HETEROGENEOUS CATALYTIC OXIDATION OF METHYLENE BLUE BY AMINE-FUNCTIONALIZED TITANIUM-TEREPHTHALATE METAL ORGANIC FRAMEWORK, NH_2-MIL-125(Ti)

TEO SZEA ERR

THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE

FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
2017

DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

08 August 2017

TEO SZEA ERR
MS1421118T

CERTIFICATION

NAME : **TEO SZEA ERR**

MATRIC NO. : **MS1421118T**

TITLE : **HETEROGENEOUS CATALYTIC OXIDATION OF METHYLENE BLUE BY AMINE-FUNCTIONALIZED TITANIUM-TEREPHTHALATE METAL ORGANIC FRAMEWORK, NH_2-MIL-125(Ti)**

DEGREE : **MASTER OF SCIENCE (INDUSTRIAL CHEMISTRY)**

VIVA DATE : **17 JULY 2017**

CERTIFIED BY

SUPERVISOR SIGNATURE

DR. MOH PAK YAN

ACKNOWLEDGEMENTS

First and foremost, I would like to express my thanks and respect for my supervisor and mentor, Dr Moh Pak Yan. He was always looking out for me, showed me respect and treated me as equals.

I would also like to acknowledge University Malaysia Sabah for providing me with the facilities to conduct my research. To the lab staff, Mr. Abdul Rahim Bin Ahmad, Mr. Jerry Alexander, Mr. Recheidy and Mr. Taipin for their expertise and technical support.

I would like to express my gratitude to MyBrain15 and Exploratory Research Grant Scheme (ERGS) for financial support.

I would like to thank God Almighty, for without His countless graces and blessings, this thesis would not have been completed.

I would like to thank my family for their unrelenting support.

My mum, with her never-ending support of my pursue of knowledge.

My cousin and friend, Yuan, for always being there during my busiest of moments. If it were not for you, my work would have been completed much earlier.

My best friend, Shane, sticking with me through every highs and lows, ups and downs, good and bad.

And finally, my esteemed colleagues. Von Fei, my comrade in arms through every step, leap and milestone. Yang, my Santa Claus, giving me what I need when I needed it the most. And Wai Hung, for simply being there.

Teo Szea Err

21 August 2017

ABSTRACT

Iron oxide sludge formation, high pH dependency, and poor catalyst reusability have always been critical drawbacks of Fenton's reagent. In this work, titanium-terephthalate metal organic framework, NH_2-MIL-125(Ti), was proposed as heterogeneous Fenton-like catalyst for methylene blue degradation. NH_2-MIL-125(Ti) is a metal-organic compound possessing high surface area, photocatalytic properties and unique dual-porosity. MIL-125(Ti) and NH_2-MIL-125(Ti) was prepared through reflux method and activated using conventional solvent exchange method. Both samples were confirmed by XRD and FTIR. SEM images showed that NH_2-MIL-125(Ti) has spherical morphology with size ranging from 250 to 500 nm which is at least half of the size of MIL-125(Ti). NH_2-MIL-125(Ti) is stable under water with superior adsorption and photocatalytic activities upon visible and UV-A irradiation. Furthermore, the results revealed that NH_2-MIL-125(Ti) is an effective non-ferrous Fenton-like catalyst. Synergistic effect was observed between NH_2-MIL-125(Ti) and H_2O_2, with 84 % of removal efficiency in 40 ppm of methylene blue. Results showed that •OH and h^+ are the dominant species in Fenton-like oxidation of NH_2-MIL-125(Ti)/H_2O_2 catalytic system. Photoenhancement was proven to be effective where up to 92 % removal was obtained when exposed to UV-A light. NH_2-MIL-125(Ti) showed low pH dependency with stable degradation from pH 3 to 9. Negligible amount of titanium leaching was detected which indicates the high stability of heterogeneous NH_2-MIL-125(Ti) catalyst with reusability up to three runs. The heterogeneous titanium-terephthalate metal organic framework catalyst can overcome the disadvantages of traditional homogeneous Fenton catalyst. The results indicate that NH_2-MIL-125(Ti) can be a new material for Fenton-like oxidation processes.

ABSTRAK

PEMANGKIN PENGOKSIDAAN HETEROGEN BAGI METILENA BIRU MELALUI KERANGKA ORGANIK LOGAM BERFUNGSIAN-AMINA TITANIUM TEREFTALAT, NH_2-MIL-125(Ti)

Pembentukan enapcemar ferum oksida, kebergantungan kepada pH dan guna semula pemangkin yang lemah merupakan beberapa kesusahan reagen Fenton yang ketara. Dalam kajian ini, kompaun logam-organik titanium-tereftalat, NH_2-MIL-125(Ti), telah dicadangkan sebagai pemangkin heterogen "Fenton-like" untuk degradasi metilena biru. NH_2-MIL-125(Ti) adalah satu sebatian logam-organik yang mempunyai luas permukaan yang tinggi, sifat-sifat fotomangkin dan juga dua jenis liang yang unik. MIL-125(Ti) dan juga NH_2-MIL-125(Ti) telah disediakan melalui kaedah reflux dan diaktifkan dengan kaedah pertukaran pelarut konvensional. Kedua-dua sample tersebut telah pencirian melalui XRD dan FTIR. SEM imej telah menunjukkan bahawa NH_2-MIL-125(Ti) mempunyai morfologi sfera dengan saiz di antara 250 nm ke 500 nm, di mana ia adalah lebih kurang separuh dari saiz MIL-125(Ti). NH_2-MIL-125(Ti) juga menunjukkan kestabilan yang tinggi di dalam air sehingga 24 jam. Apabila cahaya visible dan UV-A digunakan, aktiviti penjerapan dan fotoaktif yang tinggi telah diperhatikan. Di samping itu, NH_2-MIL-125(Ti) telah dibuktikan sebagai suatu pemangkin "Fenton-like" yang bukan-ferum yang cekap. Kesan sinergi telah diperhatikan di antara NH_2-MIL-125(Ti) dan H_2O_2, dengan penyingkiran dan penguraian 40 ppm metilena biru sehingga 84 %. Keputusan telah menunjukkan bahawa , dalam sistem pemangkin NH_2-MIL-125(Ti)/ H_2O_2, $\bullet OH$ dan h^+ merupakan spesies yang dominan dalam oksidasi "Fenton-like". Peningkatan-foto telah dibuktikan berkesan di mana 92 % penyingkiran telah dicapai apabila cahaya UV-A telah digunakan. NH_2-MIL-125(Ti) telah mempunyai pergantungan kepada pH yang rendah di mana penguraian yang stabil boleh dicapai di antara pH 3 hingga 9. Larut lesap titanium yang amat rendah telah dikesan menunjukkan NH_2-MIL-125(Ti) mempunyai stabiliti yang tinggi serta penggunaan semula sehingga tiga kali. Oleh itu pemangkin sebatian logam-organik heterogen boleh mengatasi kelemahan-kelemahan pemangkin homogen "Fenton" yang tradisional. Keputusan yang didapati telah menunjukkan bahawa NH_2-MIL-125(Ti) merupakan satu bahan yang baru didalam proses oksidasi "Fenton-like".

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

$(CH_4)_4$-BDC	2,3,5,6-tetramethylterephthalate Linker
$(NH_2)_2$-BDC	2,5-diaminoterephthalate Linker
€	Porosity
•OH	Hydroxyl Radical
α	Adsorption Coefficient
α-Fe_2O_3	Hematite
α-FeOOH	Goethite
γ-Fe_2O_3	Maghemite
λ	Wavelength
λ_{max}	Maximum Absorbance Wavelength
2D	2-dimensional Coordination Network
3D	3-dimensional Coordination Network
Al^0	Zero-valent Aluminium
AOPs	Advance Oxidation Processes
BDC	Terephthalate Linker
$BiFeO_3$	Bismuth Ferrite
c	speed of light
$C_2O_4^{-\bullet}$	Oxalyl Radical Anions
C_i	Concentration at Time t
C_0	Initial Concentration
CB	Conduction Band
DFT	Density Functional Theory
DOE	Department of Environment
DR UV-Vis	Diffuse Reflectance UV-Visible Spectrophotometer
e^-	Electron

E_g	Energy Band Gap
Fe^0	Nanoscale Zero-Valent Iron Particles
Fe_3O_4	Magnetite
Fe(II)	Ferrous Ion
Fe(III)	Ferric Ion
$Fe(OH)^{2+}$	Aquated Fe(III) Species
$Fe\text{-}OOH^{2+}$	Fe(III)-peroxide
FTIR	Fourier Transform Infrared Spectroscope
g-C_3N_4	Graphite-like Carbon Nitride
h^+	Hole
H_2BDC	Terephathalic Acid
H_2O_2	Hydrogen Peroxide
$HO_2\bullet$	Hydroperoxyl Radical
HSO_5^-	Peroxymonosulfate
h	Planck Constant
hv	Photon Energy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
IRMOF	Isoreticular MOFs
IUPAC	International Union of Pure and Applied Chemistry
k	Reaction Rate Constant
LCCT	Ligand-to-Cluster Charge Transfer
LMCT	Ligand-to-Metal Charge Transfer
MB	Methylene Blue
MIL	Materials of Institut Lavoisier
MIL-125(Ti)	Titanium (IV) Dicarboxylate
MOF	Metal Organic Framework
MOFs	Metal Organic Frameworks

MY	Metanil Yellow
NH_2-BDC	2-aminoterephthalate Linker
NH_2-H_2BDC	2-aminoterephathalic Acid
NH_2-MIL-125(Ti)	Amine-functionalized Titanium (IV) Dicarboxylate
NPs	Nanoparticles
$O_2^{-\bullet}$	Superoxide Anion
PCPs	Porous Coordination Polymers
PEF	Photo-Electro-Fenton Process
POMs	Polyoxometalates
PSM	Post-Synthesis Modified
R-CO_2-Fe^{3+}	Fe(III)-polycarboxylate
R•	Carbon-centered Radical
R^2	Correlation Coefficient
rGO	Reduced Graphene Oxide
RhB	Rhodamine B
RR195	Reactive Red Dye 195
$S_2O_8^{2-}$	Persulfate
SBU-8	Cyclic Octamers
SBUs	Secondary Building Units
SEF	Sono-Electro-Fenton Process
SEM	Scanning Electron Microscope
SPEF	Solar-Photo-Electro-Fenton
SPF	Sono-Photo-Fenton Process
$t_{½}$	Half-life
UV-Vis	UV-Visible Spectrophotometer
XRD	X-Ray Diffraction
WHO	World Health Organization

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Fenton-catalyzed Processes

Over the past few decades, advanced oxidation processes (AOPs) have gained in popularity as one of the clean approaches in pollution control (Wang, 2008). AOPs often recognized as superior to other treatment methods because of its destructive nature that can lead to almost complete mineralization in wide range of pollutants (Ai *et al.*, 2014; Dutta *et al.*, 2001; Stasinakis, 2008). AOPs mechanism involves in-situ generation of highly reactive radicals which attack pollutants rapidly and non-selectively into less harmful substances that can be further biodegraded or, in some instance, decomposed into water and carbon dioxide (Contreras *et al.*, 2002).

Generally, AOPs utilizes a combination of powerful oxidants with catalysts and/or irradiation (Stasinakis, 2008). H_2O_2 is one of the common oxidants which frequently used in AOPs (Ai *et al.*, 2014). Hydrogen peroxide (H_2O_2) is highly active oxidant with only water as a sole by-product (Lei *et al.*, 2005). As an environmentally benign oxidant, it is also inexpensive and safer to use than organic peroxides or peracids (Saedi *et al.*, 2012). H_2O_2 by itself however, is insufficient. Activation of H_2O_2 by transition metals, semiconductor, UV light or ultra-sonication is required to promote H_2O_2 decomposition into hydroxyl radicals (•OH) (Ai *et al.*, 2014; Dionysiou *et al.*, 2000; Lei *et al.*, 2005).

Fenton's reagent has attracted increasing attention in the activation of H_2O_2 since its discovery a century ago (Neyens and Baeyens, 2003). It is refers to the redox reaction between ferrous [Fe(II)] ion and H_2O_2 which lead to the formation of powerful oxidants which includes •OH (Pignatello, Oliveros, and MacKay, 2006; Stasinakis, 2008). With in-situ generation of highly reactive radicals, Fenton-catalyzed reaction has been proven to be an effective treatment in many organic

pollutants including aromatic compounds, phenols, chlorine-containing compounds, formaldehyde and synthetic dyes (Dutta *et al.*, 2001).

1.2 Limitations of Fenton-catalyzed Processes

Fenton-catalyzed treatment is an established practice with high effectiveness and low energy consumption (Bauer and Fallmann, 1997; Contreras *et al.*, 2002; Wang, 2008). Also, Fenton's reagent is more economic when compared to other AOPs which required O_3 or UV (Wang, 2008). Nonetheless, this approach is not without its drawbacks. Some of the drawbacks encountered include iron oxide sludge formation, pH limitations, large amount of reagents needed, sophisticated system required for catalyst-product separation process, poor catalyst reusability and recoverability (Dutta *et al.*, 2001; Munter, 2001; Ramirez *et al.*, 2007; Saedi *et al.*, 2012; Strlič *et al.*, 2003). As a result, many researchers are looking for new catalyst able to activate H_2O_2 while overcoming the critical drawbacks such as modification of current Fenton processes or utilization of other non-iron based materials with Fenton properties.

1.3 Modified Fenton Processes

Throughout the years, different approaches have been made to develop a more efficient Fenton catalyst. Some approaches have proven to be effective in expanding the effective pH range of Fenton reactions and prevent the sludge formation. These modifications including immobilizes of iron on materials, forms iron complexes with chelating agents and utilizes heterogeneous Fenton catalyst such as solid iron compounds and inorganic iron minerals (Babuponnusami and Muthukumar, 2014; Pignatello, Oliveros, and MacKay, 2006). However, the modified Fenton catalyst largely reduced its accessible surface active sites hence causing a decline in its catalytic activity (Pignatello, Oliveros, and MacKay, 2006). Also, instability of heterogeneous Fenton catalyst can cause iron leaching during the process which makes the reaction mainly homogeneous and leads to poor catalyst reusability (Babuponnusami and Muthukumar, 2014; Hartmann, Kullmann, and Keller, 2010).

Irradiation is another common method to improve the effectiveness of Fenton reactions. By utilizing light irradiation and sonication, enhancement can be observed in most cases in Fenton reactions. Photo-Fenton process and sono-Fenton process both can increase the rates of regeneration of Fe(II) ions (Equation 2.2 and 2.3) and reactions between Fe(II) ions and H_2O_2 (Equation 2.1). To reduce the amount of reagent required for the reactions, Fenton process can also combine with electrochemical reactions to in-situ generate Fe ions or/and H_2O_2 oxidants which is commonly known as electro-Fenton process (Pignatello, Oliveros, and MacKay, 2006).

According the Department of Environment (DOE) Malaysia directive, the discharge limit of iron content in industrial effluent is only range from 1 to 5 ppm. Therefore, in homogeneous Fenton reactions where 50 to 80 ppm of ferrous ions is normally required, sophisticated system for catalyst-product separation process is needed (Department of Environment, 2010; Hartmann, Kullmann, and Keller, 2010). To overcome the problems, researchers have expanded their studies to non-ferrous Fenton catalysts. Many metal ions and its complex forms have been identified as potential candidates such as aluminum (Al), chromium (Cr), copper (Cu), manganese (Mn), ruthenium (Ru) and cerium (Ce). The mixtures of these metal compounds with H_2O_2 were named "Fenton-like" reagents (Bokare and Choi, 2014; Goldstein, Meyerstein, and Czapski, 1993).

1.4 MOF-based Fenton Catalysts

Many researchers have been studying the effects of metal–organic frameworks (MOFs) and H_2O_2 as a co-dependent system aiming to increase catalytic performance. MOFs are hybrid materials which connect metal–ion clusters with multitopic ligands forming a three-dimensional network with a molecular-defined porosity (Wang *et al.*, 2015). Many researchers consider MOFs to be superior to other porous coordination polymers (PCPs) in terms of internal surface area, micropore volume, tunable properties and functionalities (Ai *et al.*, 2014; Jeremias *et al.*, 2013; Li *et al.*, 2017). Previous studies have shown that Fenton-like behavior is found in a number of iron–based MOFs like Fe-bpydc, MIL-100(Fe), NH_2-MIL-88B(Fe), MIL-53(Fe) and MIL-101(Fe) (Ai *et al.*, 2014; Li *et al.*, 2017; Li *et al.*, 2016;