Faculty of Engineering

MODELING AND SIMULATION OF A PHOTOCATALYTIC REMOVAL OF AMMONIACAL NITROGEN USING CARBON CATALYST

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AMIRAH AFIQAH BINTI AMAN

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of the requirement for the degree of
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ABSTRACT

The rapid urbanization in Malaysia has led to the rise in solid waste generation which eventually increase the generation of leachate in landfill. Apparently, the leachate in landfill comprises of organic and inorganic substances in which its properties depend on the landfill age. In the recent years, advanced oxidation process (AOP) has gained substantial attention in wastewater treatment for pollutant removal. Photocatalysis which is categorized under AOPs is seen to be a promising technique in eliminating a wide range of contaminants. Substantial amount of study of photocatalysis in wastewater treatment has been conducted in laboratory based experimental but has very limited study on simulation-based experiment. This study aimed to simulate the behavior of the photocatalytic removal of ammoniacal nitrogen using carbon catalyst through process simulation. By that, a set of model equations including the hydrodynamic, radiative transfer equation and kinetics reaction were developed based on the literature. Process simulation was performed in ANSYS R1 2022 Workbench to simulate the hydrodynamic field, radiation field and species distribution in the designed annular photoreactor. The comparison study between the simulation results and existing experimental data shows that the model developed has a better agreement at higher flow rate of the fluid. Furthermore, the sensitivity analysis was also conducted to study the effect of initial concentration of ammoniacal nitrogen on its removal efficiency. It was observed that at higher concentration of ammoniacal nitrogen, the removal efficiency is decreased. To conclude, all the objectives were achieved in this project and some recommendations were provided in order to improve the modeling and simulation study of the photocatalytic reaction for the application in the future studies.

Keywords: Photocatalysis, Ammoniacal Nitrogen, Computational Fluid Dynamic

ABSTRAK

Pembandaran yang pesat di Malaysia telah membawa kepada peningkatan penjanaan sisa pepejal yang akhirnya meningkatkan penjanaan larut resapan di tapak pelupusan sampah. Dalam pada itu, bahan larut lesap di tapak pelupusan terdiri daripada bahan organik dan bukan organik di mana sifatnya bergantung pada umur tapak pelupusan tersebut. Dalam beberapa tahun kebelakangan ini, proses pengoksidaan lanjutan (AOP) telah mendapat perhatian ramai dalam rawatan air sisa untuk penyingkiran bahan pencemar. Fotokatalisis yang dikategorikan di bawah AOP dilihat sebagai teknik yang berkebolehan dalam menghapuskan pelbagai jenis bahan cemar. Sebilangan besar kajian fotokatalisis dalam rawatan air sisa telah dijalankan melalui eksperimen berasaskan makmal tetapi mempunyai kajian yang sangat terhad pada eksperimen berasaskan simulasi. Kajian ini bertujuan untuk menyimulasi tingkah laku penyingkiran fotokatalitik ammoniakal nitrogen menggunakan mangkin karbon melalui proses simulasi. Oleh itu, satu set model persamaan termasuk hidrodinamik, pemindahan sinaran dan tindak balas kinetic telah diungkapkan berdasarkan literatur. Simulasi telah dilakukan dalam ANSYS R1 2022 Workbench untuk menggambarkan medan hidrodinamik, medan sinaran dan taburan spesies kimia dalam fotoreaktor anulus yang direka bentuk. Kajian perbandingan di antara hasil simulasi dan data eksperimen sedia ada menunjukkan bahawa model yang diungkapkan mempunyai persetujuan yang lebih baik pada kadar aliran bendalir yang lebih tinggi. Tambahan pula, analisis sensitiviti juga dijalankan untuk mengaji kesan kepekatan awal ammoniacal nitrogen ke atas kecekapan penyingkirannya. Adalah diperhatikan bahawa pada kepekatan ammoniacal nitrogen yang lebih tinggi, kecekapan penyingkirannya berkurang. Sebagai kesimpulan, semua objektif telah dicapai dalam projek ini dan beberapa cadangan telah disediakan untuk menambah baik pemodelan dan kajian simulasi tindak balas fotomangkin untuk aplikasi dalam kajian akan datang.

Kata Kunci: Fotokatalisis, Ammoniakal Nitrogen, Pengiraan Bendalir Dinamik

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LIST OF ABBREVIATIONS

AOP	-	Advanced Oxidation Process
AN	-	Ammoniacal nitrogen
ANSYS	-	Analysis System
ASPEN	-	Advanced System for Process Engineering
BET	-	Brunauer Emmett teller
CFD	-	Computational Fluid Dynamic
COMSOL	-	Computer Solution
COD	-	Chemical Oxygen Demand
gPROMS	-	General Process Modeling System
LSSE	-	Linear Source Spherical Emission
LVRPA	-	Local Volumetric Rate of Photon Absorption
POME	-	Palm Oil Mill Effluent
RANS	-	Reynolds Averaged Navier-Stokes (RANS)
Re	-	Reynold number
RhB	-	Rhodamine B
RSM	-	Reynold Stress Equation Model

NOMENCLATURE

^{o}C	-	Degree Celcius
%	-	Percentage
eV	-	Electronvolt
J/kmol	-	Joule per kilo mol
K	-	kelvin
kg/m^3	-	Kilogram per cubic meter
m	-	meter
m/s	-	Meter per second
m/s^2	-	Meter per second square
m^2	-	Meter square
m^2/s	-	Meter square per second
m^2g^{-1}	-	Meter Square per Gram
mg/L	-	Milligram per liter
mL/min	-	Milliliter per minute
mm	-	Millimeter
mm^3	-	Cubic millimeter
nm	-	Nanometer
Pa.s	-	Pascal second
S	-	Second
W/m^2	-	Watt per meter square

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Solid waste management is one of the major environmental challenges in Malaysia due to the increasing trend in solid waste generation. According to Ghani(2021), the amount of solid waste production in Malaysia is estimated at 49,670 tonnes per day in 2020. Comparatively in 2010, the amount of solid waste produced in Malaysia was 28,102 tonnes per day which is half from those in 2020 (Aja & Al-Kayiem, 2014). One of the factors which contributes to the increased in solid waste generation in Malaysia is the population growth. Based on the Department of Statistics Malaysia (2011), the population size of Malaysia in 2010 is 28.3 million which increases to 32.6 million in 2020 and the population is projected to increase to 41.5 million in 2040. Adding to that, rapid urbanisation in Malaysia has also led to the rise in solid waste generation due to the economic development, the living standard of citizen has been improved which further increase the food consumption and trendy clothing habit (J. Liu et al., 2019). Another contributing factor for solid waste generation especially in Malaysia is the variety of races and ethnicity in Malaysia society as different races have their custom festivities in different time (Tarmudi et al., 2009). Therefore, the solid waste generated will significantly increase during the festive season such as Hari Raya, Chinese New Year and Deepavali which occurred at different period of time in a year.

Based on a study by Nasir et al.(2021), majority of the municipal solid waste generated is allocated for landfills and only about 17.5% of it is recycled while the remaining is composted (**Figure 1.1**). The flow of solid waste started from its generation, collection, treatment and eventually disposed to the environment (Ghani, 2021).

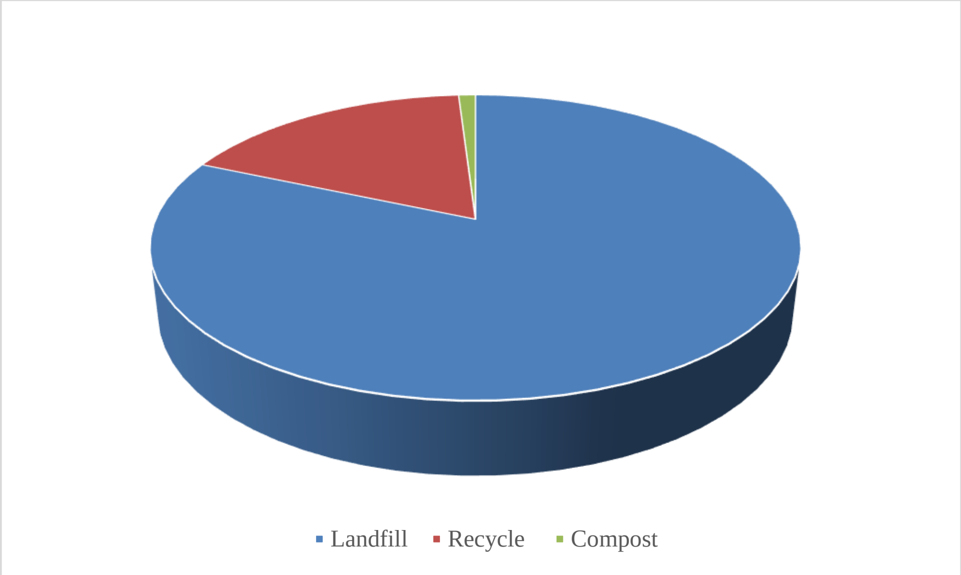

Figure 1.1: Distribution for Solid Waste Generation (Nasir et al., 2021)

Landfill is the primary solution of the municipal solid waste management in Malaysia due to its easy implementation and cost effectiveness. However, this technique will lead to significant environmental impact including the greenhouse gases emission and leachate propagation (Aja & Al-Kayiem, 2014). Leachate in landfill is generated due to the percolation of water into the site which contains high concentration of pollutants (Banch et al., 2019). It is also regarded as the by-product of sanitary landfill whereby its generation has reached 30 million tons per year and require proper treatment before discharging it to the waterbody (Wang et al., 2018). There is a possibility of leakage or unwanted discharge of leachate from sanitary landfill which may happen due to the failure of certain equipment that eventually cause ground water or surface water contamination (Dalun & Abdullah, 2021). The leachate composition can be characterized according to the landfill age which are young, intermediate and old. Basically, the landfill at young age is in acidogenic phase while the old landfill is in methanogenic phase (Kamaruddin et al., 2016). **Table 1.1** shows the characteristics of leachate in landfill with different ages. Based on the table, it can be observed that the chemical oxygen demand (COD) value decreases as the landfill age increases. Meanwhile the ammoniacal nitrogen value rises with the landfill age. Apparently, the abundancy of ammoniacal nitrogen in old landfill are derived from hydrolysis and fermentation of nitrogenous substances which cause lowered the concentration of dissolved oxygen (Petry et al., 2020).

Table 1.1: Characteristics of leachate in landfill with different ages (Tejera et al., 2019)

Landfill age (years)	**<1 (young)**	**1-5 (intermediate)**	**>5 (old)**
pH	<6.5	6.5-7.5	>7.5
COD (mg/L)	10000	4000-1000	<4000
NH_3-N (mg/L)	<400	400	>400
TOC/COD	<0.3	0.3-0.5	>0.5
BOD/COD	0.5-1	0.1-0.5	<0.1
Heavy metals (mg/L)	Medium	Low	Low

Ammoniacal nitrogen is a water quality measure for nitrogenous content which is usually associated in leachate. The high concentration of ammoniacal nitrogen in leachate negatively affect the pollutant removal due to the obstruction of nitrification process of microorganism (Haslina et al., 2021). Furthermore, the released of this pollutant into the waterbody will extensively affect the ecology system and also poisonous for human(Patil et al., 2021). It may pollute the waterway through eutrophication and accelerate the algal bloom which making it not suitable for the living of aquatic life (Petry et al., 2020). Generally, there are two types of landfills in Malaysia including non-sanitary landfill which also could be regarded as open dumping landfill and sanitary landfill (Ahmad et al., 2019).This sanitary landfill is obligated to comply with Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 whereby the discharge standard for leachate is specified in second schedule. Specifically, the permissible limit of ammoniacal nitrogen for leachate discharge is 5 mg/L. Therefore, the removal of ammoniacal nitrogen is important in order to minimize the associated environmental impact as well as to comply with the regulation subjected to leachate disposal.

1.2 Research Gap and Problem Statement

The released of leachate from landfill has the potential to contaminate the surface and groundwater. Prior to its discharge into the waterway, the wastewater must be treated with a proper treatment method. Generally, leachate can be treated through biological method and physiochemical method (Haslina et al., 2021). Biological treatment is commonly used to eliminate the organic compound which include the aerobic and anaerobic treatment (Raghab et al., 2013). Nevertheless, this method is not suitable for removal of ammoniacal nitrogen due to its less effectiveness (Detho et al., 2021). Hence, the physical-chemical treatment method is opted for the removal of ammoniacal nitrogen. Among the physical-chemical treatment method, photocatalysis has a great potential in wastewater treatment due to its high efficiency and ability in removing wide range of contaminants (Dong et al., 2015). Photocatalytic reaction is governed by the absorption of photons emitted from light sources which will be absorbed by photocatalyst (Rueda-Marquez et al., 2020). However, the study on photocatalytic removal of ammoniacal nitrogen is limited to laboratory-based study (Gong et al., 2015; Hashemi et al., 2021; He et al., 2018; Ye et al., 2019;Yu et al., 2021). Furthermore, laboratory-based research may be costly and time consuming due to the set up and involvement of many numbers of trials. As a result, it generates waste from the experiment which may be toxic. Therefore, this study is encouraged to proceed with simulation-based experiment in conducting the removal of ammoniacal nitrogen using carbon catalyst.

1.3 Research Questions, Aim and Objectives

The research questions for this study can be addressed as in the followings:

i. How to describe the model equations for species transport, radiation transport and rates of photocatalytic reaction for ammoniacal nitrogen removal?
ii. How to visualize the photocatalysis reaction of ammoniacal nitrogen over carbon catalyst?
iii. What is the effect of performing sensitivity analysis on the reaction parameter towards its removal efficiency?

Hence, the overall aim of this research project is to study on the removal of ammoniacal nitrogen using carbon catalyst through photocatalysis method and below are the research objectives:

i. To develop models which describe the species transport, radiation transfer and reaction rates for photocatalytic removal of ammoniacal nitrogen removal.
ii. To simulate the hydrodynamics, radiation field and species distribution in the reaction across the photocatalytic system by applying the model equations in computational fluid dynamic (CFD) software.
iii. To perform sensitivity analysis of the reaction parameter on the removal efficiency of ammoniacal nitrogen.

1.4 Scope of Study

This study will be focused on the ammoniacal nitrogen removal in wastewater by photocatalysis process using carbon catalyst. It will include the formulation of the flow problem based on the research objectives in which it comprises of reaction rates, radiation transfer and species transport. Thereafter, the model equations will be numerically solved using computational fluid dynamics in a CFD platform to observe the fluid flow and its interaction within the associated phenomenon. Afterwards, a sensitivity analysis will be conducted on the reaction parameters on the removal efficiency which is also be performed using the constructed model equations.

1.5 Research Significance

The research significance of this study can be listed as in the followings:

i. The simulation-based experiment conducted on photocatalysis will ensure to be economically viable due to the no experimental set up required.
ii. The in-depth understanding in behaviour of photocatalytic reaction for ammoniacal nitrogen removal in wastewater through simulation study will help in prototype development for future application.
iii. The modelling and simulation process of the photocatalysis reaction for the removal of ammoniacal nitrogen using carbon catalyst will provide external data sources to be applied in the future studies.

1.6 Summary

Leachate with high ammoniacal nitrogen content is one of the environmental concerns associated in solid waste management. This is due to its toxicity and poisonous characteristics which could possess hazard towards human and aquatic life. Hence, the removal of ammoniacal nitrogen is vital prior to discharging it into the environment. Nevertheless, there was limited research regarding the modelling and simulation of photocatalytic removal of ammoniacal nitrogen using carbon as its implementation bounded to laboratory-based study. As such this study is carried out to perform a computational fluid dynamic modelling and simulation on the hydrodynamics, radiation transfer and species distribution in the photocatalytic system. This research is hoped to provide an in depth understanding in the reaction behaviour for the future study application.

Chapter 2

LITERATURE REVIEW

2.1 Photocatalysis

Photocatalysis can be defined as a process that utilizes light from the irradiation sources to activate the semiconductor materials which can be regarded as photocatalyst by photon absorption and initiate a chemical reaction under ambient condition (Ameta et al., 2018;Escobedo & de Lasa, 2020). It is categorized under advanced oxidation process (AOPs) which is based on the generation of radical species that is readily combined with the substrate involved and this feature is seen to be promising in wastewater treatment for pollutant removal (Ghime & Ghosh, 2020). Apparently, photocatalysis method could potentially mitigate for the concern over environmental and energy issue (K. Qi et al., 2020). The rapid urbanization and industrialization have brought the need for the treatment system to be equipped with an advanced technology for the removal of diverse, complex and harmful pollutants in order to ensure the public safety and environment protection (Ghime & Ghosh, 2020). Accordingly, this technique has the ability to eliminate wide range of contaminants in a simultaneous occurrence (Kim & Jang, 2018). Another underlying benefits of photocatalysis is that it is cost effective and has simple operational method (Qi et al., 2020). Alternatively, solar has the potential to be utilized as the energy resources in this reaction which is eco-friendly due to the no air emission (Kim & Jang, 2018). Furthermore, there is no supplementary energy input needed for this process which is highly feasible (Gao & Meng, 2021).

Apart from water and wastewater treatment, the implementation of photocatalysis also can be found in indoor air purification. The air contaminants which cause indoor air pollution including pathogens, volatile organic compound, particulate matter and others could possibly lead to the respiratory problems towards the occupant (Escobedo & Lasa, 2020). Xu et al. (2018) employed vacuum ultraviolet photocatalytic oxidation (VUV-PCO) using nano-porous TiO_2 film for volatile organic compounds (VOCs) removal in the indoor air in which the system's schematic diagram is shown in **Figure 2.1**. This system comprises of air purifier unit (A), photocatalytic unit (B) and ozone removal unit (C). Subsequently, the system employed in this study was proved to be highly efficient and stable in continuous operation. Similarly in Kim and Jang(2018)'s study whereby they employed the same system to inactivate the airborne viruses present in the indoor air using Pd-TiO_2 photocatalyst which resulted to 90% of inactivation efficiency. Hence, photocatalysis could be implemented as part of air quality management for the abatement of wide range of indoor air pollutants.

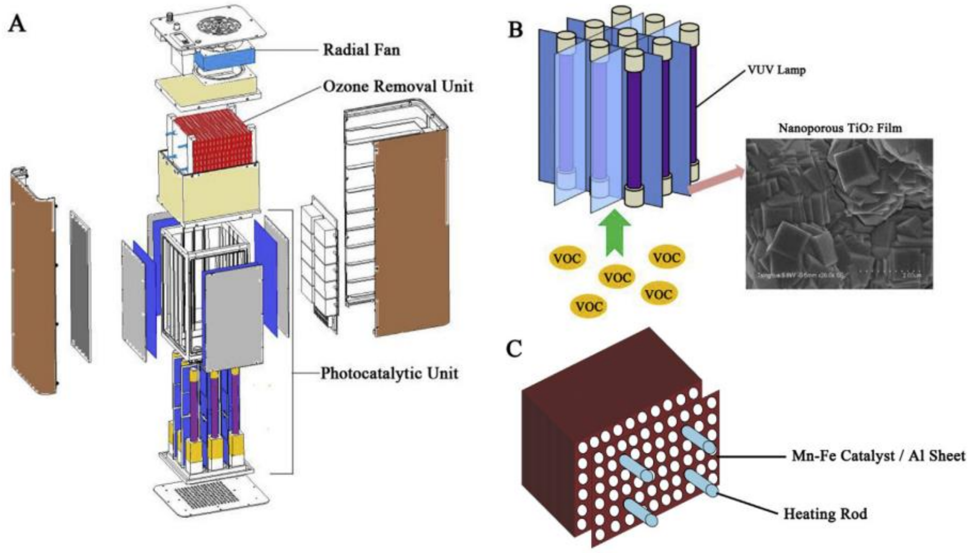

Figure 2.1: Schematic Diagram of the Vacuum Ultraviolet Photocatalytic Oxidation (VUV-PCO) (Xu et al., 2018)

Next, photocatalysis also can be implemented for hydrogen production in which it is considered as the feasible alternative for clean energy due to the utilization of renewable energy resource which is solar and no generation of adverse by products (Deng et al., 2019). Accordingly, hydrogen produced from this method is known as the energy carrier which are applied for heating and power generation. The mechanism involves the recombination of electron and hole pair for production of hydrogen (Rusinque et al., 2020). In the aforementioned study, the best performance achieved for hydrogen production through photocatalysis is 1.58% quantum yield by the reduction of Pd/TiO_2 under visible light (Rusinque et al., 2020). Meanwhile, Nishiyama et al.(2021) conducted an optimization study on hydrogen production through photocatalysis for safety and scaling up purposes using aluminum doped strontium titanate photocatalyst. **Figure 2.2** shows the 100 m^2 of the prototype of solar photoreactor used for water splitting and it visualizes the panel reactor unit(a), structure of panel reactor unit(b) and solar