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

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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,
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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_2O_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 seharian 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 penyahtepuan seterusnya dengan nanopartikel silika meso-struktur (MSN) memberi α-FeOOH/MSN. Pemangkin tersebut telah dicirikan menggunakan pembelauan sinar-X (XRD), mikroskopi transmisi elektron (TEM), spektroskopi inframerah transformasi Fourier (FT-IR), ^{29}Si putaran sudut ajaib resonans magnet nuklear (MAS ^{29}Si NMR), analisis penjerapan nitrogen, resonans elektron spin (ESR), dan spektroskopi fotoelektron sinar-X (XPS). Keputusan menunjukkan bahawa surfaktan kationik dikekalkan 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 menghalang 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 H_2O_2. Sebaliknya, telah ditemui bahawa dengan memperkenalkan α-FeOOH itu kepada sokongan MSN, penyingkiran silika berurutan dalam rangka kerja MSN dan penukargantian 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 (R^2). 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.

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LIST OF ABBREVIATIONS

AOP – Advanced Oxidation Process

BET – Brunauer–Emmet–Teller

CP – Chlorophenol

CTAB – Cetyltrimethyl ammonium bromide

DTABr – Dodecyltrimethylammonium bromide

EG – Ethylene Glycol

ESR – Electron Spin Resonance

FTIR – Fourier–Transform Infrared Spectrometer

g – Gram

$g\ L^{-1}$ – Gram per liter

K_{LH} – Langmuir–Hinshelwood constant

k_{app} – Apparent first order rate constant

k_r – Reaction rate constant

LH – Langmuir–Hinshelwood

mL – Mililiter

min – Minutes

MSN – Mesoporous silica nanoparticles

NMR – Nuclear Magnetic Resonance

TEM – Transmission Electron Microscope

TEOS – Tetraethylorthosilicate

UV–Vis/DRS	–	Ultraviolet–Visible/Diffuse Reflectance Spectrophotometer
wt%	–	Weight percentage loading
XPS	–	X–Ray Photoelectron Spectroscopy
XRD	–	X–ray Diffraction
α–FeOOH	–	α–FeOOH without support
α–FeOOH/MSN	–	α–FeOOH supported on MSN

LIST OF SYMBOLS

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

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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 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 (LD_{50}) 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 H_2O_2 concentration can result in negative effects of the photo–Fenton–like system (Burbano *et al.*, 2003). Since the selection of a reduced H_2O_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 H_2O_2 required for efficient degradation.

The α–FeOOH and α–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 α–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 α–FeOOH and α–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 α–FeOOH and α–FeOOH/MSN catalysts
    i. The α–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 α–FeOOH was also supported on mesostructured silica nanoparticles (MSN) to give α–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 (Brunnauer–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}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 photoluminescence 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, H_2O_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 (•OH), photogenerated holes (H^+), and hydroxyl radicals adsorbed on the catalyst surface ($•OH_{ads}$), 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_{LH}) 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

Abbott, A. P. and McKenzie, K. J. (2006). Application of Ionic Liquids to the Electrodeposition of Metals. *Physical Chemistry Chemical Physics.* 8: 4265–4279.

Akpan, U. G., and Hameed, B. H. (2009). Parameters Affecting the Photocatalytic Degradation of Dyes using TiO_2–based Photocatalysts: A Review. *Journal of Hazardous Materials.* 170(2–3): 520–529.

Aishah, A. J., Kurono, N., and Tokuda, M. (2002). Facile Synthesis of Ethyl 2–Arylpropenoates by Cross–Coupling Reaction using Electrogenerated Highly Reactive Zinc. *Tetrahedron.* 58(37): 7477–7484.

Al Duri, B. (1995*). Reviews in Chemical Engineering*. 11(2): 101.

Annachhatre, A. P., and Gheewala, S. H. (1996). Biodegradation of Chlorinated Phenolic Compounds. *Biotechnology Advances.* 14(1): 35–56.

Annadurai, G., Juang, R. S., and Lee, D. J. (2002). Factorial Design Analysis of Adsorption of Activated Carbon on Activated Carbon Incorporated with Calcium Alginate. *Advanced Inorganic Environmental Research.* 6: 191–199.

Anpo, M. (1989). Photocatalysis on Small Particle TiO_2 Catalysts. Reaction Intermediates and Reaction Mechanisms. *Research on Chemical Intermediates.* 11(1): 67–106.

Aziz, M. A. A., Jalil, A. A., Triwahyono, S., Mukti, R. R., Taufiq−Yap, Y. H., and Sazegar, M. R. (2014). Highly Active Ni−Promoted Mesostructured Silica Nanoparticles for CO_2 Methanation. *Applied Catalysis B: Environmental.* 147: 359–368.

Bandara, J., Mielczarski, A., Lopez, A. and Kiwi, J. (2001a). 2. Sensitized Degradation of Chlorophenols on Iron Oxides Induced by Visible Light:

Comparison with Titanium Oxide. *Applied Catalysis B: Environmental,* 34(4): 321–333.

Bandara, J., Klehm, U., and Kiwi, J. (2007b). Raschig Rings–Fe_2O_3 Composite Photocatalyst Activate in the Degradation of 4–Chlorophenol and Orange II Under Daylight Irradiation. *Applied Catalysis B: Environmental.* 76(1–2): 73–81.

Bayarri, B., Giménez, J., Maldonado, M. I., Malato, S., and Esplugas, S. (2013). 2,4-Dichlorophenol Degradation by Means of Heterogeneous Photocatalysis. Comparison Between Laboratory and Pilot Plant Performance. *Chemical Engineering Journal.* 232: 405–417.

Bertelli, M. and Selli, E. (2006). Reaction Paths and Efficiency of Photocatalysis on TiO_2 and of H_2O_2 Photolysis in the Degradation of 2–Chlorophenol. *Journal of Hazardous Material.* 138(1): 46–52.

Bishop, J. L. and Murad, E. (2004). Characterization of Minerals and Biogeochemical Markers on Mars: A Raman and IR Spectroscopic Study of Montmorillonite. *Journal of Raman Spectroscopy.* 35: 480–486.

Bourlinos, A. B., Karakassides, M. A., and Petridis, D. (2000). Synthesis and Characterization of Iron–Containing MCM–41 Porous Silica by the Exchange Method of the Template. *Journal of Physical Chemistry B.* 104: 4375–4380.

Burbano, D. D., Suidam, M., Richardson., T. (2003). Chemical Destruction of MTBE using Fenton's reagent: Effect of Ferrous Iron/Hydrogen Peroxide Ratio. *Water Science and Technology.* 47: 165–171.

Carey, F. A. (2000). *Organic Chemistry*, 4th Edition, McGraw–Hill, USA.

Chang, M. C. and Tanaka, J. (2002). FT−IR Study for Hydroxyapatite/Collagen Nanocomposite Cross−Linked by Glutaraldehyde. *Biomaterials.* 23: 4811–4818.

Chen, H. F., Wei, G. D., Han, X., Li, S., Wang, P. P., Chubik, M., Gromov, A., Wang, Z. P., and Han, W. (2011). Large-Scale Synthesis of Hierarchical Alpha-FeOOH Flowers by Ultrasonic-Assisted Hydrothermal Route. *Journal of Materials Science: Materials in Electronics.* 22: 252–259.

Cheng, W., Dong, S., and Wang, E. (2003a). Synthesis and Self–Assembly of Cetyltrimethylammonium Bromide–Capped Gold Nanoparticles. *Langmuir.* 19(22): 9434–9439.

Cheng, Y., Sun, H., Jin, W., and Xu, N. (2007b). Photocatalytic Degradation of 4–Chlorophenol with Combustion Synthesized TiO_2 under Visible Light Irradiation. *Chemical Engineering Journal.* 128(2–3): 127–133.

Chia, N−C. and Mendelsohn, R. (1996). Conformational Disorder in Unsaturated Phospholipids by FTIR Spectroscopy. *BBA–Biomembranes.* 1283: 141–150.

Cho, I.–H., and Zoh, K.–D. (2007). Photocatalytic Degradation of Azo Dye (Reactive Red 120) in TiO_2/UV System: Optimization and Modeling using a Response Surface Methodology (RSM) Based on the Central Composite Design. *Dyes and Pigments.* 75(3): 533–543.

Christensen, A. N., Jensen, T. R., Bahl, C. R. H., and DiMasi, E. (2007). Nano Size Crystals of Goethite, α–FeOOH: Synthesis and Thermal Transformation. *Journal of Solid State Chemistry.* 180(4): 1431–1435.

Cong, H., Toftegaard, R., Arnbjerg, J.,and Ogilby, P. R. (2010). Silica–Coated Gold Nanorods with a Gold Overcoat: Controlling Optical Properties by Controlling the Dimensions of a Gold−Silica−Gold Layered Nanoparticle, *Langmuir.* 26: 4188–4195.

Cornell, R.M. and Schwertmann, U. (2003). *The Iron Oxides: Structure, Properties, Reactions, Occurrances and Uses*. 2^{nd} Edition: Wiley–VCH.

Dai, C., Zhang, A., Li, L., Hou, K., Ding, F., Li, J., Mu, D., Song, C., Liu, M., and Guo, X. (2013). Synthesis of Hollow Nanocubes and Macroporous Monoliths of Silicalite–1 by Alkaline Treatment. *Chemistry of Materials.* 25: 4197–4205.

Daneshvar, N., Rabbani, M., Modirshahla, N., and Behnajady, M. A. (2004). Kinetic modeling of Photocatalytic Degradation of Acid Red 27 in UV/TiO_2 Process. *Journal of Photochemistry and Photobiology A: Chemistry.* 168(1–2): 39–45.

Das, S., and Hendry, M. J. (2011). Changes of Crystal Morphology of Aged Goethite Over a Range of pH (2–13) at 100°C. *Applied Clay Science.* 51(1–2): 192–197

Deng, Y., Cai, Y., Sun, Z., and Zhao, D. (2011). Magnetically responsive Ordered Mesoporous Materials: A Burgeoning Family of Functional Composite Nanomaterials. *Chemical Physics Letters.* 510(1–3): 1–13.

Dorfman, L., M., and Adams, G., E. (1973). Reactivity of the Hydroxyl Radical in Aqueous Solutions. *National Standard Reference Data System, National Bereau of Standards.* 46: 1.

Durand, A.–P. Y., and Brown, R. G. (1995). Photoreactions of 4–Chlorophenol in Aerated and Deaerated Aqueous Solution: Use of LC–MS for Photoproduct Identification. *Chemosphere.* 31(7): 3595–3604.

Eisenhauer, H. R. (1964). Oxidation of phenolic wastes. *Journal of Water Pollution Control*. 36: 1117–1127.

Elghniji, K., Hentati, O., Mlaik, N., Mahfoudh, A., and Ksibi, M. (2012). Photocatalytic Degradation of 4–Chlorophenol under P–Modified TiO_2/UV System: Kinetics, Intermediates, Phytotoxicity and Acute Toxicity. *Journal of Environmental Sciences.* 24(3): 479–487

Endud, S. and Wong, K−L. (2007). Mesoporous Silica MCM−48 Molecular Sieve Modified with $SnCl_2$ in Alkaline Medium for Selective Oxidation of Alcohol. *Microporous and Mesoporous Material.* 101: 256–263.

Feng, J., Hu, X., and Yue, P. L. (2003). Novel Bentonite Clay–Based Fe−Nanocomposite as a Heterogeneous Catalyst for Photo–Fenton Discoloration and Mineralization of Orange II. *Environmental Science & Technology.* 38(1): 269–275.

Ferroudj, N., Nzimoto, J., Davidson, A., Talbot D., Briot, E., Dupuis, V., Bée, A., Medjram, M.S., Abramson, S. (2013). Maghemite Nanoparticles and Maghemite/Silica Nanocomposite Microspheres as magnetic Fenton Catalysts for the Removal of Water Pollutants. *Applied Catalysis B: Environmental.* 136: 9–18.

Gao, J. and Teplyakov, A. V. (2014b). Thermal Transformations of 2–Chlorophenol on a Surface of ZnO Powder Catalyst. *Catalysis Today.* 238: 111–117.

Gao, Y., and Hao, J. (2009a). Electrochemical Synthesis of Zinc Nanoparticles via a Metal−Ligand–Coordinated Vesicle Phase. *The Journal of Physical Chemistry B. 113*(28): 9461–9471.

Garrido–Ramírez, E. G., Theng, B. K. G., and Mora, M. L. (2010). Clays and Oxide Minerals as Catalysts and Nanocatalysts in Fenton–like Reactions — A Review. *Applied Clay Science.* 47(3–4): 182–192.

Gaya, U. I., Abdullah, A. H., Zainal, Z., and Hussein, M. Z. (2009). Photocatalytic Treatment of 4–Chlorophenol in Aqueous Zno Suspensions: Intermediates, Influence of Dosage and Inorganic Anions. *Journal of Hazardous Materials.* 168(1): 57–63

Gordon, T.R. and Marsh, A.L. (2009). Temperature Dependence of the Oxidation of 2–Chlorophenol by Hydrogen Peroxide in the Presence of Goethite. *Catalysis Letter*. 132: 349–354

Goswami, D., Sen, R., Basu, J. K., and De, S. (2010). Surfactant Enhanced Ricinoleic Acid Production using Candida Rugosa Lipase. *Bioresource Technology*. 101(1): 6–13

Groen, J. C., Peffer, L. A. A, Moulijn, J. A, and Pérez–Ramírez, J. (2004a). Mesoporosity Development in ZSM–5 Zeolite upon Optimized Desilication Conditions in Alkaline Medium. *Colloids and Surfaces A: Physicochemical and Engineering. 241*: 53–58.

Groen, J. C., Hamminga, G. M., Moulijn, J. A, and Pérez–Ramírez, J. (2007b). In Situ Monitoring of Desilication of MFI–type Zeolites in Alkaline Medium. *Chemistry Chemical Physics*. 9: 4822–4830.

Guettaï, N., and Ait Amar, H. (2005). Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part I: Parametric Study. *Desalination*. 185(1–3): 427–437.

Guo, Y., Quan, X., Lu, N., Zhao, H., and Chen, S. (2007a). High Photocatalytic Capability of Self–Assembled Nanoporous WO3 with Preferential Orientation of (002) Planes. *Environmental Science & Technology*. 41(12): 4422–4427.

Guo, P., Wang, X., & Guo, H. (2009b). TiO_2/Na–HZSM–5 Nano–Composite Photocatalyst: Reversible Adsorption by Acid Sites Promotes Photocatalytic Decomposition of Methyl Orange. *Applied Catalysis B: Environmental*. 90(3–4): 677–687.

Guo, J–F., Ma, B., Yin, A., Fan, K., and Dai, W–L. (2012c). Highly Stable and Efficient Ag/AgCl@TiO_2 Photocatalyst: Preparation, Characterization, and Application in the Treatment of Aqueous Hazardous Pollutants. *Journal of Hazardous Materials*. 77: 211–212.

Gupta, V. K., Srivastava, S. K., and Tyagi, R. (2000a). Design Parameters for the Treatment of Phenolic Waste by Carbon Columns (Obtained from Fertilizerwaste Material), *Water Research*. 34: 1543–1550.

Gupta, C. K. (2003b). *Chemical Metallurgy Principles and Practice*. Weinheim, Germany, Wiley–VCH.

Hariharan, C. (2006). Photocatalytic Degradation of Organic Contaminants in Water by ZnO Nanoparticles: Revisited. *Applied Catalysis A: General.* 304: 55–56.

Hashimoto, K., and Cohen, M. (1974). Anodic Deposition of Ferric Oxy–Hydroxide Films on Platinum from Perchlorate Solutions. *Journal of The Electrochemical Society.* 121(1): 37–42.

Hassan, H., and Hameed, B. H. (2011). Fenton–like Oxidation of Acid Red 1 Solutions Using Heterogeneous Catalyst Based on Ball Clay. *International Journal of Environmental Science and Development*. 2: 218–222.

He, Z., Wang, C., Wang, H., Hong, F., Xu, X., Chen, J., and Song, S. (2011). Increasing the Catalytic Activities of Iodine Doped Titanium Dioxide by Modifying with Tin Dioxide for the Photodegradation of 2–Chlorophenol under Visible Light Irradiation, *Journal of Hazardous Materials.* 189(1–2): 595–602.

Holladay, D. W., Hanchen, C. W., Scott, C. D., and Chilcote, D. D. (1978). Biodegradation of Phenolic Waste Liquors in Stirred–Tank, Packed–Bed and Fluidized–Bed Bioreactors. *Journal WPCF.* 50: 2573–2589.

Howard, P. H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Micha– lenko, E.M. (1991). *Handbook of Environmental Degradation Rates*. Lewis Publishers, Chelsea, MI.

Hu, P., Pan, D., Zhang, S., Tian, J., and Volinsky, A. A. (2011a). Heat Treatment Effects on Fe_3O_4 Nanoparticles Structure and Magnetic Properties Prepared by Carbothermal Reduction. *Journal of Alloys and Compounds.* 509(5): 3991–3994.

Hu, S., Liu, G., Zhu, D., and Chen, C. (2012b). Synthesis, Characterization, and Evaluation of Boron–Doped Iron Oxides for the Photocatalytic Degradation of Atrazine under Visible Light. *International Journal of Photoenergy.* 598713.

Huh, S., Wiench, J. W., Yoo J–C., Pruski, M., and Lin, V.S.–Y. (2003). Organic Functionalization and Morphology Control of Mesoporous Silicas via a Co–Condensation Synthesis Method. *Chemistry of Materials.* 5(22): 4247–4256.

Idris, A., Kormin, F., and Noordin, M. Y. (2006). Application of Response Surface Methodology in Describing the Performance of Thin Film Composite Membrane. *Separation and Purification Technology.* 49: 271–280.

Idris, A., Hassan, N., Rashid, R., and Ngomsik, A.–F. (2011b). Kinetic and Regeneration Studies of Photocatalytic Magnetic Separable Beads for Chromium (VI) Reduction Under Sunlight. *Journal of Hazardous Materials.* 186(1): 629–635.

Ilisz, I., Dombi, A., Mogyorósi, K., Farkas, A., and Dékány, I. (2002). Removal of 2-Chlorophenol from Water by Adsorption Combined With TiO_2 Photocatalysis. *Applied Catalysis B: Environmental.* 3: 247–256.

Imoberdorf, G. E., Cassano, A. E., Irazoqui, H. A., and Alfano, O. M. (2007). Optimal Design and Modeling of Annular Photocatalytic Wall Reactors. *Catalysis Today.* 129(1–2): 118–126.

Jaafar, N. F., Abdul Jalil, A., Triwahyono, S., Muhd Muhid, M. N., Sapawe, N., Satar, M. A. H., and Asaari, H. (2012). Photodecolorization of Methyl Orange over α–Fe2O3–Supported HY Catalysts: The Effects of Catalyst Preparation and Dealumination. *Chemical Engineering Journal.* 191:112–122.

Jal, P. K., Patel, S., and Mishra, B. K. (2004). Chemical Modification of Silica Surface by Immobilization of Functional Groups for Extractive Concentration of Metal Ions. *Talanta.* 62: 1005–1028.

Jalil, A. A., Kurono, N., and Tokuda, M. (2001). Facile Synthesis of 2–Arylpropenoic Acid Esters by Cross–Coupling using electrogenerated Highly Reactive Zinc and a Palladium Catalyst. *Synlett.* 12: 1944–1946.

Jia, C–J. and Schüth, F. (2011). Colloidal Metal Nanoparticles as a Component of Designed Catalyst. *Physical Chemistry Chemical Physics.* 13: 2457–2487.

Jiao, S., Xu, L., Hu, K., Li, J., Gao, S., and Xu, D. (2009). Morphological Control of α–FeOOH Nanostructures by Electrodeposition. *The Journal of Physical Chemistry C.* 114(1): 269–273.

Jusoh, N. W. C., Jalil, A. A., Triwahyono, S., Setiabudi, H. D., Sapawe, N., Satar, M. A. H., Karim, A. H., Kamarudin, N. H. N., Jusoh, R., Jaafar, N. F., Salamun, N., and Efendi, J. (2013). Sequential Desilication–Isomorphous Substitution Route to Prepare Mesostructured Silica Nanoparticles Loaded with ZnO and Their Photocatalytic Activity. *Applied Catalysis A: General.* 468: 276–287.

Joshi, S., Yadav, S. and Desai, A. J., (2008). Application of Response–Surface Methodology to Evaluate the Optimum Medium Components for the

Enhanced Production of Lichenysin by Bacillus Licheniformis R2. *Biochemical Engineering Journal.* 41(2): 122–127

Kalota, D. J., and Silverman, D. C. (1994). Behavior of Aspartic Acid as a Corrosion Inhibitor for Steel. *Corrosion.* 50: 138–145.

Kamarudin, N. H. N., Jalil, A. A., Triwahyono, S., Artika, V., Salleh, N. F. M., Karim, A. H., Jaafar, N. F., Sazegar, M. R., Mukti, R. R., Hameed, B. H., and Johari, A. (2014). Variation of the Crystal Growth of Mesoporous Silica Nanoparticles and the Evaluation to Ibuprofen Loading and Release. *Journal of Colloid and Interface Science.* 421: 6–13.

Kang, N., Lee, D. S., and Yoon, J. (2002). Kinetic Modeling of Fenton Oxidation of Phenol and Monochlorophenols. *Chemosphere.* 47(9): 915–924.

Karge, H. G. (1998). Characterization by infrared spectroscopy, *Microporous and Mesoporous Material*. 22: 547–549.

Karim, A. H., Jalil, A. A., Triwahyono, S., Sidik, S. M., Kamarudin, N. H. N., Jusoh, R., Jusoh, N. W. C., and Hameed, B. H. (2012). Amino Modified Mesostructured Silica Nanoparticles for Efficient Adsorption of Methylene Blue. *Journal of Colloid and Interface Science.* 386: 307–314.

Kasiri, M. B., Aleboyeh, H., and Aleboyeh, A. (2008). Degradation of Acid Blue 74 using Fe–ZSM5 Zeolite as a Heterogeneous Photo–Fenton Catalyst. *Applied Catalysis B: Environmental.* 84(1–2): 9–15.

Kaur, R. and Mehta, S. K. (2014). Self Aggregating Metal Surfactant Complexes: Precursors for Nanostructures. *Coordination Chemistry Reviews.* 62: 37–54.

Kerker, M. (2012). *Colloid and Interface Science V3: Adsorption, Catalysis, Solid Surfaces, Wetting, Surface Tension, and Water*. Academic Press. London.

Khalil, L. B., Mourad, W. E., and Rophael, M. W. (1998). Photocatalytic Reduction of Environmental Pollutant Cr(VI) over Some Semiconductors Under UV/Visible Light Illumination. *Applied Catalysis B: Environmental.* 17(3): 267–273.

Khan, M. Z., Mondal, P. K., and Sabir, S. (2011). Bioremediation of 2–Chlorophenol Containing Wastewater by Aerobic Granules–Kinetics and Toxicity. *Journal of Hazardous Materials.* 190(1–3): 222–228.

Kim, J. R. and Kan, E. (2015). Heterogeneous Photo–Fenton Oxidation of Methylene Blue using CdS–Carbon Nanotube/TiO_2 Under Visible Light. *Journal of Industrial and Engineering Chemistry.* 21: 644–652.

Kingsley, J. J. and Patil, K. C. (1988). A Novel Combustion Process for the Synthesis of Fine Particle α–Alumina and Related Oxide Materials. *Material Letters.* 6*:* 427.

Kitis, M., Kaplan, S. S., Karakaya, E., Yigit, N. O., and Civelekoglu, G. (2007). Adsorption of Natural Organic Matter from Waters by Iron Coated Pumice. *Chemosphere.* 66(1): 130–138.

Krehula, S., Popović, S., and Musić, S. (2002). Synthesis of Acicular α–FeOOH Particles at a Very High pH. *Materials Letters.* 54(2): 108–113.

Kwon, B. G., Lee, D. S., Kang, N., and Yoon, J. (1999). Characteristics of *p*–Chlorophenol Oxidation by Fenton's Reagent. *Water Research.* 33(9): 2110–2118.

Lang, N., Delichere, P., and Tuel, A. (2002). Post−Synthesis Introduction of Transition Metals in Surfactant−Containing MCM−41. *Microporous and Mesoporous Materials.* 56: 203–217.

Laoufi N. A., Tassalit, D. and Bentahar, F. (2008). The Degradation of Phenol in Water Solution by. TiO_2 Photocatalysis in a Helical Reactor*, Global NEST Journal.*

Lee, I., Morales, R., Albiter, M. A., and Zaera, F. (2008). Synthesis of Heterogeneous Catalysts with Well Shaped Platinum Particles to Control Reaction Selectivity. *Proceedings of the National Academy of Sciences USA.* 105: 15241–15246.

Leibenguth, J. L. and Cohen, M. (1972). The Anodic Deposition of Oxide Films on Platinum from Ferrous Sulfate Solutions. *Journal of the Electrochemistry Society.* 119(8): 987–991

Li, N., N. (1968a). Separating Hydrocarbons with Liquid Membrane. *US Patent 3 (410)*, 794.

Li, J.–M., Meng, X.–G., Hu, C.–W., and Du, J. (2009b). Adsorption of Phenol, *p*–Chlorophenol and *p*–Nitrophenol onto Functional Chitosan. *Bioresource Technology.* 100(3): 1168–1173.

Li, B., Wu, K., Yuan, T., Han, C., Xu, J., and Pang, X. (2012c). Synthesis, Characterization and Catalytic Performance of High Iron Content Mesoporous Fe–MCM–41. *Microporous and Mesoporous Material.* 151: 277–281.

Liou, M.–J., and Lu, M.–C. (2008). Catalytic Degradation of Explosives with Goethite and Hydrogen Peroxide. *Journal of Hazardous Materials.* 151(2–3): 540–546.

Litter, M., I. (1999). Heterogeneous Photocatalysis: Transition Metal Ions in Photocatalytic Systems. *Applied Catalysis B: Environmental.* 23(2–3): 89–114.

Liu, G., Liao, S., Zhu, D., Liu, L., Cheng, D., and Zhou, H. (2011). Photodegradation of Aniline by Goethite Doped with Boron Under Ultraviolet and Visible Light Irradiation. *Materials Research Bulletin.* 46(8): 1290–1295.

Liu, T–X., Li, X–M., Li, F–B., Zhang, W., Chen, M–J., and Zhou, S–G. (2011). Reduction of Iron Oxides by Klebsiella pneumoniae L17: Kinetics and Surface Properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 379(1–3): 143–150

Lu, M–C. (2000a): Oxidation of Chlorophenols with Hydrogen Peroxide in the Presence of Goethite, *Chemosphere.* 40. 125–130.

Lu, M–C., Chen, J–N., and Huang, H–H. (2002b). Role of Goethite Dissolution in the Oxidation of 2–Chlorophenol with Hydrogen Peroxide, *Chemosphere.* 46: 131–136.

Maarof, H. I, Hameed, B. H., and Ahmad, A. L. (2004). Single and Binary Adsorption of Phenol and 3–Chlorophenol onto Granular Activated Carbon.

Maji, S. K., Sreejith, S., Mandal, A. K., Dutta, A. K., and Zhao, Y. (2014). Synthesis of Ag_2S Quantum Dots by a Single–Source Precursor: An Efficient Electrode Material for Rapid Detection of Phenol. *Analytical Methods.* 6: 2059–2065.

Mangrulkar, P. A., Kamble, S. P., Meshram, J., and Rayalu, S. S. (2008). Adsorption of Phenol and *o*–Chlorophenol by Mesoporous MCM–41. *Journal of Hazardous Materials.* 160: 414–421.

Martinez, L., Leinen, D., Martin, F., Gabas, M., Ramos–Barrado, J. R., and Quagliata, E. (2007). Electrochemical Growth of Diverse Iron Oxide (Fe_3O_4, alpha–FeOOH, and gamma–FeOOH) Thin Films by Electrodeposition Potential Tuning. *Journal of The Electrochemical Society.* 154(3): D126–D133.

Mastalir, Á., Király, Z., Szöllösi, G., Bartók, M. (2001). Stereoselective Hydrogenation of 1–Phenyl–1–Pentyne over Low–Loaded Pd–Montmorillonite Catalysts. *Applied Catalysis A: General.* 213: 133–140

Maugans, C. B. and Akgerman, A. (2003). Catalytic Wet Oxidation of Phenol in a Trickle Bed Reactor over a Pt/TiO_2 Catalyst. *Water Research.* 37(2): 319–328

McCullagh, C., Skillen, N., Adams, M., and Robertson, P. K. J. (2011). Photocatalytic Reactors for Environmental Remediation: A Review. *Journal of Chemical Technology & Biotechnology.* 86(8): 1002–1017.

Metz D. H., Meyer M., Dotson A., Beerendonk E., Dionysiou D. D. (2011).The Effect of UV/H_2O_2 Treatment on Disinfection By–Product Formation Potential Under Simulated Distribution System Conditions, *Water Resource.* 45: 3969–3980.

Mohapatra, P., Samantaray, S. K. and Parida, K. (2005). Photocatalytic Reduction of Hexavalent Chromium in Aqueous Solution over Sulphate Modified Titania. *Journal of Photochemistry and Photobiology A: Chemistry.* 170(2): 189–194.

Mozia, S., Bubacz, K., Janus, M., Morawski, A. W. (2012). Decomposition of 3–Chlorophenol on Nitrogen Modified TiO_2 Photocatalysts. *Journal of Hazardous Materials.* 203: 128–136.

Muller, F. and Caillard, L. (2011). *Chlorophenols*. Ullmann's Encyclopedia of Industrial Chemistry. John Wiley & Sons, Inc.

Munoz M., Pedro Z. M., Casas J. A., Rodriguez, J. J., Assessment of the Generation of Chlorinated Byproducts upon Fenton–Like Oxidation of Chlorophenols at Different Conditions. *Journal of Hazardous Material.*190: 993–1000.

Nie, Y., Hu, C., Qu, J., and Zhao, X. (2009). Photoassisted Degradation of Endocrine Disruptors over CuOx–FeOOH with H_2O_2 at Neutral pH. *Applied Catalysis B: Environmental.* 87(1–2): 30–36.

Nikoobakht, B., and El–Sayed, M. A. (2001). Evidence for Bilayer Assembly of Cationic Surfactants on the Surface of Gold Nanorods. *Langmuir.* 17(20): 6368–6374.

Nuñez, N. O., Tartaj, P., Morales, M. P., Gonzalez–Carreño, T., and Serna, C. J. (2006). Correlation Between Microstructural Features and Magnetic Behavior of Fe–Based Metallic Nanoneedles. *Acta Materialia.* 54(1): 219–224.

Ollis, D. F. (1985). Contaminant Degradation in Water, Heterogeneous Photocatalysis Degrades Halogenated Hydrocarbon Contaminants. *Environmental Science and Technology.* 19(6): 480–84.

Ortiz de la Plata, G. B., Alfano, O. M., and Cassano, A. E. (2008a). Optical Properties of Goethite Catalyst for Heterogeneous Photo–Fenton Reactions: Comparison with a Titanium Dioxide Catalyst. *Chemical Engineering Journal.* 137(2): 396–410.

Ortiz de la Plata, G. B., Alfano, O. M., and Cassano, A. E. (2010b). Decomposition of 2–Chlorophenol Employing Goethite as Fenton Catalyst. I. Proposal of a Feasible, Combined Reaction Scheme of Heterogeneous and Homogeneous Reactions. *Applied Catalysis B: Environmental.* 95(1–2): 1–13.

Ortiz de la Plata, G. B., Alfano, O. M., and Cassano, A. E. (2010c). Decomposition of 2–Chlorophenol Employing Goethite as Fenton Catalyst II: Reaction Kinetics of the Heterogeneous Fenton and photo–Fenton Mechanisms. *Applied Catalysis B: Environmental.* 95(1–2): 14–25.

Ortiz de la Plata, G. B., Alfano, O. M., and Cassano, A. E. (2010d). The Heterogeneous Photo–Fenton Reaction Using Goethite As Catalyst. *Water Science and Technology.* 258: 3019–3116.

Palma, R. D., Peeters, S., Van Bael, M. J., den Rul, H. V., Bonroy, K., Laureyn, W., Mullens, J., Borghs, G., and Maes, G. (2007). Silane Ligand Exchange to Make Hydrophobic Superparamagnetic Nanoparticles Water–Dispersible. *Chemistry of Materials.* 19: 1821–1831.

Park, J., Joo, J., Soon, G. K., Jang, Y., and Hyeon, T. (2007). Synthesis of Monodisperse Spherical Nanocrystals. *Angewandte Chemie–International Edition*. 46(25): 4630–4660.

Pavia, D. L., Lampman, G. M., and Kriz, G. S. (2001). *Introduction to spectroscopy: a guide for students of organic chemistry*. Fort Worth, Tex: Harcourt College Publishers.

Pera–Titus, M., García–Molina, V., Baños, M. A., Giménez, J., and Esplugas, S. (2004). Degradation of Chlorophenols by Means of Advanced Oxidation Processes: A General Review. *Applied Catalysis B: Environmental.* 47(4): 219–256.

Pereira, J. H. O. S., Vilar, V. J. P., Borges, M. T., González, O., Esplugas, S., and Boaventura, R. A. R. (2011). Photocatalytic Degradation of Oxytetracycline using TiO_2 Under Natural and Simulated Solar Radiation. *Solar Energy.* 85(11): 2732–2740.

Pérez–Moya, M., Graells, M., del Valle, L. J., Centelles, E., and Mansilla, H. D. (2007). Fenton and Photo–Fenton Degradation of 2–Chlorophenol: Multivariate Analysis and Toxicity Monitoring. *Catalysis Today.* 124(3–4): 163–171.

Peter, O. I., Chidi, O., and Iheanacho, M. A. (2012). The Preparation and Application of Environmentally Benign Titanium Pillared Clay Catalyst for Esterification of Ethanol and Acetic Acid. *American Chemical Science Journal.* 2: 45–59.

Peulon, S., Baraize, Q., and Chaussé, A. (2007). Iron Compounds Electrodeposited Onto a Transparent Semiconductor: Synthesis and Characterisation by UV–Vis Spectroscopy. *Electrochimica Acta.* 52: 7681–7688.

Poerschmann, J., Trommler, U., Górecki, T., and Kopinke, F.–D. (2009). Formation of Chlorinated Biphenyls, Diphenyl Ethers and Benzofurans as a Result of Fenton–Driven Oxidation of 2–Chlorophenol. *Chemosphere.* 75(6): 772–780.

Porta, F., Prati, L., Rossi, M., and Scar, G. (2002). Synthesis of Au(0) Nanoparticles from W/O Microemulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 211: 43–48.

Poulopoulos, S. G., Nikolaki, M., Karampetsos, D., and Philippopoulos, C. J. (2008). Photochemical Treatment of 2–Chlorophenol Aqueous Solutions Using Ultraviolet Radiation, Hydrogen Peroxide and Photo–Fenton Reaction. *Journal of Hazardous Material.* 153(1–2): 582–587.

Prasad, P. S. R., Shiva Prasad, K., Krishna Chaitanya, V., Babu, E. V. S. S. K., Sreedhar, B., and Ramana Murthy, S. (2006). In Situ FTIR Study on the Dehydration of Natural Goethite. *Journal of Asian Earth Sciences.* 27(4): 503–511.

Prélot, B., Villiéras, F., Pelletier, M., Gérard, G., Gaboriaud, F., and Ehrhardt, J.–J.(2003). Morphology and Surface Heterogeneities in Synthetic Goethites. *Journal of Colloid and Interface Science.* 261(2): 244–254

Proverbio, Z. E., Messina, P. V., Ruso, J., Prieto, G., Schulz, P. C., Sarmiento, F., and Argent, J. (2006). Aggregation in Dodecyltrimethylammonium Bromide–Didodecyldimethylammonium Bromide Aqueous Mixtures. *Chemical Society.* 94(4–6): 19–30.

Padhi, D.K., Parida, K. (2014). Facile Fabrication of α–FeOOH Nanorod/RGO Composite: A Robust Photocatalyst for Reduction of Cr(VI) Under Visible Light Irradiation. *Journal of Materials Chemistry A.* 2:10300–10312.

Puangpetch, T., Sreethawong, T., and Chavadej, S. (2010). Hydrogen Production Over Metal–Loaded Mesoporous–Assembled $SrTiO_3$ Nanocrystal Photocatalysts: Effects of Metal Type and Loading. *International Journal of Hydrogen Energy*. 35(13): 6531–6540.

Rădiţoiu, V., Diamandescu, L., Corobea, M. C., Rădiţoiu, A., Popescu–Pogrion, N., and Nicolae, C. A. (2012). A Facile Hydrothermal Route for the Synthesis of α–FeOOH with Controlled Morphology. *Journal of Crystal Growth*. 348(1): 40–46.

Rashid, J., Barakat, M. A., Salah, N., and Habib, S. S. (2015). ZnO-Nanoparticles Thin Films Synthesized by RF Sputtering for Photocatalytic Degradation of 2-Chlorophenol in Synthetic Wastewater. *Journal of Industrial and Engineering Chemistry*. 23: 134–139.

Rieger, P. (1998). *Electron Spin Resonance*, Brown University.

Ristić, M., Music, S., and Godec, M. (2006). Properties of γ–FeOOH, α–FeOOH and α–Fe_2O_3 Particles Precipitated by Hydrolysis of Fe^{3+} Ions in Perchlorate Containing Aqueous Solutions. *Journal of Alloys and Compounds*. 417(1–2): 292–299

Santana, M. C.; Ferrera, S. Z.; Padrón, E. T. M.; and Rodríguez, J. S. J. (2009). Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches. *Molecules*. 14: 298–320.

Sapawe, N., Jalil, A. A., Triwahyono, S., Adam, S. H., Jaafar, N. F., and Satar, M. A. H. (2012). Isomorphous Substitution of Zr in the Framework of Aluminosilicate HY by an Electrochemical Method: Evaluation by Methylene Blue Decolorization. *Applied Catalysis B: Environmental*. 125: 311–323.

Sato, H., Ohtsu, T., Komasawa, I. (2002). Preparation of Ultrafine Palladium Particles in Reverse Micelles and Application for Hydrogenation Catalysts. *Journal of chemical engineering of Japan*. 35(3): 255–262.

Schellin, M., and Popp, P. (2005). Membrane–Assisted Solvent Extraction of Seven Phenols Combined with Large Volume Injection–Gas Chromatography–Mass Spectrometric Detection. *Journal of Chromatography A*. 1072(1): 37–43.

Scherrer, P. (1981). Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*. 26: 98–100.

Sen, R. K. and Swaminathan, T. (2004). Response Surface Modeling and Optimization to Elucidate and Analyze the Effects of Inoculum Age and Size on Surfactin Production. *Biochemical Engineering Journal.* 21: 141–148.

Sepúlveda–Guzmán, S., Pérez–Camacho, O., Rodríguez–Fernández, O., and García–Zamora, M. (2005). In Situ Preparation of Magnetic Nanocomposites of Goethite in a Styrene–Maleimide Copolymer Template. *Journal of Magnetism and Magnetic Materials.* 294(2): 47–50.

Setiabudi, H. D., Jalil, A. A., Triwahyono, S., Kamarudin, N. H. N., and Mukti, R. R. (2012). IR Study of Iridium Bonded to Perturbed Silanol Groups of Pt−HZSM5 for *n*−pentane Isomerization. *Applied Catalysis A: General.* 417: 190–199.

Shao, M.–W., Ban, H.–Z., Tong, Y.–H., Hu, H., Niu, L.–L., and Gao, H.–Z. (2007). Synthesis of Single–Crystalline alpha–FeOOH Nanorods with Semi–Hard Magnetic Property. *Materials Letters.* 61(21): 4318–4320.

Sheydaei, M., Aber, S. and Khataee, A. (2014). Preparation of a Novel γ–FeOOH–GAC Nano Composite for Decolorization of Textile Wastewater by Photo Fenton–like Process in a Continuous Reactor. *Journal of Molecular Catalysis A: Chemical Volume.* 392: 229–234.

Shinde, S. S., Bhosale, C. H., and Rajpure, K. Y. (2011). Photocatalytic Oxidation of Salicylic Acid and 4–Chlorophenol in Aqueous Solutions Mediated by Modified $AlFe_2O_3$ Catalyst Under Sunlight. *Journal of Molecular Catalysis A: Chemical.* 347(1–2): 65–72.

Simonsen, M. E., Sønderby, C., Li, Z., and Søgaard, E. G. (2009). XPS and FT–IR Investigation of Silicate Polymers. *Journal of Materials Science.* 44: 2079–2088.

Singh, S. B., and Kulshrestha, G. (1997). Gas Chromatographic Analysis of Polychlorinated Dibenzo–P–Dioxins and Dibenzofurans. *Journal of Chromatography A.* 774(1–2): 97–109.

Sleiman, M., Vildozo, D., Ferronato, C., and Chovelon, J.–M. (2007). Photocatalytic Degradation of Azo Dye Metanil Yellow: Optimization and Kinetic Modeling using a Chemometric Approach. *Applied Catalysis B: Environmental.* 77(1–2): 1–11.

Song, L. and Zhang, S. (2009). Formation of α–Fe_2O_3/FeOOH Nanostructures with Various Morphologies by a Hydrothermal Route and Their Photocatalytic

Properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 348(1–3): 217–220.

Srivastava, R., Fujita, S., and Arai, M. (2009). Synthesis and Adsorption Properties of Smectite–Like Materials Prepared using Ionic Liquids. *Applied Clay Science.* 43(1): 1–8.

Sultan, S., and Tikoo, P. K. (1984). Hardness and Structure of Nickel Electrodeposited from a Nickel Acetate–N,N–Dimethylformamide–Water Bath. *Surface Technology.* 21(3): 239–244.

Sun, J–H., Sun, S–P., Wang, G–L., and Qiao, L–P. (2007). Degradation of Azo Dye Amido Black 10B in Aqueous Solution by Fenton Oxidation Process. *Dyes and Pigments.* 74(3): 647–652.

Taleb, M. F. A. (2014). Adsorption and Photocatalytic Degradation of 2-CP in Wastewater onto CS/$CoFe_2O_4$ Nanocomposite Synthesized using Gamma Radiation. *Carbohydrate Polymers.* 114: 65–72.

Taranto, J., Frochot, D., and Pichat, P. (2007). Modeling and Optimizing Irradiance on Planar, Folded, and Honeycomb Shapes to Maximize Photocatalytic Air Purification. *Catalysis Today.* 122(1–2): 66–77.

Tauc, J., Grigorovici, R., and Vancu, A. (1966). Optical Properties and Electronic Structure of Amorphous Germanium. *physica status solidi (b).* 15(2): 627–637.

Thomas, J. K. (1990). The Structure, Dynamic and Equilibrium Properties of Colloidal Systems. *Kluwer Dordrecht.* 759.

Thomas, O. and Burgess, C. (2007). *UV–Visible Spectrophotometry of Water and Wastewater:* Amsterdam; Boston: Elsevier.

Tokuda, M., Mimura, N., Karasawa, T., Fujita, H., and Suginome, H. (1993). The Effect of the Composition of Tri-Elemental Doping (K, Al, S) on the Photocatalytic Performance of Synthesized TiO_2 Nanoparticles in Oxidizing 2-Chlorophenol over Visible Light Illumination. *Applied Catalysis A: General.* 401(1–2): 233–238.

Tolosa, N. C., Lu, M-C, Mendoza, H. D., and Rollon, A. P. (2011). New Preparation of Reactive Zinc Metal by Electrolysis and Its Use for a Facile Isoprenylation of Aldehydes and Ketones. *Tetrahedron Letters.* 34(47): 7607–7610.

Tseng, R.–L., Wu, K.–T., Wu, F.–C., and Juang, R.–S. (2010). Kinetic Studies on the Adsorption of Phenol, 4–Chlorophenol, and 2,4–Dichlorophenol from Water

Using Activated Carbons. *Journal of Environmental Management.* 91(11): 2208–2214.

Ueno, K., Tokuda, H., and Watanabe, M. (2010). Ionicity in Ionic Liquids: Correlation with Ionic Structure and Physicochemical Properties. *Physical Chemistry Chemical Physics.* 12(8): 1649–1658.

Ursachi, I., Stancu, A., and Vasile, A. (2012). Magnetic α–Fe_2O_3/MCM–41 Nanocomposites: Preparation, Characterization, and Catalytic Activity for Methylene Blue Degradation. *Journal of Colloid and Interface Science.* 377(1): 184–190.

Vollmer, C., and Janiak, C. (2011). Naked Metal Nanoparticles from Metal Carbonyls in Ionic Liquids: Easy Synthesis and Stabilization. *Coordination Chemistry Reviews.* 255(17–18): 2039–2057

Vollmer, C., Redel, E., Abu–Shandi, K., Thomann, R., Manyar, H., and Hardacre, C.(2010). Microwave Irradiation for the Facile Synthesis Of Transition–Metal Nanoparticles (NPs) in Ionic Liquids (ILs) from Metal–Carbonyl Precursors and Ru–, Rh–, and Ir–NP/IL Dispersions as Biphasic Liquid–Liquid Hydrogenation Nanocatalysts for Cyclohexene. *Chemistry – A European Journal.* 16(12): 3849–3858.

Wang, Y., Deng, K., and Zhang, L. (2011a). Visible Light Photocatalysis of BiOI and Its Photocatalytic Activity Enhancement by In Situ Ionic Liquid Modification. *Journal of Physical Chemistry C.* 115(29): 14300–14308.

Wang, C, Liu, H., Sun, Z., Huang, J., Liao, Y. (2012b). Supported Nanosized α–FeOOH Improves Efficiency of Photoelectro–Fenton Process with Reaction–Controlled pH Adjustment for Sustainable Water Treatment. *International Journal of Photoenergy.* 2012: 689807.

Wei, M., Tian, D., Liu, S., Zheng, X., Duan, S., and Zhou, C. (2014). β–Cyclodextrin functionalized graphene material: A Novel Electrochemical Sensor for Simultaneous Determination of 2–Chlorophenol and 3–Chlorophenol. *Sensors and Actuators B: Chemical.* 195: 452–458.

Wu, H., Dou, X., Deng, D., Guan, Y., Zhang, L., and He, G. (2011). Decolourization of the Azo Dye Orange G In Aqueous Solution via a Heterogeneous Fenton–Like Reaction Catalysed by Goethite. *Environmental Technology.* 1–8.

Xia, M., Chen, C., Long, M., Chen, C., Cai, W., and Zhou, B. (2011). Magnetically Separable Mesoporous Silica Nanocomposite and Its Application In Fenton Catalysis. *Microporous and Mesoporous Materials.* 145(1–3): 217–223.

Xu, B., Gao, N–Y., Cheng, H., Xia, S–J., Rui, M., and Zhao, D–D. (2009). Oxidative Degradation of Dimethyl Phthalate (DMP) by UV/H_2O_2 Process. *Journal of Hazardous Materials.* 162(2–3): 954–959.

Xu, H–Y., Prasad, M., and Liu, Y. (2009). A Novel Catalyst in Mineral–Catalyzed Fenton–Like System for Dyeing Wastewater Discoloration. *Journal of Hazardous Materials.* 165(1–3): 1186–1192.

Xue, Z., Ma, J., Hao, W., Bai, X., Kang, Y., Liu, J., and Li, R. (2012). Synthesis and Characterization of Ordered Mesoporous Zeolite LTA with High Ion Exchange Ability. *Journal of Material Chemistry.* 22: 2532–2538.

Ye, F–X. And Shen, D–S. (2004). Acclimation of Anaerobic Sludge Degrading Chlorophenols and the Biodegradation Kinetics During Acclimation Period. *Chemosphere.* 54(10): 1573–1580.

Yoneyama, H., Haga, S., and Yamanaka, S. (1989). Photocatalytic Activities of Microcrystalline Titania Incorporated In Sheet Silicates of Clay. *The Journal of Physical Chemistry.* 93(12): 4833–4837.

Yoshikawa, N., Kimura, T., and Kawase, Y. (2003). Oxidative Degradation of Nonionic Surfactants with TiO_2 Photocatalyst in a Bubble Column Reactor. *The Canadian Journal of Chemical Engineering.* 81(3–4): 719–724.

Zanjanchi, M. A., Golmojdeh, H., and Arvand, M. (2009a). Enhanced Adsorptive and Photocatalytic Achievements in Removal of Methylene Blue by Incorporating Tungstophosphoric Acid–TiO_2 into MCM–4. *Journal of Hazardous Materials.* 169(1–3): 233–239.

Zanjanchi, M. A., Ebrahimian, A., and Arvand, M. (2010b). Sulphonated Cobalt Phthalocyanine–MCM–41: An Active Photocatalyst for Degradation of 2,4–Dichlorophenol. *Journal of Hazardous Materials.* 175(1–3): 992–1000.

Zarei, M., Khataee, A. R., Ordikhani–Seyedlar, R., and Fathinia, M. (2010). Photoelectro–Fenton Combined with Photocatalytic Process for Degradation of an Azo Dye using Supported TiO_2 Nanoparticles and Carbon Nanotube Cathode: Neural Network Modeling. *Electrochimica Acta.* 55(24): 7259–7265.

Zhang, H., Fu, H., and Zhang, D. (2009a). Degradation of C.I. Acid Orange 7 by Ultrasound Enhanced Heterogeneous Fenton–Like Process. *Journal of Hazardous Materials.* 172(2–3): 654–660.

Zhang, J., Li, X., Rosenholm, J. M., and Gu, H–C. (2011b). Synthesis and Characterization of Pore Size–Tunable Magnetic Mesoporous Silica Nanoparticles. *Journal of Colloid and Interface Science.* 361(1): 16–24.

Zhao, D., Sheng, G., Chen, C., Wang, X. (2012). Enhanced Photocatalytic Degradation of Methylene Blue Under Visible Irradiation on Graphene@TiO_2 Dyade. *Applied Catalysis B: Environmental.* 111: 303–308.

Zhong, L., Haghighat, F., Blondeau, P., and Kozinski, J. (2010). Modeling and Physical Interpretation of Photocatalytic Oxidation Efficiency in Indoor Air Applications. *Building and Environment.* 45(12): 2689–2697.

Zhou, T., Li, Y., Ji, J., Wong, F.–S., and Lu, X. (2008). Oxidation of 4–Chlorophenol in a Heterogeneous Zero Valent Iron/H_2O_2 Fenton–Like System: Kinetic, Pathway and Effect Factors. *Separation and Purification Technology.* 62(3): 551–558.