REMOVAL OF PARACETAMOL AND TETRACYCLINE FROM SYNTHETIC WASTEWATER USING HETEROGENEOUS TiO$_2$/SOLAR PHOTOCATALYST

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UNIVERSITI SAINS MALAYSIA
2017
REMOVAL OF PARACETAMOL AND TETRACYCLINE FROM SYNTHETIC WASTEWATER USING HETEROGENEOUS TiO₂/SOLAR PHOTOCATALYST

by

LEE CHEE MEI

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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<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Final concentration</td>
</tr>
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<td>CdS</td>
<td>Cadmium sulfide</td>
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<td>$e_{cb}$</td>
<td>Negative conduction band electron</td>
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<td>g</td>
<td>Gram</td>
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<td>$H_2O_2$</td>
<td>Hydrogen peroxide</td>
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<tr>
<td>hr</td>
<td>Hour</td>
</tr>
<tr>
<td>hv</td>
<td>Photon energy</td>
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<td>$h_{vb}^+$</td>
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LIST OF ABBREVIATIONS

ANOVA  Analysis of variance
AOPs   Advanced oxidation processes
AOX    Adsorbable organic halides
APHA   American Public Health Association
BOD₅   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
EC₅₀   Half maximal effective concentration
GC-MS  Gas chromatography - mass spectrometry
HPLC   High performance liquid chromatography
HUSM   Hospital Universiti Sains Malaysia
IC₅₀   Half maximal inhibitory concentration
ITDD   Infectious and Tropical Diseases Department
LC₅₀   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
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 [TiO₂]/suria dalam penyingkirkan parasetamol dan tetrasiklin dari air sisa sintetik secara berasingan. Kesan dari setiap pembolehubah yang dipilih (tempoh pendedahan terhadap cahaya matahari, pH, kepekatan TiO₂ 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 penyingkirkan parasetamol dan tetrasiklin. Seterusnya, rekaan pusat rencam (CCD) berdasarkan kaedah permukaan sambutan (RSM) telah digunakan untuk mengoptimumkan pembolehubah bagi kepekatan TiO₂ dan farmaseutikal. Penyingkiran parasetamol sebanyak 82% diperolehi dalam keadaan optimum 1.0 g/L kepekatan TiO₂ dan 0.06 g/L kepekatan parasetamol, manakala sebanyak 75% tetrasiklin telah disingkirkan dalam keadaan optimum 2.64 g/L kepekatan TiO₂ dan
0.07 g/L kepekatan tetrasi klin. Akhir sekali, kinetik degradasi fotopemangkin parasetamol dan tetrasi klin didapati mematuhi kinetik model Langmuir-Hinshelwood. Pemalar kadar (k) dan pemalar jerapan (K) dalam proses degradasi fotopemangkin parasetamol dan tetrasi klin 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 TiO₂ 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.