MESOSTRUCTURED SILICA NANOPARTICLES SUPPORTED ELECTROSYNTHESIZED GOETHITE IN CATIONIC SURFACTANT FOR PHOTODEGRADATION OF 2–CHLOROPHENOL

ROHAYU BINTI JUSOH

UNIVERSITI TEKNOLOGI MALAYSIA
MESOSTRUCTURED SILICA NANOPARTICLES SUPPORTED ELECTROSYNTHESIZED GOETHITE IN CATIONIC SURFACTANT FOR PHOTODEGRADATION OF 2–CHLOROPHENOL

ROHAYU BINTI JUSOH

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

MAY 2015
For Mak and Ayah,
Thank you for always being there; your endless love, faith, and encouragement never fail to strengthen me

Abg Li, Kak Yati, Kak Na, Abg Madi, Kak Nani with
Kak Long, Abg Ngah, Abg Man and Kak Elly,
Your continuous helps, cares, motivations, and supports can never be repaid

and specially for my husband, Norsyazwan Mohamed,
Thank you for always standing next to me, lifting me up whenever I couldn’t reach
ACKNOWLEDGEMENT

Alhamdulillah, all praise to Allah. Peace and blessing to Prophet Muhammad S.A.W, his families and all muslims. Endless thanks and gratefulness to my supervisors; Assoc. Prof. Dr. Aishah Abdul Jalil, Prof. Dr. Sugeng Triwahyono and Prof. Dr. Ani Idris for the never ending advises and helps during the study. Their patience, criticism and ideas throughout this study are greatly appreciated. Without their continuous support, this thesis would not be completely finished.

A million thanks and appreciation goes to all the Green Technology and Advanced Materials research group members for giving me a helping hand in the process of doing this research. A lot of appreciation also goes to the staffs of Chemical Reaction Engineering Laboratory at Faculty of Chemical Engineering and Ibnu Sina Institute for their valuable help and aiding me in technical works throughout this study. My appreciation also goes to Yang di-Pertuan Agong for the King’s Scholarship Award and Universiti Malaysia Pahang (UMP) for Fellowship Scheme that were financially helpful in finishing this study.

Last but not least, I would like to extend my deepest gratitude and appreciation to my family and my close friends for their continuous support and endless attention. Thank you for everything.
ABSTRACT

2–chlorophenol (2–CP) which had been widely used in industry and daily life is a priority toxic pollutant that has caused considerable damage to the aquatic ecosystem and human health. Due to this reason, continuing study on efficient catalyst for degradation of this recalcitrant pollutant has been conducted in these recent years. In this study, goethite (α–FeOOH) was synthesized by an electrochemical method in a cationic surfactant solution and subsequent impregnation with mesostructured silica nanoparticles (MSN) gave α–FeOOH/MSN. The catalysts were characterized using X–ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform–infrared (FT–IR), $^{29}$Si magnetic angle spin nuclear magnetic resonance ($^{29}$Si MAS NMR), nitrogen physisorption analysis, electron spin resonance (ESR), and X–ray photoelectron spectroscopy (XPS). The results indicate that the cationic surfactant was retained around α–FeOOH surface with a free swinging alkane tail pointing outward from the catalyst. The performance of the catalysts were tested on the photodegradation of the 2–CP in a batch reactor under visible light irradiation. The results showed that the α–FeOOH were able to inhibit electron–hole recombination to give complete degradation of 50 mg L$^{-1}$ 2–CP at pH 5 when using 0.03 g L$^{-1}$ catalyst and 0.156 mM of H$_2$O$_2$. In contrast, it was found that by introducing the α–FeOOH to the MSN support, sequential silica removal in the MSN framework and isomorphous substitution of Fe ion was occurred, which able to effectively degrade the 2–CP with degradation percentage of 92.2, 79.3, 73.1, and 14.2%, with the loading of α–FeOOH in the following order: 10 wt% > 15 wt% > 5 wt% > MSN, respectively. Beside the retainment of the cationic surfactant structure on the catalysts, the MSN was also elucidated to play an important role as an electron acceptor that enhanced the electron–hole separation. Response surface methodology (RSM) analysis for the α–FeOOH and α–FeOOH/MSN catalysts showed good significance of model with low probability values (<0.0001) and a high coefficient of determination ($R^2$). The kinetic studies of both catalysts illustrated that surface reaction was the controlling step of the process. Reusability study showed that both catalysts were still stable after more than 4 subsequent reactions. The upscaling study using 10–fold upscale system indicate superior performance of the catalysts with almost complete degradation of 2–CP. The employment of the catalysts on degradation of various pollutants such as phenol, cationic dye and anionic dye has also showed remarkable performance, suggesting the potential use of the catalysts for various applications. Significantly, the synthesis method of these catalysts could be a great advantage in the future development of nanotechnology.
ABSTRAK

2-klorofenol (2-CP) yang telah digunakan secara meluas dalam industri dan kehidupan sehari-hari adalah pencemar toksik utama yang telah menyebabkan kerosakan besar kepada ekosistem akuatik dan kesihatan manusia. Oleh itu, kajian berterusan mengenai pemangkin yang berkesan untuk penurunan pencemar tegar ini telah dijalankan pada tahun-tahun kebelakangan ini. Dalam kajian ini, goethite (α-FeOOH) telah disintesis oleh kaedah elektrokimia dalam larutan surfaktan kationik dan penyait tepat seterusnya dengan nanopartikel silika meso-struktur (MSN) memberi α-FeOOH/MSN. Pemangkin tersebut telah dicirikan menggunakan pembelauan sinar-X (XRD), mikroskopi elektron (TEM), spektroskopi inframerah transformasi Fourier (FT-IR), 29Si putaran sudut ajaib resonans magnet nuklear (MAS 29Si NMR), analisis penjerapan nitrogen, resonans elektron spin (ESR), dan spektroskopi fotoelektron sinar-X (XPS). Keputusan menunjukkan bahawa surfaktan kationik dikekal di seluruh permukaan α-FeOOH dengan ekor alkana berayun bebas menunjuk ke luar pemangkin. Prestasi pemangkin diuji dengan penurunan 2-CP dalam reaktor kelompok di bawah sinaran cahaya tampak. Hasil kajian menunjukkan bahawa α-FeOOH dapat menghalangi penggabungan semula elektron-lubang untuk memberi penurunan lengkap 50 mg L–1 2-CP pada pH 5 apabila menggunakan 0.03 g L–1 pemangkin dan 0.156 mM H2O2. Sebaliknya, telah ditemui bahawa dengan memperkenalkan α-FeOOH itu kepada sokongan MSN, penyingkiran silika berurutan dalam rangka kerja MSN dan penukaran isomorf ion Fe telah berlaku, yang berkesan menurunkan 2-CP dengan peratusan penurunan 92.2, 79.3, 73.1 dan 14.2%, dengan pemuatan α-FeOOH mengikut susunan yang berikut: 10% berat> 15% berat> 5% berat> MSN, masing-masing. Selain pengekalan struktur surfaktan kationik pada pemangkin, MSN juga memainkan peranan penting sebagai penerima elektron yang meningkatkan pemisahan elektron-lubang. Analisis kaedah permukaan respon (RSM) untuk α-FeOOH dan α-FeOOH/MSN menunjukkan penemuan baik dengan nilai kebarangkalian yang rendah (<0.0001) dan pekali penentu yang tinggi (R²). Kajian kinetik kedua-dua pemangkin menunjukkan bahawa tindak balas permukaan adalah langkah kawalan proses. Kajian kebolehgunaan semula menunjukkan bahawa kedua-dua pemangkin masih stabil selepas lebih dari 4 tindak balas. Kajian penskalaan menggunakan sistem 10 kali ganda menunjukkan prestasi yang membanggakan daripada pemangkin dengan penurunan 2-CP yang hampir lengkap. Penggunaan pemangkin dalam penurunan pelbagai bahan pencemar seperti fenol, pewarna kationik dan pewarna anionik juga telah menunjukkan prestasi luar biasa, menunjukkan potensi penggunaan pemangkin untuk pelbagai aplikasi. Nyata, kaedah sintesis pemangkin ini boleh menjadi satu kelebihan yang besar dalam pembangunan masa depan teknologi nano.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td></td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td></td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td></td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td></td>
<td>vi</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td></td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF ABREVIATIONS</td>
<td></td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td></td>
<td>xxi</td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td></td>
<td>xxii</td>
</tr>
</tbody>
</table>

## 1 INTRODUCTION

1.1 Research Background | 1 |
1.2 Problem Statement and Hypothesis | 5 |
1.3 Objective of the Study | 7 |
1.4 Scope of the Study | 8 |
1.5 Significance of Study | 10 |
1.6 Thesis Outline | 11 |

## 2 LITERATURE REVIEW

2.1 Introduction | 12 |
2.2 Phenolic Compound
   2.2.1 Chlorophenol
   2.2.2 2–chlorophenol (2–CP)
2.3 Degradation Method
   2.3.1 Biological Method
   2.3.2 Physical Method
   2.3.3 Chemical Method
2.4 Advanced Oxidation Process
   2.4.1 Fenton Degradation
   2.4.2 Fenton–like Degradation
   2.4.3 Photocatalytic Degradation
   2.4.4 Photo–Fenton–like Degradation
   2.4.5 Optimization of Process Conditions
   2.4.6 Kinetic Analysis
   2.4.7 Mechanism of 2–CP Photodegradation
   2.4.8 Scaling Up System
2.5 Photocatalyst Synthesis and Modification
   2.5.1 α–FeOOH as Photocatalyst
   2.5.2 Preparation of α–FeOOH
   2.5.3 Electrolysis as Preparation Method
   2.5.4 Cationic Surfactant as Electrolyte
   2.5.5 Mesostructured Silica Nanoparticles as Support Material
2.6 Summary

3 METHODOLOGY

3.1 Introduction
3.2 Materials
3.3 Catalyst Preparation
   3.3.1 Preparation of Mesoporous Silica Nanoparticles (MSN)
   3.3.2 Preparation of α–FeOOH
   3.3.3 Preparation of α–FeOOH/MSN
3.4 Catalyst Characterization
   3.4.1 Crystallinity, Phase and Structural Studies
   3.4.2 Morphological Properties
   3.4.3 Vibrational Spectroscopy
   3.4.4 Study of Textural Properties
   3.4.5 Chemical Environment Determination
   3.4.6 Chemical Oxidation State Determination

3.5 Catalytic Activity
   3.5.1 Preparation of 2-CP Solution
   3.5.2 Photoreactor System
   3.5.3 Photodegradation Activity

3.6 Optimization of Process Conditions

3.7 Scale–up Process

4 RESULTS AND DISCUSSION

4.1 Introduction

4.2 Synthesis and Characterization
   4.2.1 Crystallinity, Phase and Structural Studies
   4.2.2 Morphological Properties
   4.2.3 Vibrational Spectroscopy
   4.2.4 Study of Textural Properties
   4.2.5 Chemical Environment Determination
   4.2.6 Chemical Oxidation State Determination
   4.2.7 Proposed Structure of Photocatalysts

4.3 Photodegradation Performance Evaluations
   4.3.1 Performance of Photocatalyst
   4.3.2 Effect of Metal Loading
   4.3.3 Effect of pH
   4.3.4 Effect of H₂O₂ Concentration
   4.3.5 Effect of Catalyst Dosage
   4.3.6 Effect of Initial Concentration
   4.3.7 Effect of Reaction Temperature
   4.3.8 Proposed Photodegradation Mechanism
4.4 Response Surface Methodology 112
4.5 Kinetic Analysis 129
4.6 Reusability Study 134
4.7 Scaling Up System 137
4.8 Application to Various Pollutant 139

5 CONCLUSION 141
5.1 Result Summary 141
  5.1.1 Synthesis and Characterization 141
  5.1.2 Catalytic Performance Evaluation 142
5.2 Future Study 143
  5.2.1 Synthesis and Characterization 143
  5.2.2 Photodegradation of Organic Pollutants 144

REFERENCES 145
Appendices A-G 164-170
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Previous studies for 2–CP degradation using α–FeOOH</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>List of chemicals</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>Variables showing operating conditions used in two–level factorial design employing α–FeOOH photocatalyst</td>
<td>54</td>
</tr>
<tr>
<td>3.3</td>
<td>Variables showing operating conditions used in two–level factorial design employing α–FeOOH/MSN photocatalyst</td>
<td>54</td>
</tr>
<tr>
<td>3.4</td>
<td>Two–level factorial design of experiments of four variables employing α–FeOOH photocatalyst</td>
<td>55</td>
</tr>
<tr>
<td>3.5</td>
<td>Two–level factorial design of experiments using α–FeOOH/MSN catalyst</td>
<td>55</td>
</tr>
<tr>
<td>3.6</td>
<td>Central composite design (CCD) design of experiments employing α–FeOOH photocatalyst</td>
<td>57</td>
</tr>
<tr>
<td>3.7</td>
<td>Central composite design (CCD) design of experiments employing α–FeOOH/MSN photocatalyst</td>
<td>58</td>
</tr>
<tr>
<td>4.1</td>
<td>Textural properties of catalysts</td>
<td>81</td>
</tr>
<tr>
<td>4.2</td>
<td>Calculated band gap value for each catalyst</td>
<td>94</td>
</tr>
<tr>
<td>4.3</td>
<td>Response for two–level factorial of four variables (X₁–X₄)</td>
<td>112</td>
</tr>
<tr>
<td>4.4</td>
<td>Response for central composite design (CCD)</td>
<td>114</td>
</tr>
<tr>
<td>4.5</td>
<td>ANOVA of photodegradation of 2–CP by α–FeOOH</td>
<td>115</td>
</tr>
<tr>
<td>4.6</td>
<td>Response for two–level factorial of five variables</td>
<td>119</td>
</tr>
<tr>
<td>4.7</td>
<td>Central composite design of experiments of four</td>
<td></td>
</tr>
</tbody>
</table>
variables

4.8 Analysis of variance (ANOVA) for central composite design for α–FeOOH/MSN catalyst

4.9 Analysis of variance (ANOVA) for central composite design for α–FeOOH/MSN catalyst (reduced)

4.10 Confirmation experiments

4.11 Pseudo–first order apparent constant values for 2–CP photodegradation for α–FeOOH

4.12 Pseudo–first order apparent constant values for 2–CP photodegradation for 10wt% α–FeOOH/MSN

4.13 Comparison of the catalysts performances in the scale–up system
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Phenolic compounds considered priority pollutants by US EPA and EU</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Interaction between variable $X_1$ and $X_2$ over the response</td>
<td>28</td>
</tr>
<tr>
<td>2.3</td>
<td>A mechanism to account for the pathways of photoproducts in the course of mineralisation of 2–CP (Bandara et al., 2001a)</td>
<td>31</td>
</tr>
<tr>
<td>2.4</td>
<td>Illustration of heterogeneous photocatalytic processes on the semiconductor (Litter, 1999).</td>
<td>33</td>
</tr>
<tr>
<td>2.5</td>
<td>Illustration of surfactant showing hydrophilic (head) and hydrophobic (tail) components</td>
<td>38</td>
</tr>
<tr>
<td>3.1</td>
<td>Flow chart of the research activity</td>
<td>44</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic diagram of electrolysis cell</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic diagram of laboratory scale photoreactor</td>
<td>52</td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic diagram of pilot scale photoreactor</td>
<td>60</td>
</tr>
<tr>
<td>4.1</td>
<td>XRD patterns of $\alpha$–FeOOH nanoparticles</td>
<td>63</td>
</tr>
<tr>
<td>4.2</td>
<td>XRD patterns in region 2–10° of MSN and $\alpha$–FeOOH/MSN catalysts at different $\alpha$–FeOOH loading</td>
<td>64</td>
</tr>
<tr>
<td>4.3</td>
<td>XRD patterns in region 2–10° of MSN$<em>{\text{APTES}}$ and $\alpha$–FeOOH/MSN$</em>{\text{APTES}}$ catalysts as compared to its pristine catalysts</td>
<td>65</td>
</tr>
<tr>
<td>4.4</td>
<td>(A) and (B) TEM image of $\alpha$–FeOOH nanoparticles; (C) HRTEM image and the FFT image (as inset)</td>
<td>66</td>
</tr>
</tbody>
</table>
4.5 TEM image of (A) MSN; (B and C) 10 wt% α–FeOOH /MSN; (D) HRTEM image of 10 wt% α–FeOOH /MSN

4.6 FT–IR spectra of (a) ionic surfactant, (b) α–FeOOH, (c) P–FeOOH, and (d) C–FeOOH. (A) Region 3800–2700 cm⁻¹; (B) region 1800–1400 cm⁻¹; (C) region 1100–400 cm⁻¹

4.7 FT–IR spectra of α–FeOOH in evacuated system at (a) 303 K, (b) 313 K, and (c) 323 K. (A) Region 3900–2700 cm⁻¹; (B) region 1800–900 cm⁻¹

4.8 FT–IR spectra of catalysts. (A) Region 3800–2700 cm⁻¹; (B) region 1800–1360 cm⁻¹; (C) region 1300–400 cm⁻¹; (D) in evacuated system for region 3770–3700 cm⁻¹

4.9 FT–IR spectra of (A) MSN, (B) 5wt% α–FeOOH /MSN, (C) 10wt% α–FeOOH /MSN and (D) 15wt% α–FeOOH /MSN and Gaussian curve–fitting of band at 960 cm⁻¹

4.10 FT–IR spectra of catalysts. (a) MSN; (b) MSNAPT conversion in (c) α–FeOOH/MSN; (d) α–FeOOH/MSNAPT conversion in (A) N₂ adsorption–desorption isotherm; (B) pore size distributions of the catalysts

4.11 Pore distribution of catalysts

4.12 Pore distribution of catalysts

4.13 \(^{29}\text{Si MAS NMR spectra of (a) MSN and (b) 10wt% α–FeOOH/MSN}

4.14 ESR spectra of (a) 5wt% α–FeOOH/MSN, (b) 10wt% α–FeOOH/MSN, (c) 15wt% α–FeOOH/MSN, and (d) α–FeOOH

4.15 XPS spectra of (B) Fe₂p and (C) Si₂p for 10 wt% α–FeOOH/MSN catalyst

4.16 The proposed reaction pathways for electrosynthesis of α–FeOOH

4.17 Proposed structure of α–FeOOH/MSN
The performance of catalysts under light irradiation for photocatalysis of α–FeOOH, photo–Fenton–like reaction of C–FeOOH, P–FeOOH, and α–FeOOH catalysts [pH 5; H$_2$O$_2$ concentration 0.156 mM; catalyst dosage 0.30 g L$^{-1}$; initial concentration 50 mg L$^{-1}$; temperature 303K].

Effects of cationic surfactant on the photo–Fenton–like activity [pH 5; H$_2$O$_2$ concentration 0.156 mM; catalyst dosage 0.30 g L$^{-1}$; initial concentration 50 mg L$^{-1}$; temperature 303K].

The 2–CP photodegradation performance of the catalysts [pH 5; H$_2$O$_2$ concentration 0.156 mM; catalyst dosage 0.30 g L$^{-1}$; initial concentration 50 mg L$^{-1}$; temperature 303K].

The 2–CP photodegradation performance of the catalysts [pH 5; H$_2$O$_2$ concentration 0.156 mM; catalyst dosage 0.30 g L$^{-1}$; initial concentration 50 mg L$^{-1}$; temperature 303K].

Photoluminescence spectra for α–FeOOH/MSN catalysts

Influence of pH on 2–CP photodegradation over α–FeOOH (H$_2$O$_2$ molar concentration is 0.156 mM; catalyst dosage 0.375 g L$^{-1}$; initial concentration is 10 mg L$^{-1}$; temperature 30°C).

Effect of pH on 2–CP photodegradation over α–FeOOH/MSN (metal loading is 10wt%; H$_2$O$_2$ molar concentration is 0.156 mM; catalyst dosage 0.375 g L$^{-1}$; initial concentration is 50 mg L$^{-1}$; temperature 30°C).

Influence of H$_2$O$_2$ molar concentration on 2–CP photodegradation over α–FeOOH (pH 5; catalyst dosage 0.375 g L$^{-1}$; initial concentration is 10 mg L$^{-1}$; temperature 30°C).
4.26 Effect of H$_2$O$_2$ molar concentration on 2–CP photodegradation over α–FeOOH/MSN (metal loading is 10wt%; catalyst dosage 0.375 g L$^{-1}$; initial concentration is 50 mg L$^{-1}$; temperature 30°C).

4.27 Influence of α–FeOOH dosage on 2–CP photodegradation (pH 5; H$_2$O$_2$ molar concentration is 0.156 mM; initial concentration is 10 mg L$^{-1}$; temperature 30°C).

4.28 Effect of catalyst dosage on 2–CP photodegradation over α–FeOOH/MSN (metal loading is 10wt%; H$_2$O$_2$ molar concentration is 0.156 mM; initial concentration is 50 mg L$^{-1}$; temperature 30°C).

4.29 Influence of initial concentration of 2–CP on 2–CP photodegradation over α–FeOOH (pH 5; H$_2$O$_2$ molar concentration is 0.156 mM; catalyst dosage 0.3 g L$^{-1}$; temperature 30°C).

4.30 Effect of initial 2–CP concentration on 2–CP photodegradation over α–FeOOH/MSN (metal loading is 10wt%; H$_2$O$_2$ molar concentration is 0.156 mM; temperature 30°C).

4.31 Influence of reaction temperature on 2–CP photodegradation over α–FeOOH (pH 5; H$_2$O$_2$ molar concentration is 0.156 mM; catalyst dosage 0.3 g L$^{-1}$; initial concentration is 50 mg L$^{-1}$).

4.32 Effect of reaction temperature on 2–CP photodegradation over α–FeOOH/MSN (metal loading is 10wt%; pH is 5; H$_2$O$_2$ molar concentration is 0.156 mM; initial concentration is 50 mg L$^{-1}$).

4.33 Plot of activation energy as a function of metal loading for 2–CP degradation.

4.34 Photodegradation efficiencies of 2–CP in the presence of hole scavenger, •OH scavenger, and electron scavenger by (A) α–FeOOH and (B) C–FeOOH [pH
5, H₂O₂ concentration 0.156 mM; catalyst dosage 0.30 g L⁻¹; initial concentration 50 mg L⁻¹; temperature 303 K].

4.35 Schematic illustration of 2–CP photodegradation over (A) C–FeOOH, and (B) photogenerated electron trapping by cationic surfactant headgroups of α–FeOOH

4.36 Photodegradation efficiencies of 2–CP in the presence of hole scavenger, 'OH scavenger, electron scavenger, and 'OH ads scavenger by 10 wt% α–FeOOH /MSN catalyst [pH 5; H₂O₂ concentration is 0.156 mM, catalyst dosage 0.40 g L⁻¹; initial concentration is 50 mg L⁻¹]

4.37 Schematic illustration of 2–CP photodegradation over α–FeOOH/MSN

4.38 The studentized residuals and predicted response plot for 2–CP photodegradation

4.39 Normal % probability and studentized residual plot for 2–CP photodegradation

4.40 The actual and predicted plot for 2–CP photodegradation.

4.41 3D response plot showing effect of temperature, catalyst dosage, and H₂O₂/2–CP ratio at fixed pH

4.42 Residual diagnostics for 2–CP photodegradation of normal probability plot

4.43 Residual diagnostics for 2–CP photodegradation of residual vs. predicted response plot

4.44 Response surface plot of (A and B) pH and reaction temperature; and (C and D) α–FeOOH metal loading and pH

4.45 Linear transform ln C₀/Cₜ = f(t) of 2–CP photodegradation over α–FeOOH.

4.46 Relationship between 1/r₀ and 1/C₀ at different initial
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.47</td>
<td>Plot of ( \ln \frac{C_0}{C_t} ) as a function of time ( (t) ).</td>
</tr>
<tr>
<td>4.48</td>
<td>Plot of ( \frac{1}{r_0} ) as a function of ( \frac{1}{C_0} )</td>
</tr>
<tr>
<td>4.49</td>
<td>Proposed degradation mechanism of 2-CP over the catalysts</td>
</tr>
<tr>
<td>4.50</td>
<td>Stability of ( \alpha )-FeOOH catalyst after subsequent reactions [pH 5; ( \text{H}_2\text{O}_2 ) concentration 0.156 mM, catalyst dosage 0.30 g L(^{-1}); initial concentration 50 mg L(^{-1}), temperature is 323 K].</td>
</tr>
<tr>
<td>4.51</td>
<td>Stability of ( \alpha )-FeOOH catalyst after subsequent reactions [pH 5; ( \text{H}_2\text{O}_2 ) concentration 0.156 mM, catalyst dosage 0.30 g L(^{-1}); initial concentration 50 mg L(^{-1}), temperature is 323 K].</td>
</tr>
<tr>
<td>4.52</td>
<td>Scale-up performance of the catalysts in 10-fold pilot scale system</td>
</tr>
<tr>
<td>4.53</td>
<td>Performance of catalysts for various pollutants</td>
</tr>
</tbody>
</table>
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmet–Teller</td>
</tr>
<tr>
<td>CP</td>
<td>Chlorophenol</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethyl ammonium bromide</td>
</tr>
<tr>
<td>DTABr</td>
<td>Dodecyldimethylammonium bromide</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier–Transform Infrared Spectrometer</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>g L$^{-1}$</td>
<td>Gram per liter</td>
</tr>
<tr>
<td>$K_{LH}$</td>
<td>Langmuir–Hinshelwood constant</td>
</tr>
<tr>
<td>$k_{app}$</td>
<td>Apparent first order rate constant</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>LH</td>
<td>Langmuir–Hinshelwood</td>
</tr>
<tr>
<td>mL</td>
<td>Mililiter</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>MSN</td>
<td>Mesoporous silica nanoparticles</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>UV–Vis/DRS</td>
<td>Ultraviolet–Visible/Diffuse Reflectance Spectrophotometer</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage loading</td>
</tr>
<tr>
<td>XPS</td>
<td>X–Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X–ray Diffraction</td>
</tr>
<tr>
<td>α–FeOOH</td>
<td>α–FeOOH without support</td>
</tr>
<tr>
<td>α–FeOOH/MSN</td>
<td>α–FeOOH supported on MSN</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

α       –   Alpha
Å       –   Angstrom
β       –   Beta
°       –   Degree
γ       –   Gamma
%       –   Percentage
θ       –   Theta
λ       –   Wavelength
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The properties of 2–CP (Muller and Caillard, 2011)</td>
<td>164</td>
</tr>
<tr>
<td>B</td>
<td>Calculations of electrolysis time run for wt%</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>loading</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Standard calibration of 2-chlorophenol</td>
<td>166</td>
</tr>
<tr>
<td>D</td>
<td>UV-vis reflectance spectrum of catalysts</td>
<td>167</td>
</tr>
</tbody>
</table>
| E            | The isoelectric points (pH
|              | PZC) of photocatalysts                             | 168  |
| F            | Calculation of ANOVA table                         | 169  |
| G            | F-table                                             | 170  |
CHAPTER 1

INTRODUCTION

1.1 Research Background

Within the last decade, there has been a growing concern related to the health impact and environmental damage due to phenolic compounds. The occurrence and widespread use of the phenolic compound and its derivatives as aromatic solvents, cleaning agents, biocides, preservatives and pesticides in the environment represents a serious problem owing to their toxicity, perseverance and accumulation in the environment while soluble phenolic compounds have revealed their absolute potential to enter the food chain (Santana et al., 2009). Adverse effects of the phenolic compounds and its derivatives on human, environment, as well as aquatic life have been recently reported (Maji et al., 2014) and have been associated to numerous biological disorders (Mangrulkar et al., 2008).

Chlorophenols as derivatives of the phenolic compound were identified as a pollution concern due to their high toxicity, high stability, and potentially carcinogenic. For this reason, United States Environmental Protection Agency (US EPA) had listed them as priority pollutants (Gordon and Marsh, 2009). In Malaysia, Department of Environment (DOE) has enacted allowable limits as in Environmental
Quality Act 1979 (Sewage and Industrial Effluent) that this pollutant should be treated to be less than 1 mg L\(^{-1}\) for inland water discharged.

Among chlorophenols, 2–chlorophenol (2–CP) has been considered to be the most toxic and carcinogenic. It is widely used in industry and daily life, and has caused considerable damage and threat to the aquatic ecosystem and human health (He et al., 2011). Due to the severe toxicity of 2–CP, there is a continuing study over appropriate methods to be used when eliminating this organic compound from aqueous systems. Several removal techniques including adsorption and solvent extraction are available for removing chlorophenols. However, these techniques suffer from the possibility for the generation of secondary pollution (Khan et al., 2011). Other than that, biological treatment which commonly used for the decomposition of many chlorinated phenols has proven ineffective since chlorinated phenols are resistant to biodegradation in a satisfactory time period (Bandara et al., 2001a). Therefore, other treatment technologies have received increased interest to substitute the conventional treatment method.

Among diverse alternative treatment technologies, advanced oxidation process (AOP) has shown absolute potential during the last decades as an abatement method for the degradation of the chlorinated phenols. The term “AOP” is used to describe the production of very active species like hydroxyl radicals (•OH) which depends on the oxidation mechanism. The treatment process provide a great advantage that they completely degrade the organic pollutants from the environment, which not only from the aqueous phase, but also by substituting them into other organic compounds before transforming them into innocuous inorganic species (Bertelli and Selli, 2006). Among various types and combinations of AOPs, the integration of two different AOPs (photocatalytic and Fenton–like), which commonly known as photo–Fenton–like, often offers synergistic reaction routes for the production of •OH and has been shown to be suitable for the degradation of various chlorinated phenol pollutants (Munoz et al., 2011, Metz et al., 2011).
The most extensively studied photocatalyst for the photodegradation of organic and inorganic contaminants in wastewaters is titania–based catalysts, especially titanium dioxide, TiO$_2$ (Khalil et al., 1998). However, the commercial utilization of this catalyst is limited due to the fact that TiO$_2$ aggregates rapidly in suspension which cause them to losing its surface area as well as the catalytic efficiency. Moreover, titania was proven to be unavailable for wider applications since it is only active with light radiation with wavelength approximately below 387 nm. Furthermore, due to the high costs required for separating and recovering these particles from the treated water, TiO$_2$ particles is not suitable to be used as the photocatalyst in a commercial suspension reactor system. Thus, there is an urgent need to develop a photocatalyst with high efficiency in employment of visible light irradiation, narrow band gap, stable in operation, and requires relatively low cost for the preparation (Guo et al., 2007a).

Iron oxides/oxyhydroxides are relevant in many scientific and technical applications and have been widely used in AOP technology. Among them, goethite, also known as α–FeOOH, is a type of iron oxyhydroxide with band–gap around 2.2 eV that seems to be a realistic candidate to be used as photocatalyst for degradation of 2–CP (Hu et al., 2012b). It is considered as one of the most environmentally friendly catalysts and thermodynamically stable which important upon photocatalysis illumination (Prasad et al., 2006). α–FeOOH also combines attractive properties for large–scale application such as resistance to photocorrosion, have wide range of operating pHs and proven to have almost undetectable leaching of iron into the solution.

The commercialized method for the preparation of α–FeOOH was known to be precipitation technique. However, this preparation technique may have several drawbacks related to longer time consumption, high temperature, and the precipitation conditions require extremely careful control (Gupta, 2003b). Therefore, it is necessary to find a simple and rapid route for the preparation of α–FeOOH. Electrosynthesis is a simple method that has been explored for a few decades for the synthesis of nano–sized α–FeOOH. Nano–sized α–FeOOH particles with structures
ranging from 1 to 100 nm in size have been shown to have unique physicochemical, surface, and optoelectronic properties, as well as excellent visible light photocatalytic activity (Ortiz de la Plata et al., 2010c). Regarding these factors, there is an urgent need in synthesizing α–FeOOH nanomaterials by electrosynthesis method. Previously, gamma phase of FeOOH were successfully synthesized by electrosynthesis method as reported by Hashimoto and Cohen (1974). More recent, simpler electrolysis method for the preparation of metal nanoparticles was reported by Aishah et al., (2002) employing dimethylformamide, naphthalene, and triethylammonium phosphate as its electrolyte.

Although electrosynthesis of α–FeOOH have been explored for few decades (Jiao et al., 2009), the use of surplus organic solvents urges the needs of investigating other alternatives in substituting the conventional solvents. Moreover, small (< 5 nm) nanoparticles tend to agglomerate due to high surface energy and the large surface area. In these scenarios, surfactant can be an alternative. Surfactants are composed of both hydrophilic and hydrophobic groups, with the presence of charged hydrophilic component. Cationic surfactants, which contain positive charged ions, have always sparked researcher’s interest due to their peculiar and interesting properties which include—contrasting hydrophobic and hydrophilic nature; tendency to self associate; ability to solubilize both polar as well as non polar components, etc. (Kaur and Mehta, 2014). It has abundance of charge–carrying ions which allows its usage as solvent without the need for supporting electrolyte. Moreover, cationic surfactants has been extensively used as templates in the preparation of various materials as it provide electrosteric protection through strongly coordinating protective ligand and can be efficiently used as scaffolds for nanostructure materials (Nikoobaht and El–Sayed, 2001).

Besides the needs of synthesizing iron nanometal, research has been oriented to the iron compounds immobilization on different carriers. This is to facilitate iron separation and to avoid more complex post–treatments (Feng et al., 2003). Recently among commonly employing solid supporters, mesostructure materials have been attracted interest as functional carrier due to their high surface area, assessable pore
channels, simple pore chemistry and enhanced powder recoverability (Deng et al., 2011). Moreover, it was proven that mesoporous–assembled structure with incorporation of metal catalyst offer better light–induced hydrophilicity, which therefore exhibiting higher photocatalytic activities than non–mesoporous–assembled catalyst (Puangpetch et al., 2010).

System upscaling is a critical factor in order to demonstrate the practicability of synthesized photocatalysis and the catalytic system for environmental remediation. The reality of research based photodegradation system is that very few systems for laboratory scale test are ultimately viable in terms of industrial scale up (McCullagh et al., 2011). Therefore, it is necessary to study the capability of the laboratory scale system to be used in pilot scale which will provide the benchmark for industrially practicable applications.

1.2 Problem Statement and Hypothesis

2–CP have been widely used in agriculture, paper, cosmetic, biocide, public health industries and can also be formed as a result of chlorination in water. Because of its toxicity, carcinogenicity, yet poor biodegradability, 2–CP is among the priority pollutants of major environmental concern. The individual dose requires to kill 50% of a population of mice (LD50) values determined indicate that 2–CP is considerably more toxic than dichlorophenols (Mozia et al., 2012). Moreover, 2–CP is known to be the starting materials to dioxins and furans, the most toxic chemicals ever studied. Therefore, it is very important to degrade the 2–CP into harmless species.

Various techniques including solvent extraction, membrane filtration, adsorption, and biological degradation have been developed for degrading 2–CP from waters. However, these techniques suffer from several drawbacks related to
high cost, time consuming, and have the possibility of producing secondary pollutant. Furthermore, 2–CP do not undergo direct sunlight photolysis in the natural environment since they only absorb light below 290 nm. Thus, there are needs in searching other possible degradation method and recently, semiconductor–based photocatalysis has shown promise in degrading the toxic compounds into innocuous inorganic species.

Meanwhile, the commercialized method for preparation of α–FeOOH was known to be precipitation technique but it may have several disadvantages related to longer time consumption, high temperature, and the precipitation conditions require extremely careful control. Therefore, it is necessary to find a simple and rapid route for the preparation of α–FeOOH. Although electrosynthesis of α–FeOOH have been explored for few decades, the use of surplus organic solvents and the tendency of nanoparticles to agglomerate urge the needs of investigating other alternatives in substituting the conventional solvents. In these scenarios, cationic surfactant can be an alternative.

Moreover, the study on the interaction of electrosynthesized metal oxide in cationic surfactants with a mesostructured silica nanoparticles support is still rare. Although several studies have been conducted to deposit the metal–surfactant catalyst onto several supports including clay (Mastalir et al., 2001), metal oxide (Sato et al., 2002), and activated carbon (Porta et al., 2002), the interaction between the metal oxides and the support material was not well studied. Moreover, the properties of the catalyst are known to be strongly affected by the support, which makes it very complicated to understand its reaction mechanism. Thus, detail investigation on supported metal catalyst is very crucial.

For many iron oxides–based catalysts employed in photo–Fenton–like system, the fastest rates in solution were observed at strong acidic pH (Ortiz de la Plata et al., 2010a). This selection, however, introduces the need for acidification of the reacting medium and subsequent neutralization after treatment. Thus, nearly
neutral condition appears as more favorable in employing photo–Fenton–like system which suggests an attempt to conduct the system at mild pH condition (Kolata et al., 1994). On the other hand, insufficient amount or a disproportionate excess of \( \text{H}_2\text{O}_2 \) concentration can result in negative effects of the photo–Fenton–like system (Burbano et al., 2003). Since the selection of a reduced \( \text{H}_2\text{O}_2 \) concentration for the degradation of pollutants is important from practical point of view due to the cost and toxicity (Sun et al., 2007), an attempt is necessary to investigate the behavior of the system and to reduce the amount of \( \text{H}_2\text{O}_2 \) required for efficient degradation.

The \( \alpha\text{–FeOOH} \) and \( \alpha\text{–FeOOH/MSN} \) catalysts synthesized in cationic surfactant was hypothesized to endow extra properties on the characteristics of the catalyst which is believed can hinder the electron–hole recombination, as well as induce the capability of the catalysts to be used in visible light regions. The high surface area of MSN provides well distributions of the iron oxides on the surface of MSN besides the ability of MSN to act as an electron acceptor to synergically perform with the loaded \( \alpha\text{–FeOOH} \) to enhance the photodegradation activity. Along this line, herewith we proposed to focus on the “Electrosynthesis of goethite supported on mesostructured silica nanoparticles in cationic surfactant for photodegradation of 2–chlorophenol”.

### 1.3 Objective of the Study

The objectives of this study are:

1. To synthesize and characterize nanosized \( \alpha\text{–FeOOH} \) and \( \alpha\text{–FeOOH/MSN} \) catalysts.
2. To optimize the photocatalytic degradation of 2–chlorophenol over the synthesized catalysts by Response Surface Methodology (RSM).
3. To study the degradation mechanism and kinetic modeling of the photocatalytic process.
4. To study the potential of the synthesized catalysts for pilot plant scale applications.

1.4 Scope of the Study

The scopes of this study consist of four parts which are;
1. Synthesis and characterize nanosized \( \alpha \)-FeOOH and \( \alpha \)-FeOOH/MSN catalysts
   i. The \( \alpha \)-FeOOH was synthesized in cationic surfactant via electrosynthesis method in a normal compartment cell fitted with a cathode and anode plate at a constant current density of 120 mA cm\(^{-2}\) under ambient atmosphere at 0°C. The \( \alpha \)-FeOOH was also supported on mesostructured silica nanoparticles (MSN) to give \( \alpha \)-FeOOH/MSN catalyst using impregnation method.
   ii. The physicochemical properties of the catalysts were determined by different means of characterizations. The crystallographic structure, crystallite size, and structural orientation of the prepared catalysts were recorded using X-ray diffraction (XRD) analysis. The morphological properties and distribution of metal oxides onto supportive material were examined using transmission electron microscopy (TEM). The vibration information of the catalysts was elucidated by Fourier transform infrared (FTIR) spectroscopy. Nitrogen adsorption–desorption isotherms (Brunauer–Emmett–Teller, BET) was used to obtain the textural properties of catalysts. The chemical oxidation state of the catalysts was determined using X-ray photoelectron spectroscopy (XPS). The chemical environments of Si atoms were detected using \(^{29}\)Si magic angle spin nuclear magnetic
resonance ($^{29}\text{Si MAS NMR}$). The band gap energy determination of the catalysts were studied using ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) while the optical properties of the catalysts were analysed by photoluminescense spectroscopy (PL). The mechanistic pathway for the structure formations were also proposed based on the characterizations results.

2. The catalytic activity of the catalysts were tested on photodegradation of 2–CP in aqueous solution. The screening process was conducted to identify crucial process conditions including the effect of metal loading, pH, catalyst dosage, $\text{H}_2\text{O}_2$ concentration, 2–CP initial concentration, and temperature. Optimization of the photodegradation system was done via Response Surface Methodology (RSM) using statistical software package Design–Expert, by employing sequence optimization of full factorial design and central composite design.

3. The mechanisms of the 2–CP photodegradation over the catalysts were studied by using several scavengers. Four types of scavengers were used for the system: potassium dichromate (PD); isopropanol (IP); sodium oxalate (SO); and potassium iodide (PI), with the role as a scavenger of photogenerated electrons, hydroxyl radicals ($\bullet\text{OH}$), photogenerated holes ($\text{H}^+$), and hydroxyl radicals adsorbed on the catalyst surface ($\bullet\text{OH}_{\text{ads}}$), respectively. The kinetic modeling of the photocatalytic process was investigated using Langmuir–Hinshelwood model to accommodate reactions occurring at solid–liquid interface. The reaction rate constant ($K_R$) and the adsorption equilibrium constant ($K_{LIH}$) were calculated to determine the type of reaction occurs during the photodegradation process.

4. The potential of the catalysts for applications in pilot scale was studied in the aspects of reusability, upscaling feasibility, and degradation ability on various pollutants. The reusability of the catalysts were investigated to indicate the robustness of the catalysts towards the photodegradation process. Repeated experiments were carried out using same operating
conditions and the performances of the catalysts at each reaction cycles were compared. The feasibility of up–scaled system for photocatalytic degradation of 2–CP was investigated using a pilot scale reactor system with a 10–fold upscale system of the laboratory scale. Lastly, the potential applications of the catalysts to various target pollutants were investigated using cationic dye, anionic dye, and phenol.

1.5 Significance of Study

In this study, detailed investigation on the 2–CP degradation using α–FeOOH and α–FeOOH/MSN catalysts via photo–Fenton–like process was conducted. The employment of the photocatalysts to give complete degradation of 2–CP under mild operating conditions provide new insight in reducing the use of oxidizing agents which normally employed in huge amounts for this catalytic system. This study also provides a platform to eliminate the subsequent neutralization process which commonly required in most of the 2–CP degradation processes. Furthermore, the proposed degradation mechanism using the catalysts offers better understanding of the catalytic process employing metal–surfactant catalyst supported on a silica material.

The simple and rapid route for the synthesis of the catalysts offers new alternative to current commercial synthesis process since this electrosynthesis method using cationic surfactant as a single electrolyte avoids the surplus use of the organic solvents. The study on the mechanistic pathways for the formation of the electrosynthesized metal–surfactant catalyst presents additional knowledge in current progress in this research area. Moreover, the study on the interaction of electrosynthesized metal oxide in cationic surfactants with a mesostructured silica nanoparticles support may provide new insight to the current understanding in the metal–surfactant field.
1.6 Thesis Outline

This thesis is divided into five chapters. In Chapter 1, introduction is given about the wide usage of phenolic compound and the importance on the degradation of the chlorinated phenolic compound, especially 2–chlorophenol which caused severe problems to human and environment. Several techniques were reported to potentially overcome this problem including physical, biological, and chemical treatment. The potential of α–FeOOH and α–FeOOH/MSN as semiconductor for photo–Fenton–like process are highlighted. The problem statement of the current research was stated which subsequently provide a clear objective of the present study. The scope of study covers the research which was done to meet the objectives. The significance of research was also clearly mentioned.

Chapter 2 or literature review covers the conventional method of 2–CP degradation, basic information of 2–CP and characteristics of α–FeOOH and MSN as previously studied. The previous studies on photoreactor scaling up also included. Chapter 3 or methodology describes the chemicals and materials used in the research work, instrumentations, catalysts preparation and characterizations, experimental setup, photodegradation testing, and it also includes the procedure for the analysis calculations.

Chapter 4 concerned with the results and discussion which in further divided into seven parts. The first part is synthesis and characterization, followed by the photodegradation performance evaluation, optimization of reaction conditions, kinetic analysis, reusability study, scaling up system, and the last part is the capability study of the catalysts towards various pollutants. The results are presented and discussed comprehensively. Finally, Chapter 5 covers the results summary and future study.
REFERENCES


