REMOVAL OF PARACETAMOL AND TETRACYCLINE FROM SYNTHETIC WASTEWATER USING HETEROGENEOUS TiO_2/SOLAR PHOTOCATALYST

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2017

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by

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Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science

June 2017

ACKNOWLEDGMENTS

First and foremost, I would like to express my deepest gratitude to my supervisor, Dr. Puganeshwary Palaniandy, for her encouragement and continual support throughout this study. Her guidance and patience in conducting this thesis are much appreciated. I am also very grateful to my co-supervisor, Dr. Irvan Dahlan for his guidance and advice.

Secondly, I would like to acknowledge Ministry of Higher Education (MOHE) for funding this project under grant Fundamental Research Grant Scheme (FRGS, Grant number: 203/PAWAM/6071256) as well as the support of MyBrain15 and USM Fellowship for funding my study.

Besides, I would like to express my appreciation to all the technicians and friends (Mr. Razak, Mr. Mohad, Mrs. Samsiah, Mr. Zaini, Mr. Nizam, Mr. Dziauddin, Mr. Zabidi, Aiin, Kia and Aini) for their assistance and support throughout this study.

My warmest feeling is addressed to my beloved parents and siblings. Last but not least, I would like to dedicate my deepest appreciation to my best friend, Moon Wei Chek who always being supportive and helpful whenever I needed his help.

Thank you very much to all of you.

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LIST OF SYMBOLS

°C	Degree Celsius
C_o	Initial concentration
C_t	Final concentration
CdS	Cadmium sulfide
e^-_{cb}	Negative conduction band electron
g	Gram
H_2O_2	Hydrogen peroxide
H_2O	Water
H_2SO_4	Sulphuric acid
$HO^\bullet_2$	Hydrogen peroxide radical
H^+	Hydrogen ion
hr	Hour
hv	Photon energy
h^+_{vb}	Positive valence band hole
IrO_2	Iridium(IV) oxide
kg	Kilogram
k_{app}	Apparent rate constant
k	Reaction rate constant
K	Adsorption constant
L	Liter
MgO	Magnesium oxide
mg	Miligram
NaOH	Sodium hydroxide
NH_4^+	Ammonium

ng	Nanogram
nm	Nanometers
O_2	Oxygen
$^{\bullet}OH$	Hydroxyl radical
$O_2^{-\bullet}$	Superoxide radical anion
OH^-	Hydroxide ion
R^2	Coefficient of determination
r_o	Initial degradation rate
SnO_2	Tin (IV) oxide
TiO_2	Titanium dioxide
μg	Microgram
WO_3	Tungsten trioxide
Y_{exp}	Actual value
Y_{cal}	Predicted value
ZnO	Zinc oxide
λ	Wavelength

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
AOX	Adsorbable organic halides
APHA	American Public Health Association
BOD_5	Biochemical oxygen demand
BDD	Boron-doped diamond
CCD	Central composite design
CPCR	Compound parabolic collecting reactor
COD	Chemical oxygen demand
DO	Dissolved oxygen
eV	Electron-volt
EE2	Steroid estrogen ethinyl estradiol
EC_{50}	Half maximal effective concentration
GC-MS	Gas chromatography - mass spectrometry
HPLC	High performance liquid chromatography
HUSM	Hospital Universiti Sains Malaysia
IC_{50}	Half maximal inhibitory concentration
ITDD	Infectious and Tropical Diseases Department
LC_{50}	Half maximal lethal concentration
L-H	Langmuir Hinshelwood
mol	Mole
m/z	Mass-to-charge ratio
NEP	New emerging pollutant
NTU	Nephelometric turbidity units

ppm	Parts per million
PVDF	Polyvinylidene fluoride
PSA	Plataforma Solar de Almeria
PTR	Parabolic trough reactor
ROSs	Reactive oxygen species
RSM	Response surface methodology
SVAT	Single-variable-at-a-time
SPH	Sewerage pump house
STP	Sewage treatment plant
TFFBR	Thin film fixed bed reactor
TSS	Total suspended solid
UV	Ultraviolet
USMKK	Universiti Sains Malaysia, Kubang Kerian
WHO	World Health Organization
WWTP	Wastewater treatment plant

PENYINGKIRAN PARASETAMOL DAN TETRASIKLIN DARI AIR SISA SINTETIK MENGGUNAKAN FOTOPEMANGKIN HETEROGEN TiO_2/SURIA

ABSTRAK

Parasetamol dan tetrasiklin terkenal dari segi penggunaan serta pengeluaran tahunan yang amat tinggi di seluruh dunia. Kehadiran kedua-dua bahan farmaseutikal ini di dalam pelbagai jenis sumber air telah dilaporkan di negara yang berlainan. Dalam kajian ini, pencirian air kumbahan telah membuktikan bahawa loji rawatan kumbahan konvensional berkesan dalam degradasi parameter konvensional ke tahap yang selamat, namun ia tidak berupaya untuk menyingkirkan sisa farmaseutikal (seperti parasetamol dan tetrasiklin) yang muncul di dalam air sisa kumbahan. Selain itu, kajian ini menyelidik keberkesanan proses rawatan fotopemangkin heterogen titanium dioksida [TiO_2]/suria dalam penyingkiran parasetamol dan tetrasiklin dari air sisa sintetik secara berasingan. Kesan dari setiap pembolehubah yang dipilih (tempoh pendedahan terhadap cahaya matahari, pH, kepekatan TiO_2 dan kepekatan farmaseutikal) dalam proses rawatan fotopemangkin telah dikenalpasti dengan menggunakan kaedah pemboleh ubah tunggal pada satu masa (SVAT). Hasil kajian menunjukkan bahawa semua pembolehubah yang dipilih mempengaruhi kecekapan penyingkiran parasetamol dan tetrasiklin. Seterusnya, rekaan pusat rencam (CCD) berdasarkan kaedah permukaan sambutan (RSM) telah digunakan untuk mengoptimumkan pembolehubah bagi kepekatan TiO_2 dan farmaseutikal. Penyingkiran parasetamol sebanyak 82% diperolehi dalam keadaan optimum 1.0 g/L kepekatan TiO_2 dan 0.06 g/L kepekatan parasetamol, manakala sebanyak 75% tetrasiklin telah disingkirkan dalam keadaan optimum 2.64 g/L kepekatan TiO_2 dan

0.07 g/L kepekatan tetrasiklin. Akhir sekali, kinetik degradasi fotopemangkin parasetamol dan tetrasiklin didapati mematuhi kinetik model Langmuir-Hinshelwood. Pemalar kadar (k) dan pemalar jerapan (K) dalam proses degradasi fotopemangkin parasetamol dan tetrasiklin masing-masing adalah 0.00052 g/L.min, 131.58 L/g dan 0.0028 g/L.min, 71.43 L/g. Hasil kajian ini telah membuktikan kebolehpercayaan cahaya suria sebagai sumber UV semulajadi dalam proses degradasi fotopemangkin.

REMOVAL OF PARACETAMOL AND TETRACYCLINE FROM SYNTHETIC WASTEWATER USING HETEROGENEOUS TiO_2/SOLAR PHOTOCATALYST

ABSTRACT

Paracetamol and tetracycline are well known with tremendous annual worldwide production and high global consumption rate. Their occurrence in the various water compartments has been reported in different countries. In this study, sewage characterization showed that the conventional wastewater treatment plant was effective to degrade the conventional parameters to the acceptable conditions, but it was unable to remove the pharmaceutical compounds (paracetamol and tetracycline) appeared in the sewage treatment plant (STP). Next, this study investigated the performance of heterogeneous photocatalysis titanium dioxide [TiO_2]/solar treatment process in removing the paracetamol and tetracycline individually from the synthetic wastewater. In the batch study, the effects of the selected variables (sunlight exposure period, pH, TiO_2 concentration and initial concentration of pharmaceutical) on the photocatalytic degradation efficiencies of paracetamol and tetracycline were investigated by using the single-variable-at-a-time (SVAT) method. Results showed that all of these selected factors greatly affected the removal efficiencies of paracetamol and tetracycline. Next, central composite design (CCD) based on the response surface methodology (RSM) were used to optimize the TiO_2 and pharmaceutical concentrations. Under the optimum conditions of 1.0 g/L of TiO_2 concentration and 0.06 g/L of initial concentration of paracetamol, around 82% of paracetamol removal efficiency was attained, whereby, approximately 75% of tetracycline removal efficiency was achieved under the optimum conditions of 2.64

g/L of TiO_2 concentration and 0.07 g/L of initial concentration of tetracycline. Finally, the kinetic of the photocatalytic degradation of paracetamol and tetracycline fitted well with the Langmuir-Hinshelwood kinetic model. The reaction rate constant (k) and adsorption constant (K) for the photocatalytic degradation process of paracetamol and tetracycline were 0.00052 g/L.min, 131.58 L/g and 0.0028 g/L.min, 71.43 L/g, respectively. The results from these in situ experiments have proven the reliability of the solar in the photocatalysis treatment process.

CHAPTER ONE
INTRODUCTION

1.1 Background

Water is one of the important resources on earth where human beings and ecological systems rely on it for survival. If there is no water, there will be no life on earth. Nowadays, the demand of water increases with the rapid growth of population and vigorous industrial development. High-quality water sources are necessary particularly in maintaining healthy ecosystems and assurance for safe drinking water.

In recent years, water pollution from the emerging contaminants of pharmaceuticals has been recognized as one of the most important aspects of environmental research (Borges et al., 2015). Pharmaceutical is one of the most indispensable elements with undeniable benefits in modern life. They are extensively and increasingly used as an integral component to establish and maintain a healthy population of both humans and livestock. However, due to the widespread application of pharmaceuticals and their inadequate removal from wastewater, low levels of pharmaceuticals (ranging from the low ng/L to mg/L) have been ubiquitously detected (in both original and metabolized forms) in various aquatic compartments such as surface water, groundwater, effluents of sewage treatment plant (STP), sea water and even in the drinking water (Cardoso et al., 2014).

The occurrence of the pharmaceutical compounds in the natural water sources has been reported as early in the year 1980 (Richardson and Bowron, 1985). Pharmaceuticals are known as the "new emerging pollutants" (NEP) since they are recently detected in the environment in increasing amount and not covered by regulations until nowadays (Quadra et al., 2016; Sangion and Gramatica, 2016). The retained pharmaceuticals in different water sources may lead to some adverse effects

on the biological balance and human health such as aquatic toxicity, resistance development in pathogenic bacteria, acute and chronic damage, hormonal and endocrine disruption (K'oreje et al., 2016). This situation is getting even worse when these persistent pharmaceuticals are unable to be eliminated by using conventional wastewater treatment techniques due to the typical characteristics of the pharmaceuticals (Achilleos et al., 2010; Al-Odaini et al., 2013; Mozia and Morawski, 2012). For example, pharmaceuticals which are lipophilic (tending to combine with or dissolve in lipids or fats) can easily pass through the membranes during the filtration process and facilitate the absorption. They can also escape from the biological treatment process since they are designed to be biologically active and persistent to maintain their therapeutic activity until the specific physiological function on the human and animals has been performed (Aguilar et al., 2011). Thereby, they have the properties to bioaccumulate and cause negative effects to aquatic or terrestrial ecosystems, such as immobilization, mortality, inhibition of growth and reproduction (Quadra et al., 2016).

Other advanced treatment methods such as activated carbon adsorption, air stripping and reverse osmosis have also been investigated for the elimination of retained pharmaceuticals. Yet, studies have found out that these processes are less effective for the overall mineralization of pharmaceutical into the end product. This is due to the fact that those processes only transfer the pharmaceutical compounds from one phase to another or just collecting the pharmaceutical compounds without eliminating them (Elmolla and Chaudhuri, 2010b). The continuous input and persistence of pharmaceuticals in the aquatic ecosystem indicates an environmental challenge even their retained concentrations only range from the low ng/L to mg/L.