2006

DESTRUCTION STUDY OF TOXIC CHLORINATED ORGANICS USING BIMETALLIC NANOPARTICLES AND MEMBRANE REACTOR: SYNTHESIS, CHARACTERIZATION, AND MODELING

Yit-Hong Tee
University of Kentucky, yhfee0@yahoo.com

Right click to open a feedback form in a new tab to let us know how this document benefits you.

Recommended Citation
https://uknowledge.uky.edu/gradschool_theses/420

This Thesis is brought to you for free and open access by the Graduate School at UKnowledge. It has been accepted for inclusion in University of Kentucky Master's Theses by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.
DESTRUCTION STUDY OF TOXIC CHLORINATED ORGANICS USING BIMETALLIC NANOPARTICLES AND MEMBRANE REACTOR: SYNTHESIS, CHARACTERIZATION, AND MODELING

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Yit-Hong Tee
Lexington, Kentucky

Director: Dr. Dibakar Bhattacharyya, Alumni Professor of Chemical Engineering
Lexington, Kentucky
2006

Copyright © Yit-Hong Tee 2006
Zero-valent metals such as bulk iron and zinc are known to dechlorinate toxic organic compounds. Enhancement in reaction rates has been achieved through bimetallic nanosized particles such as nickel/iron (Ni/Fe) and palladium/iron (Pd/Fe). Batch degradation of model compounds, trichloroethylene (TCE) and 2,2’-dichlorobiphenyls (DCB), were conducted using bimetallic Ni/Fe and Pd/Fe nanoparticles. Complete degradation of TCE and DCB is achieved at room temperature. Zero-valent iron, as the major element, undergoes corrosion to provide hydrogen and electrons for the reductive catalytic hydrodechlorination reaction. The second dopant metals of nickel and palladium (in nanoscale) act as catalyst for hydrogenation through metal hydride formation that produces completely dechlorinated final product. Different compositions of bimetallic Ni/Fe and Pd/Fe nanoparticles were synthesized and their reactivity was characterized in terms of reaction rate constants, hydrogen generation through iron corrosion, and products formation. The observed TCE degradation rate constant was two orders of magnitude higher than the bulk iron and nanoiron, indicating that the bimetallic nanoparticles are better materials compared to the monometallic iron systems. Longevity
study through repeated cycle experiments showed minimum loss of activity. The surface area-normalized rate constant was found to have a strong correlation with the hydrogen generation by iron corrosion reaction. A mathematical model was derived that incorporates the reaction and Langmuirian-type sorption terms to estimate the intrinsic reaction rate constant and rate-limiting step in the degradation process. Bimetallic nanoparticles were also immobilized into the chitosan matrix for the synthesis of a nanocomposite membrane reactor to achieve membrane-phase destruction of chlorinated organics under convective flow condition. Formation of uniformly distributed nanosized particles is confirmed by high resolution transmission electron microscopy. The membrane-phase degradation results demonstrated similar trends with the previous solution phase analysis with the observed enhanced reaction rates. The advantage of the membrane system is its ability to prevent the agglomeration of the nanoparticles in the membrane matrix, to minimize the loss of precious metals into the bulk solution phase, and to prevent the formation of precipitated Fe(III) hydroxide. These are due to the chelating effect of the amine and hydroxyl functional groups in the chitosan backbones.

KEYWORDS: Bimetallic Nanoparticles, Chlorinated Organics, Catalytic Hydrodechlorination, Langmuirian – Type Sorption Isotherm, Nanocomposite Membrane Reactor

Yit-Hong Tee

12/08/2006
DESTRUCTION STUDY OF TOXIC CHLORINATED ORGANICS USING BIMETALLIC NANOPARTICLES AND MEMBRANE REACTOR: SYNTHESIS, CHARACTERIZATION, AND MODELING

By

Yit-Hong Tee

Dr. Dibakar Bhattacharyya
Director of Dissertation

Dr. Babara Knudson
Director of Graduate Studies

12/08/2006
RULES FOR THE USE OF DISSERTATIONS

Unpublished dissertations submitted for the Doctor's degree and deposited in the University of Kentucky Library are as a rule open for inspection, but are to be used only with due regard to the rights of the authors. Bibliographical references may be noted, but quotations or summaries of parts may be published only with the permission of the author, and with the usual scholarly acknowledgements.

Extensive copying or publication of the dissertation in whole or in part also requires the consent of the Dean of the Graduate School of the University of Kentucky.

A library that borrows this dissertation for use by its patrons is expected to secure the signature of each user.

<table>
<thead>
<tr>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
<tr>
<td>______________________</td>
<td>______________________</td>
</tr>
</tbody>
</table>
DISSERTATION

Yit-Hong Tee

The Graduate School
University of Kentucky
2006
DESTRUCTION STUDY OF TOXIC CHLORINATED ORGANICS USING BIMETALLIC NANOPARTICLES AND MEMBRANE REACTOR: SYNTHESIS, CHARACTERIZATION, AND MODELING

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Yit-Hong Tee

Lexington, Kentucky
Director: Dr. Dibakar Bhattacharyya, Alumni Professor of Chemical Engineering
Lexington, Kentucky
2006

Copyright © Yit-Hong Tee 2006
ACKNOWLEDGEMENTS

I would like to thank my advisor, Professor Dibakar Bhattacharyya, for his guidance, encouragement, and challenging assignments over the past five years. His extensive knowledge and ideas have advanced my technical skills and scientific backgrounds immensely in order to prepare me for the coming future. I would like to acknowledge the funding provided by the National Institute of Environmental Health Sciences (NIEHS) and US-Environmental Protection Agency (US-EPA) for the completion of my research at the University of Kentucky. In addition, I would like to say that working in the lab for the past five years will be so different without all the jokes and laughter I shared with all of my lab mates. Thank you: Aaron, Abhay, Ajay, Dave, Deepak, Jian, Morgan, Li, Melody, Nathan, Oscar, Saurav, Scott, and Vasile. Lastly, I would like to express my deepest gratitude and thank to my family back in Malaysia, especially my mom, for all the support I received when I needed it the most.
Table of Contents

Acknowledgements ........................................ iii
List of Tables ........................................... vii
List of Figures ............................................ viii

Chapter 1: Introduction .................................... 1
1.1. Remediation Technology and Bimetallic Nanoparticles ...... 1
1.2. Nanoparticles-Immobilized Membrane Reactor .............. 3
1.3. Research Objectives .................................. 5

Chapter 2: Background .................................... 7
2.1. Chemical Remediation Systems .......................... 7
2.1.1. Oxidative Approach ................................ 7
  2.1.1.1. Hydroxyl Radical Systems (OH\textsuperscript{-}) .... 7
  2.1.1.2. Permanganate method (MnO\textsubscript{4}\textsuperscript{-}) ... 9
2.1.2. Reductive Approach ................................ 10
  2.1.2.1. Vitamin B\textsubscript{12} ........................... 10
  2.1.2.2. Zero-Valent Metal-Based Systems ................. 12
2.2. Synthesis of Nanoparticles ............................ 18
  2.2.1. Solution Phase Synthesis .......................... 18
  2.2.2. Polymer Phase Synthesis .......................... 22
2.3. Long Term Reactivity ................................ 25
  2.3.1. Precipitation/Morphological Changes ............... 26
  2.3.2. Mixed Matrix Membrane System .................... 27

Chapter 3: Reaction Mechanisms and Kinetic Models .......... 30
3.1. TCE Degradation Mechanism under Batch Study .......... 30
3.2. Batch Degradation Model Derivation ...................... 31

Chapter 4: Experimental Section .......................... 35
4.1. Experimental Setups and Chemicals ...................... 35
4.2. Nanoparticles Characterization ......................... 37
  4.2.1. Brunauer, Emmett, and Teller (BET)
       Surface Area Analysis ............................... 37
4.2.2. X-Ray Diffraction (XRD) Analysis
4.2.3. Thermogravimetric (TGA) Analysis
4.2.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis
4.2.5. Atomic-Adsorption (AA) and Inductively-Coupled Plasma (ICP) Analysis
4.2.6. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS) Analysis
4.2.7. High Resolution Transmission Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (HRTEM-EDS) Analysis
4.3. Solution Phase Synthesis of Nanoparticles
4.3.1. Bimetallic Ni/Fe Nanoparticles
4.3.2. Bimetallic Pd/Fe Nanoparticles
4.4. Synthesis of Membrane
4.4.1. Chitosan Membrane with Silica Gel
4.4.2. Chitosan-Immobilized Iron Nanoparticles Membrane with Silica Gel
4.4.3. Chitosan-Immobilized Nanoparticles (Ni/Fe, Pd/Fe) Membrane with Silica Gel
4.5. Batch Degradation Study
4.5.1. Trichloroethylene (TCE)-Kinetic Analysis
4.5.2. TCE and DCB-Hydrogen Analysis
4.6. Degradation Study (DCB) by Membrane Reactor
4.7. Method of Analysis
4.7.1. TCE Analysis
4.7.2. DCB Analysis
4.8. Hydrogen Analysis
Chapter 5: Results and Discussion
5.1. Nanoparticles
5.1.1. Characterization of Bimetallic Nanoparticles
5.1.2. Batch TCE Degradation
List of Tables

Table 4.4.3.a, Characteristics and metal loading of chitosan-immobilized bimetallic Ni/Fe nanoparticles mixed matrix membranes with silica for TCE degradation study . . . . . 46
Table 4.4.3.b, Characteristics and metal loading of chitosan-immobilized bimetallic Pd/Fe nanoparticles mixed matrix membranes with silica for DCB degradation study . . . . . 47
Table 5.1.2.a, TCE Degradation Study of Fe(0) and Ni/Fe Nanoparticles . . 72
Table 5.1.3.a, Surface Areas of Ni/Fe, Ni, and Fe Nanoparticles from SEM Image Estimation and BET Analysis . . . . . 74
Table 5.1.5.a, 2,2'-dichlorobiphenyls dechlorination study by Pd/Fe nanoparticles with different surface-coated Pd content . . . . . 81
Table 5.1.5.b, Selected literature summary for PCBs dechlorination using different palladized iron systems . . . . . 83
Table 5.2.2.a, Hydrogen generation for nanoiron and Ni/Fe nanoparticles at acidic conditions . . . . . . . . . . . . . 94
Table 5.2.2.b, Iron-normalized hydrogen generation rate and the surface area-normalized reaction rate constant for Fe and Ni/Fe nanoparticles . . . . . . . . . . . . . 95
Table 5.3.1.a, Elemental analysis of Figure 5.3.1.h-(b) and (c) for chitosan-immobilized bimetallic Ni/Fe nanoparticles (Ni/Fe weight ratio = 1/4) mixed matrix membranes with silica . . . . . . . . . . . . . 114
Table 5.3.2.a, Metal mass-normalized pseudo first-order reaction rate constants of TCE degradation by Ni/Fe nanoparticles . . . . . . . . . . . . . 120
Table 5.3.3.a, Elemental analysis for membrane-immobilized bimetallic nanoparticles in the degradation study of chlorinated organics . . . . . . . . . . . . . 128
Table 5.4.1.a, Cycle studies for TCE degradation on Ni/Fe (Ni = 20 wt%) nanoparticles physical and chemical reactivity . . . . . . . . . . . . . 132
**List of Figures**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.2.2.a</td>
<td>Schematic for the electron transfer reductive mechanism of zero-valent metal systems</td>
<td>13</td>
</tr>
<tr>
<td>2.1.2.2.b</td>
<td>Enhanced catalytic reaction mechanism of bimetallic nanoparticles with TCE as the targeted compound</td>
<td>17</td>
</tr>
<tr>
<td>2.2.2.a</td>
<td>Schematic illustrates the steps used in the synthesis of hybrid polymer-metal systems</td>
<td>23</td>
</tr>
<tr>
<td>2.2.2.b</td>
<td>Schematic for the different hybrid polymer-metal systems: (a) polymer-supported nanoparticles, (b) polymer-immobilized nanoparticles, and (c) polymer-encapsulated nanoparticles</td>
<td>24</td>
</tr>
<tr>
<td>2.3.2.a</td>
<td>Schematic for the degradation of chlorinated organics by iron-based immobilized nanoparticles and chelating of Fe ions species in the nanocomposite mixed matrix membrane</td>
<td>29</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic for batch TCE sorption and degradation reaction by the Ni/Fe (Ni = 20 wt%) nanoparticles</td>
<td>32</td>
</tr>
<tr>
<td>4.1.a</td>
<td>Schematic for convective degradation study</td>
<td>36</td>
</tr>
<tr>
<td>4.4.2.a</td>
<td>Flow chart for the synthesis of chitosan-immobilized iron nanoparticles membrane with silica</td>
<td>43</td>
</tr>
<tr>
<td>4.4.3.a</td>
<td>Flow chart for the synthesis of chitosan-immobilized bimetallic (Ni/Fe and Pd/Fe) nanoparticles mixed matrix membrane with silica</td>
<td>48</td>
</tr>
<tr>
<td>5.1.1.a</td>
<td>SEM image of Ni/Fe nanoparticles with 20 wt% nickel</td>
<td>57</td>
</tr>
<tr>
<td>5.1.1.b</td>
<td>TEM image of Ni/Fe nanoparticles with 20 wt% nickel (20,000 magnification)</td>
<td>58</td>
</tr>
<tr>
<td>5.1.1.c</td>
<td>SEM image of nickel nanoparticles</td>
<td>59</td>
</tr>
<tr>
<td>5.1.1.d</td>
<td>SEM image of iron nanoparticles</td>
<td>60</td>
</tr>
<tr>
<td>5.1.1.e</td>
<td>SEM-EDS spectrum for Ni/Fe nanoparticles with 20 wt% nickel</td>
<td>62</td>
</tr>
<tr>
<td>5.1.1.f</td>
<td>TEM-EDS analysis of Ni/Fe nanoparticles with 20 wt% nickel (20,000 magnification)</td>
<td>63</td>
</tr>
<tr>
<td>5.1.2.a</td>
<td>Degradation of TCE by Ni/Fe nanoparticles with different Ni wt%. Initial TCE concentration = 10±0.1 mg/L, bimetallic loading for all experiments = 100 mg/40 ml, reaction volume = 40 ml, initial pH = 6.5</td>
<td>65</td>
</tr>
<tr>
<td>5.1.2.b</td>
<td>Quantitative analysis of ethane for Ni/Fe nanoparticles with (a) 20 wt% Ni, (b) 15 wt% Ni, and (c) 4 wt% Ni. Experimental conditions: 10±0.1 mg/L TCE (Initial TCE = 3.1 mmol), metal loading = 100 mg / 40 ml, reaction volume = 40.0 ml, and initial pH = 6.5</td>
<td>67</td>
</tr>
<tr>
<td>5.1.2.c</td>
<td>Time-independent plot of ethane yield and TCE conversion by Ni/Fe nanoparticles</td>
<td>69</td>
</tr>
<tr>
<td>5.1.2.d</td>
<td>Reaction pathways for TCE degradation by (a) bulk Fe(0) (adapted from Arnold et al., 2000) and (b) Ni/Fe nanoparticles</td>
<td>70</td>
</tr>
<tr>
<td>5.1.3.a</td>
<td>Effect of nickel compositions in Ni/Fe nanoparticles on the surface area-normalized reaction rate constant</td>
<td>76</td>
</tr>
<tr>
<td>5.1.3.b</td>
<td>STEM-EDS line profiles: (a) Ni/Fe nanoparticles with 80 wt% nickel and (b) Ni/Fe nanoparticles with 20 wt% nickel</td>
<td>77</td>
</tr>
</tbody>
</table>
Figure 5.1.4.a, Normalization of TCE degradation rate by different metal mass per liquid volume of 500 mg/L, 750 mg/L, 1500 mg/L, 2000 mg/L, and 2500 mg/L. Ni/Fe used = 20 wt% nickel. Initial TCE concentration = 10 ± 0.1 mg/L. Total reaction Volume = 40 ml. Initial pH = 6.5 . . . 79

Figure 5.2.1.a, Total hydrogen generation normalized with iron for different bimetallic Ni/Fe nanoparticles versus time under anaerobic aqueous solution. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5 . . . . 85

Figure 5.2.1.b, Iron-normalized hydrogen generation of iron nanoparticles with (open diamond symbols) and without acid treatment (solid diamond symbols) under anaerobic condition. Nanoiron = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5 . . . . . 88

Figure 5.2.2.a, Total hydrogen produced normalized by iron versus time for Ni/Fe (Ni = 20 wt%) nanoparticles with TCE degradation reaction (open diamond symbols) and TCE-free aqueous solution (solid diamond symbols). Insert is the hydrogen produced at high initial TCE degradation reaction (open square symbols) and TCE-free aqueous solution (solid square symbols). Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5 . . . . . 90

Figure 5.2.2.b, Effect of pH on hydrogen generation for Ni/Fe nanoparticles (Ni = 20 wt%) and iron nanoparticles (acid-treated and non-treated) under anaerobic aqueous solution. Analysis time is 2 hours. Nanoiron and Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5 . . . . . 92

Figure 5.2.2.c, Volcanic profile of surface area-normalized TCE reaction rate and hydrogen generation rate with respect to Ni wt% of the Ni/Fe nanoparticles. Insert is the linear correlation between $k_{\text{SA}}$ and $(k_{H_2} N_{\text{Ni}})$ . . . . . . 98

Figure 5.3.1.a, SEM surface image for chitosan-silica membrane without iron nanoparticles . . . . . . . 101

Figure 5.3.1.b, FTIR analysis of the (a) dried polymer solution of chitosan, silica, Fe$^{2+}$, and sulfosuccinic acid. (b) chitosan-immobilized iron nanoparticles with silica membrane . . . . . . . . 103

Figure 5.3.1.c, (a) Electron dispersive spectroscopy (EDS) spectra for the dried chitosan film with elemental analysis before NaBH$_4$ reduction. (10 wt% silica gel, 1.30 mmol Fe$^{2+}$/g membrane, 40 wt% of sulfosuccinic acid). (b) scanning electron microscopy (SEM) surface image for the dried chitosan film . . 105

Figure 5.3.1d, (a) Electron dispersive spectroscopy (EDS) spectra with elemental analysis for the cross-section of the chitosan-immobilized iron nanoparticles with silica (6.0 wt% silica gel, 73 mg Fe/g membrane. (b) scanning electron microscopy (SEM) of cross-section image and surface image (shown as insert) for the membrane . . . . . . . . . . . 106
Figure 5.3.1.e, XRD analysis for: (a) chitosan membrane, (b) 1.30 mmol \( Fe^{2+} \) / g chitosan membrane, (c) 3.25 mmol \( Fe^{2+} \) / g chitosan membrane, (d) iron nanoparticles by NaBH\(_4\), and (e) Fisher electrolytic iron . . . . . . . . . . 107

Figure 5.3.1.f, TGA analysis for: (a) chitosan membrane, (b) chitosan membrane with silica (6 wt% silica of membrane weight), and (c) chitosan-immobilized iron nanoparticles with silica (6 wt% silica and 7.5 wt% Fe of membrane weight) . . . . . 109

Figure 5.3.1.g, SEM surface images of: (a) porous chitosan membrane, (b) 0.25 mmol \( Fe^{2+} \) / g chitosan, (c) 1.00 mmol \( Fe^{2+} \) / g chitosan, and (d) 3.25 mmol \( Fe^{2+} \) / g chitosan . . . . . 112

Figure 5.3.1.h, (a) High resolution transmission electron microscopy (HRTEM) image of chitosan-embedded bimetallic Ni/Fe nanoparticles (Ni/Fe weight ratio = 1/4) mixed matrix membrane (Insert shows enlarged image for the squared area of the same membrane). (b) and (c) electron dispersive spectroscopy (EDS) spectra with elemental analysis (shown in Table 5.3.1.a) of the membrane with silica at different positions . . . . . . . . . . 113

Figure 5.3.1.i, Volumetric flux vs. transmembrane pressure normalized by solution viscosity of different solvents for chitosan-immobilized Pd/Fe nanoparticles under pressurized condition. Each data points represent flux after 96 hours of continuous operation . . . . . . . . . . 116

Figure 5.3.2.a, Batch TCE degradation study of chitosan-immobilized Ni/Fe nanoparticles (Ni = 20 wt%) mixed matrix membrane. Initial TCE concentration = 10 mg/L, reaction volume = 40 ml + 2 ml headspace, initial pH = 6.5 . . . . . . . . . . 118

Figure 5.3.2.b, Batch TCE degradation study of chitosan-immobilized Ni/Fe nanoparticles (Ni = 4 wt%) mixed matrix membrane. Initial TCE concentration = 10 mg/L, reaction volume = 40 ml + 2 ml headspace, initial pH = 6.5 . . . . . . . . . . 122

Figure 5.3.3.a, Degradation study of 2,2'-dichlorobiphenyl (DCB) vs. inverse solvent flux under pressure induced operation. Initial DCB concentration = 10 mg/L, solvent = 1/1 (v/v) of ethanol and water, and applied pressure of 0.35 bar to 11.0 bar . . . . . . . . . . 125

Figure 5.3.3.b, Degradation study of 2,2'-dichlorobiphenyl (DCB) vs. residence time under pressure induced operation. Initial DCB concentration = 10 mg/L, solvent = 1/1 (v/v) of ethanol and water, solvent permeability = 0.50 x 10\(^{-4}\) cm\(^3\) s\(^{-1}\) cm\(^{-2}\) bar\(^{-1}\) . . . . . . . . . . 126

Figure 5.4.1.a, Batch cycle study for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles corrected by consumption of iron content. Ni/Fe (Ni = 20 wt%) = 0.10 g, initial TCE = 10 mg/L, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the raw data for TCE degradation. . . . . . 130
Figure 5.4.1.b, Time-independent plot of TCE degradation by Ni/Fe nanoparticles (Ni= 20 wt%): ethane yield and TCE conversion. Insert shows the time-dependent plot of ethane/ethylene formation with respect to TCE degraded. 133

Figure 5.4.1.c, SEM images of TCE degradation by Ni/Fe nanoparticles (Ni = 20 wt%) at 1st (reaction time = 120 min), 2nd (reaction time = 140 min), and 3rd (reaction time = 140 min) cycles for a total reaction time of approximately 7 hours. 135

Figure 5.5.1.a, Langmuirian-type quasi sorption isotherm for TCE batch experiment study by Ni/Fe nanoparticles (Ni = 20 wt%) at high initial concentration. Insert shows the close ups of the low initial TCE concentration region. The solid line is the isotherm fit obtained by linear regression ($R^2 = 0.9904$). Ni/Fe = 0.1 g, volume = 40 ml, initial pH = 6.5. 137

Figure 5.5.1.b, TCE degradation and modeling by Ni/Fe (Ni = 20 wt%) nanoparticles at high initial TCE concentration (Initial TCE = 500 mg/L) with eq 4.3c. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in insert is only “guide to the eye”. 139

Figure 5.5.1.c, Modeling for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles at low TCE concentration (initial TCE = 10 mg/L) with eq 4.3d. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in insert is only “guide to the eye”. 141
List of Files

Yit Hong Tee PhD Dissertation.pdf (about 5.52 MB)
Chapter 1: Introduction

1.1. Remediation Technology and Bimetallic Nanoparticles

Remediation of toxic chlorinated organics such as carbon tetrachloride, trichloroethylene, chlorophenols, polychlorinated biphenyls etc. is one of the utmost important environmental goals specified by the United States Environmental Protection Agency (U.S. EPA). Different remediation methods have been studied and used in pilot plant while others are being applied in actual contaminated areas such as groundwater plume, Superfund sites, and dense non-aqueous-phase liquids (DNAPL) contaminated sites. In general, *in-situ* remediation of chlorinated compounds can be generalized into two main categories: (1) natural attenuation and biological systems, and (2) physical-chemical treatments. The former consists of phytoremediation and biodegradation by plantations (poplar, cottonwood trees et al.) and by active microbial populations (Dehalobacter, Sulfurospirillum, Desulfuromonas, Desulfitobacterium, Clostridium, Dehalococcoides, etc.) under aerobic and anaerobic environments (Christ et al., 2005; Godsy et al., 2003; Harkness et al., 1999; Jackson et al., 2005; and Wang et al., 2004). The biodegradation systems mentioned above often required years to achieve satisfactory results in terms of toxicity level of the initial substrate concentration that are tolerable to human. On the other hand, physical-chemical treatment technologies have been used to achieve immediate and effective degradation of toxic compounds and are extensively documented by National Research Council (NRC 1994, 1997, 1999). Selected approaches include air-sparging, thermal treatment, co-solvent flushing, surfactant-enhanced aquifer remediation, and chemical reduction and oxidation processes. The main chemical aspect used in this study involves the electron-assisted reductive destruction coupled with catalytic hydrodechlorination mechanism using nanosized bimetallic particles.
The use of zero-valent metals as the reducing agent in the degradation of chlorinated organics was first reported by Sweeny in the late 70’s (Sweeny, 1979 and 1980) followed by the works of Senzaki in the late 80’s (Senzaki et al., 1988 and 1989). Since then numerous studies were conducted to examine the degradation kinetics, effect of reaction conditions, and structural/morphological influences on the performance of zero-valent metals in the remediation of chlorinated compounds. The monometallic systems studied include zero-valent iron (Arnold et al., 2000; Gilham et al., 1994; Johnson et al., 1996; Matheson et al., 1994; and Robert et al., 1996), zinc (Arnold et al., 1998; and Schlimm et al., 1996), and tin (Su et al., 1999). Among all these methods, iron-based system has been receiving much attention due to its relatively low cost and negligible metal toxicity. Even though promising reaction kinetics have been reported by many, dechlorination by zero-valent metals also produce measurable amounts of less-chlorinated intermediates and by-products such as dichloroethylenes and vinyl chloride.

New and improved techniques for higher reaction kinetics and negligible formation of chlorinated intermediates were achieved using bimetallic systems. The use of bimetallic systems as reported in the literature for the remediation of chloro-organics include zero-valent iron or zinc as the base component with the addition of a catalyst metal such as nickel, palladium, platinum, silver, and copper. It is hypothesized that the enhancement of reaction kinetics with the absence of any toxic by-products formation was based on the different physical and chemical properties of the bimetallic systems. In view of the promising results achieved in the bimetallic study, nanosized systems with higher surface area per unit volume as compared to the bulk particles have been synthesized and analyzed for the degradation of chlorinated organics. Higher surface area will increase the availability of surface reaction sites for degradation process. With the
presence of a second catalytic dopant such as nickel or palladium, the reaction mechanisms is hypothesized to be altered from the simple electron transfer to the catalytic reductive hydrodechlorination pathways. The catalytic agent will alter the electronic properties of the base metal and enhance the formation of the active atomic hydrogen or hydride on the particles surface. This will facilitate the reductive pathways of the degradation reactions that involved the transfer of both electrons and atomic hydrogen or hydride to the chlorinated organics that are sorbed on the metal surface.

1.2. Nanoparticles Immobilized Membrane Reactor

The use of organic polymers to synthesize nanostructured materials as well as membrane reactor systems is receiving considerable attention lately. The presence of negatively-charged carboxylic acid group or amine and hydroxyl functional groups with lone-pair electrons on the polymer backbone can be used as chelating/ion exchange agent as well as imposing stabilizing effect on the synthesized nanoparticles. Various methods have been used to synthesize and study the chemical and physical properties of the hybrid polymeric membrane reactor with immobilized nanoparticles. These include sono-chemical, UV and $\gamma$-irradiation, and chemical reduction using reducing agents such as borohydrides and hydrazine. Polymers such as polyacrylic acid (Kidambi et al., 2005; Shuetz et al., 2004; and Xu et al., 2005), poly(vinyl alcohol) (Korchev et al., 2004; and Porel et al., 2005), poly(vinyl pyridine) (Bronstein et al., 1998; and Malynych et al., 2002), polyaniline (Drelinkiewicz et al., 1998; and Gan et al., 1995), poly(vinyl pyrrolidone) (Isabel et al.,2002; and Suslick et al., 1996), and polyamines such as polyethyleneimine (Kidambi et al., 2005; Bao et al., 2003; and Sidorov et al., 1999) are most commonly used in this area of studies. For reactive membrane systems, reports are
available on the successful synthesis of cellulose acetate thin film with immobilized bimetallic nanoparticles such as Ni/Fe, Pd/Co, and monometallic Pd for the catalytic dechlorination and hydrogenation processes (Liu et al., 1997 and 2000; and Meyer et al., 2004). Catalytically active nanoparticles and bimetallic nanoclusters incorporated into poly(amide imide) film have been reported by Fritsch et al. (1995), and Tröger et al. (1997). Formation of catalytically active nanoparticles immobilized in poly(dimethylsiloxane) matrix for the hydrodechlorination of chlorobenzene have also been reported by Fritsch et al. (2003).

Chitosan, poly(β-[1-4]-2-amino-2-deoxy-D-glucopyranose), is a biodegradable, non-toxic polysaccharide consisting of a linear chain of six-membered ring structure with both the hydroxyl and amine functional groups on its backbone. The unique chemical and physical properties of chitosan have been the subject of numerous studies. These include the use of chitosan as clinically applicable biomaterials (Denuziere et al., 1998; and Schmuch et al., 1998), separation polymers such as pervaporation and protein-separation membranes (Jegal et al., 1999; Kittur et al., 2005; and Zeng et al., 1998), as well as ion-exchange beads (Beppu et al., 2004; Guibal et al., 1998; and Ngah et al., 1999). The presence of hydroxyl and amine functional groups as possible chelating/ion exchange agent for metal ions has also attracted interest to study the use of chitosan for the synthesis of nanoparticles. Reports have shown that silver and other precious metals such as gold, palladium, and platinum have been successfully coated and stabilized by polymeric chitosan forming nanosized particles (Adlim et al., 2004; and Huang et al., 2004). These kinds of chitosan-supported nanoparticles have been shown to be catalytically active.
The use of chitosan-Pd nanocomposites for heterogeneous catalytic reactions is the most extensively reported system in the literature. For example, allylic substitution reactions of \((E)\)-cinnamyl ethyl carbonate by morpholine was reported by Quignard et al. (2000) using chitosan-supported palladium complex. Dechlorination reaction of chlorophenol to phenol, degradation of nitrophenol, and reduction of chromate were studied by Vincent et al. using chitosan-supported metal nanoparticles (2002, 2003, and 2004). Hydrogenation of nitrobenzene to aniline by chitosan-impregnated palladium composites was also reported by Jin et al. (1994). Excellent review of chitosan-based materials used in the heterogeneous catalytic reactions is detailed by Guibal (2005). Most of these catalytic systems were in the form of beads or flakes supported on silica or zeolites. Yet very few studies were conducted using chitosan in the form of membrane with active nanoparticles immobilized in the polymer matrix for catalytic reactions. These were largely due to the relatively dense structure of the final membrane formed by chitosan. The low porosity of the thin film increases the diffusion resistance of the target compound from contacting the nanoparticles immobilized in the membrane if the compounds have low partition coefficient with chitosan. These will render the nanoparticles in the polymer matrix ‘inactive’ and limit the catalytic reaction on the external surface of the membrane. The diffusion limitation of chitosan film can be reduced by inducing porosity during or after the formation of the membrane. This can be achieved by using silica as the pore-inducing agent as reported by Zeng et al. (1996) for the formation of macroporous chitosan membranes.

1.3. Research Objectives

In view of the promising results achieved by zero-valent iron-based system in the remediation of chlorinated organics and the successful application of polymeric
membrane for the immobilization of nanoparticles, this work focus on the degradation study using bimetallic nanoparticles and the integration of nanotechnology with membrane science to develop a hybrid mixed matrix membrane reactor. The experimental study and analyses to accomplish these goals include:

• To synthesize and characterize bimetallic nanoparticles with enhanced reaction kinetics and minimized toxic by-products formation.
• To study and establish the synergistic compositional effect of the bimetallic nanoparticles in the degradation reaction.
• To correlate the hydrogen generation rate through iron oxidation with the degradation kinetics of TCE by Ni/Fe nanoparticles.
• To derive a general mathematical model incorporating reaction coupled with sorption term for the estimation of intrinsic reaction rate constant and rate-limiting step.
• To determine the effect of deactivation on reaction kinetics and products formation through cycle study.
• To immobilize the nanoparticles into the chitosan polymeric matrix for the development of a hybrid membrane reactor capable of degrading chlorinated organics.
Chapter 2: Background and Literature Reviews

2.1. Chemical Remediation Systems

Different chemical methods have been studied for the remediation of chlorinated compounds. They are generally divided into two main categories, those that involve electron transfer and those that do not. Selected discussion on the process of electron-assisted abiotic remediation will be provided due to the large scope of information entailed in this area of study and the focus of our project that involved only the reductive electron-transfer mechanisms using non-biological systems. Remediation processes that involved electron transfer can be subdivided into another two different aspects, namely the oxidative and reductive pathways.

2.1.1. Oxidative Approach

The most common chemical oxidative methods studied for the remediation of toxic halogenated organics are processes based on ozone (O₃, O₃ + UV, O₃ + catalysis), hydrogen peroxide (Fenton chemistry, photo-Fenton, H₂O₂ + UV), and permanganate systems.

2.1.1.1. Hydroxyl Radical Systems (OH⁻)

Processes based on ozone and hydrogen peroxide possess some degree of similarity. The degradation kinetics and pathways are highly influenced by pH in both of the systems. At acidic conditions (pH < 4), direct ozonation occurred through electrophilic, nucleophilic or dipolar addition reactions. At basic conditions (pH > 9), dechlorination is achieved by the decomposition of ozone forming hydroxyl radicals (OH⁻) as strong oxidizing agent (Hoigné, 1998; and Langlais et al., 1991). Likewise, at
low pH (2 < pH < 4), Fenton’s reaction between H₂O₂ and a homogeneous catalyst such as iron also generates the hydroxyl radicals that are capable of oxidizing almost all except some small and simplest organic compounds to carbon dioxide and water as final products (Bigda, 1995; Safarzadeh-Amiri et al., 1996; and Walling, 1975). In addition to being highly dependent on the solution pH, the reaction kinetic of oxidative degradation by hydroxyl radicals is also a strong function of initial reactants concentration and temperature. The reaction kinetics for both of the systems that involved radical species is very complex in nature are consists of initiation, propagation, and termination steps in addition to the degradation process. The main reaction pathways are represented as the following:

**Hydrogen Peroxide System (Fenton):**

Initiation: H₂O₂ + Fe²⁺ → Fe³⁺ + OH⁻ + OH•

Propagation: OH• + H₂O₂ → HO₂• + H₂O

\[ \text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{OH}\cdot + \text{H}_2\text{O} + \text{O}_2 \]

Termination: Fe²⁺ + OH• → Fe³⁺ + HO⁻

\[ \text{HO}_2\cdot + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \]

Organics Degradation: R-Clₙ + OH• → Intermediates

Intermediates + OH• → CO₂ + H₂O + nCl⁻

**Ozone System:**

Initiation: O₃ + OH• → O₂⁻ + HO₂•

Propagation: O₃ + O₂⁻ → O₃⁻ + O₂

\[ \text{O}_3^- + \text{H}^+ \leftrightarrow \text{HO}_3\cdot \]

\[ \text{HO}_3\cdot \rightarrow \text{OH}\cdot + \text{O}_2 \]

Termination: OH• + CO₃²⁻ → HO⁻ + CO₃⁻
Organics Degradation: $\text{R-Cl}_n + \text{OH}^\bullet \rightarrow \text{Intermediates},$

$\text{Intermediates} + \text{OH}^\bullet \rightarrow \text{CO}_2 + \text{H}_2\text{O} + n\text{Cl}^-$

In addition, the ozonation and hydrogen peroxide systems can be coupled to achieve enhanced reaction rate. An excellent review on the oxidative degradation by ozone and hydrogen peroxide is reported by Pera-Titus et al. (2004).

The modified Fenton reaction was being studied to extend the application to near neutral pH conditions. This method involved the use of different ligands and macrochelates such as citrate, EDTA, polyacrylic acid etc. to control the consumption rate of $\text{H}_2\text{O}_2$ by forming a stable metal-chelate complex and effectively preventing the undesirable precipitation of metal hydro(xides) (Li et al., 2005; Smith, et al., 2006; Sun et al., 1992; and Watts, et al., 2005). This new system will lower the reaction rate between $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ and subsequently lead to the controlled formation of hydroxyl radicals used in the degradation process according to the following:

$$\text{Fe}^{2+}X + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}X + \text{OH}^- + \text{OH}^\bullet$$

where X is the active ligand that act as the rate-controlling and ferric-chelating agent as the pH increases with reaction time.

2.1.1.2. Permanganate method ($\text{MnO}_4^-$)

The oxidative dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE) using permanganate ions, $\text{MnO}_4^{-1}$, as the chemical oxidant in the contaminated soil was successfully demonstrated by Schnarr et al. (1998). They proposed in-situ chemical oxidation by flushing the soils with high concentrations of KMnO$_4$ that can rapidly oxidize TCE and PCE in the groundwater. The reaction kinetics and pathways for the oxidative degradation process was reported in the literature (Huang et al., 2002;
and Yan et al., 2000). It is based on the electrophilic attack of the electron-rich oxygen of MnO$_4^-$ on the C=C bond, forming a cyclic hypomanganate ester. Subsequent dechlorination reactions depend on the pH environment of the medium. It is shown that the cleavage of C=C bond occurred at acidic conditions with the formation of formic acid. As the pH increases, the cyclic ester will transform to acyclic ester followed by hydrolysis forming oxalic and glyoxylic acids. Eventual transformation of the formic, oxalic, and glyoxylic acids to carbon dioxide is possible lower pH due to the high oxidation rate of organic acids at acidic condition. The degradation reaction can be generalized as the following:

$$
R-\text{Cl} + \text{MnO}_4^- \rightarrow I \rightarrow x\text{CA} + \text{MnO}_2 + \text{Cl}^-
$$

where R and I is the chlorinated C$_2$ alkenes and reaction intermediates, respectively; $x$ and $y$ are stoichiometric coefficients; and CA is different carboxylic acids species. Continuous improvement on the oxidation of TCE by permanganate was reported by different modified system such as using surfactant micelles and co-solvent enhanced oxidation to increase the solubility of TCE in the aqueous phase containing the MnO$_4^-$ oxidant that lead to rapid degradation kinetics (Li, 2004; and Zhai et al., 2006).

### 2.1.2. Reductive Approach

Two of the most widely studied chlorinated organics degradation systems that are based on reductive electron-transfer mechanisms involve the use of vitamin B$_{12}$ and zero-valent metals as the reducing agent.

#### 2.1.2.1. Vitamin B$_{12}$

Vitamin B$_{12}$ with Co (III) located at the center of the tetrapyrrole ring can be reduced to powerful nucleophilic agent of Co (I) alamin in the presence of bulk reductants according to the following mechanisms:
where M is the bulk reductant. Most commonly used and studied reductants are the titanium (III) chelates such as titanium (III) citrate, titanium (III)-triacetic acid, titanium (III) ascorbate, titanium (III) EDTA etc. The reductive degradation of chlorinated organics such as perchloroethylene (PCE) and trichloroethylene (TCE) is achieved by the transfer of electron from Co (I) to the substrate forming Co (II) and vinylic intermediates. Subsequent degradation is accompanied by sequential hydrogenolysis forming non-toxic products such as acetylene and ethylene. The first reported study using vitamin B₁₂ for reductive dechlorination was by Gantzer et al. (1991). This was later followed by numerous studies that provided different insights regarding the reaction kinetics and mechanistic pathways for the degradation of various chlorinated organics. In brief, all of these studies have shown that the possible occurrence of different mechanisms such as the nucleophilic substitution, reductive β-elimination, pure electron transfer mechanism etc. that result in the formation of different final products which is similar to those observed in the zero-valent metal-based reduction system. The reactions involved are also reported to depend strongly on the stability of the alkylcobalamin intermediates and bulk reductant present during the degradation process, which is directly related to its ability to reduce Co (III) to Co (I). For instance, Lesage et al. (1998) have shown the effect of different reducing agent on the vitamin B₁₂-catalyzed reductive dechlorination in terms of the final product formation. While some authors (Glod et al., 1997; and Smith et al., 1994) suggested that only the reduced form of Cob (I) alamin is capable of initiating reductive dechlorination. Others (Assaf-Anid et al., 1994; and Chiu et al., 1996) have shown that the Cob (II) abalamin with the presence of thio reductants such as cysteine
and dithiothreitol (DTT) can also degrade chlorinated organics reductively through electron transfer mechanisms. In addition, Vitamin B$_{12}$-immobilized system using different supports that are more efficient in terms of regenerating the catalyst have been studied. Many have reported negative results such as low dechlorination reactivity and the occurrence of rapid deactivation (Habeck et al., 1995; and Marks et al., 1992). However, improved supported system was reported by Burris et al. (1996) with dechlorination reactivity comparable to those of the non-supported vitamin B$_{12}$ study with the observed minimum loss of reactivity through repeated usage.

2.1.2.2. Zero-Valent Metal-Based Systems

Zero-valent metals such as iron, zinc, and tin have been reported to degrade different chlorinated organics such as saturated and unsaturated aliphatics, benzenes, and phenolic compounds. Figure 2.1.2.2.a. shows that for chlorinated aliphatics (saturated and unsaturated) study, the toxic organics will undergo electron-assisted dechlorination through reductive elimination (substitution of two chloride atoms from carbon atoms), hydrogenolysis (replacement of a chloride atom with hydrogen atom), or hydrodechlorination (simultaneous cleavage of unsaturated carbon bonds with addition of hydrogen atoms) mechanisms. During the remediation reaction, iron is being progressively oxidized to generate electron necessary to degrade the chlorinated organics according to the following reactions:

\[
\begin{align*}
n \text{Fe} & \rightarrow n \text{Fe}^{2+} + 2n e^- \\
\downarrow & \\
\text{R-Cl}_n + n \text{H}^+ + 2n e^- & \rightarrow \text{R-H} + n\text{Cl}^- \quad (n \leq 4)
\end{align*}
\]

where R is any saturated or unsaturated aliphatic C$_1$ or C$_2$ compounds such as carbon tetrachloride, tetrachloroethylene, etc. Numerous studies showed that reductive
Figure 2.1.2.2.a. Schematic for the electron transfer reductive mechanism of zero-valent metal systems.
elimination is the dominant and preferred reaction pathway from a thermodynamic point of view as well as from the point of view of the distributed of products obtained at the end (Arnold et al., 1998, 2000 and 2002; Boronina et al., 1995; Fennelly et al., 1998; Matheson et al., 1994; and Robert et al., 1996). The reaction pathways are also found to be highly dependent on the degree of halogenation, with the common observation of an increase in degradation rate of compounds with a higher number of chlorine atoms (Arnold et al., 2000; Bylaska et al., 2002; Gillham et al., 1994; Roberts et al., 1996; and Schlimm et al., 1996).

Similar to other heterogeneous reactions, degradation of chlorinated organic using zero-valent metals involves (1) the transfer of the targeted compound from bulk solution phase to the solid phase, (2) adsorption on the metal surface, (3) degradation reactions, and (4) desorption of the products from the metal surface back to the solution phase. Under suitable experimental conditions, the mass transfer resistance in (1) and (4) can be neglected and the process can be assumed to be reaction-limited. Experimental data obtain in this situation can be used to obtain the observed reaction rate constant as a starting point to study the effect of different variables on the degradation activity of the particles. This include the initial reactant concentration, metal loading, solution pH, intra and interspecies competitive effects, presence of different cosolutes, etc. (Arnold et al., 2000; Matheson et al., 1994; and Song et al., 2005) The kinetic data is analyzed using the pseudo first-order reaction model and different observed reaction rate constants for similar targeted compounds were obtained. However, when the observed first-order reaction constants were normalized by the surface area of the particles, it was found that a general trend was observed with the surface area-normalized reaction constant obtained for each of the chlorinated compounds that deviates only by an order of magnitude as
reported in the literature and demonstrated in this study. Based on this observation, surface area-normalized rate constant has been used to characterize the reaction kinetics obtained experimentally. Further theoretical analysis has also been attempted to obtain the structure-activity correlation but the lack of sufficient empirical data coupled with the fact that the surface area-normalized rate calculated cannot accurately characterize the collective impact of experimental variables have impeded such effort (Arnold et al., 2002; Johnson et al., 1996; and Song et al., 2005).

In depth modeling of degradation kinetic that incorporates the mass transfer effect, non-linear sorption behavior, and surface heterogeneity of particles has been reported (Bandstra et al., 2004; and Murzin, et al., 2002 and 2005). It was found that the reaction kinetic is first-order in nature with respect to the targeted compound at low concentration after accounting all of the external variables. However, the first-order model will gradually shift to zero-order with the increase in concentration as shown by the experimental and mathematical modeling analysis. This observation is expected in heterogeneous reaction and can be explain by the effect of surface saturation of the targeted compound. Satisfactory results were obtained using simple models such as the Langmuir, Freundlich, and Temkin isotherms to include the quasi and most often non-linear sorption behavior of the studied compound on the particles surface (Janda, et al., 2004; and Lynggaard, et al., 2004). More advanced approach such as the Langmir-Hinshelwood and combined first and zero-order model were derived and used to estimate the rate constants and to analyze the effect of variables on the reaction kinetics and mechanisms. One of theses studies is conducted by Gotpagar et al. (1997) in which they have introduced a term called the fraction active sites parameter and demonstrated the ability of their model to predict the intrinsic reaction rate by assuming the new parameter
to be constant. Another pair of studies by Burris et al. (1995, 1998) assumed that the sorption of TCE is to non-reactive sites, effectively separating the non-reactive sorption from the reactive sites responsible for degrading the TCE. The authors have also shown that the quasi equilibrium sorption of TCE to be non-linear and can be fitted to a generalized Langmuir isotherm.

Nanosized particles, especially nanoiron, have been synthesized for the use in degradation studies. High surface area and other special physicochemical properties of the nanoparticles have shown to be able to enhance the degradation kinetics by orders of magnitude over bulk zero-valent metals (Liu et al., 2005; and Schrick et al., 2002). Due to the improved degradation results achieved by monometallic nanoiron, incorporating a second dopant such as nickel and palladium as a catalytic agent have been shown to further enhance the degradation kinetics and minimize the formation of other toxic by-products (Schrick et al., 2002; and Zhang et al., 1998). This advancement achieved by bimetallic nanoparticles is hypothesized to be the change in the reaction mechanisms. Conventional electron-transfer mechanism of nanoiron as shown in Figure 2.1.2.2.b is shifted to catalytic reductive hydrodegradation using the bimetallic nanoparticles such as nickel/iron or palladium/iron. The synergistic effect achieved by the bimetallic nanoparticles is due to the enhanced electronic interactions as well as structural/morphological properties of the systems. This is evidenced by the reported results where physical mixture of separately synthesized nickel and iron nanoparticles showed lower degradation kinetic as compared to the bimetallic particles (Schrick et al., 2002; and Zhang et al., 1998).
Figure 2.1.2.2.b. Enhanced catalytic reaction mechanism of bimetallic nanoparticles with TCE as the targeted compound.
2.2. Synthesis of Nanoparticles

Synthesis of nanoparticles in this study can be categorized into two main approaches: (1) direct solution phase synthesis by metal salt reduction, and (2) *in-situ* reduction of Fe\(^{2+}\) during the formation of membrane matrix followed by post-coating with nickel or palladium on the nanoiron surface. The solution phase synthesis of nanoparticles is well-studied and will be detailed in the following section. Publications on the use of organic polymers as protective and particles size-controlling agent are also widely available. One of the main focuses of this work is to integrate solution phase nanoparticles synthesis with an organic polymer for the formation of a hybrid mixed matrix membrane reactor with immobilized bimetallic nanoparticles for the remediation of chlorinated organics.

2.2.1. Solution Phase Synthesis

The solution synthesis of nanoparticles can be divided into two main categories: chemical and physical methods. The chemical approach involves reduction of metal ions using reducing agents such as hydrazine and metal borohydrides. The physical method is the thermolysis of organometallic precursors in the presence of a polymeric non-aqueous solvent.

In the chemical method, the use of suitable reducing agent depends on the reduction potential of different metal ions with respect to the standard reduction potential. The standard reduction potentials for iron and nickel are -0.44 V and -0.24 V, respectively:

\[
\begin{align*}
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe} \quad E^0 = -0.44 \text{ V} \quad (2.2.1.a) \\
\text{Ni}^{2+} + 2e^- & \rightarrow \text{Ni} \quad E^0 = -0.25 \text{ V} \quad (2.2.1.b)
\end{align*}
\]
In theory, synthesis of iron or nickel nanoparticles at room temperature is possible using a reducing agent with standard reduction potential more negative than -0.44 V.

The reduction potential of hydrazine, N₂H₄, is a function of solution pH and the reaction is usually conducted at temperature above 70 °C to favor the formation of nanoparticles with narrow size distribution (Boudjahem et al., 2004; Degen et al., 1999; Li et al., 1999; and Yang et al., 2004):

\[
\begin{align*}
N_2 + 4H^+ + 4e^- &\rightarrow N_2H_4 & E^0 = -0.23 \text{ V} & (2.2.1.c) \\
N_2 + 4H_2O + 4e^- &\rightarrow N_2H_4 + 4OH^- & E^0 = -1.16 \text{ V} & (2.2.1.d)
\end{align*}
\]

Based on the reduction potential of Fe²⁺ and Ni²⁺, the synthesis of iron and/or nickel nanoparticles is favored at alkaline conditions:

\[
2 \text{M}^{2+} + N_2H_4 + 4OH^- \rightarrow 2\text{M} + N_2 + 4H_2O \quad (2.2.1.e)
\]

One major advantage of using hydrazine is the absence of any metal subspecies formation. However, hydrazine is highly toxic and undergoes self-oxidation and reduction at all pH conditions according to the following reaction mechanism:

\[
3N_2H_4 \rightarrow N_2 + 4NH_3 \quad (2.2.1.f)
\]

The final synthesized nanoparticles are reported to be highly crystalline in nature and have not been studied as active agents in the degradation of toxic organics (Li et al., 1999; and Yang et al., 2004).

Metal borohydrides such as KBH₄ and NaBH₄ is the most widely studied reducing agent for the synthesis of nanoparticles for use in the degradation of chlorinated organics. Literature is available for studies of effects such as pH, solvent, borohydride addition rate etc. on the structural/morphological, magnetic, and catalytic properties of the final nanoparticles (Glavee et al., 1995; Li et al., 1999; Shen et al., 1993). Glavee et al. (1995) showed that nanosized amorphous zero-valent iron is synthesized under aqueous solution
of sodium borohydride but Fe₂B particles are obtained in non-aqueous solvent such as
diglyme and tetrahydrofuran (Bönemann et al., 1993; and Glavee et al., 1995). Another
study by Liu et al. (2005) showed that highly disordered and catalytic Fe/B nanoparticles
were synthesized by drop-wise addition of metal solutions into the borohydride solution.
The standard method involved the use of borohydride concentration at least two times
higher than the metal ions concentration at room temperature and was conducted at
neutral pH (Schrick et al., 2002; Tee et al., 2005; and Zhang et al., 1998). Similar to
hydrazine, the reduction reaction of borohydride ions is favorable at alkaline condition
according to its standard electrode potential:

\[
\begin{align*}
\text{HBO}_2 + 3\text{H}^+ + 2\text{H}_2 + 4\text{e}^- & \rightarrow \text{BH}_4^- + 2\text{H}_2\text{O} & E^0 = -0.98 \text{ V} & (2.2.1.g) \\
\text{BO}_2^- + 2\text{H}_2\text{O} + 2\text{H}_2 + 4\text{e}^- & \rightarrow \text{BH}_4^- + 4\text{OH}^- & E^0 = -1.67 \text{ V} & (2.2.1.h)
\end{align*}
\]

However, at alkaline conditions iron hydroxides can form that may adversely affect the
physicochemical properties for the end use of the final nanoparticles. In addition, the
formation of metal borides is dependent on the metal species as well as the experimental
procedure used. The overall reduction reaction by borohydride ions is written as the
following:

\[
\begin{align*}
\text{BH}_4^- + 2\text{M}^{2+} + 2\text{H}_2\text{O} & \rightarrow 2\text{M} + \text{BO}_2^- + 4\text{H}^+ + 2\text{H}_2 & (2.2.1.i) \\
2\text{BH}_4^- + 2\text{M}^{2+} + 2\text{H}_2\text{O} & \rightarrow \text{M}_2\text{B} + \text{HBO}_2 + 2\text{H}^+ + 4.5\text{H}_2 & (2.2.1.j)
\end{align*}
\]

Besides hydrazine and borohydrides, other reducing agent such as sodium
hypophosphite, NaH₂PO₂, have been reported to reduced metal ions under alkaline
condition (pH > 10) based on the oxidation reaction of phosphite ion (Drovosekov et al.,
2004; and Wang et al., 2002):

\[
\text{HPO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{PO}_2^- + 3\text{OH}^- & (2.2.1.k)
\]
However, no extended reports are available and conclusive remarks cannot be drawn from this chemical compound in the synthesis of nanoparticles. Reverse micelle solution that involved the use of different surfactants has also been used to synthesize nanoparticles with uniform particles size (Chen et al., 2000; Chen et al., 1994; and Li et al, 2003). This method also utilized hydrazine or borohydride as the reducing agent and the reaction mechanism are similar to those mentioned previously.

In non-aqueous phase study, the use of the right solvent, reductant, and stabilizing agent is critical to the successful reduction of metal ions. Non-polar solvents such as $N,N$-dimethylformamide (DMF), tetrahydrofuran (THF) etc. as well as polyalcohols such as ethylene glycol, 1,2-propanediol have been used as the solvent/reducing/stabilizing agents (Bönnemann et al., 1993 and 2002; Pastoriza-Santos et al., 1999; and Viau et al., 1996). Other powerful active reducing agent such as the alkalide and electride generated under the complexation reaction of alkali metals and chelate ethers ($A^+\cdot C\cdot A^\cdot e^-$, $A$ = alkali metals, $C$ = ethers as complexing agent) (Tsai et al., 1993; and Kirkpatrick et al., 1999), trialkylborohydride ($A$BEt$_3$H, $A$ = Li, Na, K) (Bönnemann et al., 1993; and Zeng et al., 1993), and organoaluminum compounds ($A$Ir$_3$) (Bönnemann et al., 2002; and Haubold et al., 2003) have also been used as reducing agents.

The most common physical approach used in the synthesis of nanoparticles is the thermolysis of organometallic compounds of carbonyl ($M_a(CO)_b$; $M$ = Fe, Co, Ni; subscript $a$ and $b$ = stoichiometric coefficients) with the presence of a polymeric or surfactant/capping ligand dissolved in organic solvents (Smith et al., 1980; and van Wonterghem et al., 1985). During the decomposition process, the polymer or ligand serve as the nucleation sites and catalyze the nucleation and growth of the particles. Both processes will affect the final particles size. This suggests the importance of the
functionality of the polymer or ligand used for the particles’ physicochemical properties. Bimetallic nanoparticles can also be synthesized by this method and the formation of Ni/Fe and Co/Pt has been reported in the literature (Ge et al., 1997; Park et al., 2001). The thermal decomposition of the metallic carbonyl compounds is achieved at elevated temperature, usually between 130 °C and 170 °C. Decomposition of organometallic precursors at room temperature can also be achieved by using alkene (olefin) complexes. Different monometallic and bimetallic particles have been synthesized by the Chaudret group (Pan et al., 2001; and Zitouan et al., 2002) through decomposition of alkene ligand-complexes generating zero-valent metal and olefin ligands.

**2.2.2. Polymer Phase Synthesis**

The synthetic route for the preparation of polymer-encapsulated or polymer-supported nanoparticles is similar in nature with the solution phase approaches mentioned above. It generally involves two processes as depicted in Figure 2.2.2.a:

a) dissolution of the polymeric and metal precursors followed by mixing.

b) reduction of the metal ions in the polymeric solution phase or casting of the polymer-metal ions complex forming a thin film followed by the final reduction step.

The solvent used in the first step can be aqueous or organic in nature but has to be miscible and compatible for both of the polymer and metal precursors. The final product of the hybrid polymer-metal nanoparticles can be divided into three different physical categories as shown in Figure 2.2.2.b, depending on the desired final end use of the material.

The selection of polymer is important because different functionalities of the organic groups will impart different properties of the final hybrid materials. Some may
Figure 2.2.2.a. Schematic illustrates the steps used in the synthesis of hybrid polymer-metal systems.
Figure 2.2.2.b. Schematic for the different hybrid polymer-metal systems: (a) polymer-supported nanoparticles, (b) polymer-immobilized nanoparticles, and (c) polymer-encapsulated nanoparticles.
not significantly alter the original nature of the metal elements while others may have undesirable effect such as lowering the activity of the metal catalyst. Polymeric systems with negatively charged carboxylic acid group, hydroxyl and amine functional groups with lone-pair electrons that can serve as a chelating agents as well as imposing stabilizing effect are most commonly used and studied.

Reduction methods using alcohol and borohydrides as reducing agent as well as the photochemical, electrochemical, and low-temperature thermal decomposition of zero-valent organometallic compounds without any reducing agent are also reported in literature. For the synthesis of hybrid membrane immobilized Ni/Fe nanoparticles, borohydride reduction is the preferred approach due to its rapid reaction kinetic with metal ions at room temperature that will maintain the integrity of the interaction between the polymer and the metal ions (Shimotori et al., 2004; and Yoon et al., 2003). Other methods that require higher temperature operation are also reported. These include the solvothermolysis and non-aqueous polyol reduction (Hou et al., 2004; and Lu et al., 1999).

2.3. Long Term Reactivity

Attenuation of activity for heterogeneous reaction that will affect the overall reaction selectivity and product conversion often happened after prolonged usage. Mechanisms responsible for the loss of activity can be divided into three main categories: (1) deactivation by aging/sintering, (2) deactivation by fouling, and (3) deactivation by poisoning. Qualitative analysis for these deactivating mechanisms is often conducted by surface characterization techniques such as X-ray photoelectron spectroscopy (XPS), electron diffraction spectroscopy (EDS), scanning electron microscopy (SEM) etc. (Chen
et al., 2006; Hu et al., 2005; and Teixeira et al., 1999). In some cases one of the mechanisms described above will dominate others but most often they occurred simultaneously and interconnected that contribute to the attenuation in activity (Al-Dalama et al., 2006; Corrella et al., 1988; and Rossetti et al., 2005). Some of the activity loss is irreversible while others can be partially reactivated and reused with repeated regeneration cycles.

2.3.1. Precipitation/Morphological Changes

Studies have been conducted to analyze the long term reactivity of the degradation reaction by zero-valent iron with different solution chemistry. Iron as the active reagent acts as electron donor in the degradation process through oxidation/corrosion and further reacts with other cosolutes/electrolytes that are present in the solution, thus forming other iron-based subspecies. Most of these subspecies are insoluble compounds that will precipitate on the active particle’s surface causing the loss of activity. Long term reactivity study with the presence of cosolutes/electrolytes such as carbonate, chloride, nitrate, sulfate, silicate, and other natural organic matter have been reported in the literature (Farrell et al., 2000; Klausen, et al. 2003; Köber et al., 2002; and Kohn et al., 2005). The documented results showed that the precipitation of insoluble matters will decrease the reactivity as analyzed by kinetic study.

Under anaerobic condition and the absence of other impurities in the solution, the most distinguish factor for the attenuation in activity for remediation of chlorinated organics using iron-based systems is the precipitation of iron hydr(oxides) \([\text{Fe(OH)}_n, \text{Fe}_9\text{O}_m]\) forming inactive layers on the particles surface. Most notable species include wüstite (FeO), magnetite (Fe$_3$O$_4$), and maghemite (\(\gamma\)-Fe$_2$O$_3$). In addition, hydrated forms
of ferric oxides such as akaganeite ($\beta$ - FeOOH), goethite ($\alpha$ - FeOOH), and lepidocrocite ($\gamma$ - FeOOH) have also been detected on the surface of spent iron (Roh et al., 2000). The formation of deactivating surface precipitates is a complex process governed by thermodynamic and kinetic factors. For example, magnetite is known to be produced by the oxidation of iron hydroxide and ferrihydrite:

$$\text{Fe}^0 + 2 \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2 \text{H}^+ + 2e^-$$

$$3 \text{Fe(OH)}_2 \leftrightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2 \text{H}_2\text{O}$$

$$2 \text{Fe}_3\text{HO}_8 + 5 \text{Fe}^{2+} + 4 \text{H}_2\text{O} \leftrightarrow 5 \text{Fe}_3\text{O}_4 + 10 \text{H}^+$$

The degradation of chlorinated organics will produce chloride ions that will also react with iron hydroxide forming insoluble green rust according to the following:

$$4 \text{Fe(OH)}_2 + \text{Cl}^- \leftrightarrow \text{Fe}_4(\text{OH})_6\text{Cl} + e^-$$

In addition, morphology and structural alteration caused by the precipitation reaction that can lead to the changes in total surface area also contributed to the activity loss. Attenuation in reactivity due to the reduction in surface area and surface pore clogging are observed in longevity studies of zero-valent iron (Kamolpornwijiy et al., 2003; and Vikesland et al., 2003).

### 2.3.2. Mixed Matrix Membrane Systems

From economical, environmental, and material preservation standpoint of view, it is important to be able to prevent or minimize the loss of activity of the many reagents/catalyst used in industries. Studies have been conducted to recover or regenerate the deactivated catalyst. Reported methods include thermal treatment, chemical refluxing-washing, supercritical fluids system, etc. (Jackson, 2006; Liu et al., 2005; and Zheng et al., 2004). Depending on the catalyst, reaction conditions, and reactor unit used,
in-situ regeneration is sometimes possible to avoid downtime caused by ex situ recovery approach (Burch et al., 1999). Advancement in material sciences for the synthesis of novel and better-resistant catalyst is a continuous process and is crucial for the development of more efficient and cost effective catalytic treatment systems.

Nanocomposite mixed matrix membranes with immobilized reactive particles is a novel material for treating chlorinated organics. Different membrane platforms have been synthesized. These include the cellulose acetate and polyacrylic acid supported on PVDF with immobilized bimetallic/monometallic iron nanoparticles that are shown to be able to remediate chlorinated organics such as TCE and polychlorinated biphenyls (Meyer et al., 2004; and Xu et al., 2005). Membrane systems will be able to better control the size of nanoparticles by preventing aggregation during particles formation and minimize the leaching of ferrous or ferric ions through metal chelating or ion exchange properties of the functional groups. Enhanced reaction kinetics was observed in the membrane-based systems with a rate constant that was orders of magnitude higher than the bulk/granular zero-valent iron (Meyer et al., 2004; and Xu et al., 2005). This observation can be explained by two hypotheses. The high partitioning effect of the organics into the polymeric membrane can increase the surface-sorbed concentration, as more molecules will be able to concentrate in one reactive substrate by leaving the low affinity bulk aqueous phase. Another hypothesis is that the polymeric backbone with different chelating/ion exchange functional groups can prevent the agglomeration of the nanoparticles during the degradation reaction, subsequently minimizing the precipitation and structural/morphological alteration that lead to the attenuation in activity as discussed in section 2.3.1. Figure 2.3.2.a shows the schematic for the degradation coupled with metal ions recapturing in the membrane-immobilized nanoparticles system.
Figure 2.3.2.a. Schematic for the degradation of chlorinated organics by iron-based immobilized nanoparticles and chelating of Fe ions species in the nanocomposite mixed matrix membrane.
3: Reaction Mechanisms and Kinetic Models

3.1. TCE Degradation Mechanism under Batch Study

Similar to a heterogeneous catalytic reaction, the batch degradation processes of TCE include (a) the transport of reactants from the bulk solution to the liquid-solid interface follow by adsorption to surface sites, (b) catalytic hydrodechlorination on the active surface sites, and (c) desorption of the products and transport back to the bulk solution.

(a1): Adsorption of TCE from solution phase to particles surfaces forming a $\pi$-bonded substrate:

\[
\text{C}_2\text{HCl}_3 + \text{S} \xrightleftharpoons[k_{al}]{k_{al}} \text{C}_2\text{HCl}_3\text{-S} \quad (3.1a)
\]

(a2): Formation of a di-$\sigma$-bonded species from the $\pi$-bonded intermediate:

\[
\text{C}_2\text{HCl}_3\text{-S} \rightarrow \text{C}_2\text{HCl}_3^*\text{-S} \quad (3.1b)
\]

(b): Reductive hydrodechlorination reactions on the surface by active nickel hydride (Ni-H) with the formation of ethane as the final product.

\[
\frac{5}{2} \text{Fe} + 5 \text{H}_2\text{O} + 5 \text{Ni} \rightarrow \frac{5}{2} \text{Fe}^{2+} + 5 \text{OH}^- + 5 \text{Ni-H} \quad (3.1c)
\]

\[
\frac{3}{2} \text{Fe} \rightarrow \frac{3}{2} \text{Fe}^{2+} + 3 \text{e}^- \quad (3.1d)
\]

\[
\text{C}_2\text{HCl}_3^*\text{-S} + 5 \text{Ni-H} + 3 \text{e}^- \rightarrow \text{C}_2\text{H}_6^*\text{-S} + 5 \text{Ni} + 3\text{Cl}^- \quad (3.1e)
\]

(c): Desorption of product from surface and transfer back to the bulk solution phase.

\[
\text{C}_2\text{H}_6^*\text{-S} \rightarrow \text{C}_2\text{H}_6 + \text{S} \quad (3.1f)
\]

Combining the hypothesized surface-mediated catalytic mechanisms, the overall TCE degradation with iron oxidation is written as the following:

\[
\text{C}_2\text{HCl}_3 + 4 \text{Fe} + 5 \text{H}_2\text{O} \xrightarrow[k_{int}]{k_{int}} \text{C}_2\text{H}_6 + 4 \text{Fe}^{2+} + 5 \text{OH}^- + 3 \text{Cl}^- \quad (3.1g)
\]
3.2. Batch Degradation Model Derivation

Derivation of the mathematical model for the heterogeneous degradation reaction of TCE in the batch solution study is illustrated in Figure 3.3. According to the schematic, TCE is first sorbed (physical sorption and/or chemisocption) on the particles surface followed by the degradation reaction. The main equation consisting of reaction coupled with adsorption can be represented as the following:

\[
m_{Ni/Fe} \frac{dq_{TCE}}{dt} = -k_{int} m_{Ni/Fe} q_{TCE} - V_{aq} \frac{dC_{aq}}{dt}
\]  

(3.2a)

where \( C_{aq} \) (µmol/L) and \( q_{TCE} \) (µmol/g) is the TCE aqueous phase concentration and surface-sorbed TCE per metal mass, respectively; \( k_{int} \) (hr\(^{-1}\)) is the intrinsic reaction rate constant; \( V_{aq} \) (L) is the total reaction volume; and \( m_{Ni/Fe} \) (g) is the total metal mass used.

In addition to the sorption on the metal surface according to 3.1a, TCE can also form inactive sorbed species on nanoparticles according to the following:

\[
C_2HCl_3 + Si \xrightleftharpoons[k_{a2}][k_{a2}^{-1}] C_2HCl_3-Si
\]

(3.2b)

The TCE aqueous concentration can then be written as the following:

\[
V_{aq} \frac{dC_{aq}}{dt} = -k_{a1} V_{aq} m_{Ni/Fe} C_{aq} C_v - k_{a2} V_{aq} m_{Ni/Fe} C_{aq} C_v
\]

\[
+ k_{a1}^{-1} m_{Ni/Fe} q_{TCE} + k_{a2}^{-1} m_{Ni/Fe} q_{si}
\]

(3.2c)

The definition for the rate constants can be found in appendix (nomenclature). Transmigration of the inactive-sorbed TCE in 3.2b between adjacent reactive sites can occur on the metal surface and such phenomena is observed and reported in the literature.
Figure 3.3. Schematic for non-reactive sorption and reactive sites transformation of TCE by the Ni/Fe (Ni = 20 wt%) nanoparticles
If we assume that the transmigration process of 3.2d is rapid, we can write:

\[ \frac{dq_{si}}{dt}_{FeNi} \approx 0 \approx -k_{si}m_{Ni/Fe}q_{si} + k_{-si}m_{Ni/Fe}q_{TCE} \]  \hspace{1cm} (3.2e)

and we get:

\[ q_{si} = K_{si}q_{TCE}, \quad \left( K_{si} = \frac{k_{-si}}{k_{si}} \right) \]  \hspace{1cm} (3.2f)

Substituting eq 3.2f into eq 3.2c and further rearrangements we obtain the following TCE aqueous concentration equation:

\[ V_{aq} \frac{dC_{aq}}{dt} = -K_{A}m_{Ni/Fe}C_{aq}C_{V} + K_{B}m_{Ni/Fe}q_{TCE} \]  \hspace{1cm} (3.2g)

with:

\[ K_{A} = (k_{a1} + k_{a2})V_{aq}, \quad K_{B} = (k_{-a1} + k_{-a2}K_{si}) \]  \hspace{1cm} (3.2h)

Combining eq 3.2a and eq 3.2g we obtain the representative equation for degradation of surface-sorbed TCE:

\[ m_{Ni/Fe} \frac{dq_{TCE}}{dt} = -(k_{int} + K_{B})m_{Ni/Fe}q_{TCE} + K_{A}m_{Ni/Fe}C_{aq}C_{V} \]  \hspace{1cm} (3.2i)

The surface-sorbed TCE can be characterized by Langmuirian-type quasi sorption isotherm written as the following (the sorption of aqueous TCE to particles surface is termed quasi due to the simultaneous sorption and degradation reactions):

\[ q_{TCE}(t) = \frac{KQC_{aq}(t)}{1 + KC_{aq}(t)} \]  \hspace{1cm} (3.2j)
where $K$ (L/$\mu$mol) and $Q$ ($\mu$mol/g) is sorption parameter and maximum sorption concentration, respectively. Equation 3.2i is transformed into aqueous phase TCE concentration by using eq 3.2j. After some mathematical operations the final equation becomes:

$$\frac{dC_{aq}}{dt} = -(k_{int} + K_b)C_{aq} (1 + KC_{aq}) - \frac{K_A C_v}{K} C_{aq} (1 + KC_{aq})^2$$  \hspace{1cm} (3.2k)

This is the general model derived for batch degradation reaction with surface sorption and rapid transmigration of inactive-sorbed TCE to near-by active sites, which is different from the pseudo first-order reaction model without the sorption effect that is commonly used and reported in the literature for TCE study (Arnold et al., 1998 and 2000; Tee et al., 2005; Schrick et al., 2002; and Gotpagar et al., 1997). The assumptions used in deriving the model for the complex heterogeneous surface reactions are summarized as followed:

1. Mass transfer resistance between the aqueous and solid boundary layer are negligible
2. Degradation reactions for TCE and any surface-sorbed intermediates are irreversible.
3. TCE dechlorination occurred on the particles surface before desorption of products to the bulk solution.
4. Reactions are at isothermal condition.
5. Absence of inter and intraspecies competitive effects.
6. Gaseous products such as ethylene and ethane are assumed to accumulate only at the headspace due to its low solubility in the aqueous phase.
Chapter 4: Experimental Section

4.1. Experimental Setups and Chemicals

Experimental setup for batch and convective flow degradation study are illustrated in Figure 4.1.a. Chemicals obtained from Aldrich Chemical Inc. were: granular sodium borohydride (NaBH₄ = 99.995%), methylene chloride (CH₂Cl₂ = 99.6%, A.C.S. reagent), high molecular weight chitosan flakes (Mw ≈ 1,000,000 with >75% deacetylation), sulfosuccinic acid (70 wt% in aqueous solution), nickel chloride (NiCl₂.6H₂O = 99.99%), palladium (II) acetate ((CH₃COO)₂Pd = 99.98%), silica gel (Davisil® Grade 710, pore size 60 Å, pore volume 0.75 cm³/g, particle size 4-20 µm), ultrapure grade tris(hydroxymethyl)-aminomethane (purity = 99.9+%), and ethanol (denatured reagent grade, water < 0.0003%). Trichloroethylene (TCE, C₂HCl₃ = 99.99%), ferrous chloride (FeCl₂.4H₂O = 102.00%), sodium hydroxide solution (certified as 0.2490-0.2510 N), hydrochloric acid solution (certified as 0.2 N), nitric acid (trace metal grade), glacial acetic acid (HPLC grade), hexane (GC-MS grade), and deionized ultra filtered water were purchased from Fisher Scientific. Potassium hexachloropalladate (K₂PdCl₆, Pd assay as 26.8%) was obtained from Alfa Aesar. 2,2’-dichlorobiphenyls (DCB: 99.9 purity), 2-chlorobiphenyls (99.9% purity), and biphenyls (99.9% purity) were from Ultra Scientific. All of the chemicals and materials were used without further treatment. DIUF were deoxygenated by heating at ~60 °C and bubbling with nitrogen gas overnight before used in the study.
Figure 4.1.a. Schematic for convective degradation study
4.2. Nanoparticles Characterization

4.2.1. Brunauer, Emmett, and Teller (BET) Surface Area Analysis

BET (Nitrogen Brunauer-Emmet-Teller) surface area analysis was performed using Micromeritics ASAP 2000 to determine the surface area of the nanoparticles. Samples were dried under vacuum at 120 °C overnight and subsequently purged with N₂ before each measurement.

4.2.2. X-Ray Diffraction (XRD) Analysis

Thin films X-ray diffraction for all chitosan membranes were characterized using a Siemens diffractometer interfaced with a DACO-Kristalloflex using Cu Kα (λ = 0.1541 nm) as radiation source generated at 40 kV and 30 mA. The XRD data were collected using a scanning rate of 1.0° min⁻¹ and a scanning mode with a step size of 0.08° in the 2θ ranged from 5° to 85° for chitosan-silica gel membranes and 10° to 90° for all other samples.

4.2.3. Thermogravimetric (TGA) Analysis

The membranes thermal properties were evaluated using Perkin-Elmer Thermogravimetric Analyzer (TGA-7) interfaced with Pyris Thermal Analysis software Version 7. The membrane samples were freeze-dried and crushed into pieces using liquid nitrogen. This was followed by weighing approximately 5.0 mg of sample and heating it from 40 °C to 800 °C at 10°C/min under nitrogen atmosphere.

4.2.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

ThermoNicolet Nexus 470 spectrometer was used for FTIR analysis to detect the presence of functional groups in the membranes. Thin membrane samples were attached
to a polyethylene substrate FT-IR card from Thermo Electron Corp. and analyzed at ambient temperature. All spectra were obtained from 100 scans at 4.0 cm\(^{-1}\) resolution with spectrum ranged from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

4.2.5. Atomic-Adsorption (AA) and Inductively-Coupled Plasma (ICP) Analysis

The total metal loading of iron and nickel in the membrane was analyzed using Varian Fast Sequential AA Spectrometer (SpectraAA 220/FS) interfaced with SpectraAA V-3.0 for quantitative analysis. The palladium content in the membrane was determined using Varian Vista-Pro Simultaneous ICP-OES machine. The use of ICP for palladium analysis is due to the expected low Pd content in the membrane that required analytical method with high sensitivity at low detection limit. Five-point linear calibration curves for iron, nickel, and palladium were constructed and the results were correlated accordingly. The calibration curves were periodically checked with solutions appropriately diluted using standards obtained from Ultra Scientific (Pd\(^{2+}\) = 1,000 mg/L) and Fisher Scientific (Fe\(^{2+}\) and Ni\(^{2+}\) = 1,000 mg/L).

4.2.6. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS) Analysis

High resolution SEM and SEM-EDS analyses were performed by Hitachi S-900 operated at 3 kV and Hitachi S-3200 at 20 kV, respectively. Both machines were pumped to near vacuum at ~50 mTorr. Samples for high resolution SEM imaging were sputter-coated with a thin layer of gold coating with a thickness of ~2 nm to 5 nm (~20 seconds sputter time) by an EmScope SC 400 sputter coater to reduce electrostatic charging. SEM-EDS elemental analysis was conducted using a Noran Voyager EDS detector.
interfaced with Noran Voyager Easy Spectra V-4.2.2 for qualitative and quantitative analyses.

4.2.7. High Resolution Transmission Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (HRTEM-EDS) Analysis

A JEOL 2010F FasTEM field emission electron microscopy equipped with an EDS detector operated at 200 kV was used to carry out the HRTEM-EDS analysis. Electron beam with point-to-point resolution of 0.5 nm was used for the EDS elemental analysis of iron, nickel, and silica at different membrane areas. Lacey carbon copper grid (Lacey Carbon Type-A, Ted Palla, Inc.) was coated with membrane solution and dried under vacuum. This was followed by the reduction of Fe$^{2+}$ and the dissolution of silica gel using borohydride solution. After the reduction process, the iron nanoparticles were doped with nickel and re-dried under vacuum. The vacuum-dried sample was dipped into another borohydride solution. The copper grid with chitosan-immobilized Ni/Fe nanoparticles was washed with ethanol and dried in the hood before the HRTEM-EDS analysis.

4.3. Solution Phase Synthesis of Nanoparticles

4.3.1. Bimetallic Ni/Fe Nanoparticles

Different compositions of Ni/Fe nanoparticles were synthesized by the sodium borohydride reduction of 0.05 M aqueous mixture of Ni$^{2+}$ and Fe$^{2+}$ solution. Initial pH of the mixture was 3.8. The solution was stirred for 15 minutes without pH adjustment under nitrogen purging for homogeneous mixing and to eliminate oxygen in the reaction vessel. Reduction of Ni$^{2+}$ and Fe$^{2+}$ were proceeded by slowly adding 0.20 M of sodium borohydride (pH = 10.0) which is in four fold molar excess of the combined Fe$^{2+}$ and
Ni$^{2+}$ into the mixture with intense stirring. Nitrogen gas was circulated in the reaction vessel to prevent the accumulation of hydrogen gas generated during the reduction process. Rapid increase in the solution pH from 3.8 to 6.3 was observed when approximately 2.0 mmol of borohydride was added into the solution. This was followed by a decrease in pH to 4.4 in which the reduction of Fe$^{2+}$ and Ni$^{2+}$ begins to take place. During the reduction reaction, color was observed to change from brownish-green to black solution with the formation of dark colloidal particles. The final solution pH with Ni/Fe nanoparticles was around 9.8. The solution was stirred for an additional 15 minutes followed by vacuum-filtration using Durapore ultrafiltration membrane with 0.1 µm pore size. The nanoparticles were washed with excess amount of deoxygenated water and rinsed with ethanol and acetone before being dried at 50 °C under vacuum overnight. The vacuum-dried nanoparticles were then used immediately for TCE degradation studies. Reproducibility of the nanoparticles synthesized was shown by the consistent results obtained in the TCE degradation studies and the characterization analysis of SEM, TEM, and BET.

### 4.3.2. Bimetallic Pd/Fe Nanoparticles

Palladized nanoparticles were synthesized by post-coating the acid-treated nanoiron (synthesized by sodium borohydride solution) with different Pd$^{2+}$ concentrations (using 550 mg/L Pd$^{2+}$ from K$_2$PdCl$_6$) in solvent mixture of water/ethanol (1/9) under continuous stirring. Different surface-coated palladium nanoparticles were obtained by changing the concentration of Pd$^{2+}$ coating solution. The coating process was completed when the visible yellow brownish Pd$^{2+}$ became a clear solution (about 30 min to 40 min). The Pd/Fe nanoparticles were filtered and washed with deoxygenated water.
and ethanol. This was followed by drying under vacuum overnight and used in the next day for degradation analysis.

4.4. Synthesis of Membrane

4.4.1. Chitosan Membrane with Silica Gel

Chitosan membrane was synthesized by dissolving 1.0 g of chitosan flakes in a 100 ml total volume of 1 vol% acetic acid solution. The mixture was vigorously stirred for 2 hours with a mechanical stirrer to dissolve the chitosan. This was followed by the addition of 1.0 ml of 70 wt% sulfosuccinic acid in the solution and stirred for another 2 hours. Silica gel was then added slowly into the mixtures and allowed to mix for 30 minutes under intense stirring for homogeneity. The final pH of the solution was about 2.2. A specific weight of the solution (8.00 g) was poured on a Petri dish (diameter = 7.5 cm) and dried in the hood. The dried chitosan film was soaked in 500 ml aqueous solution of 0.20 M NaBH₄ twice for a total immersion time of 3 hours. Chitosan membrane was formed and detached easily from the Petri dish once being soaked in the NaBH₄ solution. The resulting membrane was thoroughly washed with deoxygenated water followed by the rinsing with ethanol before further analysis.

4.4.2. Chitosan-Immobilized Iron Nanoparticles Membrane with Silica Gel

Solution mixture of chitosan, sulfosuccinic acid, and silica gel was prepared by the same procedure outlined previously (section 4.2.1). 10 ml of 0.18 M Fe²⁺ aqueous solution was added to the chitosan mixture and mechanically stirred for 2 hours. The final pH of the solution mixture was 3.00. Specific amount of the mixture was poured on a Petri dish (diameter = 7.5 cm) and allowed to dry overnight in the hood. The synthesis of
chitosan-immobilized iron nanoparticles membrane was achieved by immersing the dried film in a 500 ml of 0.40 M NaBH₄ solution (pH ≈ 10). Intense reaction with bubbling accompanied by the gradual formation of a dark and rigid membrane was observed at the beginning. Reduction reaction of Fe²⁺ to zero-valent iron nanoparticles and the dissolution of silica gel in alkaline medium continued as the membrane immersed in the BH₄⁻ solution. This process is repeated a second time for a total of 3-hour immersion of the membrane in the borohydride solution. After the immersion process, the membrane was placed in a pressure cell with a filter paper as support. The cell was filled with 50 ml of 0.40 M NaBH₄ (50 vol% in ethanol) and pressurized to 5.8 bar using nitrogen gas. This second step is to ensure the complete reduction of Fe²⁺ in the membrane matrix to zero-valent iron nanoparticles as the BH₄⁻ convectively passed through the membrane in the pressure cell. This process was also repeated twice with a total volume of 100 ml of 0.40 M NaBH₄. Four batches of 50 ml ethanol were added and convectively passed through the membrane to wash the membrane thoroughly in the cell. The synthesis flow chart is shown in Figure 4.4.2.a.
Step 1: Solution Mixture

Dissolution of Chitosan in Acetic Acid
(1g in 100 ml of 1 vol% acetic acid)

Mechanically Stir for 2 hours

10 ml of 0.18 M Fe²⁺ (Fe²⁺ = 1.80 x 10⁻³ mol) +
Sulfosuccinic Acid (7.0 vol% of total volume) to
Enhance the Stability of Thin Film During
Membrane Formation

Addition of 0.25 g Silica Gel (6 nm pore size, 0.75 cm³/g pore volume, 4-20 µm particle size) into Mixture
(20 wt% of Silica gel with respect to Chitosan)

Mechanically Stir for 30 minutes

Drying Part of the Solution (6g) Overnight in Hood Forming Thin Film on Petri Dish (Diameter = 7.5 cm)  (Refer
to Figure 5.3.1.c-(a)  for EDS elemental analysis and Figure 5.3.1.c-(b) for SEM surface image)

Step 2: Chitosan-Embedded Fe Nanoparticles Membrane

Soaking in 500 ml of 0.40 M NaBH₄ (pH = 9.8-10.5) twice for a total of 3 hours duration:
  a. Chitosan Membrane Formation
  b. Complete leaching of Sulfosuccinic acid
  c. SiO₂ Dissolution
  d. Fe(H₂O)₆²⁺ + 2BH₄⁻ → Fe⁰ + 2B(OH)₃ + 7H₂

Formation of Chitosan-Embedded Fe Nanoparticles Membrane with
Silica (Refer to Figure 5.3.1.d-(a) for EDS elemental analysis and
Figure 5.3.1.d-(b) for SEM surface image)

100 ml of 0.40 M NaBH₄ (50 vol % in ethanol)
Convectively Passed through Membrane Matrix in
Pressure Cell (Flux = 1.55 x 10⁻⁴ cm³ s⁻¹ cm⁻² at 5.8 bar)

200 ml of Ethanol Washing of
Membrane in the Pressure Cell
(Flux = 1.20 x 10⁻⁴ cm³ s⁻¹ cm⁻² at
5.8 bar)

Figure 4.4.2.a. Flow chart for the synthesis of chitosan-immobilized Fe nanoparticles membrane with silica
4.4.3. Chitosan-Immobilized Ni/Fe and Pd/Fe Nanoparticles Membrane with Silica Gel

The doping of chitosan-immobilized iron nanoparticles membrane with nickel was conducted using 60 ml of 0.50 x 10^-3 M Ni^{2+} in ethanol solution (Ni^{2+} from stock of 12000 mg/L aqueous solution prepared from NiCl_2.6H_2O). The Ni^{2+} was allowed to convectively pass through the membrane in the cell under pressurized condition (5.8 bar). After the doping process, 100 ml of 0.20 M NaBH_4 solution (50 vol% ethanol) was added in the cell and convectively passed through the membrane at 5.8 bar. The chitosan-immobilized Ni/Fe nanoparticles hybrid mixed matrix membrane was washed with copious amount of ethanol in the cell followed by rinsing with deoxygenated water before being used in the TCE degradation study. Post coating of the chitosan-immobilized iron nanoparticles with palladium is similar as described above. In brief, the membrane in the pressure cell was filled with 6 ml of 0.05 x 10^-3 M Pd^{2+} (550 mg/L Pd^{2+} from palladium (II) acetate) in acetone. The cell was pressurized and post coating of iron nanoparticles with palladium was achieved as the Pd^{2+} convectively passed thorough the membrane. No NaBH_4 was used after the post coating of Fe nanoparticles with Pd. This is due to the ability of zero-valent iron to reduce Pd^{2+} based on the difference in the reduction potential:

\[
Pd^{2+} + 2e^- \rightarrow Pd^0 \quad E^o = + 0.98 \quad (4.4.3.a)
\]

\[
Fe^{2+} + 2e^- \rightarrow Fe^0 \quad E^o = - 0.44 \quad (4.4.3.b)
\]

\[
Fe^0 + Pd^{2+} \rightarrow Fe^{2+} + Pd^0 \quad (4.4.3.c)
\]
The chitosan-immobilized Pd/Fe nanoparticles membrane was thoroughly washed with ethanol in the cell. This was followed by rinsing with deoxygenated water once the membranes were taken out from the cell and used immediately in the DCB degradation study. Table 4.4.3.a and Table 4.4.3.b showed the characteristics of the membranes used in the TCE and DCB degradation studies, respectively. Figure 4.4.3.a showed the flowchart for the doping and post-coating of nickel and palladium.

4.5 Batch Degradation Study

4.5.1 Trichloroethylene (TCE)-Kinetic Analysis

Degradation study of TCE was conducted using 100 mg of Ni/Fe nanoparticles with initial TCE concentration of 10 mg/L in a 42-ml total volume serum-seal glass vial. The initial pH of the solution was 6.5. Two ml headspace was left in the vial for gas phase analysis. The reaction vials were clamped to a shaker and samples were collected at different time intervals. Control experiments without the Ni/Fe nanoparticles were performed and the total TCE balance in the liquid phase was 98% of the initial TCE concentration. This showed that the volatility of TCE in the headspace is negligible in this study. TCE degradation study for each of the Ni/Fe bimetallic systems was conducted by two separate batches of Ni/Fe nanoparticles. Same experimental procedure was used in the study of the effect of metal loading on TCE degradation using five batches of separately prepared Ni/Fe nanoparticles with 20 wt% nickel.

For the chitosan-immobilized Ni/Fe study, batch experiments were conducted in 42-ml total volume serum-seal glass vial using two pieces of the membranes with an initial TCE concentration of 10 mg/L. The metal loading and Ni/Fe ratio for each of the
Table 4.4.3.a. Characteristics and metal loading of chitosan-immobilized bimetallic Ni/Fe nanoparticles mixed matrix membranes with silica for TCE degradation study

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane weight</td>
<td>65.00 ± 4.50 mg</td>
</tr>
<tr>
<td>Membrane diameter</td>
<td>6.50 cm</td>
</tr>
<tr>
<td>Membrane surface area</td>
<td>33.20 cm²</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>60.50 ± 5.50 µm</td>
</tr>
<tr>
<td>Fe weight</td>
<td>3.60 ± 0.25 mg</td>
</tr>
<tr>
<td>Ni weight</td>
<td>1.20 ± 0.15 mg</td>
</tr>
<tr>
<td>Silica weight</td>
<td>3.50 ± 0.15 mg</td>
</tr>
</tbody>
</table>
Table 4.4.3.b. Characteristics and metal loading of chitosan-immobilized bimetallic Pd/Fe nanoparticles mixed matrix membranes with silica for DCB degradation study

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane weight</td>
<td>39.00 ± 2.0 mg</td>
</tr>
<tr>
<td>Membrane diameter</td>
<td>4.15 cm</td>
</tr>
<tr>
<td>Membrane surface area</td>
<td>13.50 cm²</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>58.50 ± 6.50 μm</td>
</tr>
<tr>
<td>Fe weight</td>
<td>2.80 ± 0.15 mg</td>
</tr>
<tr>
<td>Pd weight</td>
<td>0.015 ± 0.005 mg</td>
</tr>
<tr>
<td>Silica weight</td>
<td>2.20 ± 0.05 mg</td>
</tr>
</tbody>
</table>
Figure 4.4.3.a. Flow chart for the synthesis of chitosan-immobilized bimetallic (Ni/Fe and Pd/Fe) nanoparticles mixed matrix membrane with silica.
membrane was determined by atomic adsorption (AA) analysis (metal loading = 5.20 mg, Ni/Fe ratio = 1/3). Initial and final pH of the solution was 6.5 and ~7.2, respectively. Two ml headspace was left in the vial for gas phase analysis. The reaction vials were clamped to a shaker and samples were collected at different time intervals. Control experiments were performed using chitosan membrane without the Ni/Fe nanoparticles. The total TCE balance in the liquid phase was 96.00 % of the initial TCE concentration. This showed that TCE has negligible partition coefficient in the chitosan and the volatility of TCE in the headspace can be neglected in the mass balance calculation. Reproducibility of the TCE degradation study was checked by using different membranes synthesized from three batches of separately prepared membrane solutions and doping with Ni\textsuperscript{2+} under the same experimental conditions.

For TCE cycle study, a new set of seven batches of TCE solutions were used for each of the cycle analysis. 4 ml of reacted sample from each of the TCE solutions at the end of first cycle (120 min) was withdrawn and another 4 ml of stock TCE solution (100 mg/L) was added back into the vial for a fresh TCE initial concentration of 10 mg/L. New septa vial was used at the beginning of each cycle study. Same procedure was used at the end of second cycle (140 min) where 4 ml of reacted volume was withdrawn from seven new batches of TCE solutions and replenished with 4 ml of 100 mg/L TCE stock solution for the third cycle study. Nitrogen purging was used during the transferring of TCE to prevent oxidation of iron that will affect the hydrogen generation analysis.

4.5.2. TCE and DCB-Hydrogen Analysis

A 120 ml EPA certified vial with Mininert® septa valve is used for trichloroethylene (TCE) and 2,2’-dichlorobiphenyls (DCB) batch degradation study. Two
initial aqueous TCE concentrations (10 mg/L and 500 mg/L) occupied a total volume of 40 ml with 80 ml headspace were used in the TCE study. In the study of pH effect on hydrogen generation rate, initial solution pH of 6.50 was adjusted to 5.0 and 8.0 using HCl or NaOH and tris(hydroxymethyl)- aminomethane (TRIS) as buffer. This organic buffer was chosen because of its reported weak interaction with ferrous in solution (Arnold et al., 2000; and Matheson et al., 1994). Bimetallic Ni/Fe nanoparticles of 0.10 g were added into the TCE solution while under nitrogen purging and the container was immediately sealed with the Mininert® valve to prevent oxygen from entering the vial. Similar approach was used for DCB analysis at room temperature where the degradation of 15 mg/L DCB in 40 ml of ethanol/water (vol=1/1) solvent mixture was conducted using 0.10 g of Pd/Fe nanoparticles. No pH adjustment was made in the DCE study.

4.6 DCB Degradation Study by Membrane Reactor

A high pressure cell with an inner diameter of 4.15 cm (active surface area = 13.50 cm²) was used for the degradation study of DCB under pressure induced operation. The metal loading and Pd weight percentage for the chitosan-immobilized Pd/Fe nanoparticles membrane were determined by ion-coupled plasma (ICP) analysis (metal loading = 2.30 mg, Pd = 0.50 wt% with respect to the total metal loading). The pressure cell was filled with DCB with an initial concentration and total volume of 15 mg/L and 100 ml, respectively. Different transmembrane pressures ranged from 0.35 bar to 11.0 bars were applied to the dead-end flow cell using nitrogen gas. For each of the pressures studied, the first 10 ml of the sample was collected and the collection time was recorded to determine the volumetric flux of the membrane. This was followed by the collection of different sample volumes at different time intervals. The volumetric fluxes were
determined and compared with the initial value to study the flux fluctuation. DCB’s GC-MS analysis for the initial 10 ml sample and the samples collected at later time were conducted to study the steady-state nature of the degradation reaction. It was found that the volumetric fluxes determined at different time intervals for each of the pressures studied were within ±10 % deviation. The DCB’s GC-MS analysis also showed that the reaction has reached its steady-state value as the results showed that the first 10 ml-sample were ±6 % to the sample collected thereafter. Control experiment was conducted using chitosan membranes with silica gel and the results showed that the adsorption of DCB in the membrane phase was 20.00 ± 4.5% relative to the initial concentration of DCB. In contrast to the negligible sorption of TCE in chitosan, the adsorption of DCB in the membrane was taken into account when reporting the degradation results in later kinetic analysis.

4.7 Method of Analysis

4.7.1. TCE Analysis

Liquid phase TCE analysis was performed by Hewlett Packard 5890 Series II gas chromatograph equipped with a Series 6150 mass spectrometer and coupled with OI Analytical Purge-and-Trap Model 4560. The column used was Supelco-1.4 µm SPB-624 with 60 m x 0.25 mm. Initial GC temperature was 35°C and increased to 200°C with a ramping rate of 6 °C/min. Ultra high purity Helium was used as the carrier gas with a flowrate of 7.5 ml/min. MS scan was ranged from m/z = 35 to 260 at 0.6 sec/scan. The TCE detection limit of the OI purge-and-trap instrument was 0.1 µg/L. An internal standard of methylene chloride (0.1 mg/L) was used. It was mixed with the diluted liquid sample during the purging stage of the purge-and-trap analysis. The error associated with
the GC/MS analysis was determined to be 5% based on the initial TCE concentration. Reproducibility of the liquid phase analysis was checked by periodically analyzing TCE standard obtained from Ultra Scientific (HC-270). The TCE balance relative to the initial standard value was 96.0 ± 0.5%.

A cryogenic-capable HP 5890 Series II GC equipped with a Series 6150 mass spectrometer was used for ethane analysis. The GC was cooled to -5 °C by liquid CO2 and maintained for 5 minutes. The temperature was then increased to 200 °C with a ramping rate of 8 °C/min. Ethane analysis was conducted by drawing 0.5 ml of sample volume from the headspace using an air-tight syringe and injected manually into the GC’s sampling port. A five-point ethane standard curve was constructed ($R^2 = 0.996$) by five different known volumes of 100 ppm C1-C6 parafins standard gas mixture purchased from Supelco. The results obtained from the headspace analysis were then correlated with the ethane standard curve. Reproducibility of the standard curve was ensured by injecting known ethane concentrations that fall within the range of the curve. The results obtained were compared with the standard curve and the calculated values were 92.0 ± 0.3 % relative to the actual values.

For the TCE-hydrogen study, aqueous phase TCE concentration was determined using the previous mentioned analytical method. To determine the total TCE concentration (aqueous phase plus solid phase), specific sample volume was withdrawn from the same reaction vial until 20 ml of solution was remained in the container. 20 ml of hexane was added into the vial containing both the TCE solution and nanoparticles. The extraction process was allowed to run overnight. Total TCE concentration was determined using the hexane phase solution and analyzed by a GC-ECD from Varian CP3800 equipped with a RTX-624 capillary column from Restek Corp. coupled with a
CP8300 autosampler. Temperature program used was: 4 minutes holding at initial 40 °C, 7.0 °C/min ramping rate from 40 °C to 100 °C, 30 °C/min from 100 °C to 220 °C, and 1 minute holding at 220°C before return to the initial temperature of 40°C. A standard curve with Cl⁻ ranging from 1 mg/L to 50 mg/L was constructed from Ultra Scientific’s TCE standard (100.40 ± 0.50 mg/L in methanol). Periodic curve-check was conducted at 15 mg/L and 25 mg/L Cl⁻ prepared from dilution of the same standard.

For the TCE cycle study, gaseous degradation products such as ethylene, and ethane were analyzed using another calibration curve constructed by standard gas (1% of acetylene, carbon monoxide, carbon dioxide, ethane, ethylene, methane, and the balance nitrogen) from Scotty Specialty Gases.

### 4.7.2. DCB Analysis

For the batch DCB study, a Varian CP-3800 gas chromatography (column = Varian EZ-Guard capillary column CP-9012) coupled with Varian Saturn-2200 GC/MS was used to measure the aqueous concentration of DCB and its degradation products of 2-chlorobiphenyl and biphenyl. The temperature profile used was: initial temperature of 100 °C increased to 210 °C with a ramping rate of 12 °C/min, from 210 °C to the final 300 °C at 30 °C/min. At different time intervals, 2 ml of sample was added into an 8 ml vial containing 2 ml of hexane for overnight extraction. After extraction, 1 ml aliquot from the hexane phase was transferred to a 1.5 ml GC auto-sampler vial. This was followed by the addition of 10 µl of naphthalene d-8 (~5000 mg/L in methylene chloride from Ultra Scientific) into the auto-sampler vial as internal standard for the GC-MS analysis. The concentrations of DCB and the degradation products of 2-chlorobiphenyls and biphenyls were correlated using a calibration curve ranged from 0.5 mg/L to 20 mg/L
constructed from external standards obtained from Ultra Scientific. Periodic check was conducted to ensure the reproducibility of the calibration curve using 5 mg/L and 10 mg/L standards prepared by diluting the pre-made 100 mg/L DCB, 2-chlorobiphenyls, and biphenyls.

Similar method was used for the aqueous phase DCB analysis in the chitosan-immobilized Ni/Pd membrane analysis. At the end of the degradation study, the used membrane was removed from the convective cell and placed into a 20 ml vial with 10 ml of hexane for membrane phase extraction. The same extraction and sampling procedures described previously was conducted for the membrane’s GC-MS analysis.

### 4.8. Hydrogen Gas Analysis

Quantification of hydrogen gas evolved due to the oxidation of nanoiron and bimetallic nanoparticles (Ni/Fe and Pd/Fe) was conducted using a GC-TCD from Agilent 6890N Network GC System interfaced with ChemStations software and equipped with a Carboxen 1004 micropacked column from Supelco Inc. The temperature program used was: One min holding at 50 °C followed by a ramping rate of 5 °C/min to 120 °C and remained at 120 °C for another minute. Ultra high purity argon was used as the carrier gas. A Hamilton air-tight lock syringe was used to withdraw 1 ml of headspace volume from the vials (with and without degradation analysis) and injected directly to the manual injection port. The total mole of hydrogen generated was correlated with a five-point calibration curve constructed using standard gas of 1% hydrogen in nitrogen (analytical accuracy = ±0.02 %) from Scott Specialty Gasses. To check the accuracy of the calibration curve, a known mass of Fisher electrolytic iron was digested in a 120 ml-vial with 40 ml of 1.0 M nitric acidic. One ml of the headspace sample was analyzed and the
total hydrogen generated was determined using the standard curve. Theoretical value and calculated results using the standard curve was within 96.50 ± 0.50 % accuracy. Imbalance may be due to the surface impurities such as oxides upon exposure of Fisher iron in the air. Leakage through the Mininert® septa vial was checked by injecting a known volume of hydrogen standard gas into the vial filled with 40 ml of deoxygenated water and 80 ml headspace. The headspace hydrogen gas was re-drawn from the headspace at different time intervals (5hr and 10 hr) and its concentration was analyzed using the hydrogen standard curve. Neglecting the solubility of hydrogen in water, percent errors between the initial and time-elapsed value were determined to be less than 5%.
Chapter 5: Results and Discussion

5.1. Nanoparticles

5.1.1. Characterization of Bimetallic Nanoparticles

The morphology and structure of bimetallic Ni/Fe nanoparticles with 20% nickel by weight are shown in Figures 5.1.1.a and Figure 5.1.1.b by SEM and TEM, respectively. The spherical nanoparticles with 20 nm to 40 nm in diameter are connected in chains of beads. This observation is due to the magnetic and electronic interactions between the metals (Zhang et al., 1997). Identical structure and fairly uniform size distribution were observed for different compositions of Ni/Fe nanoparticles. This can be explained by the low molarity of Ni$^{2+}$ and Fe$^{2+}$ together with four fold molar excess of borohydride used in the synthesizing process. This will cause the rapid reduction rate of M$^{2+}$ for the formation of more nuclei, and thus less metal atoms for particle growth. This will produce Ni/Fe with uniform particle size, and hence, uniform surface area as obtained by BET analysis (22 m$^2$/g to 27 m$^2$/g). This observation agreed with the results reported by Nafis et al. (1990) and Hu et al. (1991). They have shown the synthesis of ultrafine Ni/Fe particles with uniform size distribution by the reduction of low concentration of Ni$^{2+}$ and Fe$^{2+}$ aqueous mixture using excess borohydride. Pure nickel and iron nanoparticles having similar chain structure were also synthesized using the same method as shown in Figure 5.1.1.c and Figure 5.1.1.d, respectively. It is observed that the nickel nanoparticles have more uniform size distribution and higher specific surface area than the nanoiron (Ni = 21.12 m$^2$/g, Fe = 12.40 m$^2$/g). This can be explained by the higher reduction rate of nickel by sodium borohydride due to the higher reduction potential of nickel as compared to iron. Same observations were made by Shen et al. (1993) where the reduction of Fe$^{2+}$ and
Figure 5.1.1.a. SEM Image of Ni/Fe Nanoparticles with 20 wt% Nickel
Figure 5.1.1.b. TEM Image of Ni/Fe Nanoparticles with 20 wt% Nickel (20,000 magnification)
Figure 5.1.1.c. SEM Image of Nickel Nanoparticles
Figure 5.1.1.d. SEM Image of Iron Nanoparticles
Ni$^{2+}$ by borohydride produced larger iron nanoparticles than Ni that can be explained by the higher reaction rate of Ni$^{2+}$ with BH$_4^-$.

Semi-quantitative information of the Ni/Fe nanoparticles is provided by EDS analysis and is shown in Figure 5.1.1.e and Figures 5.1.1.f. SEM–EDS analysis in Figure 5.1.1.e was taken from multiple particles due to the electron beam spread ranged from 0.5 µm to 30 µm in diameter (Williams et al., 1996). This will generate an overall elemental analysis on a relatively large area ranging in micron size and provide us with an averaged result that is closely related to the bulk value. Figure 5.1.1.e indeed shows that the SEM–EDS spectra correlated well to the actual nickel weight percentage of 20 wt% in the bimetallic nanoparticles. TEM-EDS with a focused electron beam of 0.5 nm in diameter directed at different spots on the nanoparticles was used to obtain better elemental analysis. Three EDS spectra with different nickel and iron compositions are included in Figures 5.1.1.f. The results indicated that the nanoparticles have different surface compositions. It is hypothesized that the surface reactivity of TCE degradation may be affected by the inhomogeneous surface compositions of the nanoparticles in terms of kinetics and product formation. Detail and thorough analysis of the different surface reactive site responsible for TCE degradation is beyond the scope of this study.

The appearance of oxygen in the elemental analyses is probably due to the oxidation reaction when the nanoparticles were exposed to air during the preparation of the SEM and TEM samples. The reduction of nickel by borohydride is known to be a complex process. In addition to the formation of elemental nickel, Ni$_2$B and insoluble boron species have also been reported as the end products (Legrand et al., 2002). The presence of Ni (JCPDS: 4-0805) and nickel borides (NiB – JCPDS: 6-567, Ni$_2$B –
Figure 5.1.1.e. SEM-EDS Spectrum for Ni/Fe Nanoparticles with 20 wt% Nickel

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom%</th>
<th>Element</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O -K</td>
<td>10.80</td>
<td>3.32</td>
<td></td>
</tr>
<tr>
<td>Fe -K</td>
<td>74.50</td>
<td>80.07</td>
<td></td>
</tr>
<tr>
<td>Ni -K</td>
<td>14.70</td>
<td>16.61</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.1.1.f. TEM-EDS Analysis of Ni/Fe Nanoparticles with 20 wt% Nickel (20,000 magnification)
JCPDS: 25-576, and Ni$_3$B – JCPDS: 19-834) were detected by XRD analysis of the nickel reduced by borohydride. XRD analysis of the bimetallic Ni/Fe (4:1 weight ratio) showed the presence of pure Fe (JCPDS: 6-696) and Ni (JCPDS: 4-0805). The solid solution phases of the bimetallic Ni-Fe also being detected (FeNi$_3$ – JCPDS: 38-419, Fe$_3$Ni$_3$B – JCPDS: 36-979, and Fe$_4$$_3$Ni$_{18.5}$B$_6$ – JCPDS: 19-613) together with the expected borides formation: nickel borides and iron boride (Fe$_2$B – JCPDS: 39-1314).

Elemental analysis obtained by TEM also showed the presence of boron in Figures 5.1.1.f. Both of the figures demonstrated that boron was detected in areas with high nickel content. In contrast, no boron was observed in regions with high iron concentration as shown in Figure 5.1.1.f. These observations are consistent with the studies of Fe$^{2+}$ and Ni$^{2+}$ reduction by borohydride (Legrand et al., 2002; and Glavee et al., 1994 and 1995):

\[
\text{Fe (H}_2\text{O)}_6^{2+} + 2 \text{BH}_4^- \rightarrow \text{Fe} + 2 \text{B(OH)}_3^- + 7 \text{H}_2 \quad (5.1.1.c)
\]

\[
\text{Ni}^{2+} + 2 \text{BH}_4^- + 6 \text{H}_2\text{O} \rightarrow \text{Ni} + 3 \text{B(OH)}_3^- + 7 \text{H}_2 \quad (5.1.1.d)
\]

\[
2 \text{Ni}^{2+} + 4 \text{BH}_4^- + 9 \text{H}_2\text{O} \rightarrow \text{Ni}_2\text{B} + 12.5 \text{H}_2 + 3 \text{B(OH)}_3 \quad (5.1.1.e)
\]

Low boron content shown in this study as compared to other reported values could be the result of different particle synthesis methods. The results obtained by TEM-EDS and XRD showed that the boron peak is highly related to the nickel in the nanoparticles. The absence of boron in the SEM-EDS spectra in Figure 5.1.1.e. is due to the limitations of the scanning probe that can only detect boron at high concentration.

**5.1.2. Batch TCE Degradation**

Rapid TCE degradation by Ni/Fe nanoparticles is showed in Figure 5.1.2.a. Ni/Fe nanoparticles with 20 wt% nickel content completely degraded the TCE in 2-hour period. The degradation rate gradually decreased with decreasing nickel content in the bimetallic systems. The control case in Figure 5.1.2.a was zero-valent iron. The results showed that
Figure 5.1.2.a. Degradation of TCE by Ni/Fe Nanoparticles with Different Ni wt%. Initial TCE Concentration = 10±0.1 mg/L. Bimetallic Loading for all Experiments = 100 mg/40 ml. Reaction Volume = 40 ml. Initial pH = 6.5
the bimetallic Ni/Fe systems have higher TCE degradation rates as compared to the commercially available bulk zero-valent particles such as iron and zinc (Su et al., 1999; Campbell et al., 1997; Roberts et al., 1996; and Arnold et al., 1998 and 2000).

Quantitative analysis of ethane produced in the TCE degradation are shown in Figure 5.1.2.b. Simultaneous degradation of TCE and conversion to ethane was observed for the bimetallic systems consist of 20 wt%, 15 wt%, and 4 wt% nickel. Figure 5.1.2.b-(a) shows the maximum conversion of ethane at 2-hour time period for the 20 wt% nickel particles where complete TCE degradation is also being observed. Similar observation was obtained for nanoparticles with 15 wt% nickel as shown in Figure 5.1.2.b-(b). In contrast, Figure 5.1.2.b-(c) shows the continuous formation of ethane together with TCE degradation in 6-hour time period for 4 wt% nickel particles. This showed that the formation of ethane as the main product is a function of the nickel composition in the Ni/Fe nanoparticles. Total carbon mass balance as C₂ relative to the initial TCE concentration for the systems with 20 wt%, 15 wt%, and 4 wt% nickel was 97.3%, 90.1%, and 87.4%, respectively. Losses of some of the volatile organics may have occurred by experimental errors during sampling through the septa. The formation of ethane as the major final product in the TCE degradation by Ni/Fe was also reported by Schrick et al. (2002). They also showed qualitative indications of the formation of alkenes in short period of degradation. This is followed by the observed straight and branched-chain alkanes in the GC-MS chromatograms as the reaction progressed before the complete conversion of TCE to ethane. The difference between the reported results (Schrick et al., 2002) and our study may be explained by the conditions used in the synthesis and TCE degradation study. These include: no pH adjustment during our nanoparticles synthesis process; direct addition of solid borohydride into the Ni²⁺/Fe²⁺
Figure 5.1.2.b. Quantitative Analysis of Ethane for Ni/Fe Nanoparticles with (a) 20 wt% Ni, (b) 15 wt% Ni, and (c) 4 wt% Ni. Experimental Conditions: 10±0.1 mg/L TCE (Initial TCE = 3.1 mmol), metal loading = 100 mg / 40 ml, reaction volume = 40.0 ml, and initial pH = 6.5
solution by Schrick et al. (2002); and an initial concentration of TCE in our study which was three orders of magnitude lower than Schrick et al. (2002). In the course of our TCE degradation study, the formation of ethane as the final product coupled with the absence of chlorinated by-products indicated that bimetallic Ni/Fe nanoparticles may alter the conventional reaction pathways of the monometallic systems.

The kinetic data for both of the TCE degradation and ethane formation were converted into a time-independent plot as shown in Figure 5.1.2.c. The results show that the ethane yield is directly related to the TCE conversion in Figure 5.1.2.b. Based on these observations and the absence of intermediates in the degradation process, the reaction pathway illustrated in Figure 5.1.2.d-(a) is simplified to Figure 5.1.2.d-(b) and the first-order reaction rate model can be written as:

$$\frac{dC_{aq}}{dt} = -k_{TCE} C_{aq} \approx \frac{dC_{C_2H_6}}{dt} (5.1.2.a)$$

where $C_{aq}$ and $C_{C_2H_6}$ represents the TCE and ethane concentration ($\mu$mol/L), respectively; and $k_{TCE}$ is the pseudo first-order reaction rate constant of TCE (1/hr).

It is hypothesized that the rapid TCE degradation achieved by Ni/Fe nanoparticles is due to the incorporation of nickel as the second dopant metal. In the presence of the catalytic nickel, metal-carbon bonds are expected to be strengthened. This will favor the chemisorptions and the dissociations of C=C intermediates on the metal surface (Agrawal et al., 1996; Burke et al., 1998; Chourasia et al., 1988; and Park et al., 1998). Hydrogenation of the unsaturated intermediates is also greatly enhanced by the active metal hydride formed on the nickel surface where the atomic hydrogen on the metal surface is reported and well-known to be a very powerful reducing agent (Gui et al., 2000; Odziemkowski et al., 2000; Shin et al., 1999; and Wang et al., 2003). These will
Figure 5.1.2.c. Time-Independent Plot of Ethane Yield and TCE Conversion by Ni/Fe Nanoparticles
Figure 5.1.2.d. Reaction Pathways for TCE Degradation by (a) Bulk Fe(0) (adapted from Arnold et al., 2000) and (b) Ni/Fe Nanoparticles
prevent the formation of chlorinated intermediates as well as increasing the TCE degradation rate.

TCE study using nanoiron synthesized by the solution method was also performed. In contrast to the rapid degradation observed by Ni/Fe nanoparticles, the synthesized nanoiron has degradation rate that is two orders of magnitude lower coupled with the formation of acetylene and ethylene as the final products. This shows that bimetallic Ni/Fe was better than the bulk and nanoiron in terms of degradation kinetics. Table 5.1.2.a verifies this observation by showing that the surface area-normalized reaction rate constant of Ni/Fe nanoparticles with 20 wt% nickel is at least one order of magnitude higher than bulk iron and nanoiron. This indicates that nickel is indeed a catalytic dopant metal in the Ni/Fe system, which enhances the TCE degradation. The TCE degradation by nanoiron in this study is lower than the one reported by Schrick et al. (2002). This can be explained by the different synthesis and experimental procedures used in the studies (pH, concentration, etc.), as well as the methods performed in the handling and pretreatment of the nanoparticles (Su et al., 1999; Matheson et al., 1994; Tamara et al., 2004; and Butler et al., 2001).

5.1.3. Effect of Ni Content on TCE Degradation

In section 5.1.2., the composition of Ni/Fe nanoparticles is shown to have a profound effect on TCE degradation. In this study, surface area-normalized reaction rate constant from the pseudo first-order reaction rate model is determined to characterize the TCE degradation by Ni/Fe systems:

\[
\frac{dC_{aq}}{dt} = k_{SA} a_s \rho_m C_{aq} \tag{5.1.3.a}
\]

and according to eq 5.1.2.a, \(k_{SA}\) can be written as:
Table 5.1.2.a. TCE Degradation Study of Fe(0) and Ni/Fe Nanoparticles.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference</th>
<th>BET Surface Area (m²/g)</th>
<th>$k_{SA}$ (L/m²/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peerless Fe(0)</td>
<td>Su et al. (1999)</td>
<td>0.70</td>
<td>8.7 x 10⁻⁵</td>
</tr>
<tr>
<td>Master Builders Fe(0)</td>
<td>Su et al. (1999)</td>
<td>1.20</td>
<td>8.7 x 10⁻⁵</td>
</tr>
<tr>
<td>Fisher Fe(0)</td>
<td>Su et al. (1999)</td>
<td>0.10</td>
<td>9.0 x 10⁻⁴</td>
</tr>
<tr>
<td>Nanoiron</td>
<td>this study</td>
<td>12.40</td>
<td>4.8 x 10⁻⁴</td>
</tr>
<tr>
<td>Nanoiron</td>
<td>Schrick et al. (2002)</td>
<td>18.00</td>
<td>2.0 x 10⁻³</td>
</tr>
<tr>
<td>20 wt% Nickel Nanoparticles</td>
<td>this study</td>
<td>21.22</td>
<td>3.7 x 10⁻²</td>
</tr>
</tbody>
</table>
where $a_s$ is specific surface area of the Ni/Fe (m$^2$/g) obtained by BET surface area analysis, $\rho_m$ is mass concentration of metal (g/L), and $k_{SA}$ is the surface area-normalized reaction rate constant (L/m$^2$/hr). According to eq 5.1.3.b, an estimate of the actual surface area per gram of the catalytic material is needed to complete the kinetic model.

This was done by two methods: (1) average particle size was determined from SEM photomicrographs and converted to surface area per gram, and (2) BET surface area measurement was made using conventional adsorption apparatus. In the first approach, 120 spherical nanoparticles were randomly chosen from the SEM image and an average diameter was estimated. The estimated surface areas shown in Table 5.1.3.a are consistent with the BET measurements. Small differences between the estimates and the BET values are expected due to the presence of cracks or crevices that cannot be observed in the SEM image. This justifies the use of BET surface area in obtaining the $k_{SA}$ for the characterization of TCE degradation.

The reported surface area-normalized reaction rate of 9.80 x $10^{-2}$ L/m$^2$/hr by Schrick et al. (2002) for Ni/Fe (1:3 weight ratio) agreed well with our data of 5.70 x $10^{-2}$ L/m$^2$/hr as shows in Figure 5.1.3.a. Other reported data (Kim et al., 2003) showed the $k_{SA}$ of 1.15 x $10^{-2}$ L/m$^2$/hr by using 0.05 Ni wt% surface coated on the iron powder. These results are two orders of magnitude higher than the $k_{SA}$ reported in the literature (Su et al., 1999; Johnson et al., 1996; Lien et al., 2001; and Schrick et al., 2002) using commercial bulk and powdered iron. $k_{SA}$ for TCE degradation by nanoiron in the literature (Zhang et al., 1998; and Schrick et al., 2002) is also lower by an order of magnitude than the nickel coated iron. This shows the catalytic property of nickel and the effect of different
Table 5.1.3.a. Surface Areas of Ni/Fe, Ni, and Fe Nanoparticles from SEM Image Estimation and BET Analysis

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Average Diameter Observed (nm)</th>
<th>Estimated Surface Area (m²/g)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Fe with 20 wt% Nickel</td>
<td>35</td>
<td>21.22</td>
<td>24.42</td>
</tr>
<tr>
<td>Ni/Fe with 80 wt% Nickel</td>
<td>28</td>
<td>24.63</td>
<td>25.66</td>
</tr>
<tr>
<td>nanonickel [(Ni(0),Ni₂B]</td>
<td>39</td>
<td>17.27</td>
<td>21.12</td>
</tr>
<tr>
<td>nanoiron</td>
<td>58</td>
<td>13.14</td>
<td>12.40</td>
</tr>
</tbody>
</table>
methods used in the synthesis of bimetallic systems to enhance the TCE degradation rate.

Different values of surface area-normalized rate constant were reported in the literature for each of the systems of commercial bulk irons, nanoirons, and bimetallic nanoparticles with almost identical structural, morphological, and physical properties. This is because the $k_{SA}$ determined by eq 5.1.3.b corresponds to the overall particles’ surface reactions and does not distinguish the distributions of different surface sites reactivity. Thus, a more rigorous model that accounts for the surface inhomogeneity is needed in order to obtain the true nature of the TCE degradation by each of the specific systems studied. Gasper et al (2002) has attempted to analyze the reactive sites distribution for the reduction of carbon tetrachloride by granular iron and reported the localization effect in their study. Figure 5.1.3.a showed the compositional effect of nickel on the surface area-normalized reaction rate constants and the STEM-EDS line profiles in Figure 5.1.3.b are used to explain the obtained observations. The $k_{SA}$ values in Figure 5.1.3.a increase with the nickel content in the bimetallic nanoparticles. At 25 wt% Ni the optimum catalytic effect of nickel in the bimetallic system is reached and a decrease in $k_{SA}$ is observed for higher nickel loading. Figures 5.1.3.b-(1a) and Figures 5.1.3.b-(1b) showed that both of the 20 wt% and 80 wt% Ni nanoparticles has higher nickel concentration than iron at the edge. On the contrary, line profiles in Figures 5.1.3.b-(2a) and Figures 5.1.3.b-(2b) show that the continuous domain of the nanoparticles corresponded closely to the actual Ni/Fe weight ratio. Equilibrium phase diagram for iron-nickel alloy reported in the literature demonstrated distinct solution phases that are in accordance to the bimetallic compositions of the two elements (Swartzendruber et al., 1991). Although the study is conducted in bulk alloy systems and at temperatures > 100 °C, it is expected that the bimetallic nanoparticles also possess similar solid solution
Figure 5.1.3.a. Effect of Nickel Compositions in Ni/Fe Nanoparticles on the Surface Area-Normalized Reaction Rate Constant
Figure 5.1.3.b. STEM-EDS Line Profiles: (a) Ni/Fe Nanoparticles with 80 wt% Nickel and (b) Ni/Fe Nanoparticles with 20 wt% Nickel
phase characteristics with respect to the iron-nickel in bulk domain, as is also being reported by Zysler et al. (2001). Thus, the change of reaction rate in the bimetallic systems can be attributed by the different Ni/Fe ratio of the particles (BET surface area for different Ni content bimetallic nanoparticles are between 22.00 m²/g and 28.00 m²/g). In this study, it is hypothesized that the TCE degradation rates for both 20 wt% and 80 wt% Ni particles will be lower at the edges due to high Ni content. With the surface-area normalized reaction rate for the 20 wt% nickel particles close to the optimum value in Figure 5.1.3.a, we can deduce from the line profile that the $k_{SA}$ for this nanoparticles represents highly reactive surface with Ni/Fe at approximately 1/5 ratio, assuming that that surface Ni/Fe composition is similar to the bulk composition as shown in Figure 5.1.3.b-(2b). On the other hand, the low $k_{SA}$ for nanoparticles with 80 wt% Ni is due to the high Ni/Fe ratio on all of the areas as shown by the STEM-EDS analysis. These results clearly demonstrated the surface effect of nickel as the second dopant metal. To be an effective catalyst, the nickel has to be in a close electronic contact with the Fe and maintaining a synergistic Ni/Fe ratio. In addition, structural factors may also play a role in the degradation activity posses by the nanoparticles.

5.1.4. Effect of Metal loading on the Surface Area-Normalized Reaction Rate

The use of surface area-normalized reaction rate constant in the studies of heterogeneous reactions is a common practice. Degradation rate as characterized by $k_{SA}$ should be independent of the mass, surface area of the metal, and the total reaction volume used. Analysis of TCE degradation as shown in Figure 5.1.4.a indeed verified the mentioned characteristics of $k_{SA}$. The results were obtained from five Ni/Fe mass per reaction volumes of 500 mg/L, 750 mg/L, 1500mg/L, 2000 mg/L, and 2500 mg/L using different batches of 20 wt% nickel nanoparticles. Experimental procedures and initial
Figure 5.1.4.a. Normalization of TCE Degradation Rate by Different Metal Mass per Liquid Volume of 500 mg/L, 750 mg/L, 1500 mg/L, 2000 mg/L, and 2500 mg/L. Ni/Fe Used = 20 wt% Nickel. Initial TCE Concentration = 10 ± 0.1 mg/L. Total Reaction Volume= 40 ml. Initial pH = 6.5
conditions were maintained the same for all of the analyses. The observed first-order rate constants determined for each of the five metal loadings are different, as expected. This is due to the increase in surface areas available for TCE adsorption and reaction for systems with higher metal loading. On the other hand, normalization of the degradation results with the metal surface volumes in Figure 5.1.4.a showed an overall $k_{SA}$ value of $(3.30 \pm 0.60) \times 10^{-2}$ L/m$^2$/hr for the 20 wt% nickel nanoparticles. This justifies the use of $k_{SA}$ to determine the compositional effect of nickel in the Ni/Fe systems for TCE degradation.

5.1.5. DCB Degradation by Pd/Fe Nanoparticles

Different palladium-coated nanoiron particles were used to study the degradation of 2,2’-dichlorobiphenyls (DCB) in anaerobic environments. Some general trends are established based on the data obtained in this analysis. Increase in total hydrogen evolved with the presence of DCB degradation was observed in the DCB study for all of the iron nanoparticles coated with different amount of palladium. The surface-coated palladium is hypothesized to adsorb as H$_2$ produced from iron corrosion and to dissociate it into atomic hydrogen forming the active surface palladium hydride that is able to cleave the halogen-carbon bond catalytically (Campbell, 1988; Jobic et al., 1987; Kishore et al., 2005; and Nag, 2001). The bimetallic nature of Pd/Fe also increases the palladium activity through the enhanced electronic effect as reported in the literature (Benedetti et al., 1991). With the presence of palladium on the surface of nanoiron that are in close electronic contact with each other, DCB degradation can be achieved at room temperature in contrast to the inactive nanoiron as shown in Table 5.1.5.a.

An excessive increase in palladium coating on the nanoiron is shown to have a detrimental effect on the total hydrogen generation. Assuming that the atomic diameter of
Table 5.1.5.a. 2,2’-dichlorobiphenyls dechlorination study by Pd/Fe nanoparticles with different surface-coated Pd content

<table>
<thead>
<tr>
<th>Pd wt%</th>
<th>Pd surface area coverage&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Hydrogen generated without Reaction&lt;sup&gt;a&lt;/sup&gt; (µmol)</th>
<th>Hydrogen generated with Reaction&lt;sup&gt;b&lt;/sup&gt; (µmol)</th>
<th>[DCB]&lt;sup&gt;0&lt;/sup&gt;</th>
<th>[2-CB]&lt;sup&gt;0&lt;/sup&gt;</th>
<th>[BP]&lt;sup&gt;0&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>8.60</td>
<td>10.06</td>
<td>no observable degradation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.73%</td>
<td>8.30</td>
<td>16.61</td>
<td>0.93</td>
<td>0.006</td>
<td>0.026</td>
</tr>
<tr>
<td>0.5</td>
<td>7.3%</td>
<td>11.88</td>
<td>19.80</td>
<td>0.82</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>3.0</td>
<td>44%</td>
<td>9.30</td>
<td>16.56</td>
<td>0.70</td>
<td>0.07</td>
<td>0.16</td>
</tr>
<tr>
<td>6.5</td>
<td>95%</td>
<td>0.84</td>
<td>1.26</td>
<td>0.83</td>
<td>0.04</td>
<td>0.07</td>
</tr>
</tbody>
</table>

2- CB = 2-chlorobiphenyls; BP = biphenyls

* reaction condition: Pd/Fe = 0.1 g, volume = 40 ml, ethanol/water = 1:1, headspace = 80 ml, initial DCB = 15 mg/L, initial pH = 6.3, 22 °C
*# analysis/collection time = 120 min
<sup>1</sup> based on Pd cross sectional surface area of 0.072 nm<sup>2</sup> (atomic diameter = 0.15 nm), initial nanoparticles surface area = 28 m<sup>2</sup>/g
Pd is 0.15 nm, Table 5.1.5.a showed the calculated surface coverage of Pd on the nanoiron with a surface area of \( \approx 30 \, \text{m}^2/\text{g} \). As the amount of palladium approached the monolayer surface coverage limit, degradation is observed to diminish in terms of lower DCB conversion to biphenyl. This shows the importance of the bimetallic nature of Pd/Fe where the oxidation of iron provides the hydrogen that is needed by the palladium to remediate the chlorinated biphenyls. This kind of bimetallic synergistic effect is also reported by Nutt et al. (2005) where gradual loss of degradation activity of the gold supported palladium nanoparticles toward TCE hydrodechlorination was observed when the surface Pd exceeded the monolayer coverage.

Successful degradation of polychlorinated biphenyls (PCBs) by palladized iron was first reported by Grittini et al. (1995). A more detail study was conducted by Lowry et al. (2004) and Kim et al. (2004) where the surface area-normalized reaction rate for different polychlorinated biphenyls was obtained. A summary of literature results is listed in Table 5.1.5.b showing the effect of solvents, degree of chlorination and the location of chlorine atom, hypothesized reaction mechanisms, and materials other than palladized iron used in the PCBs study. The general trends include (1) higher degradation rate with increase in the degree of chlorination, (2) ortho-positioned chlorine atoms is least susceptible to dechlorination due to steric factor, and (3) the observed lower degradation kinetics with the increase of non-aqueous solvents in the reacting solution. While the data collected in this analysis is limited to draw any conclusive remark regarding the reaction kinetics and any structure-reactivity correlations, we have confirmed that the degradation reaction will induce iron oxidation in the bimetallic system and established the reactivity for different surface-coated palladium nanoiron in the remediation of chlorinated biphenyls.
Table 5.1.5.b. Selected literature summary for PCBs dechlorination using different palladized iron systems

<table>
<thead>
<tr>
<th>Pd/Fe sample</th>
<th>Pd wt%</th>
<th>Reaction Conditions</th>
<th>$k_{SA}$ (L/m²hr)</th>
<th>PCBs Studied Compounds</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>palladized peerless iron¹</td>
<td>0.05</td>
<td>Pd/Fe = 2 g, volume = 10 ml, methanol/water = 3:7, initial PCBs = 1.55 mg/L, 22 °C</td>
<td>$4.33 \times 10^{-6}$</td>
<td>2,2'-dichloro</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.94 \times 10^{-5}$</td>
<td>3,4'-dichloro</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.60 \times 10^{-5}$</td>
<td>2,3,2',5'-tetrachloro biphenyls</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.44 \times 10^{-5}$</td>
<td>2,4,2',5'-tetrachloro biphenyls</td>
<td>NA</td>
</tr>
<tr>
<td>palladized zero-valent Iron²</td>
<td>0.05</td>
<td>Pd/Fe = 2 g, volume = 20 ml, water &gt; 90 vol%, initial PCBs = 6 mg/L, 23 °C</td>
<td>$1.45 \times 10^{-3}$</td>
<td>2,3-dichloro</td>
<td>&gt;90% dechlorination after 210 hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.55 \times 10^{-3}$</td>
<td>2,4-dichloro</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.85 \times 10^{-3}$</td>
<td>3,4-dichloro biphenyls</td>
<td>NA</td>
</tr>
<tr>
<td>palladized Fisher Scientific iron filling³</td>
<td>0.25</td>
<td>Pd/Fe = 2 g, volume = 5 ml, acetone/water = 1:5, initial PCB = 1.5 mg/L, 20 °C</td>
<td>NA</td>
<td>2,3,2',5'-tetrachlorobiphenyl</td>
<td>Complete dechlorination in 9 hr</td>
</tr>
<tr>
<td>Pd/Fe nanoparticles⁴</td>
<td>NA</td>
<td>Pd/Fe = 0.1 g, volume = 2 ml, ethanol/water = 1:9, initial PCB = 5 mg/L, 22 °C</td>
<td>NA</td>
<td>Aroclor 1254</td>
<td>Complete dechlorination in 17 hr</td>
</tr>
<tr>
<td>palladized Aldrich iron particles⁵</td>
<td>0.05</td>
<td>Pd/Fe = 2 g, volume = 5 ml, methanol/water/acetone = 1:3:1, initial PCB = 20 mg/L, 25 °C</td>
<td>NA</td>
<td>Aroclor 1260</td>
<td>Complete dechlorination in 5 – 10 min</td>
</tr>
</tbody>
</table>

5.2. Hydrogen Analysis

5.2.1. Hydrogen Generation by Ni/Fe Nanoparticles

Degradation of chlorinated organics such as TCE by zero-valent iron is hypothesized to be the surface-mediated electron transfer mechanism assisted by the electrochemical oxidation of iron in anaerobic aqueous condition (Matheson et al., 1994; and Arnold et al., 2000):

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (5.2.1.a)
\]
\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (5.2.1.b)
\]
\[
\text{R-Cl} + \text{H}^+ + 2e^- \rightarrow \text{R-H} + \text{Cl}^- \quad (5.2.1.c)
\]

In addition to the oxidation reaction of 5.2.1a, water under anaerobic condition can serve as an oxidizing agent that corrodes iron generating hydrogen gas according to the following reaction:

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (5.2.1.d)
\]

Thus, in the absence of dechlorination reactions, the total zero-valent iron mass can be assessed by the number of hydrogen evolved through the anaerobic iron oxidation according to eq 5.2.1.d. Figure 5.2.1.a shows the total amount of hydrogen generated by Ni/Fe nanoparticles with different nickel content normalized with iron mass under anaerobic condition. The results represent the sum of the gas phase and aqueous phase hydrogen gas produced:

\[
\text{H}_2 = \text{H}_2(g) + \text{H}_2(aq) \quad (5.2.1.e)
\]

where the gas phase hydrogen, \( \text{H}_2(g) \), is determined directly from the headspace GC-TCD analysis and the aqueous phase hydrogen, \( \text{H}_2(aq) \), is obtained as the following:

\[
\text{H}_2(aq) = (7.515 \times 10^{-6}) \text{H}_2(g) R T M_{\text{H}_2\text{O}} / V_{\text{HS}} \quad (5.2.1.f)
\]

where \( 7.515 \times 10^{-6} \text{ mol kg}^{-1} \text{kPa}^{-1} \) is the solubility of hydrogen in water at 100 kPa at 25
Figure 5.2.1.a. Total hydrogen generation normalized with iron for different bimetallic Ni/Fe nanoparticles versus time under anaerobic aqueous solution. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.
$^\circ$C; $R$ is the gas constant; $T$ the operating temperature; and $M_{H_2O}$ and $V_{HS}$ is the mass of the total solution and headspace volume, respectively. Solid phase hydrogen due to the diffusion and entrapment of $H_2$ by the nanoparticles is assumed to be negligible in short-term analysis (2-hour duration). This assumption is justifiable since the solubility of $H_2$ in metal particles is relatively low, e.g. $< 10^{-5}$ cm$^3$ kg$^{-1}$ at 100 kPA $H_2$ for pure iron; and $< 10^{-2}$ cm$^3$ kg$^{-1}$ at 100 kPA $H_2$ for nickel. Initial hydrogen generated by the anaerobic iron oxidation increased linearly with time within the first two hours for four of the bimetallic systems (20 wt%, 25 wt%, 50 wt%, and 75 wt% nickel) with the 20 wt% and 25 wt% Ni nanoparticles being two of the highest hydrogen generating systems. Lower hydrogen generation with increase in nickel content can be explained by the enriched nickel concentration at the edge of the particles that act as a protective layer to minimize the oxidation of iron. This observation is expected since the simultaneous reduction of $Ni^{2+}$ and $Fe^{2+}$ mixture will generate nanoparticles with nickel predominantly concentrated at the outer layer as reported in the literature (Tee et al., 2005). It is interesting to observe that in Figure 5.2.1.a the total hydrogen generation for $Ni = 20$ wt%, 25 wt%, and 50 wt% falls on a relatively linear trend line ($R^2 = 0.905$) when normalized by the iron mass and the obtained iron-normalized hydrogen generation rate, $k_{H_2}$, based on the regression line is 63.20 $\mu$mol H$_2$/ g Fe hr. This showed that the bimetallic system with up to 50 wt% nickel content still provide satisfactory iron surface concentration in producing hydrogen under anaerobic condition. In contrast, the 75 wt% Ni nanoparticles has had significantly lower iron-normalized H$_2$ generation ($k_{H_2} = 6.70$ $\mu$mol H$_2$/ g Fe hr). This observation confirmed the particles structural properties of enriched surface nickel with respect to higher nickel content that lead to a decrease in the surface iron concentration.
In anaerobic and low temperature environments, iron hydroxides may be metastable phases and are favored thermodynamically to undergo further oxidation:

\[ 3 \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2 \text{H}_2\text{O} \tag{5.2.1.g} \]

Nonetheless, the above process, known as the Schikorr reaction (Stumm et al., 1981), is slow due to kinetic limitation and proceeds satisfactorily only at > 373 K. Thus the hydrogen generated by the reaction in eq 5.2.1g is excluded in our analysis and we assumed that the total \( \text{H}_2 \) gas is dependent only on the corrosion of zero-valent iron.

Hydrogen analysis of pure iron nanoparticles in Figure 5.2.1.b shows that \( \text{H}_2 \) production rate for the acid-treated sample is close to two times higher than the non-treated nanoparticles. As anticipated, the acid treatment will remove any passive surface materials that might affect the oxidation of iron and effectively increase the hydrogen generation rate from 25.10 \( \mu \text{mol H}_2/\text{g Fe hr} \) to 44.64 \( \mu \text{mol H}_2/\text{g Fe hr} \). The passive surface species may include the boron/boride due to the borohydride synthesis method and surface oxides by the oxidation of iron exposed to air. The surface area-normalized hydrogen generation rate \((k_{\text{H}_2})\) for the acid-treated nanoiron in Fig. 5.2.1.b and 20 wt% Ni bimetallic nanoparticles in Fig. 5.2.1.a is 44.64 \( \mu \text{mol H}_2/\text{g Fe hr} \) and 64.32 \( \mu \text{mol H}_2/\text{g Fe hr} \), respectively. However, five times lower surface area-normalized TCE degradation rate \((k_{\text{SA}} = 0.72 \times 10^{-2} \text{L/m}^2\text{hr})\) for the acid-treated nanoiron as compared to \((k_{\text{SA}} = 3.50 \times 10^{-2} \text{L/m}^2\text{hr})\) the 20 wt% bimetallic nanoparticles indicated that the hydrogen generated from the oxidation process cannot be utilized effectively in the absence of a second catalytic metal dopant for the degradation of chlorinated organics. It is hypothesized that hydrogen disproportionates into atomic hydrogen on the nickel forming nickel hydride that hydrogenate the chlorinated organics adsorbed on the metal surface (Odziemkowski et al., 2000; Wang et al., 2003; and Campbell, 1998).
Figure 5.2.1.b. Iron-normalized hydrogen generation of iron nanoparticles with (open diamond symbols) and without acid treatment (solid diamond symbols) under anaerobic condition. Nanoiron = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.

\[ k_{H2} = 44.64 \mu\text{mol} \text{ H}_2 / \text{g Fe hr} \]

\[ k_{H2} = 25.10 \mu\text{mol} \text{ H}_2 / \text{g Fe hr} \]

final pH = 7.85

final pH = 7.20
5.2.2 TCE Degradation and Its Effect on Hydrogen Generation

Degradation of TCE by Ni/Fe nanoparticles has been studied previously and its reaction kinetics is reported in terms of surface area-normalized reaction rate (Tee et al., 2005). Iron as the electron donor oxidized and consumed in the degradation process while the nickel serves as the catalyst that simultaneously enhances the reaction kinetically and alters the degradation mechanisms. To the best of our knowledge, the effect of TCE degradation on the hydrogen generation and its utilization by the bimetallic Ni/Fe nanoparticles in assisting the reaction have not yet been fully established. Figure 5.2.2.a shows the degradation of TCE by Ni/Fe (20 wt% Ni) in anaerobic conditions increases the hydrogen generation and has a lower pH as compared to the TCE-free solution. The analysis was conducted with two initial TCE concentrations of 10 mg/L and 500 mg/L. Increase in the total hydrogen generation in the presence of TCE degradation can be attributed to the complex heterogeneous reactions occur in the aqueous solution. As the reaction proceeds, breaking of the carbon chlorine bond occurs on the metal surface generating Cl\(^{-}\) according to 3.1g. Chloride ion is well known for its corrosive nature that is capable of inducing pitting corrosion and increasing the iron reactivity (Gotpagar et al., 1999; and Scherer et al., 2000). The effect Cl\(^{-}\) on iron oxidation may explain the increase of hydrogen generation from 61.40 \(\mu\)mol H\(_2\)/g Fe hr to 186.40 \(\mu\)mol H\(_2\)/g Fe hr for low TCE concentration; and 108.80 \(\mu\)mol H\(_2\)/g Fe hr to 214.00 \(\mu\)mol H\(_2\)/g Fe hr for high TCE concentration. Under the experimental conditions used in this study, approximately 7.75 \(\mu\)mol and 382 \(\mu\)mol of H\(_2\) are needed for the complete degradation of 10 mg/L and 500 mg/L TCE, respectively. Hydrogen collected in the headspace was in excess of 26 mol% (30 \(\mu\)mol H\(_2\)) for the complete degradation at low initial TCE concentration. On the other hand, significant lower amount of hydrogen collected (180 \(\mu\)mol H\(_2\)) at high
Figure 5.2.2.a. Total hydrogen produced normalized by iron versus time for Ni/Fe (Ni = 20 wt%) nanoparticles with TCE degradation reaction (open diamond symbols) and TCE-free aqueous solution (solid diamond symbols). Insert shows the hydrogen produced in degradation of high initial TCE concentration (open square symbols) and TCE-free aqueous solution (solid square symbols). Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.
TCE concentration for longer time period (10 hr) indicates that the pitting corrosion induced by Cl\(^-\) is not sustainable in the long run.

The pH of solution in which iron undergoes oxidation is expected to increase due to the formation of OH\(^-\). It is interesting to observe that the increase in pH for the TCE-degradation study is lower than the pure aqueous hydrogen analysis of Ni/Fe nanoparticles as shown in Figure 5.2.2.a. In the absence of any cosolutes in the reaction solution, this observation can only be attributed to the complex heterogeneous reactions of TCE such as the Cl\(^-\)-effect generated during the degradation reaction and the formation of metal-hydride that act as catalytic reducing agent. The detail mechanisms responsible for the lower pH observed in the TCE study cannot be determined in this study.

Analysis of the hydrogen generated by the 20 wt% Ni bimetallic nanoparticles and nanoiron under TCE-free anaerobic condition at different solution pH (<1.0, 5.0, 6.5, and 8.0) was conducted. Figure 5.2.2.b showed that the overall total H\(_2\) generation for the buffered solution is not a strong function on the solution pH from 5.0 to 8.0. This observation is similar to the results reported in the literature (Uhlig, 1971) where iron corrosion at room temperature is independent of the pH ranged from 4.0 to 10.0. In addition, solution pH is also found to exert negligible effect on the electrical properties of zero-valent iron (Slater et al., 2005). It is expected that the iron oxidation rate will increase in the presence of a catalytic metal such as nickel based on the galvanic cell hypothesis, where iron is the sacrificial metal protecting the nickel. Figure 5.2.2.b indeed shows that higher hydrogen generation was observed for the bimetallic Ni/Fe as compared to the nanoiron. The consistency in the total hydrogen generated by the Ni/Fe (Ni = 20 wt%) nanoparticles irrespectively of the solution pH (5.0 to 8.0) supports the hypothesis that the higher H\(_2\) generation in Figure 5.2.2.a is indeed due to the Cl\(^-\).
Figure 5.2.2.b. Effect of pH on hydrogen generation for Ni/Fe nanoparticles (Ni = 20 wt%) and iron nanoparticles (acid-treated and non-treated) under anaerobic aqueous solution. Analysis time is 2 hours. Nanoiron and Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5.
induced corrosion.

Figure 5.2.2.b also showed that the acid treatment improved the total amount of hydrogen generation by as much as more than twice comparing with the non-treated nanoiron at different pH conditions. This observation complements with the results shown in Figure 5.2.1.b, where the iron-normalized H₂ rate is higher for the acid-treated sample. Table 5.2.2.a showed the complete digestion study under pH < 1.0 condition for different iron-based nano systems. The results in Table 5.2.2.a showing the total hydrogen produced from the complete oxidation of zero-valent nanoiron indicates that the method used in the nanoiron synthesis cannot totally prevent the formation of surface oxides impurities upon exposure to air. On the other hand, the bimetallic Ni/Fe nanoparticles (20 wt% and 50 wt% Ni) synthesized under the same method possess higher oxidation resistance when exposed to the air, as indicated by the similar level of hydrogen generation with the acid-washed nanoiron as shown in Table 5.2.2.a. The digestion study indicated that enhanced air-stability of the nanoparticles can be achieved with the presence of nickel in addition to the catalytic effect Ni has on the degradation kinetics and reaction pathways. The deviation between the experimentally calculated results and the theoretical values can be attributed to the formation of metal borides during the metal ions-borohydride reduction process and trace amount of oxides formation on the surface iron atoms that are not in close electronic contact with the nickel.

Table 5.2.2.b show that a strong correlation exists for the surface area-normalized TCE reaction rate \( (k_{SA}, \text{ L/ m}^2 \text{ hr}) \) and hydrogen generation \( (k_{H_2}, \mu \text{mol H}_2/ \text{ m}^2 \text{ hr}) \) for different bimetallic Ni/Fe systems. As discussed in section 5.1 the edge of the nanoparticles will become more saturated with nickel as the nickel content increases. This will diminish the oxidation of iron to produce the electrons and protons needed in
Table 5.2.2.a. Hydrogen generation for nanoiron and Ni/Fe nanoparticles at acidic conditions

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Hydrogen generation at 2 hrs** (µmol H₂)</th>
<th>Percent deviation of experimental and theoretical total hydrogen generation at complete digestion ***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH &lt; 1 (complete digestion)</td>
<td></td>
</tr>
<tr>
<td>Nanoiron</td>
<td>1.556 x 10³</td>
<td>86.44 %</td>
</tr>
<tr>
<td>Acid-treated nanoiron</td>
<td>1.742 x 10³</td>
<td>96.78 %</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles (Ni = 20 wt%)</td>
<td>1.720 x 10³</td>
<td>95.56 %</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles (Ni = 50 wt%)</td>
<td>1.705 x 10³</td>
<td>94.72 %</td>
</tr>
</tbody>
</table>

* Sample weights = 0.10 g  
** 1N nitric acid was used for pH < 1 solution  
*** Assuming Fe and Ni are in zero-valent state, hydrogen generated at complete digestion = 1.80 x 10³ µmol H₂
Table 5.2.2.b. Iron-normalized hydrogen generation rate and the surface area-normalized reaction rate constant for Fe and Ni/Fe nanoparticles.

<table>
<thead>
<tr>
<th>Iron-based nanoparticles</th>
<th>Surface area-normalized hydrogen generation rate* $k_{H2}$ (mmol H$_2$/m$^2$ hr)</th>
<th>Surface area-normalized TCE degradation rate $k_{SA}$ (L / m$^2$ hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-washed Fe from Fisher$^1$</td>
<td>$0.10 \times 10^{-4}$</td>
<td>$0.03 \times 10^{-2}$</td>
</tr>
<tr>
<td>Fe/B nanoparticles$^2$</td>
<td>$8.50 \times 10^{-4}$</td>
<td>$1.40 \times 10^{-2}$</td>
</tr>
<tr>
<td>Fe nanoparticles$^3$</td>
<td>$9.12 \times 10^{-4}$</td>
<td>$0.05 \times 10^{-2}$</td>
</tr>
<tr>
<td>Acid–treated Fe nanoparticles</td>
<td>$16.10 \times 10^{-4}$</td>
<td>$0.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^4$ (Ni = 25 wt%)</td>
<td>$0.21 \times 10^{-4}$</td>
<td>$9.80 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^3$ (Ni = 20 wt%)</td>
<td>$22.30 \times 10^{-4}$</td>
<td>$3.50 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^3$ (Ni = 25 wt%)</td>
<td>$25.74 \times 10^{-4}$</td>
<td>$5.75 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^3$ (Ni = 50 wt%)</td>
<td>$19.00 \times 10^{-4}$</td>
<td>$2.35 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^3$ (Ni = 75 wt%)</td>
<td>$2.50 \times 10^{-4}$</td>
<td>$1.25 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni/Fe nanoparticles$^3$ (Ni = 80 wt%)</td>
<td>$0.40 \times 10^{-4}$</td>
<td>$0.09 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

*initial $H_2$ generation rates were determined from measurements obtained up to 120 minutes where linear increase with time was observed. Initial pH = 6.5


$^4 k_{SA}$ and $k_{H2}$ from Schrick et al. Chem. Mater., 2002, 14, 5140.
the degradation process, which subsequently leads to lower reaction kinetics and hydrogen generation. Reported literature results of $k_{SA}$ and $k_{H2}^*$ for iron, nanoiron and Ni/Fe systems are listed in Table 5.2.2.b as well. As anticipated, nanoparticles with higher surface area (from 25 m$^2$/g to 50 m$^2$/g) compared to the iron powder (< 1 m$^2$/g) have higher H$_2$ generation rate. Nano Fe/B synthesized by Liu et al. (2005) is able to utilize the H$_2$ generated by iron corrosion during TCE degradation that enhanced the reaction kinetics. This observation is hypothesized to be the catalyzing effect of the highly disordered Fe/B solid phase. Current analysis and previously reported results of TCE study by iron nanoparticles as shown in Table 5.2.2.b demonstrate that the hydrogen generation rate is similar to those reported by Liu et al. (2005) but with reaction kinetics that are an order of magnitude lower (Tee et al., 2005). This may be explained by the lack of catalyzing effect of the synthesized nanoparticles that can utilize the H$_2$ produced by the oxidation of iron. This observation can be attributed to the method used in the nanoparticles synthesis, as different $k_{SA}$ values were reported by authors that have dissimilar synthesis procedures. As expected, the acid-treated nanoiron showed great improvement in both of the $k_{H2}^*$ and $k_{SA}$ values as compared to the fresh nanoiron synthesized in this study. However, the observed lower $k_{SA}$ value even after the acid-treatment as compared to the results reported by Liu et al. (2005) is another indication of the presence of structural and surface compositional differences between the nanoirons. The presence of nickel as the catalyzing agent was clearly demonstrated by the study of the acid-treated nanoiron and Ni/Fe nanoparticles, especially the Ni = 50 wt% particles. Both of these nanoparticles showed relatively similar $k_{H2}^*$ value but the bimetallic Ni/Fe system demonstrated enhanced reaction kinetic in terms of $k_{SA}$ that are an order of magnitude higher than the nanoiron. TCE degradation study using bimetallic Ni/Fe
reported by Schrick et al. (2002) demonstrated high reaction kinetic but has significantly lower $k_{H2}^*$ that are similar in magnitude to the bulk Fisher iron powder. In this case, other explanations and analysis have to be used to clarify the observed results besides using the reported $k_{H2}^*$.

Figure 5.2.2.c shows that both of the surface area-normalized degradation and hydrogen generation rates demonstrated ‘volcano’ like characteristic with respect to the nickel content in the nanoparticles. Based on this observation, derivation of a functional representation that incorporates relevant parameters such as the hydrogen generation rate and bimetallic composition is attempted in this study. With the previous assumption that the hydrogen generation is solely from the oxidation of zero-valent iron and and undetermined fraction of the $H_2$ produced undergo diatomic dissociation on the nickel surface forming active metal hydride for the degradation reaction:

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$   \hspace{1cm} (5.2.2a)

$$2Ni + H_2 \rightarrow 2Ni–H$$   \hspace{1cm} (5.2.2b)

the first-order surface area-normalized reaction constant, $k_{SA}$, is hypothesized to be a function of the aforementioned experimental parameters expressed as the following:

$$k_{SA} = N_{Ni} V_{aq} k_{H2}^* (F_s \eta) + k_{SA/Fe} , \quad (N_{Ni} < 1.00)$$   \hspace{1cm} (5.2.2c)

where $k_{H2}^*$ ($\mu$mol $H_2$/ m$^2$ hr) is the surface area-normalized hydrogen generation rate obtained experimentally; $V_{aq}$ (L) is the total reaction volume; $N_{Ni}$ is the weight fraction of nickel in the bimetallic particles; the product $F_s$ and $\eta$ (1/$\mu$mol $H_2$) is constant where each of its physical meaning is defined as the following:

$$F_s = \frac{H_2 \text{ adsorbed on metal surface}}{non-adsorbed H_2}$$   \hspace{1cm} (5.2.2d)
Figure 5.2.2.c. Volcanic profile of surface area-normalized TCE reaction rate and hydrogen generation rate with respect to Ni wt% of the Ni/Fe nanoparticles. Insert is the linear correlation between $k_{SA}$ and $(k_{H2}N_{Ni})$. 

<table>
<thead>
<tr>
<th>Ni wt%</th>
<th>$k_{SA} \times 10^{-2}$ (L/m² hr)</th>
<th>$k_{H2}^{*}$ (µmol H₂/m² hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.05</td>
<td>1.03</td>
</tr>
<tr>
<td>80</td>
<td>0.09</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\[ \eta = \frac{1}{\text{adsorbed } H_2 \text{ undergoing diatomic dissociation on nickel and being used in the degradation reaction}} \]  
(5.2.2e)

and the last term in eq 5.2.2c is the surface area-normalized reaction rate constant for the iron nanoparticles:

\[ k_{SA}^{Ni} = k_{SA}^{Fe} \]  
(5.2.2f)

The insert in Figure 5.2.2.c shows the linear relation with a correlation coefficient of 0.98 and the constant \((F_s \eta)\) obtained is 8.40 (\(\mu\)mol \(H_2\)) \(^{-1}\). The parameters of \(F_s\) and \(\eta\) are dynamic in nature, depend on nickel composition, and may account for the geometric and electronic effects of the bimetallic nanosized nature of the particles. We can approximate the maximum hydrogen adsorption capacity by estimating the surface nickel atoms of the bimetallic nanoparticles. Using the reported molar volume for nickel (6.59 cm\(^3\)), the Avogrados number (6.02 x 10\(^{23}\) atoms/mol), nanoparticles surface area (30 m\(^2\)/g), and assuming that the surface area coverage of nickel atoms is similar in magnitude with its weight fraction \((N_{Ni})\); the calculated surface nickel atoms for nanoparticles with 20 wt% Ni is 2.10 x 10\(^{18}\) (3.48 \(\mu\)mol Ni). Based on the reported analysis of nickel-adsorbed surface hydrogen atoms that is close to one mono layer and assuming that hydrogen adsorbed dissociatively on nickel forming Ni-H, the maximum number of hydrogen molecules adsorption for 20 wt% Ni nanoparticles was 1.72 \(\mu\)mol \(H_2\) (Panczyk et al., 2005). Based on the reaction mechanism of 3.1e, about 7.75 \(\mu\)mol \(H_2\) is needed in order to completely degrade 3.1 \(\mu\)mol TCE. This indicates that the formation of nickel-hydride of 3.1c is rapid as compared to other surface reactions and it is not the rate-limiting step in the degradation reaction. Needed to mention is that nickel nanoparticles \((N_{Ni} = 1.00)\)
should not be considered in the correlation in eq 5.2.2c due to the inability of nickel to produce H₂ at near neutral pH condition for the degradation reaction.

5.3. Chitosan-Immobilized Nanoparticles

5.3.1. Characterization

The synthesis of chitosan membrane with immobilized iron nanoparticles is achieved by the simultaneous pore formation utilizing silica particles as porogen and the reduction of Fe²⁺ by sodium borohydride. The polymeric chitosan formed a hydrophilic yet mechanically stable thin film with nanoparticles randomly distributed on the surface and in the membrane. The use of silica gels to induce porosity in the chitosan membrane has been previously reported by Zeng et al. (1996). They reported that stable macroporous membranes can be synthesized when the silica particles were extracted out of the dried chitosan membrane by immersion in alkaline medium. The synthesis of porous chitosan membrane has also been studied and used as ion-exchange agent in the adsorption of Cu(II) (Beppu et al., 2004) and the separation of protein (Zeng et al., 1998). In this study, only aqueous sodium borohydride as the alkaline medium was used to form porous chitosan membrane and simultaneously reducing Fe²⁺ to zero-valent iron. This is different from the approach used by Zeng et al. (1996) where dissolution of silica was attained using warm bath of aqueous NaOH. Partial dissolution of silica gel was observed at the end with approximately 60% loss of silica weight. SEM analysis of the membrane without the iron nanoparticles showed that the silica particle size was 60 nm to 70 nm (Figure 5.3.1.a) vs. the initial value of 4 μm to 20 μm. This is close to the silica weight loss in the chitosan-immobilized iron nanoparticles membrane and assumption was made that the silica has roughly similar particle size in both of the membranes with and without
Figure 5.3.1.a. SEM Surface Image for Chitosan-Silica Membrane without Iron nanoparticles
the iron nanoparticles. Table 4.4.3.a. shows the structural characteristics and metal loading of the chitosan-immobilized iron nanoparticles membrane with silica after the doping and post coating with Ni and Pd.

The FTIR analysis in Figure 5.3.1.b shows the spectrums for the dried polymer solution and the chitosan-immobilized iron nanoparticles membrane with silica. The results in Figure 5.3.1.b for both the dried polymer solution and the membrane exhibit quite similar stretching bands and are outlined with its wave number (cm$^{-1}$) as follows:

1. broad peaks range from 3450 cm$^{-1}$ to 3390 cm$^{-1}$ (region in line a):
   - OH and NH group stretching

2. 2960 cm$^{-1}$ (region in line b): CH stretching of CH$_3$

3. 1590 cm$^{-1}$ (line d): NH$_2$ in amino group

4. 1020 cm$^{-1}$ to 1150 cm$^{-1}$ (region in line f): C-O-C ether linkage and Si-O-Si stretching vibrations

5. 800 cm$^{-1}$ (line g): CH$_3$OH group

In Figure 5.3.1.b-(a) of the dried polymer solution, the characteristic bands correspond to the C=O and SO$_3^-$ groups from sulfosuccinic acid were observed at 1750 cm$^{-1}$ (line c in Figure 5.3.1.b-(a)) and 1250 cm$^{-1}$ (line e in Figure 5.3.1.b-(a)), respectively. A small shoulder at 1620 cm$^{-1}$ appeared next to the NH$_2$ stretching band at 1590 cm$^{-1}$ was attributed to the symmetric deformation of NH$_3^+$. This indicated that the SO$_3^-$ group of the sulfosuccinic acid can form a complex with NH$_3^+$ in chitosan via electrostatic interaction. This will increase the stability of thin film during membrane formation where intense reduction reaction of Fe$^{2+}$ and dissolution of silica occurred in the borohydride solution. Due to the small molecule size of the sulfosuccinic acid, gradual leaching were occurred during the synthesis process. This is confirmed by the FTIR spectra in Figure
Figure 5.3.1.b. FTIR Analysis of the (a) Dried polymer solution of chitosan, silica, Fe$^{2+}$, and sulfosuccinic acid. (b) Chitosan-immobilized iron nanoparticles with silica membrane
5.3.1.b-(b) and the SEM image coupled with EDS analysis in Figure 5.3.1.c and Figure 5.3.1.d showing the presence and complete leaching of sulfosuccinic acid before and after the synthesis, respectively. XRD analysis for chitosan membranes with and without the immobilized iron nanoparticles was performed and shown in Figure 5.3.1.e. It is observed that the chitosan membrane in Figure 5.3.1.e-(a) shows two relatively broadened diffraction peaks at approximately 10° (2θ) and 20° (2θ) which are attributed to the hydrated and anhydrous crystals, respectively. This is consistent with the observations made by Ogawa et al. (1993) and Nunthsnid et al. (2001). They reported the loss of crystallinity of the chitosan membranes by the observed peak broadening at the diffraction angles of 2θ = 10° and 20°. The loss of crystalline structure together with the formation of amorphous phase is due to the reprecipitation and restructuring of the chitosan after the dissolution in acidic medium. The same observations are made for the chitosan membranes with immobilized nanoparticles with similar diffraction patterns as shown in Figure 5.3.1.e-(b) and 5.3.1.e-(c). The increased intensity of the hydrated phase accompanied by weaker and broader diffraction of the anhydrous region can be attributed to the morphological changes of the chitosan membrane. These changes can be attributed to the dissolution of silica and iron nanoparticles formation in the membrane when it is treated with NaBH₄. This kind of phenomena has been reported by Ogawa et al. (1993). Based on the XRD analysis, it is concluded that the chitosan-immobilized iron nanoparticles membrane has more amorphous and less oriented structure than the chitosan thin film.

XRD analysis for Fisher electrolytic iron and nanoirons synthesized by the solution method of NaBH₄ reduction were also obtained for comparison purpose.
Figure 5.3.1.c (a) Electron dispersive spectroscopy (EDS) spectra for the dried chitosan film with elemental analysis before NaBH4 reduction. (10 wt% silica gel, 1.30 mmol Fe²⁺/g membrane, 40 wt% of sulfosuccinic acid). (b) Scanning electron microscopy (SEM) surface image for the dried chitosan film.
Figure 5.3.1.d. (a) Electron dispersive spectroscopy (EDS) spectra with elemental analysis for the cross-section of the chitosan-embedded Fe nanoparticles with silica (6.0 wt% silica gel, 73 mg Fe/g membrane). (b) Scanning electron microscopy (SEM) of cross-section image and surface image (shown as insert) for the membrane.
Figure 5.3.1.e. XRD Analysis for: (a) Chitosan Membrane, (b) 1.00 mmol Fe$^{2+}$ / g chitosan Membrane, (c) 3.25 mmol Fe$^{2+}$ / g chitosan Membrane, (d) Iron Nanoparticles by NaBH$_4$, and (e) Fisher Electrolytic Fe
Diffraction patterns for the Fisher electrolytic Fe in Figure 5.3.1.e-(e) were confirmed by the data files of the International Centre for Diffraction Data (ICDD) (formerly Joint Committee on Powder Diffraction Standards, JCPDS) (ICDD card number: 6-696). The iron nanoparticles synthesized by the solution method shows a strong and broadened peak at a diffraction angle of approximately 45° in Figure 5.3.1.e-(d), which is similar with the most intense diffraction peak (2θ = 44.788°, d_{spacing} = 2.022, RI = 100%) of the electrolytic Fe. The peak broadening is due to the amorphousity and the different solid phases detected on the particles. Neglecting peak broadening due to microstrain in the structure and stripping undesirable peaks caused by Cu Kα2 radiation using TracersV6 software from Diffraction Technology, the solid phases with its respective diffraction patterns were examined. The results showed the presence of iron oxides (Fe_{0.98}O – ICDD: 39-1088, FeO (wüstite) – ICDD: 6-615, Fe_2O_3 (maghemite) – ICDD: 25-1402, and Fe_3O_4 (magnetite) – ICDD: 19-629) in addition to zero-valent iron. The presence of oxides in the sample is assumed to be attributed by the oxidation of surface iron atoms during the handling and sample preparation. The appearance of similar diffraction angle with less peak broadening is observed for the chitosan-immobilized iron nanoparticles membrane. With the presence of polymeric chitosan, fewer solid oxide phases were found on the surface of membrane-immobilized nanoparticles. The only oxide phase detected was Fe_{0.98}O and the nanoparticles on the surface were predominantly Fe(0). When the metal loading on the membrane increases, the protective and stabilizing effect of the polymeric chitosan gradually decreases. This is confirmed by the detection of more oxide phases in membranes with higher iron mole per unit mass of membrane (mmol Fe / g membrane).

Thermal stability and the amount of nonvolatile components in the chitosan membranes could be inferred from the TGA thermograms in Figure 5.3.1.f. The initial
Figure 5.3.1.f. TGA Analysis for: (a) Chitosan Membrane, (b) Chitosan Membrane with Silica (6wt% silica of membrane weight), and (c) Chitosan-Immobilized Iron Nanoparticles with Silica (6 wt% silica and 7.5 wt% Fe of membrane weight)
weight loss from 50 °C to 140 °C for all of the membranes was attributed to the dehydration of water in the chitosan. This agreed with the observation made by Nunthanid et al. (2001). A rapid weight loss at higher temperature of 260 °C was due to the chitosan chain degradation. Degradation of chitosan continued with the increase in temperature and complete decomposition was observed at 640 °C and 700 °C for the chitosan (Figure 5.3.1.f-(a)) and chitosan mixed matrix membranes (Figure 5.3.1.f-(b) and (c)), respectively. It is observed in Figure 5.3.1.f that with the addition of nanoparticles in the membrane matrix, the physical and mechanical properties of chitosan was slightly improved by decomposing at a higher temperature. The final weight percentage of the nonvolatile silica in the membrane shown in Figure 5.3.1.f-(b) was around 6.0 wt% relative to the initial membrane mass. The combined weight of the silica and iron nanoparticles retained in the mixed matrix membrane in Figure 5.3.1.f-(c) was approximately 14.0 wt%. Both of the results are consistent with the AA and ICP analyses (data not shown) by digestion technique conducted using the same mixed matrix membranes (chitosan-silica and chitosan-immobilized iron with silica membranes).

The formation of iron nanoparticles in the membrane domain with silica was observed by the SEM as shown in Figure 5.3.1.d. The distinction between the nanoiron and silica in the image was not possible since both particles are in close contact with each other. Based on the previously reported results for the membrane systems with immobilized nanoparticles (Meyer et al., 2004; and Xu et al., 2005) and the solution phase synthesis studies using borohydride as the reducing agent (Tee et al., 2005; and Schrick et al., 2004), bimetallic nanoparticles obtained in this study is in the range of 30 nm to 70 nm in diameter. However, nanoparticles size is strongly affected by the initial iron concentration used in the synthesis. Higher iron concentration will result in larger
nanoparticle size as indicated in Figure 5.3.1.g. This is due to the chitosan reaching its particles immobilizing limit with the increase in Fe$^{2+}$ concentration. The presence of polymers can prevent the agglomeration of the metal nanoparticles immobilized in the membrane. In order to investigate the effect of membrane on nanoparticles formation, HRTEM was used to study the structural characteristic of the synthesized iron nanoparticles. HRTEM image in Figure 5.3.1.h shows that nanoparticles shown in the SEM image were actually consisted of nanoclusters with smaller silica and Ni/Fe particles with diameter of 5 nm to 10 nm in the membrane domain. The bimetallic Ni/Fe nanoparticles in Figure 5.3.1.h synthesized by doping the iron nanoparticles with stoichiometric amount of Ni followed by NaBH$_4$ treatment (Ni/Fe weight ratio = 1/4) seems to be deposited on the larger silica particle surface. Elemental analysis of the nanoclusters in Table 5.3.1.a shows that the bimetallic Ni/Fe compositions of the 5 nm to 10 nm size particle was indeed close to 1/4 weight ratio with high concentration of Si in the background.

The membrane solvent permeation property for the chitosan-immobilized Pd/Fe nanoparticles was determined using water and ethanol solutions. In this study, water has the highest permeability ($1.42 \times 10^{-4}$ cm$^3$ s$^{-1}$ cm$^{-2}$ bar$^{-1}$) followed by ethanol ($1.00 \times 10^{-4}$ cm$^3$ s$^{-1}$ cm$^{-2}$ bar$^{-1}$) and mixture of 1/1 volume ratio of ethanol and water solution ($0.50 \times 10^{-4}$ cm$^3$ s$^{-1}$ cm$^{-2}$ bar$^{-1}$). It is reported that the transport of solvent through polymeric porous membrane is influenced both by the membrane characteristics and the properties of solvents (Bhanushali et al., 2001). This includes the hydrophilicity and porosity of the membrane as well as the viscosity and polarity of the solvent. High water permeability is expected due to the high degree of hydrophilicity of the chitosan membrane. The ethanol flux through the hydrophilic chitosan would be lower than the water as anticipated due to
Figure 5.3.1.g. SEM Surface Images of: (a) Porous Chitosan Membrane, (b) 0.25 mmol Fe$^{2+}$/g Chitosan, (c) 1.00 mmol Fe$^{2+}$/g Chitosan, and (d) 3.25 mmol Fe$^{2+}$/g Chitosan
Figure 5.3.1.h. (a) High resolution transmission electron microscopy (HRTEM) image of chitosan-embedded bimetallic Ni/Fe nanoparticles (Ni/Fe weight ratio = 1/4) mixed matrix membrane (Insert shows enlarged image for the squared area of the same membrane). (b) and (c) Electron dispersive spectroscopy (EDS) spectra with elemental analysis (shown in Table 5.3.1.a) of the membrane with silica at different positions.
Table 5.3.1.a. Elemental analysis of Figure 5.3.1.h-(b) and (c) for chitosan-immobilized bimetallic Ni/Fe nanoparticles (Ni/Fe weight ratio = 1/4) mixed matrix membranes with silica

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td>Element wt %</td>
<td>Atomic %</td>
</tr>
<tr>
<td>Figure 5.3.1.h-(b)</td>
<td>2.65</td>
<td>3.22</td>
<td>77.10</td>
</tr>
<tr>
<td>Figure 5.3.1.h-(c)</td>
<td>85.26</td>
<td>81.67</td>
<td>12.08</td>
</tr>
</tbody>
</table>
the limited hydrogen bonding of the organic polar solvent and lower polymer-solvent interaction. The lowest solvent permeation for the 1/1 volume mixture of ethanol and water can be attributed to the increased viscosity of the solution (2.50 x 10^{-3} \text{ Pa.s at 25} °\text{C}) with respect to water (0.85 x 10^{-3} \text{ Pa.s at 25} °\text{C}) and ethanol (1.10 x 10^{-3} \text{ Pa.s at 25} °\text{C}). The addition of ethanol in the water also decreases the mixture polarity and subsequently increases the resistance at the membrane-solvent interphase (Geens et al., 2005). Based on this observation, the solvent effect is more important on the permeation properties for the mixture of ethanol and water solution (1/1 volume ratio), which is the solvent used in the DCB degradation study.

The simplest model describing the volume flux through porous membrane is the viscous flow based on the Hagen-Poiseuille equation:

\[
J_w = \left( \frac{\varepsilon r^2}{8l \tau} \right) \left( \frac{\Delta P}{\mu} \right) = \frac{1}{R_m} \left( \frac{\Delta P}{\mu} \right)
\]  

(5.3.1.a)

where \(J_w\) is the solvent flux, \(\Delta P\) the applied transmembrane pressure, \(\mu\) is the solvent viscosity, and \(R_m\) is the intrinsic membrane resistance which includes the membrane thickness (\(l\)), surface porosity (\(\varepsilon\)), pore radius (\(r\)), and tortuosity factor (\(\tau\)). It assumes an ideal situation where the solvent flow through a uniformly distributed and evenly sized pores in the membrane, without concentration polarization, fouling etc. (Mulder, 1995). Based on these assumptions, the permeation of solvent should be dependent only on the membrane properties, the inverse of membrane resistance, \(1/R_m\). Figure 5.3.1.i shows the expected linear relation for the different solvent fluxes vs. the viscosity-normalized transmembrane pressure with different observed membrane resistances. Based on the permeation data, water showed the lowest membrane resistance of 57.47 cm\(^{-1}\) (\(R^2 = \)}
Figure 5.3.1.i. Volumetric flux vs. transmembrane pressure normalized by solution viscosity of different solvents for chitosan-immobilized Pd/Fe nanoparticles under pressurized condition. Each data points represent flux after 96 hours of continuous operation.
0.9789) followed by ethanol with $R_m$ of 87.00 cm$^{-1}$ ($R^2 = 0.9712$). The highest resistance observed was the mixture of 1/1 volume ratio of ethanol and water with $R_m$ of 131.60 cm$^{-1}$ ($R^2 = 0.9893$). The difference in the membrane resistances for different solvents shows that the flux through the chitosan-immobilized nanoparticles membrane is affected not only by the polymeric materials used, but also by the solvent properties (viscosity, molar volume, polarity) and polymer-solvent interactions (surface tension, etc.). The influence of these parameters is being studied and reported in the literature (Robinson et al., 2004; and Machodo et al., 1999).

**5.3.2. Batch TCE Degradation by Ni/Fe**

The results of the batch degradation experiments by chitosan-immobilized Ni/Fe nanoparticles in Figure 5.3.2.a shows the simultaneous dechlorination of TCE and formation of ethane as the main product, consistent with the results obtained in the reported literature using colloidal bimetallic Ni/Fe nanoparticles (Schrick et al., 2004; and Tee et al., 2005) and different systems of membrane-immobilized Ni/Fe nanoparticles (Meyer et al., 2004; and Xu et al., 2005). This shows that the bimetallic Ni/Fe nanoparticles of the chitosan membranes are catalytically active for the degradation of hazardous chlorinated organics. In this study where the catalytically active nanoparticles are immobilized in the membrane matrix, considerations have to be taken to account the mass transfer phenomena such as the sorption and diffusion of TCE and other degraded products in the membrane phase. In order to check that the decrease of TCE concentration in the aqueous phase GC-MS analysis is actually due to the degradation reaction by the Ni/Fe nanoparticles and not the sorption of TCE in the chitosan membrane, control experiments were conducted using chitosan membrane without the nanoparticles. The aqueous phase GC-MS analysis for the control study
Figure 5.3.2.a. Batch TCE degradation study of chitosan-immobilized Ni/Fe nanoparticles (Ni = 20 wt%) mixed matrix membrane. Initial TCE concentration = 10 mg/L, reaction volume = 40 ml + 2 ml headspace, initial pH = 6.5
showed that the TCE concentration was 92.00 ± 0.53 % relative to the initial total TCE used. Hexane extraction of the chitosan recovered approximately 4.0 ± 0.65 % of TCE in the membrane phase. The combined GC-MS analysis and extraction study showed that the TCE balance obtained was approximately 96.00 % of the TCE used in the control experiments. The volatility and loss of TCE during the sampling procedure might account for the difference in the TCE balance. Based on the results obtained in the control study, the sorption of TCE in the membrane and the loss due to the volatility of TCE is neglected in the kinetic analysis. The decrease of TCE in the aqueous phase is expected to be the degradation reaction by the active Ni/Fe nanoparticles in the chitosan membrane. Quantitative gas phase analysis showed that the mass balance based on C₂ is 90.0 ± 2.5 % relative to the initial value of GC-MS analysis.

Kinetic studies were conducted by measuring the rate of TCE degraded over time and is modeled based on the pseudo first-order reaction rate law as described in section 5.1.3:

$$-\frac{dC_{TCE}}{dt} = k_{obs} C_{Ni/Fe} C_{TCE}$$

(5.3.2.a)

where $C_{TCE}$ and $C_{Ni/Fe}$ represent the TCE (mol/L) and catalyst concentration (g/L), respectively, and $k_{obs}$ is the observed pseudo-first-order reaction rate constant (L/g hr).

Combining eq 5.1.3.a with eq 5.3.2.a:

$$k_{obs} C_{Ni/Fe} = k_{SA} a_s \rho_m$$

(5.3.2.b)

Table 5.3.2.a shows the metal mass-normalized reaction rate of the batch TCE degradation study using Ni/Fe nanoparticles (Tee et al., 2005) and membrane-immobilized nanoparticles for different polymeric systems reported in the literature (Meyer et al., 2004; and Xu et al., 2005). It is observed that the peudo first-order reaction rate in our study has the same order of magnitude with the reported result in Xu et al.
<table>
<thead>
<tr>
<th>Ni/Fe Ratio</th>
<th>$k_{obs}$ (L/g$_{Ni/Fe}$ hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tee et al. (2005)</td>
<td>1/4, (nanoparticles)</td>
</tr>
<tr>
<td>Meyer et al. (2004)</td>
<td>1/4, (cellulose acetate-immobilized nanoparticles)</td>
</tr>
<tr>
<td>Xu et al. (2005)</td>
<td>1/4, (polyacrylic acid-immobilized nanoparticles supported on PVDF)</td>
</tr>
<tr>
<td>This Study</td>
<td>1/4, (chitosan-immobilized nanoparticles with Silica)</td>
</tr>
</tbody>
</table>
(2005) and three times higher than those in Tee et al. (2005) and Meyer et al. (2004). The difference in the rate constants of the TCE degradation study can be caused by different factors. These include the synthesis method and the use of membrane systems with different polymeric properties that might affect the transport of TCE to the nanoparticles.

The Ni/Fe weight ratio of 1/4 used in this study is based on the previously established optimum compositions showing the highest TCE degradation rate with the formation of ethane as the main product (Tee et al., 2005). It is assumed that the Ni/Fe nanoparticles synthesized by the solution reduction method and the bimetallic Ni/Fe nanoparticles in the chitosan membrane synthesized in-situ by doping the iron nanoparticles with nickel possess similar degradation characteristics toward chlorinated organics. To verify that membrane reactor with bimetallic Ni/Fe of lower nickel loading will have a diminished TCE degradation kinetic as reported in the nanoparticles study (Figure 7 of Tee et al., (2005)), chitosan-immobilized Ni/Fe nanoparticles with 4 wt% Ni was synthesized and used to degrade the TCE under the same experimental conditions. As anticipated, bimetallic Ni/Fe nanoparticles with 4 wt% Ni showed lower degradation rate for the complete conversion of TCE to ethane as shown in Figure 5.3.2.b. The kinetic results characterized by the pseudo first-order reaction constant for the 25 wt% and 4 wt% Ni was 5.58 L/g_cat hr ($R^2 = 0.9969$) and 0.12 L/g_cat hr ($R^2 = 0.9900$), respectively. The lower reaction kinetic with higher Ni content can be explained by the high Ni surface composition that will hinder the electrochemical process of the zero-valent iron that generates electrons and assists in the production of hydrogen needed for the reduction of TCE:

\[
Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (5.3.2.c)
\]

\[
Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (5.3.2.d)
\]
Figure 5.3.2.b. Batch TCE degradation study of chitosan-immobilized Ni/Fe nanoparticles (Ni = 4 wt%) mixed matrix membrane. Initial TCE concentration = 10 mg/L, reaction volume = 40 ml + 2 ml headspace, initial pH = 6.5
\[ Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \]  \hspace{1cm} (5.3.2.e)

\[ Cl_2C\equiv CHCl + \frac{3}{2} H_2 + 3e^- \xrightarrow{Ni} CH_4 + 3Cl^- \]  \hspace{1cm} (5.3.2.f)

As described earlier, the presence of Ni as dopant is hypothesized to be able to strengthen the metal-carbon bonds on the metals surface. This will enhance the chemisorptions and subsequently increase the dissociation of C=C intermediates on the surface (Agrawal et al., 1996; Park et al., 1998; and Burke et al., 1991). The observed optimum degradation was reported previously by Tee et al. (2005) and Xu et al. (2005) at approximately 25 wt% Ni loading. Beside the observed compositional effect of the bimetallic Ni/Fe nanoparticles on TCE degradation as shown in this study, Grenier et al. (2004) also reported the reaction kinetics in the vapor-phase reduction of organohalides (\textit{cis}-1,2-dichloroethylene) by Ni/Fe as a function of the nickel loading of the bimetallic system.

Different studies showing the dependent of reaction rates on the compositions of the bimetallic systems were also reported in literature. These include the hydrogenation of nitrobenzene derivatives by Ni/Pd bimetallic nano-cluster in Lu et al. (2000), reduction of chlorophenols by Pd/Fe in Liu et al. (2005), and TCE hydrodechlorination by Pd/Au nanoparticles in Nutt et al. (2005). All of these studies, including our results, have indicated the importance of the second dopant metal and the synergistic compositions of the bimetallic systems in achieving the optimum physical and chemical properties for the dechlorination reactions.

**5.3.3. Convective DCB Degradation by Pd/Fe**

DCB degradation is conducted under pressure induced condition. As the solution convectively passed through the membrane by applying pressure at the cell reservoir, mass transfer of the chlorinated DCB to the active Pd/Fe nanoparticles in the membrane
is enhanced. It is observed that the DCB degradation and biphenyl formation as the end product increased with the reciprocal of volumetric flux, $1/J_w$, as shown in Figure 5.3.3.a. As expected, lower volumetric flux (higher $1/J_w$) corresponds to longer residence time of DCB in the membrane phase containing the bimetallic Pd/Fe nanoparticles. This will increase the contact time of the targeted DCB with the catalytically active Pd/Fe and subsequently lead to higher DCB degradation and formation of biphenyl as shown in Figure 5.3.3.b. Based on the flux data with the 60 µm thick membrane with diameter of 4.15 cm (membrane volume = 0.081 cm$^3$), the calculated residence time for 80% DCB degradation was 12.5 minutes. This corresponds to a flux of $0.12 \times 10^{-4}$ cm$^3$ s$^{-1}$ cm$^{-2}$ at transmembrane pressure of 0.5 bar. DCB degradation of 50% was observed at 1.5 minutes residence time that corresponds to applied pressure of 2 bar with solvent flux of $0.78 \times 10^{-4}$ cm$^3$ s$^{-1}$ cm$^{-2}$.

The hypothesized reductive hydrodechlorination reaction process of DCB with chitosan-immobilized bimetallic Pd/Fe nanoparticles at room temperature followed a step-wise reaction pathway as reported in the literature (Korte et al., 2002; and Kim et al., 2004) and is expected to be the same in this investigation. The palladized iron nanoparticles in the chitosan are in close electronic contact with each other and dechlorination is assumed to occur at the Pd/Fe interface, not on the iron or palladium surfaces alone. Electron and hydrogen generated by elemental iron are used by palladium forming the powerful reducing agent of surface-bound metal hydride, Pd-H$^*$:

\[
\begin{align*}
H^+ + e^- & \xrightarrow{Pd} Pd-H^* \\
H_2 & \xrightarrow{2Pd} 2Pd-H^* \\
R-Cl_2 + 2Pd-H^* + 2e^- & \rightarrow R-H_2 + 2Cl^- + 2Pd
\end{align*}
\]
Figure 5.3.3.a. Degradation study of 2,2'-dichlorobiphenyl (DCB) vs. inverse solvent flux under pressure induced operation. Initial DCB concentration = 10 mg/L, solvent = 1/1 (v/v) of ethanol and water, and applied pressure of 0.35 bar to 11.0 bar
Figure 5.3.3.b. Degradation study of 2,2’-dichlorobiphenyl (DCB) vs. residence time under pressure induced operation. Initial DCB concentration = 10 mg/L, solvent = 1/1 (v/v) of ethanol and water, solvent permeability = $0.50 \times 10^{-4} \text{ cm}^3 \text{s}^{-1} \text{ cm}^{-2} \text{ bar}^{-1}$
In addition, the possible formation of strong palladium-chlorine bonds as reported in the literature (Muftikian et al., 1995; Bodnariuk et al., 1989; and Coq et al., 1986) may also enhance the removal of atomic chlorine from DCB.

Based on the hypothesized reductive dechlorination mechanism of DCB on the Pd/Fe surface, palladium as the catalytic agent is not consumed in the reaction and the iron as the electron donor and reductant for water is transformed into soluble ionic species (Fe$^{2+}$, Fe(OH)$^-$). In contrast to the gradual dissolution of ionic species into the aqueous medium as is observed in the solution phase dechlorination study of colloidal nanoparticles, leaching is minimized by immobilizing the bimetallic Pd/Fe nanoparticles in the membrane matrix. This can be explained in the recapturing properties of the polymers with chelating functional groups. Chitosan with hydroxyl and amine functional groups on its backbone is expected to be able to recapture the water soluble Fe$^{2+}$ ions that are being “consumed” in the dechlorination process. The elemental analysis (AA for Fe ions and ICP for Pd ion) of the permeates and the remaining solution in the cell reservoir indeed showed negligible leaching of metals with respect to the initial loading of the bimetallic Pd/Fe nanoparticles in the membrane, with less than 1% for Fe$^{2+}$ and below the ICP detection limit for Pd$^{2+}$. The total metal mass balance of the used membranes was 98.00 ± 0.05 % relative to the fresh membranes by elemental analysis of digestion study. Table 5.3.3.a shows the elemental analysis that indicates the negligible leaching of metal ions for the membrane phase degradation study of TCE and DCB by Ni/Fe and Pd/Fe nanoparticles, respectively.
Table 5.3.3.a. Elemental analysis for membrane-immobilized bimetallic nanoparticles in the degradation study of chlorinated organics

<table>
<thead>
<tr>
<th>Degradation Study</th>
<th>Solution Phase (Leached Metal)</th>
<th>Membrane Phase (Fresh and Recaptured)</th>
<th>Total Balance with respect to Initial Weight*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE (Ni/Fe)</td>
<td>Fe$^{2+}$ 0.020 mg</td>
<td>Ni$^{2+}$ 0.060 mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.55 mg</td>
<td>97.50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.13 mg</td>
<td></td>
</tr>
<tr>
<td>DCB (Pd/Fe)</td>
<td>Fe$^{2+}$ 0.025 mg</td>
<td>Pd$^{2+}$ NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.745 mg</td>
<td>98.00%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0142 mg</td>
<td></td>
</tr>
</tbody>
</table>

* initial content of immobilized Ni/Fe: Ni = 1.20 mg, Fe = 3.60 mg
initial content of immobilized Pd/Fe: Pd = 0.015 mg, Fe = 2.80 mg
5.4. Long-Term Degradation Study

5.4.1. TCE Cycle Study by Ni/Fe Nanoparticles

Batch TCE cycle study is conducted to assess the effect of activity loss on reaction mechanism. Using the hydrogen data in Figure 5.2.2.a \( (k_{H2} = 184.60 \, \mu\text{mol H}_2/\text{g Fe hr}) \) and the amount of TCE degraded forming ethane/ethylene at different time intervals in each cycles, Figure 5.4.1.a shows the degradation kinetic corrected with the loss in iron mass due to the consumption of iron as electron donor and reductant in the aqueous phase degradation and oxidation reactions. Interpretation of kinetic data without correcting the loss of iron will overestimate the effect of deactivation and is demonstrated by the insert in Figure 5.4.1.a. As expected, gradual decrease in reaction kinetic with successive cycles study was observed indicating the progressive deactivation by the precipitation of by-products on the metal surface. Precipitation of different iron subspecies in long-term degradation study with different solution chemistry have been documented and was found to have a profound impact on the reaction kinetic (Farrell et al., 2000; and Klausen et al., 2003). Some of the cosolutes are found to be able to enhance the degradation. However most of them lower the reactivity by forming a mixed surface layer of precipitate which is mostly consists of ferrous or ferric related compounds (Furukawa et al., 2002; Kohn et al., 2005; and Satapanajaru et al., 2003). With the absence of any inorganic or organic cosolutes in this study, the attenuation in reactivity is mainly caused by the precipitation of corrosion products of insoluble hydroxides that passivated the metal surface. This indicates that the chloride-corrosion promoting effect as mentioned earlier that enhanced the hydrogen generation is relatively short-lived (decreasing \( k_{H2}^* \) as shown in Table 5.4.1.a) and doesn’t prevent the formation of passivating layer in the long run. This observation is also reported by others where
Figure 5.4.1.a. Batch cycle study for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles corrected by consumption of iron content. Ni/Fe (Ni = 20 wt%) = 0.10 g, initial TCE = 10 mg/L, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the raw data for TCE degradation.
initial increase in the degradation kinetics was achieved in chloride-containing solution but such rate-enhancing effect cannot be sustained in the long term study (Klausen, J., 2001 and 2003). In addition, the gradual increase in pH from 6.50 to the final pH of 8.20 at the end of third cycle as the reaction progress may also contribute to the decrease in reactivity as the generation of more OH− accelerated the formation of hydroxides species. It is interesting to observe that even though the reactivity gradually decreased over time, no chlorinated intermediates were detected in the aqueous phase by GC analysis for each of the three cycles and ethane remained as the major product with respect to the TCE degraded at different time intervals (shown in Table 5.4.1.a). This implied that the passivation of the bimetallic nanoparticles does not adversely modify the reaction mechanism of the TCE degradation process where ethane/ethylene remained as the major product. This is indeed indicated in Figure 5.4.1.b showing the time-independent plot of TCE conversion and ethane yield as well as the ratio of ethane formation and TCE degraded with respect to time. In addition to the decrease in reactivity, the shift in products formation is also expected with the increase in reaction times that are also being mentioned by authors studying the longevity of zero-valent iron for dechlorination reaction (Farrell et al., 2002; and Klausen et al., 2003). This hypothesis is shown as insert in Figure 5.4.1.b where the formation of ethylene accounted for most of the product balance in the gas phase for second and third cycles. The absence of less completely reduced compounds in aqueous solution coupled with the gas phase products balance analysis is hypothesized to be due to the rapid transmigration of the surface-sorbed intermediates from the surface-passivated site to another reactive site before it can be desorbed and transferred to the bulk solution phase.

A surprising observation in the cycle study is the increase of particles surface area
Table 5.4.1.a. Cycle studies for TCE degradation on Ni/Fe (Ni = 20 wt%) nanoparticles physical and chemical reactivity

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Initial pH</th>
<th>BET (m²/g)</th>
<th>$k_{H_2}^*$ (µmol / m² hr)</th>
<th>$\frac{[\text{TCE}]}{[\text{TCE}_0]}$</th>
<th>$\frac{[\text{C}_2\text{H}_6]}{[\text{TCE}_0]}$</th>
<th>$\frac{[\text{C}_2\text{H}_4]}{[\text{TCE}_0]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.50</td>
<td>28.28</td>
<td>6.65</td>
<td>Complete degradation after 120 min</td>
<td>0.92</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>6.90</td>
<td>60.66</td>
<td>3.18</td>
<td>&gt; 95% degradation after 140 min</td>
<td>0.87</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>7.60</td>
<td>90.80</td>
<td>1.32</td>
<td>&gt; 70% degradation after 140 min</td>
<td>0.56</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Figure 5.4.1.b. Time-independent plot of TCE degradation by Ni/Fe nanoparticles (Ni= 20 wt%): ethane yield and TCE conversion. Insert shows the time-dependent plot of ethane/ethylene formation with respect to TCE degraded.
(N\textsubscript{2}-BET analysis) as the reaction progressed (listed in Table 5.4.1.a.). This observation counters to the anticipated decrease in surface area as a result of the expected occurrence of processes such as the deposition of inactive layers on the particles surface, reduced porosity due to pore clogging, and dissolution of metal in the deactivation study of heterogeneous catalysis as reported in the literature (Kamolpornwijit et al., 2003; Murzin et al., 2004; and Vikesland et al., 2003). In the absence of any cosolutes effect, the increase in surface area in this case can only be attributed to the complex corrosion chemistry of iron in deoxygenated water coupled with the degradation reaction. One hypothesis is that the insoluble iron (hydr)oxides formed in the oxidation of iron are highly porous. The porous nature of the corroded precipitates is recently confirmed in the literature (Díez-Pérez et al., 2006). Porous precipitation of corroded oxides that increased the BET surface area and enhanced the conduction and interfacial polarization of zero-valent iron is also reported by Wu et al. (2005). Additionally, Cl\textsuperscript{–} may also induced nickel corrosion forming porous nickel oxides layer as well as cracked surfaces that are observed by Hsu et al (1987) and Barbosa et al. (1998). SEM images in Figure 5.4.1.c clearly revealed the oxidation of the nanoparticles and precipitation reactions. It shows the bimetallic Ni/Fe underwent morphological changes from the initial spherical nanosized particles to the indistinguishable agglomerates of colloidal clusters. Changes in metal surface morphology resulting from oxidation and precipitation are expected and reported in the literature (Kanel et al., 2006; Taman et al., 2005; and Wu et al., 2005).
Figure 5.4.1.c. SEM images of TCE degradation by Ni/Fe nanoparticles (Ni = 20 wt%) at 1st (reaction time = 120 min), 2nd (reaction time = 140 min), and 3rd (reaction time = 140 min) cycles for a total reaction time of approximately 7 hours.
5.5. Batch Degradation Modeling

5.5.1. Langmuirian-Type Sorption Isotherm and Reaction

Figure 5.5.1.a shows the quantitative analysis of the sorption study obtained experimentally through extraction of the nanoparticles in organic solvent. TCE sorption per metal mass, $q_{TCE}$ (µmol/g), is determined by the difference between the extracted and aqueous concentration according to the following expression:

$$ q_{TCE} = \frac{C_{TCE} - (C_{aq} V_{aq})}{m_{Ni/Fe}} $$

(5.5.1a)

The results demonstrated a Langmuirian-type quasi sorption isotherm. The coefficients of $K$ and $Q$ in eq 3.2j are determined by linear regression and the value obtained is 0014 L/µmol and 135.14 µmol/g, respectively. In addition, nonlinear regression analysis is also conducted (nlinfit function in Matlab 7.0 based on the Gauss-Newton and Levenberg-Marquardt algorithm) for comparison purpose and the value obtained for $K$ and $Q$ with 95% confidence limit is 0.0015 L/µmol and 140.21 µmol/g, respectively. The sorption isotherm plateau of Ni/Fe nanoparticles was about 120 µmol/g. The cross section area of a TCE molecule laying flat on a surface was estimated to be 40 Å²/molecule (Karanfil et al., 2004). Ni/Fe has a surface area of about 30 m²/g. Assuming monolayer coverage and the particles has similar energy of interactions with the adsorbent, the surface area coverage of TCE based on the sorption plateau is estimated to be around 90%. This indicates that the surface of Ni/Fe is closely packed with TCE molecules at initial concentration of 500 mg/L, which include both of the inactive and reactive sites sorption. Based on the reported study of TCE sorption to iron surface by Farrell et al. (2004), the fractional surface coverage of TCE may be lower due to the shortening of carbon-carbon bond after the formation of sigma bonding which is similar in magnitude in the
Figure 5.5.1.a. Langmuirian-type quasi sorption isotherm for TCE batch experiment study by Ni/Fe nanoparticles (Ni = 20 wt%) at high initial concentration. Insert shows the close ups of the low initial TCE concentration region. The solid line is the isotherm fit obtained by linear regression ($R^2 = 0.9904$). Ni/Fe = 0.1 g, volume = 40 ml, initial pH = 6.5.
conversion of a double to triple bond.

Degradation of TCE at low and high initial concentrations was experimented and mathematical modeling was conducted to study the reaction kinetic and sorption effect. At high initial concentration (TCE = 500 mg/L, 0.16 mmol), the total surface of nanoparticles approached the monolayer saturation limit and no more vacant sites will be available for TCE sorption. Using eq 3.2k with $C_V$ equal to zero, we obtain the expression for degradation with surface sites saturated with TCE:

$$\frac{dC_{aq}}{dt} = -(k_{int} + K_p)C_{aq}(1 + KC_{aq}) \quad (5.5.1b)$$

Another realistic assumption is that desorption is negligible when the particles surface are saturated with TCE, where $k_{a1}$ and $k_{a2}$ are approximately zero. Then eq 5.5.1b is further simplified to eq 5.5.1c:

$$\frac{dC_{aq}}{dt} = -k_{int}C_{aq}(1 + KC_{aq}) \quad (5.5.1c)$$

Experimental results were correlated with eq 5.5.1c by numerical integration technique using Matlab 7.0 (ODE15s solver) to estimate the intrinsic reaction rate constant. Figure 5.5.1.b shows that agreement between the experimental and calculated results was obtained with $k_{int}$ of about 0.10 hr$^{-1}$. The observed intrinsic surface area-normalized rate constant was determined to be $1.60 \times 10^{-3}$ L/m$^2$hr. This is an order of magnitude lower than the $k_{SA}$ value of $3.60 \times 10^{-2}$ L/m$^2$hr obtained previously in section 5.1.3. This is because the $k_{SA}$ determined earlier is considered a lumped parameter that includes the effect of surface sorption/transmigration and reaction. This will overestimate the true degradation rate constant of the reaction. At low initial concentration (TCE = 10 mg/L, 3.10 µmol), less than 10% of the total surface areas were adsorbed by TCE molecules. Equation 3.2k can then be further simplified to eq 5.5.1d with the following assumptions:
Figure 5.5.1.b. TCE degradation and modeling by Ni/Fe (Ni = 20 wt%) nanoparticles at high initial TCE concentration (Initial TCE = 500 mg/L) with eq 4.3c. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in insert is only “guide to the eye”.

$C_{aq} \times 10^{-2}$ ($\mu$mol/L)

$\text{Time (hr)}$

$\text{(C}_2\text{H}_6 + \text{C}_2\text{H}_4 \text{)} \text{formed}$

$\text{TCE degraded}$

$\text{Experimental Data}$

$k_{int} = 0.05 \text{ hr}^{-1}$

$k_{int} = 0.10 \text{ hr}^{-1}$

$k_{int} = 0.20 \text{ hr}^{-1}$

0 2 4 6 8 10 12

0 2 4 6 8 10 12

0 2 4 6 8 10 12

0 2 4 6 8 10 12

0 2 4 6 8 10 12
The modeling results in Figure 5.5.1.c show that excellent agreement between the calculated results and experimental data was obtained with the lumped parameter $k'$ value of 3.60 hr$^{-1}$ (5.76 x 10$^{-2}$ L/m$^2$hr). Based on the previously obtained estimated $k_{int}$ value (0.10 hr$^{-1}$), $K$ parameter (0.0015 L/µmol), and fractional occupied sites ($C_V / Q \approx 0.90$), the magnitude of the sorption effect from the bulk solution onto the particles surface can be estimated using eq 5.5.1.e. After substitution of all the appropriate parameters into eq 5.5.1.e and assumed that $k_{a1}$ is negligible, the sorption rate of TCE is 0.15 µmol hr$^{-1}$, which is close to the magnitude with the reaction rate under the experimental conditions used in this study. This implied that the degradation reaction by nanoparticles is not truly a rate-limiting step where TCE will undergo transformation once it was surface-bounded at the same rate it was sorbed onto the surface.

Inserts in Figure 5.5.1.b and Figure 5.5.1.c showing the time-dependent plot for the ratio of ethane and/or ethylene formation with respect to the TCE degraded also provide some insight regarding the reaction mechanism. Complete TCE degradation was achieved in 2-hour period with the formation of ethane that accounted for more than 92% of the total carbon balance at low TCE aqueous concentration. However at high concentration where the surface of nanoparticles was saturated with TCE molecules, complete TCE degradation only achieved after 10 hours of reaction time with shift in product formation. Ethylene and ethane are the main products formed within the first four
Figure 5.5.1.c. Modeling for TCE degradation by Ni/Fe (Ni = 20 wt%) nanoparticles at low TCE concentration (initial TCE = 10 mg/L) with eq 4.3d. Ni/Fe = 0.1 g, volume = 40 ml, headspace = 80 ml, initial pH = 6.5. Insert shows the ratio of gaseous products formation and TCE degraded with respect to time. Solid line in insert is only “guide to the eye”.
hours of reaction time that accounted for about 70% of the degraded TCE balance. As the reaction progressed, ethylene and ethane formation was in relation to the degraded TCE. However, chlorinated intermediates were not detected in the aqueous phase for the whole degradation duration. The main hypothesis from this observation is that the surface sites saturation will not strongly affect the reaction mechanism. As the surface was filled with TCE molecules, no vacant sites will be available for further sorption and transmigration. Degraded intermediates will continue to be strongly adsorbed on the same sites where its parent TCE molecule were first sorbed and undergo further reductive hydrodegradation reaction forming gaseous products of ethylene and ethane.

It should be noted that the model derived does not account the formation of any intermediates and are used to characterize the concentration of TCE degraded in aqueous phase with respect to time. However, based on the absence of any chlorinated by-products in the aqueous phase together with the quantitative analysis of ethylene and ethane formation, we can hypothesized that TCE undergoes reaction pathways involving the rapid elimination and hydrogenation reactions that form chloroacetylene, acetylene, and finally ethylene/ethane as shown in Figure 2.1.2.2.a. The observed formation of dichlorinated intermediates and acetylene as well as lower reaction rates by bulk iron suggest that TCE undergoes different reaction mechanisms (non-acetylene pathway) as compared to the bimetallic nanoparticles.
Chapter 6: Conclusions

This research work has been based on the hypothesis that the unique electronic and physicochemical properties of nanosized particles can be used to enhance the degradation kinetic and alter the reaction mechanistic pathways of chlorinated organics. Iron-based nanoparticles with a second dopant metal were shown to be able to catalyze the reaction kinetic significantly. The feasibility of combining nano and membrane science for the development of a better remediation technology of nanocomposite mixed membrane reactor has been demonstrated in this study through the successful synthesis of membrane-immobilized nanoparticles and its reactive separation analysis of chlorinated organics. The benefits of using nanoparticles for toxic organics remediation were retained by the hybrid membrane reactor with the added advantages of alleviating metal leaching problem and its potential application for convective mode reactive separation.

Fundamental Science and Engineering Advancements:

- Nano sized/structured particles can be used to enhance the reaction kinetically.
- A second catalytic dopant can be incorporated to enhance the physical and chemical properties of the base metallic element.
- Nanostructured materials can be immobilized into the membrane matrix to achieve reactive separation goals.
- Metal leaching can be minimized by nanocomposite membrane reactors through chelation by the membrane’s electronegative functional groups.

Specific conclusions drawn from this work include:

- The synthesized bimetallic Ni/Fe nanoparticles was shown to enhance the reaction kinetic in terms of surface area-normalized rate constant based on the pseudo first-order
reaction model. Reaction mechanism was altered to the hypothesized reductive hydrodechlorination by gas phase quantification analysis of ethane/ethylene formation and aqueous phase TCE degradation. Rate constants with orders of magnitude higher than the micron-sized iron demonstrated the superior characteristics of the particles in nanosized domain and the presence of nickel as catalytic agent. Additional study using different bimetallic mass concentration showed that the surface area-normalized reaction rate constant is a function of the nickel composition in the bimetallic Ni/Fe nanoparticles.

- The electron microscopic characterization of the nanoparticles coupled with kinetics analysis showed the importance of Ni/Fe ratios (in particles) on the reaction rates. As expected, very high nickel content in the Ni/Fe nanoparticles was observed to have a detrimental effect on the degradation reaction. This is due to the formation of less reactive nickel-rich surface layer on the nanoparticles. The compositional distribution of bimetallic Ni/Fe nanoparticles is complemented by the iron oxidation analysis where increase in the overall nickel content will lead to surface nickel saturation that diminished the hydrogen generation and subsequently decreased the TCE degradation rate. Reactivity of bimetallic Ni/Fe nanoparticles expressed in terms of surface area-normalized rate constant can be correlated with iron-normalized hydrogen generation rate. The presence of chloride-induced pitting corrosion that leads to higher iron oxidation was observed in this study but this effect was not sustainable in the long run.

- Mathematical analysis using the derived equation of reaction coupled with sorption term indicated that the rate of sorption and surface reaction were similar in magnitude with each other implying the absence of a true rate-limiting step. Surface saturation where TCE approaching the monolayer coverage limit will not affect the reaction mechanistic pathways. The less completely reduced intermediates continued to
be surface-sorbed and undergo further transformation into ethane/ethylene. In addition, TCE cycle analysis showed that the deactivation process did not adversely affect the mechanistic pathways where ethane remained as the major product formed at the end. This study showed that the deactivation process will affect the kinetic but not the chemical reactivity of the bimetallic nanoparticles.

- Degradation study of dichlorobiphenyls (DCB) by Pd/Fe nanoparticles and its associated iron oxidation analysis demonstrated similar trends with those observed in the TCE study. Hydrogen generated by iron oxidation depended strongly on the palladium surface coverage, in which total hydrogen generation decreased with higher palladium surface coverage that lowered DCB conversion to biphenyls.

- Chitosan membrane-immobilized bimetallic Ni/Fe nanoparticles were effective in degrading TCE and complete degradation was achieved using milligrams quantity of the nano materials with the formation of ethane as the major end product. The observed pseudo first-order reaction rate was similar with the PVDF-supported polyacrylic acid-immobilized nanoparticles but was higher than the naked nanoparticles and the cellulose acetate-based nanocomposite membrane systems. This showed that the immobilized nanoparticles reactivity is a strong function of the membrane-platform used.

- DCB degradation with the formation of biphenyl and monochlorinated product by chitosan-immobilized Pd/Fe nanoparticles was achieved under pressure induced operation and its conversion was related to the applied transmembrane pressure (residence time). As expected, lower applied pressure that corresponds to longer residence time will lead to higher DCB degradation and biphenyl formation and vise versa.
Appendix

Nomenclature

\( \alpha_s \) = specific surface area \( (m^2/g) \)

\( C_{Ni/Fe} \) = catalyst mass concentration in eq 5.3.2.a \( (g/L) \)

\( C_{aq} \) = aqueous phase TCE concentration \( (\mu mol/L) \)

\( C_{TCE} \) = total TCE concentration from organic phase extraction analysis \( (\mu mol/L) \)

\( C_v \) = vacant surface concentration \( (\mu mol/g) \)

\( J_w \) = solvent flux \( (cm^3 s^{-1} cm^{-2}) \)

\( k_{a1} \) = active surface sorption rate \( (1/\mu mol hr) \)

\( k_{-a1} \) = active surface desorption rate \( (1/hr) \)

\( k_{a2} \) = inactive surface sorption rate \( (1/\mu mol hr) \)

\( k_{-a2} \) = inactive surface desorption rate \( (1/hr) \)

\( k_{H2} \) = iron mass-normalized hydrogen generation rate \( (\mu mol / g \ Fe \ hr) \)

\( k_{H2}^* \) = surface area-normalized hydrogen generation rate \( (\mu mol / m^2 \ hr) \)

\( k_{int} \) = intrinsic TCE degradation rate constant \( (1/hr) \)

\( k_{obs} \) = observed pseudo first-order rate constant \( (L/g \ hr) \)

\( k_{ka} \) = surface area-normalized reaction rate constant \( (L/m^2 \ hr) \)

\( k_{Si} \) = forward transmigration rate \( (1/hr) \)

\( k_{Si}^{-} \) = reverse transmigration rate \( (1/hr) \)

\( k_{TCE} \) = observed pseudo first-order rate constant \( (1/hr) \)

\( K \) = Langmuirian-type sorption coefficient \( (L/\mu mol) \)

\( K_A \) = parameter defined in eq 2.2h \( (L/\mu mol hr) \)

\( K_B \) = parameter defined in eq 2.2h \( (1/hr) \)

\( K_{Si} \) = equilibrium transmigration sorption constant \( (k_{Si} / k_{Si}) \)
\( m_{\text{Ni/Fe}} \) = mass of Ni/Fe nanoparticles for degradation study (g)

\( q_{\text{TCE}} \) = surface-sorbed TCE concentration (\( \mu \text{mol/g} \))

\( q_{\text{si}} \) = surface-sorbed inactive TCE concentration (\( \mu \text{mol/g} \))

\( Q \) = maximum sorption concentration for surface-sorbed TCE (\( \mu \text{mol/g} \))

\( R_m \) = intrinsic membrane resistance (1/cm)

\( V_{\text{aq}} \) = total solution volume (L)

\( \Delta P \) = applied transmembrane pressure (bar)

\( \tau \) = residence time in convective degradation study (min)

\( \mu \) = solvent viscosity (kg /m min)

\( \rho_m \) = mass concentration of metal (g / L)
Matlab Programs

Determination of Langmuir Coefficients:

function Langmuir = GL(beta, x)
% Langmuir Sorption Coefficients
b1 = beta(1);
b2 = beta(2);
% Langmuir Sorption Isotherm
Langmuir = (b1*b2*x)./(1+(b1*x));

% Experimental Determined Aqueous Phase Concentration (µmol/L)
x = [ 22.97 8.74 4.28 0.99 0.175 2291.22 381.87 2917.49 2031.55 982.68 311 87.5 ];
% Experimental Determined Surface Sorbed Concentration (µmol/g)
y = [11.27 5.64 4.13 2.48 0.81 109.7 59.5 115.23 105.14 77.26 38.56 16.3 ];

% Initial Guesses for Langmuir Coefficients, K and Q
beta = [ 0.005 100 ];

betahat = nlinfit (x, y, ‘GL’, beta);
References


Lowry, G. V.; and Johnson, K. M., Congener-Specific Dechlorination of Dissolved PCBs by Microscale and Nanoscale Zerovalent Iron in a Water/Methanol Solution, 2004, 38, 5208-5216.


Vita

Yit-Hong Tee was born on June 15, 1975, in Kuala Lumpur, Malaysia. He attended the College of Damansara Utama in Malaysia for his freshman year before transferring to the University of Kentucky in Fall 1995. He received both his bachelors of science and masters of science degree from the university in 1998 and 2002, respectively. He continued his PhD study in 2002 at the University of Kentucky.

Publications:

• Degradation of Trichloroethylene and Dichlorobiphenyls by Iron-Based Bimetallic Nanoparticles, Tee, Y-H., and Bhattacharyya, D., to be submitted to Chemistry of Materials in December 2006.


Presentations:


• *Carbon Dioxide-Selective Membranes Containing Mobile and Fixed Carriers*, Tee, Y-H., and Ho, W.S. Winston, Annual Meeting of the American Institute of Chemical Engineers, Indianapolis, IN, November 3-8, 2002.
