Carbon-nZVI nanocomposites for dechlorination of halogenated hydrocarbons

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A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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CARBON-SUPPORTED ZERO VALENT IRON NANOPARTICLE NANOCOMPOSITES AS NOVEL MATERIALS FOR DECHLORINATION OF HALOGENATED HYDROCARBONS

(Thesis Format: Integrated Article)

By

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ABSTRACT

A family of hybrid nanocarbon/nanoiron composites has been developed with the aim to carry out simultaneous adsorption and dechlorination of chlorinated hydrocarbons from aqueous solutions. Several methodologies for the synthesis of these materials are evaluated in terms of their adsorption capacities and dechlorination activities. Detailed spectroscopic and microscopy studies indicate that the adsorption ability of the carbonaceous support is greatly improved after acid oxidization, attributed to the formation of oxygenated functional groups on their surfaces. When iron nanoparticles are incorporated on the composites, the materials show a much higher trichloroethylene (TCE) removal efficiency compared to bare metallic nanoiron particles or nanocarbon. It is proposed that in this hybrid nanomaterial system, the carbonaceous material serves as a highly efficient adsorbent and an effective support to immobilize iron nanoparticles simultaneously. Thermal programmed reduction studies suggest a strong support interaction with the nanoiron particles, which diminishes the possibility of agglomeration in solution and thus maintains their high reactivity for redox TCE dechlorination.

Keywords: multi-walled carbon nanotubes, nanoscale zero valent particles, granular activated carbon, adsorption, TCE dechlorination
CO-AUTHORSHIP

Chapter 2: Literature Review


Chapter 3: Adsorption of Trichloroethylene onto Multi-walled Carbon Nanotubes

All the experimental and theoretical work was carried out by Jing Cheng under the guidance of Dr. Jose E. Herrera. The initial draft and the followed modifications of this manuscript were conducted by Jing Cheng under the supervision of Dr. Jose E. Herrera.

The final version of this manuscript will be submitted as a peer reviewed publication.

Chapter 4: Simultaneous Adsorption and Degradation of Trichloroethylene by Bimetallic Pd/nZVI Supported on Multi-walled Carbon Nanotubes

Jing Cheng has performed all the experiments, collected and analyzed data and wrote the draft of this chapter. Dr. Jose E. Herrera guided the experiments and revised the chapter.

The final version of this manuscript will be submitted as a peer reviewed publication.
Chapter 5: Simultaneous Adsorption and Degradation of Trichloroethylene over Granular Activated Carbon-Nanoscale Zero-valent Particle Composite: Synthesis, Characterization and Reactivity

Jing Cheng conducted the experiments, collected and interpreted the results and wrote the draft of this chapter. Dr. Jose E. Herrera supervised the laboratory tests and reviewed the chapter. The final version of this manuscript will be submitted as a peer reviewed publication.
DEDICATION

To the memory of my ever-loving grandmother, Daozhen Wang and my dearest grandfather Pingan Cheng, for their precious love, continuous encouragement and confidence, which are always of the greatest worth and have already rooted in my life.
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1, 2-DCE: 1,2-dichloroethene
2-CIBP: 2-Chlorobiphenyl
-COOH: Carboxyl
-OH: Hydroxyl
α-Fe₂O₃: Hematite
γ-Fe₂O₃: Maghemite
α-FeO(OH): Goethite
AC: Activated Carbon
Ag: Silver
ATSDR: Agency for Toxic Substances and Disease Registry
BET: Brunauer-Emmett-Teller
BJH: Barrett-Joyner-Halenda
CₓHᵧClₜ: Chlorinated Hydrocarbons
CA: Cellulose Acetate
CCVD: Catalytic Chemical Vapor Decomposition
CEP: Completed Exposure Pathway
cis-1,2-DCE: cis-1,2-dichloroethene
CMC: Carboxymethyl Cellulose
CNTs: Carbon Nanotubes
CT: Carbon Tetrachloride

CVD: Chemical Vapor Decomposition

DCB: Dichlorobenzene

DI: Deionized Water

DFT: Density Functional Theory

DNAPLs: Dense Non-aqueous Phase Liquids

DO: Dissolved Oxygen

USEPA: US Environmental Protection Agency

Fe₀: Zero Valent Iron

Fe (II): Ferrous iron

Fe (III): Ferric iron

FeCl₃: Ferric Chloride

FeO: Wustite

Fe₃O₄: Magnetite

FeSO₄: Ferrous Sulfate

FeSO₄ · 7H₂O: Ferrous Sulphate Heptahydrate

Fe(NO₃)₃ · 9H₂O: Ferric Nitrate Nonahydrate

FTIR: Fourier Transform Infrared Spectroscopy

GAC: Granular Activated Carbon

GC: Gas Chromatography

GC-ECD: Gas Chromatography-Electron Capture Detector
HCl: Hydrochloric Acid

HNO₃: Nitric Acid

HRTEM: High-resolution Transmission Electron Microscopy

H₂SO₄: Sulphuric Acid

IPA: Isopropanol

IR: Infrared Spectroscopy

IUPAC: International Union of Pure and Applied Chemistry

MAC: Maximum Acceptable Concentration

MCL: Maximum Contaminant Level

MWCNTs: Multi-walled Carbon Nanotubes

N₂: Nitrogen

NaBH₄: Sodium Borohydride

NaOH: Sodium Hydroxide

Ni: Nickel

nZVI: Nano-scale Zero Valent Iron

PAA: Polyacrylic Acid

PAC: Powdered Activated Carbon

PAHs: Polycyclic Aromatic Hydrocarbons

PBDEs: Polybrominated Diphenyl Ethers

PCBs: Polychlorinated Biphenyls

PCE: Tetrachloroethene
Pd: Palladium

Pd(ac)$_2$: Palladium Acetate

Pd/NZVI: Palladized Nanoscale Zero Valent Iron

PRBs: Permeable Reactive Barriers

Pt: Platinum

PV3A: Polyvinyl Alcohol-co-vinyl Acetate-co-itaconic Acid

RAC: Reactive Activated Carbon

Raman: Raman Spectroscopy

SAED: Selected Area Electron Diffraction

SEM: Scanning Electron Microscopy

SWCNTs: Single-walled Carbon Nanotubes

THMs: Trihalomethanes

TCD: Thermal Conductivity Detector

TCDD: 2,3,7,8-tetrachlorodibenzo-p-dioxin

TCE: Trichloroethylene

TEM: Transmission Electron Microscopy

TPR: Temperature Programmed Reduction

VC: Vinyl Chloride

XRD: X-ray Diffraction

ZVI: Zero Valent Iron
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Chapter 1 Introduction

1.1 Background on Groundwater Contamination

The level and complexity of water contamination worldwide has reached unprecedented levels in such a way that the complexity of the problem seems intractable. While there is a wide variety of different contaminant species, the US environmental protection agency divides most of the common contaminants found in surface water into six categories [1]:

- Inorganic compounds: these include toxic heavy metal ions (e.g. cadmium, chromium, lead, copper, mercury), oxoanions (arsenates, chromates) and nonmetal anions such as fluoride.

- Organic compounds: benzene, 1, 2-dichloroethene (1, 2-DCE), dioxins, polyaromatic hydrocarbons, tetrachloroethene (PCE), trichloroethylene (TCE), polychlorinated biphenyls (PCBs), etc.

- Disinfection byproducts: trihalomethanes and haloacetic acids.

- Disinfectants: chlorine (as Cl), chloramines and chlorine dioxide.

- Radionuclides: atoms with unstable potentially radioactive nuclei, such as phosphorous-32, promethium-147 or americium-243.
• Microorganisms: these include bacteria, fungi and archaea, but not viruses nor prions.

In particular, the widespread occurrence of chlorinated hydrocarbons, such as TCE or PCE, poses a potential threat to public health and the environment [2]. Initially highly valued for their high chemical stability and strong resistance to combustion and explosion, these chlorinated compounds have been widely utilized as degreasing solvents by a number of industries such as electronics, machinery, metal finishing and dry cleaning. The combination of past extensive use, leakage from storage drums, accidental spills and improper discharge has left a legacy of widespread contamination of groundwater by these ubiquitous and recalcitrant pollutants in Canada, the U.S. and several other industrialized nations [3]. Among these, TCE, one of the most ubiquitous chlorinated compounds, has been found at 301 out of the 1444 ATSDR’s (Agency for Toxic Substances and Disease Registry) CEP (Completed Exposure Pathway) sites by 2007 [4].

Chlorinated hydrocarbons are normally categorized as dense non-aqueous phase liquid (DNAPL) toxic contaminants in soil and groundwater. They have densities greater than water and therefore are capable to transport deeper into sediments by gravity from which they gradually leach out into aquifers. Due to their low aqueous solubility and low rate of dissolution, chlorinated pollutants are persistent to natural degradation, causing long-term environmental pollution. Additionally, chlorinated compounds are suspected carcinogens
and pose a significant health threat. As a class of the priority pollutants, U.S. Environmental Protection Agency (USEPA) set a maximum contaminant level (MCL) in drinking water of 5 ppb (or 0.005mg/L) for both TCE and PCE, which is readily exceeded at contaminant sites by orders of magnitude [5].

1.2 Nanoscale Zero-valent Iron Technologies

The cleanup of aquifers contaminated with DNAPLs is of utmost importance and is a challenging task due to subsurface heterogeneity and complex site architecture [6]. Various techniques have been explored to dechlorinate DNAPLs, including bioremediation [7], pump-and-treat methods [8], thermal treatment [9] and air sparging-soil vapor extraction [10]. However, these methods are either relatively expensive, time consuming, or limited by the production of secondary waste streams that require subsequent disposal or treatment. Compared to these conventional approaches, permeable reactive barriers (PRBs) are a potentially simple, cost-effective, and environmentally benign technology that has become a preferred method for remediation of chlorinated compounds [11]. The foremost advantage of PRBs is that the contaminated water can be treated in-situ without pumping out for above-ground treatment and disposal, resulting in relatively low operational and maintenance costs [12]. Various reactive materials have been suggested for PRBs, among these micro-scale zero valent iron (ZVI)
particles in the form of filings or granules are inexpensive and readily available. One of the most attractive features is that ZVI particles can be readily incorporated into reactive subsurface barriers by the “funnel and gate” approach, in which a porous wall of granular iron is constructed in the path of a contaminated groundwater plume [13]. As contaminated groundwater flows through the permeable wall bearing iron particles, the organic contaminants react with the surface sites on iron thoroughly to form environmentally innocuous end products: hydrocarbons, chloride ions and water.

However, due to their limited reactivity, the reduction rate of granular iron particles is very slow [14]. As a result, production and accumulation of some toxic and carcinogenic intermediate byproducts, such as vinyl chloride (VC) and cis-1, 2-dichloroethene (cis-1, 2-DCE) takes place [15]. One of the primary parameters dominating the reaction rate is the number of active sites on the surface of ZVI particles presented to the groundwater plume. Since the reaction on Fe⁰-based particles is a surface-mediated process, the dechlorination rate strongly depends on the available surface area of the ZVI particles. In other words, increasing the fraction of active iron atoms located on the particle surface would result in an increase in dechlorination activity. This can be achieved by decreasing the iron particle size.
In order to enhance the dechlorination reaction rate and minimize byproducts formation, Zhang et al. [16] at Lehigh University investigated the application of nano-scale ZVI (nZVI) particles, prepared by reductive precipitation of iron salts with sodium borohydride (NaBH₄) solution, for the removal of TCE. He reported that the nanoparticles, with a broad size distribution of 1-100nm, showed much higher TCE dechlorination reactivity than that observed on micro ZVI. Compared to conventional bulk iron, nZVI could potentially eliminate the need for PRBs, resulting in lower costs and greater remedial effectiveness.

nZVI comprises a core of primarily zero-valent metallic iron (Fe⁰) with a mixed-valence oxide shell. The shell mainly consists of ferrous or ferric ion hydroxides, which are formed from oxidation of the metallic iron through contact with oxygen or oxygenated water [17]. The formed hydroxide or oxide layer can potentially reduce the reactivity of nZVI particles and thus decrease the effectiveness of the Fe⁰ particles and increase the possibility of harmful byproducts formation. Deposition of a second metal, such as palladium (Pd), platinum (Pt) or nickel (Ni) prevents the formation of this oxide layer and enhances the dechlorination efficiency, which consequently prevent the formation of toxic intermediates [18].
In a bimetallic nZVI system, Fe\textsuperscript{0} nanoparticles behave as reducing agents through their corrosion reactions, releasing electrons that reductively dechlorinate TCE, PCE and other chlorinated compounds, while the dopant more noble metal serves as a catalyst that accelerates the dechlorination rate. Palladized zero-valent iron bimetallic nanoscale particles (Pd/Fe\textsuperscript{0} BNPs) are commercially available and are among the most commonly used BNPs in site remediation. These bimetallic nanoparticles offer dechlorination rates that are orders of magnitude higher than the corresponding monometallic nanoparticles. For example, Chin et al. [19] illustrated that the use of Pd/Fe\textsuperscript{0} BNPs increased TCE degradation by up to two orders of magnitude, when compared to monometallic nZVI particles. The introduction of a second metal not only increases the reactivity and reduces the accumulation of toxic byproducts, but also has been reported to make the particles more stable in air by inhibiting their surface oxidation [18].

In addition to the core-shell structure, another important characteristic of nZVI is its strong tendency to aggregate to form larger clusters or chains in the micrometer scale, which subsequently leads to a significant and rapid loss in reactivity and decreases its mobility [20]. The process of agglomeration of the magnetic metal nanoparticles normally takes place through direct inter-particle interactions such as \textit{van der Waals} or magnetic forces [21]. In order to be effective, nZVI particles thus need to be in the form of stable dispersion in water so that they can to be delivered to water-saturated porous
material in the contaminated areas. Therefore, scientists and engineers are increasingly interested in engineering nZVI with various surface modifications in order to minimize their aggregation [22].

1.3 Surface Modification of Zero-valent Iron Nanoparticles

To facilitate soil delivery and mobility of nZVI particles, various particle modification techniques have been explored. Surfactants, polymers, and polyelectrolytes are among the main types of stabilizers commonly used to modify the surface of nZVI. Some of the examples reported in the literatures include polyacrylic acid (PAA) [23], potato starch [22], carboxymethyl cellulose (CMC) [24], cellulose acetate (CA) [25] and guar gum [26]. It is well accepted that mechanisms commonly exploited to enhance the dispersion of nanoparticles in aqueous suspension are electrostatic repulsion and steric hindrance [24]. Stabilizations of nZVI particles with these coatings rely mainly on either electrostatic repulsion where adsorption of a charged stabilizer (e.g. surfactant) increases the repulsive forces between particles, or steric hindrance where a sterically bulky stabilizer (such as polymer) hinders particle attraction [27].
Recently, immobilization of nZVI particles on a solid supports is receiving a lot of attention, because of its advantages in preventing agglomeration of particles by preserving a higher iron surface area. These solid support materials include polymeric resins, silica gel or sand [28]. The support itself is intended to disperse the iron nanoparticles, thereby increasing its total specific surface area and to provide for greater hydraulic conductivity. Nanoparticles can also be immobilized or impregnated onto a high surface area support, such as zeolites, compressed carbon black and activated carbon [29-31]. The use of carbon-functioned iron oxide nanoparticles presents many advantages over polymeric resins or silica, in terms of much higher chemical and thermal stability as well as biocompatibility [32]. The carbon shell not only protects the iron nanoparticles from rapidly degradation by the surrounding environment, but it also prevents their agglomeration.

1.4 Field Application of nZVI Technology

As discussed above, well-documented laboratory studies have demonstrated that iron-based nanoparticles (e.g. nZVI, bimetallic nZVI and surface-modified nZVI) can effectively dechlorinate a range of chlorinated hydrocarbons [16, 19, 23, 24, 25 and 26]. Although these lab-bench studies on the experimental stage indicated the superior capability of iron-based materials, their feasibility for implementation and application in
fields needs to be further evaluated. Consequently, there has been a considerable attention devoted in the past few years to develop pilot- and full-scale field tests. US-EPA reported that totally 26 sites have been effectively undertaken or are being considered for remediation by Fe-based nanoparticles in the U.S. [33]. Glazier et al. [34] carried out a field trial of nZVI for in-situ groundwater treatment of a site contaminated with chlorinated VOCs at the Research Triangle Park, North Carolina. They reported that nZVI were injected by pumping as a slurry suspension into the wells and over 90% reduction of the CVOCs concentration was achieved within several days. PCE, TCE and DCE concentrations were also reduced to levels near or below groundwater quality standards within six weeks of injection. Elliott and Zhang [35] initially reported a field assessment of bimetallic nZVI (Pd/Fe, BNPs) on the treatment of a TCE-contaminated site located in Trenton, New Jersey. Approximately 1.7 kg of the BNPs particles was gravity-fed into the aquifer over a 2-day period. The main contaminant (TCE) was effectively removed (96% drop in concentration) within four weeks of injection.

Moreover, the U.S. Navy conducted an extensive field test using BNPs (Pd/Fe) to remediate two contaminated sites located in Naval Air Station, Jacksonville, Florida and Naval Air Engineering Station, Lakehurst, New Jersey [36]. In the first pilot-scale study, a nontoxic polymer-coated Pd/Fe BNPs suspension was injected and TCE concentrations were observed to reduce up to 90% monitored from a well located approximately 20 feet from the source zone, suggesting that some nanoparticles migrated outside of the
treatment zone through preferential pathways. The second pilot trial indicated that two primary contaminants of concern, TCE and DCE, decreased with an average of 79% and 83%, respectively, after direct-push injection of BNPs. Furthermore, Quinn et al. [37] and O’Hara et al. [38] monitored a field-scale demonstration of emulsified ZVI (EZVI) to remediate a source zone dominated by TCE at Cape Canaveral Air Force Station, Florida. Using pressure-pulse injection of EZVI, they observed a high remediation efficiency (>80%) of TCE-contaminated soil and up to 100% reduction of TCE concentrations in groundwater. Additionally, Su et al. [39] conducted a field test of EZVI at Parris Island, South Carolina for two and half years to assess the treatment of subsurface source zone dominated by PCE and TCE. EZVI was delivered by pneumatic injection and direct injection and they observed significant reductions of PCE (>85%) and TCE (>85%) concentrations with a corresponding increase in the concentration of degradation products (e.g. ethane). In summary, the results of these field-scale treatability tests all agree favorably with those of previously published laboratory tests, indicating that in-situ application iron-based technology can be successfully implemented on the field.
1.5 Hybrid Carbon-based Materials-Nanoscale Zero-valent Iron

Carbon-based hybrid nanomaterials are one of the most active research fields in nanotechnology. It covers a broad field from conventionally used activated carbon (AC) to novel materials like carbon nanotubes (CNTs) [40]. Based on the route of synthesis and its chemical and physical structure, properties of hybrid nanomaterial vary tremendously. Therefore, they have been widely applied in liquid phase adsorption, separation and purification and catalysis [41-42]. The combination of carbonaceous material such as CNTs or AC and nZVI particles could lead to a novel integration of the unique characteristics and functions of the two components and further exhibit important features and properties caused by cooperative effects [43].

1.5.1 Hybrid of CNTs-supported nZVI

Since discovered in 1991 by Iijima [44], CNTs have been the subject of an increasing number of experimental and theoretical studies due to their unique morphology and various potential applications. The novel structure of CNTs, with perfect lattice alignment and closed topology, endows them with outstanding properties, in terms of high electrical conductivity, excellent strength and stiffness as well as unusual electronic and chemical
properties as well as with an outstanding thermal conductivity [44]. Owing to their specific properties, CNTs have been applied to many fields, including electron field emitters [45], quantum nanowire [46], catalysts support [47], chemical sensors [48] and as adsorbent for hydrogen and other gases storage [49]. Recently, because of the extremely high surface area (\(\sim 1500 \text{ m}^2/\text{g}\)) [50], CNTs have been explored as promising adsorbents for distinct contaminants in aqueous solutions.

A number of contributions have been devoted to the experimental and theoretical study of contaminant adsorption by CNTs. One of the earliest studies by Long et al. [51] initially reported that CNTs had significantly higher dioxin removal efficiencies than activated carbon. Li et al. [52] later indicated that CNTs had a high adsorption capacity for lead removal from water. The same group [53] also showed that CNTs were excellent fluoride adsorbents and their removal capability was superior to that of activated carbon. Peng et al. [54] reported that CNTs were efficient adsorbents for 1, 2-dichlorobenzene from water and that these materials could be used in a wide pH range. Lu and coworkers [55] indicated CNTs also displayed significantly high trihalomethane removal efficiencies. Recently, Lv et al. [56] adopted a new nano-composite consisting of nZVI and multi-walled CNTs (MWCNTs) to remove Cr (VI) from wastewater. The results indicated nZVI-MWCNTs composites exhibited around 36% higher efficiency on Cr (VI) removal, compared to bare nZVI. The characterization analysis showed that nZVI
particles could disperse on the surface or into the network of MWCNTs. Thus this nZVI-MWCNTs composite provides a promising alternative material for the removal of heavy metal ions from aqueous solutions.

1.5.2 Activated Carbon-impregnated with nZVI

Alternatively, activated carbon is another type of carbon primarily derived from charcoal with an exceptionally high surface area (e.g. typically $\sim 500 \text{ m}^2$), and a large amount of micro-porosity [57]. Due to their extremely high surface area and large pore size, AC has been one of the most widely used materials for environmental applications. For instance, it has been extensively used for environmental applications in air and water treatment, such as spill cleanup, groundwater remediation, drinking water filtration, air purification, and capture of volatile organic compounds [57-59].

Recent interests on nanoscale materials have greatly influenced AC research as well. Scientists at Helmholtz Center for Environmental Research in Germany [60] developed a new method combining iron nanoparticles with AC to produce “Carbon-Iron” platelets of between 50-200 nm in diameter. The combined DNAPL sorbent properties of the activated carbon with the reductive capacity of Fe$^0$ proved very promising for the reduction of a range of chlorinated organics whilst also exhibiting mobility comparable to
surfactants and polyelectrolyte coatings. Moreover, Hyeok et al. [61] developed an effective strategy, employing a series of innovative granular activated carbon (GAC) composites incorporated with palladized Fe\(^0\) nanoparticles and further studied their removal effectiveness of PCBs.

### 1.6 Research Objectives

In this study, a simple, inexpensive approach was explored to fabricate reactive carbon-based hybrid nanomaterials using MWCNTs or GAC and monometallic or bimetallic Fe\(^0\) nanoparticles. Their applications in environmental remediation were tested by probing their ability to dechlorinate TCE in aqueous solutions.

The following objectives of this research were formulated and achieved:

1. **Develop a new strategy, employing two categories of materials (MWCNTs and GAC) for the creation of hybrid carbon-based Fe\(^0\) and Pd/Fe\(^0\) bimetallic nanoparticles;**
   
   (Refer to Chapter 4 and 5)

2. **Characterize the chemical and physical properties of the two hybrid nanomaterial (nZVI-MWCNTs and GAC-nZVI) using a battery of characterization techniques including TEM (transmission electron microscopy), BET (Brunauer-Emmett-Teller)
isotherm measurement, XRD (X-ray diffraction), TPR (temperature programmed reduction) and Raman spectroscopy; (Refer to Chapter 4 and 5)

(3) Estimate the adsorption capacities of as-grown and oxidized MWCNTs supports for TCE removal under equilibrium conditions; (Refer to Chapter 3)

(4) Assess the effect of incorporation of monometallic and bimetallic Fe\textsuperscript{0} nanoparticles over as-grown and oxidized MWCNTs on TCE removal performance; (Refer to Chapter 4 and 5)

(5) Evaluate the impact of nZVI incorporation over GAC on TCE removal capacity;

(Refer to Chapter 4 and 5)

This thesis is presented in the format of “Integrated Article Format”. A brief description of each chapter is expressed as follows:

Chapter 1 provides an introduction to this study including background information and the primary research objectives.

Chapter 2 reviews the synthesis, characterization and properties of nZVI particles, CNTs and two types of novel hybrid of carbon-based nano-composite (nZVI-CNTs and GAC-nZVI). Previous studies on the reactivity of monometallic and bimetallic Fe\textsuperscript{0} nanoparticles and adsorption performance of CNTs are also reviewed.
Chapter 3 studies the TCE adsorption capacity of as-grown and acid oxidized MWCNTs, additionally compares them to a commercially available powder activated carbon. Several factors are evaluated to test the adsorption capacity in terms of initial TCE concentration, MWCNTs dosage and influence of modification process. Kinetic and adsorption isotherm studies are also used to model TCE adsorption mechanism over these materials.

Chapter 4 investigates the TCE removal efficiency of a new hybrid nano-composite based on MWCNTs-supported Fe$^0$ and Pd/Fe$^0$ nanoparticles. Synthesis, characterization and reactivity are discussed.

Chapter 5 introduces the concept of a reactive GAC-nZVI composite. The preparation, characterization and effectiveness for dechlorination of TCE are investigated. Observed TCE removal efficiencies are compared to bare nZVI, bare Pd/nZVI and raw GAC, respectively.

Chapter 6 summarizes and discusses the outcomes of this study and presents recommendations for further work.
1.7 References


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Chapter 2 Literature Review

2.1 Introduction

Contamination of water is a widespread problem in the United States and throughout the world as a result of industrials, agricultural and non-agricultural pollution. Thousands of sites worldwide have been contaminated with a wide range of toxic organic compounds. In particular, chlorinated organic contaminants, such as TCE and PCE, are identified as the priority pollutants in drinking water system [1], due to their considerable human carcinogenicity. These contaminants are persistent in the environment and transformed or degraded extremely slowly by natural processes [2]. Conventional remediation technologies include ex-situ soil washing and pump-and-treat operations, as well as in-situ thermal treatment, chemical oxidation and use of reactive barriers with iron. However, these technologies have some disadvantages such as high operational and maintenance cost, expensive equipment, incomplete removal, high-energy requirement and generation of toxic residual sludge. Therefore, it is crucial to develop and implement innovative water technologies treating water with high efficiency and low energy consumption.
Recently, nanoscience and nanotechnology has introduced as a new dimension to scientific disciplines and technology sectors due to its ability to exhibit super functional properties of materials at nano-scale. This eco-friendly technology is considered to be an effective alternative to the current practices of site remediation. Due to their subcolloidal size and unique molecular or atomic structures, many nanomaterials have been shown to possess distinctive chemical, catalytic, electronic, magnetic, mechanical and optical properties that contribute to promising applications in machinery, energy, optics, electronics, drug delivery and medical diagnostics [3-5].

The large surface-to-volume ratio of nanomaterial can lead to surprising surface and quantum size effects. As particle size decreases, the proportion of atoms located at the surface increases, which raises its tendency to adsorb, interact and react with other atoms, molecules and complexes to achieve charge stabilization [6]. Derived from their characteristics of enhanced reactivity, much higher specific surface area and subsurface transport, nZVI particles have been extensively used for rapid and cost-effective cleanup of groundwater compared to conventional approaches. Over the past decade, extensive studies have demonstrated that ZVI nanoparticles are effective for the transformation and detoxification of a wide variety of pollutants commonly identified in groundwater, including PCE, TCE, and carbon tetrachloride (CT) [7-9]. Dozens of pilot and large-scale in-situ applications have also been conducted and demonstrated that rapid in-situ
remediation with nZVI can be achieved. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the rate and efficiency of remediation, and reduce the possibility of agglomeration and aggregation.

In addition, carbonaceous nanomaterial can serve as a high capacity and selective sorbent for the common organic contaminants. Adsorption offers high efficiency, cost-effectiveness and easy handling. A number of adsorbents such as activated carbon [10], zeolite [11] and alumina [12] have been reported for the removal of different categories of pollutants from groundwater. Due to its high surface area and wide pore size distribution, granular activated carbon (GAC) have been of the great interest to removal of organic contaminants from groundwater. Recently, carbon nanotubes (CNTs), a new member of carbon family, have generated broad and interdisciplinary attentions due to their unique physicochemical properties. Because of their highly porous and hollow structure, large specific surface area, light mass density and strong interaction between CNTs and pollutant molecules [13], CNTs become relatively a new class of adsorbents and hold interesting positions in carbon-based adsorptive materials.

Nanocomposite materials based on carbonaceous materials and nZVI integrate the unique characteristics and properties of two types of components and further present some novel properties and applications for environmental remediation. In this chapter, we highlight a
few recent literatures of hybrid nanocomposite constituting of CNTs or GAC with nZVI for environmental remediation of pollutants in groundwater. Beginning with a brief review of the synthetic methodologies to fabricate two representatives of combination of carbon-based nanomaterials, we further explore the prospects of their structure, characteristics and properties.

2.2 Nanoscale Zero-valent Iron (nZVI)

With the development of emerging nanotechnologies, nZVI represents a new generation of remediation technology to remove the persistent chlorinated organic contaminants, such as TCE and PCE, in groundwater and sediment. Compared to the conventional technologies applied, nZVI technology has a great potential in reduction and removal of chlorinated pollutants more rapid and effectively, thereby providing a cost-effective solution.

2.2.1 Synthesis of Monometallic and Bimetallic nZVI

To date, numerous methods have been developed for the manufacture of metallic nanoparticles to generate different sizes and shapes. These synthetic methods could be classified into two main categories: either a physical synthesis approach or a chemical
fabrication method. The physical synthesis methods include: inert gas condensation, sever plastic deformation, high-energy ball milling and ultrasound shot peening. On the other hand, the chemical synthesis methods consist of reverse micelle, controlled chemical co-precipitation, chemical vapor condensation, pulse electro-deposition liquid flame spray and liquid-phase reduction.

Primarily, there are two strategies to preparation of ZVI nanoparticles, divided into “top-down” and “bottom-up” approaches. “Top-down” refers to the preparation of nanoparticles by mechanical and/or chemical steps including milling, etching, or machining. It starts with a suitable bulk material of large size (e.g. granular or microscale), and then breaks them into small pieces. For the latter approach of “bottom-up”, it entails the “grown” of nanostructures atom-by-atom or molecule-by-molecule by chemical synthesis, self-assembling and positional assembling [14]. However, for “top-down” method, broad size distribution, varied shape or geometry, and impurities from the milling medium are the main factors of concern for the products. Therefore, a more convenient approach of “bottom-up”, production of nZVI on a commercial scale has great potentials for the use in the creation of technologically advanced and useful materials.
Because of its simplicity and productivity, liquid-phase reduction method is most thoroughly investigated and widely used in the environmental applications. The basic idea of liquid-phase reduction, referring to borohydride reduction, is to add a strong reductant into a metallic ion solution to reduce it into nanoscale metal particles. For example, the most common method to generation of nZVI is by reduction of aqueous ferric (Fe (III)) [15] or ferrous (Fe(II)) [7] salt with sodium borohydride (NaBH₄) at ambient temperature (Eq.(1) & Eq.(2)):

\[
4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \quad \text{Eq.(1)}
\]

\[
2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 \downarrow + H_2BO_3^- + 4H^+ + 2H_2 \uparrow \quad \text{Eq.(2)}
\]

A major advantage of this method is its simplicity with the need of only two common reagents and no requirements for any special equipment or instruments. The procedure starts with slowly adding freshly made ferric chloride (FeCl₃) or ferrous sulfate (FeSO₄) solution into a reaction vessel containing a solution of NaBH₄ [16] or adding a NaBH₄ solution into a ferric chloride or ferrous sulfate solution [17]. The process is normally carried under an inert atmosphere of nitrogen (N₂) to avoid oxidation of the metallic iron surface.
Typically, a 1:1 volumetric ratio of NaBH$_4$ and FeCl$_3$ ⋅ 6H$_2$O solutions are vigorously mixed in a flask reactor under these conditions [15], while the synthesis needs to be conducted in a close environment because the chemical reactions produce gaseous H$_2$ as a byproduct and to avoid reoxidation of the reduced Fe$^0$ particles by surrounding oxygen. Experimentally the ratio between borohydrate and ferric ions exceeds the stoichiometric requirement by a factor of approximately 7 (Eq. (1)). The excess mass ratio is necessary in order to achieve rapid and uniform growth of iron nanoparticles. The harvested nZVI is then washed with a large amount of distilled water and at the end, with diluted ethanol, to remove the excess residual NaBH$_4$ and for short storage purpose. If FeSO$_4$ is used as precursor, nZVI is also prepared by mixing a 1:1 volumetric ratio of NaBH$_4$ and FeSO$_4$ (Eq. (2)) [7]. A stoichiometric excess of borohydrate is used as well, although considerably less that used in the reaction with ferric chloride. The finished nanoparticles are washed with copious amounts of distilled water, then by ethanol for further use.

Bimetallic iron nanoparticles, in which a second and often less reactive metal such as Pd, Ni, Pt or silver (Ag) is prepared simply by soaking the freshly prepared nZVI in a solution of the second metal salt [18]. It has been demonstrated that the second noble metal promotes iron oxidation and acts as a catalyst for electron transfer and hydrogenation. Zhang et al. [15] reported the synthesis of iron nanoparticles partially coated with palladium (Pd/Fe). The reduction and subsequent deposition of Pd on the
surface of nZVI was proposed to achieve as indicated below:

\[
Pd^{2+} + Fe^0 \rightarrow Pd^0 \downarrow + Fe^{2+} \quad \text{Eq. (3)}
\]

In their experiment, aqueous precipitates of nZVI, prepared by Eq. (1), were soaked with an ethanol solution containing 1 w.t. % of palladium acetate ([Pd(C₂H₃O₂)₂]₃) at room temperature to achieve deposition of Pd over the nZVI surface.

### 2.2.2 Structure and Characterization of nZVI

#### 2.2.2.1 Structure of nZVI

Typically, nZVI exhibits a core-shell structure. It is composed of a core that consists primarily of zero-valent or metallic iron while the mixed valence (e.g. Fe (II) or Fe (III)) oxide shell is formed as a result of oxidation of the metallic ions, as indicated in Fig. 2.1 [14].
Under ambient conditions, nZVI is fairly reactive in water and serves as an excellent electron donor, which makes it a versatile remediation material [19]. The core consisting of mainly zero-valent iron nanoparticles has the capability of chemically reduce environmental contaminants. Meanwhile, the shell is largely iron oxides/hydroxides formed from the oxidation of nZVI, which provides sites for chemical complex formation and protects nZVI from rapid oxidation.
2.2.2.2 Characterization of nZVI

Properties of nZVI depend on their synthesis and preparation methods and can be characterized by several techniques and instruments such as transmission electron microscope (TEM), scanning electron microscope (SEM), powder X-ray diffraction (XRD), Raman spectroscopy (Raman) and Brunauer-Emmett-Teller isotherm (BET) measurement. These instruments help to quantify the properties of particles in terms of particle size, specific surface area and shape/morphology.

Wang and Zhang [15] used TEM to analyze the morphology of the chemically synthesized nZVI by reduction of FeCl$_3$ with NaBH$_4$. As shown in Fig. 2.2, the nanoparticles are mostly spherical in shape and exist as chain-like aggregates. Measurements of over 400 representatives from TEM images yielded a mean value of particle diameter at 66.6±12.6 nm with the median size of 60.2 nm, average size of 70.2 nm and standard deviation about 49.6 nm. Over 80% of the nanoparticles have diameter less than 100 nm, whereas 50% are less than 60 nm. Generally, TEM analysis revealed that synthetic nZVI particles obtained through the NaBH$_4$ aqueous reduction method are in the size range of 1-100 nm.
As with particle size, specific surface area is also an important factor affecting the chemical and physical properties of nanoparticles. nZVI was proven to have relatively large specific surface area, determined with the classic BET measurement. Zhang et al. [18] compared the surface area of Fe$^0$ nanoparticles with the commercially available microscale iron particles. It was concluded that the average BET surface area of nZVI was about 33.5 m$^2$/g, which was 1-2 orders higher than that of commercial microsize particles. Additionally, they also examined the specific surface area of Pd/Fe bimetallic nanoparticles, which was about 35±2.7 m$^2$/g. Such a much larger specific surface area provides more active sites where reaction occurs, which is one of the reasons why nZVI might exhibit greater reaction rates with contaminants [20].
Moreover, XRD technique was used further to characterize the particle composition. An example of the XRD spectrum of nZVI particles is shown in Fig. 2.3. [21] XRD diffractogram indicates that the major surface species of freshly prepared nZVI particles is zero-valent iron (Fe⁰, diffraction angle (2θ) equals to 44.9°), while a small amount of iron oxide crystalline phase (FeO, 2θ=35.8°) is also observed. The broadness of the peaks indicates the existence of an amorphous phase of iron.

![X-ray diffractogram of the synthesized iron nanoparticles](image)

**Fig. 2.3 X-ray diffractogram of the synthesized iron nanoparticles**

(Reprinted from [21] with permission from Elsevier Limited)

A detailed knowledge of the surface properties is vital for understanding the most important reaction mechanisms, kinetics, and intermediate product profiles. The transport, distribution and fate of nanoparticles in the environment also depend on these surface
properties. nZVI particles produced with different methods will exhibit widely varying properties. The surface properties of some common nZVI particles synthesized by chemical reduction in lab are summarized in **Table 2.1**.

### Table 2.1 Summary of physical properties of common lab synthesized nZVI

*Fe^{BH} refers to Fe⁰ nanoparticles produced by borohydride reduction*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source Ref.</th>
<th>Particle Size (nm)</th>
<th>BET Surface Area (m²/g)</th>
<th>Shape</th>
<th>Composition</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{BH}</td>
<td>[18]</td>
<td>10-100</td>
<td>33.5</td>
<td>Spherical</td>
<td>Mainly Fe⁰ some goethite and wustite</td>
<td>Preici w/ NaBH₄</td>
</tr>
<tr>
<td>nZVI</td>
<td>[21]</td>
<td>30-50</td>
<td>36.5</td>
<td>Spherical</td>
<td>Fe 60 wt.% O 36 wt.% B 4 wt. %</td>
<td>FeCl₃ + NaBH₄</td>
</tr>
<tr>
<td>Fe^{BH}</td>
<td>[20]</td>
<td>59-67</td>
<td>33.5</td>
<td>Spherical aggregates, chain of particles</td>
<td>Small crystallites, an amorphous coating</td>
<td>NaBH₄ reduction</td>
</tr>
<tr>
<td>Pd/Fe</td>
<td>[20]</td>
<td>3-30</td>
<td>35 ± 2.7</td>
<td>Roughly spherical</td>
<td>Primarily Pd metal, Fe metal and iron corrosion products</td>
<td>NaBH₄ reduction</td>
</tr>
</tbody>
</table>
2.2.3 Reactivity of nZVI with Chlorinated Compounds

Fe$^0$ particle has been recognized as an excellent electron donor, regardless of their particles size it can react with both dissolved oxygen and oxygenated water [22]. Fe$^0$ exhibits a strong tendency to slowly oxidize to ferrous irons (Fe$^{2+}$) and release electrons in the environment in accordance with the following oxidation half reaction:

$$Fe^0(s) \rightarrow Fe^{2+}(aq) + 2e^-(aq) \quad \text{Eq.}(4)$$

In the subsurface environment, the predominant electron acceptors are water and to some extent residual dissolved oxygen (DO) [23].

$$Fe^0(s) + 2H_2O(aq) \rightarrow Fe^{2+}(aq) + H_2(g) + 2OH^-(aq) \quad \text{Eq.}(5)$$

$$2Fe^0(s) + O_2(g) + 2H_2O(aq) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq) \quad \text{Eq.}(6)$$

Under both aerobic and anaerobic conditions, Fe$^0$ particle reacts with DO or H$_2$O to form Fe$^{2+}$ and release electrons. These electrons thus can potentially carry a variety of reactions that lead to the transformation of target chlorinated compounds. The importance
of electron donors in the reduction of chlorinated hydrocarbons has received significant attention in the research and environmental remediation communities. In general, three potential transformation mechanisms are proposed during the reactivity of nZVI particles [24]:

1. Direct reduction at the metal surface: direct transfer of electrons from the iron metal to chloride organic molecules adsorbed on the metal surface, leading to the production of chloride ions and formation of hydrocarbons;

2. Reduction by ferrous ions: reduction by the Fe\textsuperscript{2+}, which results from corrosion of the metal;

3. Catalyze hydrogenolysis by H\textsubscript{2} that is formed by reduction of H\textsubscript{2}O during anaerobic corrosion: hydrogenation of the chlorinated organics with adsorbed hydrogen produced during metal corrosion by water, in which the metal serves as a catalyst [25]

Most researchers support the dechlorination procedure via electron transfer mechanism, where the electrons transfer from the metal to the chlorinated compounds [24]. It is intended that toxic contaminants (e.g. TCE) would be reductively dechlorinated to an essentially nontoxic mixtures of hydrocarbons, such as ethane, ethane, and acetylene [24]. A generalized chlorinated hydrocarbon, labeled as RCl, as an example, would be reduced in accordance with the following reaction (Eq.(7)): 
$RCl + Fe^0 + H^+ \rightarrow R - H + Fe^{2+} + Cl^- \quad \text{Eq.(7)}$

A schematic of the reduction of TCE is illustrated in Fig. 2.4 [18], showing the reductive ability of element Fe with a chlorinated hydrocarbon. In this example, $Fe^0$ transforms TCE into ethane and releases $Fe^{2+}$ ions and chloride ions.

![Fig. 2.4 Reaction of iron in a bimetallic nanoscale particle with TCE](image)

(Reprinted from [18] with permission from John Wiley and Sons)

The proposed mechanistic steps for the reduction of TCE by zero-valent iron (ZVI) are presented in Fig. 2.5. They are primarily divided into a sequential hydrogenolysis pathway and reductive β-elimination pathway [26]. Hydrogenolysis is the chemical reaction whereby the halogen is replaced by hydrogen (as shown in Fig. 2.5, Pathway A.).

In the process, the intermediate products, dichloroethene (DCE) and vinyl chloride (VC),
are produced in a sequential pathway. DCEs and VC are slower toward degradation than TCE itself. Therefore, DCEs and VC are detected as major intermediate products when hydrogenolysis is the pathway of TCE degradation. By contrast, reductive β-elimination (Fig. 2.5, Pathway B) leads to the transformation of TCE directly into ethene via the production of some short-lived intermediates, such as chloroacetylene and acetylene. The reductive β-elimination pathway accounts for the rapid conversion of TCE into ethane and ethane with relatively minor intermediate products formation. Tratnyek et al. [27] reported that β-elimination was the preferred pathway because it favored under abiotic-reducing conditions. His experimental observations also indicated that intermediates products DCEs and VC were not formed, supporting the proposed β-elimination pathway.
Fig. 2.5 Hypothesized reaction pathways for TCE dechlorination by nZVI

(Reprinted from [26] with permission from American Chemical Society)
2.2.4 Degradation of Chlorinated Compounds by nZVI

As discussed above, the greater reactivity often ascribed to nZVI is the result of larger overall surface area, greater density of reactive sites on the particle surface, and higher intrinsic reactivity of the reactive surface sites. In addition, due to their ability to remain in suspension, nZVI can be injected directly into contaminated soils, sediments and aquifers [28]. Therefore, the application of nZVI instead of micro/macro-scale Fe$^0$ materials could potentially eliminate the need or using PRBs and be more effective in both cost feasibility and contaminant remediation. Laboratory studies indicated that a wide array of chlorinated hydrocarbons could be degraded by nZVI, including chlorinated methane, ethane, benzene, and potentially polychlorinated biphenyls (PCBs) [29]. Several factors play a role in determining the reactivity of nZVI, including particle size, the amount of reactive surface area, the presence of hydrogenation catalysts (e.g. palladium), the method of fabrication, the morphology or porosity of the particle, the crystalline structure of the particle, and impurities and coatings [30].
2.2.4.1 Degradation of TCE by Monometallic nZVI

nZVI particles have been illustrated to be more reactive toward halogenated hydrocarbon than commercial Fe⁰ powders and reduce almost all halogenated hydrocarbons to benign compounds, such as hydrocarbons, chloride and water.

Choe et al. [31] evaluated the feasibility of using nZVI particles to reductively degrade TCE in anaerobic batch experiments. The nZVI particles were synthesized by chemical reduction method with a diameter range of 1 to 200 nm. BET specific surface area was 31.4 m²/g, which is much greater than the value of commercially available iron particles (0.0634 m²/g). After 30 min, 90% of TCE was degraded and 70% of TCE was converted to non-toxic final products. Because of their high conversion efficiency of TCE to non-toxic final products, the harmful intermediates, such as 1,2-dichloroethene (1,2-DCE), represented only a small amount of the final dechlorination products. The results demonstrated that nZVI particles have high capacity of transforming chlorinated organic compounds into harmless final products, which was largely due to they possess higher specific surface areas than micro-scale ZVI particles.
Liu et al. [32] further investigated the effect of structure (crystalline or amorphous) on the reactivity of TCE remediation. The study applied high-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) to characterize the morphology of the particles. It is shown that fresh nZVI particles exhibited amorphous structure while annealed nZVI was crystalline in structure. The rate of dechlorination of different particles with TCE was also evaluated. The results indicated that the crystalline nanoirons were able to activate hydrogen and made use of any externally additive hydrogen, which made them more reactive to TCE than non-crystalline particles.

TCE concentration is another important factor in dechlorination by nZVI. Liu et al. [33] synthesized Fe^{BH} by chemical reduction method and used them in TCE degradation under two different conditions of high TCE concentration (limited iron) and low TCE concentration (excess iron). Their results indicated that faster reduction could be achieved through lower TCE concentrations and smaller particle sizes. According to their calculation, Fe^{BH} displayed pseudo-first-order kinetics for excess iron and zero-order kinetic for limited iron. They also studied the final products, with a composition of 70–80% ethane and 20–30% C₃–C₆ products. Moreover, Li et al. [34] investigated the degradation of TCE using two types of nZVI particles. They found that nZVI was an effective tool for degradation of TCE and the time required for complete reduction of TCE was distinct for different initial TCE concentrations, Fe⁰ loading, and particle sizes. Their result proved
that the reduction time was lower with lower initial TCE concentrations, smaller particle sizes and higher Fe\(^0\) loading.

### 2.2.4.2 Degradation of TCE by Bimetallic nZVI

In addition to transformation by Fe\(^0\), bimetallic coupling with a second catalytic metal has also been used to degrade a variety of contaminants as environmental cleanup. The incorporation of a noble or catalytic metal, such as Pd, Ni, Pt, or Ag, can substantially enhance the overall nZVI reaction rate. The fast reactions generated by the bimetallic nanoparticles also reduced the possibility of toxic byproduct formation and accumulation. **Fig. 2.6** gives an example of the reaction of a chlorinated compound with a bimetallic particle. In this system, one metal (e.g. Fe, Zn) serves primarily as an electron donor while the dopant metal (e.g. Pd, Pt) acts as a catalyst [18].

![Fig. 2.6 A nanoscale bimetallic particle for chlorinated solvent removal](image)

(Reprinted from [18] with permission from John Wiley and Sons)
Elliott et al. [7] reported that the degradation of TCE could be greatly enhanced when a small portion of Pd of 0.1 w.t. % was coated on the Fe\(^0\) particle surface. Wang et al. [35] found that TCE was degraded in 1.7 h, when reacted with Fe\(^0\) nanoparticles, whereas TCE was degraded in 0.25 h when reacted with Pd/Fe nanoparticles, under the same reaction conditions. It was also discovered that TCE reacted with both Fe\(^0\) and Pd/Fe nanoparticles to yield hydrocarbons including ethene, ethane, propene, propane, butene, butane, and pentane. The results demonstrated that bimetallic Pd/Fe nanoparticles displayed clear advantages over pure nZVI particles. Zhang et al. [18] further confirmed that physically simple mixture of Fe and Pd particles together performed no better than bare Fe\(^0\) particles, and that reactivity can be enhanced only by coating Pd on the surface of nZVI to form bimetallic particles. A comparison on dechlorination of chlorinated methanes by Fe\(^0\) nanoparticle, Fe/Pd, and microscale Fe\(^0\) is presented in Table 2.2, which reveals that Pd/Fe nanoparticle is more effective than nZVI particles [37].
Table 2.2 Comparison on dechlorination of chlorinated methane by microscale, nanoscale Fe\(^0\) and Pd/Fe\(^0\) nanoparticles (Reprinted from [37] with permission from American Chemical Society)

<table>
<thead>
<tr>
<th></th>
<th>Initial concentration</th>
<th>Reduction Time (h)</th>
<th>Percentage reduced (%)</th>
<th>Final products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCl(_4)</td>
<td>CHCl(_3)</td>
<td>CCl(_4)</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>Micro Fe(^0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe loading (g/20ml)</td>
<td>20</td>
<td>15.9</td>
<td>N/A</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano Fe(^0)</td>
<td></td>
<td>0.25</td>
<td>15.86</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/Fe(^0)</td>
<td></td>
<td>0.25</td>
<td>15.4</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Besides Pd metal, other noble metals, such as Ni and Pt have also been used to promote dechlorination by nZVI. Mallouk et al. [36] used Ni/Fe nanoparticles for the dechlorination of TCE. The author observed an increase in the dechlorination rate of TCE using Ni/Fe in comparison to Fe\(^0\) nanoparticles. They attributed the enhanced reactivity to Ni-catalyzed hydrodechlorination. Furthermore, Xu et al. [37] investigated the dechlorination of chlorinated benzenes using nanoscale Fe–Ag bimetallic particles. At room temperature, 4 mg/L hexachlorobenzene was reduced below detectable limits after 4 days. Tetrachlorobenzene and trichlorobenzene were the most abundant by-products,
accounting for more than 80%. Only a trace amount was degraded to be dichlorobenzene. To date, nZVI has been developed and used to degrade a wide range of organic and inorganic soil and water contaminants. In particular, degradation of chlorinated solvents has been given significant attention, because they are some of the most common soil and groundwater contaminants and the degradation end products are often relatively harmless hydrocarbons. Moreover, although incomplete dechlorination of highly chlorinated compounds could produce some intermediate products (e.g. VC), which are more hazardous and persistent than the parent compounds, it has been recognized that the production of less toxic intermediate products is an added advantage of the use of nZVI compared to larger iron particles. Furthermore, surface modification by adding a second metal to Fe\(^0\) surface gives the additional benefit of protecting the surface from oxidation, thus improving the long-term activity of the iron species. In the case of Pd/Fe\(^0\) nanoparticles, it is thought that Pd metal not only prevents the formation of oxides on the Fe\(^0\) nanoparticle surface but also promotes dechlorination reactions by serving as a catalyst that accelerates the dissociation of chlorine-carbon bonds. A summary of nanoiron application in TCE degradation is presented in Table 2.3.
Table 2.3 Summary of monometallic and bimetallic nZVI for application of TCE degradation (Fe^{BH} refers to the nano-Fe⁰ produced by borohydride reduction, Fe^{H2} refers to the nano-Fe⁰ synthesized by reduction with heat and H₂)

<table>
<thead>
<tr>
<th>nZVI Type</th>
<th>Fe loading (g/L)</th>
<th>TCE conc. (mg/l)</th>
<th>Removal Efficiency</th>
<th>Final Products</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe^{BH}</td>
<td>13.75</td>
<td>4.68</td>
<td>&gt;99% in 24hr</td>
<td>C₂H₆</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>Fe^{BH}</td>
<td>1.5</td>
<td>20</td>
<td>100% in 54hr</td>
<td>C₂H₄</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100% in 75hr</td>
<td></td>
<td>C₂H₆</td>
<td>First order kinetics</td>
<td>[16]</td>
</tr>
<tr>
<td>Fe^{BH}</td>
<td>5</td>
<td>20</td>
<td>100% in 1hr</td>
<td>C₃H₆</td>
<td>First order kinetics</td>
<td>[16]</td>
</tr>
<tr>
<td>Fe^{BH}</td>
<td>1.9</td>
<td>4.4</td>
<td>90% in 1.5hr</td>
<td>70-80% C₂H₆, 20-30% C₃-C₆ products</td>
<td>Pseudo-first order kinetics under both conditions</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>0.36</td>
<td>290</td>
<td>80% in 2day</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe^{H2}</td>
<td>1.9</td>
<td>4.4</td>
<td>85% in 4.5 days</td>
<td>74.5% C₂H₄, 20.9% C₂H₆, 84.3% C₂H₂, 7.8%C₂H₄</td>
<td>Pseudo-first order kinetics</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>0.36</td>
<td>290</td>
<td>52% in 8 days</td>
<td></td>
<td>zero-order kinetics</td>
<td></td>
</tr>
<tr>
<td>Fe^{BH}</td>
<td>20</td>
<td>20</td>
<td>100%</td>
<td>C₂H₆, C₂H₄, C₃H₆, C₄H₁₀, C₄H₈, C₅H₁₂</td>
<td>Pseudo-first order kinetics</td>
<td>[35]</td>
</tr>
<tr>
<td>Pd/Fe</td>
<td>0.1</td>
<td>52</td>
<td>98% in 17hr</td>
<td>TCE destroyed completely, chloride as an indicator</td>
<td>Starch stabilized</td>
<td>[39]</td>
</tr>
<tr>
<td>Pd/Fe</td>
<td>0.1</td>
<td>52</td>
<td>78% in 2hr</td>
<td>TCE destroyed completely, chloride as an indicator</td>
<td>Non-starch</td>
<td>[39]</td>
</tr>
<tr>
<td>Pd/Fe</td>
<td>5</td>
<td>20</td>
<td>100% in 90min</td>
<td>80% C₂H₆</td>
<td>Non-starch</td>
<td>[17]</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>0.1</td>
<td>23.4</td>
<td>98% in 2hr</td>
<td>C₆H₁₀, C₆H₁₄, C₄H₈</td>
<td></td>
<td>[36]</td>
</tr>
</tbody>
</table>


2.2.5 Stability of nZVI

Due to their extremely high reactivity, initially formed nZVI particles are prone to rapid aggregation and agglomeration to form micro-sized fractal aggregates, which subsequently lead to a significant loss in reactivity and decreased their environmental mobility [40]. Agglomeration of magnetic metal nanoparticles results primarily from direct inter-particle interactions such as van der Waals forces and magnetic interactions [41]. In order to prevent or reduce agglomeration of nanoparticles, two common mechanisms are explored to improve particle stability in aqueous suspension include electrostatic repulsion and steric hindrance. The formed mechanism occurs when charged stabilizer molecules are adsorbed to the metal core, resulting in an enhanced electrical double layer and thus increasing the electrostatic repulsion between the capped particles. For the mechanism of steric hindrance, it is the process in which particle attractions are impeded by coating the metal core with sterically bulky stabilizers (e.g. polymers).

Researchers have been studied extensively to modify the surface of nZVI to ensure their adequate reactivity and mobility, which guarantee to deliver them into the contaminated subsurface zones. One of the common used modified nZVI is EZVI (also called as emulsified nZVI). It is termed as a surfactant-stabilized emulsion, consisting of nZVI
surrounded by an oil-liquid membrane that facilitates its treatment of chlorinated hydrocarbons [42](Fig. 2.7.). The exterior oil membrane of the emulsion is hydrophobic, which is miscible with DNAPL, allowing the contact time increased between the chlorinated compounds and nZVI within the droplet. Along with the more complete reaction, the oils could also be used to enhance biological reaction, which contribute to destruction of the contaminants. This is particularly important when using nZVI in a permeable barrier where the contaminated water usually flows through [43].

![Fig. 2.7 Magnified image of an EZVI](image)

**Fig. 2.7 Magnified image of an EZVI** (Reprinted from [42] with permission from John Wiley and Sons)
Besides EZVI, other surfactants are also widely employed to passivate the surface of nanoparticles during or after the synthesis to avoid agglomeration. After they are applied to nZVI, the steric hindrances provided by such coating molecules counteract with the electrical and dipolar attraction between particles and promote colloidal stability. Schrick et al. [44] used poly (acrylic acid) (PAA) and anionic hydrophilic carbon supported nZVI for the removal of chlorinated hydrocarbons. They indicated that the delivery vehicle was able to lower the aggregation and sticking coefficient of nZVI. However, PAA has limited applications due to its reversible adsorption characteristics. Sun et al. [45] used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A) led to significant enhancements in particle stability and subsurface mobility of nZVI.

As an alternative to surfactants, the controlled coating of nZVI with high molecular weight polymers are considered as an irreversible process and therefore provides a more appropriate method for increasing the hydraulic mobility of nZVI in subsurface systems [46]. Numerous polyelectrolyte (polymer) coatings have been tested with varying success, including butyl methacrylate [46], carboxymethyl cellulose [47], guar gum [48], poly (4-styrenesulphonate) [49], poly (acrylic acid) [44], polyaspartate [50], polyoxyethylenesorbitanmonolaurate [51], polymethylmethacrylate [46], polymethacrylic acid [46], polyvinyl alcohol-co-vinyl acetate-co-itaconic [52], triblock copolymers [53] and xanthan gum [54]. Carboxymethyl cellulose (CMC) is one of the most commonly
used stabilizers to modify nZVI. Cellulose is a carbohydrate consisting of a series of hydro-glucose units interconnected by an oxygen linkage (known as a beta linkage) to form a linear molecular chain structure. Cellulose can easily be modified to CMC by replacing the native CH$_2$OH group in the glucose unit with a carboxymethyl group. CMC is water-soluble, low-cost and environmentally friendly, therefore, it has been successfully used as an effective stabilizer by strongly interacting with Fe$^0$ nanoparticles. He et al. [47] developed a new strategy for stabilizing Pd/Fe$^0$ nanoparticle with CMC as a stabilizer. The complexation between carboxylate groups with metals and the intermolecular hydrogen bond between CMC and the Fe$^0$ particle surface were identified to be the major mechanisms for stabilizing bimetallic nanoparticles to yield stable dispersions with sizes smaller than 17.2 nm.

Another strategy for enhancing the stability and reactivity of nZVI is to immobilize them on a support. The use of porous microfiltration membranes as the support is of great interest because of their open structures and large pore sizes [55]. Several techniques including coating, grafting, and blending have been used to modify membrane surfaces [56]. Xu et al. [55] verified that immobilization of Ni/Fe bimetallic nanoparticles onto microfiltration membranes is a novel strategy for environmental application because of effectively reduction and less agglomeration of nanoparticles, long-term stability and protection of nanoparticles from oxidation. Li et al. [57] reported that attachment of
metallic particles onto polymer membranes to avoid problems, such as the reduction of particle loss, prevention of particles agglomeration, and potential application of convective flow, which occurred by freestanding ZVI. Recently, modification approaches by coating nZVI particles with silica [58], zeolite [57] and carbon [59] have been preferred due to their high stability in acidic or basic media and proven biocompatibility. Kim et al. [60] revealed that nZVI might be supported onto larger particles such as activated carbon in order to improve its mobility.

**2.2.6 Summary**

nZVI technology can be a suitable remedy for eliminating or mitigating a contaminant source zone (e.g. DNAPL). Due to their higher specific surface area, nZVI particles have much better degradation activity of the chlorinated organic compounds, such as TCE and PCE, than that of micro-scale ZVI particles. The high reactivity of nZVI allows them to rapidly degrade TCE or PCE into harmless or less toxic degradation products. Fe$_0$ nanoparticles have shown improved reactivity by coupling with a second catalytic metal, such as Pd. The second metal not only reacts with contaminants, but also protects the iron surface from oxidation, thus improving long-term activity. To avoid their high tendency of aggregation, it is clearly demonstrated that nZVI particles can be tailored by surface modification for specific environmental remediation applications.
2.3 Carbon Nanotubes

Carbon nanotubes (CNTs), a new member of the carbon family, was first discovered by Iijima in 1991 [61]. Since its discovery, CNTs has attracted great attentions due to its unique properties, such as functional mechanical, thermal, electrical and optoelectronic properties depend on atomic arrangement, the diameter and length of the tubes, and the morphology or nanostructure [62-63]. Increasing studies have indicated that CNTs possess an enormous potential for applications in environmental remediation. Since this dissertation focuses on the use of a hybrid CNTs (or Carbon)- nZVI material, we present in this subchapter an overview of recent progress in laboratory studies of CNTs for contaminant removal from water. Discussed aspects concentrate on the preparation, characterization and use of nanotube materials for the removal of water contaminants.

2.3.1 Structure and Synthesis of Carbon Nanotubes

CNTs can be formally depicted as a graphene honeycomb rolled either into a seamless single-walled cylinder or into several concentric cylinders. The former structure is termed a single-walled carbon nanotubes (SWCNTs) (Fig. 2.8) [64] and the latter a multi-walled carbon nanotubes (MWCNTs) (Fig. 2.9) [65]. The diameters of a typical MWCNTs range
from a few to a few tens of nanometers and their length is of the order of a micrometer, while for the case of SWCNTs, the diameter is in the order of a nanometer but length can reach several micrometers or more.

Fig. 2.8 Transmission electronic microscopy image of single-walled carbon nanotubes rope (Reprinted from [62] with permission from John Wiley and Sons)
Fig 2.9 MWCNTs as seen by transmission electron microscopy, the different walls constituting the material appear in a longitudinal view, a micrograph of SWCNTs is included for comparison (Reprinted from [63] with permission from John Wiley and Sons)

Each SWCNTs structures are fully described by two integers \((n, m)\), which specify the number of unit vectors \(\vec{a}_1\) and \(\vec{a}_2\) in the graphene structure that constitute the chiral vector \(V = n\vec{a}_1 + m\vec{a}_2\). The graphene structure is rolled-up in such a way that the chiral vector V forms the nanotube circumference. These indices determine the nanotube
diameter, and also the orientation of the carbon hexagons with respect to the nanotube axis; this orientation is the termed the “chirality” of the nanotube.

SWCNTs have unique chemical, electronic and mechanical properties, combined with a very lightweight. Depending on their chirality and diameter, the nanotubes may be either electrically metallic or semiconductor. At the same time, they have shown evidence for high stiffness (Young’s modulus), a very high resilience, and an ability to reversibly buckle and collapse. These properties have led to SWCNTs becoming promising candidates in the fabrication of strong fibers with a lightweight and high electrical conductivity. Nanotube can also be functionalized with different chemical moieties, and this greatly broadened the scope of their applications in fields ranging from conductive coatings to molecule specific nano-sensing.

The synthesis of CNTs materials can be divided into high-temperature routes (laser ablation, arc discharge) [61, 66-70] and medium-temperature processes, based on either catalytic decomposition or a carbon-containing molecule (a saturated or unsaturated hydrocarbon or carbon monoxide) [71, 72]. For the high-temperature routes, pure graphite or a mixture of graphite and a metallic catalyst are vaporized at very high temperatures (2000–4000°C), and the nanotubes are formed during the cooling process at
lower temperatures [73]. The catalytic decomposition of a carbon-containing molecule requires a relatively low temperature, and has the potential for high-yield productions.

Iijima [61] was the first to report the presence of multi-walled CNTs in the soot of an arc-discharge chamber. The tubes were produced using an electric arc-discharge evaporation method similar to that used for the synthesis of fullerene. In this method, an electric arc discharge is generated between two graphite electrodes under an inert atmosphere of helium or argon (Fig. 2.10(a)) [74]. The first successful production of MWCNTs at the gram-level was developed by Ebbesen and Ajayan in 1991 [75]. To synthesize SWCNTs, a metal catalyst is required [76] and the first report of the synthesis of substantial amounts of these materials, by Bethune and coworkers, appeared in 1993 [77].

In 1996, Smalley and coworkers produced high yields (>70%) of SWCNTs by utilizing the laser-ablation (vaporization) of graphite rods doped with small amounts of Ni and Co catalysts (Fig. 2.10(b)) [78]. In this process, a piece of graphite is vaporized by laser irradiation under an inert atmosphere. The resultant soot containing the nanotubes is deposited on the walls of a quartz tube when the reaction mixture has cooled. Although this process is known to produce CNTs of the highest quality and highest purity,
purification step is generally required to eliminate any carbonaceous impurities from the as-produced material. This purification is normally achieved by carbon gasification.

Since 1960, carbon filaments and fibers have also been produced by the thermal decomposition of carbon-containing molecules (this process is also known as chemical vapor decomposition; CVD) in the presence of a catalyst [79, 80]. A similar approach was used by Yacaman in 1993 [81] and later by Nagy and collaborators [82, 83], to grow MWCNTs. Following these initial reports, the CVD technique has been subsequently improved and optimized such that, in general, these processes involve the catalyst-assisted decomposition of hydrocarbons (usually ethylene or acetylene) in a tube reactor at temperatures between 550-1000°C. The growth of CNTs occurs on the catalyst surface as the gas molecule decomposes (Fig. 2.10(c)). This process has several advantages over the arc discharge and laser ablation techniques. In fact, its amenable nature has led to its use in the large-scale synthesis of aligned CNTs [84, 85].

Since all of these synthesis methods generate, in addition to the nanotubes, relatively large amounts of impurities, a number of techniques have been proposed to improve the quality of the materials through post-synthesis purification. These methods range from concentrated acid treatments, dispersion by sonication in a surfactant and filtration, to high-temperature heating under neutral or lightly oxidizing conditions [86, 87].
Unfortunately, a detailed account of the different methods for CNTs synthesis and purification is beyond the scope of this chapter, and these topics will be addressed only in the context of the synthesis or chemical treatment affecting the adsorption properties of the materials.

Fig. 2.10 Schematic representations of various processes used to produce CNTs (a) electric-arc method apparatus [74] (b) schematic representation of an oven laser-vaporization apparatus [78] (c) a chemical vapor deposition set-up in which the catalytic bed is fluidized [88] (Reprinted from [74, 78, 88] with permission from John Wiley and Sons)
2.3.2 Properties of Carbon Nanotubes

As described above, CNTs has unique structures, with remarkable properties that can be grouped as electronic, mechanical, thermal, and optical. Most of the physic-mechanical properties of CNTs are dependent on the $sp$ bond network present on their structure [89] and their diameter, length, and chirality. As these properties have been discussed extensively elsewhere [90-92], some of the most important results in this area will be discussed briefly, with emphasis placed on those properties that affect the adsorption capacity of the materials.

The mechanical properties of a solid must ultimately depend on the strength of its interatomic bonds. Both, experimental and theoretical, results have predicted that CNTs have the highest Young’s modulus of all different types of nanostructures, with similar tubular forms such as BN, BC3, BC2N, C3N4, CN, and so on. Furthermore, due to the high in-plane tensile strength of graphite, both SWCNTs and MWCNTs are expected to have large bending constants. The results of experimental and theoretical studies have indeed indicated that CNTs can be very flexible, able to elongate, twist, flatten, or bend into circles, before fracturing [90].
The thermal and electrical properties of CNTs include conductivity. The specific heat and thermal conductivity are determined primarily by the nanotube’s electronic and phononic structures [91] with theoretical and experimental results having demonstrated superior electrical properties for these materials. CNTs have electric current-carrying capacities, which are 1000-fold higher than that of copper wires [93]. In fact, theoretical calculations based on the tight binding model approximation within the zone folding scheme show that one-third of the possible SWCNTs structures are metallic, while two thirds are semi-conducting [89, 94].

2.3.2.1 Adsorption-related Properties of Carbon Nanotubes

Early studies investigating the adsorption of nitrogen onto both MWCNTs [95, 96] and SWCNTs [97] have highlighted the porous nature of these materials. Indeed, due to their uniformity in size and surface properties, CNTs are considered as ideal model sorbent systems to study the effect of nanopore size and surface morphology on sorption and transport properties.

The surface area of CNTs has a very broad range, depending on the nanotube number of walls, the diameter, length, wall defects and in the case of SWCNTs, the number of nanotubes in a nanotube bundle [98]. Isolated SWCNTs with an open end (this may be
achieved through oxidation treatment) has a theoretical surface area equal to that of a single, flat graphene sheet of 2700 m$^2$/g [99], however, reported experimental values indicate lower adsorption capacities [100]. In the case of SWCNTs, the diameters of the tubes and number of tubes in the bundle have the strongest effects on the nanotube surface area. In the case of MWCNTs, chemical treatments are reported to be useful for promoting micro-porosity. Surface areas as high as 1050 m$^2$/g have been reported for MWCNTs subjected to alkaline treatment [101]. A two-step activation treatment (acid + CO activation) has been also reported to increase the specific surface area of MWCNTs materials. It has been proposed that these treatments open the ends of the nanotube structure, enabling adsorption onto the nanotube inner openings [102]. Some representative results of the surface area and pore volume of SWCNTs and MWCNTs are listed in Table 2.4.
Table 2.4 Adsorption properties and types of adsorption sites in SWCNTs and MWCNTs (Reprinted from [102] with permission from John Wiley and Sons)

<table>
<thead>
<tr>
<th>Type of nanotube</th>
<th>Porosity (cm³/g)</th>
<th>Surface area (m²/g)</th>
<th>Adsorption site</th>
<th>Surface area per site (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs bundle</td>
<td>Microporous</td>
<td>400-900</td>
<td>Surface Groove</td>
<td>483</td>
</tr>
<tr>
<td></td>
<td>$V_{\text{micro}}$: 0.15-0.3</td>
<td></td>
<td>Pore Interstitial</td>
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<tr>
<td></td>
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<td>785</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Mesoporous</td>
<td>200-400</td>
<td>Surface Pore</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aggregated pores</td>
<td></td>
</tr>
</tbody>
</table>

$V_{\text{micro}}$ = micropore volume

An important issue to address when considering adsorption onto nanotubes is to identify the adsorption sites. For instance, the adsorption of gases into a SWCNTs bundle can occur inside the nanotubes (pore), in the interstitial triangular channels between the tubes, on the outer surface of the bundle, or in the grooves formed at the contacts between adjacent tubes outside of the bundle (Fig. 2.11) [103].
In addition, the surface functionalization of CNTs by chemical methods has been found to be a powerful tool for improving the adsorption capacity. Selective adsorption can be achieved through a controlled modification of the nanotube’s physical and chemical properties, such as surface area, hydrophilicity, and permeability. For instance, Vermisoglou and Georgakilas [104] have studied the sorption properties of pristine and chemically modified (functionalized with oleylamine and poly (sodium 4-styrene sulfonate)) nanotubes using adsorbates with different polarities. Based on their measurements, these authors concluded that the sorption behavior of the CNTs was greatly modified by chemical treatment. In fact, a chemical modification that increased the hydrophilicity of the nanotube walls enhanced the adsorption selectivity for water.
over n-hexane. Chemical modification of the nanotube wall was verified using infrared (IR) spectroscopy (Fig. 2.12). When comparing the IR spectra of pristine SWCNTs with those of chemically treated CNTs, new peaks corresponding to aliphatic chains were observed in the case of hydrophobic nanotubes, whereas peaks corresponding to more polar bonds were observed in the case of hydrophilic materials.

![Infrared spectra of (a) pristine and (b, c) modified CNTs](image)

**Fig. 2.12** Infrared spectra of (a) pristine and (b, c) modified CNTs (Reprinted from [51] with permission from John Wiley and Sons)
Yu et al. [105] have investigated the adsorptive performance on modified MWCNTs by using mechanical ball milling. For these materials, the adsorptive performance for aniline in aqueous solution indicated that the adsorptive capacity of milled, short open-ended MWCNTs increased from 15 mg/g to 36 mg/g compared to the unmilled MWCNTs. The measurements of pore size distribution proved that the inner pore diameter of 3nm remained constant after milling, but the aggregated pore diameter had decreased.

### 2.3.3 Carbon Nanotube as Adsorbents

Carbon nanotube have superior capabilities for the adsorption of a wide range of toxic substances. The earliest reports of CNTs use related to the removal of organic pollutants, notably dioxins, from water [106], though later they were reported also as having an exceptional ability to adsorb inorganic contaminants, such as fluoride [107]. In both cases, the CNTs displayed a superior performance compared to “traditional” adsorbents, such as activated carbon. These pioneering studies opened a new field of CNTs applications, with many subsequent reports noting CNTs to be excellent adsorbents for the removal of other contaminants. For example, CNTs was shown to adsorb up to 30 mg of a trihalomethane molecule per gram from a 20 mg/L solution [108]. Other reports indicated that SWCNTs could act as “molecular sponges” for small organic molecules, such as CCl₄ [109]. A similar case was demonstrated for inorganic contaminants, with CNTs again showing
superior performance; measurements of the adsorption capacity of a MWCNTs material showed that it could adsorb 13.5-fold more fluoride than a typical high-surface-area alumina adsorbent. These early results led to the suggestion that CNTs might indeed serve as an effective adsorbent for removing polluting agents from water, and consequently during the past few years some extensive laboratory studies have established the role of CNTs as an effective adsorbent for common contaminants from water, including a wide variety of organic compounds and inorganic ions. Herein, we will focus on the discussion of the potential applications of CNTs for the removal of organic compounds.

Compared to the comprehensively detailed studies about the potentials of CNTs for the removal of inorganic substances from water, the number of researches conducted on the adsorption of organic pollutants onto CNTs is relatively small. A report published by the U.S. Environmental Agency in 2002 [110] stated that the most common organic contaminants found in drinking water ranged from disinfection byproducts (e.g. trihalomethanes) to other organic chemicals, including carbon tetrachloride, benzene, polychlorinated benzenes, dioxins, and pesticides. The similar chemical characteristics of most of these organic pollutants give rise to similar acute health effects at high doses, with the primary target organ generally being the central nervous system. Sustained or very high exposures to these organic chemicals can be fatal. An overview of the results
obtained on the removal of some of these chemicals from water, using CNTs as an 
adsorbent, is provided in the following sections.

2.3.3.1 Adsorption of Dioxins

Dioxins and related compounds (e.g. polychlorinated dibenzofurans and biphenyls) are 
highly toxic pollutants. The toxicity of dioxins varies with the number of chlorine atoms; 
for example, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is a known human carcinogen. 
In addition to cancer, dioxins also adversely affect the immune and endocrine systems, as 
well as normal fetal development [111]. Dioxins are mainly generated from the 
combustion of organic compounds in waste incinerators. Due to the extreme toxicity and 
chemical inertness of dioxins, it is necessary to improve any current technologies based 
on activated carbon adsorption.

Long et al. [106] have reported that CNTs can attract and trap a large amount of dioxins 
in a more efficient manner than the activated carbon or other adsorbents currently used. 
Long’s group attributed this observation to the stronger interaction forces that exist 
between dioxin molecules and the curved hydrophobic surface of the nanotubes. Another 
series of investigations, based on dioxin temperature-programmed desorption [106, 112], 
reported that the interaction of dioxins with CNTs was much stronger than that with
activated carbon. The desorption temperatures, desorption activation energy and
Langmuir constants obtained for dioxin desorption on CNTs, activated carbon and
\( \gamma - \text{Al}_2\text{O}_3 \) are clearly indicated that the interaction of dioxins with CNTs is significantly
higher that with the other adsorbents.

A density functional theory (DFT) study conducted by Kang et al. [113] focused on the
molecular interactions between dioxin and metal-doped (Li, Na, Fe) SWCNTs. The
calculations indicated that doping large-diameter SWCNTs with calcium atoms could
introduce a strong cooperative binding of the carbon \( \pi \) system with the dioxin. A band
structure analysis suggested that the charge transfer model could explain these
observations. Iron atoms, which are commonly used as a catalyst for CNTs synthesis, can
also significantly facilitate dioxin binding. In a sense, this suggests that the adsorption of
small molecules, particularly those with delocalized \( \pi \) electrons, can be significantly
enhanced by the presence of metallic catalyst remnants following the accomplishment of
SWCNTs synthesis.

More recently, a theoretical \textit{ab initio} calculation of 2,3,7,8-tetrachlorinated
dibenzo-\( p \)-dioxin interaction with pristine, “defective” as well as B-, N-, and Si- doped
SWCNTs, was reported by Fagan et al. [90]. Their results predicted that the interaction
between SWCNTs and dioxins would depend on the geometric configuration of the
approaching dioxin, the dopant metal, and the number of defects in the nanotube wall.

The results suggested that the adsorption of dioxin was more effective for the case of defective nanotubes. This theoretical prediction shows promise from a practical point of view, as structural defects on the tube walls are naturally formed during nanotube growth and purification processes. Moreover, the results also indicated that doping with B, N, and Si does not improve the absorption capacities of dioxins.

2.3.3.2 Adsorption of 1, 2-Dichlorobenzene

Chlorobenzenes, such as mono-chlorobenzene, dichlorobenzene (DCB), and trichlorobenzene, which are present in some surface and groundwater, have been identified as priority pollutants by the US Environmental Protection Agency [115]. Among chlorobenzenes, DCB is one of the most chemically stable, and its degradation in soil and aquatic environments is extremely limited [116]. The widespread use of chlorinated aromatic chemicals over several decades has resulted in contamination of the environment and human exposure to DCB. The methods employed to remove DCB from water are either destructive oxidation or adsorption.
Peng et al. [108] reported the use of as-grown CNTs and graphitized CNTs as adsorbents to remove 1, 2-DCB from water. As-grown CNTs was prepared by catalytic pyrolysis of a propylene–hydrogen mixture at 750 °C using Ni particles as catalysts. The graphitized CNTs were prepared by treating as-grown CNTs in a nitrogen atmosphere at 2200°C for 2 h. The maximum amounts of DCB adsorbed by the as-grown and graphitized CNT were 30.8 and 28.7 mg/g, respectively. The short time required to achieve equilibrium suggested that the CNTs had very high adsorption efficiencies, with the removal rate remaining almost constant over a pH range from 3 to 10. The adsorption isotherms obtained are reproduced in Fig. 2.13. Taken together, the results indicated that the as-grown CNTs were superior to the graphitized material in terms of DCB adsorption.

![Fig. 2.13 Isotherms for DCB adsorption onto as-grown and graphitized CNTs at 25°C (pH = 5.5, t = 24h)](Image)

(Reprinted from [106] with permission from John Wiley and Sons)
Recently, \textit{ab initio} theoretical calculations of 1, 2-DCB adsorption onto metallic SWCNTs were reported by Fagan et al. [117] The values for the binding energies obtained in terms of interaction between the DCB and SWCNTs, indicated that a decrease in nanotube diameter and a consequent enhancement in tube curvature favored a more effective adsorption of DCB on the tube surface. Charge distribution calculations indicated that the adsorption of DCB occurred through $\pi - \pi$ stacking; the calculations also suggested that the DCB–SWCNTs interaction was larger for metallic nanotubes than for semi-conducting nanotubes.

\textbf{2.3.3.3 Adsorption of Trihalomethanes}

Trihalomethanes (THMs) are generated during the disinfection of drinking water with chlorine [118], and are recognized as potentially hazardous and carcinogenic substances [119]. More stringent requirements for the removal of THMs from drinking water in recent years have led to the development of innovative, cost-effective alternatives to remove these byproducts. In 2004, Lu et al. [120] reported the use of CNTs materials to remove THMs from water, where the nanotube samples were fabricated by the catalytic decomposition of a CH$_4$/H mixture at 700°C using Ni particles as catalyst. Based on FTIR spectra the authors noted that, after a mild acid treatment, the CNTs material became more hydrophilic and effective for the adsorption of the relatively polar THMs.
molecules. It was also suggested that the diffusion mechanisms controlled the adsorption of THMs onto the CNTs. In fact, the smallest molecule, CHCl$_3$, was seen to adsorb preferentially onto the nanotubes, followed by CHBrCl$_2$, CHBr$_2$Cl, and CHBr$_3$. The adsorption isotherms obtained in these studies are shown in Fig. 2.14. The observed adsorption capacity for CHCl$_3$ was highest, followed by CHBrCl$_2$, CHBr$_2$Cl and CHBr$_3$. The maximum adsorbed amounts of CHCl$_3$, CHBrCl$_2$, CHBr$_2$Cl and CHBr$_3$ were 2.41, 1.23, 1.08 and 0.92 mg/g, respectively, from an initial concentration of 1mg/l of each THM.

Fig. 2.14 Adsorption isotherms for four trihalomethanes onto CNTs (Reprinted from [120] with permission from John Wiley and Sons)
Another study conducted by the same group [121] included a comparison of the adsorption of THMs on powdered activated carbon. In contrast to data obtained with CNTs, for activated carbon, the largest molecule (CHBr$_3$) has been preferentially adsorbed, followed by CHBr$_2$Cl, CHBrCl$_2$ and CHCl$_3$. With an initial concentration of 1mg/l, the amounts of CHCl$_3$, CHBr$_2$Cl, CHBrCl$_2$ and CHBr$_3$ adsorbed were 1.2, 1.68, 2.19, and 2.75 mg/g CNTs, respectively. The adsorption of THMs onto CNTs also occurred more rapidly compared to activated carbon. Although the surface area of the nanotube material (295 m$^2$/g) was much less than that for activated carbon (900 m$^2$/g), the adsorption capacity of CHCl$_3$ onto CNTs was approximately twice that for activated carbon. The thermodynamic and kinetic parameters of the adsorption processes of THMs on MWCNTs were also reported [121]. Here, the amount of THMs adsorbed onto CNTs was seen to decrease with a rise in temperature, with the highest adsorption capacities observed at 5°C and 15°C. Under the same conditions, the purified CNTs material displayed two- to three-fold greater adsorption capacities for CHCl$_3$ than did activated carbon. A thermodynamic analysis revealed the adsorption of THMs onto CNTs to be exothermic in nature.
2.3.3.4 Adsorption of Polyaromatic Compounds

A recent study [122] has been reported to investigate the adsorption of polycyclic aromatic hydrocarbons (PAHs) (e.g., naphthalene, phenanthrene, pyrene) from water onto six different carbon nanomaterials, including fullerenes, SWCNTs and MWCNTs. The results showed that the adsorption capacities of the nanomaterials for the different polycyclic aromatic molecules was related to the PAH molecular size, which prompted the authors to suggest that, due to their size, some of these aromatic molecules could not access the nanomaterial pores. Among the different carbon nanomaterials, adsorption appeared to relate well with the adsorbent surface area, micro-pore, and mesopore volume. Except for the SWCNTs, a linear relationship was observed between the adsorbed capacity and the carbon nanomaterial.

2.3.4 Summary of CNTs Adsorption Results and Conclusions

Among the above described data, some of which are summarized in Table 2.5, it appears that, except for those used by Peng et al. [108], all CNTs employed in these experiments have been purified by pretreating with acid, before adsorption measurements were made. Such pretreatment had a major impact on the adsorption capacity of the CNTs in terms of
contaminant removal. An analysis of the afore-mentioned results indicated that the acid treatment not only removed the amorphous carbon that coats the CNTs surface but also increased the specific nanotube surface area and pore volume. However, it seems that the most important factor responsible for the improved adsorption capacities seen with oxidized CNTs is the incorporation of surface functional groups (hydroxyl, carboxyl and carbonyl) generated by their treatment with oxidizing acids.

**Table 2.5 Summary of selected cited results**

<table>
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<tr>
<th>Ref</th>
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<td>Acid treatment</td>
<td>Structure &amp; electronic properties of CNT</td>
</tr>
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<td>Acid treatment</td>
<td>pH of solution</td>
</tr>
<tr>
<td>[114]</td>
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<td>1,2-DCB</td>
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<td>Theoretical study</td>
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<td>[120]</td>
<td>CNT</td>
<td>THMs</td>
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<tr>
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<td>THMs</td>
<td>Acid treatment</td>
<td>Temperature</td>
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<tr>
<td>[122]</td>
<td>CNT &amp; fullerenes</td>
<td>PAHs</td>
<td>Acid treatment</td>
<td>Adsorbed volume capacity &amp; molecular size of adsorbate</td>
</tr>
</tbody>
</table>
2.4 Integration of nZVI into a Carbonaceous Nanomaterial Matrix

As discussed above, nZVI technology has been widely explored for the remediation of chlorinated compounds, such as TCE, because of the extremely small particle size, large specific surface area and in-situ reactivity. However, nZVI particles without a stabilizer are actually agglomerated into macroscale aggregates, resulting in a significant decrease of reactivity. Therefore various methods have been developed to modify their surface properties and enhance their reactivity. Although to date, most studies have focused on the development of polymers or silica protective coatings, recently carbon-protected nZVI particles are receiving more attention, because they have many advantages over polymers or silica, such as much higher chemical and thermal stability as well as biocompatibility. The carbon matrix not only protects the nZVI from rapid oxidized by the surrounding environment, but it also prevents the particles from agglomeration caused by van der Waals attraction.

Among the carbon-based materials, activated carbon (AC) and CNTs have been proposed to be the most viable candidates due to their unique chemical and physical properties. As its name implies, activated carbon is one of the most active members of the carbon family, because it possesses the special characteristics of exceptionally high surface area and a
large amount of micro-porosity. AC has been studied extensively and employed in a wide range of industrial applications in terms of purification of gases and removal of organic pollutants from water, because of its excellent adsorption capacity, a result of high porosity and internal surface area. In the case of CNTs, as reviewed above, they provide a large specific surface area (around 1500 m$^2$/g) and a strong *van der Waals* binding energy for molecular adsorbates on well-defined adsorption sites, including interior sites, groove sites, exterior sites and interstitial sites. Thanks to large efforts in experimental and theoretical research, much progress has been made over the last few years in the area of CNTs environmental application.

Combination of the two classes of nanomaterial (AC or CNTs and nZVI) will lead to a successful integration of the properties of two components into a new class of hybrid materials, presenting an important benefit for applications in environmental remediation and catalysis. Beyond the scope of treating carbonaceous nanomaterial as an adsorbent media and nZVI as a reductant, respectively, hybrid nanomaterials are considered as a potential candidate by prospective utilization of simultaneous adsorption and dechlorination for chlorinated contaminants.
2.4.1 Synthesis of Carbon-based Hybrid Nanomaterial

So far, techniques used to synthesize a carbon shell onto metallic nanoparticles divide into physical and chemical routes. The employment of a range of different physical techniques includes microwave irradiation [141], high-energy milling [142], pulsed laser ablation [143] and supercritical fluids [144]. But all of these physical methods are expensive and time-consuming, which limit their applications. Some economic and easy-handling chemical approaches have been recently introduced to fabricate hybrid nano-materials. The classical methods are impregnation [145], co-precipitation [146] and deposition-precipitation [147]. Some other novel routes include precipitation from reverse micelle (e.g. water-in-oil) emulsions [148], chemical vapor impregnation [149] and electrochemical reduction [150]. As one of the most popular approaches, impregnation has been employed to prepare a variety of carbon-based nanomaterials. It is commonly referred to as “wetness incipient impregnation” by entailing the “wetting” of the solid support with a solution containing the metal precursor. The metal nanoparticle precursor, typically a salt, (e.g. ferric chloride) is dissolved in the minimum quantity of solvent to afford its complete dissolution. The resulting solution is then added to the porous solid support, until a thick paste is formed. The solvent is then removed and the final solid is subject to thermal chemical treatment to obtain the final material [145, 151].
Choi et al. [151] initially introduced this approach to prepare Pd/Fe\textsuperscript{0} nanoparticle supported on granular activated carbon (GAC) (depicted in Fig. 2.15) The author successfully embedded Fe\textsuperscript{0} nanoparticle in 7–40 nm GAC using Fe (NO\textsubscript{3})\textsubscript{3} as the Fe\textsuperscript{0} source (Fig. 2.15(a)), followed by calcination (at 300°C) of the material to produce GAC-nZVI composite precursor (mainly as GAC-Fe\textsubscript{2}O\textsubscript{3}) (Fig. 2.15(b)). This was subsequently reduced with NaBH\textsubscript{4} to produce GAC-nZVI composite (Fig. 2.15(c)). Pd nanoparticles were prepared by reductive deposition of Pd(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2} at the ZVI surface (Fig. 2.15(d)). These materials showed good adsorption capacity and good activity for the dechlorination of 2-chlorobiphenyl.

![Fig. 2.15 Incipient wetness impregnation approach for the preparation of Pd/Fe\textsuperscript{0} mixed metal nanoparticles supported on GAC](image)

(Reprinted from [151] with permission from American Chemical Society)
2.4.2 Characterization of Hybrid Nanomaterial

Appropriate physical and chemical characterization of hybrid nanomaterial is fundamental to determine their intrinsic properties [152]. The most important physicochemical properties of hybrid nanomaterial, such as average particle size, particle size distribution, specific surface area, porosity, elemental composition and crystallinity, are essential elements to elucidate their homogeneity, stability, reactivity and potential applications of hybrid nanomaterial [153]. Numerous analytical techniques and instruments are being applied in the filed of characterization, including transmission electron microscopy (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET) measurement and Raman spectroscopy. From electron microscopy techniques, two of the most valuable tools are TEM and SEM, which allow the corroboration of structure and morphology of hybrid nanomaterial. Additional techniques widely used to determine the nanoparticle phases and compositions are XRD, Raman and Fourier transform infrared spectroscopy (FTIR).

Morphologies of MWCNTs and nZVI–MWCNTs composite before and after reaction with Cr (VI) are presented in Fig. 2.16. [15] It was revealed that MWCNTs with a diameter less than 50 nm has a smooth surface (Fig. 2.16(a)). As nZVI loaded, some
bright spherical spots became visible, which were proven to be nZVI particles by TEM image. (Right bottom of Fig. 2.16(b)) These nZVI particles, with a diameter of 20-80 nm, were located on the surface or inside of the nanotube network.

Fig. 2.16 (a) SEM and TEM images of MWCNTs; (b) SEM and TEM images of nZVI supported on MWCNTs before reaction; (c) SEM images of nZVI supported on MWCNTs after reaction with Cr (VI) for 2 h and (d) XRD patterns of bare MWCNTs, nZVI–MWCNTs before and nZVI–MWCNTs after reaction.

(Reprinted from [15] with permission from Elsevier Limited)
XRD patterns from the same study are shown in Fig. 2.16d [15]. The results indicated that the nZVI–MWCNTs composite kept typical structure and framework of MWCNT.

(Fig. 2.16d, curve a) An apparent peak at $2\theta = 44.90^\circ$ (Fig. 2.16d, curve b) indicated the presence of nZVI and the existence of peaks (Fig. 2.16d, curve c) suggested the formation of iron oxides after reaction, in terms of $\gamma$-Fe$_2$O$_3$ ($2\theta = 36^\circ$), Fe$_3$O$_4$ ($2\theta = 36^\circ/57^\circ/62.5^\circ$) and Cr$_2$FeO$_4$ ($2\theta = 35.50^\circ$). The authors concluded that the appearance of Fe (II), Fe (III), Cr (III) and the diminishment of Fe$^0$ demonstrated that the occurrence of redox reactions between nZVI and Cr (VI) where nZVI particles acted as reductants.

Tseng et al. [154] studied the characteristics of GAC-nZVI composite, prepared of wetness impregnation approach. TEM technique was used to observer the morphology and size of four different nanocomposite samples. Fig. 2.17 showed a TEM image of one of GAC-nZVI composite samples (GAC-nZVI700P), which comprised by roughly spherical nZVI particles with a diameter of 10-100nm, situated within the pores. XRD analysis (Fig. 2.18), presented that the main reflection occurred at 44.7, ($2\theta=44.7$) for nZVI and all GAC–ZVI composites, which is consistent with literatures regarding to the position of bare Fe$^0$ nanoparticle.
Fig. 2.17 TEM image of GAC-nZVI700P composite (100,000X) (Reprinted from [154] with permission from Elsevier Limited)

Fig. 2.18 XRD analysis of GAC–nZVI composites (Reprinted from [154] with permission from Elsevier Limited)
2.4.3 Applications of Hybrid Nanomaterial

2.4.3.1 Environmental Applications of Hybrid Nanomaterial

The simultaneous adsorption and dechlorination that can potentially take place on the combined hybrid nanomaterial is a promising approach for in-situ groundwater and sediment remediation of chlorinated contaminants. Recent studies have shown that hybrid activated carbon media containing nZVI (Fe\textsuperscript{0}-AC) can simultaneously remove some organic compounds.

For instance, Hyeok et al. [54] revealed that physical adsorption of polychlorinated biphenyls (PCBs) to GAC and their electrochemical dechlorination by Fe/Pd bimetal on the GAC could be simultaneously achieved on a GAC-supported Pd/Fe\textsuperscript{0} system. The results showed that neat GAC and GAC-Fe\textsuperscript{0} exhibited only adsorption of 2-chlorobiphenyl (2-CIBP), whereas GAC-Pd/ZVI showed a significant dechlorination of 2-CIBP of 90% efficiency after 2 days and complete adsorption of remaining 2-CIBP with the final product biphenyl formed. They demonstrated that hybrid GAC-Pd/ZVI system could be used for the fabrication of an efficient “reactive capping barrier” to in-situ treat sediment and groundwater contaminated with hydrophobic organic
compounds via reductive pathways.

More recently, Tseng and co-workers [154] studied the coupling adsorption and degradation of TCE through dechlorination using synthetic GAC–ZVI composites. Their results indicated that TCE compounds, attracted by GAC adsorption, were firstly accumulated around ZVI particles imbedded in pores on the surface of the GAC. They were then dechlorinated by ZVI, which degraded both adsorbed and dissolved TCE compounds. The experiment confirmed that GAC–ZVI composites combined the physical adsorption capacity of GAC with the dechlorination reactivity of ZVI and could be used as a reactive GAC, which was not subject to the limitations of using GAC and ZVI separately.

In the case of CNTs-ZVI composite, Lv et al. [15] initially adopted nZVI-MWCNTs composite to remove Cr (VI) from wastewater. The characterization of TEM, SEM and XRD showed that nZVI particles could disperse on the surface or into the network of MWCNTs. Compared to bare nZVI or AC-nZVI composites, nZVI–MWCNTs composites exhibited around 36% higher efficiency on Cr (VI) removal. They also discovered that low pH and initial Cr (VI) concentration could increase both removal efficiency and rate constants. Overall, their study proved that nZVI particles could be supported by MWCNTs, which exerted excellent acceleration effect on Cr (VI) removal.
2.5 Summary

Because of their high efficiency in the removal or reduction of chlorinated contaminants, nZVI particles have advantages over regular microscale iron particles in both in-situ and ex-situ environmental engineering applications. Since the initial field demonstration of nZVI technology in 2001, significant progress has been made in research and development of iron nanoparticle for soil and groundwater treatment. CNTs, on the other hand, providing a large specific surface area and a strong \textit{van der Waals} binding energy, has attracted great attentions in the filed of removal and adsorption of both inorganic and organic contaminants.

In recent years, hybrid nanomaterials have become one of the main focuses of research. There is a great potential to use this technology to clean up the contaminated sites and protect the environment from pollution. The combination of carbonaceous nanomaterial and ZVI generates a family of composite materials with extraordinary properties. In this chapter, we reviewed two types of hybrid nanomaterials, GAC-nZVI and CNTs-nZVI, in terms of synthesis process, characterization and their remediation applications. However, so far, there is only few publications discussing their potential for environmental remediation, and more work is required to fully exploit this technology.
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Adsorption of Trichloroethylene onto Multi-walled Carbon Nanotubes

3.1 Introduction

Chlorinated hydrocarbons, such as trichloroethylene (TCE), form a category of dense non-aqueous phase liquid (DNAPL) contaminants in groundwater and soil that are persistent to natural degradation due to their low aqueous solubility and low rate of dissolution. They have a density higher than that of water and have the capability to be settled deeper into the sediments by their gravities, from which they gradually leach out into aquifers, therefore causing the problems of long-term environmental pollution. Trichloroethylene, which is detected as one of the most commonly chlorinated organic compounds in surface water, groundwater and soil, has been widely utilized as a degreasing agent for metalworking, machine and electronic industries due to its non-flammability and ability to dissolve various organic materials [1]. The combination of extensively use in the past, unconscious leakage from storage drums, accidental spills and improper discharge has resulted in a legacy of the widespread contamination of groundwater by this ubiquitous and recalcitrant pollutant in several industrialized nations, including Canada [2]. Moreover, TCE is suspected as carcinogenic and possess a
significant health threat, mainly affecting the central nervous system and causing headache, nausea, dizziness, clumsiness and drowsiness [3]. Heavy exposure to TCE can cause the damage to human livers and kidneys. Listed as a priority pollutant by the US Environmental Protection Agency (USEPA), TCE has been set the maximum contaminant level (MCL) of 5 ppb (0.005 mg/L), which is readily exceeded at the contaminant sites by orders of magnitude [4].

Cleanup of TCE-contaminated groundwater sites is of utmost importance and could be a challenging task due to the subsurface heterogeneity and complex site architecture [5]. Commonly adopted technologies represented for the removal of TCE organic compounds include bioremediation [6], air stripping [7], photosonochemical degradation [8] and advanced oxidation processes, etc. However, these technologies have distinct disadvantages, such as considerably high operational and maintenance cost, expensive equipment, incomplete removal, high-energy requirement and generation of toxic residual sludge. Therefore, it is extremely crucial to develop and implement innovative technologies with high removal efficiency and low energy consumption for remediating TCE-contaminated aquifers.
Among the depuration technologies for groundwater remediation, adsorption has been widely used because it conjugates good efficiencies with a reliable and robust process configuration [9]. Numerous adsorbents, such as activated alumina [11], zeolites [12], manganese oxides [13], silica [14], iron oxides [15], granular activated carbon and powder activated carbon [16-17], have been developed. Their large surface areas and physicochemical interactions between adsorbates and adsorbents have been investigated for their potential applications for adsorbing TCE compounds from aqueous systems. For instance, activated carbon is the most commonly used adsorbent for water purification treatment. However, it fails to remove many organic pollutants including TCE at concentration levels of nanograms per liters [18]. Therefore, low TCE adsorption capacities and increasingly stringent standards limit its applications as well as that of traditional adsorbents.

Carbon Nanotubes (CNTs), a fascinating new member of carbon family, have been come under intense multidisciplinary study since their discovery in 1991 [19] due to their unique morphology and exceptional properties. Generally, CNTs are considered as needlelike cylindrical tubules of concentric graphitic carbon capped by fullerene-like hemispheres, and are normally classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [20]. The novel structure of CNTs with perfect lattice alignment and closed topology endows them with outstanding physical and
chemical properties including high electrical and thermal conductivity, excellent strength and stiffness, and high thermal and chemical stability [20]. Their large specific surface area, cylindrically hollow cores and layered tubule nanostructure presents tremendous potentials for future engineering applications in the field of catalyst supports [21], hydrogen storage [22] and composite materials [23], etc. At present, increasing theoretical and experimental investigations indicate that CNTs have great potential adsorbents for distinct contaminants removal from aqueous systems. Unlike most traditional adsorbents, CNTs possess unique features that contribute to superior removal capacities, such as fibrous shape with high aspect ratio [24], large accessible external surface area, and well-developed mesopores [25].

Because of their specific features, CNTs have been extensively studied by many researchers for their applicability in removing different types of water contaminants. Long et al. [26] initially reported that MWCNTs had significantly higher dioxin removal efficiency than that of activated carbon, which was attributed to stronger interactions between dioxins and MWCNTs. Li et al. [27] indicated that CNTs showed exceptional adsorption capability and high adsorption efficiency for lead removal from water. The same group [28] further reported that CNTs were excellent adsorbents for fluoride, cadmium (II), and chromium (II) and their removal capability was superior to that of activated carbon. Peng et al. [29] confirmed that CNTs were efficient adsorbents for 1,
2-dichlorobenzene removal from water and that it can be used in a wide pH range. Lu and coworkers [30] evaluated that CNTs displayed significantly high trihalomethanes (THMs) removal efficiencies. However, because of their comparatively low water solubility, raw CNTs had difficulties to disperse homogeneously in aqueous phase, causing much inconvenience in their practical applications. In order to take the best advantages of CNTs in aqueous systems it is necessary to modify CNTs to decrease their hydrophobicity.

As-synthesized CNTs are dominantly produced by chemical vapor deposition (CVD), arc discharge and laser ablation, which inevitably lead to the formation of carbonaceous impurities and metal catalyst particles, including amorphous carbon, fullerenes, carbon nanoparticles and metal nanoparticle residues from the transition meal catalysts [31]. These impurities significantly influence the adsorption properties of CNTs and limit their application. Thus, several purification and functionalization protocols have been developed to enhance CNT material’s performance. One of the most common approaches relies is the use of concentrated acids [32], such as a mixture of concentrated \( \text{H}_2\text{SO}_4/\text{HNO}_3 \) (3:1 by volume) and concentrated \( \text{HCl} \) or \( \text{HNO}_3 \) acid solutions [33]. Acid treatment of CNTs purifies and enhances the chemical reactivity of the nanotube graphitic network. Thus through acid treatment the pristine CNTs can be effectively purified through efficient elimination of the amorphous carbon and residual metal
nanoparticles [34]; while the simultaneous incorporation of oxygenated functional groups, mainly carboxyl (-COOH) and hydroxyl (-OH), onto the graphitic surface facilitates the exfoliation of CNT bundles, and increases their solubility in water [35].

A number of contributions have been devoted to the experimental and theoretical studies on the adsorption of various contaminants by modified MWCNTs. They are relatively new adsorbents that have been proven to possess great potential for removing heavy metal ions. Li et al. [36-37] reported that surface oxidized MWCNTs by nitric acid at 140 °C for 1h showed exceptional adsorption capability and high adsorption efficiency for lead (II) and cadmium (II) removal from water. Li and co-workers [38] concluded that the adsorption of Pb (II), Cu (II) and Cd (II) onto acid-treated MWCNTs were 3-4 times larger than those of conventionally used powdered activated carbon (PAC) and granular activated carbon (GAC). In addition, MWCNTs have shown exceptional adsorption capability and high adsorption efficiency for various organic contaminants. Peng et al. [29] demonstrated that the modified MWCNTs could be used as a good adsorbent for the removal of 1,2-dichlorobenzene in a wide pH range of 3-10 and it only took 40 min to attain equilibrium. Lu et al. [39] employed MWCNTs purified by mixed HNO₃/H₂SO₄ solution as adsorbents to study adsorption kinetics and thermodynamics of THMs from chlorinated drinking water and they indicated that modified CNTs possessed 2-3 times higher adsorption capacities than that of commercially available PAC suggesting that
MWCNTs were efficient adsorbents. Moreover, Liao et al. [40] reported the adsorption of ortho-chlorophenol, meta-chlorophenol and para-chlorophenol onto HNO₃ and NH₃ treated MWCNTs and compared with the adsorption on ACs. The results revealed that HNO₃-treated MWCNTs possessed the highest adsorption capacity, supposed to be attributed to the large mesopore volume and enhanced hydrophilic interactions. Salam and Burk [41] used oxidized MWCNTs to study the removal of pentachlorophenol from aqueous solution and found that oxidized tubes could be considered as good adsorbents for the uptake of pentachlorophenol from large volumes of solutions. The comparison of MWCNTs with other carbonaceous adsorbents, such as bonded silica (C₁₈) [42], AC [43, 44] and carbon molecular sieves [45] suggest that the MWCNTs are promising organic adsorbents for environmental protection applications.

These studies indicate MWCNTs are promising candidates for the removal of water pollutants through adsorption. However, limited work has been conducted on the adsorption of TCE compounds from aqueous solution by pristine or/and modified MWCNTs. In this chapter we discuss the results obtained on the use of pristine and modified MWCNTs for the adsorption of TCE in aqueous phase. The main objectives of this study are to evaluate TCE adsorption behavior on MWCNTs as a function of batch contact time, initial TCE concentrations, different MWCNTs chemical modification approaches and various tube dosages and further model the TCE adsorption kinetics and
the adsorption isotherms to describe the mechanism and thermodynamic of TCE adsorption by MWCNTs materials. To accomplish the goals of this investigation, a series equilibrium batch adsorption experiments were conducted to elucidate TCE removal capabilities by pristine and various modified MWCNTs. The adsorption kinetics was analyzed by experimental data fitting with a pseudo-first-order equation, a pseudo-second-order rate equation and intra-diffusion equation, respectively. The adsorption performance was determined by estimating the coefficients of Langmuir and Freundlich adsorption isotherms, respectively.

### 3.2 Materials and Methods

#### 3.2.1 Chemicals

All solvents and reagents used in this study were obtained from supplies with commercially analytical grade and used as received without any further purification. Trichloroethylene (≥99.5% purity, ACS reagent) and n-hexane (anhydrous solvents, 95% purity) were purchased from Sigma-Aldrich (WI, USA). Isopropyl alcohol (2-propanol, 99.5% min. assay, ACS reagent, BDH) and methanol (99.8% min. ACS Grade, BDH) were obtained from VWR Company (USA). All ultrapure water used in this study was deionized by a Barnstead Easypure II system. All the chemical solutions used in this
study were prepared using deionized water.

3.2.2 Materials

3.2.2.1 Multi-walled Carbon Nanotubes (MWCNTs)

As-grown MWCNTs used in present study were procured commercially from Cheap Tubes Inc. (Brattleboro, VT). According to the product information provided by the manufacturer, the MWCNTs samples were synthesized using a catalytic chemical vapor deposition (CCVD) method with metal catalysts. The mass ratio of the amorphous carbon of MWCNTs was less than 5%. Their specifications were provided by the manufacturer and are summarized in Table 3.1.

Table 3.1 Specifications of the commercial MWCNTs

<table>
<thead>
<tr>
<th>Outer Diameter (nm)</th>
<th>Inside Diameter (nm)</th>
<th>Length (µm)</th>
<th>Purity</th>
<th>Specific Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-20</td>
<td>3-5</td>
<td>10-30</td>
<td>&gt;95 wt.%</td>
<td>233</td>
</tr>
</tbody>
</table>
The suspensions of as-grown MWCNTs were prepared by dispersing received raw-MWCNTs into ultrapure deionized water and then sonicated using an ultrasonic probe (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY) to archive the initial suspension of MWCNTs in water. To obtain homogenous suspensions of as-grown MWCNTs, 60 mg of as-grown MWCNTs were added to a 100 mL beaker containing 60 mL of deionized water and sonicated under the condition of 200 watts (max. 400 watts) within an ice-water bath for 45-60 min. As-grown MWCNTs are usually hydrophobic and tend to agglomerate in bundles resulting in poor solubility and are therefore difficult to handle. Even though sonication is useful, but without the addition of a surfactant or chemical modification, MWCNTs will fall out of water suspension within hours.

3.2.2.2 Powder Activated Carbon

In order to compare TCE adsorption capacity by MWCNTs with other adsorbents, a commercially available powder activated carbon, (HYDRODARCO®C, HD-PAC), was obtained from Norit Americas, Inc. (Marshall, TX). HD-PAC had a specific surface area of 600±10 m²/g and minimum 65% of the samples have the mesh size less than 45 µm. PAC samples were first pulverized, washed with deionized water to remove surface impurities. Wet PAC samples were oven-dried at 105°C for 12-hour, then cooled to room
temperature and stored in glass jars. To prepare homogeneous PAC suspensions, 60 mg of both PAC samples were dispersed into 60 mL of deionized water, and then sonicated for about 1 hour by an ultrasonic probe in an ice-water bath at 280 watts (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY).

3.2.2.3 Preparation of Modified MWCNTs

Due to its poor solubility in aqueous solutions and lack of reactivity, surface chemical modification on the as-grown MWCNTs was performed by acid-oxidation following standard literature methods [39]. In a typical preparation process, the suspension of as-grown MWCNTs was transferred into a mixture of concentrated sulphuric acid (HSO₄, 95%-97%) and concentrated nitric acid (HNO₃, 70%) with a volume ratio of 3:1 (H₂SO₄:HNO₃=3:1, v/v). The suspension was then homogenized using an ultrasonic bath for 2 hours (AQUASONIC Ultrasonic Cleaner, VWR Scientific Products, West Chester, PA), followed by subsequently several cycles of washing with deionized water until the pH value was close to neutral. The solid material was separated from the suspension by centrifuging using a model of IEC-B-20A Centrifuge at a rotation speed of 9000 rpm for 15 min. Finally, the treated MWCNTs were dried overnight in an oven at 100°C and stored in a desiccator for further studies. The resulting MWCNTs were denoted as “acid-oxidized MWCNTs”.
An additional acid oxidation protocol was carried by refluxing pristine MWCNTs suspension either in concentrated HNO$_3$ or concentrated hydrochloric acid (HCl) solution, respectively. In the process of acid oxidation, 50 mL of pristine MWCNTs suspension were transferred into a 125 mL three-neck, round-bottomed glass flask equipped with a reflux condenser, magnetic stirrer and a thermometer. 10 mL of concentrated HNO$_3$ (ACS, 68%) or HCl (ACS, 36.5-38%) were slowly added and the solution was continuously heated at 85°C (HCl) or 70°C (HNO$_3$) overnight, respectively. Oxidized MWCNTs were denoted as “HNO$_3$-refluxed MWCNTs” or “HCl-refluxed MWCNTs”, separately. After cooling down to ambient temperature, acid-refluxed oxidized MWCNTs suspensions were repeatedly rinsed with doubly distilled water to remove excess free oxidants until the solutions reached a pH value about 7. Finally, the oxidized MWCNTs suspensions were both subjected to centrifugal separation using IEC-B-20A Centrifuge at about 7000 rpm for 10 min. The centrifugation step was repeated three times. The MWCNTs slurry were thus separated from water and the recovered residues were collected and dried at 100°C in an oven for 24 hours to drain the excess water and then stored in a desiccator for subsequent use.

Weight losses of all acid-oxidized MWCNTs were calculated to be less than 5%. Such oxidation treatment is known to not only purify the bulk MWCNTs material by dissolving carbon nanoparticles, metal catalyst support and amorphous carbon, but also to
enhance their hydrophilicity and enhance their suspension ability through the intentional addition of oxygen-containing functional groups onto the surface of the nanotubes. These oxidized MWCNTs suspensions prepared following this protocol were stable toward sedimentation in aqueous phase for up to several months.

3.2.3 Characterization of MWCNTs

Diameters and morphology of as-grown and modified MWCNTs were elucidated by transmission electron microscopy (TEM) using Philips CM10 Transmission Electron Microscopy. For TEM measurements, a very dilute suspension of as-produced or modified MWCNTs was prepared in methanol by sonication for 20-30 min. A few drops of MWCNTs suspension were deposited onto a Lacey carbon-coated copper grid followed by the complete evaporation of methanol from grid in air at room temperature. For each MWCNTs sample, a representative set of micrographs (roughly 20-30 TEM images) was chosen and the diameter of each particle on those micrographs was measured and analyzed in order to obtain the nanotubes diameter distribution. The diameters and diameter distribution were calculated using Imaging software (Gatan Microscopy Software, Gatan Inc.) by manually examining nearly 20-30 TEM images for each MWCNTs sample.
Raman spectra of MWCNTs before and after modification were obtained in a Raman spectrometer. (Renishaw micro-Raman 2000) The spectra were obtained using 632.8 nm line of a He-Ne laser in the range of 120 cm\(^{-1}\) to 2000 cm\(^{-1}\).

The specific surface area of HNO\(_3\)-oxidized MWCNTs was measured by N\(_2\) adsorption/desorption at 77 K using a BET Model ASAP 2010 surface area analyzer. (Micromeritics Inc., Norcross, GA, USA). The Brunauer-Emmett-Teller (BET) method was employed to determine the specific surface area of MWCNTs samples.

### 3.2.4 Batch Adsorption Experiments

Batch equilibrium adsorptive capacity (isotherm) experiments were performed on a mixture of either as-grown MWCNTs or modified-MWCNTs and various TCE solutions with different initial concentrations. The effects of modification approaches of MWCNTs, TCE initial concentration, and MWCNTs dosage were evaluated to investigate the effectiveness of MWCNTs chemical treatment on their TCE adsorption capability. All the batch adsorption experiments were conducted at room temperature (25°C) at neutral pH environment (pH=7) in 60 mL glass serum bottles capped with a Teflon mininert valve to minimize the loss of TCE during repetitive sampling.
The pre-weighted as-grown MWCNTs or modified-MWCNTs were dispersed into deionized water to obtain stable suspensions. This was achieved under sonication (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY) at 250 watts for 45 min. For each reaction bottle, 60 mL of as-grown or modified MWCNTs suspensions were transferred into the reaction bottles, and pre-determined amounts of TCE stock solution (0.15 mL of TCE in 10 mL of 2-propanol) was added to obtain a preset initial TCE concentration. The headspace in the reaction vial was set to nearly zero to minimize volatilization losses. The bottles were mounted on a wrist-action shaker (MISC-CAEQUIP, BURRELL 24 place wrist action shaker-115V, VWR) for vigorous mixture to keep good homogenization for the solutions. Subsequently shaken for predetermined time intervals, the shaker was stopped, and the reaction bottles were placed vertically to allow the particles to settle. The clear supernatant containing TCE was extracted by n-hexane, transferred to a 2 mL GC vial and ready for further measurements. The optimal sampling times were estimated by a sequential estimation procedure, in which a set of preliminary trails was conducted to determine the optimal time intervals for sampling. Parallel blank experiments without added MWCNTs were carried for each experiment.
In addition, the effect of MWCNTs dosage on TCE adsorption was carried out by adding predetermined amounts of MWCNTs in 60 mL deionized water solutions with initial TCE concentration of 20 mg/L at pH value of about 7. Comparative batch adsorption experiments of as-grown MWCNTs, modified-MWCNTs and commercially available HD-PAC were conducted under the same conditions. The pre-treatment on PAC was the same as that employed for the MWCNTs. The comparative studies were accomplished in a series of reaction bottles containing 60 mL of as-grown MWCNTs, modified MWCNTs and PAC suspensions, respectively. All experiments have been conducted in duplicates to check the consistency of the results and the average values are reported as the final result. The coefficient of variation is estimated less than 5% for all of the adsorption kinetics and isotherms. A discussion on reproducibility and data analysis is shown in Appendix A. Table 3.2 indicates the different experimental conditions used for TCE adsorption testing.
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>TCE initial concentration $C_i$, (mg/L)</th>
<th>Adsorbent Dosage, $m$, (mg)</th>
<th>Total Contact Time, $t$, (hr)</th>
<th>Volume $V$, (mL)</th>
<th>$T$ (°C)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown MWCNTs</td>
<td>20, 50, 80, 100, 120, 150</td>
<td>5, 10, 30, 60, 80, 100, 120, 150</td>
<td></td>
<td>168</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>Acid-oxidized MWCNTs</td>
<td>20</td>
<td>5, 10, 30, 60, 80, 100, 120, 150</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>HNO$_3$-refluxed MWCNTs</td>
<td>20, 50, 80, 100, 120, 150</td>
<td>5, 10, 30, 60, 80, 100, 120, 150</td>
<td></td>
<td>168</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>HCl-refluxed MWCNTs</td>
<td>20</td>
<td>5, 10, 30, 60, 80, 100, 120, 150</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>HD-PAC</td>
<td>20, 50, 80, 100, 120, 150</td>
<td>5, 10, 30, 60, 80, 100, 120, 150</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>
3.2.5 Analytical Methods

3.2.5.1 TCE Calibration Curve

Initially, stock solutions of TCE were prepared by dissolving reagent-grade TCE into 2-propanol and appropriate volumes of the stock solutions were spiked by dilution through gas-tight syringes into a series volumes of glass vials in order to achieve the desired TCE concentrations. The glass vials were sealed with a 20 mm rubber stopper to minimize solvent evaporation.

Prior to analysis of the samples by gas chromatography (GC), the response factor and the detection linearity for the internal standard were established. Standard calibration curves for TCE were generated in 2-propanol and DI water by using solutions containing known concentrations of TCE. The linear range of detection for the internal standard of TCE was determined as 15-155 mg/L with a detection limit of 0.5 mg/L, and all the sample extracts were analyzed within this range [46]. The calibration curves were used to calculate the aqueous concentrations of TCE in the reaction solutions and analyzed using the same method for all the samples.
3.2.5.2 Solvent Extraction Analysis

In this study, the residual TCE after adsorption was determined by a solvent extraction method. Hexane was used as the extracting solvent. Briefly, at selected time intervals, 250 µL of the aqueous aliquot was sampled from both the reaction and blank bottles and transferred to a 2 mL GC vial containing 1mL of n-hexane. This GC vial was shaken for about 10 seconds and then kept undisturbed for about 1hr to allow for equilibration. Upon phase separation, organic phase containing TCE was extracted from the eluent with n-hexane using the liquid-liquid extraction technique. A 1µL of extract was withdrawn by the auto-sampler for GC analysis.

3.2.5.3 Analysis of TCE by Gas Chromatography

An Agilent 7890 Gas Chromatography equipped with an electron capture detector (GC-ECD) was used to analyze TCE concentrations in the extracted samples of TCE/n-hexane. Helium gas (HP, Praxair) was used as carrier gas, and the flow rate was set at 6.38 mL/min. In order to meet the requirements of adsorption at infinite dilution, corresponding to zero coverage and GC linearity [40], the samples injected were in the range of 0.05-0.2 µL and chromatographic separation was performed in a DB-624
capillary column (30 m × 0.53 mm × 3 µm, J&W Scientific). The flow in the detector (argon+CH₄ (5%)) was set to 60 mL/min. The temperature program used for the analysis of TCE by GC-ECD using an isothermal stage at 35°C for 4 min, subsequently increased to 180°C at a rate of 18°C/min and finally held at this temperature for 5 min. A sample volume of 1µL of extracted TCE was injected into a splitless mode of GC-ECD in order to determine the concentrations of residual TCE in sample after adsorption. Similarly, 1µL of a standard blank solution (without adsorption) was also injected into the GC-ECD. The retention time of TCE found was about 8.5 minute for this temperature program.

3.3 Results and Discussion

3.3.1 Surface Characteristics of As-grown and Modified MWCNTs

To evaluate the structural morphology, purity, dimension, defects and efficiency of modification with respect to changes in structure of MWCNTs, characterization techniques with rapid, convenient and unambiguous features are urgently required. Normally, characterization of MWCNTs evaluates three different aspects: non-carbonaceous impurities such as residual metal catalysts, carbonaceous impurities and MWCNTs structural variation, including defects, functional groups, cap opening and cutting, etc. [41] In this article, characteristics of MWCNTs before and after acid
oxidation modification by HNO$_3$ were analyzed and discussed based on TEM studies and Raman spectroscopy.

3.3.1.1 Transmission Electron Microscopy (TEM)

Shape and dimension are two key factors to identify the characteristics of MWCNTs since these parameters determine their specific surface area and thus influence on TCE adsorption capacity [41]. Among the most common tools to characterize the shape and dimension of MWCNTs, TEM is by far one of the most useful techniques. The advantage of TEM over other microscopy techniques is that it is simple and could be carried out routinely. At present, TEM imaging is used to characterize the morphology of MWCNTs with respect to the direct observations of impurities, local structures and MWCNTs defects [41]. TEM allows determining the way in which the tubular structures are arranged (for example: concentric or nested tubes, scrolled sheets, stacked cup arrays, herringbone-type, etc.) [41] In addition, by use of TEM it is also possible to estimate the inner and outer diameters of concentric tubes and the presence of amorphous carbon and metal catalysts coating on the outer layers of the tubes.
Morphology Study

Fig. 3.1 and Fig. 3.2 represents the TEM images of as-grown MWCNTs (as received from Cheap. Tubes. Inc.) and HNO$_3$-oxidized MWCNTs, respectively. As illustrated in the TEM micrographs, there was no significant difference between as-grown MWCNTs and oxidized MWCNTs. It is obviously observed that both MWCNTs were curved and possessed a multiple atomic structure with hollow inner tubes. Although the nanotubes were entangled round each other, their structures were quite integrated and graphite layers of the tube walls could be discerned clearly. For both as-grown MWCNTs and modified MWCNTs, their lengths are found within the micrometer range. Aviles et al [47] reported that the lengths of MWCNTs would generally become shorten after acid treatment. The length measurements are conducted if the tube samples are straight and distinguishable. However, it is observed that the isolated MWCNTs are usually curved and entangled with each other and they are tend to form the aggregated structures due to intermolecular forces. Thus, it is difficult to determine their lengths definitively, but they are in the range of hundreds of nanometers to micrometers.
Fig. 3.1 Transmission electron micrograph of as-grown MWCNTs (duplicate from Cheap. Tubes. Inc.)

Fig. 3.2 Transmission electron micrograph of HNO₃-refluxed oxidized MWCNTs
The TEM micrographs of the as grown material indicate the presence of some impurities (such as amorphous carbon, metal catalyst particles and soot, etc.), which could be adsorbent materials on their own, thus their presence can misrepresent adsorption properties of MWCNTs for TCE [48]. A closer look at the TEM images indicates that MWCNTs were of high purity, with uniform diameter distribution and little structural deformity. The amorphous carbon was observed as an unstructured material on the TEM images of as-grown MWCNTs, which was eliminated after oxidization process. The metal catalyst particles, which were usually residues from the transition metal catalysts, are evident as the darkest spots in the micrographs. Some of them were deposited on the walls of the MWCNTs and left as defective sites after acid oxidization [48]. Others were encapsulated by the carbon layers, which varied from disordered carbon layers to graphite shells, making them impervious and unable to dissolve in acids. After chemical oxidation with concentrated acid (Fig. 3.2) some bundles appeared exfoliated and curled, and fragmentation of the MWCNTs structure took place. The graphitic surface of MWCNTs seems to be etched by the strong oxidants, leading to a shorter length of the nanotubes and opening of their tips. Destruction of the caps exposed the terminated cylinder walls, which could be further attacked to form thinner tubes, increasing the surface area per unit volume [49]. Associated to the cap opening and additionally defective sites generated, a large population of various functionalities are expected to form onto the reactive sites of modified MWCNTs, improving their solubility and chemical reactivity.
Other studies characterized the modified MWCNTs and the TEM images showed the similar observations as ours. Lu et al. [50] modified MWCNTs by thermal treatment and the morphology of raw and purified MWCNTs were analyzed by high-resolution TEM. As seen from the images, a large amount of metal catalysts and amorphous carbon appeared within raw MWCNTs and removed after purification. Moreover, Wu et al. [51] prepared the oxidized MWCNTs with 65% nitric acid and the TEM images demonstrated that both the MWCNTs were cylindrical and the impurities were removed after oxidization. In addition, Li et al. [37] prepared the modified MWCNTs by refluxing with concentrated nitric acid. TEM analysis showed that as-grown MWCNTs usually curved and entangled around each other and length ranging from hundreds of nanometers to micrometers. They also observed that after oxidization, tips of MWCNTs were open and fracture took place. Lu et al. [52] purified the as-prepared MWCNTs by concentrated HCl solution and reported that the tubes possessed multiple walls containing a concentrically nested array of SWCNTs with the hollow inner tube and an average external diameter of around 25 nm.
Diameter and Diameter Distribution

The representatively average values of diameter and diameter distributions of MWCNTs before and after acid oxidization were roughly estimated from a multiple of the recorded TEM images and analyzed using Imaging software after manually examining at least 20-30 independent nanotubes measured from a homogeneous sample. Fig. 3.3 represents a comparable histogram of diameter distributions of both as-grown MWCNTs and HNO₃-oxidized MWCNTs, which were obtained by the analysis of a series of TEM micrographs. The external diameters of the as-grown MWCNTs (Fig. 3.1) and modified MWCNTs (Fig. 3.2) varied from 20-30 nm and 5-25 nm, respectively. The average tube diameters of as-grown and modified MWCNTs were calculated as 25 nm and 15 nm, respectively. Modified MWCNTs were smaller in diameter and had a broader diameter distribution than those of as-grown MWCNTs. In the case of as-grown MWCNTs, more than 85% of tubes spread in the range of 20-30 nm and a few tubes were as large as 30-35 nm. The average diameter of MWCNTs after oxidization decreased and nearly 90% of the nanotubes appeared in the range of 10-25 nm, and less than 10% were smaller than 10 nm in diameter. The decrease in the diameter of the modified MWCNTs may be due to the removal of amorphous carbon from the as-grown MWCNTs by the oxidation of concentrated acids. The phenomenon might be also explained by proposing that the
oxidation treatment would partially break up the as-grown MWCNTs into small pieces and cut short most of raw MWCNTs [51]. This is supported by the observed better suspensibility of modified MWCNTs compared to that of as-grown MWCNTs.

Our measurement of as-grown MWCNTs and modified MWCNTs are in consistent with those reports. Li et al. [36] refluxed the as-grown MWCNTs with a mixture of HNO₃ and H₂SO₄ solution and analyzed the tube diameter distribution. The comparable results of the as-grown and modified MWCNTs showed that the average tube diameter decreased from 30 nm to 12 nm, and the diagram also suggested that most of the modified tubes had

![Fig. 3.3 Diameter distribution of as-grown MWCNTs and modified MWCNTs from TEM images](image-url)
the diameters less than 15 nm. Wu et al. [51] measured the diameters of MWCNTs and indicated that the main external diameters declined from 50-60 nm (as-produced) to 20-30 nm (modified MWCNTs). Di et al. [53] calculated the outer diameter of tubes with the average value of 30 nm and Li et al. [54] reported the oxidized MWCNTs exhibited cylindrical shape and curve features.

### 3.3.1.2 Raman Spectroscopy

Raman spectroscopy, a fast, conventional and non-destructive analysis technique, was employed to characterize the quality of the MWCNTs. The technique is well known as a tool able to describe the structural properties of MWCNTs, and assisting in the identifying the presence of impurities and defects [48]. Raman spectroscopy can evaluate the quality of MWCNTs by semi-quantifying the relative fractions of impurities in the measured MWCNTs using the intensity ratio of D/G band under fixed laser power density. We thus used this technique to investigate the changes of structure features of MWCNTs before and after acid oxidization.

**Fig. 3.4** depicts typical Raman spectra, in the range of 800-2000 cm$^{-1}$, obtained from the as-grown MWCNTs and HNO$_3$-oxidized MWCNTs. The spectra indicate that MWCNTs before and after oxidization, both have two characteristic sharp peaks located at 1320
These peaks correspond to the so-called D-bands and G-bands. The D-band located near 1320 cm\(^{-1}\), is attributed to the presence of amorphous carbon or structurally disordered sp\(^2\)-hydridized carbon atoms of MWCNTs. The intensity of the D-band is thus often considered as a measure of “disorder” in graphite and is linked to the structural defects on the nanotube walls, the presence of carbon vacancies, heptagon-pentagon pairs, kinks and heteroatoms [55]. On the other hand, the G-band present at 1580 cm\(^{-1}\), originates from the in-plane tangential vibration of the carbon-carbon bonds in graphene sheets. It is associated with the ordered graphite E\(_{2g}\) symmetry of the interlayer mode reflecting the structure integrity of sp\(^2\)-hybridized carbon atoms of the MWCNTs [56]. The D-band and G-band ratio is thus used to evaluate the extent of carbon-containing physical defects in the MWCNTs. In order to calculate the individual intensity of D-band (I\(_D\)) and G-band (I\(_G\)), and their peak intensities ratio (I\(_D\)/I\(_G\)) in our samples, a linear baseline subtraction was carried and both spectra were normalized with respect to the D-band intensity [57].
For the as-grown MWCNTs, D-band displayed a highly intense, broad and strong peak, which indicated that the as-grown MWCNTs contained a reasonable amount of disordered carbon atoms, which is a typical observation on as-grown MWCNTs with nanotubes opening or characteristic defects [55]. The $I_D/I_G$ ratio of as-grown MWCNTs and oxidized MWCNTs were 0.796 and 0.756, respectively. The lower $I_D/I_G$ of modified-MWCNTs could be interpreted as an indication of a decrease on the number of impurities as a result of acid oxidization. This result has been previously observed after acid oxidization treatments where the amounts of amorphous carbon in raw nanotube materials decreased resulting in a material with a higher graphitization degree [56]. These observations are supported by the TEM micrographs (Fig. 3.1 and 3.2), which
corroborate that less disordered carbon and structure defects are present in the nanotubes after acid treatment, thus resulting in a smoother nanotube surface.

Similarly, in previous study of Lu et al. [58], the structural information of MWCNTs was evaluated by a Raman spectrometer, and the spectra obviously indicated that there were two sharp peaks located at ~1350 cm\(^{-1}\) and ~1580 cm\(^{-1}\), respectively, relating to the so-called D-band and G-band. The intensity of D and G bands (I\(_D\)/I\(_G\)) of modified MWCNTs was lower than that of raw tubes, implying less impurities and more smooth carbon surface. Another study conducted by the same group [52] using purified MWCNTs by thermal treatment displayed the similar Raman spectra. After purification, the I\(_D\)/I\(_G\) ratio of MWCNTs decreased, indicating a more graphitized structure and thereby improving their surface properties. Therefore, these observations suggested by previous studies are in good agreement with the results obtained in our study.

### 3.3.1.3 BET Surface Area

The specific surface area of HNO\(_3\)-oxidized MWCNTs measured by BET yielded a value of 313.5±3.8 m\(^2\)/g, which is larger than that obtained on the received raw MWCNTs (233 m\(^2\)/g). An increase of specific surface area after oxidization is consistent with the TEM and Raman observations (Fig. 3.2 and 3.4 respectively), which indicates that
amorphous carbon introduced by CVD preparation process is removed and the inner cavities of MWCNTs are probed, resulting in the exposure of MWCNTs internal surface area. Another possible reason may be proposed by suggesting that the oxidization of MWCNTs with HNO$_3$ unties the entwined MWCNTs and thus increases it available the surface area [59]. Similar results are obtained by Lu et al. [60], in which the as-grown MWCNTs were oxidized by nitric acid and the specific surface area was measured by BET method. They found that the BET surface area largely increased to 297 m$^2$/g. Di et al. [53] reported that the specific surface area of MWCNTs was increased from 196.3 to 250.6 m$^2$/g after acid treatment. Another study of Lu et al. [50] demonstrated that the BET surface area of MWCNTs was increased from 225 to 295 m$^2$/g after acid treatment, which had the similar specific surface areas and same decline trend as our tube samples.

Generally, as-grown MWCNTs are hydrophobic and likely to aggregate into bundles or clusters, primarily due to the strong electrostatic and van der Waals interactions between the neighboring nanotube walls [61]. It is very difficult to achieve an efficient dispersion of as-produced MWCNTs agglomerates in aqueous solutions, remaining it a great obstacle to the manipulation and application of MWCNTs. In the preparation stage of as-grown MWCNTs suspension, we initially dispersed nanotubes by sonication to provide a mechanical energy leading to the exfoliation of tubes from the original bundles. As-grown MWCNTs prepared by CVD method exist as agglomerates because of their
physically curved and entangled morphology. Sonication overcomes van der Waals attractions among adjacent tubes to separate them from each other, disentangle and fragment the tubes, thus improving their dispersion to some extent. However, this mechanical dispersion method is not sufficient to uniformly disperse as-grown MWCNTs for a long period, confirmed with the phenomenon that MWCNTs suspension settled down within minutes. In the case of modified MWCNTs, by covalent attachment of oxygenated functional groups onto the sidewalls or defect sites of the tube surfaces, the interactions between tubes and surrounding has been influenced to reduce their tendency to agglomerate in the phase solvents and enhance nanotubes dispersion. Also these functional groups are hydrophilic, making modified MWCNTs dispersed more easily in water. With this chemical method, modified MWCNTs suspension could be homogeneously stable for up to months, confirmed by the visual observations. Because of the nature of agglomeration for as-grown MWCNTs, the characterization results obtained in solid or gas/solid samples might not accurately explain the experimental observations in the aqueous solution. However, the magnitude of the differences is very small related to the observation data and therefore the effect of agglomeration of as-grown MWCNTs could be considered almost negligible. Moreover, for the continuous experiments, as-grown MWCNTs suspension was controlled with well mixing by a wrist-action shaker to minimize agglomeration of tubes.
In summary, the physical properties of as-grown MWCNTs have been effectively improved after acid oxidation process by means of eliminating impurities such as amorphous carbon and residual metal catalyst particles, exfoliating and disentangling some curved bundles, breaking down and fragment the tubes and open the tips to expose their terminally cylinder walls. Additionally, the average tube diameter of MWCNTs decreases from 25 nm to 15nm and their specific surface area increases accordingly from 233 to 313.5 m$^2$/g. On the other hand, by incorporation of the oxygenated functional groups, mainly carboxyl and hydroxyl, onto the surface of the nanotubes, the surface chemistry of MWCNTs are greatly improved in terms of hydrophilicity, aqueous solubility and enhanced chemical reactivity. After modification by acid oxidation, the wettability of MWCNTs surface improved, which made tubes more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar TCE molecules. Acid oxidation, in addition, increased the suspension dispersion, stability and solubility of MWCNTs in aqueous solutions and thus enhanced the contact between the carbon nanotubes and TCE molecules.
3.3.2 Factors Affecting the Adsorption Ability of TCE onto MWCNTs

Adsorptive interactions between MWCNTs and TCE pollutants are influenced by many factors, such as contact time, TCE initial concentration, MWCNTs dosage and MWCNTs modification methods. In present study, we studied TCE adsorption over MWCNTs during a fixed contact time (0-168 hours) using different TCE initial concentrations (20-150 mg/L) and MWCNTs materials (before and after acid oxidization). The adsorption capacity of TCE onto MWCNTs \( q \), mg/g at any specific time \( t \) was calculated from the differences between initial concentration \( C_i \) and final concentration at time \( C_t \) by the following equation [62]:

\[
q = \frac{(C_i - C_t)V}{m}
\]

Where:

- \( q \) : Adsorption capacity, amount of TCE adsorbed by MWCNTs (mg/g);
- \( C_i \) : Initial TCE concentration (mg/L);
- \( C_t \) : TCE concentration after a certain period of time \( t \) (mg/L);
- \( V \) : volume of solution (L);
- \( m \) : MWCNTs dosage (g);
3.3.2.1 Evaluation of Optimal Contact Time

As depicted in Fig. 3.5, a batch experiment was conducted to evaluate the effect of contact time (0-168 hours) on the adsorption behavior of TCE by HNO$_3$-refluxed oxidized MWCNTs. This was carried out by adding a dose of 60 mg of oxidized-MWCNTs into 60 mL of a solution with a TCE initial concentration of 20 mg/L at a pH value of 7. During the initial 12-hour, it can be noticed that a lag-phase was presented and adsorption of TCE only about 0.2 mg/g occurred. This observation of the occurrence of a lag-phase is very interesting, which isn’t in agreement with those of Lu et al. [39] and Salam et al. [41], who studied other organics-CNTs adsorption systems. Whereas, two reports indicated the similar observation on adsorption curves and explained it to some extent. Chegrouche et al. [63] studied the removal of strontium from aqueous solutions by adsorption onto activated carbon. They stated that the initial slow adsorption step, in which adsorption capacity reached 1.5 mg/g within 4 h, could be explained by the slow diffusion of the studied solution, and also the large Sr (II) cationic radii within it (r = 2.19 A). Moreover, Ball et al. [64] measured the adsorption of lysozyme onto Si(Ti)O$_2$ surface in the presence of sodium thicyanate. They characterized the adsorption kinetics by the presence of a lag phase whose duration time was estimated around 33min, followed by a rapid adsorption. They proposed that the lag-phase could be
suggested by the occurrence of a possible nucleation regime before adsorption to the surface. In our study, the effect of lag-phase created a delay in the adsorption process and thus it is important to explore the possible sources of this observation. At present, we do not know what originate the observed phenomenology and hence the question of the sources of a reasonable explanation needs to be considered in our forthcoming studies.

![Kinetic curve for TCE adsorption over HNO$_3$-oxidized MWCNTs](image)

**Fig. 3.5 Kinetic curve for TCE adsorption over HNO$_3$-oxidized MWCNTs**

(MWCNTs dosage = 60 mg/60 mL; initial TCE concentration ($C_i$) = 20 mg/L; pH = 7, at $T = 25^\circ$C). The error bars are the standard deviation of duplicate results.
With further increase in time, the adsorption rate increased rapidly for the sequent 72 hours and an equilibrium adsorption capacity at 5.1 mg/g was achieved. After 84 hours of reaction, the rate of the amount of TCE adsorbed onto the modified MWCNTs equilibrium was gradually approached at a final adsorption capacity of 6 mg/g. After 144 hours, the amount of adsorbed TCE did not significantly changed with time. According to the above results, the 168h contact time was selected to establish the batch experiments conditions, which would ensure that the TCE equilibrium isotherms were fully reached as evidenced in Fig. 3.5. A careful inspection of Fig. 3.5 indicates that during the contact time of 12-60 hours, TCE adsorption is initially rapid, perhaps because a large number of externally vacant surface sites are available for the direct adsorption of TCE molecules. After this stage, the curve approaches a plateau with a slower adsorption, which may be interpreted by the reason that the remaining vacant surface sites are difficult to occupy because of the repulsive forces between the TCE molecules on the MWCNTs and the bulk phase [65]. Moreover, after the full occupancy of the surface adsorption sites had been achieved, TCE molecules would have to diffuse from the exterior surface to the interstitial channel spaces and grooves, which considered as the pores of MWCNTs possible for adsorption [65, 66]. Therefore, the observed adsorption kinetic curve seems to indicate that the adsorptive interactions between TCE molecules and MWCNTs occurred not only on the external surfaces but also on the inner cavities and the open ends of MWCNTs, which are also accessible to TCE molecules diffusion. Finally, as contact
time increased (≥130 hours.), TCE molecules fully saturate the MWCNTs surface and adsorption equilibrium is reached.

This adsorption process is quite similar to that had been reported for THMs [39], 1,2-dichlorobenzene [29], aromatic compounds [67] and reactive dyes [68], etc. Sheng et al. [67] investigated the adsorption of 1-naphthylamine, 1-naphthol and phenol on MWCNTs. The adsorption kinetics illustrated that the adsorption was initially rapid, followed by a slower adsorption stage and stagnated with the increase in contact time. They explained that the initial adsorption primarily occurred on the external graphene surface of MWCNTs. The following slow adsorption stage was contributed to the slow diffusion of TCE molecules into the interstitial channel space regarded as pore-like structure. Furthermore, Lu et al. [39] observed the similar adsorption pattern for the purified MWCNTs-THMs system. They suggested that the initially steep adsorption was attributed to the available outmost surface adsorption sites and then the repulsive forces between the adsorbed molecules and the bulk phase made the remaining vacant sites difficult to occupy and THMs molecules slowly diffused into the pore-like structure of MWCNTs.
3.3.2.2 Effect of Initial TCE Concentration

**Fig. 3.6** illustrates the effect of TCE initial concentration on the adsorption of TCE by HNO$_3$-oxidized MWCNTs. The TCE initial concentrations ($C_i$) were set as 20, 50 and 100 mg/L with a total contact time in the range of 0-168 hours at pH value of 7 at room temperature (25°C). For all the experiments, it was noted that nearly no adsorption occurred at the beginning 12-hr of the experiments. The TCE adsorption rates increased steeply in the sequent 48 hours for various initial concentrations, followed by a slower uptake regime. Finally, they reached equilibrium gradually at the time of 144, 132, 120 hours, depending of the initial TCE concentration (i.e. 20, 50 and 100 mg/L respectively). The equilibrium adsorption capacities ($q_e$) of TCE onto MWCNTs observed were 6, 16 and 25 mg/g, for $C_i$ equaled of 20, 50 and 100 mg/L respectively.
Fig. 3.6 Effect of TCE initial concentration on the amount of TCE adsorbed onto HNO₃-oxidized MWCNTs (Modified MWCNTs dosage = 60 mg/60 mL; pH = 7, at T = 25°C). The error bars, in some cases smaller than the symbols, represent the standard deviations of duplicate samples.

Fig. 3.6 suggests that adsorption equilibrium of TCE onto MWCNTs is reached faster at a higher $C_i$ and that calculated $q_e$ increased with the increase of $C_i$. The longer contact time to achieve equilibrium for lower $C_i$ could be probably interpreted by suggesting a regime controlled by a diffusion mechanism. Reid et al. [66] studied several binary mixtures of relatively non-volatile absorbates, which indicated that the mass diffusivity decreased with decreasing concentration and that low concentrations were responsible for a decrease in the diffusion flux of absorbents onto the absorber’s surface. In other words,
the diffusion driving force of TCE molecules onto MWCNTs surface would be greater at higher $C_i$. As a consequence, the time needed for TCE molecules to reach the active adsorption sites of MWCNTs is shorter for higher $C_i$, causing a faster diffusion rate of TCE molecules across the external boundary layer and within the pores of MWCNTs [66]. Arastech et al. [69] has reported a similar trend on the adsorption of 2-nitrophenol to modified MWCNTs with different initial concentrations in the range of 30 mg/L to 300 mg/L. They revealed that the amount of adsorbed 2-nitrophenol onto MWCNTs increased with a rise in initial concentration and a shorter time needed to reach the equilibrium with a higher initial concentration. They explained the phenomenon, in which the faster diffusion rate was caused by a higher diffusivity driving force. Lu et al. [58] and Lu et al. [50] further confirmed the observation by studying the adsorption of natural organic matter by MWCNTs and THMs by MWCNTs, respectively. Both of the research groups observed adsorption efficiency of MWCNTs increased as the initial concentration increased, accordingly.
3.3.2.3 Effect of MWCNTs Modification Process

The results of the adsorption experiments using MWCNTs subject to different acid treatment protocols are presented in Fig. 3.7. In these sets of experiments, as-grown MWCNTs, acid-oxidized MWCNTs, HCl-refluxed oxidized MWCNTs and HNO₃-refluxed oxidized MWCNTs were tested for their capabilities to adsorb TCE from water. Other parameters, such as TCE initial concentration, contact time and MWCNTs dosage, were kept constant at 20 mg/L, 0-168 hours and 60 mg/60 mL, respectively. It was noticed clearly that, for all types of MWCNTs, TCE uptake increased quickly with time after a 12h “lag-time” and adsorption equilibrium was reached within 156 hours for as-grown MWCNTs and 144 hours for modified MWCNTs. Generally, it took a longer time for TCE over as-grown MWCNTs to achieve adsorption equilibrium, in contrast to modified MWCNTs. Fig. 3.7 also indicates that the TCE adsorption capability on non-treated MWCNTs was low compared to the acid treated materials. Indeed, an equilibrium value of 3.5 mg/g was observed on the as-grown MWCNTs. This observed poor adsorption capacity for TCE removal by as-grown MWCNTs is consistent with previous reports [50]. By contrast under the same conditions, modified MWCNTs showed good ability for removal of TCE from aqueous solutions with a final adsorption capacity of 4.9, 5.7 and 6 mg/g for acid-oxidized, HCl-refluxed and HNO₃-refluxed
MWCNTs samples, respectively.

Fig. 3.7 Adsorption kinetics of TCE onto different MWCNTs (Conditions: \( C_i = 20 \) mg/L; MWCNTs dosage = 60 mg/60 mL; pH = 7 and \( T = 25^\circ\)C); error bars, in some data points smaller than the symbols, represent the standard deviations of duplicate samples.

These results clearly indicate that, under the experimental conditions applied in this study, the oxidization treatment has an evident impact on the MWCNTs adsorption capacity of TCE. Oxidized MWCNTs had far better performance on the TCE adsorption than as-grown MWCNTs. It was also noted that the adsorption capacity of TCE on acid-refluxed oxidized MWCNTs was higher than that of acid-oxidized MWCNTs. The
nature of the acid used for reflux (HCl vs. HNO₃) did not appreciably affected adsorption capacity, although MWCNTs reflux-oxidized with HNO₃ performed slightly better. These observations can be rationalized in terms of the formation of additional of adsorption sites in the form of oxygen-containing functional groups generated during acid treatment at reflux temperature. These observations are in full agreement with the results of TEM and Raman spectra presented above. During the course of acid oxidization, the tips of MWCNTs are opened and a large number of oxygenated functional groups (e.g. –COOH and –OH) are generated on the reactive site of MWCNTs’ surface. Generation of the oxygen-containing functional groups promoted MWCNTs to become more hydrophilic and suitable for adsorption of TCE molecules and correspondingly enhanced TCE adsorption capacities. Among them, HNO₃-refluxed MWCNTs generated the largest amount of functional groups on their surfaces and offered most hydrophilic surface structure, thus they had a superior TCE adsorption capability than the other types of CNTs materials evaluated in this study. The observations are well matched with the previous study conducted by Lu et al. [50]. The author prepared the modified MWCNTs by refluxing with a mixture of concentrate HNO₃ and H₂SO₄ solution (30mL HNO₃+10mL H₂SO₄) and employed as adsorbents to study the adsorption of THMs. The adsorption isotherms showed that acid treated MWCNTs possessed higher adsorption capacity (1.6 mg/g) than that of the pristine MWCNTs (0.6 mg/g). They explained the adsorption capacity increased in accordance with an increase in BET surface areas of
MWCNTs from 225 to 295 m²/g. In addition, they also suggested that the adsorption capacity was not only dependent on the physical structure, but also on the surface chemistry (i.e. the carboxyl groups produced by acid refluxing). Another study carried out by Li et al. [36] investigated the effect of different oxidization of MWCNTs via H₂O₂ and HNO₃ solutions on the removal of cadmium (II) from aqueous solutions. They concluded that HNO₃ treated MWCNTs performed better than that of H₂O₂ treated tubes. This may be due to that the oxidation with HNO₃ gives the larger specific surface area and introduced more oxygen containing function groups, which increased the adsorption to tube surfaces.

3.3.2.4 Effect of MWCNTs Dosage

Fig. 3.8 shows the results obtained when evaluating the effect of MWCNTs dosage (m) on TCE adsorption efficiency by different types of MWCNTs. The batch adsorption experiments were carried out using various amounts of MWCNTs ranging from 5 to 150 mg added into 60 mL water samples spiked with 20 mg/L of TCE. As seen in Fig. 3.8, the adsorption capacity increased with an increase in the MWCNTs dosage. For all types of MWCNTs, an obvious increase of TCE removal capacity takes place at the dosage value varied from 5 to 60 mg per 60 mL. However, for the as-grown MWCNTs, the adsorption uptake increased very slowly and reached only 3.9 mg/g at a MWCNTs
dosage of 150 mg per 60 mL. The observed trends for HCl and HNO₃ oxidized MWCNTs were almost identical and obtained TCE adsorption capacities were 6 and 6.3 mg/g, respectively, at a dosage of 150 mg per 60 mL. The removal capacity for HNO₃-oxidized MWCNTs was the highest at equilibrium, which once again suggests that the oxidization with concentrated HNO₃ is an effective method to improve TCE adsorption capability.

Fig. 3.8 Effect of MWCNTs dosage on the adsorption of TCE by different types of MWCNTs (MWCNTs dosage: 5-150 mg/60 mL; Cᵢ: 20 mg/L; contact time: 168 hours at pH=7 and T=25°C); error bars, in some data points smaller than the symbols, represent the standard deviations of duplicate samples.
Previously, in some reports, similar observations can be obtained well, such as nickel (II) (Lu et al. [70]) and cadmium (II) (Li et al. [36]) adsorption by MWCNTs. Wu et al. [68] utilized MWCNTs to study the adsorption efficiency to a reactive dye, Procion Red MX-5B. He suggested that the amount adsorbed initially increased with the MWCNTs dosage and reached the maximum adsorption capacity (30 mg/g) at MWCNTs dosage of 0.25 g/L. In our case, the adsorbed amount reached a maximum at dosage of 150 mg/60 mL, which is consistent with Wu et al. Moreover, Kuo and Wu [71] examined the feasibility of removing direct dyes, Direct Yellow 86 (DY86) and Direct Red 224 (DR224) from aqueous solutions using MWCNTs. They evaluated that for DY86, the adsorption percentage increased from 42 to 74% when the MWCNTs dosage increased from 0.33 to 0.67 g/L and for DR224, the adsorption percentage increased from 29 to 79%. They suggested that the increase in percentage of dye removed with an adsorbent dosage could be attributed to an increase in the adsorbent surface, which increased the availability of adsorption sites.
### 3.3.3 Adsorption Kinetics

Adsorption kinetics of as-grown MWCNTs (initial TCE concentration is 20 mg/L) and HNO₃-oxidized MWCNTs were investigated under three different initial TCE concentrations (20, 50 and 100 mg/L) with a MWCNTs concentration of 1 mg/mL at pH of 7 and ambient temperature. TCE adsorption capacity was monitored for up to 168 hours. In order to evaluate the adsorption rates of TCE onto MWCNTs, two extensively used kinetic models, namely the pseudo-first order and pseudo-second order, were employed to characterize the dynamic of the adsorption process in terms of the order of the rate constant based on the experimental data. Recently, both models have been widely applied to the adsorption of pollutants from aqueous solutions. The pseudo-first order kinetic model, suggested by Lagergren in 1898 [72], is the first rate equation to describe the adsorption kinetics for the solid/liquid system based on solid capacity. It is one of the most widely used adsorption rate equations for the adsorption of a solute from a liquid solution. It is generally expressed as follows:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]
After integrating and applying the boundary conditions \((t=0, q_i=0\) and \(t=t, q_i=q_e)\) to this equation, the linear form of the rate equation can be rewritten as:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

The pseudo-second order model, proposed by Ho and Mckay [73], was introduced for the description of adsorption kinetics and has been applied in liquid-phase adsorption systems. Ho et al. [74] proposed that the pseudo-second order rate expression based on the adsorption capacity on the solid phase could be used to describe the chemisorption process. This rate expression has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions. The pseudo second-order kinetic rate equation is expressed as:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

Integration of the rate equation with the boundary conditions \(t=0\) to \(t=t\) and \(q_i=0\) to \(q_i=q_e\) gives the linear form:
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

Where:

- \( q_e \): amount of TCE adsorbed at equilibrium, (mg-TCE/g-MWCNTs)
- \( q_t \): amount of TCE adsorbed at time \( t \), (mg/g)
- \( k_1 \): pseudo-first order rate constant of adsorption, (h\(^{-1}\))
- \( k_2 \): pseudo-second order rate constant of adsorption, (g/(mg \cdot h))
- \( t \): adsorption time, (h)

The straight lines were expected to yield from the plots of \( \ln(q_e - q_t) \) vs. \( t \) and \( t/q_e \) vs. \( t \) and shown in **Fig. 3.9 (a)** and **(b)**, respectively. The calculated kinetic parameters \( (k_1, k_2, \text{ and } q_e) \) under different conditions are determined from the slopes and the intercepts of regression lines and are tabulated in **Table 3.3**. It can be seen that the linear plots of the pseudo-first order kinetic model deviate considerably from the theoretical data, whereas in case of the pseudo-second order adsorption equation, all of the data converged well into a straight line. The correlation coefficient \( (R^2) \) of the linear regression expresses the conformity between the experimental data and the model-predicted values. A relatively high \( R^2 \) value indicates that the model successfully describe the kinetics. Analysis of tabular data reveals that \( R^2 \) values for the pseudo-second order model are
closer to unity than that for the pseudo-first order model. Moreover, the $q_{e,cal}$ values calculated from the pseudo-second order model are more consistent with the experimental values ($q_{e,exp}$). Hence, these results indicate that the pseudo-second order model could be approximated more appropriately to describe the adsorption kinetics of TCE onto MWCNTs. Since the pseudo-second order was developed on the premise that chemisorption is the operative reaction mechanism [73], the chemical interactions are possibly involved in the adsorption processes and the adsorption capacity is proportional to the number of active sites on MWCNTs.
Fig. 3.9 Adsorption kinetics of TCE by MWCNTs: (a) Tests of pseudo-first-order rate equation; (b) Tests of second-order rate equation ($C_i$: 20, 50 and 100 mg/L for HNO$_3$-oxidized MWCNTs and $C_i=20$ mg/L for as-grown MWCNTs); error bars, in some data points smaller than the symbols, represent the standard deviations of duplicate samples.
Table 3.3 Kinetics parameters for TCE adsorption onto as-grown MWCNTs and oxidized MWCNTs with different initial TCE concentrations

<table>
<thead>
<tr>
<th>Initial TCE conc. (mg/L)</th>
<th>As-grown MWCNTs</th>
<th>HNO₃ oxidized MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Exp. $q_{e,exp}$ (mg/g)</td>
<td>3.5±0.13</td>
<td>6±0.14</td>
</tr>
<tr>
<td>Pseudo-first order model</td>
<td>$k_1$ (h⁻¹)</td>
<td>0.0116</td>
</tr>
<tr>
<td></td>
<td>$q_{e,cal}$ (mg/g)</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.930</td>
</tr>
<tr>
<td>Pseudo-second order model</td>
<td>$k_2$ (g/(mg ⋅ h))</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>$q_{e,cal}$ (mg/g)</td>
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</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
</tr>
<tr>
<td>Intra-particle diffusion model</td>
<td>$K_{id}$ (mg/g h₀.5)</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>I (mg/g)</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.989</td>
</tr>
</tbody>
</table>
As reported in the previous studies [73, 75], the pseudo-first order equation did not fit well for the adsorption data obtained experimentally over the whole range of contact time, which is also consistent with the observation in this study (presented in Fig. 3.9 (a)). Ho et al. [76] discussed that the possible interpretation for this deviation is because that the parameter lnqₑ is an adjustable parameter. It is often found not equal to the intercept of a plot of ln(qₑ-qₜ) vs. t, however in a true pseudo-first order model, ln(qₑ) should be exactly equal to the intercept from the plot of ln(qₑ-qₜ) against t. The calculated equilibrium adsorption capacity qₑ,cal is an unknown parameter and could be adjustably obtained by a “best-fit” trail and error method. Initially, experimental qₑ (qₑ,exp), determined from the equilibrium isotherms, are substituted into equation. By using the “trail and error” strategy, the rate constant k₁ and equilibrium adsorption capacity qₑ,cal are determined, accordingly. Moreover, as explained by Rudzinski and Plazinski [77], the pseudo-first order model has been widely used on the ground of one-site-occupancy adsorption (i.e. one adsorbed molecule occupies one adsorption site). Lagergren proposed that this kinetic equation represented in fact the exact solution of Langmuir isotherm equation at equilibrium. In our following analysis on adsorption isotherms, we demonstrated that the adsorption of TCE on the MWCNTs used in the present study did not follow the Langmuir model but was fitted well with the Freundlich model. The conduction further confirms the results mentioned above. Because the adsorption sites on these MWCNTs are not energetically homogeneous, the pseudo-first order model failed to describe the
adsorption kinetics. Therefore, for the pseudo-first order equation, the theoretical curve is considerably deviated from the experimental data, and the pseudo-second order model offers a better fitting.

Various observations and interpretations in the applications of different adsorption models to the kinetic data have been reported, in which a common observation from the previous studies is that the pseudo-second model fit the adsorption kinetic best. Sheng et al. [67] applied three kinetic models (pseudo-second order model, pseudo-first order model, and Elovich model) to simulate the adsorption kinetics of three aromatic compounds onto MWCNTs. They represented that the pseudo-second order model fitted the adsorption kinetics well with consistently $R^2 > 0.99$. However, the other two models failed to describe the experimental data well, as indicated by consistently lower $R^2 < 0.9$, implying that the adsorption kinetic followed a pseudo-second order rate law. Lu et al. [60] studied the adsorption kinetic of Zinc (II) onto the as grown and oxidized MWCNTs and similar results have been observed. They also indicated an increased in adsorption kinetic parameter ($k_2$) from 0.0107 to 0.0127 g/(mg • min) after oxidization, contributed to the changes in the surface chemistry of tubes after HNO$_3$ oxidization. Moreover, Zhang et al. [78] studied the adsorption kinetics of biphenyl adsorption by MWCNTs with different initial concentrations of biphenyl. They suggested that the adsorption rate was faster at higher concentrations in comparison with low concentrations. Comparing the pseudo-first
order kinetic model and pseudo-second kinetic order model, the pseudo-second kinetic
order model fitted the experimental kinetic curves better and this phenomenon is
consistent with our results.

Although the pseudo-second order model has been widely applied to describe the kinetics
of adsorption by well fitting the experimental data, it cannot identify the diffusion
mechanism during the adsorption process. To better understand the mechanism of the
adsorption, it is important to predict the rate-limiting step involved in an adsorption
process. It is well documented in the reports [79,80], for a solid-liquid system, the
adsorption process mainly consisted of three consecutive stages as follows: external
diffusion, mass transfer of the solute from the bulk solution to the adsorbent surface
across the boundary layer; intra-particle diffusion, transport of the adsorbate within the
interior pore-like structure of the adsorbent; adsorption of the adsorbate on the external
surface and within the pores of the adsorbent. Crank et al. [81] stated that the last step
was considered fast enough and usually can be negligible. Therefore, the overall rate of
adsorption is governed by the slowest transport step, which would be either external
diffusion or intra-particle diffusion or combination of both steps. In order to distinguish
these different steps, the intra-particle diffusion model based on the theory proposed by
Weber and Morris has been tested as [82]:
\[ q_t = k_{id} t^{0.5} + I \]

where:

- \( q_t \): amount of TCE (mg/g) adsorbed at a given time (t)
- \( I \): a constant related to the thickness of the boundary layer (mg/g)
- \( K_{id} \): intra-particle diffusion rate constant (mg/g h^{0.5})

Fitting the experimental data into an intraparticle diffusion model and plotting \( q_t \) versus \( t^{0.5} \), a so-called Weber-Morris plot [82] is generated, in which the dependency of adsorption on the intra-particle diffusion could be indicative. Weber and Morris [82] reported that if the plot produced a straight line and passed through the origin, the adsorption process was dominated by intra-particle diffusion solely, whereas, if it exhibited a multi-linear nature, which indicated that there were two or more steps with different rate constants affecting the adsorption process. **Fig. 3.10** shows the Weber-Morris plots of the amount of TCE adsorbed against the square root of time for adsorption of TCE onto as-grown MWCNTs and oxidized MWCNTs. It has been observed that all plots were nonlinear for the whole adsorption period and reflected a three-stage nature, with an initial linear portion followed by an intermediate linear region and a plateau. Different authors observed the multi-linearity of Weber-Morris plot for CNTs adsorption for various contaminants [68, 69, 71, 78]. They suggested that the initial
linear portion (0-60h) was contributed to the external surface adsorption process, due to the diffusion of TCE molecules through the aqueous solution to the external surface of MWCNTs. The gradual linear region was followed up to 120h, representing the stage of intra-particle diffusion within the pore-like structure of MWCNTs. Finally, an equilibrium adsorption was attained. Therefore, all of these features implied that the adsorption of TCE onto MWCNTs was controlled by external mass transfer followed by intra-particle diffusion mass transfer.

![Intra-particle diffusion modeling of TCE on MWCNTs](image)

Fig. 3.10 Intra-particle diffusion modeling of TCE on MWCNTs ($C_i$: 20, 50 and 100 mg/L for oxidized MWCNTs and $C_i$=20mg/L for as-grown MWCNTs); error bars, in some data points smaller than the symbols, are the standard deviations of duplicate samples.
Moreover, the values of intraparticle diffusion rate constants $k_{id}$ and parameters $I$ are determined from the slopes and interprets of the second straight-line portions of plots, respectively, and tabulated in Table 3.3. It can be seen from the table that all values of correlation coefficients ($R^2$) are greater than 0.9, indicating that the adsorption mechanism well followed the intra-particle diffusion model. It may be concluded that, according to Weber-Morris plot, the adsorption of TCE by MWCNTs is governed by a multi-step process, involved the external mass transport and intraparticle diffusion. It is further found that the diffusion rate constant for the as-grown MWCNTs is the lowest compared with that of the oxidized tubes, may indicating the less dependency of the as-grown MWCNTs on the intraparticle diffusion. In the case of oxidized MWCNTs, the constant values increase with higher initial TCE concentration, corresponding to an enhanced diffusion of TCE through interior pores at higher TCE concentration. The intercept (the value of $I$) provides the measure of the boundary layer effect. The higher value of $I$, the greater the boundary layer effect, and thus the greater the contribution of the external mass transport in the rate-controlling step.

Several authors have applied the intraparticle diffusion model for the adsorption kinetics of different compounds onto CNTs. Most of them proposed a two or three-segment plot and suggested that intra-particle diffusion involved in the adsorption but was not sole rate-determining mechanism. Arastech et al. [69] established that the adsorption
rate-controlling mechanism of 2-nitrophenol onto MWCNTs and suggested a two-stage adsorption process in terms of surface adsorption and intraparticle diffusion. A similar phenomenon has been observed in the adsorption of direct dyes (by DY86 and DR224) onto MWCNTs. Kuo et al. [71] applied the intraparticle diffusion model to study the rate-controlling step and found that adsorption involved intraparticle diffusion. However, that was not the only rate-controlling step and other kinetic mechanisms may control the adsorption rate. They also observed that the intraparticle diffusion rate constants ($k_{id}$) increased from 0.57 to 1.08 mg/g min$^{0.5}$ as the initial concentration of dye increased (10-20mg/L). Moreover, a similar finding has been obtained Zhang et al. [78], in which they investigated the adsorption kinetics of aromatic compounds to CNTs. The piecewise linear plot of intraparticle model was observed, which is consistent with other studies.

### 3.3.4 Adsorption Isotherms

Equilibrium studies in the adsorption of TCE onto MWCNTs were applied to predict the adsorption capacities of MWCNTs during acid oxidization process. Evaluation of isotherm data was used to investigate the maximum adsorption capacities and develop an equation to accurately describe the adsorption behaviors of TCE on MWCNTs [57]. In this set of experiments, TCE adsorption isotherms were conducted to study the effect of MWCNTs acid oxidization as well. **Fig. 3.11** shows the equilibrium adsorption isotherms
of TCE onto as-grown MWCNTs and HNO₃-refluxed MWCNTs, which were expressed as a relationship between the observed amount of TCE adsorbed per unit mass of MWCNTs at equilibrium (qₑ, mg/g) and the equilibrium concentration of TCE in aqueous solution (Cₑ, mg/L). According to our preliminary kinetic studies, a reaction time of 168 hours was used for the adsorption isotherms to achieve complete equilibrium. Initial TCE concentrations were used in a range from 20-150 mg/L while the MWCNTs dosage used was fixed at 1mg/mL with pH adjusted to 7. Within the examined concentration range, it could be seen that both TCE adsorption capacities increased with increasing TCE concentration. As-grown MWCNTs show a relative poor adsorption capacity of 18 mg/g at TCE equilibrium concentration of 132 mg/L. Under the same conditions, adsorption capacity of HNO₃-refluxed MWCNTs was observed to reach 30 mg/g for TCE equilibrium concentration of 120 mg/L. The higher adsorption capability of modified MWCNTs is expected, due to the presence of functional groups generated during acid treatment. This observation is in good agreement of the studies conducted by Lu et al. [50] and Li et al. [36], in which they revealed that adsorption capacity of modified MWCNTs was higher than as-grown MWCNTs was contributed both the larger BET surface area and introduction of oxygenated functional groups.
In order to study the adsorption mechanism, both the Langmuir and Freundlich models have been applied to evaluate the data derived from the adsorption isotherms of TCE by MWCNTs with different parameters. Langmuir [83] theoretically derived the isotherm based upon the assumptions in which the adsorption occurs on a homogeneous solid surface with the adsorption sites are energetically identical and equivalent; and the lateral interactions between adsorbate molecules are negligible. A further implication is that each site can accommodates at most one adsorbed molecule and the maximum adsorption
capacity corresponds to monolayer coverage, i.e. the adsorbed layer is one molecule in thickness. When monolayer coverage reaches, no further adsorption can occur. The mathematical expression for the Langmuir isotherm is written as [83]:

\[ q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \]

The linear form can be rearranged as below:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \]

Where:

\( C_e \): Equilibrium concentration of adsorbate in aqueous solution, (mg/L);

\( q_e \): Mass of solute adsorbed per unit mass of adsorbent at equilibrium (adsorption capacity), (mg adsorbate/g adsorbent);

\( q_{max} \): Theoretical maximum adsorption capacity, corresponding to complete monolayer coverage (mg/g);

\( K_L \): Langmuir adsorption constant, related to the energy of adsorption (affinity of binding sites), (L/mg);
The Freundlich isotherm has been widely used to describe the equilibrium adsorption relationship for the non-ideal systems, especially for organic compounds adsorbed onto carbons. It is originally proposed as an empirical formula and widely applicable to describe the general features of the adsorption systems with different geometric and energetic surface heterogeneity. In its derivation, the Freundlich model assumes that the inequivalent sites are present on a rough non-uniform surface and therefore the adsorption energy of a given molecule varies between groups of adsorption sites [84]. The adsorption isotherms lacking a plateau indicate that the Freundlich model could be applied to a multi-layer adsorption. The Freundlich isotherm equation is represented as following [84]:

\[ q_e = K_F C_e^{1/n} \]

The linearized form of this equation leads to:

\[ \ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \]

Where:

\( C_e \): Equilibrium concentration of adsorbate in aqueous solution, (mg/L);

\( q_e \): Mass of solute adsorbed per unit mass of adsorbent at equilibrium (adsorption
capacity), (mg adsorbate/g adsorbent);

$K_F$: Freundlich adsorption constant, representing the adsorption capacity $[(mg/g)(L/mg)^{1/n}]$

$1/n$: empirical constant (dimensionless);

From this perspective, Freundlich isotherm is applicable to the adsorption systems, in which the adsorption sites on the solids are distributed exponentially with respect to the adsorption energy. The exponential constant $1/n$ is a measure of adsorption intensity, which represents the parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorptive surface [84]. The stronger adsorption sites with higher energy tend to be occupied first and the adsorption strength decreases exponentially with the increasing degree of site occupation. Furthermore, the magnitude of $1/n$ is interpreted to represent the mutual interaction among the adsorbent molecules. A value of “$1/n$” lower than unity generally suggests a competitive adsorption regime, where the adsorbed molecules repulse each other [89]. Oppositely, value above one is an indicative of cooperative adsorption.

In this study, both Langmuir and Freundlich models were used to fit the experimentally obtained adsorption isotherms. To this end, the batch experimental data for TCE adsorption onto as-grown and HNO$_3$-oxidized MWCNTs was analyzed and fitted to the isotherm models of Langmuir and Freundlich, respectively (shown in Fig. 3.12 (a)). Fig.
3.12 (b) present the linearized plots of Langmuir model and the values of $K_L$ and $q_{max}$ can be calculated, respectively, from the intercepts and slopes of the linear plots of $C_e$ against $\frac{C_e}{q_e}$. In the case of Freundlich isotherms (Fig. 3.12 (c)), the linear plots are obtained by plotting $lnC_e$ versus $lnq_e$ and the isotherm constants, $K_F$ and $1/n$, are produced from their intercepts and slopes. The parameters of the Langmuir model ($q_{max}$ and $K_L$) and Freundlich model ($K_F$ and $1/n$) as well as the corresponding correlation coefficients ($R^2$) are tabulated in Table 3.4.
Fig. 3.12 Langmuir and Freundlich isotherm models for TCE adsorption: (a) fittings to the experimental data; (b) Langmuir model for as-grown and modified MWCNTs; (c) Freundlich model for as-grown and modified MWCNTs; error bars are standard deviation for duplicate samples.
Table 3.4 Langmuir and Freundlich adsorption isotherm parameters for TCE adsorption on MWCNTs

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir Model</th>
<th>Freundlich Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_max (mg/g)</td>
<td>K_L (L/mg)</td>
</tr>
<tr>
<td>MWCNTs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-grown</td>
<td>40.82</td>
<td>6.39×10^{-3}</td>
</tr>
<tr>
<td>HNO_3-acid</td>
<td>58.82</td>
<td>9.52×10^{-3}</td>
</tr>
<tr>
<td>PAC</td>
<td>54.05</td>
<td>6.52×10^{-3}</td>
</tr>
</tbody>
</table>

As observed from Table 3.4, Langmuir and Freundlich isotherm models both showed relatively good agreement with the experimental data, with R^2 values all significant and approaching to unity. R^2 values of linear regression of Langmuir and Freundlich models were 0.905, 0.972 for as-grown MWCNTs and 0.911, 0.956 for modified MWCNTs, respectively. Comparing the values of R^2, it appears that the Freundlich model provided a better fitting of the experimental data, implying that the Freundlich isotherm model could be more appropriate to describe the adsorption characteristics of TCE onto MWCNTs in our work. Langmuir isotherm assumes that monolayer coverage of TCE molecules occurs on a homogeneous surface without any interactions between TCE molecules and the
adsorption of TCE molecules occurs over sites with identical adsorption energy [84]. However, in the case of MWCNTs, the surface is energetically and structurally inhomogeneous, the assumption of the Langmuir isotherm is not fulfilled even approximately. The surface of MWCNTs is composed by several different sites and thus the site heterogeneity leads to a distribution of adsorption energies among the sites, resulting in a deviation of the Langmuir isotherm. As a result, the Freundlich model fits adsorption data on rough inhomogeneous surface better than the Langmuir’s equation. This observation is in agreement with previous work by Erto et al. [85] who investigated TCE adsorption onto activated carbon and reported that Freundlich model was the best fitting model for this system. The groups suggested that the significant deviation of model estimation from the experimental data observed for Langmuir model indicated that the adsorption was not pure monolayer type.

Different studies have been conducted to understand the adsorption isotherms of various contaminants onto MWCNTs by fitting the experimental data to the most commonly used Langmuir and Freundlich models. One of the observations from these studies was that both Langmuir and Freundlich isotherm model fit the adsorption by MWCNTs well. Sheng et al. [67] presented the adsorption isotherms of some aromatic compounds, including 1-naphthylamine, 1-naphthol and phenol onto the as-grown and oxidized MWCNTs and found that both Langmuir and Freundlich models fit the adsorption isotherms well with
most of $R^2$ is larger than 0.95. Some of the literatures, however, suggested that one model is better than another. Lu and Su [58] observed that the equilibrium data of natural organic matter adsorption by oxidized MWCNTs were very well represented by the Langmuir isotherm equation when compared to the Freundlich equation. Conversely, other studies conducted by Kuo et al. [71] and Li et al. [86] indicated that the Freundlich isotherm model predicted the experimental data better than that of Langmuir model. Kuo et al. [71] studied the adsorption isotherms of Direct Yellow 86 dye onto MWCNTs by different adsorption models and suggested that the adsorption was best fitted with the Freundlich isotherm model. Li and Zhao [86] investigated the adsorption behaviors of five structurally related ionizable organic contaminants such as perfluorooctane sulfonate, perfluorooctanoic acid, perfluorooctanesulfonamide, 2,4-dichlorophenoxyacetic acid and 4-n-nonylphenol onto MWCNTs. Based on the values of $R^2$, the Freundlich model was found more suitable to simulate the adsorption isotherms by each compound. Moreover, Yang et al. [87] showed the similar results from the adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials.

According to Table 3.4, the constants $q_{max}$ and $K_F$, represent the adsorption capacity estimated from the Langmuir and Freundlich models, respectively. These report values of 40.82 mg/g and 0.419 (mg/g)(L/mg)$^{1/n}$ for as-grown MWCNTs and 58.82 mg/g and 0.977 (mg/g)(L/mg)$^{1/n}$ for modified MWCNTs, respectively. It is once again patent that under
the same conditions of adsorption, modified MWCNTs exhibited higher TCE adsorption capacity than that of as-grown MWCNTs. The maximum adsorption capacities predicted by both models for treated MWCNTs were larger than that of the untreated MWCNTs, which could be attributed to the larger number of adsorption sites generated by acid oxidization. Two represented research reports by Lu et al. [39] and Wu et al. [88] calculated the values of $q_{\text{max}}$ and $K_F$ by fitting the experimental data with both the Langmuir and Freundlich models. From the comparison, values of $q_{\text{max}}$ and $K_F$ of the modified MWCNTs were larger than that of as-grown MWCNTs, which was in consistent with the experimental results [39, 88]. The constant $K_L$, reflecting the adsorption affinity of MWCNTs for TCE, relates to the free energy of TCE adsorption over MWCNTs; this values is predicted by the Langmuir model to be $9.52 \times 10^{-3}$ L/mg for modified MWCNTs, comparable with the value of $6.39 \times 10^{-3}$ L/mg for as-grown MWCNTs [85]. The substantially larger value of $K_L$ for modified MWCNTs suggested a higher affinity between TCE molecules and modified MWCNTs over that of as-grown MWCNTs, which matches well the work by Wu et al. Furthermore, in this study, the magnitudes of $1/n$ are all in the range of zero to unity, indicating a favorable TCE adsorption onto MWCNTs media, which is consistent with the study conducted by Wu et al. [88] This group investigated the isotherm models for adsorption of a reactive dye (Procion Red MX-5B) by MWCNTs and the magnitude of $1/n$ established from Freundlich model quantified a favorable adsorption ($1/n<1$).
3.3.5 Comparative Studies by Commercially Available Activated Carbon

In the comparative analysis, a batch experiment for TCE adsorption using commercial powder activated carbon (PAC-HYDRODARCO®C, Norit Americas. Inc., Marshall, TX) was conducted. The specific surface area of HD-PAC was equal to 600 m²/g, which is much larger than that of as-grown MWCNTs (233 m²/g). The pretreatment process and the experimental conditions of PAC were the same as that used for MWCNTs. Fig. 3.13 (a) reports the effect of contact time on the adsorption of TCE onto as-grown MWCNTs, HNO₃-oxidized MWCNTs and PAC, respectively using a TCE initial concentration of 20 mg/L. The time needed for PAC to reach equilibrium was 168 hours, which was longer than the value of 156 hours for both as-grown and 144 h for the modified MWCNTs. This might be the result of the porous structure of PAC compared to MWCNTs. This porous structure would thus require that TCE molecules move from the exterior surface to the inner surface of the pores on PAC [60]. To compare the adsorption capacity of MWCNTs and PAC, TCE adsorption studies over MWCNTs and PAC were performed. Fig. 3.13(b) show these results where experimental equilibrium TCE adsorption capacities of as-grown MWCNTs, HNO₃-oxidized MWCNTs and PAC are compared using an initial TCE concentration range of 20-150 mg/L. Under the same conditions, the observed adsorption capacities of TCE adsorbed onto as-grown MWCNTs, oxidized MWCNTs
and PAC were 18, 30 and 24 mg/g, respectively. Modified MWCNTs possess higher TCE adsorption capacity (30 mg/g), compared to PAC (24 mg/g). In contrast, as-grown MWCNTs showed the lowest adsorption capacity.

![Figure 3.13](image)

**Fig. 3.13** (a) Adsorption kinetics of TCE onto different carbonaceous materials (Adsorbant dosage = 1 mg/mL; pH = 7, at T = 25°C); (b) Adsorption isotherms of TCE on different carbonaceous materials (Contact time: t=168 h, adsorbent dosages: 1 mg/mL, pH=7, T=25°C); error bars are standard deviation for duplicates.
Langmuir and Freundlich isotherm models where fitted for the adsorption data on PAC. The results of this fitting are reported in Table 3.4. Under the same conditions, theoretical maximum adsorption capacities of TCE onto as-grown MWCNTs, oxidized MWCNTs and PAC, respectively, were 40.82, 58.82 and 54.05 mg/g. This trend was consistent with the observed experimental results. (Fig. 3.13(b)) We need to emphasize that even though the specific surface area of oxidized MWCNTs (313.5 m²/g) was lower than that of PAC (600 m²/g), oxidized MWCNTs showed a better adsorption performance. After acid oxidization, functional groups were introduced to the defective sites of the MWCNTs surface. Therefore, although the specific surface area of modified MWCNTs (313.5 m²/g) was smaller than that of PAC, their functional groups provide a suitable surface structure for TCE adsorption. These results suggest that TCE adsorption was dependent on the amounts and type of active sites on the MWCNT surface rather than the total surface area available for adsorption [90]. Taking into account observed shorter equilibrium times as well as the higher adsorption capacity of TCE compared with PAC, the modified MWCNTs tested in this study proved to be an efficient adsorbent for TCE removal from aqueous solutions.

In the reports, the comparative analysis on adsorption of various contaminants by MWCNTs was previously conducted. For example, Lu et al. [50] compared the adsorption capacity of THMs by MWCNTs with that of commercial PAC. It was evident
that MWCNTs took less contact time to reach equilibrium. The adsorption capacity of THMs onto the modified MWCNTs was 2.72 mg/g, which was much larger than onto PAC (1.32 mg/g), although the surface area of purified MWCNTs (295 m²/g) was much smaller than that of PAC (900 m²/g). Similar result was obtained from another study by testing the adsorption isotherms of natural organic matter onto both MWCNTs and GAC. Under the same conditions, Lu et al. [58] found that the adsorption capacities decreased in the order of modified MWCNTs (12 mg/g)>GAC (10 mg/g)>as-grown MWCNTs (6 mg/g), which is in accordance with the decline in the BET surface area of these adsorbents. The Langmuir and Freundlich constants (q max and K F) were calculated and compared. It can be seen that the modified MWCNTs had the greatest q max and K F followed by GAC and then the as-grown MWCNTs, which was consistent well with the experimental trend we observed in present study.
3.4 Conclusions

In this chapter, MWCNTs materials as novel adsorbents were prepared by acid oxidization. TEM and Raman spectra were used to characterize the obtained material and to evaluate their surface properties, including morphology, diameter distribution, degree of impurities and defects before and after acid oxidization treatment. Batch adsorption experiments were carried out to evaluate their adsorption performance for TCE removal from aqueous solutions. Both as-grown and modified MWCNTs were investigated for their equilibrium adsorption capacities under various experimental conditions in terms of initial TCE concentrations, modification processes and MWCNTs dosages. In addition, this study evaluated the adsorption kinetics and equilibrium adsorption isotherms and aimed to understand the basic mechanisms of TCE removal by MWCNTs. Finally, a comparative analysis was applied to study the adsorption capacities of MWCNTs with commercially available PAC. In summary, the following conclusions could be collected from this study:

1. Characterization using TEM and Raman suggested that the properties of MWCNTs such as purity, structure and nature of the carbon surface are greatly improved after acid oxidization. With the disappearance of impurities, increase of surface area, and formation of surface oxygen-containing functional groups, oxidized MWCNTs became more
hydrophilic and adsorption capacity of TCE increased correspondingly.

(2) In a batch mode, acid-oxidized MWCNTs showed exceptional adsorption capability of TCE from aqueous solutions. The highest adsorption efficiency was achieved with the HNO₃-refluxed oxidized MWCNTs.

(3) The kinetics of adsorption process was described well by the pseudo-second-order rate model. The adsorption behavior of TCE from aqueous solutions by MWCNTs was in good agreement with the Freundlich adsorption model. The constants obtained from the Freundlich isotherm model fitting indicated that the HNO₃-oxidized MWCNTs had the highest adsorption capability.

(4) The comparative study on the adsorptive performance of TCE revealed that oxidized MWCNTs exhibited superior adsorption capability than that of the commercially available PAC, whereas, as-grown MWCNTs were found to possess lower adsorption capacity than PAC.

(5) It is proposed that the predominant mechanism for improvement of MWCNTs adsorption capacity in linked to the formation of oxygenated surface functional groups by the chemical oxidization of MWCNTs during acid treatment.
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Simultaneous Adsorption and Degradation of Trichloroethylene by Bimetallic Pd/nZVI Supported on Multi-walled Carbon Nanotubes

4.1 Introduction

Trichloroethylene (TCE), categorized as a class of chlorinated hydrocarbons, has been widely utilized by a number of industries as degreasing agents and solvents in large quantities on a regular basis [1]. Because of its high toxicity and presence as a continuous long-lived source of subsurface contamination, TCE poses a significant threat to human health and ecosystem [2] and is thus listed as one of the priority pollutants of USEPA [3]. As a consequence, remediation of TCE-contaminated sites is especially critical and has become the subject of numerous research efforts. Conventional technologies, such as bioremediation [4], thermal treatment [5], oxidation [6], pump-and-treat methods and soil vapor extraction [7], pose various drawbacks and these disadvantages effectively restrict their application at the filed scale [8]. In-situ injection of zero-valent iron (ZVI) through permeable reactive barriers (PRBs) represents one of the innovatively approvable technologies for remediation of a variety of chlorinated hydrocarbon contaminants [9]. Since Gillham and O’Hannesin firstly proposed [10] that ZVI particles could act as a strong reductive agent to effectively degrade chlorinated organic compounds, extensive
research efforts have been carried out on the development and implementation of ZVI technologies for sites historically contaminated with chlorinated solvents.

Commercially available ZVI particles have the advantages of cost-effective, de-halogenation efficiency and environmentally benign impact, thus ZVI technology is considered one of the most proven alternatives to conventional physicochemical methods for remediation of contaminated sites. Generally, the overall redox reaction between chlorinated hydrocarbons (denoted as \( C_xH_yCl_z \)) and iron (\( Fe^0 \)) in aqueous environmental solutions could be expressed as [11):

\[
C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + zCl^-
\]

In this process, ZVI particles carry reduction of the chlorinated organic molecules and are oxidized to ferrous iron (\( Fe^{2+} \)) and further to ferric iron (\( Fe^{3+} \)). Chlorinated hydrocarbons are thus effectively transformed into nontoxic final products, such as ethane, ethane, chloride ions and water.

With the recent development of nanotechnology, nanoscale zero-valent iron (nZVI) particles have been identified as a promising material for the transformation and detoxification of a wide variety of chlorinated hydrocarbons [12]. nZVI particles exhibit
superior dechlorination reactivity over microsized ZVI, as a result of their smaller particle size and larger specific surface area [13]. By using nZVI instead of granular ZVI, the chemical reduction rate of chlorinated hydrocarbons per mass of iron is several orders of magnitude higher than that observed on ZVI. Zhang et al. [11] initially investigated the application of nZVI particles for the removal of TCE. They reported that nZVI prepared by a typical reduction of iron salt with sodium borohydride (NaBH$_4$) solution showed much higher TCE reduction efficiency (up to 96% of TCE removed) and attributed this observation to the relatively high nZVI surface area (33.5 m$^2$/g vs. ZVI’s 0.9 m$^2$/g).

Based on these additional bench scale tests [14-16], nZVI particles have been extensively used for rapid and cost-effective cleanup of groundwater contamination. Dozens of pilot and large-scale in-situ applications have been conducted and demonstrated that rapid in-situ remediation with nZVI could be achieved [17-19].

nZVI’s high surface area and enhanced reactivity, however, make it susceptible to oxidation by surrounding water and/or oxygen, leading to the formation of a surface passive layer of iron oxides which could potentially hinder dechlorination activity over time [20]. The results in slower and incomplete degradation of chlorinated species lead to the production and accumulation of measurable amounts of toxic and carcinogenic intermediates and by-products, such as vinyl chloride (VC) and dichloroethene (DCE), which are recognized as potentially more harmful than their parent compounds [21].
Efforts to prevent nZVI particles from surface oxidation, minimize byproducts formation and promote their dechlorination activities have led to the addition of a second catalytic metal (e.g. Pd, Ni and Cu) onto the freshly prepared nZVI [22]. In this type of bimetallic nZVI system (Pd/Fe\(^0\) for example), Fe\(^0\) nanoparticles act as reducing agents through their corrosion reactions, generating electrons that reductively degrade chlorinated compounds while the additionally dopant metal functions as a catalyst on the surface of nZVI to accelerate the reaction rate [22]. The presence of a catalytic metal in a bimetallic system greatly enhances reaction rates by orders of magnitude higher than the corresponding monometallic systems, and inhibits the production and formation of toxic intermediates and by-products [23]. Chin et al. [24], for example, illustrated that the application of Pd/Fe\(^0\) bimetallic system increased TCE degradation rates by up to two orders of magnitude, as compared to bare nZVI particles.

On the other hand, ZVI nanoparticles have a strong tendency to aggregate and form large clusters and agglomerate chains, forming domains of several microns in size through intrinsic magnetic interactions and direct inter-particle interactions (e.g. van der Waals forces) [25]. Aggregation of nZVI leads to a significant and rapid loss in chemical reactivity and inhibits their mobility in subsurface. Thus agglomeration has been identified as the primary drawback limiting the field applications of nZVI technology [26]. In an attempt to overcome these issues, engineered ZVI particles with various
surface modifications have been extensively explored. One of the common methods is to use stabilizers, such as water-soluble starch, surfactants and polymers, which are attached on the nZVI surface to inhibit agglomeration. Some of the explored stabilizers include polyacrylic acid (PAA) [27], potato starch [28], carboxymethyl cellulose (CMC) [29], cellulose acetate (CA) [30] and guar gum. [31] Alternatively, nZVI particles could be immobilized onto a solid matrix support, such as silica [32], chitosan [33], zeolite [34], bentonite [35], compressed carbon black [36] and hydrophilic carbon particles [37]. In these formulations, nZVI is chemically bounded to the support, preventing their agglomeration [38]. Among these potential solid matrix supports, carbon-based hybrid nanomaterials have caught a lot of attention in the field of environmental remediation [39]. They have the advantages of a high surface area, high chemical and thermal stability and low toxicity, compared to the conventional supports [40]. Mackenzie et al. [41] initially described an approach to synthesize carbon supported iron particles in lab sale. He used activated carbon colloids in a solution of iron (III)-ions, dried the slurry and thermally reduced the iron in hydrogen. Yue et al. [42] used a similar methodology using porous graphite as carbon support material for metals and alloy catalysts.

As a novel member of carbon family, carbon nanotubes (CNTs) are promising supports due to their internal hollow space and large specific surface areas [43]. Because of their unique nanostructure and particularly convex surface, metallic particles and metal oxides
could be encapsulated or attached to the surfaces of CNTs via covalent bonding or physical adsorption [44]. Garcoa et al. [45] reported that CNTs was an efficient support for ruthenium nanoparticles used for catalytic wet air oxidation of wastewater contaminants. Kim et al. [46] demonstrated the ability of CNTs to support iron oxide nanoparticles (Fe₃O₄ and γ-Fe₂O₃). Wildgoose et al. [47] proposed that CNTs were more suitable supports for immobilizing bimetallic nickel and iron nanoparticles compared with other kinds of carbon materials because of their stabilities and adsorption capabilities. In addition to their applications as a support, CNTs have been also explored as new adsorbents showing superior adsorption capabilities than those of classic carbon-based adsorptive materials [48]. Due to their highly porous and hollow structure as well as large specific surface area, CNTs can strongly interact with a wide range of adsorbates. Thus, adsorption-related applications of CNTs have being studied extensively by theoretical calculations, experimental measurements and molecular simulations. For instance, Long et al. [49] reported that CNTs had significantly higher dioxin removal efficiency than activated carbon. Peng et al. [50] indicated later that CNTs was an efficient adsorbent for 1, 2-dichlorobenzene removal from water and that these materials could be used in a wide pH range. Lu and co-workers [51] reported CNTs displayed significantly high THMs removal efficiencies.
As previously discussed in Chapter 3, we employed the as-grown and modified MWCNTs to effectively remove TCE from the aqueous solutions. The results indicated that the modified MWCNTs were a good adsorbent compared to those conventional activated carbon materials. Furthermore, a new concept called “hybrid nZVI-CNTs material” (nZVI-CNTs composite) has been proposed for the removal of chlorinated organic contaminants, involving the integration of simultaneous adsorption and dechlorination. In this hybrid nanomaterial system, CNTs serves simultaneously as highly efficient and selective adsorbents for contaminants and as supports to immobilize nZVI particles. Monometallic Fe$^0$ or bimetallic Pd/Fe$^0$ nanoparticles perform as an effective redox material for the detoxification of pollutants in the same aqueous solution. In this context, Lv et al. [52] has most recently reported the application of nanocomposites consisting of nZVI and MWCNTs to remove Cr(VI) from wastewater. They prepared such nanocomposites through depositing nZVI particles onto as-received MWCNTs by in situ reduction of ferrous sulfate. The results indicated that the nZVI-MWCNTs composites exhibited around 36% higher efficiency for Cr(VI) removal, compared to that of nZVI particles. The characterization analysis showed that nZVI particles dispersed well on the MWCNTs network.

Moreover, Xiao and Shen [53] created a new approach to immobilize ZVI nanoparticles into electrospun polymer nanofibers and presented its environmental applications for
TCE removal. In their study, MWCNTs are mixed with polyacrylic acid (PAA)/polyvinyl alcohol (PVA) mixture polymer solution for subsequent electrospinning to form uniform nanofibers. The MWCNTs-incorporated PAA/PVA nanofibers were reported to be crosslinked and used as a nanoreactor to complex Fe(III) ions through binding with the PAA carboxyl groups for the reductive formation of ZVI nanoparticles. They found that the nanofibrous mats effectively degraded TCE with a degradation efficiency approaching 93%. In this chapter, we have developed a simple and efficient strategy to introduce ZVI nanoparticles into MWCNTs by means of a wet chemical method. For the first time, a hybrid of nZVI-MWCNTs composite is used to remove TCE from aqueous solution by a combination of simultaneous adsorption and dechlorination mechanisms. The primary objectives of this study are to synthesize the monometallic nZVI-MWCNTs composite and bimetallic Pd/Fe$^{0}$ nanoparticle-MWCNTs composite and additionally to investigate the kinetics of TCE dechlorination by these composites and the impact of Pd loading over Fe$^{0}$ in the composites on the performance of TCE removal.
4.2 Materials and Methods

4.2.1 Materials and Reagents

Ferrous sulphate heptahydrate (FeSO₄·7H₂O, 99.5%) was used as iron precursor and supplied by Acros Organics. Trichloroethylene (TCE, ≥99.5%, ACS reagent), sodium borohydride (NaBH₄), sodium hydroxide (NaOH, EMD, Chemicals Inc.) and n-hexane (anhydrous solvents, 95%) were purchased from Sigma-Aldrich (WI, USA). Isopropyl alcohol (2-propanol, 99.5% min. assay, ACS reagent, BDH) and ethanol (99.8% min. ACS Grade, BDH) were obtained from VWR Company (USA). Palladium (II) acetate (Pd(ac)₂, [Pd (C₂H₅O₂)₂]₃, 99.98%, trimer, Pd min. 46%) was received from Alfa Aesar Company. All solvents and reagents used were obtained with commercially analytical grade and used as received. All water used in this experiment was deionized by a Barnstead Easypure II system. In order to remove dissolved O₂ and prevent further oxidation, deionized (DI) water was deoxygenated by purging with nitrogen gas (ultra high purity, Praxair) for at least 2 hours and used immediately prior to use. All the chemical solutions and suspensions used in this study were prepared using deoxygenated water.
4.2.1.1 Multi-walled Carbon Nanotubes (MWCNTs)

As-grown MWCNTs were received commercially from Cheap Tubes Inc. (Brattleboro, VT). They were synthesized using a catalytic chemical vapor deposition (CCVD) method with metal catalysts. Their specifications, as provided by the manufactures, are: outer diameter: 10-20 nm; inside diameter: 3-5 nm; length: 10-30 µm; specific surface area: 233 m²/g; purity: > 95 wt.% and amorphous carbon content: < 5% wt.%. To obtain homogenous suspensions of as-grown MWCNTs, 100 mg of as-received MWCNTs were dispersed into 100 mL of DI water and sonicated using an ultrasonic probe (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY) at 250 watts (max. 400 watts) in an ice-water bath for 1 h.

4.2.1.2 Oxidized MWCNTs

Acid-oxidized MWCNTs were prepared following the method reported by Wilson’s et al. [54] Briefly, 100 mL of as-grown MWCNTs suspension were transferred into a three-neck, round-bottomed glass flask equipped with a reflux condenser, magnetic stirrer and a thermometer. 20 mL of concentrated HNO₃ (ACS, 68%) was slowly added and the solution was continuously heated at 140°C for 12 hours. After cooling down to room
temperature, oxidized-MWCNTs suspensions were repeatedly rinsed with DI water until the pH value was close to neutral. Finally, the solid phase was separated from the suspension of oxidized-MWCNTs by centrifuging using a model of IEC-B-20A Centrifuge at a rotation speed of 7000 rpm for 15 min. Finally, the oxidized-MWCNTs was dried overnight in an oven at 100°C to drain the excess water and stored in a desiccator.

4.2.2 Preparation of Pd/nZVI-MWCNTs Composites

Four types of nano-scale Fe⁰ materials (monometallic nZVI, bimetallic Pd/Fe⁰ nanoparticles, monometallic nZVI-MWCNTs composite and bimetallic Pd/nZVI-MWCNTs composite) were synthesized using the NaBH₄ reduction method described in Chapter 2. All synthesis was conducted in a reactor flask at room temperature inside an anaerobic chamber under N₂ atmosphere to avoid Fe⁰ oxidation.

4.2.2.1 Monometallic Fe⁰ Nanoparticles (nZVI)

nZVI particles were prepared via the reduction of an aqueous solution of FeSO₄·7H₂O with aqueous NaBH₄, following the protocol previously described by He et al. [55] Briefly, 50 mg of FeSO₄·7H₂O was dissolved into 100 mL of deoxygenated water to
achieve a solution containing 0.0018 M of Fe$^{2+}$. After complete dissolution of the iron salt, an equal volume (100 mL) of 0.0036 M aqueous NaBH$_4$ solution was added drop-wise (1 drop per sec). During this process, the reaction flask was housed on a magnetic stirrer operating at 400 rpm. In this study, the molar ratio of NaBH$_4$ to FeSO$_4$•7H$_2$O (BH$_4^−$/Fe$^{2+}$) was controlled about 2:1, following methodology previous described by Wang at al. [56] Through the process of titration, NaBH$_4$ was introduced to reduce Fe$^{3+}$ ions to Fe$^0$, according to following reaction [56]:

$$2Fe^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 2H_2 + 4H^+$$

After the complete addition of NaBH$_4$, the mixture was stirred continuously for an additional 30 min until visible hydrogen evolution ceased. Finally, the resulting nZVI particles were thoroughly rinsed with deoxygenated water and then transferred to a 60 mL reaction bottle and immediately capped with Teflon Miniert Valves and stored inside the anaerobic chamber for further use.

4.2.2.2 Bimetallic Pd/Fe$^0$ Nanoparticles (Pd/nZVI)

To obtain bimetallic nanoparticles, the freshly prepared nZVI suspension was immediately equilibrated with 20 mL of 4.7×10$^{-6}$ M (ethanol/water, v/v, 3/1) solution
of palladium (II) acetate (Pd(ac)$_2$). This ethanolic solution was used because of the low water solubility of the palladium salt. This concentration was selected to achieve a final Pd loading rate of 0.1 w.t. % on Fe$^0$. The process for the deposition of Pd onto the surface of Fe$^0$ nanoparticles can be described according to [57]:

$$Pd^{2+}(aq) + Fe(s) \rightarrow Pd(s) + Fe^{2+}(aq)$$

The mixture was further stirred for 10-15 min to complete the redox reaction. The Pd-doped nZVI particles were then rinsed with deoxygenated water and preserved in a 60 mL reaction vial capped with Teflon Mininert Valves inside the anaerobic chamber.

4.2.2.3 MWCNTs-supported nZVI Particles (nZVI-MWCNTs)

To synthesize MWCNTs-supported nZVI composite, a multi-step procedure was developed. This methodology relays on NaBH$_4$ reduction of iron ions pre-adsorbed on the MWCNTs surface. This protocol was developed using a starting point of the strategy reported by Wang et al. [58], who synthesized the zeolite-supported nZVI composites by in-situ reduction of exchanged iron ions. Our procedure was similar with slight modifications to accommodate the MWCNTs component. Before synthesis, all aqueous solutions and MWCNTs suspension were re-purged with highly pure N$_2$ for at least 2 h.
All the reactions were performed in an N\textsubscript{2} filled anaerobic chamber to prevent the oxidation of Fe\textsuperscript{0}. As-grown or oxidized MWCNTs (0.1g) were homogeneously dispersed into 80 mL of deoxygenated water by sonication (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY) for about 30 min to assist dissolution. The Fe\textsuperscript{0} content of the composite material was set as 10 w.t. %. The iron precursor aqueous solution was prepared by homogeneously dissolving 0.05 g FeSO\textsubscript{4}·7H\textsubscript{2}O into deoxygenated water (20 mL). Subsequently this solution was added into a 250-mL amber glass/Teflon cap bottle filled with the suspension of MWCNTs and caped under N\textsubscript{2} to give a final concentration of 1 g/L of MWCNTs. The pH of the mixture was then adjusted to 7 using NaOH. The capped closed mixture was then homogenized on a temperature controlled (25°C) orbital shaker at 150 rpm for 24 h to allow equilibration. After this period of time, the vial containing the mixture was transferred to the anaerobic chamber and the contents were transferred to a reactor flask. 100 mL of a 0.0036 M NaBH\textsubscript{4} solution was added drop-wise (about 60 drops per min) into the MWCNTs-Fe solution at 25°C with parallel magnetic stirring at 400 rpm. Following the addition of the total volume of NaBH\textsubscript{4}, the mixture was allowed to homogenize for about 30 more min. After cessation of visible hydrogen evolution, the suspension was rinsed thoroughly with the deoxygenated water and immediately capped with Teflon Miniert Valves and stored in the anaerobic chamber for further use.
4.2.2.4 MWCNTs-supported Pd/Fe$^0$ Bimetallic Nanoparticles

In order to synthesize Pd-doped nZVI-MWCNTs composite, the same procedure used for the synthesis of nZVI-MWCNTs and described above was followed with the additional deposition of Pd over Fe$^0$. To this end, the freshly prepared nZVI-MWCNTs suspension were immediately equilibrated with 20 mL of $4.7 \times 10^{-6}$M ethanolic solution of Pd(ac)$_2$. The final composition of Pd/nZVI-MWCNTs composite in this study is 0.1 g/L nZVI, 0.1w.t. % Pd (w/w of nZVI) and 1 g/L MWCNTs. The mixture was further stirred for 10-15 min to complete the redox reaction. The Pd/nZVI-MWCNTs particles were then rinsed with deoxygenated water and preserved in a-60 mL reaction vial capped with Teflon Mininert Valves.

4.2.3 Batch Experiments

All the batch experiments were performed at room temperature (25°C) and at a pH of 7 in 60-mL glass serum bottles capped with a Teflon mininert valve to minimize the loss of TCE during repetitive sampling. The headspace in the reaction bottle was set to nearly zero to minimize volatilization losses. Each reaction bottle was filled with 60 mL of suspension containing a fixed amount of as-grown or oxidized MWCNTs, bare nZVI,
nZVI-MWCNTs and Pd/nZVI-MWCNTs, respectively. All the materials were synthesized immediately before use. A volume of 10 mL of 2-propanol was spiked with 0.15 mL of pure TCE to prepare a TCE stock solution, and a preset initial TCE concentration was obtained by adding the right amount of TCE stock solution into the reaction bottle. After spiking each bottle with this TCE stock solution, the valves were closed and the bottles were mounted on a wrist-action shaker (MISC-CAEQUIP, BURRELL 24 place wrist action shaker-115V, VWR) for a vigorous mixture with good homogenization of the solutions. After shaking for a pre-determined time, the shaker was stopped, and the reaction bottles were placed vertically to allow the particles to settle. 0.25 mL aliquot of the clear supernatant containing TCE was sampled and extracted with n-hexane and then transferred to a 2 mL caped GC vial for further analysis measurements. A control blank experiment was carried out along with each run under exactly similar conditions. All experiments were conducted in duplicates to check the consistency of analysis and the reported results are average values.

To investigate their performance for TCE dechlorination, comparative studies were conducted using as-grown MWCNTs, oxidized MWCNTs, bare nZVI, nZVI-MWCNTs composite and Pd/nZVI-MWCNTs composite. The effects of the addition of catalyst Pd and various TCE initial concentrations (20, 50 and 100 mg/L) were evaluated separately. A pseudo-first-order model was used to investigate the kinetic mechanism of TCE
reaction dechlorination. Blanks using 0.1 g/L nZVI solution and 1 g/L MWCNTs suspension were also tested for a comparative study.

4.2.4 Analytical Methods

Surface morphology of as-grown MWCNTs, oxidized-MWCNTs, bare nZVI and nZVI-MWCNTs composite were elucidated by TEM using a Philips CM10 Transmission Electron Microscope. For TEM measurements, a very dilute suspension of sample was prepared in methanol by sonication for 20-30 min. A few drops of suspension were deposited onto a Lacey carbon-coated copper grid followed by evaporation of methanol in air at room temperature. For each sample, a representative set of micrographs (roughly 20-30 TEM images) was chosen and the size of each particle on those micrographs was measured and analyzed. The particle size and their distributions were calculated using Imaging software (Gatan Microscopy Software, Gatan Inc.).

Specific surface areas of bare nZVI, oxidized MWCNTs and nZVI-MWCNTs composite were measured by the classic BET method. The BET surface area of the sample is mainly determined by the physical adsorption of nitrogen onto the surface of a solid and then the amount of adsorbed N\textsubscript{2} was calculated. The measurement was performed by N\textsubscript{2} adsorption/desorption at 77 K using a Model ASAP 2010 surface area analyzer.
Representative freshly prepared samples were separated from the suspension and then dried at 90°C in a vacuum overnight before use for BET analysis.

In this study, the residual TCE after dechlorination was determined by a solvent extraction method. Hexane was used as the extracting solvent. Briefly, at certain time intervals, 250-µL of the aqueous aliquot was sampled by a gas-tight syringe from both the reaction and parallel bottles and transferred to a 2 mL GC vial containing 1mL of n-hexane. After addition of the aliquot, the vial was immediately closed and manually shaken for about 10 seconds, then kept undisturbed for about 1h to allow for equilibration. Upon phase separation, the organic phase containing TCE was extracted from the vial and transferred to a GC vial. A 1µL of extract was withdrawn by the auto-sampler for GC analysis.

An Agilent 7890 Gas Chromatography equipped with an electron capture detector (GC-ECD) was employed to analyze TCE concentrations in the extracted samples of TCE/ n-hexane. Helium gas (HP, Praxair) was used as carrier gas, and the flow rate was set at 6.38 mL/min. Chromatographic separation was performed in a DB-624 capillary column (30 m × 0.53 mm × 3 µm, J&W Scientific). The flow in the detector (Argon+CH₄ (5%)) was set to 60mL/min. The temperature program used for the analysis of TCE by
GC-ECD using an isothermal stage at 35°C for 4 min, subsequently increased to 180°C at a rate of 18°C/min and finally held at this temperature for 5 min. A sample volume of 1µL of extracted TCE was injected into a split-less mode of GC-ECD in order to determine the concentrations of residual TCE in sample after adsorption. Similarly, 1µL of a standard blank solution (without adsorption) was also injected into the GC-ECD. The retention time of TCE was close to 8.5 minute under these conditions.

4.2.4.1 TCE Calibration Curve

Initially, stock solutions of TCE were spiked by dissolving reagent-grade TCE into 2-propanol and appropriate volumes of the stock solutions were diluted through gas-tight syringes into a series volumes of glass vials to achieve the desired TCE concentrations. The glass vials were sealed with a 20 mm Teflon coated rubber stopper to minimize solvent evaporation. Prior to analysis of the samples by GC, the response factor and the detection linearity for the internal standard were established. Standard calibration curves for TCE were generated in 2-propanol and DI water by using solutions containing known concentrations of TCE. The linear range of detection for the internal standard of TCE was determined as 15-155 mg/L with a detection limit of 0.5 mg/L, and all the sample extracts were analyzed within this range. The calibration curves were used to calculate the concentrations of TCE in the reaction solutions. All samples in this study were analyzed
following this protocol.

4.3 Results and Discussion

4.3.1 Characterization of nZVI-MWCNTs Composite

4.3.1.1 Morphology Study

Fig. 4.1 (a)-(c) and (b)-(f) represented the TEM images of as-grown and oxidized MWCNTs, respectively. As clearly discussed in the previous chapter (Chapter 3.3.1.1), both tubes were curved and entangled round each other. Their structures were quite integrated and possessed a multiple atomic structure with hollow inner cores. Some of the impurities including amorphous carbon and metal catalyst particles disappeared after acid oxidization. Moreover, some bundles appeared exfoliated and curled and fragmentation of the MWCNTs structure occurred. Destruction of the caps exposed the terminated cylinder walls and thus increased the specific surface area (surface area per unit volume) [59]. Associated to the cap opening and increase on specific surface area, some functional groups were introduced onto the reactive sites of the oxidized MWCNTs, further improving their solubility and chemical reactivity.
Fig. 4.1 Transmission electron micrographs (a)-(c): as-grown MWCNTs, (d)-(f): HNO$_3$-oxidized MWCNTs (Fig. 4.1 (a) is duplicated from Fig 3.1.)
Fig. 4.2 (a) presents a typical TEM image of bare nZVI particles. It has been observed that most nZVI particles were spherical in shape and relatively uniform in size. Fig 4.2 (b) clearly indicates that a representative single nZVI particle consists of a Fe\(^0\) interior core with higher density, which is surrounded by a uniformly thin shell of iron oxides with lower density. It is noticeable that nZVI forms chain-like domains, which are formed due to the magnetic and electrostatic interactions between the metallic particles, resulting in reduction of the available reactive surface area for contaminant degradation. This core-shell model and chain-like structure are typical features for nZVI particles observed in the majority of published reports [23, 60, 61, 62].
**Fig. 4.3** shows a representative TEM micrograph of nZVI-MWCNTs composite. The spherical nZVI particles (black round spots) are successfully distributed along the external surface or inside the network of MWCNTs, as depicted in **Fig. 4.3**. Unlike smooth surface of oxidized MWCNTs, the surface of nZVI-MWCNTs seems much more coarse, caused by the deposition of nZVI particles. A similar phenomenon has been observed by Lv et al. [52]. They reported that MWCNTs with a smooth surface became coarse as nZVI loaded on and some bright spherical spots were visible and they also proven these globular nodules to be nZVI particles. The TEM images additionally presented that the nZVI particles were located either on the surface of MWCNTs or inside the network of MWCNTs, which is consistent with our observations.

Acid oxidation of MWCNTs contributes to the formation of open tips of nanotubes and surface functional groups, which provide strong anchoring sites for the nZVI particles. The oxygenated functional groups, such as -COOH and -OH, are generated in the process of acid oxidization and attached onto the surface of MWCNTs. Adjusting pH to neutral (pH=7), these functional groups are partially deprotonated to generate a negative charge on the surface of the oxidized MWCNTs, which serves as an anchoring point for cationic iron oxide precursors. After a typical NaBH$_4$ reduction, nZVI particles have formed and clusters of aggregated nZVI particles are attached onto the surface of MWCNTs. Large aggregates of iron particles are not observed, which matches the observation from Lv’s
findings. [52] They found that although aggregation of nZVI particles was still observed, it much decreased compared to the case of unsupported nZVI particles. Apparently, the immobilization of nZVI particles with MWCNTs prevents their agglomeration and thus maintains their high surface area and reactivity.

Fig. 4.3 (a)-(d) TEM images of oxidized MWCNTs-supported nZVI particles
4.3.1.2 Nanotubes and nZVI Diameter Distribution

The diameter and diameter distribution of MWCNTs before and after acid oxidization were measured and shown in Fig. 3.3. A comparison histogram of diameter distributions of as-grown and oxidized MWCNTs was represented and the average diameters of as-grown and oxidized MWCNTs were calculated as 25 nm and 15 nm, respectively. As illustrated in Fig. 3.3, oxidized MWCNTs were smaller in diameter and had a broader diameter distribution than those of as-grown MWCNTs. The phenomenon could be interpreted in which the acid oxidization partially breaks up the as-grown MWCNTs into small pieces and cut short most of them, providing better suspensibility of oxidized MWCNTs compared to that of as-grown MWCNTs.

Size and size distribution of the unsupported Fe\(^0\) nanoparticles and MWCNTs-supported Fe\(^0\) nanoparticles were calculated following the same procedure previously discussed in Chapter 3. Fig. 4.4 shows the particle size and size distributions of unsupported nZVI particles and MWCNTs-supported nZVI particles, respectively. According to the results, more than 90% of particles have a diameter in the range of 1-65 nm and a few particles exist mainly as aggregates with diameters above 90 nm. Their average size was around 55 nm, which is in agreement with the values reported in the other studies. Zhang et al. [23]
analyzed over 150 individual nZVI particles prepared by a similar method. The average particle size was reported on the order of 50-70 nm, with more than 70% being in the range of 25-100 nm and 30% being larger than 150 nm. Another study carried out by Sun et al. [60], in which the authors calculated the particle size using more than 420 particles observed in their TEM images determined the average particle size about 70.2 nm with a standard deviation of ~ 19.6 nm. Compared to unsupported nZVI particles, the nZVI particles supported on MWCNTs have a smaller average diameter (40 nm). Majority of the particles were in the diameter of 30-50 nm and more than 85% of them have diameters in the size range of 1-60 nm. The particle size was in agreement with that measured by Lv and Xu [52], in which the supported-Fe\textsuperscript{0} nanoparticles were calculated to be 20-80 nm in diameter.

![Fig. 4.4 Diameter distributions of unsupported and supported nZVI particles from TEM images](image-url)
4.3.1.3 BET Surface Area

As measured in Chapter 3, the BET surface area of oxidized MWCNTs was 313.5 m$^2$/g, which was larger than that obtained on the as-grown MWCNTs (233 m$^2$/g). It has been mentioned that the BET surface area is increased after oxidization, due to the removal of the amorphous carbon and metal catalyst particles as well as to the generation of the interstitial space and grooves. In addition, the oxidization of MWCNTs with HNO$_3$ solution has been suggested to untie the entwined MWCNTs and thus increased the BET surface area [62]. When the nZVI particles were filled into the matrix of MWCNTs, the BET surface area of nZVI-oxidized MWCNTs composite decreased to 267.8 m$^2$/g. BET analysis indicates that the presence of nZVI particles results in a slightly decrease on the surface area compared to that of unsupported pure oxidized MWCNTs. This may be attributed to the incorporation of nZVI particle into the pores of MWCNTs. The decrease on the BET surface area after the introduction of Fe$^0$ nanoparticles was also observed in previous studies. Sunkara and Zhan [63] synthesized spherical Fe$^0$-carbon microsphere nanocomposite through carbothermal reduction. In their case, the BET surface area of the nZVI-carbon composite decreased from 320 to 221 m$^2$/g. They explained the decrease as a result of the association of spherical Fe$^0$ particles. Moreover, a similar trend has been observed by Laura and Mack [64]. This group prepared the iron nanoparticles supported
on carbon by reacting iron salts and the BET surface area of the composite was calculated to be 80 m²/g, which was smaller than that of the original carbon black material used as support (120 m²/g).

4.3.2 Adsorption and Dechlorination Performance of the Pd/nZVI-MWCNTs Composites

The adsorption performance of TCE using MWCNTs subject to acid oxidization was discussed in Chapter 3.3.2.3 and presented in terms of C/C₀ vs. time (t) (shown in Fig. 4.5). In the sets of experiments, as-grown and oxidized MWCNTs were comparatively tested for their capabilities to adsorb TCE from aqueous solution (a parallel blank sample was prepared without adding MWCNTs). The adsorption curves are shown as C/C₀ vs. reaction time (t), where C₀ (mg/L) is the initial TCE concentration in the solution and C (mg/L) is the concentration at time t (h). Figure 4.5 indicates that the TCE adsorption capability of non-treated MWCNTs is lower compared to that of the oxidized nanotubes. It is observed that adsorption efficiency of TCE is reached 15% for the as-grown MWCNTs after 156 hour. In contrast, 30 % of the total TCE present in aqueous solution is adsorbed onto the oxidized MWCNTs adsorption within 144 hour. The observed differences between pristine and acid treated nanotubes in terms of adsorption capacity are consistent with previous reports and can be rationalized in terms of the formation of
additional of adsorption sites in the form of oxygen-containing functional groups generated during acid oxidization [65].

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Fig. 4.5 Adsorption performance of TCE by as-grown and oxidized MWCNTs (reaction conditions: $C_0$: 20 mg/L; as-grown or oxidized MWCNTs: 1 g/L; $T=25^\circ C$, pH=7); error bars represent the standard deviation for duplicate results.

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Fig. 4.6 (a) and (b) present the results on the simultaneous adsorption and degradation of TCE by nZVI/as-grown MWCNTs and nZVI/oxidized MWCNTs composites, respectively. The degradation of TCE with nZVI particles and adsorption of TCE by MWCNTs were carried out individually to compare it with the results obtained on the nZVI/MWCNTs composite. The loading of bare nZVI particles is the same as the content
of nZVI in nZVI/MWCNTs composite. Under the same operating conditions, TCE removal efficiencies (expressed as C/C<sub>0</sub>) are measured as a function of reaction time (t).

The removal of TCE from the aqueous phase by the as-grown and oxidized MWCNTs is solely attributed to adsorption, with equilibrium reached after 156 hour and 144 hour respectively. For bare nZVI particles, a partial TCE degradation (about 14% reduction) is detected within approximately 5 days. When nZVI particles are exposed to TCE-containing solutions, there is an initial decline of TCE concentration (expressed as C/C<sub>0</sub>) to 0.84 (16%), followed by a subsequently slower degradation. Lv et al. [52] found similar results in their study, in which nZVI/MWCNTs composite was used to removal Cr (VI) from wastewater. They reported that the removal efficiency of nZVI nanoparticles was initially increased to 47% but slowed down and continually increased to 59%, which has the similar reduction process as our observation. This phenomenon was possibly attributed to the surface oxidation and aggregation of nZVI particles previously reported [26]. When Fe<sup>0</sup> particles are exposed to air/water, they easily formed an obstructive oxide film on their surface, which would reduce the reactivity of nZVI particles and thus slow the reductive degradation of TCE over the entire course of the reaction.
Fig. 4.6 Comparison of removal efficiency of TCE by (a) nZVI, as-grown MWCNTs and nZVI/as-grown MWCNTs composites (b) nZVI, oxidized MWCNTs and nZVI/oxidized MWCNTs composites (reaction conditions: \( C_0 \): 20 mg/L; as-grown/oxidized MWCNTs: 1g/L; \( \text{Fe}^0 \): 0.1g/L, \( \text{Fe}^0 \)-MWCNTs: 1g/L, 10 w.t. % \( \text{Fe}^0 \); \( T=25^\circ C, \text{pH}=7 \)); error bars represent the standard deviation for duplicate results.
On the other hand, both nZVI-as-grown MWCNTs and nZVI-oxidized MWCNTs composites show superior capability to remove TCE from aqueous solutions. Figure 4.6a suggests that for the case of the as-grown MWCNT materials, the enhanced adsorption capacity of the composite (~35% TCE removal at equilibrium) is the result of an additive contribution of the independent effects of the bare nZVI (~14% TCE removal at equilibrium) and MWCNTs (~18% TCE removal at equilibrium). While additional experiments would be necessary to corroborate this hypothesis, it is clear that for the case of the nZVI-oxidized MWCNTs composite, the enhanced TCE removal capacity (Fig. 4.6b) is not the result of an additive contribution. Indeed, up to 55% of TCE was removed using the nZVI-oxidized MWCNTs composite at equilibrium. This observation clearly indicates that nZVI-MWCNTs composite displays much higher capacity for the dechlorination of TCE than the corresponding unsupported nZVI particles and acid treated MWCNTs.

The obvious growth on removal efficiency was confirmed by Lv’s study [52] and nearly 90% of Cr (VI) was reported to successfully remove by the nZVI-MWCNTs composite. They interpreted that the MWCNTs could act as a micro-cathode while coupling with nZVI, preventing the formation of oxide film on the surface and accelerating the corrosion of nZVI particles. Furthermore, Xiao et al. [53] evaluated the remediation capability of TCE using the ZVI-immobilized polymer nanofibrous mats (PAA/PVA)
with and without MWCNTs. They showed that both ZVI-containing nanofibrous mats exhibited excellent performance for the degradation of TCE. Within the first 30 min, the reaction process reached a dynamic equilibrium, and the remaining fraction of TCE with and without MWCNTs was estimated to be 0.034 and 0.086, respectively. The higher removal efficiency and lower reaction time may be caused by the different fabrication method. In Xiao’s study, a new approach was used to incorporate ZVI to PAA/PVA-crosslinked MWCNTs, resulting in a dense distribution of ZVI across the cross section of nanofibers and a much smaller mean size of the ZVI nanoparticles was estimated. (1.6±0.28 nm vs. 40 nm in our study)

In our study, we suggested that the improvement on removal efficiency was likely due to the prevention of the nZVI particles from the surface oxidization and aggregation when they were supported in the MWCNT substrate. In addition, MWCNTs could also facilitate the dechlorination of TCE adsorbed in the vicinity of the reactive nZVI sites through strong adsorption by oxidized MWCNTs [66]. When the nZVI-MWCNTs composite was used, TCE is partitioned into the aqueous solution and the MWCNTs surface through adsorption and if the adsorbed-TCE is then accumulated in close proximity to the imbedded nZVI particles, present dechlorination would take place. This adsorptive mechanism enhances the mass transfer of TCE molecules from the aqueous solution to the solid surface and would further increase the dechlorinating ability of nZVI
particles. Thus, it is speculated that the nZVI particles would degrade either the adsorbed-TCE onto MWCNTs or dissolved-TCE in the aqueous solution. Therefore, the apparent enhancement of TCE decontamination by nZVI-MWCNTs composite might be a complex function of a simultaneous adsorption of TCE onto MWCNTs and degradation by nZVI particles.

**4.3.2.1 Effect of Pd Catalyst**

For this series of experiments, we introduced an extremely small amount of Pd over Fe$^0$ (0.1 w.t. % of Fe$^0$) to evaluate the reactivity characteristics of Pd/nZVI and Pd/nZVI-MWCNTs composite with dissolved TCE. Fig. 4.7 presents the results on TCE dechlorination by 1 g/L nZVI-MWCNTs loaded with 0.1% Pd catalyst (w/w Fe$^0$) over a reaction time of 24h. Upon the introduction of Pd onto the surface of nZVI, a significant increase of the reactivity is observed for the non-supported and supported-nZVI systems. Compared to the relatively low efficiency of bare nZVI particles, Pd/nZVI completely degraded TCE within 24h. In the case of the nZVI-MWCNTs composite, the fraction of TCE decreased dramatically and 100 % is removed within only 6h. The large improvement on removal efficiency is in good agreement with the results obtained by Sunkara et al. [63]. In their work, 0.25g of Pd/Fe$^0$-C composite (1 g/L Fe$^0$) was employed with 0.1% Pd (w/w Fe$^0$) to remove 20 ppm TCE from aqueous solutions. They observed
an initial sharp reduction (~70%) followed by a much slower decline and finally complete removal was achieved within 1h. The shorter time for this composite to reach 100% degradation is possibly due to their high nZVI/TCE ratio (50), which was much larger that the one we used (5).

**Fig. 4.7** Effect of Pd loading on the nZVI and nZVI/oxidized MWCNTs (reaction conditions: \( C_0 \): 20 mg/L; \( \text{Fe}^0 \): 0.1 g/L, \( \text{Fe}^0 \)-MWCNTs: 1g/L; Pd loading: 0.1 w.t. % of \( \text{Fe}^0 \), \( T=25 \) °C, pH=7); error bars represent the standard deviation for duplicate results.
As shown in Fig. 4.7, deposition of small amount of Pd onto nZVI surface could dramatically increase the overall TCE removal efficiency. Nyer et al. [67] reported that the degradation of TCE by Fe$^{0}$ was a surface-mediated reaction that occurred on the surface of the Fe/H$_{2}$O interface. Therefore, dopant of Pd catalyzes the dissociative chemisorption of H$_{2}$ and facilitates oxidation of nZVI by less active Pd and Pd-mediated hydrogenation by the following mechanisms [67]:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}_{\text{aq}}^- \\
\text{H}_2(\text{g}) & \rightarrow 2\text{H}_{\text{ad}} \quad (\text{Activated atomic-H}) \leftrightarrow 2\text{H}^+_{\text{(aq)}} + 2e^- \\
5\text{H}^+ + \text{C}_2\text{HCl}_3 + 3e^- & \rightarrow \text{C}_2\text{H}_6 + 3\text{Cl}^- 
\end{align*}
\]

In a monometallic NZVI system, direct reduction of TCE occurs on the Fe$^{0}$ surface, which serves as an electron donor to degrade TCE. In a bimetallic nZVI system (Pd/Fe$^{0}$), Fe$^{0}$ component serves as a reducing agent through their corrosion reactions, generating electrons that reductively degrade chlorinated compounds. The role of Pd is to catalyze the dissociative chemisorption of H$_{2}$ produced by redox reactions on the Fe$^{0}$ surface. The formation of activated atomic H$_{\text{ad}}$ acts as a powerful secondary reducing agent, which in turn facilitates the acceleration of reaction rates of TCE degradation [67].
4.3.2.2 Effect of Initial TCE Concentration

To evaluate the performance on the decontamination of TCE by nZVI-oxidized MWCNTs composites, the effect of various initial TCE concentrations was assessed in this section. TCE initial concentrations of 20, 50, 100 mg/L were used, respectively, while all other conditions were kept constant. As shown in Fig. 4.8 the removal efficiency of TCE decreased slightly with an increase of TCE initial concentration. Within reaction time of 5 d, the lowest TCE initial concentration (20 mg/L) exhibits a removal efficiency of 55 %, followed by 50 % of reduction with TCE initial concentration of 50 mg/L and 47% is removed when the initial concentration increases to 100 mg/L. A similar trend was observed by Lv and Xu [52] when evaluating the Cr(VI) removal efficiency by the nZVI-MWCNTs nanocomposites. They used Cr(VI) concentrations in the range of 10-60 mg/L and reported that the Cr(VI) could be absolutely removed at concentration of 10, 20 and 40 mg/L, while around only 60% was removed as the concentration increased to 60 mg/L. They explained the decline was a result of the limited amount of nZVI particles as initial concentration of TCE increased. As the quantity of nZVI/MWCNTs composite was fixed, the available sites for adsorption remained constant and the smaller of nZVI/Cr(VI) mass ratio decreased as the
increase on the Cr(VI) concentration, leading to low removal efficiency under a higher Cr(VI) concentration.

Fig. 4.8 Effect of TCE initial concentration on the nZVI/oxidized MWCNTs (reaction conditions: initial TCE: 20, 50 and 100 mg/L; MWCNTs-oxidized nZVI: 1 g/L, T=25°C, pH=7); error bars represent the standard deviation for duplicate results.

The phenomenon might be attributed to a competitive effect of the improved adsorption capacity by MWCNTs and lower degradation efficiency through nZVI particles with an increase on TCE initial concentration. As discussed in Chapter 3, with increasing on initial TCE concentrations from 20 to 100 mg/L, more TCE molecules were adsorbed onto the oxidized MWCNTs, resulting in a higher adsorption capacity of TCE due to the
enhanced mass diffusion at higher TCE initial concentration [68]. Thus, the performance of adsorption by nZVI-MWCNTs composites would theoretically increases with increasing TCE initial concentration. On the other hand, a decrease in reduced reactivity at a higher TCE initial concentration has been observed on bare nZVI particles due to the deactivation of nZVI particles caused by formation of a passivating Fe oxides layer during dechlorination at high TCE concentrations [69].

4.3.3 Kinetic Analysis

Previous studies have been used the first-order kinetic model to describe the reduction of TCE by nZVI and Pd/nZVI particles [70-73] and the equation is expressed as follows:

$$r_{TCE} = -\frac{dC_{TCE}}{dt} = K_{obs}C_{TCE} = k_{SA}A_{TCE}C_{TCE}$$

It can be rearranged as a linear form:

$$-\ln \left( \frac{C_{TCE}}{C_{0(TCE)}} \right) = k_{obs}t = k_{SA}A_{TCE}C_{TCE}$$

$$k_{SA} = \frac{k_{obs}}{A_{TCE}}$$
Where:

\( C_{\text{TCE}} \): TCE concentration (mg/L) in aqueous phase at time \( t \) (h),

\( C_{o(\text{TCE})} \): TCE initial concentration (mg/L),

\( k_{\text{obs}} \): observed pseudo-first-order reaction rate constant (h\(^{-1}\)).

\( k_{\text{SA}} \): surface-normalized rate constant (L h\(^{-1}\) m\(^{-2}\))

\( t \): reaction time (h)

\( \rho_m \): mass concentration of the nanoparticles (g/L)

\( a_s \): TEM-based specific surface area of nanoparticles (m\(^2\)/g)

In our experiments, we employed the pseudo-first order kinetic model to quantitatively evaluate the reaction kinetics of TCE using the nZVI-MWCNTs and Pd/nZVI-MWCNTs composites under various conditions (shown in Fig. 4.9 (a) and (c)). This pseudo-first order model describes apparent kinetics as a first-order process; however this apparent order of the reaction might be influenced by the intrinsic reaction kinetics and diffusion. The experimental conditions results in a particularly controlled regime, in which diffusion through the pore structure might occur under the same time scale of the elementary reaction. If that is the case, the apparent kinetics will indicate first order processes since diffusion is a first-order process. The experimental data of reactivity was fitted with a linear plot of \(-\ln\left( \frac{C}{C_0} \right)\) vs. \( t \) to obtain the observed reaction rate constant
The linearized plots \([ - \ln \left( \frac{c}{c_0} \right) ]\) vs. \(t\) of the model-simulated kinetic data under different conditions are shown in Fig. 4.9 (b), (d) and (e) and the values of the observed pseudo-first order reaction rate constants \((k_{\text{obs}}, \text{h}^{-1})\), surface-normalized rate constant \((k_{\text{SA}}, \text{L h}^{-1} \text{m}^{-2})\) and regression coefficients \((R^2)\) are listed in Table 4.1. As suggested by Nyer et al. [67], the dechlorination of TCE by Fe\(^0\) nanoparticles is a surface-mediated reaction, thus the specific surface area is an important factor and has a significant impact on the reaction rate. To better compare the reaction rates under various specific surface areas, the surface-normalized rate constant \((k_{\text{SA}})\) has been applied as a general descriptor to assess the surface reactivity of various nanoparticles, rather than the pseudo-first order rate constant \((k_{\text{obs}})\) [70]. In this study, the TEM-based specific surface areas \((\alpha_s)\) of the unsupported and supported Fe\(^0\) nanoparticles were calculated by the equation proposed by He and Zhao [74] \((\alpha_s = 3\times10^6/(r\times\rho))\), \(r\)=particle radius (nm), based on the mean particle diameter obtained from the TEM micrographs, \(\rho\) equals the density of Fe\(^0\), 7870 kg/m\(^3\)). The \(k_{\text{SA}}\) values were determined accordingly.
(a) C/Co vs. Time, t (h) for different samples:
- nZVI
- nZVI-as grown MWCNTs
- nZVI-oxidized MWCNTs
- Pseudo-1st order model

(b) -ln(C/Co) vs. Time, t (h) for different samples:
- nZVI-oxidized MWCNTs
- nZVI-as grown MWCNTs
- nZVI
- Linear models for nZVI, nZVI-oxidized MWCNTs, and nZVI-as grown MWCNTs
Pd/nZVI and Pd/nZVI-oxidized MWCNTs were compared in terms of their catalytic activity.

Graph (c): Pseudo-1st order model fit for the reaction kinetics.

Graph (d): Linear fit for the reaction kinetics.
Fig. 4.9 Pseudo-first-order model fittings to the experimental data: (a) nZVI and nZVI-MWCNTs ($C_o=20\,\text{mg/L}$) (c) Pd/Fe$^0$ and Pd/Fe$^0$-oxidized MWCNTs (Pd: 0.1 w.t. % of Fe$^0$); linear plots of pseudo-first order model for (b) nZVI and nZVI-MWCNTs ($C_o=20\,\text{mg/L}$) (d) Pd/Fe$^0$ and Pd/Fe$^0$-oxidized MWCNTs (Pd: 0.1 w.t. % of Fe$^0$) (e) $C_o$: 20, 50, 100 mg/L for Fe$^0$-oxidized MWCNTs (Fe$^0$: 0.1 g/L, Fe$^0$-MWCNTs: 1g/L, mass ratio of Fe$^0$/MWCNTs: 10 w.t. %; T=25°C, pH=7);
Table 4.1 Observed pseudo-first-order reaction rate constants, surface-normalized rate constants and regression coefficients under various conditions

<table>
<thead>
<tr>
<th>Composite/Particle</th>
<th>C₀ (mg/L)</th>
<th>k₀ (h⁻¹)</th>
<th>α₅ (m²/g)</th>
<th>kₛₐ (L/h/m²)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>nZVI</td>
<td>20</td>
<td>0.002</td>
<td>13.86</td>
<td>1.4×10⁻³</td>
<td>0.920</td>
</tr>
<tr>
<td>nZVI-as-grown MWCNTs</td>
<td>20</td>
<td>0.004</td>
<td>19.06</td>
<td>2.1×10⁻³</td>
<td>0.907</td>
</tr>
<tr>
<td>nZVI-oxidized MWCNTs</td>
<td>20</td>
<td>0.007</td>
<td>19.06</td>
<td>3.7×10⁻³</td>
<td>0.926</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.006</td>
<td>19.06</td>
<td>3.1×10⁻³</td>
<td>0.915</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.005</td>
<td>19.06</td>
<td>2.6×10⁻³</td>
<td>0.934</td>
</tr>
<tr>
<td>Pd/nZVI</td>
<td>20</td>
<td>0.264</td>
<td>13.86</td>
<td>0.19</td>
<td>0.926</td>
</tr>
<tr>
<td>Pd/nZVI-oxidized MWCNTs</td>
<td>20</td>
<td>0.627</td>
<td>19.06</td>
<td>0.33</td>
<td>0.903</td>
</tr>
</tbody>
</table>

In our study, TEM measurements revealed that the mean sizes of Fe⁰ nanoparticles and Fe⁰ nanoparticles in the MWCNTs-supported samples were approximately 55 nm and 40 nm, respectively. Applying He's equation [74], the specific surface areas were calculated to be 13.86 and 19.06 m²/g, respectively. The value of 19.06 m²/g was taken for the calculation as an upper limit for kₛₐ for all MWCNTs-supported samples. It has been reported by Zhuang et al. [75] that the mean sizes of Pd/Fe⁰ bimetallic nanoparticles was
slightly decreased from 50-70 nm (for nZVI particles) to 30-50 nm by using a similar NaBH₄ reduction method. Since this difference on mean size didn’t significantly change the specific surface area, we roughly assumed that the mean sizes of our Pd/Fe nanoparticle and MWCNTs-supported Pd/Fe nanoparticle were 55 nm and 40 nm, respectively. As illustrated in Fig. 4.9, it is obvious that the kinetic data is deviated from the fitting during the first 10 hours of the experiment. The initial inconsistency of the fittings could be contributed to the influence of the lag-phase of the MWCNTs, which was observed and discussed in Chapter 3.3.2.1.

As shown in Table 4.1, the pseudo-first-order reaction kinetic model fits the experimental data fairly well ($R^2 > 0.91$) under the various experimental conditions. The high $R^2$ value indicated that the reaction kinetics of TCE by nZVI-MWCNTs and Pd/nZVI-MWCNTs composites could be described well with the pseudo-first order kinetic model, which is in good agreement with the previous studies on carbon-supported nZVI nanoparticles [52, 74, 75]. For nZVI-MWCNTs composite, the observed reaction rate of TCE ($k_{obs}$) increases in the order nZVI-oxidized MWCNTs ($0.007 \text{ h}^{-1}$) > nZVI/as-grown MWCNTs ($0.004 \text{ h}^{-1}$) > nZVI ($0.002 \text{ h}^{-1}$). Furthermore, the same increased trend of the surface-normalized reaction rate ($k_{SA}$) on TCE degradation is observed. It can be seen that nZVI-oxidized MWCNTs exhibits the largest $k_{SA}$ values ($k_{SA}=3.7\times10^{-3} \text{ L h}^{-1} \text{ m}^{-2}$), followed by nZVI-as grown MWCNTs ($2.1\times10^{-3} \text{ L h}^{-1} \text{ m}^{-2}$).
and then nZVI \((1.4\times 10^{-3} \text{ L h}^{-1} \text{ m}^{-2})\). A similar study was carried out by Mackenzie and Bleyl [76], in which they developed a novel carbon-iron colloidal (CIC) composite consisting of activated carbon colloids and anchored deposit of nZVI clusters for TCE dechlorination (Fe loading: 1 g/L and initial TCE: 30 mg/L). The \(k_{SA}\) obtained values on the selected CIC types were based on the TEM-calculated surface areas (estimation of specific Fe\(^0\) surface area for CIC from mean size of Fe\(^0\) structures of 50 nm) and the highest \(k_{SA}\) value was reported to be \(1.25\times 10^{-3} \text{ L h}^{-1} \text{ m}^{-2}\). In our study, the calculated \(k_{SA}\) value for the nZVI-oxidized MWCNTs is \(3.7\times 10^{-3} \text{ L h}^{-1} \text{ m}^{-2}\), which is the same order of magnitude but has a slightly larger value than the value reported by Mackenzie et al. [76]. The larger value of \(k_{SA}\) indicates that the nZVI-MWCNTs composite has high reactivity for TCE dechlorination. It is evident that the nZVI-MWCNTs composite has higher Fe\(^0\) surface-normalized reaction rate than that of nZVI particle, indicating an enhancement on reactivity, which is a result from the combination of TCE adsorption on MWCNTs and degradation by nZVI. In addition, MWCNTs acts as an ideal support to prevent the aggregation of nZVI particles thus increasing their activity.

In addition, Table 4.1 also shows that with the deposition of small amount of Pd onto the surface of Fe\(^0\), the calculated the \(k_{SA}\) values for TCE dechlorination by Pd/Fe nanoparticles in MWCNTs support was 0.33 \text{ L h}^{-1} \text{ m}^{-2}, which was drastically increased by two orders of magnitude compared to the MWCNTs supported Fe\(^0\) nanoparticles.
(3.7×10^{-3} \text{ L h}^{-1} \text{ m}^{-2}). This great improvement on reaction rates is consistent with the experimental observation from CMC-stabilized Pd/Fe nanoparticles (Pd/Fe ratio: 0.1/100, w/w) [76], which was reported to be 17-times-greater than bare Pd/nZVI particles for the transformation of TCE. Wu et al. [78] used membrane-supported Pd/Fe nanoparticles with 0.7 w.t. % of Pd (Fe^0: 0.54 g/L) for the dechlorination of TCE and the $k_{\text{obs}}$ was 0.387 h^{-1}, corresponding to an order of magnitude increase on the dechlorination rate observed for supported Fe nanoparticles without Pd (0.0384 h^{-1}). In our study, with the presence of palladium, the reaction rate were enhanced by a factor of more than 90, which demonstrates that a relatively small dose of palladium offers a strongly catalytic impact on TCE dechlorination reactivity.

The calculated values of surface-normalized reaction rates remained roughly constant (0.003-0.004 L h^{-1} m^{-2}) for the nZVI-MWCNTs composites while the initial TCE concentrations increased from 20 to 100 mg/L. On the other hand, as expected from the discussion on Chapter 3, the intraparticle diffusion rates of TCE to MWCNTs increased from 0.455 to 0.889 mg/g h^{0.5} with the increase on TCE initial concentrations (20-100mg/L). In spite of the 5 times change in TCE initial concentration, the observed reaction rates are almost identical within an error margin, confirming a first-order dependence, suggesting that the surface-mediated reaction rather than diffusion is the rate-limiting step in the TCE dechlorination process.
4.4 Conclusions

In this chapter, a new concept of “nZVI-MWCNTs composite” is developed to remove TCE from aqueous solution involving an integration of simultaneous adsorption by MWCNTs and degradation reaction through nZVI particles. A simple and efficient strategy was established to introduce nZVI particles into MWCNTs by wet chemical method. TEM was used to characterize their morphology and particles size distributions. BET was applied to calculate the specific surface area. Batch experiments were carried out to evaluate TCE removal performance from aqueous solutions by nZVI-MWCNTs composite, compared with bare nZVI and MWCNTs. The introduction of a small amount of Pd was evaluated its impact on the composite’s TCE removal efficiency. Finally, a pseudo-first-order kinetic model was employed to investigate the basic mechanism of TCE removal by nZVI-MWCNTs. In summary, the following conclusions can be collected from this study:

(1) TEM characterization suggests that the MWCNTs morphological properties relevant to adsorption are greatly improved after acid oxidization. With the disappearance of impurities, increase of surface area, and formation of surface oxygen-containing functional groups, oxidized MWCNTs become more hydrophilic and adsorption capacity of TCE increase correspondingly;
TEM images of bare nZVI indicate that most nZVI particles are spherical in shape and relatively uniform in size. A representative single nZVI particle consists of a Fe$^0$ interior core, surrounded by a uniformly thin shell of iron oxides. nZVI particles have a strong tendency to aggregate and form a chain-like structure, resulting in the reduction of the available reactive surface area for TCE degradation;

BET analysis indicates that specific surface area of nZVI with the presence of MWCNTs is much larger than those unsupported particles. Therefore, the immobilization of nZVI particles with MWCNTs prevents their agglomeration and thus maintains their high surface area and reactivity;

Acid oxidation of MWCNTs contributes to the formation of open tips of nanotubes and surface functional groups, which provide a strong association with nZVI particles. With the immobilization of nZVI particles with MWCNTs, their high surface area and reactivity are maintained, preventing nZVI agglomeration.

In a batch mode, nZVI-MWCNTs composite shows much higher TCE removal efficiency compared to bare nZVI and MWCNTs. In this hybrid nanomaterial system, MWCNTs serves as a highly efficient adsorbent and also an effective support to immobilize nZVI particles, simultaneously, Fe$^0$ nanoparticles perform as an effective redox material for the dechlorination;

The deposition of small amount of Pd (0.1 w.t. %) onto nZVI surface could dramatically increase the overall TCE removal efficiency. The role of Pd is to
catalyze the dissociative chemisorption of hydrogen produced by redox reactions on Fe\textsuperscript{0}. The activated atomic H-species acts as a powerful secondary reducing agent, which in turn can contribute to increase the degradation rates of TCE; (7) The kinetics of TCE degradation over the nZVI-MWCNTs composites are described fairly well by a pseudo-first-order rate model;
4.5 References


[42] Li, W., Han, C. and Liu, W., *Catal Today.*, 125, 278-281, 2007


5.1 Introduction

Among several chlorinated compounds, trichloroethylene (TCE) is ubiquitous in groundwater and soil [1]. Due to its chemical stability and density, it persists and gradually accumulates as a continuous long-term environmental contaminant. Environment Canada has listed it as a priority pollutant and established 0.005 mg/L as the maximum acceptable concentration (MAC) for TCE in drinking water [2]. Because of its significant threat to the environment and health, a large effort has been put on the remediation of TCE-contaminated sites. During the last decade, the application of reactive zero-valent iron (ZVI)-based systems represent one of the innovative strategies used to address this issue [3]. Zhang et al. [4], in 1998, firstly proposed that ZVI particles could act as a strong reductive agent to effectively and passively degrade organic chlorinated compounds such as TCE. The simplified redox mechanism between TCE ($C_2HCl_3$) and iron (Fe$^0$) in aqueous solutions could be expressed as following [4]:
\[ C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^- \]

In the above reaction, ZVI particles mediate successive reduction and are oxidized to ferrous iron \((Fe^{2+})\) and further to ferric iron \((Fe^{3+})\), while TCE compounds are effectively reduced, leading to the eventually innocuous products, such as ethane, ethane, chloride ions and water. ZVI particles are thus initially thought to be simple, cost-effective, and environmentally benign, and proposed as the best alternative to conventional physicochemical methods.

As discussed in the previous chapter, nanoscale ZVI (nZVI) particles have been successively synthesized and extensively used as an effectively promising material for the transformation and detoxification of a wide variety of chlorinated hydrocarbons [5]. Due to their smaller particle size and larger reactive surface area [6], the reductive dechlorination rate of chlorinated hydrocarbons has been found several orders of magnitude higher than those conventional microscale granular ZVI particles. In addition to bench-scale experiments, nZVI has been demonstrated to successfully achieve the rapid in-situ remediation in pilot and large-scale filed applications. However, nZVI particles easily react with water and/or oxygen presented in their surrounding media to form a passivation layer, hindering its reaction with contaminants over time [7]. As a result of the slower and incomplete degradation, measurable amounts of intermediates
and by-products (e.g. VC and DCE) are produced and accumulated. These by-products are carcinogenic and some of those are potentially more harmful than their parent compounds [8]. Therefore, these major drawbacks limit the widespread applications of nZVI and further research efforts have focused on protecting nZVI particles against surface oxidation and minimizing byproducts formation. One of these strategies involves the deposition of a catalytic layer of noble metals (such as Pd, Ni or Cu) onto the surface of freshly prepared nano-Fe\textsuperscript{0} particles [9]. The addition of the noble metal onto the Fe\textsuperscript{0} surface not only significantly facilitates the iron to substrate electron-transfer required for contaminant reduction but also accelerates the reactivity rate through a parallel reduction pathway, thus eliminating byproduct accumulation [10]. Particularly for Pd/nZVI systems, Chin et al. [11] illustrated that a small amount of palladium enhances TCE dechlorination rates by two orders of magnitude and also inhibits the production and formation of toxic intermediates and byproducts.

Moreover, there is a second shortcoming that hinders the widespread applications of nZVI particles. Due to their strong tendency to agglomerate rapidly, the particles easily grow into large clusters and chain domains in the micro to millimeter scale [12], which thus results in a significant loss in available reactive surface area and inhibits their mobility in the subsurface [13]. Thus, surface modified nZVI particles have been explored with the aim of further enhancing their efficiency for remediation. These
strategies rely on stabilization by adsorption of hydrophilic or amphiphilic organic species on nZVI surface, such as water-soluble starches, surfactants and polymers. These adsorbed large organic molecules are able to prevent particles from aggregation and enhance their stability by increasing the steric and/or electrostatic repulsion. Alternatively, nZVI particles could be effectively immobilized onto a solid matrix support, such as hydrophilic carbon particles [14]. Due to their exceptionally high surface area, and high micro-porosity [15, 16], carbon-based materials provide a lot of anchoring points to prevent the agglomeration of nZVI particles [17]. Furthermore, the porous carbon materials have high chemical and thermal stability and biocompatibility [18, 19], making them effective to support nanoparticles. As a typical carbon material, activated carbon (AC) has been studied for its potential as a support for environmental applications, as a result of its high surface area (around 500 m$^2$), porous structure, unique surface properties and relatively low cost [20, 21]. Mackenzie et al. [15] firstly described an approach to synthesize carbon-supported iron particles, in which he used activated carbon colloids as supports for iron salt precursors and then thermally treated them in hydrogen to form metallic irons. Laura et al. [16] prepared a carbon-Fe$^0$ combined with CMC for the removal of Cr (VI) oxoions. These materials decreased the concentration of a 10 ppm Cr (VI) solution to about 1ppm within 3 days. Busch et al [22] developed an AC-plated nZVI material to study its transport ability. Column tests showed that high mobility of
this composite material in soil and the faster and higher transport is a result of the combination of the mobility of AC and the reactivity of nZVI particles.

In addition, AC have been extensively employed as adsorbent in a wide range of environmental applications, due to its pore structure, high specific surface area, chemical inertness and thermal stability. For instance, adsorption of various persistent organic compounds by AC is one the major technologies used in water treatment [23]. Removal of volatile organic compounds (e.g. extracted contaminated soil vapors) by AC adsorption has been often used for air treatment [24]. In particular, granular activated carbon (GAC) has been evaluated to remediate TCE compounds from groundwater by adsorption. Kilduff et al. [25] investigated the feasibility of purifying TCE by GAC. Miyake et al. [26] reported that activated carbon was very useful for the removal of TCE vapor from TCE-contaminated water. Huang et al. [27] conducted and compared the effectiveness of seven granular activated carbons in adsorptive capacities of TCE from groundwater.

Recently, a new nanocomposite so-called “reactive activated carbon” (RAC) has been proposed for the simultaneous adsorptive and reactive properties as a practical in-situ remediation strategy for contaminated sites [28]. The combination of the high adsorption capacity of AC and the electrochemically destructive reactivity of nZVI or Pd/nZVI
particles has been evaluated effective to degrade certain organic compounds in groundwater. Choi et al. [28] initially developed a new and effective strategy to synthesize a series of adsorptive GAC composites incorporated with reactive nZVI (GAC-nZVI composite) and bimetallic Pd/nZVI nanoparticles (Pd-doped GAC-nZVI composite) and studied their effectiveness for the removal of polychlorinated biphenyls (PCBs). He proposed a parallel removal mechanism that simultaneously removed PCBs from the aqueous phase by means of adsorption to GAC and dechlorination by bimetallic Pd/Fe nZVI. Zhuang et al. [29] also synthesized the Pd/nZVI impregnated-AC composite and investigated its effectiveness to remove polybrominated diphenyl ethers (PBDEs) and PCBs. Palladization of the composite promoted the dehalogenation kinetics for mono-, tri-BDEs and 2,3,4-trichlor-obiphenyl (PCB 21) by 2-, 3-, and 4-orders of magnitude, respectively. Chang et al. [30] synthesized bimetallic Cu-amended nZVI particles and incorporated them with GAC to prepare supported nanoparticles. They used the composites to remove hexachlorocyclohexane and around 99% of the target-contaminant was removed within 165 min. They proposed that AC as a support was effective for increasing the dispersion of nZVI particles and avoiding the agglomeration of the metallic nanoparticles and AC could also adsorb the degradation products.

Most of the studies have been focused on the application of RAC composite for the remediation of highly hydrophobic organic compounds (e.g. PCBs). However, to the best
of our knowledge, few papers so far have published on the application of RAC system to
the C2-chlorinated hydrocarbons. Mackenzie and Bleyl [31] introduced a novel
Carbon-Iron® colloidal composite consisting of activated carbon colloids (ACC) and
anchored deposits of zero-valent iron clusters. This study discussed the principal material
properties of CIC relevant for groundwater treatment of TCE in comparison to
commercially available nZVI particles and they discovered that the interplay of sorption
and reaction contributed to the higher reactivity, providing a more efficient utilization of
the iron reagent. Most recently, Tseng and Su [32] studied the coupling adsorption and
degradation of TCE through dechlorination using synthetic GAC-ZVI composites with
the use of a PEG-4000 (polyethylenglykol-4000) dispersant. They reported that the
composite displayed a greater capacity for the reductive chlorination of TCE than the
individual use of ZVI but had a similar reaction rate as that of GAC. The published study
has paid little attention to the morphology of the iron phases anchored in the carbon
support and interaction between iron particles with GAC with various Fe loadings, and as
well as the influence of palladium on the reaction rates, even though all of the
information is critical for the rational development of effective materials for
environmental remediation.

In this chapter we describe our efforts on the integration of the simultaneous physical
adsorption by GAC and chemical degradation through nZVI particles for the remediation
of chlorinated organic compounds in a RAC system. The primary objectives are in terms of synthesizing the GAC-nZVI and Pd-impregnated GAC-nZVI composites, respectively; characterizing and comparing the properties of the hybrid GAC-nZVI composites to their parent substrates (nZVI and GAC) by TEM, Raman spectroscopy, XRD, BET surface area and temperature programmed reduction (TPR), evaluating the removal efficiency of TCE by these composites and studying the effect of the mass ratio of nZVI particles to GAC on TCE removal, assessing the impact of palladium over GAC-nZVI composites on the performance of TCE removal and elucidating the possible mechanism involving in the supported and unsupported nZVI system by the pseudo-first-order kinetics model.

5.2 Materials and Methods

5.2.1 Materials and Reagents

All water used was deionized using a Barnstead Easypure II system. To remove the dissolved O$_2$ and prevent oxidation, deionized (DI) water was further deoxygenated by purging it with nitrogen gas (ultra high purity, Praxair) for at least 2 hours prior to use. All the chemical solutions used in this study were prepared using deoxygenated water. All solvents and chemicals used were obtained as commercially analytical grade reagents and used as received without any further treatment. Ferric nitrate nonahydrate
(Fe(NO₃)₃·9H₂O, ACS grade reagent, minimum purity 98 wt.%) used as iron precursor was supplied by Sigma–Aldrich. Trichloroethylene, (TCE, ≥99.5%, ACS grade reagent), sodium borohydride (NaBH₄) and n-hexane (anhydrous solvents, 95%) were purchased from Sigma-Aldrich (WI, USA). Isopropyl alcohol (2-propanol, 99.5% min. assay, ACS grade reagent, BDH) and methanol (99.8% min. ACS grade, BDH) were obtained from VWR Company (USA). Palladium (II) acetate (Pd(ac)₂, [Pd(C₂H₃O₂)₂]₃, (99.98%, trimer, Pd min. 46%wt.) was received from Alfa Aesar. Sodium hydroxide (NaOH, ACS grade, EMD) and nitric acid (ACS grade, 68%) were purchased from Sigma Aldrich.

A commercially lignite-based granular activated carbon (GAC, HD-3000, US mesh 8×30) was obtained from Norit Americas, Inc. (Marshall, TX). The received HD-3000 has a graphite crystal phase with surface area of 600-675 m²/g, effective size range of 0.7-0.9 mm and iodine number of 500 mg/g. The advantages of their mesoporous structure, large surface area and low cost of lignite coal make GAC as an ideal impregnation support material. Before use, GAC was washed thoroughly with deionized water to remove soluble impurities. Wet GAC was then dried in the oven at 110 °C overnight, cooled to room temperature and stored in desiccator for further use. To prepare homogeneous GAC suspensions, 60 mg of GAC sample was dispersed into 60 mL of deionized water, and then sonicated for about 1h by an ultrasonic probe in an ice-water bath at 280 watts (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY).
5.2.2 Synthesis of GAC-nZVI Composites

To synthesize the GAC-nZVI and Pd-doped GAC-nZVI composites, a multi-step procedure was developed to impregnate the mesoporous GAC with nZVI particles. We adapted the method reported by by Choi et al. [28], in which a certain amount of iron was impregnated into the matrix of GAC. Generally, nZVI particles were incorporated into the pores of lignite-based HD 3000-GAC by a typical incipient wetness impregnation method. Ferric nitrate (Fe(NO$_3$)$_3$•9H$_2$O) was adopted as the precursor solution rather than other Fe salts (e.g. ferric chloride, ferrous sulfate) because other counterpart anions (Cl$^-$ and SO$_4^{2-}$) could not be completely removed during the heat treatment procedure at 300°C, which might affect Fe-GAC metal-support interaction [33]. The amount of Fe(NO$_3$)$_3$•9H$_2$O required to be dissolved in deionized water and added to the support to give the required Fe loading (w/w) is calculated by the following equation:

$$m_{Fe(NO_3)_3•9H_2O} = \frac{y_{Fe} \times M_{Fe(NO_3)_3•9H_2O} \times m_{GAC}}{M_{Fe} \times 100}$$

Where:

$m_{Fe(NO_3)_3•9H_2O}$: Mass of Fe(NO$_3$)$_3$•9H$_2$O (g);

$y_{Fe}$: Percentage of Fe$^0$ loading;
\[ M_{\text{Fe(NO}_3)_3\cdot 9H_2O} \]: Molecular weight of Fe(NO$_3$)$_3$•9H$_2$O, 404 g/mol;

\[ m_{\text{GAC}} \]: Mass of GAC support (g)

\[ M_{\text{Fe}} \]: Atomic weight of Fe, (55.85 g/mol)

### 5.2.2.1 GAC-supported nZVI Composites

GAC was first sieved to a particle size fraction using a no. 30 sieve (USA Standard Testing Sieve) to remove grains smaller than 0.595 mm. (A: GAC). Iron oxides were incorporated into the GAC surface and pores by an incipient wetness impregnation method at ambient temperature. In accordance with the methodology of Choi et al. [28], the aqueous precursor solution was prepared by dissolving 7.4 g of Fe(NO$_3$)$_3$•9H$_2$O at 60°C in a small quantity of deionized water (5 mL). Fe(NO$_3$)$_3$ solution was then added drop-wise manually into 10 g of GAC for 15 min. This process produced approximately 10% of Fe$^0$ loaded over GAC (w/w). Different mass ratios of GAC-nZVI composites (i.e. 5%, 10%, 15% and 20%) were prepared following the same procedure but modifying the amounts of GAC accordingly added into the precursor solutions. The purpose of the impregnation procedure is to have a complete and homogeneous wetting of the GAC by the dissolved iron salt, allowing the iron solution to penetrate the porous GAC structure and thus decrease the possibility of agglomeration due to the formation of clumps of liquid. For total incorporation of Fe to GAC, the resulting gel-like solid matrix was dried
at room temperature for 2 h, followed by 105°C in an oven overnight. (B: GAC-Fe(NO$_3$)$_3$).

After iron incorporation, the dried GAC-Fe(NO$_3$)$_3$ composite was further calcined in a tube furnace (Porter) under a steam of air to transform Fe(NO$_3$)$_3$ to Fe oxides. In a typical experiment, the flow rate of the carrier gas (air) was set at 50 mL/min. The solid salt sample B was heated to 150°C at a rate of 6°C/min and held for about 30 min to remove any solvent and moisture. The temperature was then increased to 300°C within 20 min using a linear ramp and maintained at 300°C for 4 h to remove all nitrate ions and decomposed the Fe (III) ions into Fe oxides. The generated Fe oxides were incorporated firmly into the GAC matrix of the composite. Finally, the reactor tube was allowed to cool down to ambient temperature and the resulting black powder was collected. To remove unincorporated free Fe oxides, the composite was again sieved using a no. 30 sieve (C: GAC-Fe oxides, GAC-nZVI composite precursor, mainly Fe$_2$O$_3$) and stored in a desiccator for further use. Materials with four different Fe loadings are prepared (5, 10, 15% and 20% (w.t.%)) and labeled as 5,10, 15 or 20% GAC-nZVI composite precursor, respectively.

GAC-nZVI composite was synthesized using a traditional reduction method whereby a strong reducing agent (i.e. NaBH$_4$) in excess amount was used to reduce GAC-Fe$_{3+}$ to
GAC-Fe$^0$ [26]. During this stage, Fe oxides (mainly Fe$_2$O$_3$) were reduced to elemental Fe$^0$ (GAC-nZVI). Based on the stoichiometric requirement, the complete reduction of 1 mol of Fe$^{3+}$ requires only 0.75 mol of BH$_4^-$; however, we carried out the excessive amount (mass ratio of BH$_4^-$/Fe$^{3+}$ = 7.4) to accelerate the synthesis reaction and ensure full reduction [34]. The reduction reaction is expressed as following:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2$$

Before synthesis, DI water, aqueous solutions and suspension of GAC-nZVI composite precursor were purged with highly pure N$_2$ for at least 2 h to remove dissolved O$_2$. All the reactions were performed in an anaerobic chamber filled with N$_2$ to prevent the oxidation of Fe$^0$. To reduce the iron oxides to nZVI particles, 0.1 g GAC-nZVI composite precursor was resuspended into 50 mL of methanol/DI water (30/70, v/v) and sonicated for about 45 min by an ultrasonic probe in an ice-water bath at 280 watts (Fisher Sonic Dismembrator, ARTEK System Corporation Farmingdale, NY) to obtain suspension of GAC-nZVI composite precursor. The pH value of the suspension was adjusted to about 7.0 by adding a 1 M NaOH solution drop by drop. The suspension was then purged with highly pure N$_2$ for at least 2 h to remove dissolved O$_2$. Under inert conditions, the suspension was transferred to a reactor flask, and an equal volume (50 mL) of a NaBH$_4$ solution (prepared to a BH$_4^-$/Fe$^{2+}$ ratio of 7.4) was added in a drop-wise manner (about
60 drops per min) to reduce Fe$^{3+}$ to elemental Fe$^{0}$ (nZVI). The suspension of GAC-nZVI composite precursor was then magnetically stirred at 25°C at 400 rpm. Following the addition of the total volume of NaBH$_4$, the mixture was allowed to homogenize for about 30 min more. After cessation of visible H$_2$ evolution, the suspension was rinsed thoroughly the deoxygenated water and immediately capped with Teflon Miniert Valves for further use. To recover the solid GAC-nZVI composite (D: GAC-nZVI), the slurry was centrifuged using a model of IEC-B-20A at a rotation speed of 9000 rpm for 15 min. and washed with copious amounts of methanol to remove free ZVI and other impurities. Finally, the composite D was dried overnight at room temperature and stored under N$_2$ atmosphere for further studies.

5.2.2.2 GAC-supported Pd/Fe$^{0}$ Bimetallic Nanoparticles

In order to synthesize Pd-doped GAC-nZVI composite, the same procedure was used as the synthesis of GAC-nZVI described above. The additional deposition of Pd over Fe$^{0}$ particles is 0.1 w.t. %. (Pd/ Fe$^{0}$, w/w) Pd was reductively deposited from palladium (II) acetate trimer [Pd(CH$_3$CO$_2$)$_2$] solution and elemental Pd was incorporated over the nZVI surface according to the following reaction [56]:

$$Pd^{2+} + Fe \rightarrow Pd + Fe^{2+}$$
Briefly, $4.7 \times 10^{-6}$ M of Pd(CH$_3$CO$_2$)$_2$ was dissolved in 20 ml of a 1:3 v/v water-methanol solution for 2 h. The freshly prepared suspension of GAC-nZVI composite was immediately mixed with the Pd acetate solution and further stirred for 15 min. Pd was doped onto the surface of nZVI particles by a displacement reaction [35]. The Pd-doped GAC-nZVI composite was then rinsed with deoxygenated water and preserved in a-60 mL reaction vial capped with Teflon Mininert Valves.

### 5.2.2.3 Monometallic Fe$^0$ Nanoparticles

To synthesize the unsupported nZVI particles, a similar procedure as the one described above was used, except that no GAC was added in the solution at the beginning of the reaction. nZVI particles were prepared by the reduction of an aqueous solution of FeSO$_4$•7H$_2$O with NaBH$_4$ solution [36]. Briefly, 50 mg of FeSO$_4$•7H$_2$O was dissolved into 100 mL of deoxygenated water to achieve a solution 0.0018 M in Fe$^{2+}$. After complete dissolution of the iron salt, 100 mL of a 0.0036 M aqueous NaBH$_4$ solution was added drop-wise (1 drop per sec). During this process, the reaction flask was housed on a magnetic stirrer operating at 400 rpm inside an anaerobic chamber. In this study, the molar ratio of NaBH$_4$ to FeSO$_4$•7H$_2$O ($\text{BH}_4^- / \text{Fe}^{2+}$) was fixed to 2:1. Through the process of titration, NaBH$_4$ was introduced to reduce Fe$^{2+}$ ions to Fe$^0$, according to following reaction [37]:
\[2Fe^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 2H_2 + 4H^+\]

After the complete addition of NaBH\textsubscript{4}, the mixture was stirred continuously for an additional 30 min until visible hydrogen evolution ceased. Finally, the resulting nZVI particles were thoroughly rinsed with deoxygenated water and then transferred to a 60 mL reaction bottle immediately capped with Teflon Miniert Valves and stored in the anaerobic chamber for further use.

5.2.2.4 Bimetallic Pd/Fe\textsuperscript{0} Nanoparticles

To incorporate Pd metal, the freshly prepared nZVI suspension (see description above) was mixed immediately after synthesis with 20 mL of 4.7×10^{-6} M ethanolic solution of Pd(ac)\textsubscript{2} (methanol/water, v/v, 3/1). The concentration of the solution was adjusted to achieve the loading of 0.1 w.t. % over the total iron. The mixture was further stirred for 15 min to complete the deposition of Pd. The Pd/nZVI particles were then rinsed with deoxygenated water and preserved in a-60 mL reaction vial capped with Teflon Mininert Valves inside the anaerobic chamber.
5.2.3 Characterization of GAC-nZVI and Pd-doped GAC-nZVI Composites

The GAC-nZVI composite was characterized using microscopy and spectroscopy. GAC and nZVI particles were also characterized and the results were used as references for comparison with the composite. Particle size, morphology, and crystal structure were characterized using transmission electron microscopy (TEM), Raman spectroscopy (Raman) and X-ray diffraction (XRD). The porosity of the composite was measured by nitrogen physisorption. The Brunauer–Emmett–Teller (BET) equation was used to determine the specific surface area. In addition, H₂-temperature programmed reduction (H₂-TPR) technique was used to investigate the morphology of the iron species formed over GAC upon reduction.

5.2.3.1 Transmission Electron Microscopy

Surface morphology (size and shape) and crystallographic properties of GAC, nZVI, GAC-nZVI composite precursor (GAC-Fe oxides composite) and GAC-nZVI composite were evaluated by transmission electron microscopy (TEM) using Philips CM10 Transmission Electron Microscopy. For TEM measurements, a very dilute suspension of
sample was prepared by dispersing the particles in methanol by sonication for 20-30 min. A few drops of the resultant suspension were deposited onto a Lacey carbon-coated copper grid followed by the complete solvent evaporation in air at room temperature and then introduced into the microscope sample chamber. The particle size and size distribution were calculated using Imaging® software (Gatan Microscopy Software, Gatan Inc.). For each sample, a representative set of micrographs (roughly 20-30 TEM images) was used and the size of each particle on those micrographs was measured and analyzed. Average particle size of each sample was estimated from images of at least 150 individual particles.

5.2.3.2 BET Surface Area

Brunauer–Emmett–Teller (BET) surface area, porosity, pore diameter and distribution of GAC-nZVI and palladized GAC-nZVI composites (0.1%, w/w, Pd/nZVI) with different iron loadings (5%, 10%, 15% and 20%) were measured by N2-adsorption isotherms. Pure nZVI and GAC were also analyzed for comparison. The measurements were performed at 77 K using a Model ASAP 2010 surface area and porosimetry analyzer. (Micromeritics Inc., Norcross, GA, USA). The BET surface area of the sample was determined by the physical adsorption of nitrogen onto the surface of a fixed amount of sample and then the amount of adsorbed N2 was calculated at relative pressure ranging from 10^-6 to 0.1. The
average pore size was measured by Barrett–Joyner–Halenda (BJH) method, based on a 
N₂ desorption isotherm model. Prior to the analysis, representative samples were 
separated from the suspension and then dried at 90°C in an oven overnight and then 
degassed at 573 K for 10 hours.

5.2.3.3 X-ray Diffraction

The crystal structure and crystallinity of GAC-nZVI composite precursor (GAC-Fe 
oxides composite) was characterized with a powder X-ray diffraction (XRD) instrument 
on a Rigaku Multiflex X-ray powder diffractometer (Japan) with Cu-Kα (λ = 1.5406 Å) 
monochromatic radiation from a long fine-focus Cu tube operating at 30 kV and 15 mA. 
Scans were conducted over 2θ angles in the region from 5° to 80° with a scanning rate of 
2°/min, which covers the major species of iron, iron oxides and graphite peaks of interest. 
The obtained XRD pattern was referenced to the powder diffraction files (ICDD-FDP 
data base) to identify the crystal phase of Fe oxides species and carbon in the GAC-nZVI 
composite precursor.
5.2.3.4 Raman Spectroscopy

Raman spectra of GAC-nZVI composite precursor were obtained by a Raman spectrometer (Lab-RAM HR 800) with YAG laser (double-diode pumped Nd laser). The spectra were obtained using the excitation wavelength of 532 nm in the range of 200-2000 cm\(^{-1}\).

5.2.3.5 Temperature Programmed Reduction

H\(_2\)-temperature programmed reduction (TPR) was performed by an automated catalyst characterization system (SRI-100 TPR apparatus), equipped with a thermal conductivity detector (TCD) that monitored hydrogen uptake. In a typical analysis, 50±0.5 mg of catalyst was loaded in a quartz glass tube served as a reactor, which was sat inside a commercial tube furnace unit. TPR experiments were conducted in a reducing gas mixture agent with a composition of 5% (vol. %) of ultrahigh purity hydrogen diluted in an ultrapure argon stream (All gases were supplied by Praxair). The flow rate was maintained at 50 mL/min and monitored by a mass flow controller. Prior to each TPR run, the samples were pretreated in-situ by purging with a flow of ultrahigh purity argon (99.99%) to remove trace amounts of adsorbed water. After 10 min of the baseline
stabilization, the samples were heated from room temperature up to 800°C using a linearly elevated heating rate of 10°C/min. An isothermal hold-up of 30 min at 800°C was followed until the baseline has been restored. The temperature was measured by a thermocouple placed inside the furnace unit. After the completion of temperature program, the reaction chamber was allowed to cool down to ambient temperature at the same flow rate before removing from the tube furnace.

The TPR profile is expressed as a function of temperature (°C) vs. TCD signal (a.u.) that represents hydrogen uptake. The peaks obtained were deconvoluted using PeakFit software. The H₂ consumption rate at each reduction stage was quantified by integrating the corresponding peak areas with automatic baseline fitting using Origin 6.0 software. The system was integrally calibrated using the reduction profiles of well-known amounts of CuO (ultrahigh-purity, 99.99%). A series of GAC-nZVI composite precursors were tested to probe their reduction behavior upon the variation of temperatures and to further get an insight on the interaction between the iron oxides and carbon support and its influence on their reduction behavior.
5.2.4 TCE Adsorption and Degradation Experiments

The batch adsorption/degradation experiments were carried out in 15 mL glass serum bottles at room temperature (25°C) at pH of 7 to investigate the ability of GAC-nZVI composite to remove TCE from aqueous solution. The bottles were capped with Teflon mininert valves to minimize the loss of TCE during repetitive sampling. The headspace in the reaction bottle was set to nearly zero to minimize volatilization losses. To each reaction bottle, 0.1g/L of GAC-nZVI composite was added, followed by the addition of TCE to obtain 100 mg/L TCE aqueous solution. This was achieved by spiking pure water with 68 µL of a TCE stock solution obtained by dissolving 0.15mL of TCE in 10 mL of 2-propanol. Subsequently, the bottles were mounted on a wrist-action shaker (MISC-CAEQUIP, BURRELL 24 place wrist action shaker-115V, VWR) for vigorous mixture with good homogenization of the solutions. At specific time intervals over a one-week period, the shaker was stopped, and the reaction bottles were placed vertically to allow the particles to settle. The clear supernatant containing TCE was extracted by n-hexane and the extract was transferred to a 2 mL GC vial for TCE measurement. To investigate the removal efficiency of TCE, a comparative study was carried out using GAC, nZVI and GAC-nZVI composite. The amount of GAC and Fe⁰ nanoparticles used in these experiments was adjusted to 1 g/L and 0.1 g/L respectively. Parallel blank
experiments without the addition of composite were carried for each experiment. The effect of the deposition of catalyst Pd was also evaluated. Composites with different iron loadings were tested (5%, 10%, 15% and 20% w.t.) at a constant concentration of GAC (1g/L).

5.2.5 Analytical Methods

In this study, the residual TCE concentration after degradation was determined by solvent extraction method. n-Hexane was used as the extracting solvent. Briefly, at predetermined time intervals, 250-µL of an aliquot was withdrawn using a gas-tight syringe through a septum cap (maintaining a closed system conditions), from both the reaction and blank bottles and transferred to a 2 mL GC vial containing 1mL of n-hexane. The GC vial was then shaken for about 10 seconds and kept undisturbed for about 1 h for equilibration. Upon phase separation, the organic phase containing TCE was removed from the vial. A 1µL of this extract was withdrawn by the auto-sampler for GC analysis. All experiments were conducted in duplicates to check the consistency of results and the average value was reported.

An Agilent 7890 gas chromatography equipped with an electron capture detector (GC-ECD) was used to analyze TCE concentrations in the extracted samples of TCE/
n-hexane. Helium gas (HP, Praxair) was used as carrier gas, and the flow rate was set at 6.38 mL/min. Chromatographic separation was performed in a DB-624 capillary column. (30 m × 0.53 mm × 3 µm, J&W Scientific) The flow in the detector (Argon+CH₄ (5%)) was set to 60 mL/min. The temperature program used for the analysis of TCE by GC-ECD has an isothermal stage at 35°C for 4 min, subsequently increased to 180°C at a rate of 18°C/min and is finally held at this temperature for 5 min. A sample volume of 1µL of extracted TCE was injected into a split-less mode of GC-ECD in order to determine the concentrations of residual TCE in sample after adsorption. Similarly, 1µL of a standard blank solution (without adsorption) was also injected into the GC-ECD. The retention time of TCE was close to 8.5 minutes under these conditions.

5.2.5.1 TCE Calibration Curve

Initially, stock solutions of TCE were spiked by dissolving reagent-grade TCE into 2-propanol and appropriate volumes of the stock solutions were diluted through gas-tight syringes into a series volumes of glass vials to achieve the desired TCE concentrations. The glass vials were sealed with a 20 mm Teflon coated rubber stopper to minimize solvent evaporation. Prior to analysis of the samples by GC, the response factor and the detection linearity for the standard were established. Standard calibration curves for TCE were generated in 2-propanol and DI water by using solutions containing known
concentrations of TCE. The linear range of detection for the internal standard of TCE was determined as 15-155 mg/L with a detection limit of 0.5 mg/L, and all the sample extracts were analyzed within this range [38]. The calibration curves were used to calculate the concentrations of TCE in the reaction solutions. All samples in this study were analyzed following this protocol.

5.3 Results and Discussion

5.3.1 Characterization of GAC-nZVI Composites

5.3.1.1 Morphology Study

The microstructure and morphology of uncoated nZVI particles and GAC-supported nZVI composites were analyzed through transmission electron microscopy (TEM). A typical TEM image of nZVI particles is presented in Fig. 5.1 (a). From the TEM image, it is observed that most of the particles are nearly spherical in shape and relatively uniform in size. In aqueous solution, nZVI particles easily agglomerate to form chain-like clusters and this is mainly attributed to the magnetic and electrostatic interactions between the metallic particles, resulting in reduction of the available reactive surface area for contaminant degradation. The formed spherical agglomerates have the particle size up to
1 micron. **Fig 5.1 (b)** indicates that a representative single nZVI particle consists of a Fe$^0$ interior core with higher density, which is surrounded by a relatively uniform shell of iron oxides with lower density. The average particle size of nZVI particle is approximately 50-60 nm and the oxidative shell has a thickness about 5 nm. **Fig. 5.1 (c)** shows a representative TEM image of neat GAC grain. It is clearly illustrated that the bare GAC grain exhibits distinct mesoporous morphology and poses high porosity.
Fig. 5.1 Typical TEM images: (a) nZVI particles; (b) single nZVI particle; (c) GAC grain
**Fig. 5.2** shows the representative TEM micrographs of the GAC-nZVI composite, with Fe loading of 10 w.t. %. As depicted in **Fig. 5.2**, GAC-nZVI composites are roughly spherical in shape and fairly homogeneous distributed throughout the GAC support. The presence of nZVI particles were visualized clearly as the dark spherical dots due to their high electron density, by contrast, GAC support appears as light gray regions because of the lower electron density. As clearly evidenced by the TEM image in **Fig. 5.2 (a)**, the majority of nZVI particles were incorporated inside the pores of GAC based on the observations that many pores were disappeared. Some nZVI particles are also observed attached onto the surface of the GAC grains, as illustrated in **Fig. 5.2 (b)**. In addition, no obviously large size domains of isolated nZVI particles were found and most nZVI particles were associated with GAC material. This indicates that the nZVI particles are well dispersed over the GAC support. The interaction between nZVI particles and GAC grains prevents the agglomeration of nZVI particles. Chang et al. [30] prepared Cu-doped nZVI bimetallic nanoparticles with activate carbon support by a similar method and confirmed that there was a strong association between the carbon support and the Cu/Fe\(^0\) nanoparticles from TEM images. They also indicated that the immobilization of metallic particles with AC prevented their agglomeration, which was caused by magnetic interactions between the particles and therefore maintain their high surface area and reactivity.
Fig. 5.2 TEM images of GAC-nZVI composites
5.3.1.2 Particle Size Distribution

Particle size distributions of nZVI particles and GAC-nZVI composite were manually estimated from 20-30 representative TEM images obtained by each sample, using Imaging® software. **Fig. 5.3** represents a comparison histogram of the obtained particle size distributions of nZVI particles and GAC-nZVI composite. The estimated average particle size of unsupported nZVI was calculated around 55 nm. More than 90% of particles have a diameter in the range of 1-65 nm and a few particles exist mainly as aggregates with diameters above 90 nm. Compared to the bare nZVI particles, the Fe\(^0\) nanoparticles on the GAC support have a slightly smaller average diameter (35 nm). In this composite, nearly 80% of composites appear in the range of 20-60 nm, less than 15% are smaller than 20 nm in diameter and a few particles are as large as 80 nm. This indicates not only a better dispersion of nZVI particles over GAC support but also a narrower diameter distribution. Mackenzie et al. [31] prepared a new type of CIC composite material and observed that the majority of the iron occurred as small clusters on the inner carbon surface with 30-50 nm in diameter, which is in agreement with our observations.
Fig. 5.3 Particle size distributions of nZVI particles and GAC-nZVI composite from TEM images

5.3.1.3 BET Surface Area and Pore Properties

Fig. 5.4 (a) and (b) show the N$_2$ adsorption-desorption isotherms obtained for neat GAC material and GAC-nZVI composite, respectively. Both GAC and GAC-nZVI samples exhibit a typical IV-type N$_2$ adsorption/desorption isotherm with a small hysteresis loop. According to the International Union of Pure and Applied Chemistry (IUPAC) classification [39], a IV-type isotherm with a clear hysteresis loop between adsorption and desorption isotherms indicates the presence of a well-developed mesoporous structure. This mesoporous system enables a good dispersion of nZVI particles over GAC support [40]. In addition, the adsorption capacity of GAC-nZVI composite for N$_2$ is
smaller than that of neat GAC, probably due to the presence of nZVI particles. As shown in Table 5.1, the imbedded nZVI particles within the pores of GAC likely contribute to the decrease on BET surface area. NaBH₄ solution entered into the inner pores of GAC matrix and reduce Fe³⁺ to generate nZVI particles. The disappearance of mesopores inside the GAC matrix decreases the BET surface area of GAC-nZVI composite, accordingly resulting in the decline on the N₂ adsorption capacity.
Table 5.1 summarizes the BET surface areas, total pore volumes and average pore sizes derived from N$_2$ adsorption/desorption isotherms at 77 K for GAC, GAC-nZVI composite precursor, GAC-nZVI composites with different Fe loadings and palladized GAC-nZVI composite, respectively. As shown in Table 5.1, neat GAC material has a BET surface area of 600 m$^2$/g and an average pore volume of 0.58 cm$^3$/g. The GAC-nZVI composite precursor has a slightly lower surface area (552 m$^2$/g), while the GAC-nZVI
composites have further decreased surface areas ranging from 454 to 345 m²/g. In addition, the corresponding total pore volume for GAC-nZVI composite precursor (5%, w/w) and GAC-nZVI composite (w/w, 5%) were determined to be 0.49 and 0.42 cm³/g respectively, which are smaller than that of pure GAC (0.58 cm³/g). The average pore size decreased as well from 4.34 nm of neat GAC to 3.86 nm of GAC-nZVI composites. For the palladized GAC-nZVI composite, the BET surface area, total pore volume and average pore size were 348 m²/g, 0.29 cm³/g and 3.12 nm, respectively, which are slightly smaller than the GAC-nZVI composite with the same Fe⁰ loading (15%, w/w).
Table 5.1 BET surface areas and porosities of neat GAC, GAC-nZVI composite precursor, GAC-nZVI composites and Pd-doped GAC-nZVI composite

<table>
<thead>
<tr>
<th>Composition</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume a (cm³/g)</th>
<th>Average pore size b (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>600</td>
<td>0.58</td>
<td>4.34</td>
</tr>
<tr>
<td>GAC-nZVI precursor (5%)</td>
<td>552</td>
<td>0.49</td>
<td>4.17</td>
</tr>
<tr>
<td>GAC-nZVI d (5%)</td>
<td>454</td>
<td>0.42</td>
<td>3.86</td>
</tr>
<tr>
<td>GAC-nZVI d (10%)</td>
<td>391</td>
<td>0.39</td>
<td>3.51</td>
</tr>
<tr>
<td>GAC-nZVI d (15%)</td>
<td>351</td>
<td>0.36</td>
<td>3.37</td>
</tr>
<tr>
<td>Pd-doped GAC-nZVI (0.1% Pd, 15% Fe)</td>
<td>342</td>
<td>0.29</td>
<td>3.12</td>
</tr>
<tr>
<td>GAC-nZVI d (20%)</td>
<td>345</td>
<td>0.35</td>
<td>3.36</td>
</tr>
</tbody>
</table>

a Single point adsorption total pore volume at P/Pₒ=0.98; b Adsorption average pore diameter (4 V/A by BET); c Mass ratio of iron oxide particles to GAC is 5% (Fe w/w); d Mass ratio of nZVI particles to GAC is 5% to 20% (w/w); e Mass ratio of nZVI particles over GAC is 15% (w/w) and Pd loading in the composite is 0.1% over Fe (w/w, Pd/nZVI)
In contrast to neat GAC, the BET surface area and total pore volume of GAC-nZVI composite precursor decreased from 600 to 552 m$^2$/g and 0.58 to 0.49 cm$^3$/g, respectively. This tendency can be explained by proposing that the mesoporous structure of GAC was partially occupied by the formed iron oxides particles. Further decreases on the BET surface area to 454 m$^2$/g and total pore volume to 0.42 cm$^3$/g are the results of reduction of Fe oxides to disordered Fe$^0$ nanoparticles [41]. The deposition of palladium does not significantly affect BET surface area. The values observed at these higher loadings indicate that the nZVI particles are well incorporated into the internal pores of GAC, causing partial clogging and blockage of the available GAC mesopores and micropores [41]. The average pore sizes of the GAC-nZVI composites with and without Pd are relatively smaller than that of neat GAC, further confirming this hypothesis.

Choi et al. [28] reported a similar phenomenon by synthesizing the GAC/ZVI/Pd composites using a similar incipient wetness impregnation method. The authors indicated that the composite contained 14.4% of Fe and 0.68% of Pd content and the BET surface area of GAC/ZVI decreased from 574 m$^2$/g (for GAC) to 369 m$^2$/g and further decreased slightly to 358 m$^2$/g with deposition of Pd. In addition, the pore volume (0.375 cm$^3$/g) and pore sizes (4.07 nm) of GAC/ZVI composites were smaller than those of neat GAC (0.639 cm$^3$/g and 4.45 nm). Our observed values (see Table 5.1) differ no more than 8% compared to their reported values. In our case a similar trend for a decrease on BET
surface area, pore volume and pore size is observed, further confirming that our results are consistent with the previous reports. In addition, Tseng, et al [32] measured the surface areas and porosity of the composites GAC-ZVI and GAC-ZVIP (using polyethyleneglykol as dispersant) and two different calcination temperatures. They found that the BET surface areas of the composites ranged from 782.6 to 826.1 m$^2$/g, which were smaller than that reported for neat GAC (930 m$^2$/g). The higher BET surface areas, compared to those observed in our case, can be attributed to the higher surface area of their GAC starting material.

With an increase on the Fe$^0$ loading from 5% to 20%, the surface area and pore volume of the composites were observed to decrease from 454 to 345 m$^2$/g and 0.42 to 0.35 cm$^3$/g, respectively. In other words, finally around 43% of BET surface area and 40% of pore volume of GAC were occupied by nZVI particles. The decreases are not linear and seem to be reached a plateau at the loading of 15% (shown in Fig. 5.5). The average pore size shows a similar trend as well. Composite with Fe$^0$ loadings of 15% and higher exhibited a sensible decrease on the BET surface area, total pore volume and average pore size, which could be attributed to blockage of the GAC pores. The pore blockage seems to reach its maximum at the Fe loading of 15 w.t. %. However, although the pores of GAC are blocked by the presence of nZVI particles, even at 20% iron loading, the GAC-nZVI
composite still retains relatively large surface area (345 m$^2$/g) and high pore volume (0.35 cm$^3$/g) values, which are typical for a porous material [42].
Fig. 5.5 Influences of different Fe loadings on (a) BET surface area, (b) total pore volume and (c) average pore size
5.3.1.4 Identification of Iron Species in GAC-nZVI Composites

During calcination at 300°C, four iron oxides: Fe$_3$O$_4$ (magnetite), γ-Fe$_2$O$_3$ (maghemite), α-Fe$_2$O$_3$ (hematite) and α-FeO(OH) (goethite) are possibly decomposed from the GAC-Fe oxides precursor (ferric nitrate) [43] and accumulated inside the pores of GAC support. In order to validate the composition of iron oxides formed in the calcination process, GAC-nZVI composite precursors (GAC-Fe oxides composite) were analyzed by powder X-ray diffraction (XRD). Fig. 5.6 presents the XRD patterns for GAC-nZVI composite precursor with 15% Fe$^0$ loading to identify iron oxides species. XRD patterns for the samples with lower Fe$^0$ loadings of 5% and 10% are similar to that of 15% loading, however, the Fe oxides signals are less significant at lower loadings, thus we used 15% loading of Fe$^0$ as an example. XRD pattern for 20% loading of Fe$^0$ is almost identical to that of 15% loading, and thus it is not included here.
As shown in Fig. 5.6, a major peak was observed at 26°, corresponding to the graphitic carbon structure of GAC [44]. The presence of hematite (α-Fe$_2$O$_3$) is confirmed by the peaks at 24, 33, 36, 41, 54, 62 and 64° in the XRD pattern [45]. In addition to the dominant extensive of α-Fe$_2$O$_3$ phase, minor signatures of magnetite (Fe$_3$O$_4$) (2θ=57°) and perhaps goethite (FeO(OH)) (2θ=27°) are also observed. Therefore, α-Fe$_2$O$_3$ peaks dominate the XRD patterns, indicating that the adsorbed iron salts have been decomposed to form primarily α-Fe$_2$O$_3$ nanoparticles during the calcination step for all GAC-nZVI composite precursors with different Fe$^0$ loadings. The results are in good agreement with the observations reported by Chang et al. and Choi et al. Choi et al. [28] studied the crystallographic properties of GAC composites and the XRD pattern identified that the
iron oxides phase in GAC-ZVI precursor samples was mainly hematite. Chang et al. [30] examined the XRD of the unsupported and supported nanoscale particles and further confirmed that the $\alpha$-$\text{Fe}_2\text{O}_3$ or $\text{Fe}_3\text{O}_4$ particles were main iron oxides generated from the decomposition of the GAC-Fe salt composite.

Raman spectroscopy was additionally carried out to get a deeper insight into the crystalline structure of the GAC-nZVI composite precursor. Raman spectrum of the GAC-nZVI composite precursor (15% $\text{Fe}^0$ loading) in the range of 200-2000 cm$^{-1}$ is shown in Fig. 5.7. The two characteristic broad peaks located at 1328 cm$^{-1}$ and 1584 cm$^{-1}$ are corresponded to the D-band and G-band of graphitic structures present in GAC. The three peaks observed at 211, 264 and 479 cm$^{-1}$ are assigned to hematite, which is in a good agreement with previous Raman values reported for $\alpha$-$\text{Fe}_2\text{O}_3$ in the literatures [46, 47]. Raman spectra of 5%, 10% $\text{Fe}^0$ loadings were also analyzed and the occurrence of peaks are similar to that of 15% $\text{Fe}^0$ loading with less intensities. 20% $\text{Fe}^0$ loading has an almost identical Raman spectrum to that of 15% $\text{Fe}^0$ loading. Therefore, Raman spectra of GAC-nZVI composite precursors with different $\text{Fe}^0$ loadings all confirm the presence of $\alpha$-$\text{Fe}_2\text{O}_3$ nanoparticles in the composites.
5.3.1.5 Temperature Programmed Reduction

Temperature-programmed reduction (TPR) is a well-established technique, particularly suited to characterizing metallic catalysts, including metal oxides, mixed metal oxides or metal oxides dispersed on a support. Typically, a TPR experiment provides the qualitative information on the different phases present, their reducibility and the strength of metal-support interaction. For the case of a bimetallic system, the TPR pattern can further indicate the influence of a dopant promoter and the interaction between the two components. In addition, quantitative information can be determined from the measurement of the consumption of the reducing gas (H₂).
The TPR reduction profile of GAC-nZVI composite precursor (5 w.t.%) is presented in Fig. 5.8 (a). Both XRD and Raman measurements indicate that the major phase of iron oxides present in the GAC-nZVI composite precursor is $\alpha$-Fe$_2$O$_3$. As a reference material, a TPR profile of pristine $\alpha$-Fe$_2$O$_3$ was obtained and the result is presented in Fig. 5.8 (b). For reference, the H$_2$-TPR pattern corresponding to neat GAC sample is also included (Fig. 5.8. (c)). For the neat GAC support, there is a broad peak between 350-600°C, which could be assigned to the gasification of GAC. However, the intensity of the reduction peak was much less significant compared to those peaks obtained for GAC-nZVI composite precursor, indicating that the contribution of GAC support to the reducibility of GAC-nZVI composite precursor is negligible relative to the contribution of pristine $\alpha$-Fe$_2$O$_3$ catalyst.
Fig. 5.8 TPR profiles: (a) GAC-nZVI composite precursor (5%, w/w); (b) pristine α-Fe₂O₃; (c) neat GAC support
For unsupported crystalline $\alpha$-Fe$_2$O$_3$, as shown in Fig 5.8 (b), the TPR profile consists of two characteristic fairly defined reduction peaks, which is typical of two-stage $\alpha$-Fe$_2$O$_3$ reduction to metallic $\alpha$-Fe$^0$ [48]. The first peak appeared at ca. 295°C, which is associated with a transformation stage of Fe$_2$O$_3$ to magnetite (Fe$_3$O$_4$) [48]:

$$3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$$

The second broader peak, with maxima about 405°C, corresponds to the further reductive transition of Fe$_3$O$_4$ to metallic Fe$^0$ [48]:

$$\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe}^0 + 4\text{H}_2\text{O}$$

The large width of peak B indicates that the phase transformation of Fe$_3$O$_4$ to metallic Fe$^0$ is a slow process, which is consistent with previous reports [49].

As Fe$_2$O$_3$ particles were decomposed from iron salt, the GAC-nZVI composite precursor exhibited a TPR profile with multiple reduction peaks in the temperature range of 300–800°C. Reduction starts at 300°C (Fig 5.8 (a)), showing two fairly separated temperature regions. During the low temperature range, a primarily strong H$_2$ uptake was observed at around 410°C, which could be assigned to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$. In the higher
temperature region, two heavily overlapped peaks can be observed, which could be
decovoluted into two contributions. A broader minor peak situated around 580°C, can be
attributed to the subsequent reduction of Fe₃O₄ to FeO [48]:

$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$$

A shoulder on the second peak centered about 720°C, can be interpreted as the transition
of FeO to metallic Fe⁰ [48]:

$$FeO + H_2 \rightarrow Fe^0 + H_2O$$

The comparison on the reduction behavior of crystalline α-Fe₂O₃ particles and the
GAC-nZVI composite precursor clearly indicates that the presence of the GAC support
affects the thermal stability of the iron oxide species. Indeed, the reduction of the
GAC-nZVI composite precursor was accomplished by a three-stage reduction mechanism
(Fe₂O₃ → Fe₃O₄ → FeO → Fe⁰), rather than the commonly accepted reduction
proceeding in two steps via a Fe₃O₄ intermediate observed on the unsupported Fe₂O₃
particles. It is well known that bulk-phase FeO is thermodynamically metastable below
570°C and easily decomposed into α-Fe⁰ and Fe₃O₄ [50]. Thus a FeO phase during the
reduction process of crystalline Fe₂O₃ to Fe⁰ (Fig. 5.8a) is not observed since full
reduction is accomplished below 500°C. However, in the presence of GAC support, the metastable FeO phase is stabilized [51], which can be attributed to the strong interaction between Fe oxides and GAC support [52]. Indeed, another evidence of the strong metal oxide-support interaction is the high temperature needed to accomplish full iron oxides reduction in the GAC-supported material (800°C vs. 480 °C in crystalline Fe₂O₃). Choi et al. [28] also analyzed the H₂-TPR patterns on the GAC/Fe₂O₃ composites and observed a major peak located at 450°C and a second broad minor peak ranging from 570-800°C. They assigned the first large peak to the reduction of Fe₂O₃ to Fe₃O₄, while the second broad range could be contributed to two transformations: one below 700°C explained the reduction of Fe₃O₄ to FeO, and another above 700°C referred to the reduction of FeO to Fe⁰. They suggested that the reduction temperature (450°C) of Fe₂O₃-GAC was higher than the normally reported values in literature (350-400°C), which was a result of a strong Fe-GAC metal-support interaction; this is in good agreement with our results.

Influence of Fe Loading

In order to investigate the impact of Fe loading on the reducibility, a series of GAC-nZVI composite precursors with different Fe loadings were prepared by mass ratios of 5%, 10%, 15% and 20% (w/w, Fe/GAC) and all the samples were characterized by H₂-TPR experiments. Fig. 5.9 shows the reduction profiles of GAC-nZVI composite precursors
with various Fe loadings. As exhibited, all four TPR patterns have similar shapes, showing three distinct regions in the temperature range of 250-800°C. With an increase on the Fe loading from 5% to 20%, the first reduction peak (~400°C), corresponding to the reduction of α-Fe₂O₃ to Fe₃O₄, shifts toward higher temperatures from 410°C to 450°C. The reduction peaks at ~600°C and ~700°C follow the same trend. The results qualitatively reflect a decrease in the overall reducibility of the GAC-nZVI composite precursor as Fe loading increases. As discussed previously, the comparison on the TPR patterns between GAC-nZVI composite precursor and crystalline Fe₂O₃ catalyst indicates that a significant α-Fe₂O₃-GAC interaction is taking place in the composite precursor, which suppresses the reducibility of α-Fe₂O₃ particles. As Fe loading increases, the interaction between α-Fe₂O₃ and GAC becomes pronounced, leading to a decrease in the reducibility of α-Fe₂O₃. The stronger interaction could be explained by a higher dispersion of α-Fe₂O₃ particles over GAC support. In the GAC-nZVI composite precursor, α-Fe₂O₃ particles interact well with GAC support and the dispersion of α-Fe₂O₃ on the support is very effective. This observation is consistent with the BET and TEM results and may be associated with a decrease in iron oxide particle size [53].
Fig. 5.9 TPR profiles of GAC-nZVI composite precursors with different Fe$^0$ loadings (5% to 20%, w/w)
Promotion Effect of Palladium

In addition to study on the reducibility of GAC-nZVI composite precursors, TPR technique was also used to characterize the reduction profiles of a series of palladium (Pd)-promoted GAC-nZVI composite precursors. These catalysts were prepared by the deposition of 0.1% (w/w) of Pd onto the GAC-nZVI composite precursors. For all composites, the content of Fe varied from 5% to 20% (w/w), whereas the amount of Pd for all samples kept constant at 0.1 w.t. %. (Pd/Fe, w/w) The main objective focuses on investigating the promoting effect of the dopant noble Pd metal on the reducibility of the GAC-nZVI composite precursor. The TPR profiles of 0.1% Pd-promoted GAC-nZVI composite precursors with increasing Fe loadings (5% to 20%) are presented in Fig. 5.10.

All TPR profiles display five reduction peaks in a broad profile extending from 100°C to 800°C (Fig.5.10). A small negative peak at 120°C can be observed, which could be attributed to desorption of hydrogen from the palladium surface or the decomposition of a bulk palladium hydride formed with the reduced Pd-crystallites [54]. In contrast with the GAC-nZVI composite precursor, the reduction profiles of the composites with dopant Pd metal show a hydrogen-uptake peak at 245-277°C for different Fe loadings. This distinct peak is attributed to a consumption of hydrogen by oxidized palladium [55]:
\[ H_2 + PdO \rightarrow Pd + H_2O \]
Fig. 5.10 TPR profiles of Pd-doped GAC-nZVI composite precursors with different Fe loadings (Fe⁰/GAC: 5%-20%, w/w; Pd loading is 0.1 w.t.%)

The reduction temperature is higher than the typically reported values (normally around 110°C) [56-58], probably due to the differences in terms of palladium loading, substrate type (GAC in this study), calcination temperature and ramp rate during TPR [57]. Besides
the hydrogen uptake corresponding to palladium oxide reduction, the Pd-impregnated GAC-nZVI composite precursors all present two characteristic reduction peaks. One appears at about 400°C, corresponding to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ and a second one consists of two overlapped peaks, with maxima around 580°C and 720°C, respectively. We attribute the reduction peak at ~ 580°C to the formation of intermediate FeO phase, whereas the small hydrogen consumption peak at about 720°C is linked to the final transition of FeO to metallic Fe.

Compared to the TPR profiles of Pd-free GAC-nZVI composite precursor, the Pd-doped composite precursor shows a shift of the reduction peaks corresponding to iron oxide species toward lower temperatures. This clearly indicates that Pd metal promotes the reduction of iron oxide species in the GAC-nZVI composite precursors. This is consistent with the previous observations reported that a promoting catalytic effect on the reducibility of pristine Fe$_2$O$_3$ by palladium via hydrogen activation, which especially affects the transformation of Fe$_2$O$_3$ to Fe$_3$O$_4$ [59]. This enhanced reducibility is presumably related to the spillover effect of activated hydrogen on the surface sites of the previously reduced metallic Pd promoter at relatively lower temperature and its subsequent reductive reaction with Fe$_2$O$_3$ species [60].
5.3.2 Adsorption and Dechlorination of TCE by GAC-nZVI and Pd-doped GAC-nZVI Composites

The performance on TCE removal from aqueous solution by the GAC-nZVI composite (nZVI/GAC, 10 w.t.%) is illustrated in Fig. 5.11. TCE degradation using bare nZVI particles and adsorption by neat GAC were also carried out for the purpose of comparison. Parallel blank samples were prepared as well without any reaction materials. To eliminate the influence by different iron loadings, the amount of GAC in each reaction vial was adjusted to keep the initial total content of iron constant. Under the same operating conditions, TCE removal efficiency (expressed as $C/C_0$) is measured as a function of reaction time ($t$, h), in which $C_0$ (mg/L) is the initial TCE concentration in the solution and $C$ (mg/L) is the concentration at time $t$. As illustrated in Fig. 5.11, the gentle disappearance of TCE onto GAC is attributed to adsorption, with equilibrium reached after 72 h. Because of its high surface area and large porosity, GAC acts as a good adsorbent for various contaminants, however the chemical identities of these contaminants remain intact in the GAC pores and still potentially pose a threat to the environment [26]. For bare nZVI particles, a partial TCE degradation (about 18% reduction) was observed after 3 days. In this case, when the nZVI particles were exposed to TCE-containing solutions, there was an initially rapid decline of TCE concentration
followed by a subsequently slower degradation possibly due to either the formation of a passivation layer on the surface of nZVI particles [7] or the aggregation of nZVI particles [12].

Fig. 5.11 Comparison of removal efficiency of TCE by nZVI, neat GAC and GAC-nZVI composite (Reaction conditions: $C_0$: 100 mg/L; GAC: 1 g/L; Fe$^0$: 0.1 g/L, GAC/nZVI: 1g/L, mass ratio of nZVI/GAC: 10 w.t. %; T=25 °C, pH=7); error bars are standard deviations of duplicates.
When the GAC-nZVI composite was used, a gradually increased amount of TCE (up to 48%) was effectively removed from the aqueous solution after 60 hours. This result clearly indicates that GAC-nZVI composite displays a higher capacity for the dechlorination of TCE than the corresponding unsupported nZVI or neat GAC. The apparent enhancement of TCE removal efficiency might be a combined consequence of physical adsorption by GAC and reductive degradation by nZVI particles. The commercially lignite-based GAC (HD-3000) has a surface area of 600 to 675 m$^2$/g and thus is an ideal support to enhance the dispersivity of nZVI particles. The well-developed porous structure of GAC inhibits aggregation of iron nanoparticle [25], resulting in more available reactive sites for TCE degradation. Moreover, it is well established that unsupported nZVI particles easily passivate when exposed to air or water [60, 61]. Incorporation of nZVI particles into the GAC matrix could potentially prevent the passivation of nZVI surface and accelerate the corrosion of nZVI particles. As a result, with coupling with GAC support, the reductive reactivity of the impregnated nZVI particles is promoted.

In addition to their inherent aspects of stabilizing effect, GAC could also be used as an ideal adsorbent material to provide a large number of adsorptive sites for TCE adsorption. It is speculated that the strong adsorption capacity of GAC enhances the mass transfer of TCE in the aqueous solution. The solubilized TCE is attracted by the GAC adsorption to
partition from the aqueous phase and thereby accumulate in close proximity to the imbedded nZVI particles in the pores of GAC and dispersed nZVI particles on the surface of GAC, as observed in similar systems [62]. The adsorbed TCE could be regarded as an elevation in the local concentrations of TCE in the vicinity of reactive nZVI sites and thus facilitates the reductive reactivity of nZVI particles. Overall, it is observed that the remediation efficiency of TCE is improved when the nZVI particles are incorporated into the GAC support. The plausible mechanism of TCE degradation by the GAC-nZVI composite thus would involve the adsorption of TCE on GAC followed by degradation by nZVI.

In comparison with the adsorption of TCE by MWCNTs (discussed in Chapter 3.3.2.1, Fig. 3.5), there was no obvious lag-phase for the adsorption by GAC. The chemical structure of GAC is similar to that of MWCNTs and the surface area of GAC is normally in the range of 600 m²/g, slightly higher than that of MWCNTs (233 m²/g). Thus, it seems that neither surface area nor chemical properties could be used to explain the absence of the lag-phase for GAC adsorption completely. In the case of MWCNTs, the possible explanation for the presence of lag-phase is linked to internal diffusion. In contrast to the typically porous structure of GAC, MWCNTs have a unique morphology, appearing as loose and intertwined tubular structure. Beside the surface adsorptive sites, the interstitial channels and grooves present between the tube bundles and the inner pores
of the tubes could also provide available adsorption sites. While the external surface of MWCNTs is generally accessible for adsorption, the TCE molecules need time to diffuse into the interstitial and inner pores of the tubes, potentially resulting in a lag-phase of the initial adsorption stage. This hypothesis could be explored by increasing the shaking speed of the reaction bottles. If the lag-phase becomes shorter or even disappears with higher shaking speed, we could suggest that the lag-phase of TCE adsorption by MWCNTs is a result of the internal diffusion of TCE molecules.

Tseng et al. [32] investigated the adsorption and/or dechlorination of the TCE onto ZVI, GAC and GAC-ZVI composites. They detected that complete adsorption of TCE was achieved after around 300 min. However, in our study, a maximum of 48% of TCE was adsorbed by GAC within 60 h. The lower adsorption capacity and longer adsorption time may be caused by the lower GAC content (1 g/L) and much lower surface area (600 m$^2$/g). The GAC used in our study was HD-3000 type with a surface area of 600 m$^2$/g, which was much smaller than that used in Tseng’s study (Activated Carbon Calgon Filrasorb 400, surface area: 930 m$^2$/g). Moreover, Tseng et al. [32] used 5 g/L of GAC for all experiments, which was 5 times higher than GAC concentration used in our study (1 g/L). On the other hand, they observed that TCE was partially degraded using ZVI alone (up to 20%), which was consistent with our results (18%). Although Tseng et al. [32] used larger amounts of GAC and the Fe$^0$ loading was only 3%. Thus it means that
the Fe\textsuperscript{0} content was 0.15 g/L, which is similar as the Fe\textsuperscript{0} concentration used in our experiment (0.1 g/L). They indicated that the GAC-ZVI composites exhibited a much higher dechlorination capacity for TCE removal than the individual ZVI particles, which was in good agreement with our observations.

5.3.2.1 Catalytic Effect of Palladium

In order to investigate the catalytic effect of palladium over the GAC-nZVI composite for the removal efficiency of TCE, an extremely small amount of Pd (0.1w.t.%) was impregnated onto the surface of nZVI particles. During a reaction time of 24 hours, the reactivity characteristics of the Pd-doped GAC-nZVI composite were evaluated and compared with that of unsupported Pd/nZVI particles. As shown in Fig. 5.12, with the deposition of a small amount of Pd onto the surface nZVI particles, the overall TCE removal efficiency dramatically increased for both the unsupported and supported GAC-nZVI systems. Bare Pd/nZVI particles completely degraded TCE within 36 h, whereas complete TCE removal was achieved by only 18 h for the Pd-doped GAC-nZVI composite. In contrast, Pd-free composite dechlorinated TCE much slower and eventually reached only 48% removal. Thus, it is concluded that the deposition of Pd metal to the surface of the GAC-nZVI composite greatly improved the overall reaction for TCE removal. The catalytic effect of Pd on the nZVI-MWCNTs composite was discussed in
Chapter 4. In that case it was also observed that dechlorination of TCE significantly improved with Pd addition. For the case of Pd/nZVI-MWCNTs, complete dechlorination of TCE was observed within 6h, which further demonstrated the catalytic promotion effect of palladium on carbon-supported Fe⁰ nanoparticles for TCE dechlorination.

Fig. 5.12 Effect of Pd loading on the nZVI particles and GAC-nZVI composites (reaction conditions: C₀: 100 mg/L; GAC: 1 g/L; Fe⁰: 0.1 g/L, GAC-nZVI: 1g/L, mass ratio of nZVI/GAC: 10 w.t. %; Pd: 0.1 w.t. %, T=25°C, pH=7); error bars are standard deviations of duplicates.

Nyer et al. [63] reported that the degradation of TCE by Fe⁰ particles is a surface-mediated reaction that occurred on the surface of the Fe/H₂O interface. In a monometallic nZVI system, oxidation of nZVI particles donates electrons, which are
transferred from Fe metal to directly degrade TCE compounds. With the presence of Pd on the surface of nZVI particles, gaseous H\textsubscript{2} formed via the electrolysis of water, is available to degrade TCE by hydro-dechlorination [64]. The dissociative activation of gaseous H\textsubscript{2} is catalyzed by Pd metal to produce the active atomic H\textsubscript{ad} over the Fe\textsuperscript{0} surface. The formation of H\textsubscript{ad} species results in the generation of a powerful secondary reducing agent, which in turn facilitates the acceleration of reaction rates of TCE degradation [65].

5.3.2.2 Influence of Fe Loading

To evaluate the influence of Fe loading on the performance of TCE dechlorination and get an insight on the mechanism of TCE removal form aqueous solution, GAC-nZVI composites with different nZVI loadings (i.e. 5%, 10%, 15% and 20%) were tested. To synthesize a set of composites with various Fe loadings, the amount of Fe initially added was constant, accordingly modifying the dosage of GAC added to achieve the desired mass ratios. All other conditions for the experiment remain unchanged and the results are presented in Fig. 5.13. It can be seen that all composites exhibited TCE removal efficiencies in the range of 43-58% during a reaction time of 72 h. At the lowest Fe loading (5%, w/w), the final TCE removal efficiency was observed only 40%. When the Fe loading in the composite increased to 20% (w/w), up to 60% of TCE was effectively removed.
Fig. 5.13 Effect of mass ratios of nZVI to GAC on TCE removal (Reaction conditions: initial TCE: 100 mg/L; GAC-nZVI: 1g/L, T=25°C, pH=7); error bars are standard deviations of duplicates.

In all these experiments, the absolute Fe concentration was kept constant (6 mg Fe/60 mL). As the mass ratios of Fe/GAC increased, the absolute dosage of GAC in the composite accordingly decreased. Theoretically, the smaller amount of GAC would result in a decrease on the adsorption capacity of TCE. However, the composite’s TCE removal efficiency was observed to increase at lower GAC dosages. This observation can be rationalized by proposing that the adsorption of TCE by GAC plays a minor role on the removal of TCE from aqueous solution at higher Fe loadings. Although the absolute Fe dosage is almost identical in all composites, the BET and TPR results indicated that the
composites with higher Fe loadings displayed smaller BET surface areas and smaller particle sizes. In principle, the composite with a higher Fe loading should present a lower dechlorination reactivity of TCE. Inversely, the experimental observations indicate that the reductive reactivity of TCE was enhanced at the higher Fe loadings. (i.e. Iron is easier to oxidize in the composites with higher Fe loadings.) We should also mention that this observation is in agreement with the TPR results, where the reducibility of iron decreased at higher Fe loadings. It could be proposed that at the higher Fe/GAC mass ratios, nZVI particles are primarily dispersed on the surface of the GAC grain rather than incorporated into the GAC pores, as opposed to the inner pores that would be filled first during Fe impregnation at lower Fe loadings. Reactive nZVI particles may be then readily available for TCE reduction without presenting the mass transfer limitation of TCE due to the slow diffusion that TCE will experience while trying to reach the iron species inside the GAC pore network.

Tseng et al. [32] studied the effect of different doses of the composites on the removal of TCE from the aqueous solutions. They changed the concentration on iron in their composites from 5 to 10 g/L by keeping the Fe$^0$ loading constant (ZVI content was 2.15%×weight of GAC-ZVI). As expected, the usage of a higher dosage resulted in a more reducing environment and thus a larger amount of TCE dechlorinated. However, in our study, we kept the Fe$^0$ concentration in the aqueous suspensions unchanged (0.1g/L)
but increased the Fe loading of the solid material from 5% to 20% by accordingly changing the absolute mass of Fe/GAC added to the suspension. Therefore, the higher TCE dechlorination capacity associated with higher Fe\(^0\) loadings may be linked to the improved surface morphology of the composites and enhanced interaction between iron and GAC at higher Fe\(^0\) loadings.

5.3.2.3 Kinetic Analysis

A pseudo-first-order rate kinetic model has been previously used to describe the reductive degradation of TCE by nZVI particles with or without palladium addition [66]. The expression is described as follows:

\[
- \frac{dC_{TCE}}{dt} = K_{obs} C_{TCE} = k_{SA} a_S \rho_m C_{TCE}
\]

The linear form could be rearranged and expressed below:

\[
- \ln \left( \frac{C_{TCE}}{C_{o(TCE)}} \right) = k_{obs} t = k_{SA} a_S \rho_m t
\]
Where:

\( C_{\text{TCE}} \): TCE concentration (mg/L) in aqueous phase at time \( t \) (h)

\( C_{\text{o(TCE)}} \): TCE initial concentration (mg/L)

\( k_{\text{obs}} \): observed pseudo-first-order reaction rate constant (h\(^{-1}\))

\( k_{\text{SA}} \): surface-normalized reaction rate constant (L h\(^{-1}\) m\(^{-2}\))

\( t \): reaction time (h)

\( \rho_m \): mass concentration of the nanoparticles (g/L)

\( a_s \): TEM-based specific surface area of nanoparticles (m\(^{2}\)/g)

To quantitatively describe the reaction kinetics of TCE removal, we applied a pseudo-first-order model in our experiments to characterize the dechlorination of TCE using the GAC-nZVI composites with and without palladium doping (illustrated in Fig. 5.14 (a)). Under various conditions, our experimental data is fitted with a linearized plot \([- \ln \left( \frac{C}{C_0} \right) \text{ vs. } t\)] and the model-simulated kinetic data is shown in Fig. 5.14 (b) and (c). Generally, the kinetic models for GAC-nZVI composites are in good agreement with their reaction behavior observed experimentally. The observed pseudo-first order reaction rate constants \( (k_{\text{obs}}, \text{h}^{-1}) \), surface-normalized reaction rate constants \( (k_{\text{SA}}) \) and correlation coefficients \( (R^2) \) are derived from the linear plots (Fig. 5.14 (b) and (c)) and listed in Table 5.2.
(a) [Graph showing the relationship between Contact Time, t (h) and C/Co for different treatments: nZVI, Pd/nZVI, GAC-nZVI, Pd/nZVI-GAC. The graph includes a pseudo-1st order model line.]

(b) [Graph showing the relationship between Time, t(h) and -ln(C/Co) for different treatments: nZVI, GAC-nZVI, GAC-Pd/nZVI, and linear nZVI, linear Pd/nZVI, linear GAC-nZVI, and linear GAC-Pd/nZVI.]
Fig. 5.14 (a) pseudo-first-order model fittings to the experimental data; (b) linear pseudo-first-order models for nZVI, GAC-nZVI, Pd/nZVI and Pd-doped GAC-nZVI composites; (Fe$^0$: 0.1 g/L, GAC/nZVI: 1g/L, mass ratio of nZVI/GAC: 10 w.t. %, C$_0$: 100 mg/L, Pd loading: 0.1 w.t. % of Fe$^0$) (c) various Fe loadings in the GAC-nZVI composites (C$_0$: 100 mg/L, GAC-nZVI: 1g/L, Fe$^0$: 0.1 g/L, T=25°C, pH=7); error bars are standard deviations of duplicates.
Table 5.2 Observed pseudo-first-order reaction rate constants, surface-normalized reaction rate constants and regression coefficients under various conditions

<table>
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<th>Composite</th>
<th>Fe loading (w/w, %)</th>
<th>$k_{\text{obs}}$ (h$^{-1}$)</th>
<th>$a_s$ (m$^2$/g)</th>
<th>$k_{\text{SA}}$ (L/h/m$^2$)</th>
<th>$R^2$</th>
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<tr>
<td>nZVI</td>
<td>-</td>
<td>0.006</td>
<td>13.86</td>
<td>0.004</td>
<td>0.911</td>
</tr>
<tr>
<td>GAC-nZVI</td>
<td>5</td>
<td>0.017</td>
<td>-</td>
<td>-</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.019</td>
<td>-</td>
<td>-</td>
<td>0.934</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.024</td>
<td>21.78</td>
<td>0.011</td>
<td>0.927</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.026</td>
<td>-</td>
<td>-</td>
<td>0.915</td>
</tr>
<tr>
<td>Pd/nZVI</td>
<td>-</td>
<td>0.147</td>
<td>-</td>
<td>-</td>
<td>0.981</td>
</tr>
<tr>
<td>Pd-doped GAC-nZVI</td>
<td>10</td>
<td>0.368</td>
<td>-</td>
<td>-</td>
<td>0.968</td>
</tr>
</tbody>
</table>

As shown in Table 5.2, the pseudo-first-order reaction kinetic model fits well with the experimental data, indicated by the good correlation coefficients between 0.91 and 0.98 in all cases. In this study, the TEM-based specific surface areas ($a_s$) of the unsupported and supported Fe$^0$ nanoparticles were calculated using the same method discussed in Chapter 4 (page 217-218). The mean sizes of Fe$^0$ nanoparticles and Fe$^0$ nanoparticles in the GAC-supported samples were measured approximately 55 nm and 35 nm, respectively. The observed reaction rate of TCE ($k_{\text{obs}}$) for GAC-nZVI composite was
about 0.02 h\(^{-1}\), whereas nZVI alone exhibited around 4 times lower reaction rate than that with GAC supported (0.006 h\(^{-1}\)). A similar increase in dechlorination activity has been reported by Tseng et al [32]. They reported a \(K_{\text{obs}}\) value for GAC-ZVI was 6.00 min\(^{-1}\), which was 40 times higher than that reported for bare ZVI (0.15 min\(^{-1}\)). The reported values of \(k_{\text{obs}}\) were obviously different from our results, and could perhaps be attributed to differences between their and our material’s surface morphology. However since the authors presented mainly bulk characterization data (XRD, BET, SEM and TEM) without a detailed surface characterization (TPR, Raman, etc.) we cannot carry a detailed comparison to pinpoint the specific differences.

Since surface area is taken into account by evaluating the reactivity of nanoparticles, the parameter \(k_{\text{SA}}\) based on the specific surface area of particles needs to be calculated to better describe the reactivity. In this context a study was carried out by Mackenzie and Bleyl [31] to calculate the values of \(k_{\text{SA}}\) for nZVI and selected types of CIC composites. They suggested that the highest \(k_{\text{SA}}\) value of CIC with 18% Fe content was 0.008 L m\(^{-2}\) h\(^{-1}\), which was higher than the one obtained on bare nZVI particles (0.004 L m\(^{-2}\) h\(^{-1}\)). Their reported values are on the same order of magnitude but slightly smaller than our results (0.011 L m\(^{-2}\) h\(^{-1}\)), indicating that GAC-nZVI composite in our study has high reactivity on TCE dechlorination. The enhancement on reactivity of TCE for the GAC-nZVI composite is proposed to be a combined effect of adsorption by GAC and
degradation by nZVI. GAC support additionally acts as an ideal support to prevent the aggregation and passivation of nZVI particles, thus increasing their activity.

With the deposition of a small amount of palladium onto the surface of Fe\(^0\) particles, the reaction rate constant drastically increased to 0.37 h\(^{-1}\). Compared to the Pd-free GAC-nZVI composite (0.019 h\(^{-1}\)), a nearly 20-fold improvement demonstrates that the reactivity rate is strongly catalyzed by palladium metal. The large improvement has been confirmed by another study conducted by Chang et al. [30]. The group investigated the disappearance kinetics of hexachlorocyclohexane (\(\gamma\)-HCH) in the aqueous phase by AC-supported bimetallic Cu/Fe\(^0\) nanoparticles. By comparing the \(k_{\text{obs}}\) values, Cu was found to increase the rate of dechlorination by almost 10 times (0.11 min\(^{-1}\) for Cu-amended Fe\(^0\)/AC vs. 0.01 min\(^{-1}\) for Fe\(^0\)/AC), which is consistent with our observations. Moreover, the observed rate constants (\(k_{\text{obs}}\)) are calculated using various mass ratios of Fe to GAC for the GAC-NZVI composites. The maximum value of \(k_{\text{obs}}\) (0.026 h\(^{-1}\)) was achieved when Fe loading was 20%, which confirmed that a higher Fe loading in the composite facilitated TCE dechlorination.
5.4 Conclusions

In this chapter, we developed a reactive GAC-nZVI composite to investigate the removal capability of TCE from aqueous solution. It is predicted that an integration of simultaneous adsorption by GAC and degradation reaction through nZVI particles is involved. Using an incipient wetness impregnation preparation strategy, reactive nZVI particles were incorporated into the mesopores of a GAC matrix. TEM was used to characterize their morphology and particles size distributions. N\textsubscript{2} adsorption/desorption isotherms were applied to calculate their BET surface area and porosity. XRD, Raman and TPR were used to study the composition of GAC-nZVI composite precursor. Batch experiments were carried out to evaluate TCE removal from aqueous solutions by the GAC-nZVI composite. The impact of palladium was studied on the composite’s TCE removal efficiency. A pseudo-first-order rate kinetic model is introduced to study the dechlorination mechanism of TCE by GAC-nZVI composites with and without Pd-promoter. In summary, the following conclusions could be collected from this study:

(1) TEM images indicate that nZVI particles are nearly spherical in shape and relatively uniform in size. Free nZVI particles have a strong tendency to aggregate and form chain-like domains, resulting in the reduction of the available reactive surface area for TCE degradation. After calcination, nZVI particles accumulate inside the pores of
GAC, which provides a good substrate for a better dispersion of nZVI particles.

(2) BET analysis indicates that GAC-nZVI composite has a high surface area and pore volume. The impregnation of nZVI particles within the mesopores of GAC diminishes the agglomeration of nanoparticles and thus maintains their high reactivity.

(3) XRD and Raman analysis of GAC-nZVI precursor composite indicates that the adsorbed iron salt precursors have been decomposed to primarily Fe$_2$O$_3$ nanoparticles during the calcination step. TPR implies an apparently strong interaction between Fe$_2$O$_3$ nanoparticles and GAC support.

(4) In batch mode, GAC-nZVI composite shows much higher TCE removal efficiency compared to nZVI and GAC. In this hybrid nanomaterial system, GAC serves as a highly efficient adsorbent and also as an effective support to immobilize nZVI particles, simultaneously, Fe$^0$ nanoparticles perform as an effective redox material for TCE dechlorination.

(5) The deposition of small amount of Pd (0.1 w.t. %) onto nZVI surface dramatically increases the overall TCE removal efficiency. The role of Pd is to catalyze the dissociative chemisorption of hydrogen produced by redox reactions on the Fe$^0$ surface. The activated atomic H$_{ad}$ species acts as a powerful secondary reducing agent, which in turn can contribute to increase the degradation rates of TCE.

(6) A higher loading of nZVI results in a more reducing environment, possibly indicating
that the location of nZVI particles within the composites is on the surface of GAC grain, rather than impregnating inside the GAC inner pores structure.
5.5 References


[22] Busch, J., Meibner, T. and Pottoff, A., Institute for earth and environment, University of Potsdam, Potsdam, Germany, 1999


Chapter 6 Conclusions and Recommendations

6.1 Conclusions

This study has demonstrated that multifunctional carbon-supported nZVI composites are effective for dechlorination of TCE at the bench scale. Two representative carbon materials, MWCNTs and GAC, were employed to encapsulate monometallic or bimetallic nZVI particles onto a solid matrix and significantly facilitate the reductive degradation of TCE over nanoiron. The observed improvement on the dechlorination efficiencies of TCE is clearly demonstrated and is attributed to the integration of simultaneous adsorption and degradation reactions through nZVI or palladized nZVI particles.

On the basis of our results, the following major findings and outcomes are summarized.

- Acid-oxidized MWCNTs are shown to be a suitable adsorbent for TCE removal from aqueous solutions. Among the various purification approaches of as-grown MWCNTs, HNO$_3$-refluxed oxidized MWCNTs achieved the highest TCE adsorption efficiency. A comparative study revealed that oxidized MWCNTs
exhibited superior adsorption capability than that of commercially available activated carbon.

- The kinetics of TCE adsorption over MWNTs was described well by a pseudo-second-order rate model and the thermodynamic adsorption behavior of TCE from aqueous solutions by MWCNTs was in good agreement with the Freundlich adsorption model. Based on TEM and Raman results it is proposed that the predominant mechanism for improvement of MWCNTs adsorption capacity is the result of the formation of surface oxygen-containing functional groups introduced during acid oxidization.

- nZVI-MWCNTs composite synthesis protocol was developed by using an efficient strategy to introduce nZVI particles into MWCNTs by wet chemical methods. nZVI particles were incorporated into the mesopores of GAC matrix by a multistep preparation of an incipient wetness impregnation and subsequent calcination and reduction.

- Both nZVI-MWCNTs and nZVI-GAC composites show much higher TCE removal efficiency than bare nZVI, MWCNTs or GAC. In this hybrid nanomaterial system, MWCNTs or GAC serves as a highly efficient adsorbent and also an effective
support to immobilize nZVI particles; simultaneously Fe\textsuperscript{0} nanoparticles perform as an effective redox material for the dechlorination.

- The deposition of small amount of Pd (0.1 w.t. %) onto nZVI surface dramatically increases the overall TCE removal efficiency. The role of Pd is to catalyze the dissociative chemisorption of hydrogen produced by redox reactions on Fe\textsuperscript{0}. The activated atomic H\textsubscript{ad}-species acts as a powerful secondary reducing agent, which in turn can contribute to increase the degradation rates of TCE.

### 6.2 Recommendations

The high efficiency for TCE removal by oxidized MWCNTs indicates that oxidized MWCNTs exhibit high potential as adsorbents for the removal of TCE from aqueous systems. Incorporated nZVI or palladized nZVI particles into MWCNTs or GAC matrix accelerate the removal efficiencies of TCE. However, the surrounding environmental conditions (such as pH, ionic strength, ORP, temperature, etc.) might greatly influence their performance. Therefore, continuing work in this area should focus on exploring the impacts of various environmental conditions for TCE removal to validate the effectiveness of carbon-nZVI composites in real field applications. In addition, CNTs are considered to be high cost and their environmental toxicity is still unknown. The limited
data available on their impact on human health and the environment currently limits their uses in environmental applications. Further research is required in this area thus is required before the technology can be tested in the field.

Due to technical limitation our studies focused solely on the degradation of TCE, reactions products were not monitored in our studies. Although we attributed the high dechlorination activity of the Pd catalyst to and increasing the use of active hydrogen available based in previous literature reports, this hypothesis needs to be confirmed through quantification of $\text{H}_2$ generated during dechlorination and a closed carbon balance.
Appendix A

Reproducibility of Experimental Data and Error Analysis

In order to estimate the precision and accuracy of the observation data, all of the samples in a series of batch experiments were conducted in duplicate. Only the average values of the measurements were presented as the final results. The error bars presented within the graphs indicate the standard deviation from the mean values of the data sets. Reproducibility of the experiments is considered to be significantly important because the determination of whether or not a data point is representative or anomalous (an outlier) can be statistically analyzed through the sufficient replicates within the tests. It has been suggested that the analysis of a data set required a reasonable number of data points per sample and the minimum replicates are advised by a sensitivity analysis. However, due to our experimental limitations it was not technically feasible to carry out the required replicates for each experimental test to gain an appreciation of the variance of individual data points. The reason would be interpreted by the fact that the adsorption and kinetics tests need too much amount of TCE (disposal issue of environmentally hazardous waste) too long experimental period. Therefore, we intended in the context to minimize the statistical analysis of samples to carry the experiments as duplicates, which we considered could assess the reproducibility of the experiment data. We acknowledge however that this approach might not have been the most adequate.
Duplicate batch experiments were examined for both adsorption isotherms and
degradation reactions in this thesis, and the analysis of the duplicates indicates that the
relative standard deviations from the mean values are estimated within ±5% in all cases.
Error analysis is aimed to quantify and record the errors associated with the inevitable
spread in a set of measurements. The potential sources of errors are unpredictably
encountered in the experiments, mainly divided into two categories: 1) Preparation step,
including incomplete dissolution of the analytes; loss of the analyte by volatilization;
introduction of contaminants from reaction of the solvent with vessel walls; introduction
of analyte as a solvent contaminant from overdose reactant and contamination error arises
during grinding and crushing due to mechanical wear and abrasion of the grinding
surfaces. 2) Sampling and analysis step, such as visual judgment; natural fluctuation due
to thermal motions or the random timing of single event and limited precision of
instrumental readings. Although these errors unavoidably influence the precision of the
data sets, they could be eliminated to an accepted level of variables by a careful replicate
measurement and standard statistical analysis.
APPENDIX B

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