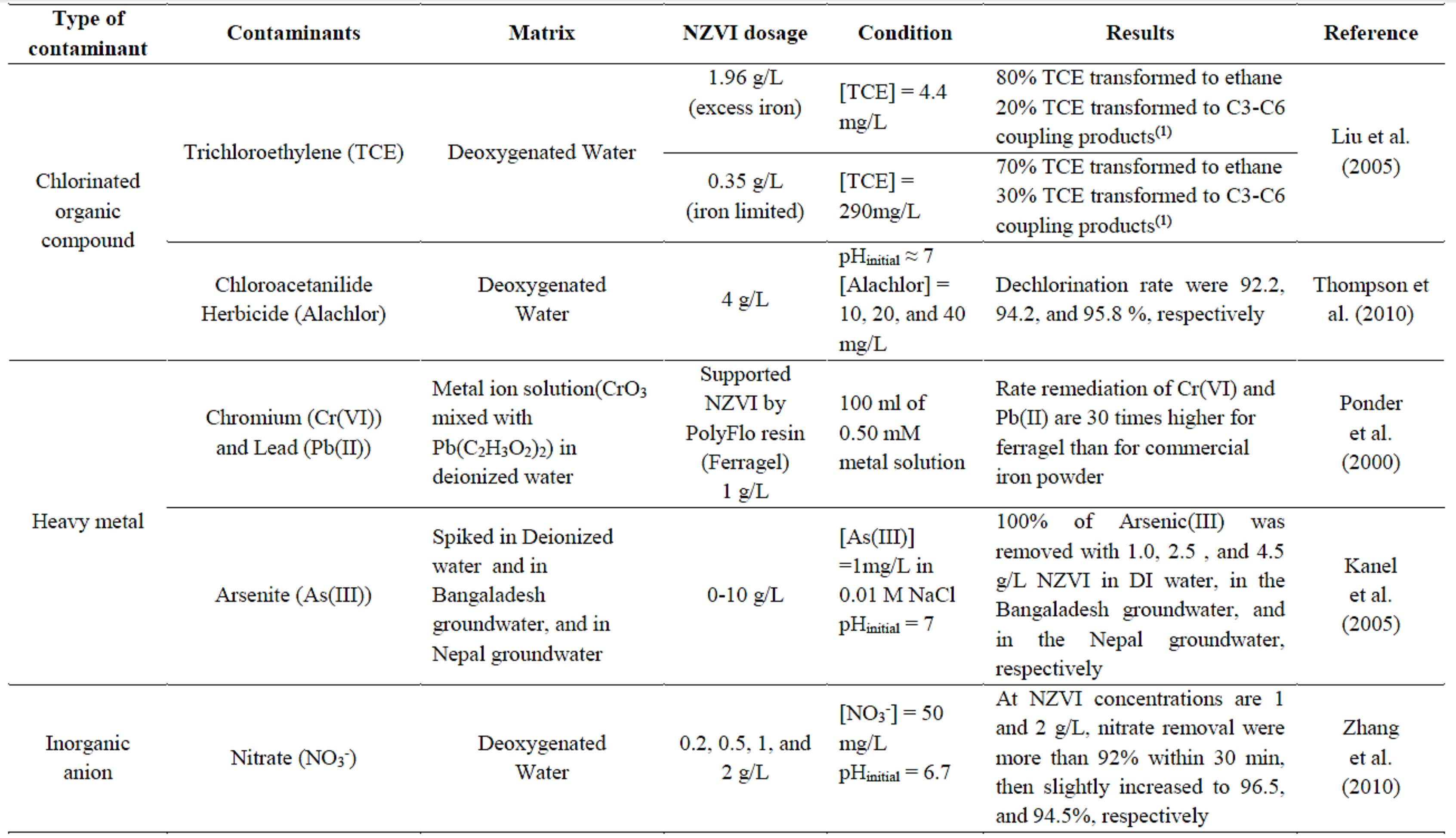


Figure 2.2 Schematic of groundwater contamination and NZVI injection well

Table 2.2 Examples of studies involving the use of NZVI for remediating contaminants



Type of contaminant	**Contaminants**	**Matrix**	**NZVI dosage**	**Condition**	**Results**	**Reference**
Chlorinated organic compound	Trichloroethylene (TCE)	Deoxygenated Water	1.96 g/L (excess iron)	[TCE] = 4.4 mg/L	80% TCE transformed to ethane 20% TCE transformed to C3-C6 coupling products(1)	Liu et al. (2005)
			0.35 g/L (iron limited)	[TCE] = 290mg/L	70% TCE transformed to ethane 30% TCE transformed to C3-C6 coupling products(1)	
	Chloroacetanilide Herbicide (Alachlor)	Deoxygenated Water	4 g/L	$pH_{initial} \approx 7$ [Alachlor] = 10, 20, and 40 mg/L	Dechlorination rate were 92.2, 94.2, and 95.8 %, respectively	Thompson et al. (2010)
Heavy metal	Chromium (Cr(VI)) and Lead (Pb(II))	Metal ion solution(CrO_3 mixed with $Pb(C_2H_3O_2)_2$) in deionized water	Supported NZVI by PolyFlo resin (Ferragel) 1 g/L	100 ml of 0.50 mM metal solution	Rate remediation of Cr(VI) and Pb(II) are 30 times higher for ferragel than for commercial iron powder	Ponder et al. (2000)
	Arsenite (As(III))	Spiked in Deionized water and in Bangaladesh groundwater, and in Nepal groundwater	0-10 g/L	[As(III)] =1mg/L in 0.01 M NaCl $pH_{initial} = 7$	100% of Arsenic(III) was removed with 1.0, 2.5 , and 4.5 g/L NZVI in DI water, in the Bangaladesh groundwater, and in the Nepal groundwater, respectively	Kanel et al. (2005)
Inorganic anion	Nitrate (NO_3^-)	Deoxygenated Water	0.2, 0.5, 1, and 2 g/L	$[NO_3^-] = 50$ mg/L $pH_{initial} = 6.7$	At NZVI concentrations are 1 and 2 g/L, nitrate removal were more than 92% within 30 min, then slightly increased to 96.5, and 94.5%, respectively	Zhang et al. (2010)

2.2 Natural Organic Matter (NOM)

2.2.1 Characteristics of NOM

Natural organic matter (NOM) is a mixture of organic compounds that are present in natural water. The concentration of NOM is usually 10 fold comparing to the contaminant found in natural water. Thus, the presence of NOM could play an important role in the contaminant removal. This includes the removal of contaminant by NZVI. NOM is derived from the decomposition of living organisms; for example, animals, and plants. NOM has heterogeneous properties which make it difficult to study the effect or behavior of NOM in environment and treatment processes. Therefore NOM should be separated into subgroups of compounds that have similar properties. As a result, its structure can be easier to characterize and its effect on natural and engineered systems can be determined. NOM can be categorized into two major fractions based on polarity to hydrophobic, and hydrophilic. Both major NOM fractions can be further divided into 3 sub-fractions based on charge to as acid, base and neutral as shown in Table 2.3.

2.2.2 Compositions of NOM

NOM can be classified into 6 fractions. Types of organic compounds belong to NOM fraction are shown in Table 2.3.

Table 2.3 Composition of NOM fractions (Barber et al., 2001)

Fraction	Abbreviation	Organic compound class
Hydrophobic acid	HPOA	C_5-C_9 aliphatic carboxylic acids; 1- and 2-ring aromatic carboxylic acids; 1- and 2-ring phenols; fulvic acid
Hydrophobic base	HPOB	Humic substances portion retained by XAD-8 resin at pH~7 which can be eluted by HCl; 1- and 2-ring aromatic amines except pyridine; proteinaceous substances; cationic surfactants
Hydrophobic neutral	HPON	Hydrocarbons; $>C_5$ aliphatic alcohols, amides, esters, ketones, and aldehydes; $>C_9$ aliphatic carboxylic acids and amines; >3-ring aromatic carboxylic acids acids and amines; chlorophyll and related pigments; LAS and optical brighteners
Hydrophilic acid	HPIA	$<C_5$ aliphatic carboxylic acids; polyfunctional carboxylic acids; LAS degradation products; mixture of various hydroxyl acids
Hydrophilic base	HPIB	$<C_9$ aliphatic amines; pyridine; amphoreticproteinaceous materials containing aliphatic amino acids, amino sugars peptides, and proteins
Hydrophilic neutral	HPIN	$<C_5$ aliphatic amides; short chain aliphatic amines, alcohols, aldehydes, esters, ketones; polyfunctional alcohols; carbohydrates; cyclic amides

2.2.3 NOM model compounds

NOM in natural water consists of many kinds of substances. To study an effect of each kind of NOM, NOM model compounds have been used as representative of each NOM fraction. For example, a group of researchers had used NOM surrogates in their works for disinfection by-production formation (Bond et al., 2009; Bond et al., 2010). A list of NOM model compounds is shown in Table 2.4.

Table 2.4 NOM fraction surrogates

Classification	**Model compound**	**Chemical group**	**Molecular weight (g/mol)**	**Reference**
HPOA	Humic acid	NA	NA	Bond et al. (2012)
HPOB	Aniline	Amine	93	Barber et al. (2001); Świetlik et al. (2004)
HPON	L-tryptophan	Amino acid	204	Bond et al. (2009b)
HPIA	Oxalic acid	Carboxylic acid	90	Barber et al. (2001); Świetlik et al. (2004); Bond et al. (2009b)
HPIB	L-asparagine	Amino acid	132	Barber et al. (2001); Świetlik et al. (2004); Bond et al. (2009b)
HPIN	D-xylose	Carbohydrate	150	Bond et al. (2009a)

Note: NA = Not available

2.3 Factors Affecting NZVI Performance

2.3.1 Effect of NOM on NZVI reactivity

During the past decade, the effects of NOM on pollutant degradation by NZVI, and modified NZVI have been investigated. However, whether NOM inhibits or enhances NZVI reactivity is still inconclusive. Most research was studied through a representative NOM including humic acid (HA) and Suwannee River NOM (SRNOM). This is because they were studied extensively by other researchers (Tsang et al., 2009; Chekli et al., 2013; Kim et al., 2014).

NOM concentration has become a factor influencing reactivity NZVI. Previous studies showed the NZVI or modified NZVI reactivity on contaminant removal was inhibited in the presence of HA. Giasuddin et al. (2007) studied the removal of arsenite (As (III)), and arsenate (As (V)) by NZVI. At initial pH of 6.5, As(III) or As(V) of 2 mg/L, NZVI of 0.3 g/L and HA of 20 mg/L, the reduction of surface-normalized rate constant (k_{sa}) of As (III) and As (V) were reduced 43%, and 68%, respectively. Zhang et al. (2009) also reported that the increasing of HA concentration decreased the efficiency of 2,4-dichlorophenol (2,4-DCP) removal by Ni-Fe (surface-modified NZVI). They found 2,4-DCP removal efficiencies of 100, 99, 95, 84 and 69% for HA concentration from 0, 5, 10, 30 to 40 mg/L as HA, respectively. Lee et al. (2009) also observed a similar finding. They found that TCE dechlorination rate by surfactant modified NZVI (SNZVI) was inhibited at HA concentrations of 1, 10, and 30 mg/L as HA. It was explained that the inhibition of NZVI reactivity by HA could be from the competition between HA and contaminants to occupy reactive sites on NZVI surface (Lee et al., 2009; Zhang et al., 2009).

On the other hand, there were evidence that certain HA concentrations promoted the reduction of contaminants. Lee at al. (2009) reported that the efficiency of TCE removal was promoted to 90% within 60 min at a high HA concentration of 50 mg/L as HA (lower HA concentrations found to inhibit the removal). Also the nitrate reduction rate was enhanced at 6.25, and 12.5 mg/L of HA (Kim et al., 2013). Wang et al. (2011) studied on a long run effect (96 hrs) of HA on 4-chlorobiphenyl (4-ClBP) reduction. Their work showed increasing 4-ClBP dechlorination in the presence of HA. At 10 mg/L HA in 96 hours, the reduction efficiency of 4-ClBP was enhanced from 65% to 87.2%. This may be because HA could act as electron shuttle which worked with oxygen and enhanced hydroxyl radical production. The hydroxyl radicals mediated oxidation of organic compound (pollutant) through Fenton’s reaction (Kang and Choi, 2009).

2.3.2 Effect of solution pH on NZVI reactivity

The influence of solution pH on HA adsorption was studied by Giasuddin et al. (2007). At initial pH in a range of 3.0-9.0, the HA adsorption was 80 mg/g whereas the adsorption rate decreased rapidly at initial pH of > 10.0. This could be explained by point of zero charges (PZC) of NZVI, HA, and NZVI-HA. NZVI had PZC at pH around 7.7. The increasing NZVI efficiency at lower pH was because of the charges on NZVI surface and HA surface. According to the opposite charges among NZVI and HA at pH lower than 7.7, it is easier for HA to adsorb onto NZVI surface (Giasuddin et al., 2007). Moreover, low solution pH enhanced more dechlorination rate of chlorinated organic compounds. Zhang et al. (2009) reported that as the initial pH values increased from 3.0, 6.0, 8.0, 9.0 to 11.0, the degradation rate of 2,4-DCP dropped from nearly 100% to 95%, 69%, 48% and 46%, respectively in the presence of HA of 10 mg/L. Wang et al.

(2011) also found that after 2 days of reaction, the 4-ClBP concentration decreased 46.2%, 52.2%, 64.3%, and 64.4% of initial reaction when the initial pH increased from 4.0, 5.5, 6.8, and 9.0, respectively. At low pH, more hydrogen ions were available.

The dechlorination reaction requires the hydrogen ion (Eq. 2.10). Therefore, the removal of 4-ClBP was enhanced at low pH (Wang et al., 2011).

$$RCl + H^+ + 2e^- \rightarrow RH + Cl^- \qquad (2.10)$$

2.3.3 Effect of ions onto NZVI reactivity

Groundwater, where NZVI is commonly applied, contains of many kinds of ions. Therefore, ions could affect the reactivity of NZVI. Giasuddin et al. (2007) studied on an influence of many kinds of ions on NZVI reactivity in presence of humic acid. The results showed that at 10 mM of NO_3^- and SO_4^{2-}, HA could be removed completely while the HA removal efficiencies were obstructed in presence of 10 mM of HPO_4^{2-}, HCO_3^-, and $H_4SiO_4^0$ (0%, 18% and 22%, respectively). This was because HPO_4^{2-} and HCO_3^- possess the reactive sites of NZVI to form inner-sphere complexes. The results showed that anions competed with HA to react with NZVI. For cations, both of the presence of Ca^{2+} and Mg^{2+} promoted HA removal (71.1% and 45.8%, respectively) by NZVI. These results were similar to the study of Liu et al. (2007). They reported that the anions (5 mN) in groundwater hindered trichloroethylene reduction in the following order $Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^{2-}$. They observed that Co^{2+}, Cu^{2+}, and Ni^{2+} promoted 4-ClBP dechlorination without humic acid by NZVI because they formed bimetals with NZVI.

2.3.4 Effect of temperature on NZVI reactivity

Temperature affects the reactivity of NZVI. Increasing temperature enhances NZVI performance. Zhang et al. (2009) reported that the dechlorination rate of 2,4-DCP increased from 82% to 100% when the temperature of solution increased from 10°C to 35°C in the presence of 10 mg/L HA using 6 g/L Ni-Fe. They claimed that higher temperatures enhanced the mobility of 2,4-DCP to react nanoparticles, increased the activation energy for electron transfer or increased the reactive site complex formation. This finding was agreeable with the study by Xu et al. (2013). They found that increasing temperature from 10°C, 20°C, 30°C to 40°C, the degradation rate of 2,4-DCP increased 39.1±1.9%, 54.3±2.0%, 76.4±0.8% to 89.7±0.7%, respectively using nanoscale magnetic Pd/Fe and without HA.

CHAPTER III

MATERIALS AND METHODS

3.1 Experimental Framework

The experimental framework of this research is shown in Figure 3.1. The experiment was divided into 3 main parts: 1) NZVI synthesis and characterizations, 2) the reactivity between NOM fraction surrogates and NZVI, and 3) the reactivity between NOM fractions, bulk NOM and NZVI. The details of NZVI synthesis and characterizations are described in sections 3.2 and 3.3. The experiment of NOM fraction surrogates is described in section 3.4. This part was divided into two subsections. The first subsection was kinetic study of NOM surrogates and the second subsection was adsorption isotherm study of NOM fraction surrogates on NZVI. Section 3.5 describes the experiment of reactivity of NOM fractions with NZVI and reactivity of bulk NOM with NZVI. NOM from two natural water sources were used in the experiment.

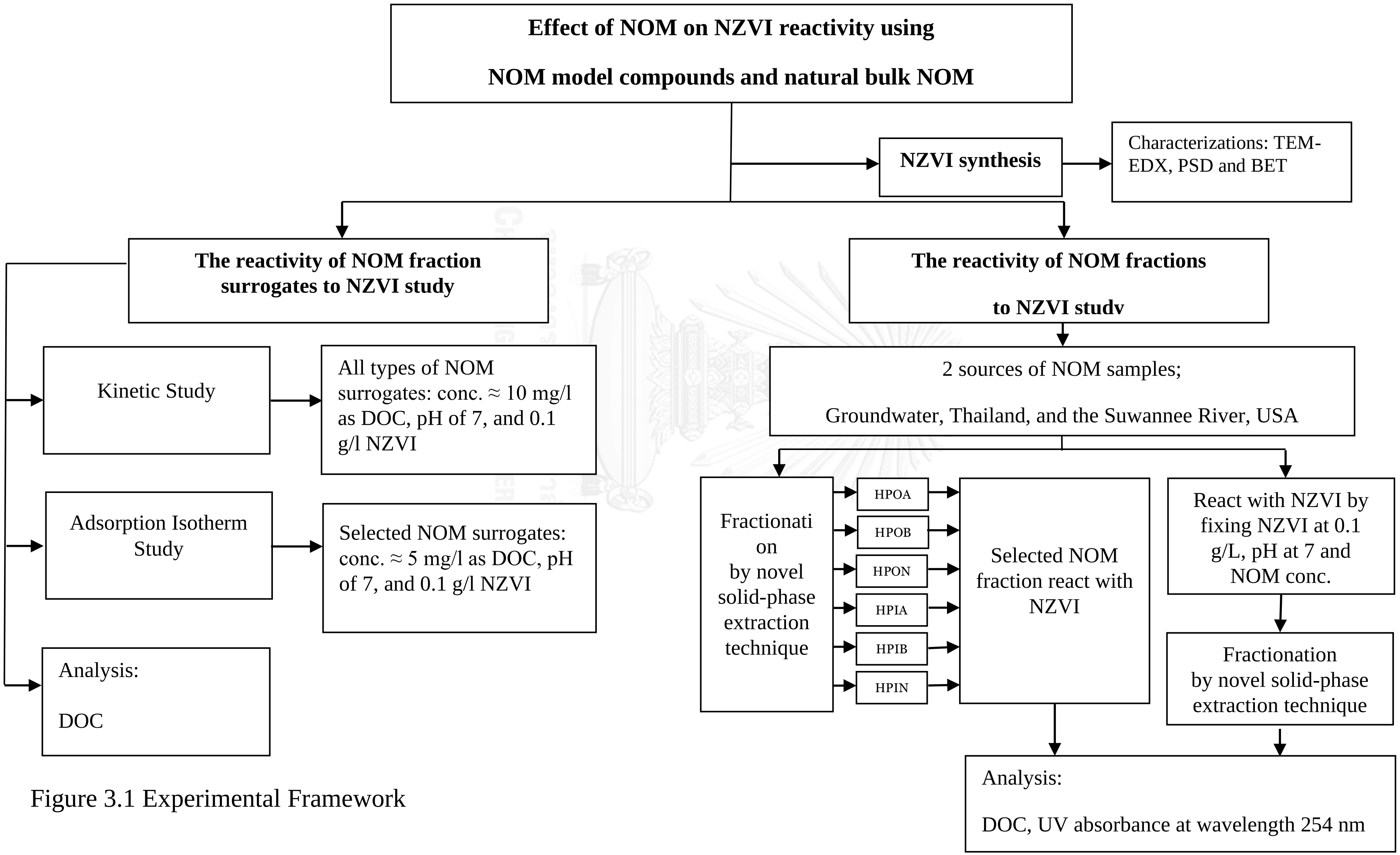


Figure 3.1 Experimental Framework

3.2 Nano-Zero Valent Iron Synthesis

The schematic diagram of nano-zero valent iron particles synthesis is shown in Figure 3.2. Nano-zero valent iron was synthesized using $NaBH_4$ (97%, Loba, India) as a reducing agent. The procedure of synthesis follows the method of Liu et al. (2005). One liter of 0.07M $FeSO_4 \cdot 7H_2O$ (99.5%, Qrec, New Zealand) was prepared in a methanol/deionized (DI) water solution (at a ratio of 30/70, v/v). Then 10 mL of 5M NaOH (99%, Merck, Germany) was dropped into the ferrous solution at a rate of 3 mL/min. After that, 50 mL of 2.1M $NaBH_4$ was added at a rate of 6 mL/min while the solution was being stirred all the time. Then, the solution was continuously stirred for 20 minutes to form NZVI. The NZVI particles were separated from the solution by centrifugation at 3,500 rpm for 5 minutes. Then NZVI particles were transferred to a round bottle flask containing methanol. Any NZVI particles attached to the flask wall were rinsed by methanol to ensure that all NZVI particles were under methanol. After that, the particles were dried under nitrogen gas at 120˚C (until methanol completely evaporated). The drying time was about 2-3 hours. Finally, all NZVI particles were ground and were kept under nitrogen gas before use to prevent the oxidation of NZVI.

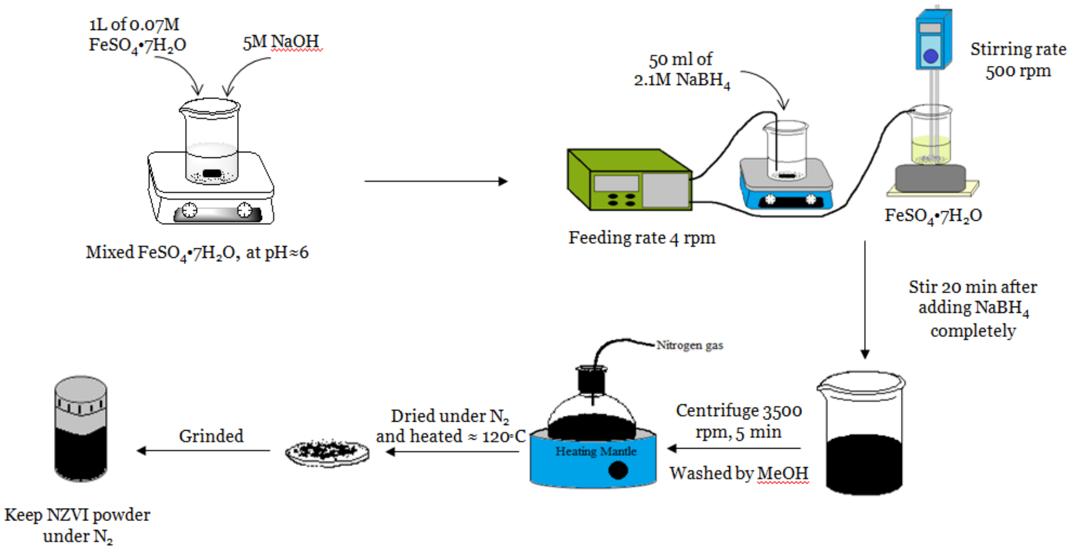


Figure 3.2 Schematic diagram of NZVI synthesis

3.3 Nano-Zero Valent Iron Characterizations

3.3.1 Transmission electron microscopy with energy-dispersive x-ray spectroscopy

Transmission electron microscopy (TEM) was performed using Tecnai G2 20 S-TWIN (FEI, Czech Republic) to observe the morphology and particle size of NZVI, whereas energy-dispersive x-ray (EDX) spectroscopy was used for detecting the elemental composition of the particles. NZVI particles were suspended in ethanol and were sonicated by Ultrasonic Cleaner for 15 min at 48 kHz (NDI ULTRAsonik 136H, USA). Then, a few drops of the solution was dropped by micropipette onto 200-mesh carbon-coated copper grid (3.05 mm diameter) and let it dry before TEM-EDX analysis. The particle size distribution of the synthesized NZVI was determined by measuring particle size through TEM images and analyzing the data using the TEM Imaging and Analysis (TIA) Offline program (FEI Company, USA.).

3.3.2 Surface area

The surface area of the synthesized NZVI was determined by a nitrogen adsorption-desorption technique using the Brunauer-Emmett-Teller (BET) theory. The procedure was carried out through a surface area and pore size analyzer (Bel-Japan, BelSorp mini II, Japan). Prior to measurement, the sample was degassed at 90°C for an hour and 200°C for 4 hours to remove the moisture. The specific surface area of sample was calculated from adsorption data by using the standard BET method. The following equation was used for surface area calculation.

$$\frac{1}{W[\left(\frac{P_0}{P}\right)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \qquad (3.1)$$

where W is weight of adsorbed nitrogen at relative pressure P/P_0

W_m is weight of adsorbed gas of monolayer coverage

C is a constant

3.4 The reactivity of NOM fraction surrogates with NZVI

3.4.1 Reaction kinetic study of NOM fraction model compounds and NZVI

The reaction kinetics between NOM model compounds and NZVI was investigated using a 1-L high-density polyethylene bottle fitted with septum under an anaerobic condition. The list of NOM model compounds representing NOM fractions is shown in Table 2.4. Unbuffered NOM model compound solutions of 1,000 mL were prepared at pH of 7, and DOC of approximately 10 mg/L. NaOH and HCl were used for pH adjustment. A pH measurement was always performed before starting the reaction. The solution was purged by nitrogen gas (99.99%) for an hour to remove dissolved oxygen before NZVI injection. NZVI (0.1 g) was added to the NOM surrogate solution and the bottles were rotated end-over-end at 20 rpm by an overhead mixer (VELP Scientifica Rotax 6.8, Italy) at room temperature. Syringes with needle were used to collect water sample at 0, 15, 30, 45, 60, 90, and 120 minutes. All water samples were centrifuged at 5,000 rpm for 5 minutes and filtered through a 0.2 µm pore-size nylon membrane syringe filter (Vertical, Thailand) (prewashed with 2 mL of DI water) prior to DOC analysis. A scheme diagram of the experimental procedure is shown in Figure 3.3.

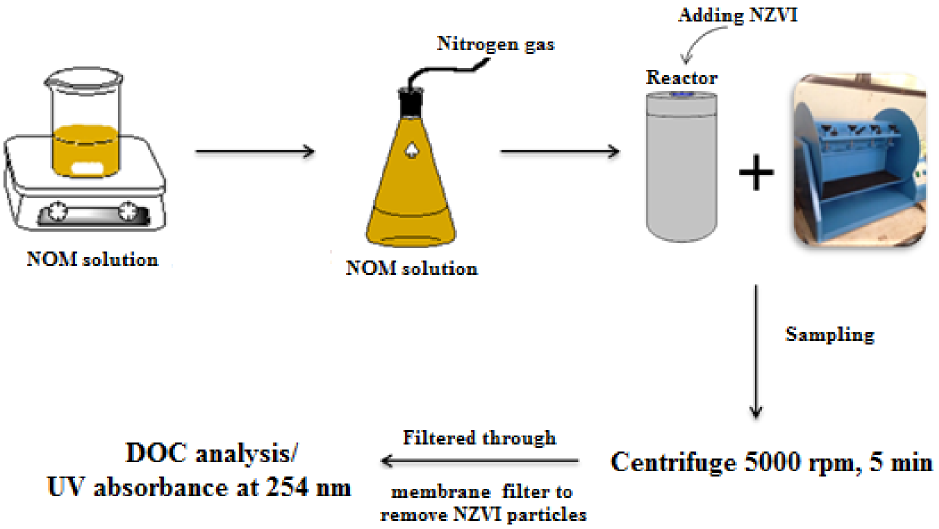


Figure 3.3 Schematic diagram of the experimental procedure

3.4.2 Adsorption isotherm of NOM surrogates and NZVI

Adsorption isotherm experiments were conducted by using 40-mL glass vial with a screw cap. NOM surrogate solutions for HPOA and HPIA fractions were prepared as described above at pH of 7 and DOC of approximately 5 mg/L. NZVI was dosed to the solution at different concentrations (0.1, 0.3, 0.5, and 0.7 g/L). The glass vials were rotated end-over-end at 20 rpm at room temperature. Water samples were collected after 2 hours of reaction, centrifuged and filtered in the similar fashion as previously described in section 3.4.1.

3.5 The Reactivity of NOM Fractions with NZVI

3.5.1 NOM fraction samples

NOM samples used in this study were collected from two different sources in order to obtain different types of NOM components. The first source of sample was collected from groundwater (GWNOM), Gud Nam Sai Sub-District, Nam Phong District, Khon Kaen Province, Thailand. The location of the site is 16°42’33.0582”, 102°45’2.1832”. This groundwater well is a shallow well. Groundwater NOM was chosen because NZVI was typically used for groundwater remediation. A GWNOM sample of 70 L was collected on June 24, 2014. The GWNOM was filtered through a series of three filters including filter paper 42 Ashless (Whatman®, UK) (prewashed with 100 mL of DI water) and a 1.2 µm pore-size GF/C filter (Whatman®, UK) (prewashed with 100 mL of DI water), and lastly a 0.45 µm pore-size cellulose nitrate membrane filter (Whatman®, UK) (soaked in 100 mL of DI water for 48 hours according to Khan and Subramania-Pillai (2007) and prewashed with 100 mL of DI water) to remove suspended solids before using it for fractionation. The other source of sample was Suwannee River NOM (SRNOM) (Georgia, USA). SRNOM was isolated by reverse osmosis and freeze dried by the International Humic Substances Society (Cat. No. 2R101N). The SRNOM was chosen in this work because it has been studied extensively (Ratpukdi et al., 2009; Chekli et al., 2013; Erhayem et al., 2014). SRNOM was obtained in a powder form. SRNOM solution was prepared by dissolving the NOM powder with DI water to obtain a desirable DOC concentration and was also filtered through a 0.45 µm pore-size cellulose nitrate membrane filter before using in experiment.

3.5.2 Natural organic matter fractionation setup

Fractionation is a method to separate NOM into 6 main fractions. In this study, a novel solid-phase extraction technique by Ratpukdi et al. (2009) was used for NOM fractionation. Table 3.1 lists 3 types of sorbent cartridge used for NOM fractionation.

Table 3.1 Solid phase extraction sorbents properties

Type of sorbent	**Category**
Bond Elute ENV (Varian, Inc.)	Nonpolar
Strata X-C (Phenomenex)	Cation exchanger
Strata X-AW (Phenomenex)	Anion exchanger

Note: Modified from Ratpukdi et al. (2009)

3.5.2.1 Cartridge preparation

All the cartridges including ENV, Strata X-C, and Strata X-AW were cleaned by 10 mL MeOH (HPLC-grade). Then, 10 mL of 1N HCl were used for only Strata X-C and Strata X-AW. Finally, the cartridges were cleaned by DI water using a vacuum pump, 1 L for ENV and Strata X-C cartridges and 1.5 L for Strata X-AW. Teflon tubing with a diameter of 1/16” (Thermo Scientific, USA) was used for transferring water sample from the water sample reservoir to the cartridges.

3.5.2.2 NOM fractionation

Figure 3.4 illustrates a setup for NOM fractionation and elution process. Before using the cartridges, approximately 20 mL of DI water was passed through each cartridge by gravity. To start the NOM fractionation, water sample was adjusted to pH 7 using NaOH and H_2SO_4. The sample was passed through the first ENV cartridge. The sample passing through the first cartridge was adjusted for pH to 10 before passing through the second ENV cartridge. The sample was adjusted for pH to 2 and drawn through the third ENV cartridge. After that, it was passed through the strata X-C cartridge without pH adjustment. Finally, it was adjusted for pH to 7. Retained NOMs in the first ENV, the second ENV, the third ENV, the strata X-C and the strata X-AW cartridges were HPON, HPOB, HPOA, HPIB and HPIA, respectively while the remaining NOM in the sample was HPIN. Twenty milliliters of the sample after passing through each cartridge were collected for DOC analysis (DOC_1, DOC_2, DOC_3, DOC_4, and DOC_5). Equations 3.2 to 3.7 show the calculations for the concentrations of NOM fractions based on DOC values.

$$\text{HPON} = \text{DOC of water sample} - DOC_1 \quad (3.2)$$

$$\text{HPOB} = DOC_1 - DOC_2 \quad (3.3)$$

$$\text{HPOA} = DOC_2 - DOC_3 \quad (3.4)$$

$$\text{HPIB} = DOC_3 - DOC_4 \quad (3.5)$$

$$\text{HPIA} = DOC_4 - DOC_5 \quad (3.6)$$

$$\text{HPIN} = DOC_5 \quad (3.7)$$

3.5.2.3 NOM elution

To obtain NOM fractions, NOM retained on each cartridge was eluted. Retained NOMs on the ENV1 and ENV2 cartridges were eluted by 10 mL MeOH (HPLC-grade) and 10 mL of 0.1N HCl, respectively whereas NOMs captured by the ENV3, Strata X-C and Strata X-AW cartridges were eluted by 10 mL of 0.1N NaOH.

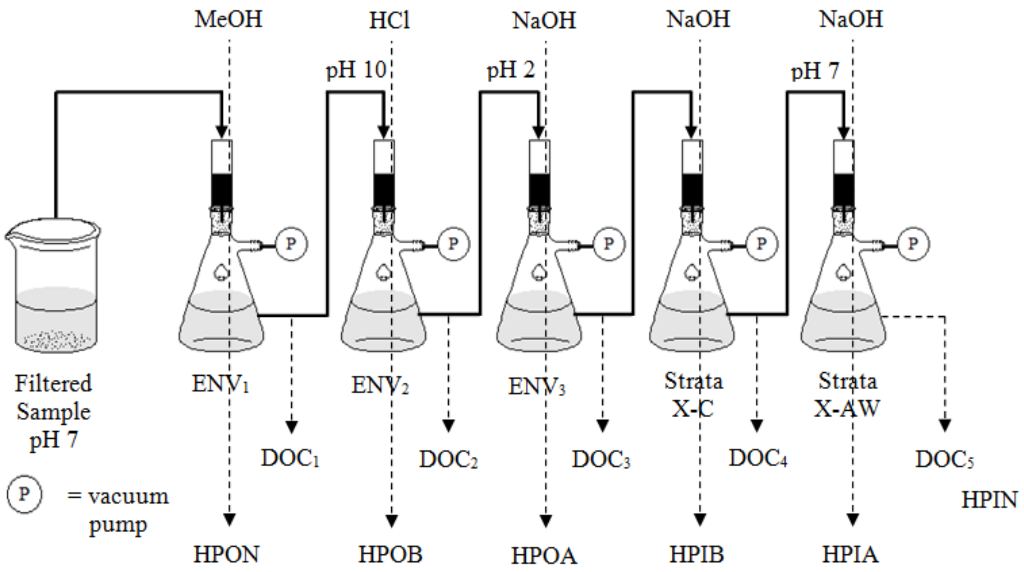


Figure 3.4 Schematic diagram of fractionation setup and elution (dashline) (Modified from Ratpukdi et al., 2009)

3.5.2.4 NOM cleanup

After elution, each NOM fraction solution had to be cleaned up before use. The HPON solution which was eluted by MeOH was evaporated by rotary vacuum evaporator (BÜCHI Rotavapor R-114, Switzerland) at 60°C and vacuum at 200 mbar until all MeOH was removed. For the HPOB solution that was eluted by HCl was cleaned up by anion exchange resin (Purolite® A400, Purolite Corporation, USA) to eliminate chloride ion. For the HPOA, HPIB and HPIA solutions which were eluted by

NaOH were subject to cation exchange resin resin (Purolite® C100, Purolite Corporation, USA) to remove sodium ion from the solution. The eluted HPIN was passed through cation exchange and anion exchange resin successively to remove sodium and chloride ions, respectively.

3.5.3 Experimental setup

Experiments on NOM fractionation were divided into two parts: 1) Effect of each NOM fraction on NZVI reactivity and 2) Effect of bulk NOM on NZVI reactivity. The first part, water sample was fractionated by a novel solid-phase extraction technique and then each fraction was reacted with NZVI at different pHs to study for effect of each NOM fraction on NZVI reactivity. The second part was conducted by reacting bulk NOM with NZVI. NOM fractions before and after the reaction with NZVI were performed. For the second part, competition among NOM fractions (within the bulk NOM) for reactivity with NZVI was possible.

3.5.3.1 NOM fraction and nano-zero valent iron reaction experiment

Batch experiments were conducted by using 40 mL glass vial with a screw cap under an anaerobic condition. The NOM fraction solution was prepared at DOC concentrations of 2-4 mg/L, at pH 5, 7 and 9. Before NZVI injection, the NOM solution was purged by nitrogen gas for 30 min in order to eliminate dissolved oxygen. Later, NZVI was added into the sample. The bottle was rotated end-over-end at 20 rpm at room temperature. A sample was collected form the vial at 0, 15, 30, 45, 60, 90 and 120 minutes of reaction time. The collected sample was centrifuged at 5,000 rpm for 5 minutes to separate NZVI particles from the solution and then filtered through a 0.2 µm pore-size nylon syringe filter (prewashed by 2 mL DI water). The filtrate was preserved for DOC analysis by HCl, 1 drop per 20 ml (of the filtrate). The un-preserved filtrate was measured for UV_{254}.

3.5.3.2. Bulk NOM and nano-zero valent iron reaction experiment

In this part, bulk NOM samples were fractionated before and after the reaction with NZVI. One liter of bulk GWNOM was prepared without DOC concentration adjustment while 1 L of bulk SRNOM was prepared at a DOC concentration of approximately 8 mg/L. Both types of water samples were adjusted to pH 7 and were purged by N_2 gas for an hour to obtain an anaerobic condition. NZVI was injected after purging and the reaction time was 2 hours. After 2 hours, the water sample was filtered through a 0.45 µm pore-size cellulose nitrate membrane filter (soaked in 100 mL of DI water for 48 hours and prewashed with 100 mL of DI water) instantly and then fractionated. All experiments were duplicated.

3.6 Analyses

DOC was analyzed according to Standard Methods for the Examination Water and Wastewater (APHA et al., 2012) using a combustion TOC analyzer (Analytik Jena-Analyzer multi N/C 2100S, Germany). Limitation of detection is 0.05 mg/L. Water samples were filtered through a 0.2 µm pore-size nylon syringe filter (Vertical, Thailand) or a 0.45 µm pore-size cellulose nitrate membrane filter (Whatman®, UK) and were preserved by HCl before the DOC analysis. DOC was analyzed triplicate. For UV_{254} measurement, filtered samples without preservation and a UV-Vis spectrophotometer (DR-6000, HACH, USA) were used.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 NZVI Characteristics

4.1.1 Structure and size distribution

The morphology of synthesized NZVI was observed by the TEM spectroscopy. Figure 4.1a and 4.1b illustrates that NZVI had a spherical shape that consists of core and shell. The core of NZVI is where the reduction of target contaminant occurs while the shell of NZVI is composed of iron oxides or hydroxides due to oxidation reaction (Li et al., 2006a; Li et al., 2006b). The agglomeration of NZVI particles due to their magnetic property was observed. The main element of synthesized NZVI was iron (Fe) (Figure A.1). Table 4.1 shows the percentage of each element which was detected by EDX spectroscopy. High percent of copper came from the TEM-carbon coated copper grid used in EDX spectroscopy. Figure 4.2 exhibits the particle size distribution of NZVI. Most particles were in a range between 5-100 nm (98%) (Figure 4.3) and the average size (± standard deviation) of synthesized NZVI particles was 40.36±18.22 nm. From particle size distribution results, the iron particles are considered nanoparticles according to a criterion by the European Commission that 50% of the particles have to be smaller than 100 nm (European Commission, 2011).

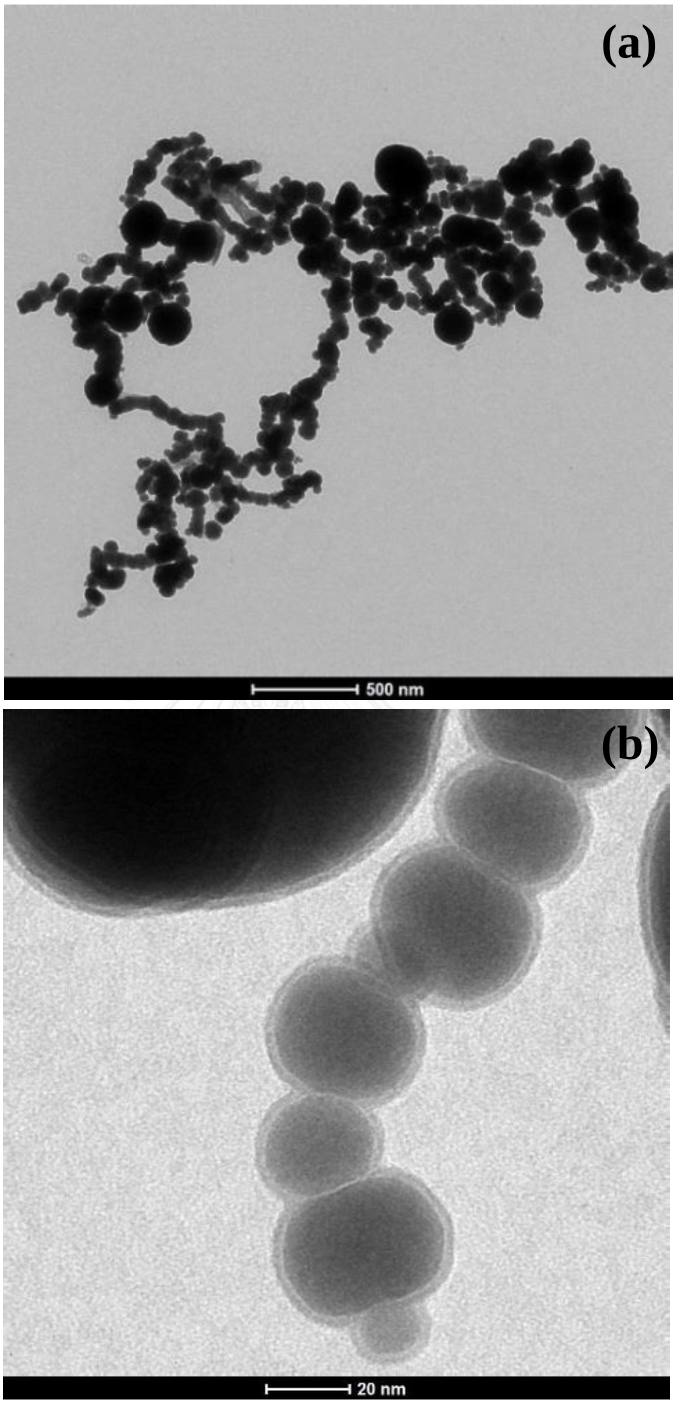


Figure 4.1 TEM images of NZVI used in the study: (a) Magnification 15000X and (b) Magnification 285000X.

Table 4.1 The percentage of each element on EDX spectroscopy

Type of element	%
Iron (Fe)	72.35
Copper (Cu)	20.29
Oxygen (O)	4.06
Carbon (C)	2.06
Sulfur (S)	1.24

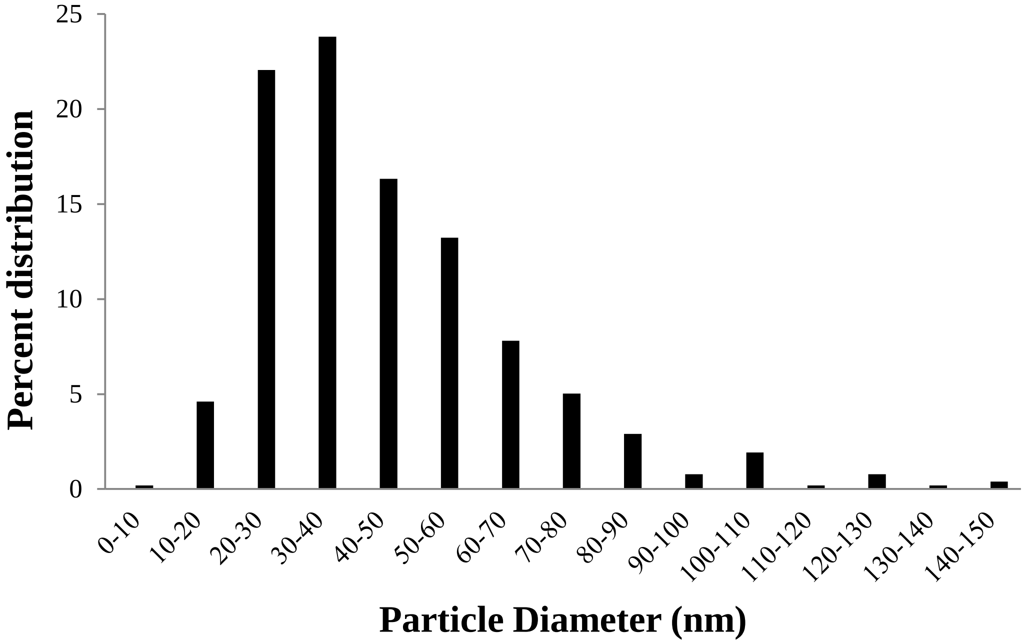


Figure 4.2 Size distribution of synthesized NZVI (n = 516 particles)

4.1.2 Specific surface area

The specific surface area of synthesized NZVI was detected through the Brunauer-Emmett-Teller (BET) method. The synthesized NZVI had a specific surface area ($a_{s,BET}$) of 29.52 m^2/g which was in the range of 12.40 to 46.27 m^2/g obtained by other researchers (Liu et a., 2005; Giasuddin et al., 2007; Zhang et al., 2010; Hwang et al., 2011; Shih et al., 2011; Kim et al., 2013).

4.2 Natural Organic Matter (NOM) Model Compound Study

4.2.1 Reaction kinetics of NOM model compounds and NZVI

The reaction kinetics of NOM model compounds and NZVI was studied using 6 NOM surrogates representing hydrophobic acid/base/neutral and hydrophilic acid/base/neutral fractions (Table 2.4). Figure 4.3 shows the change of DOC with time for each NOM surrogate. The DOC concentrations of humic acid (HPOA) and oxalic acid (HPIA) decreased by 40% and 10% over the course of experiment (120 min), respectively. The DOC reduction of humic acid agreed with the first order kinetic reaction ($R^2 = 0.9718$) while the reduction of oxalic acid did not. The DOC concentrations of other surrogate NOM fractions remained relatively unchanged (< 5% changes). The DOC reduction of humic acid and oxalic acid could be from adsorption onto active sites of NZVI (Chen et al., 2011; Lv et al., 2013; Tang et al., 2014). Humic and oxalic acids contain carboxylic functional group which has pKa around 4.2 (Abate and Masini, 2001). Experiment was conducted at pH of 7 which was more than pKa. Therefore, the carboxylic acid functional groups in HPOA and HPIA surrogates were in deprotonated (COO^-) forms and adsorbed onto oxide shell of NZVI (Giasuddin et al., 2007; Wang et al., 2014). Normally, DOM reacted with colloids; especially, humic acid to metal oxide or metal nanoparticles, by adsorption onto the surface of colloids (Philippe and Schaumann, 2014). However, for the other 4 NOM surrogates including aniline (HPOB), L-tryptophan (HPON), L-asparagine (HPIB), and D-xylose (HPIN), they had low reactivity with NZVI based on the structures of the compounds which may have less or no negatively charge to react with NZVI. This study only chose some NOM surrogates; consequently, using the NOM fractions from natural water to determine the reactivity with NZVI was necessary and was performed.

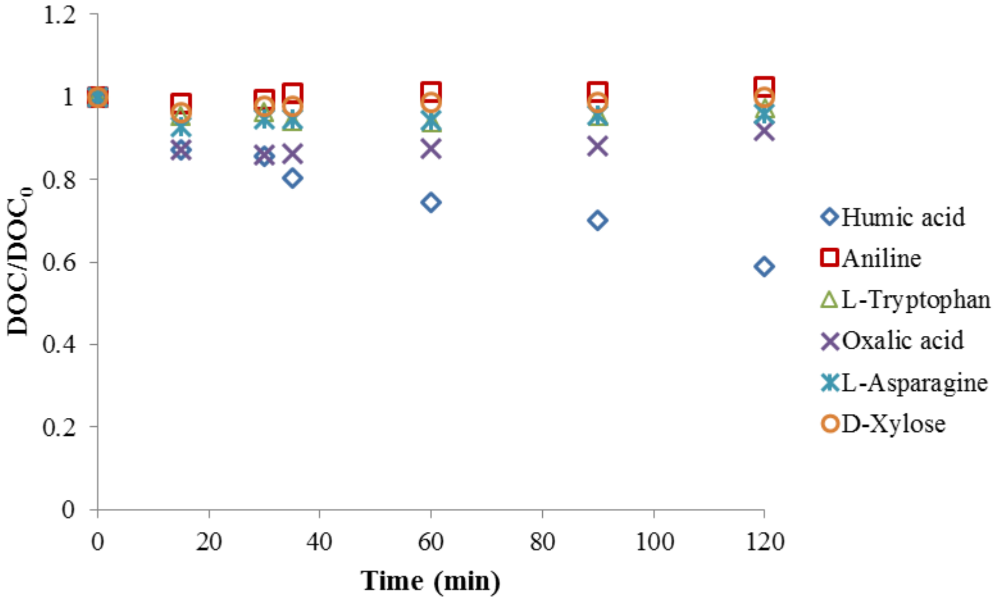


Figure 4.3 Change in DOC concentration of NOM surrogates (0.1 g/L of NZVI, pH 7)

4.2.2 Adsorption isotherm

Only humic acid (HPOA) and oxalic acid (HPIA) were chosen to study in the adsorption isotherm because their kinetics results showed reactivity with NZVI. The data were fitted with Freundlich (Equation 4.1) and Langmuir adsorption isotherms (Equation 4.2).

$$\frac{x}{m} = q_e = KC_e^{1/n} \tag{4.1}$$

$$\frac{x}{m} = q_e = \frac{abC_e}{1+bC_e} \tag{4.2}$$

where x is mass of solute adsorbed; m is mass of adsorbent

q_e is mass ratio of the solid phase – the mass of adsorbed solute per mass of adsorbent

C_e is equilibrium concentration of solute/volume (mg/L)

K, a, b, and n are constants.

The results of the Freundlich and Langmuir isotherms of humic acid and oxalic acid are shown in Figures 4.4 and 4.5, respectively. Table 4.2 presents the fitted parameters for both isotherms. Based on the correlation coefficient (R^2), the Langmuir isotherm tends to fit the data better than the Freundlich isotherm except for oxalic acid. However, the rate constants for Langmuir isotherm were negative. The negative values constants indicated the Langmuir isotherm is not appropriate for explaining the adsorption process (Ramakrishna and Viraraghavan, 1997). NOM surrogate adsorption did not follow the assumption of the Langmuir model since these constants represent the surface binding energy and monolayer coverage. Therefore, the Freundlich isotherm was a more suitable choice. Furthermore, humic acid has a complex structure. The adsorption of sophisticated chemical structures rarely occurred in monolayer which is one of the key characteristics of the Langmuir isotherm (Erhayem and Shon, 2014). Based on the K values for the Freundlich isotherm, HPOA had more adsorption capacity to NZVI than HPIA.

Table 4.2 Calculated parameters for the Freundlich and Langmuir isotherms

Surrogate (Fraction)	**Freundlich**			**Langmuir**		
	K (mg/g)(L/mg)$^{1/n}$	**n**	**R^2**	**b (L/mg)**	**a (mg/g)**	**R^2**
Humic acid (HPOA)	6.3973	0.1991	0.7565	-2.5561	-3.85E-03	0.9196
Oxalic acid (HPIA)	1.52E-03	0.886	0.8484	-0.0234	-0.0234	0.8193

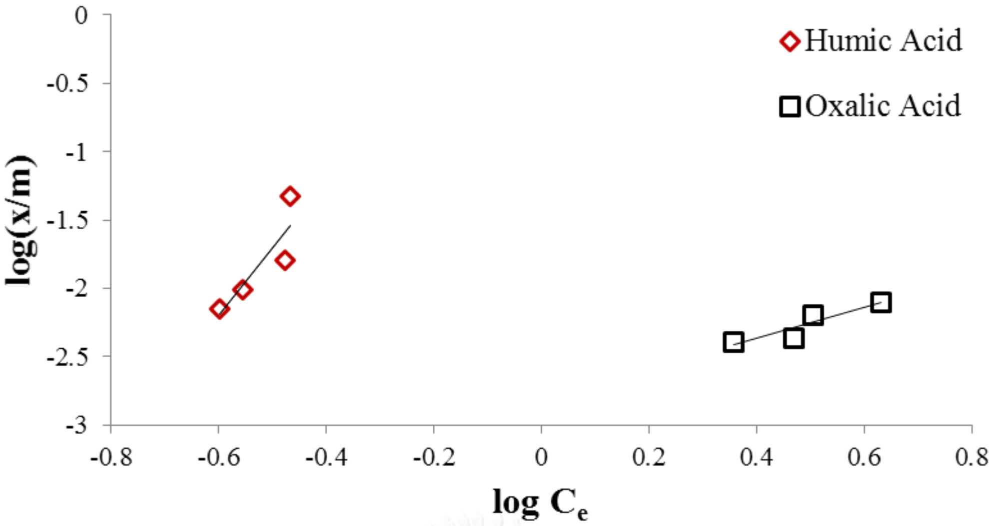


Figure 4.4 Freundlich isotherm plot of humic acid (HPOA) and oxalic acid (HPIA)

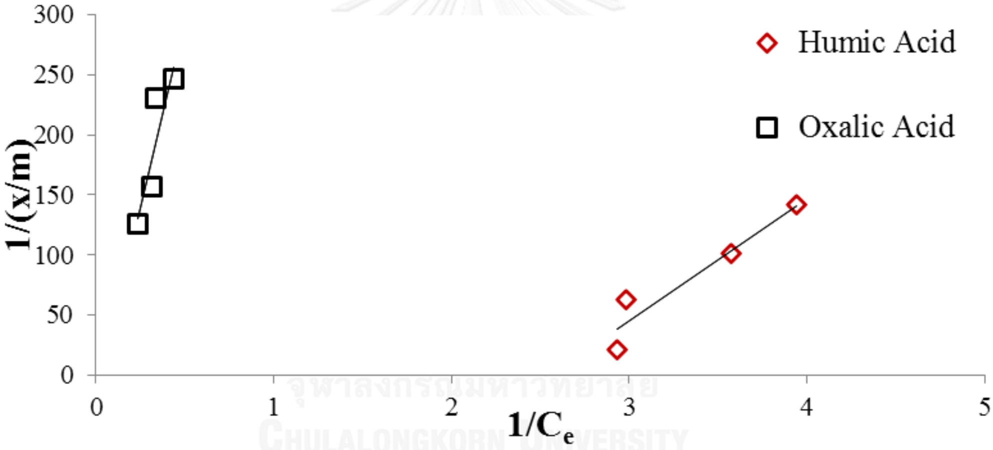


Figure 4.5 Langmuir isotherm plot of humic acid (HPOA) and oxalic acid (HPIA)

4.3 Interaction between NZVI and NOM fractions

Figures 4.6 and 4.7 show the percent of each fraction for GWNOM and SRNOM. According to very small percentages of HPOB and HPIB fractions in both samples, only 4 fractions (HPOA, HPON, HPIA and HPIN) were isolated and experimented.

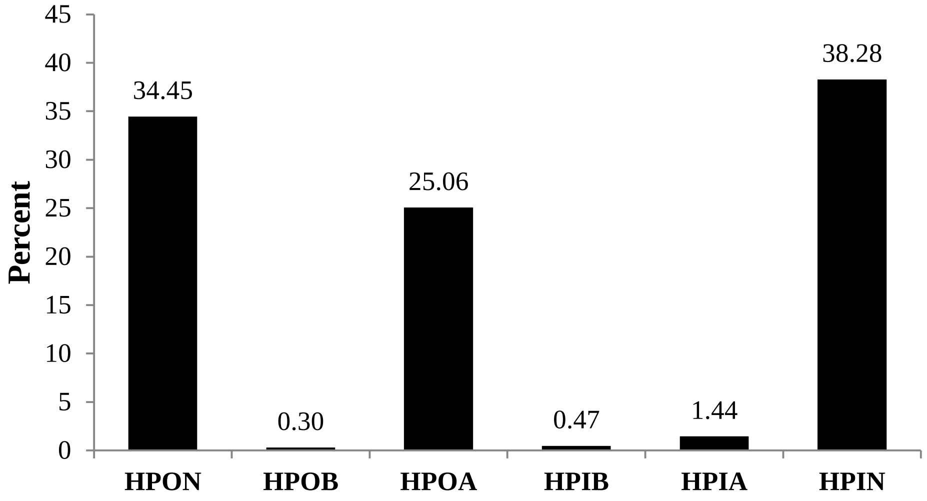


Figure 4.6 NOM fractions of GWNOM (DOC = 1.08 mg/L)

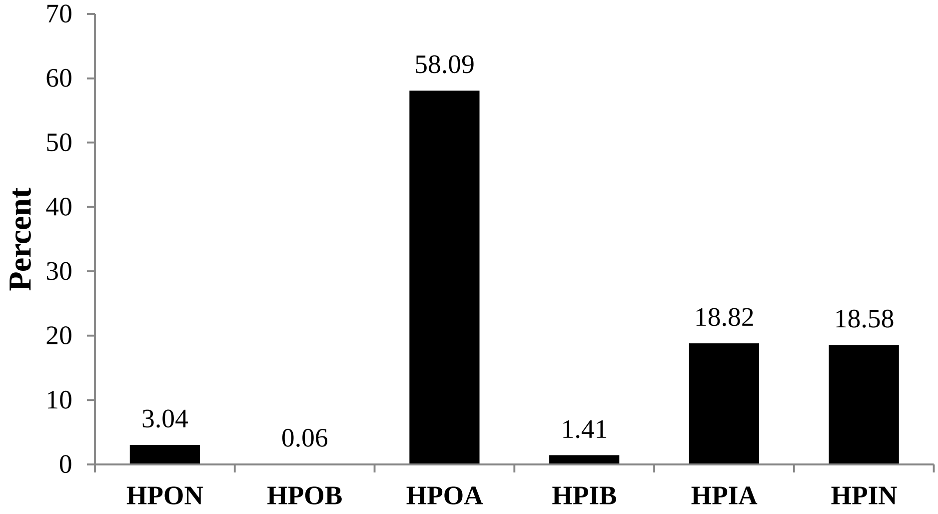


Figure 4.7 NOM fractions of SRNOM (DOC = 8.75 mg/L)

The interaction between NZVI and NOM fractions was tested by determining the reduction of DOC and UV_{254}. Figures 4.8a-c and 4.9a-c show the change in DOC of GWNOM fractions and SRNOM fractions, respectively. For GWNOM, the reduction of DOC of NOM fractions occurred during the first 15 min of the reaction. At the end of experimental run (120 min), the overall DOC reductions of NOM fractions were 0-30%. The DOC of SRNOM fractions decreased 0-60%.

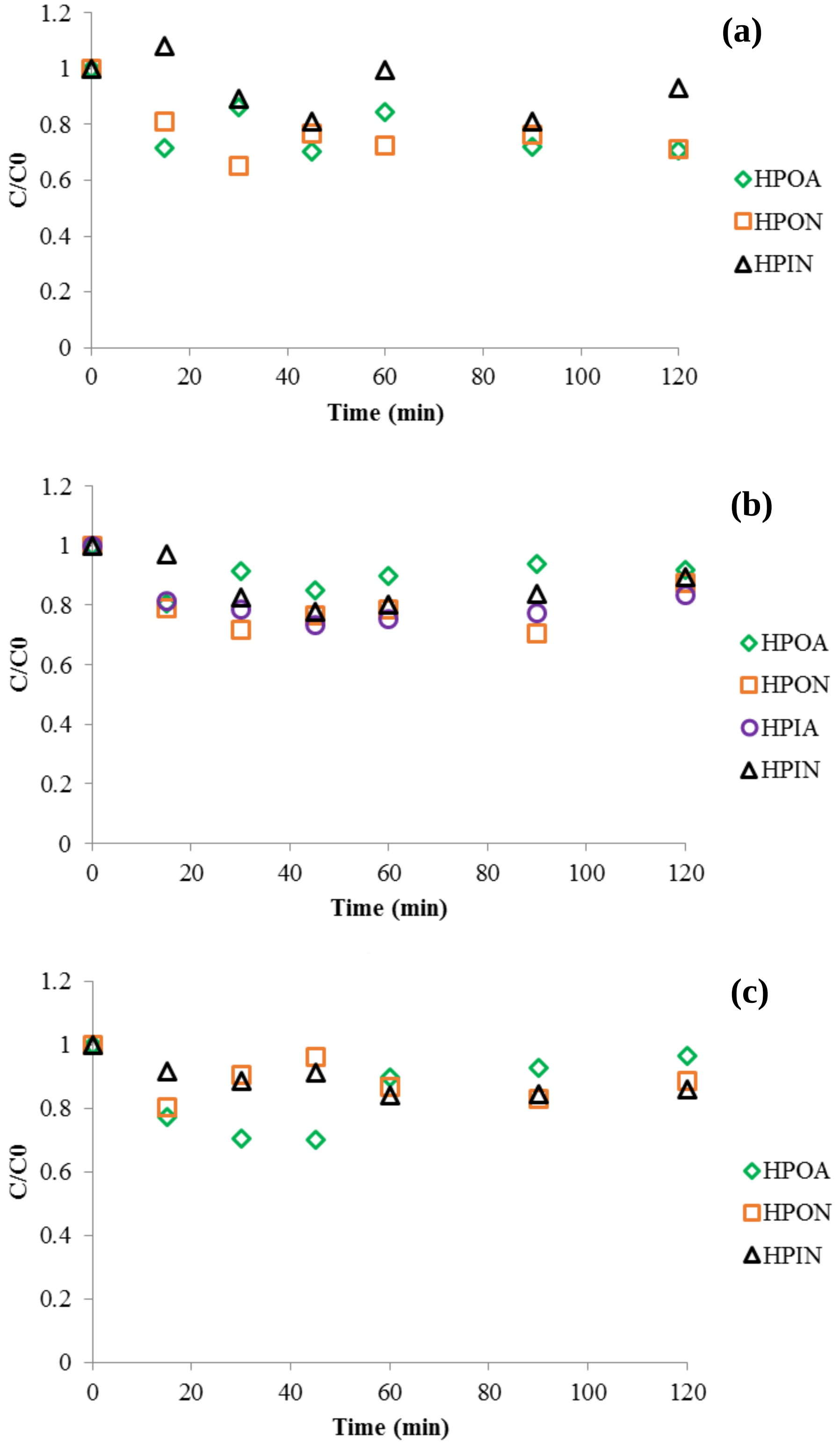


Figure 4.8 Normalized DOC reduction for GWNOM versus reaction time at (a) pH 5, (b) pH 7 and (c) pH 9

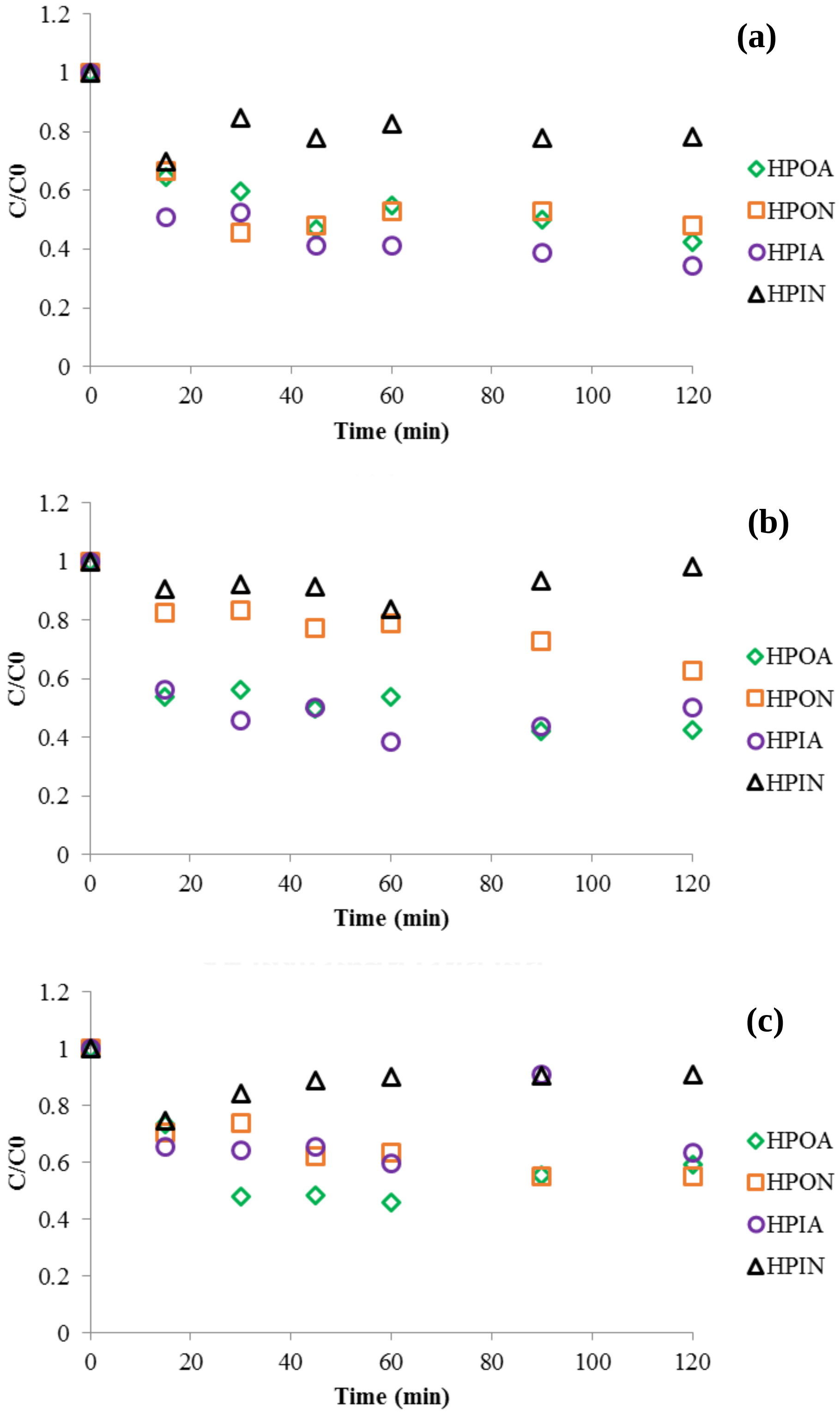


Figure 4.9 Normalized DOC reduction for SRNOM versus reaction time at (a) pH 5, (b) pH 7 and (c) pH 9

The adsorption kinetic data were best fitted with the pseudo-second-order equation. This suggests that the adsorption followed the assumption that chemisorption between adsorbent and adsorbate was the rate determining step (Wang et al., 2014). Previous studies also reported the suitability of this model for reaction between NOM and iron oxide nanoparticles (Chekli et al., 2013; Wu et al., 2014). The calculated parameters of the pseudo second order are shown in Tables 4.3 and 4.4 for GWNOM and SRNOM, respectively. It is noted that HPIA fraction of GWNOM was experimented at pH 7 only due to limited availability of this fraction. For GWNOM, the difference in the amount of NOM absorbed at equilibrium (q_e) of NOM fractions at different pH was observed. At pH 5, HPOA and HPON had the comparable adsorption while HPIN had less adsorption (4 times). The increasing of pH to 7 and 9 resulting in lower adsorption of HPOA about 3 and 5 times, respectively. The HPON adsorption decreased moderately as pH increased from 7 to 9. HPIN fraction was found to have the lowest adsorption at all pHs tested. However, some pseudo-second-order rate constant (k_2) values were negative because linear regressions of the pseudo-second-order model gave negative intercepts.

Table 4.3 Calculated parameters of the pseudo-second-order model for GWNOM fractions reacting with NZVI

GWNOM		q_e (mg/g)	k_2 (g/mg•min)	R^2
pH 5	HPOA	6.95	0.0157	0.9152
	HPON	6.49	0.0650	0.9695
	HPIA	NA	NA	NA
	HPIN	1.42	-0.0322	0.7855
pH 7	HPOA	2.16	-0.0583	0.9172
	HPON	6.63	0.0383	0.9437
	HPIA	6.29	-0.0245	0.9458
	HPIN	2.49	-0.0291	0.8946
pH 9	HPOA	1.32	-0.0503	0.9065
	HPON	4.01	-0.1954	0.9319
	HPIA	NA	NA	NA
	HPIN	3.56	-0.0275	0.9213

NA = Not available

Table 4.4 Calculated parameters of the pseudo-second-order model for SRNOM fractions reacting with NZVI

SRNOM		q_e (mg/g)	k_2 (g/mg•min)	R^2
pH 5	HPOA	17.86	0.0072	0.9753
	HPON	11.76	0.0348	0.9893
	HPIA	18.66	-0.0092	0.9908
	HPIN	3.37	0.0037	0.8794
pH 7	HPOA	15.65	0.0103	0.9817
	HPON	10.87	0.0041	0.8482
	HPIA	13.53	-0.1135	0.9844
	HPIN	1.45	-0.0154	0.9818
pH 9	HPOA	12.84	-0.0419	0.9690
	HPON	11.12	0.0081	0.9647
	HPIA	9.85	0.1015	0.9960
	HPIN	2.12	-0.0623	0.9902

The adsorption of SRNOM fraction shared common trends with that of GWNOM that the q_e values of HPOA and HPIA was the highest at pH 5 and decreased as pH increased. Also HPIN of SRNOM had the lowest absorption at all pHs tested. The effect of pH on the adsorption of NOM fraction could be from the characteristics of NOM fractions and the properties of NZVI. At low pH, NZVI was positively charged on its surface. As a result, NZVI had high interaction with the acid fractions that was negatively charged. As pH increased beyond the point zero charge of NZVI (pH 7.7), the surface of NZVI became negatively charged (Giasuddin et al, 2007). Consequently, this resulted in decreasing of adsorption for HPOA and HPIA. The charge of NOM fraction may not be the only factors that influence the adsorption of NOM onto NZVI. HPON fractions of both NOM sources were found to adsorb to NZVI more than HPIN substantially. SRNOM fractions had higher adsorption to NZVI than GWNOM fractions. This result was expected since SRNOM is more hydrophobic than GWNOM and has high contents of unsaturated carbon structure (measured by UV_{254}).

UV_{254} of GWNOM and SRNOM versus reaction time is shown in Figures 4.10a-c and 4.11a-c, respectively. The UV_{254} of HPOA and HPON fractions decreased with time; especially, at pH 5 which had the highest reduction. At pH 7 and 9, limited changes throughout the experiments were observed. The UV_{254} of SRNOM showed almost 100% decreased within the first 30 min at pH 5 while complete UV_{254} reduction was within 60 min for pH 7. The UV_{254} of HPIN fluctuated around 0.1 cm^{-1}. This may be due to the composition of HPIN that is mostly aliphatic and have less unsaturated carbon (Barber et al., 2001).

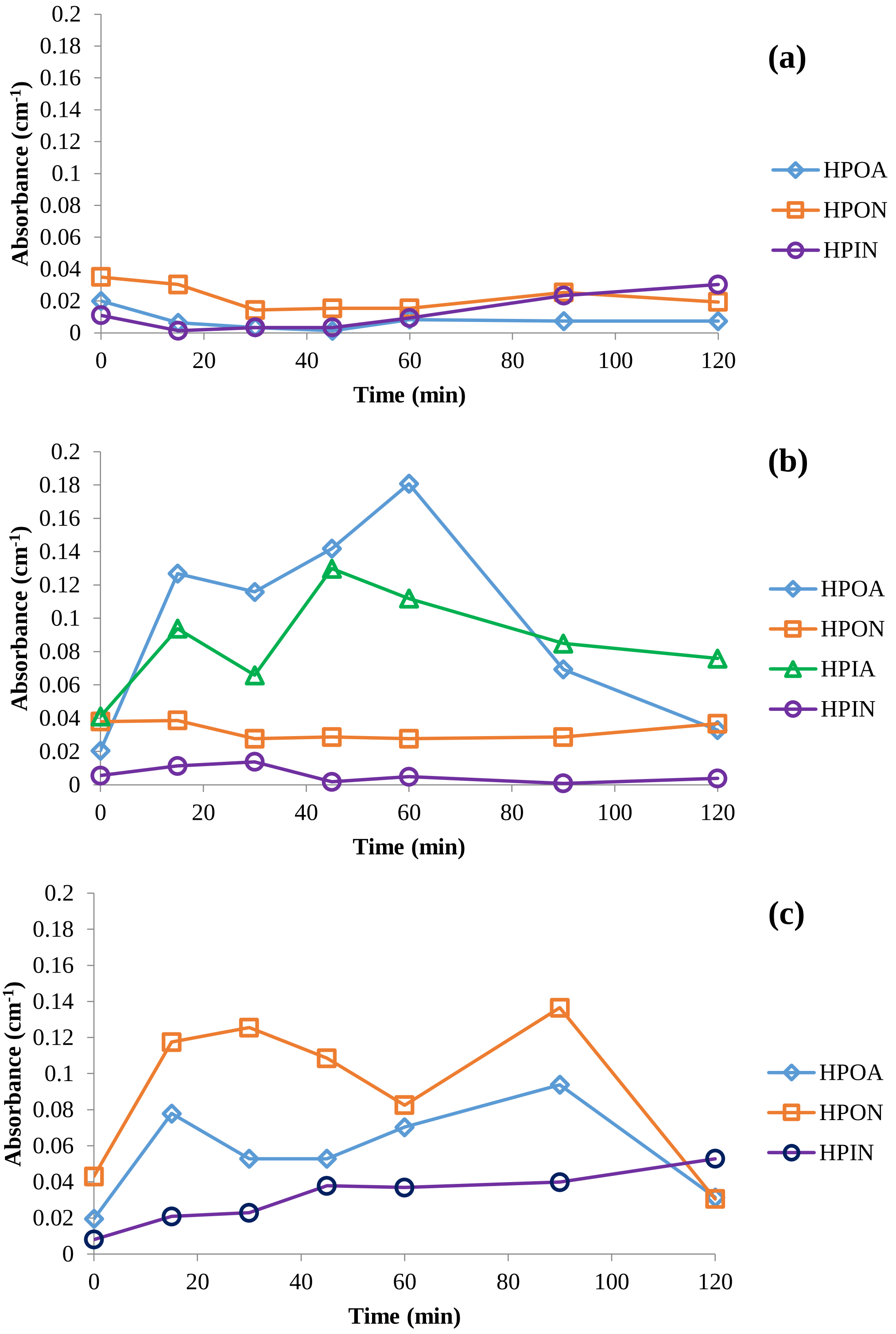


Figure 4.10 UV_{254} for GWNOM versus reaction time at (a) pH 5, (b) pH 7, and (c) pH 9

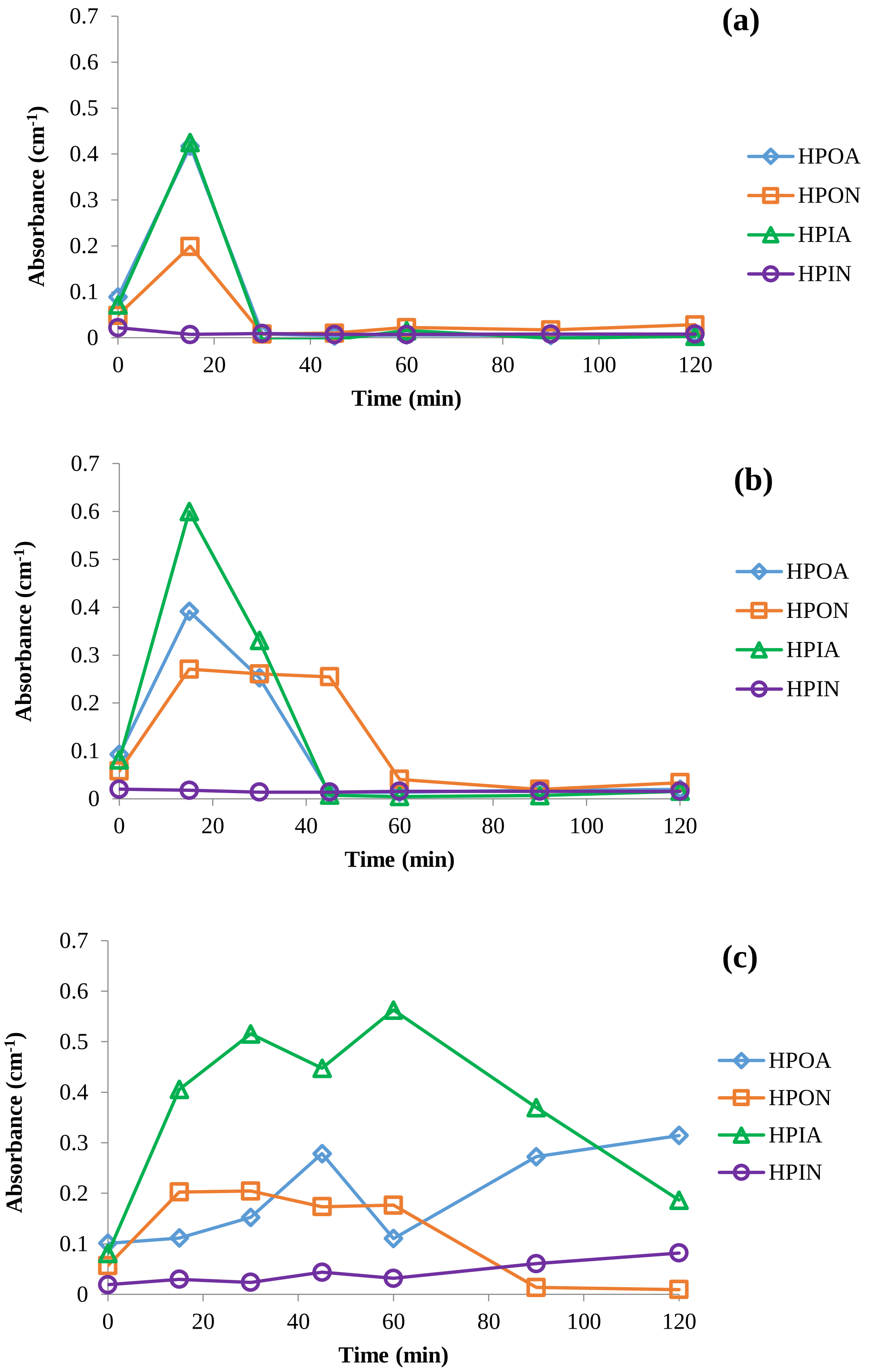


Figure 4.11 UV_{254} for SRNOM versus reaction time at (a) pH 5, (b) pH 7, and (c) pH 9

The increasing of UV_{254} during the course of experiment might be because NOM oxidized NZVI to Fe^{2+} or Fe^{3+} especially under acidic condition. After the increase, the UV_{254} decreased under some experimental conditions (SRNOM at pH 5 and 7). This could be from the precipitation of Fe^{2+} and $Fe^{3+}$with NOM. However, not all Fe^{2+} and Fe^{3+} formed complex with NOM and precipitate. Fe^{2+} and Fe^{3+} produced from the oxidation could contribute to UV_{254} (Weishaar et al., 2003). In addition, the alkaline condition can cause an error for spectroscopy; therefore, some results in basic condition might be affected. On the other hand, the decreasing of UV_{254} (after increasing, Figure 4.11a and 4.11b) could be because NOM interacted with NZVI and adsorbed onto NZVI surface (Philippe and Schaumann, 2014).

4.4 Interaction between NZVI and bulk NOM

Bulk NOM was investigated to examine the competition for reaction with NZVI among different fractions. The fraction distribution before and after GWNOM and SRNOM reacting with NZVI are shown in Figures 4.12 and 4.13, respectively. The result showed that the composition of NOM changed after reacting with NZVI. When considering the change in DOC concentration of each NOM fraction of GWNOM and SRNOM (Figures 4.14 and 4.15), it identified the fractions that had more reaction with NZVI. For GWNOM, HPON and HPOA decreased while HPIN increased. For SRNOM, HPOA and HPIA decreased while HPON, HPIB, and HPIN increased. As described above in subsection 4.3, the q_e values of GWNOM fractions at pH 7 showed that HPOA had the lowest amount of NOM adsorbed onto NZVI which meant less interaction with NZVI than the other fractions. Moreover, HPON which had the highest adsorption onto NZVI decreased from 34% to 27%. This proves that there were competitions among NOM fractions in GWNOM. HPOA preferentially reacted with NZVI while the other fractions did not compete well.

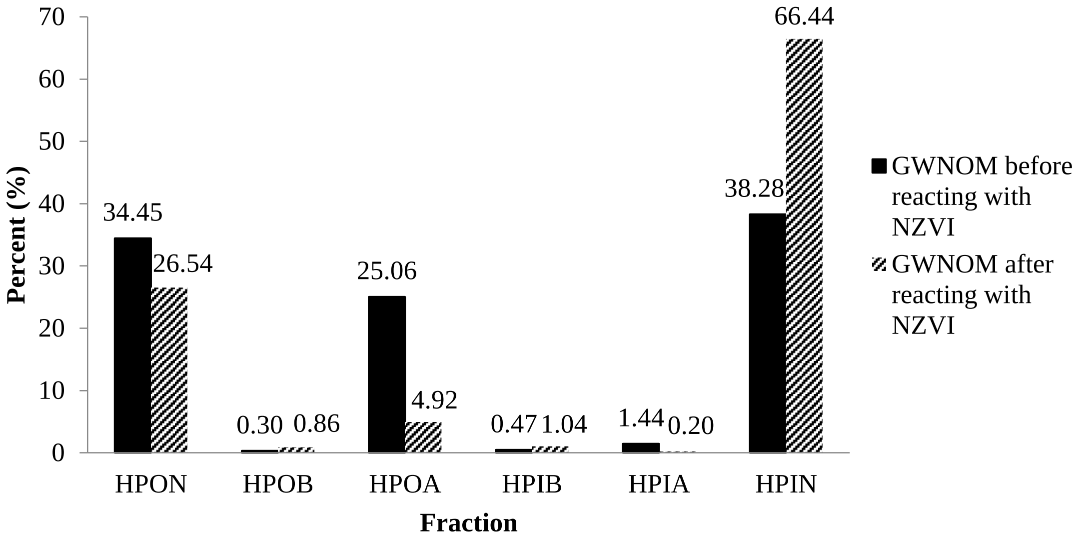


Figure 4.12 The percentage of NOM fractions of GWNOM before and after reacting with NZVI

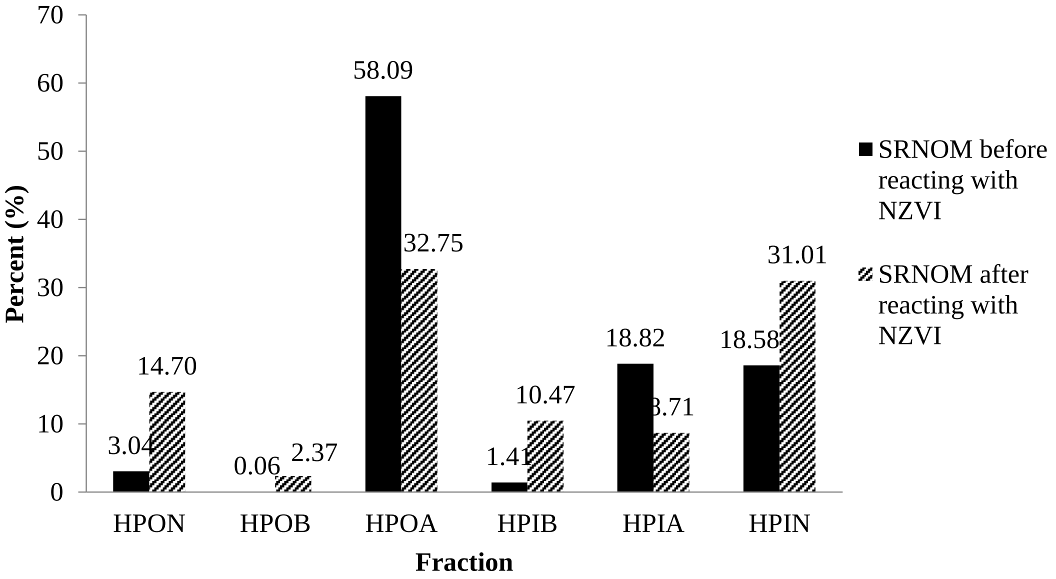


Figure 4.13 The percentage of NOM fractions of SRNOM before and after reacting with NZVI

The HPOA fraction of SRNOM decreased the most from 58% to 33%. This observation agrees with the finding described above that HPOA had the highest q_e (Table 4.4).

The results of bulk NOM fractionation indicated that adsorption may not be the only reaction occurred between NOM and NZVI. Based on the increases in DOC concentrations of HPIN of GWNOM and HPON and HPIN of SRNOM (after reacting with NZVI as shown in Figures 4.14 and 4.15, there was also the degradation of NOM. The degradation resulted in changes of NOM properties to become more hydrophilic and neutral.

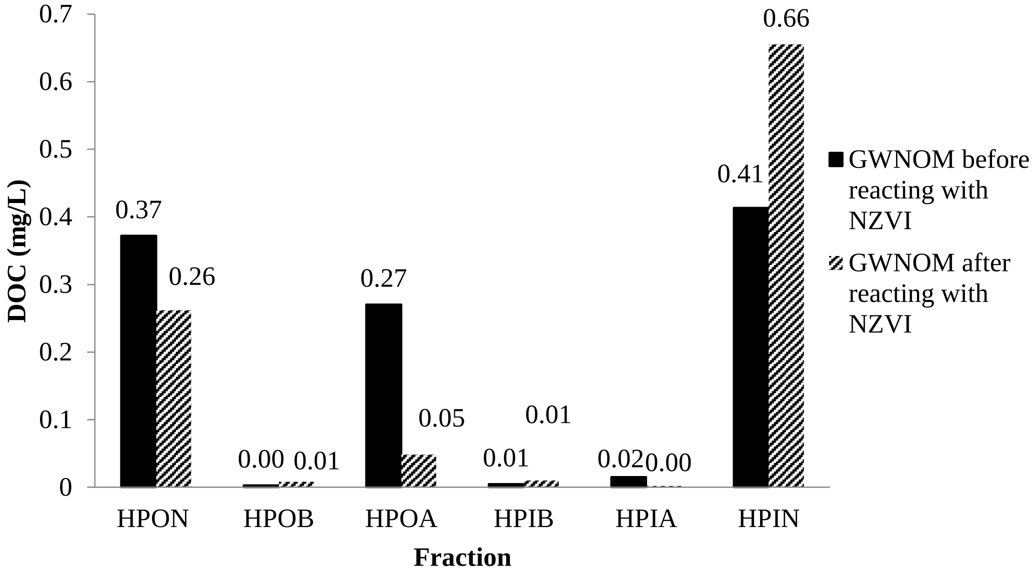


Figure 4.14 DOC mass of GWNOM fractions before and after reacting with NZVI

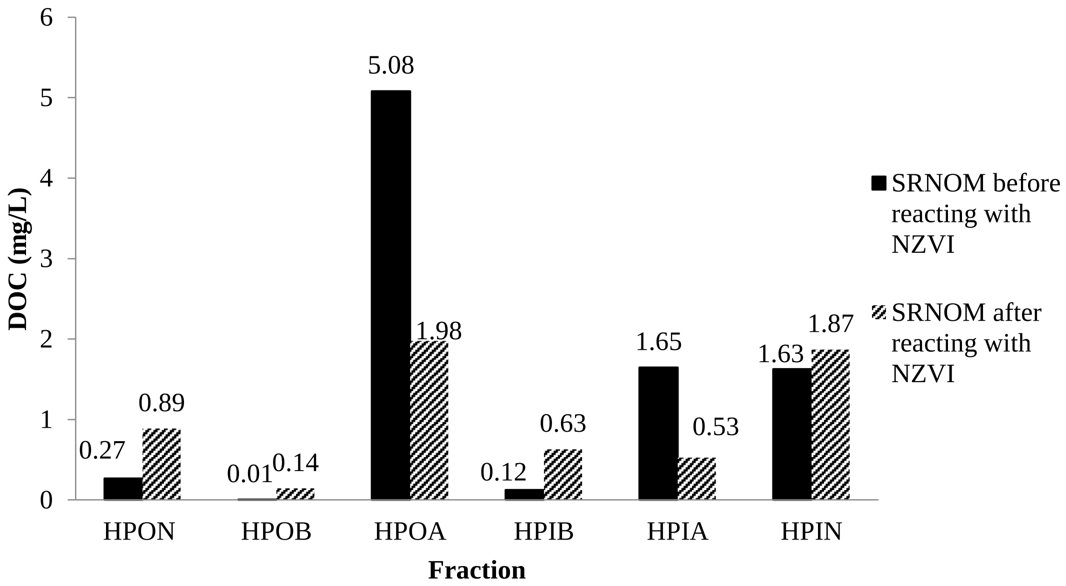


Figure 4.15 DOC mass of SRNOM fractions before and after reacting with NZVI

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

In this study, NZVI was synthesized and characterized by TEM-EDX and BET. The results showed that synthesized NZVI was in a range 5-100 nm. NZVI had a specific surface area of 29.52 m^2/g. By examining the interactions between synthesized NZVI and NOM surrogates, NOM fractions and bulk NOM from two different sources, the following conclusions can be drawn:

1) Among the NOM fraction surrogates studied, only humic acid (HPOA) and oxalic acid (HPIA) reacted with NZVI (based on DOC reduction).This result indicates that the interaction between NZVI and NOM fraction surrogates might be limited to negatively charge structures such as deprotonated carboxylic acid.
2) Adsorption of humic acid (HPOA) and oxalic acid (HPIA) onto NZVI fitted the Freundlich isotherm with $R^2 > 0.75$ rather than the Langmuir isotherm suggesting that the adsorption of humic acid and oxalic acid was not monolayer and aggregation of the organic compounds on NZVI surface was likely.
3) Different reactivity levels of the four isolated NOM fractions (HPOA, HPIA, HPON and HPIN) with NZVI were found. HPOA, HPIA and HPON fractions had high adsorption capacity while low absorption capacity was

observed for HPIN. The solution pH was an important factor influencing the adsorption of NOM fraction onto NZVI surface. Adsorption of acid NOM fractions (HPOA and HPIA) significantly decreased as the solution pH increased while the adsorption of HPON and HPIN were less affected. In addition, source of NOM affected the reactivity toward NZVI. The results showed that SRNOM fractions, which had higher UV_{254} than those of GWNOM, had higher adsorption to NZVI. Different reactivity levels of NOM fractions implies that once NZVI is applied in the field the NOM composition might play an important role in the reactivity between NZVI and target contaminants.

4) Bulk NOM fractionation before and after reacting with NZVI revealed that there were competitions among the NOM fractions to NZVI. HPOA had the highest reactivity with NZVI. Moreover, the increase of DOC concentration of HPIN after reacting with NZVI suggests that the reaction of NOM and NZVI might not be only adsorption but also degradation.

5.2 Recommendations for future work

1) The reactivity of NOM fraction surrogates was probed by DOC which did not change for several NOM fraction surrogates. Measurement of concentration of compounds directly, which could better reflect the reactivity of NOM surrogate with NZVI, should be performed.
2) Interactions between NOM fractions and NZVI should be studied under various conditions such as temperature, and NOM and NZVI concentrations.

3) Various types of modified NZVI should be studied with NOM fractions to find out what type of NZVI has the least reactivity with NZVI and in turn is potentially effective for groundwater remediation.

4) This study should be extended by experimenting NZVI, NOM fractions and a model pollutant in the same system.

5) Based on the result of bulk fractionation, adsorption of NOM by NZVI may not be the only reaction but also degradation may occur. This reaction mechanism should be further investigated.

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APPENDIX A

NZVI characterization

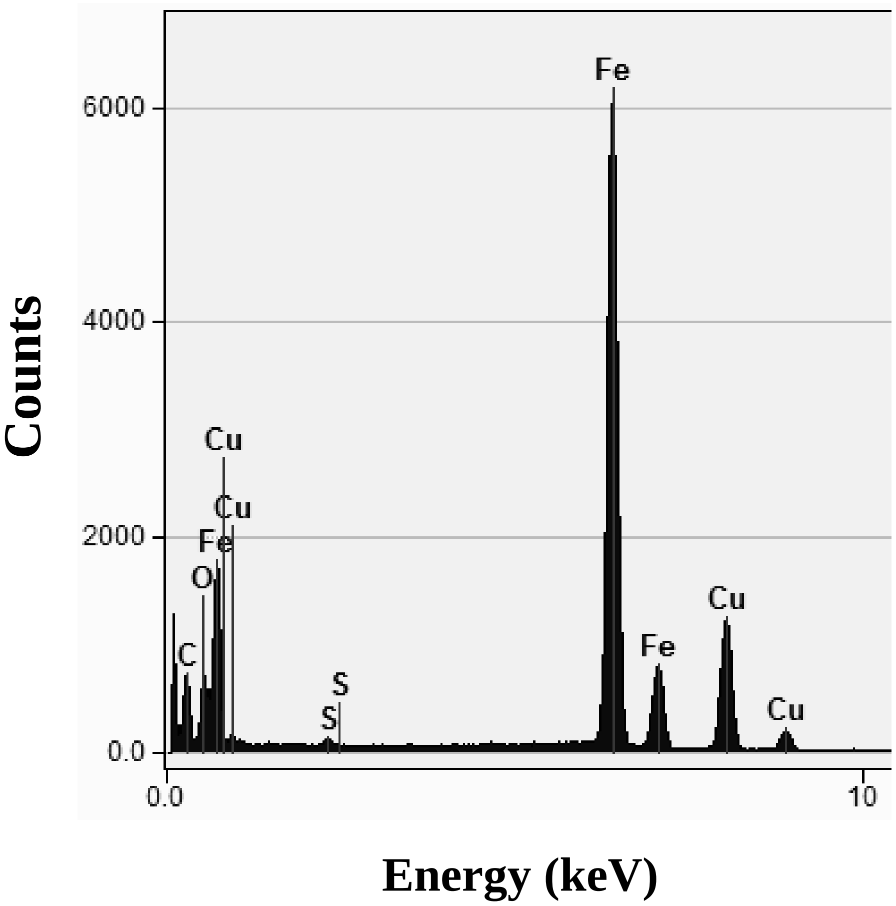
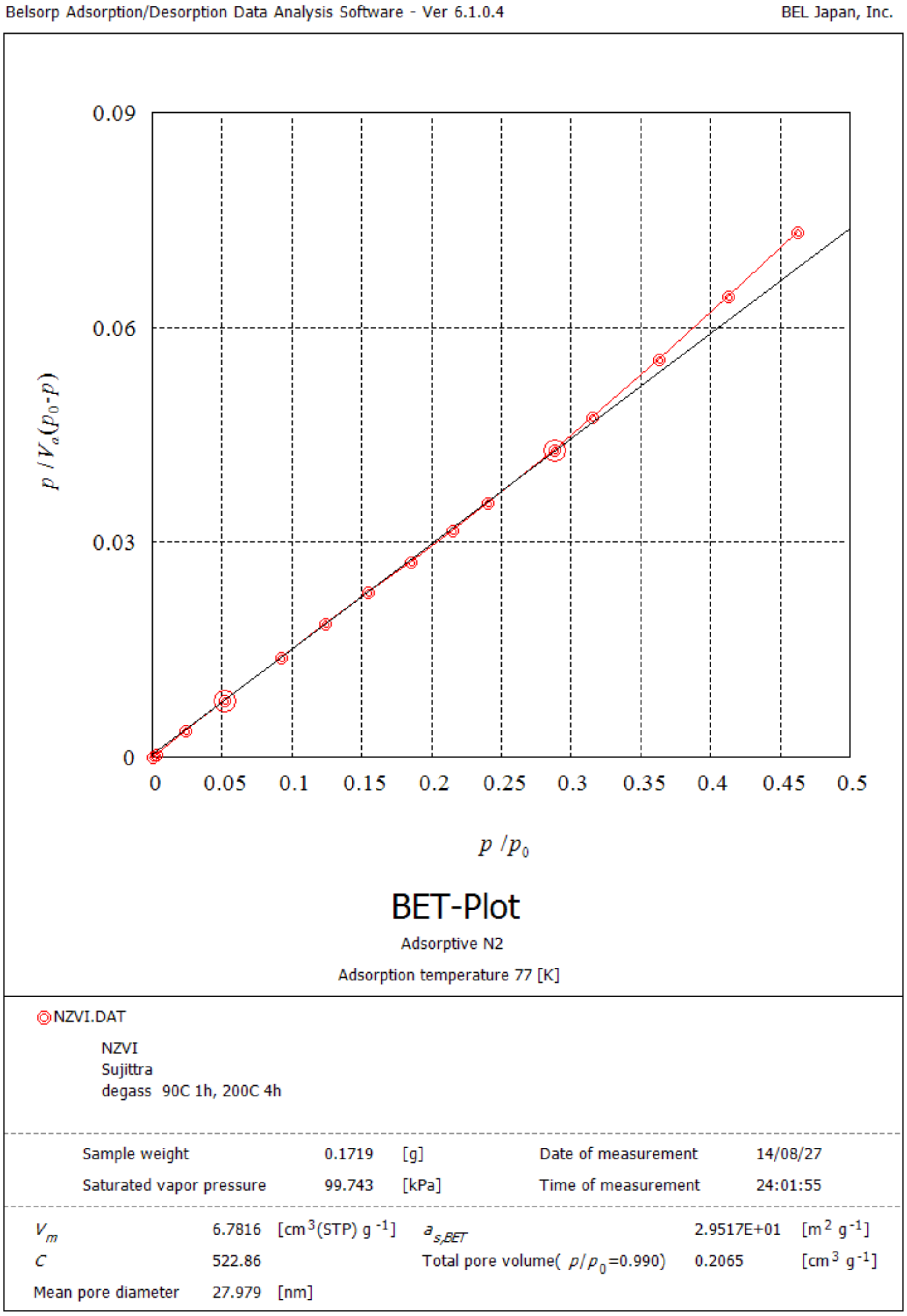


Figure A.1 EDX spectroscopy of synthesized NZVI



Belsorp Adsorption/Desorption Data Analysis Software - Ver 6.1.0.4 BEL Japan, Inc.

BET-Plot

Adsorptive N2

Adsorption temperature 77 [K]

◎NZVI.DAT

NZVI
Sujittra
degass 90C 1h, 200C 4h

Sample weight	0.1719	[g]	Date of measurement	14/08/27
Saturated vapor pressure	99.743	[kPa]	Time of measurement	24:01:55

V_m	6.7816	[cm^3(STP) g^{-1}]	$a_{s,BET}$	2.9517E+01	[m^2 g^{-1}]
C	522.86		Total pore volume(p/p_0=0.990)	0.2065	[cm^3 g^{-1}]
Mean pore diameter	27.979	[nm]			

Figure A.2 BET plot from nitrogen adsorption-desorption technique

APPENDIX B

Natural organic matter (NOM) model compound study

Table B.1 Kinetic study of NOM model compound and NZVI

NOM fraction surrogate	**Time (min)**	**DOC (mg/L)**	**NOM fraction surrogate**	**Time (min)**	**DOC (mg/L)**
Humic acid (HPOA)	0	8.15	Oxalic acid (HPIA)	0	9.31
	15	7.11		15	8.13
	30	6.98		30	8.00
	45	6.56		45	8.03
	60	6.06		60	8.14
	90	5.70		90	8.21
	120	4.81		120	8.55
Aniline (HPOB)	0	9.52	L-asparagine (HPIB)	0	9.43
	15	9.35		15	8.76
	30	9.46		30	8.91
	45	9.59		45	8.93
	60	9.64		60	8.89
	90	9.63		90	9.00
	120	9.74		120	9.03
L-tryptophan (HPON)	0	9.18	D-xylose (HPIN)	0	10.35
	15	8.76		15	9.96
	30	8.85		30	10.11
	45	8.65		45	10.12
	60	8.63		60	10.22
	90	8.77		90	10.21
	120	8.92		120	10.34

APPENDIX C

Interaction between NZVI and NOM fractions

Table C.1 Parameters of groundwater

Parameter	Unit	Value
Color	NA	Colorless
pH	NA	8.59
Electricity conductivity (EC)	µS/cm	852
Alkalinity	mg/L as $CaCO_3$	523
Total hardness	mg/L as $CaCO_3$	320
Calcium hardness	mg/L as $CaCO_3$	242
Chloride	mg/L	16.6
Sulfide	mg/L	<5.0
Manganese	mg/L	0.18
Iron	mg/L	<0.05

NA = Not available

C.2 Recovery of NOM fractions of Groundwater and Suwannee River

Table C.2 Recovery of NOM fractions of Groundwater and Suwannee River

NOM	**Fraction**	**Mass of carbon recovered (mg)**	**Mass of carbon calculated by DOC in fraction (mg)**	**Recovery (%)**
GWNOM	HPON	7.84	14.88	52.7
	HPOB	NA	NA	NA
	HPOA	5.36	10.83	49.5
	HPIB	NA	NA	NA
	HPIA	0.38	0.62	61.1
	HPIN	NA	NA	NA
SRNOM	HPON	3.81	5.32	71.8
	HPOB	NA	NA	NA
	HPOA	81.63	101.65	80.3
	HPIB	NA	NA	NA
	HPIA	21.14	32.93	64.2
	HPIN	NA	5.32	NA

NA = Not available
Mass of GWNOM was based on 40 L of sample
Mass of SROM was based on 20 L of sample

$$Recovery\ Efficiency = \frac{DOC_e \times V_e}{DOC_f \times V_s} \times 100$$

where DOC_e is DOC of eluted NOM fraction solution

V_e is Volume of eluted NOM solution

DOC_f is DOC of NOM fraction (calculated by subtraction of DOC before and after SPE cartridge

V_s is Volume of water sample fractionated

C.3 NOM fractions study

Table C.3 DOC concentration of GWNOM fractions reacting with NZVI

NOM fraction	**Time (min)**	**DOC (mg/L)**		
		pH 5	**pH 7**	**pH 9**
HPOA	0	2.25	3.01	2.74
	15	1.61	2.42	2.06
	30	1.94	2.75	1.88
	45	1.58	2.55	1.87
	60	1.90	2.70	2.46
	90	1.62	2.82	2.53
	120	1.59	2.76	2.65
HPON	0	2.37	2.40	3.14
	15	1.92	1.89	2.52
	30	1.55	1.72	2.84
	45	1.82	1.83	3.02
	60	1.72	1.88	2.72
	90	1.81	1.69	2.61
	120	1.69	2.09	2.78
HPIA	0	NA	3.50	NA
	15	NA	2.84	NA
	30	NA	2.75	NA
	45	NA	2.56	NA
	60	NA	2.63	NA
	90	NA	2.71	NA
	120	NA	2.91	NA
HPIN	0	1.88	2.26	2.26
	15	2.03	2.19	2.07
	30	1.68	1.86	2.00
	45	1.52	1.75	2.06
	60	1.87	1.81	1.90
	90	1.52	1.89	1.91
	120	1.75	2.02	1.94

NA = Not available

Table C.4 DOC concentration of SRNOM fractions reacting with NZVI

NOM fraction	**Time (min)**	**DOC (mg/L)**		
		pH 5	**pH 7**	**pH 9**
HPOA	0	3.12	2.66	2.99
	15	2.01	1.43	2.20
	30	1.86	1.49	1.44
	45	1.46	1.32	1.45
	60	1.72	1.43	1.38
	90	1.56	1.12	1.66
	120	1.33	1.13	1.77
HPON	0	2.30	2.94	2.33
	15	1.53	2.42	1.65
	30	1.05	2.45	1.72
	45	1.11	2.27	1.45
	60	1.22	2.31	1.48
	90	1.22	2.14	1.29
	120	1.11	1.84	1.29
HPIA	0	2.80	2.58	2.65
	15	1.43	1.45	1.74
	30	1.47	1.18	1.71
	45	1.15	1.29	1.74
	60	1.15	0.99	1.59
	90	1.09	1.12	2.41
	120	0.96	1.29	1.68
HPIN	0	2.72	2.26	2.42
	15	1.90	2.04	1.81
	30	2.30	2.08	2.04
	45	2.12	2.06	2.15
	60	2.25	1.89	2.18
	90	2.12	2.11	2.19
	120	2.13	2.22	2.20

Table C.5 UV_{254} absorbance of GWNOM reacting with NZVI

NOM fraction	**Time (min)**	**UV_{254} Absorbance (cm^{-1})**		
		pH 5	**pH 7**	**pH 9**
HPOA	0	0.0200	0.0205	0.0195
	15	0.0063	0.1268	0.0778
	30	0.0033	0.1158	0.0528
	45	0.0013	0.1418	0.0528
	60	0.0083	0.1808	0.0703
	90	0.0073	0.0693	0.0938
	120	0.0073	0.0328	0.0313
HPON	0	0.0350	0.0380	0.0430
	15	0.0303	0.0387	0.1175
	30	0.0143	0.0277	0.1255
	45	0.0153	0.0287	0.1085
	60	0.0153	0.0277	0.0825
	90	0.0253	0.0287	0.1365
	120	0.0193	0.0367	0.0305
HPIA	0	NA	0.0410	NA
	15	NA	0.0938	NA
	30	NA	0.0658	NA
	45	NA	0.1298	NA
	60	NA	0.1118	NA
	90	NA	0.0848	NA
	120	NA	0.0758	NA
HPIN	0	0.0110	0.0055	0.0080
	15	0.0013	0.0113	0.0208
	30	0.0033	0.0138	0.0228
	45	0.0033	0.0018	0.0378
	60	0.0093	0.0048	0.0368
	90	0.0233	0.0008	0.0398
	120	0.0303	0.0038	0.0528

NA = Not available

Table C.6 UV_{254} absorbance of SRNOM fractions reacting with NZVI

NOM fraction	**Time (min)**	**UV_{254} Absorbance (cm^{-1})**		
		pH 5	**pH 7**	**pH 9**
HPOA	0	0.0890	0.0930	0.1010
	15	0.4173	0.3917	0.1115
	30	0.0083	0.2527	0.1525
	45	0.0043	0.0137	0.2785
	60	0.0063	0.0137	0.1105
	90	0.0053	0.0177	0.2725
	120	0.0083	0.0197	0.3145
HPON	0	0.0490	0.0580	0.0570
	15	0.1993	0.2707	0.2025
	30	0.0083	0.2607	0.2045
	45	0.0103	0.2547	0.1735
	60	0.0223	0.0407	0.1765
	90	0.0173	0.0197	0.0135
	120	0.0283	0.0337	0.0095
HPIA	0	0.0720	0.0810	0.0810
	15	0.4253	0.5997	0.4055
	30	-0.0037	0.3307	0.5155
	45	-0.0037	0.0777	0.4475
	60	0.0157	0.0047	0.5625
	90	-0.0007	0.0067	0.3695
	120	0.0033	0.0157	0.1865
HPIN	0	0.0220	0.0200	0.0190
	15	0.0073	0.0178	0.0298
	30	0.0093	0.0138	0.0238
	45	0.0073	0.0138	0.0438
	60	0.0073	0.0158	0.0318
	90	0.0083	0.0158	0.0608
	120	0.0083	0.0158	0.0818

C.4 Adsorption kinetic of NOM fractions onto NZVI surface

The adsorption kinetic of NOM fractions onto NZVI surface is calculated through mass balance equation and pseudo-second order equation as described in following formulas:

Mass balance equation

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where q_t (mg/g) is the amount of NOM absorbed per gram of NZVI at time t (min)

C_0 (mg/L) is the initial concentration of NOM fraction in the solution

C_t (mg/L) is the concentration of NOM after time t of adsorption

W (g) is the mass of NZVI used

V (L) is the volume of the solution

Pseudo-second order equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where: k_2 (g/mg•min) is the pseudo-second-order rate constant

q_e (mg/g) is the amount of humic acids adsorbed at equilibrium

APPENDIX D

Interaction between NZVI and bulk NOM

Table D.1 DOC concentration of GWNOM and SRNOM fractions before and after reacting with NZVI

Source	**Fraction**	**DOC (mg/L)**		**Remark**
		Before NZVI	**After NZVI**	
GWNOM	HPON	0.3721	0.2618	DOC$_{initial}$ = 1.08 mg/L DOC$_{final}$= 0.99 mg/L
	HPOB	0.0032	0.0085	
	HPOA	0.2707	0.0485	
	HPIB	0.0051	0.0103	
	HPIA	0.0156	0.0020	
	HPIN	0.4134	0.6554	
SRNOM	HPON	0.2660	0.8866	DOC$_{initial}$ = 8.75 mg/L DOC$_{final}$= 6.03 mg/L
	HPOB	0.0053	0.1429	
	HPOA	5.0829	1.9753	
	HPIB	0.1234	0.6315	
	HPIA	1.6468	0.5253	
	HPIN	1.6258	1.8703	

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Presentation:

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