UNIVERSITI TEKNOLOGI MARA

PHOTOCATALYTIC DEGRADATION OF BENZENE-TOLUENE GASEOUS MIXTURE USING N, Fe-TiO₂ PHOTOCATALYST UNDER VISIBLE LIGHT: RESPONSE SURFACE METHODOLOGY (RSM) AND ARTIFICIAL NEURAL NETWORK (ANN) MODELLING

ARMAN BIN SIKIRMAN

Thesis submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy**

Faculty of Chemical Engineering

July 2017

ABSTRACT

Volatile organic compounds, VOCs such as benzene and toluene are hazardous to human health even when exposed at low concentration due to their carcinogenic impact. Recently, photocatalytic degradation has received great attention from researchers as one of the promising method to lower VOC concentration in the air. Common photocatalyst used for this process is titanium dioxide, TiO₂. However, TiO₂ can only be activated under UV light range due to the wide band gap energy. Limited resources are the challenge faced in implementing photocatalytic degradation. This is because only 3% of the sunlight wavelength range is of UV light while the other 45% is of visible light. The conventional method, also known as the 'one-factor-at-a-time' is a common approach taken in photocatalytic degradation. This approach is usually difficult and the interaction between process parameters is complicated to interpret as it requires numerous experiments. Besides, the complexity of photocatalytic degradation also lies in predicting the removal efficiency of the pollutants. Hence, this study is attempted to modify the TiO₂ photocatalyst and to activate it under visible light wavelength range. The modified photocatalyst was applied in the photocatalytic degradation of individual benzene or toluene, as well as their gaseous mixture under irradiation of visible light. In this research, TiO_2 was modified by co-doping with nitrogen and iron elements, prepared using sol-gel method in order to activate the photocatalyst in visible light wavelength. The modified photocatalyst was characterized using XRD, BET surface area, UV-Vis DRS, and XPS. The synthesized N, Fe-TiO₂ was applied in the photocatalytic degradation, and tested with individual benzene or toluene, and benzene-toluene gaseous mixture under irradiation of visible light. To reduce the number of experiments, as well as to optimize the degradation process, response surface methodology (RSM) was applied for each photocatalytic degradation cases. Artificial neural network (ANN) models were also developed to predict the complexity of the photocatalytic degradation process under visible light. It was found that N, Fe-TiO₂ photocatalyst is an anatase phase with crystal size of 19 nm and higher active surface sites. In addition, the energy band gap of N, Fe-TiO₂ photocatalyst is 2.33 eV, representing its ability to be activated under visible light wavelength region. RSM models have been developed to predict the removal efficiency of benzene, toluene and benzene-toluene gaseous mixture in order to optimize the responses. It was found that all independent variables that consisted of pollutant concentration, flow rate, and photocatalyst loading played a significant role in the degradation process which was evaluated based on the ANOVA, main effect, and variable interaction analysis. The optimum condition based on the RSM model of benzene-toluene gaseous mixture was 10 ppm (benzene concentration), 10 ppm (toluene concentration), 0.8 L/min (flow rate), and 25.54 (photocatalyst loading) which have successfully degraded 87.66% (desirable: 87.28%) and 90.83% (desirable: 89.95%) of benzene and toluene, respectively. Finally, the ANN models for individual benzene or toluene gas was 3-15-1, and benzene-toluene gaseous mixture was 4-15-2. The models were proven to have a good fit with high determinant coefficient, R² value for all cases, which is near to 1. The developed ANN models were good predictors for the application of the degradation process. The objectives of this research were successfully achieved, thereby marked the applicability of photocatalytic degradation of benzene-toluene gaseous mixture using N, Fe-TiO₂ photocatalyst under visible light irradiation.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praises to Allah S.W.T., The Most Greatest and The Most Merciful for His guidance and blessing as well as giving me strength and ability to complete this study. First and foremost, my special appreciation goes to my supervisors, firstly to Associate Prof. Dr. Jagannathan Krishnan, for his supervision and constant support. His invaluable help, encouragement, patience, numerous comments, criticisms and suggestion during the process in completing this study are gratefully praised. I am very indebted with his confidence and trust on my ability. Not forgotten, my appreciation to Associate Prof. Dr. Junaidah Jai for her tremendous support, belief and generosity in sharing knowledge and experience.

I would like to express my appreciation to the Dean and the Deputy Dean, Faculty of Chemical Engineering, for their support and help towards my postgraduate affairs. My acknowledgement is also extended to all the academic and non-academic staffs of Faculty of Chemical Engineering for their co-operations during my study in Universiti Teknologi MARA, Shah Alam.

I also wish to thank to Ministry of Science, Technology and Innovation (MOSTI) for funding the project through e-Science fund (Grant no.: 100-RMI/SF16/6/2 (19/2012). Without the fund, the study will not be successfully completed.

My special appreciation also goes to my best friend, Mohd Syukur Osman for his tremendous support and helping in finishing the study. His presence has always given me motivation and energy for me to complete the thesis.

I would also like to extend my sincere thanks to all my friends especially Hikmah, Nazri, Hidayu, Izni, Fazlida and all members of Postgraduate Room, Level 5 for their kindness and moral support during my study. Thanks for the cheerfulness and great memories shared.

Last but not least, my deepest gratitude goes to my beloved parents, Mr. Sikirman Jalal and and also to family members especially Ms. Sri Yanti Sikirman, my sister for their endless love, prayers and encouragement. Their love have always given me strength to face any problems or obstacles endured.

To those who indirectly contributed in this research, your kindness means a lot to me.

Thank you very much.

ARMAN SIKIRMAN, 2017

TABLE OF CONTENTS

CONFIRMATION BY PANEL OF EXAMINERS	Page i
AUTHOR'S DECLARATION	ii
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	Х
LIST OF FIGURES	xivv
LIST OF PLATES	xxii
LIST OF SYMBOLS	xxiii
LIST OF ABBREVIATIONS	xxivv

CHAPTER ONE: INTRODUCTION	1
1.1 Background Research	1
1.2 Problem Statement	4
1.3 Objectives	6
1.4 Scope And Limitations of Study	6
1.5 Significance and Novelty of the Study	8

СН	APTER TWO: LITERATURE REVIEW	9
2.1	Introduction	9
2.2	Volatile Organic Compounds (Vocs)	9
	2.2.1 Benzene Toxicity	10
	2.2.2 Toluene Toxicity	11

CHAPTER ONE INTRODUCTION

This chapter outlines the overview of the process of the photocatalytic degradation process and some important components in this process such as a photocatalyst, light sources, pollutants and photoreactor. In addition, problem statement, research objectives, the scope of the research study and the significance of the study are presented in this chapter. This research aims to utilize the available materials and technology in order to treat volatile organic compound at lower cost with high removal efficiency.

1.1 BACKGROUND RESEARCH

Volatile organic compounds (VOCs) that are present in air are emitted from various sources such as petrochemical industrial waste, landfills, transportation and household chemicals and products. All chemicals containing carbon element which exist in the atmosphere except carbon dioxide and monoxide are called VOCs (Augugliaro et al., 1999). Benzene and toluene gases are the examples of VOCs which could cause harmful effects towards human health even at low concentration. Exposure to VOCs may cause; (1) both acute and chronic health problems, thus, it is considered as carcinogenic, mutagenic and teratogenic, (2) global warming, (3) depletion of ozone layer, (4) formation of acid rain, and (5) sick building syndrome due to its existence in the indoor air (Lin et al., 2013; Peerakiatkhajohn et al., 2011; Zhong et al., 2007). Various treatments have been applied to remove VOCs from the air in the past few decades such as absorption, adsorption, condensation, bio-filtration, and incineration (Assadi et al., 2012; Sun et al., 2010; Wang et al., 1998). However, most of the conventional methods possessed disadvantages, such as producing secondary pollutants, high capital investment and operation cost for a low concentration VOCs, short and unpredictable life spans (Jeong et al., 2005).

Benzene and toluene are aromatic hydrocarbons which are classified as elements in the VOCs groups producing a very high impact on the human health. Inhaling those elements even at minute concentration could cause dizziness, eye, nose and throat