SYNTHESIS OF FIBROUS SILICA TITANIA CATALYSTS FOR PHOTODEGRADATION OF IBUPROFEN

ANEES AMEERA BT FAUZI

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Faculty of Engineering
Universiti Teknologi Malaysia

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Specially dedicated to my lovely mother, father and step-father,

Thank you for always standing next to me and give me support

&

To my beloved siblings, Izwan and friends,

Thank you for always helping me and making me smile throughout the master journey

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ABSTRACT

In recent decades, the occurrence of pharmaceutically active compounds in wastewater has emerged as one of the major environmental issues due to its toxicity and adverse impact towards human beings and aquatic life. Photocatalytic degradation is one of the promising techniques for degrading organic compounds. Among the photocatalysts, titania (TiO_2) is the most attractive since it is a non-hazardous compound and eco-friendly. However, it has a low photocatalytic performance. This present study was focused on the photodegradation of ibuprofen (IBP) using modified TiO_2 namely fibrous silica titania (FST) as photocatalyst. FST was prepared using the hydrothermal method under different molar ratios of toluene and water. The catalysts were characterised using X-ray diffraction, ultraviolet-visible spectrophotometer diffuse reflectance spectroscopy, nitrogen adsorption-desorption, field emission scanning electron microscope, transmission electron microscopy, Fourier transform infrared, and electron spin resonance. The increase in molar ratio of toluene and water has resulted in increase in particle size and surface area with reduction of crystalline anatase TiO_2. The highest distribution of active site (Si-O-Ti bond), terminal silanol and defeated site hydroxyl were observed in the catalyst FST(6:1), thereby showing the highest performance in degrading IBP. The photocatalytic performance of the catalysts towards degradation of 10 mg L^{-1} IBP under visible light at pH 7 and 0.375 g L^{-1} catalyst after 4 hours was in the following order: FST(6:1) (90%)> FST(5:1) (80%)> FST(7:1) (71%)> commercial TiO_2 (67%). Kinetic study shows that the degradation of IBP followed the pseudo first order Langmuir-Hinshelwood model. The response surface methodology study for FST(6:1) catalyst demonstrated good significance of model with a high coefficient of determination (R^2=0.937) while reusability study displayed that the catalyst was still stable after 5 cycles. The employment of catalyst on degradation of other pollutants revealed that the performance was above 20% degradation, suggesting the potential use of the catalysts for various wastewater treatments.

ABSTRAK

Pada dekad kebelakangan ini, kewujudan sebatian aktif farmaseutikal dalam air sisa merupakan salah satu isu alam sekitar yang utama akibat ketoksikannya dan kesan buruk terhadap manusia dan kehidupan akuatik. Degradasi fotopemangkinan adalah salah satu teknik yang meyakinkan untuk mengurai sebatian organik. Antara fotomangkin, titania (TiO_2) adalah yang paling menarik kerana ia adalah sebatian yang tidak berbahaya dan mesra alam. Walau bagaimanapun, TiO_2 mempunyai prestasi fotopemangkinan yang lebih rendah. Kajian ini lebih fokus kepada fotopenyahbuangan ibuprofen (IBP) menggunakan TiO_2 terubahsuai iaitu silika titania berserat (FST) sebagai fotomangkin. FST disediakan dengan mengguna kaedah hidroterma dengan nisbah molar toluena dan air yang berbeza. Sifat-sifat mangkin telah dicirikan dengan menggunakan pembelauan sinar-X, spektroskopi pantulan serakan spektrofotometer cahaya nampak-ultraungu, penjerapan-penyahjerapan nitrogen, mikroskop elektron imbasan pancaran medan, mikroskop elektron transmisi, spektroskopi inframerah transformasi Fourier, dan resonans putaran elektron. Peningkatan nisbah molar toluena dan air telah menyebabkan saiz zarah dan luas permukaan meningkat dengan pengurangan kristal anatase TiO_2. Mangkin FST(6:1) telah menunjukkan taburan yang tinggi terhadap tapak aktif (ikatan Si-O-Ti), silanol terminal dan kekurangan tapak hidroksil, justeru itu, ia telah menunjukkan prestasi tertinggi dalam degradasi IBP. Prestasi fotomangkin terhadap degradasi 10 mg L^{-1} IBP menggunakan cahaya boleh lihat pada pH 7 dan 0.375 g L^{-1} mangkin selepas 4 jam adalah dalam urutan berikut: FST(6:1) (90%)> FST(5:1) (80%)> FST(7:1) (71%)> komersil TiO_2 (67%). Kajian kinetik menunjukkan bahawa degradasi IBP mengikut model Langmuir-Hinshelwood tertib pertama pseudo. Kajian kaedah gerak balas permukaan untuk mangkin FST(6:1) menunjukkan model penemuan baik dengan pekali penentu yang tinggi (R^2 = 0.937) dan kajian kebolehan guna semula telah menunjukkan bahawa mangkin masih stabil selepas 5 kitaran. Penggunaan mangkin terhadap degradasi bahan pencemar yang lain membuktikan bahawa prestasi degradasi melebihi 20%, mencadangkan potensi penggunaan mangkin untuk pelbagai rawatan air sisa.

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LIST OF ABBREVIATIONS

ALD	-	Atomic Layer Deposited
ANOVA	-	Analysis of Variance
AOPs	-	Advanced Oxidation Processes
ASP	-	Aspirin
BET	-	Brunauer–Emmett–Teller
BPA	-	Bisphenol A
CB	-	Conduction Band
CCD	-	Central Composite Design
CdS	-	Cadmium Sulfide
CR	-	Congo Red
CTAB	-	Cetyltrimethylammonium Bromide
DFC	-	Diclofenac
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscope
FFT	-	Fast Fourier Transform
FS	-	Fibrous Silica
FST	-	Fibrous Silica Titania
FTIR	-	Fourier Transform Infrared
GCMS	-	Gas Chromatography Mass Spectrometry
IBP	-	Ibuprofen
IUPAC	-	International Union of Pure and Applied Chemistry
KBr	-	Potassium Bromide
KCC-1	-	Fibrous Silica
LH	-	Langmuir Hinshelwood
LMCT	-	Ligand-to-Metal Charge Transfer

MB	-	Methylene Blue
MET	-	Methanol
MS	-	Mesoporous Silica
MSN	-	Mesoporous Silica Nanoparticles
MW	-	Microwave
NSAIDs	-	Non-Steroidal Anti-Inflammatorys
OV	-	Oxygen Vacancy
PAR	-	Paracetamol
PhACs	-	Phamarceutically Active Compounds
PP	-	Potassium Perchlorate
RSM	-	Response Surface Methodology
SBA-15	-	Silica Based Type
SHC	-	Sodium Hydrogen Carbonate
SiO_2	-	Silica Dioxide
SOF	-	Silica Optical Fiber
SS	-	Sum of Squares
SSR	-	Sum of Squares Regression
SST	-	Sum of Squares Total
TEM	-	Transmission Emission Spectroscopy
TEOS	-	Tetraethyl Orthosilicate
TiO_2	-	Titanium dioxide
UV-vis/DRS	-	UV-visible spectrophotometer/ Diffuse Reflectance Spectroscopy
VL	-	Visible light
VB	-	Valence Band
WWTP	-	Waste Water Treatment Plant
XRD	-	X-ray diffraction

LIST OF SYMBOLS

Ɵ	-	Theta
λ	-	Wavelength
^oC	-	Degree Celsius
•OH	-	Hydroxyl Radical
C	-	Concentration
e^-	-	Electron Negative
e^-_{CB}	-	Electron Negative in the Conduction Band
eV	-	Electron Volt
G	-	Gram
g	-	Magnetic Field Strength
$g\ L^{-1}$	-	Gram per litre
h^+_{VB}	-	Hole Positive in the Valence Band
K	-	Kelvin
k_{app}	-	First-Order Rate Constant
k_r	-	Reaction Rate Constant
K_{LH}	-	Adsorption Coefficient of The Reactant
L/bed/day	-	Litre/bed/day
$mg\ L^{-1}$	-	Milligram Per litre
mM	-	Millimolar
mL	-	Millilitre
M	-	Molar
MPN/mL	-	Most Probable Number/millilitre
nm	-	Nanometre
µm	-	Micrometre
$\mu g\ L^{-1}$	-	Microgram per liter

P/P_O	-	Relative Pressure
R	-	Reaction Rate
rpm	-	Rotation per Minute
S	-	Second
T	-	Temperature
W	-	Watt

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Pharmaceuticals belong to a chemical group which are extensively used nowadays and have been a concern to the environment (Nina et al., 2017). These compounds, which comprised a huge group of human and veterinary medicinal compounds have long been used around the world. The extended and worldwide usage of hazardous pharmaceuticals has potentially increase the pollution of surface, ground and drinking water. Basically, pharmaceuticals contaminate soil, surface waters, ultimately ground and drinking water after excretion process from humans or animals through urine or faeces, as well as through the sewage system and from the influent of wastewater treatment plants (Klavarioti et al., 2009).

Pharmaceutically active compounds (PhACs) produced in surface and ground waters have been classified by many countries as an environmental problem. The pharmaceutical industry uses the designation active pharmaceutical ingredients to describe products that are pharmacologically active, resistant to degradation, highly persistent in aqueous medium and capable of producing adverse effect in water organisms as well as able to negatively impact the human health (Rivera-Utrilla et al., 2013). Ibuprofen (IBP) is one of the antipyretic pharmaceuticals that is frequently detected in the municipal wastewater systems which is biological active and has adverse impacts on the environment even in small concentrations (Choina et al., 2013). To overcome these problems, several treatment processes such as coagulation, chemical precipitation, chlorination and ozonation have been developed.

However, these methods have several drawbacks including their inability to destroy the pollutants that tend to be transferred from one phase to another (Nina et al., 2017). Besides, Tran et al. (2017) reported that the use of conventional processes could not completely remove recalcitrant pollutants.

Advanced oxidation processes (AOPs) are a promising alternative and have been extensively studied among researchers, which include homogenous and heterogeneous photocatalytic oxidation (Nina et al., 2017). AOPs are processes that generate hydroxyl radicals (•OH), which are highly oxidised agents that are very useful in reacting with a wide variety of compounds (Silva et al., 2015). Among AOPs, heterogenous photocatalysis using semiconductors like TiO_2 as catalyst is a well-developed method that provides promising results the removal and total mineralisation of various pharmaceuticals and other micro pollutants from aquatic phase (Antonopoulou et al., 2016). In addition, these methods are excellent in terms of performance and environmental friendly due to its ambient operating conditions, and the fact that the catalyst is cost effective, non-toxic and photochemically stable (Surenjan et al., 2017).

The application of TiO_2 catalyst is fascinating for an effective photocatalytic degradation of drugs and other harmful organic pollutants under UV-light irradiation. Countless treatments have been done using TiO_2 catalysts since it is less hazardous, eco-friendly with no additional chemicals required, as well as the possibility of completing abatement of drugs (Choina et al., 2012). Notwithstanding, TiO_2 suffers from several drawbacks such as wide band gap, low surface area, poor accessibility of active site, high electron-hole recombination, weak light harvesting and difficulty in isolation and reusability (Singh et al., 2016).

The synthesis of TiO_2 with mesoporous structure has been reported in improving the photocatalytic performance towards the desired reaction, owing to its high surface area and total pore volume for enhanced adsorption capacity (Li et al., 2015; Jaafar et al., 2015a). However, Dong et al. (2016) claimed that inorganic material with high surface area and pore volume usually have low strength and unsuitable for practical use. To overcome those shortcomings, researchers have sought to improve the performance of mesoporous TiO_2 by coupling it with other materials and designing different morphologies. Recently, mesoporous TiO_2/SiO_2 spheres have attracted a great deal of attention due to their benefits, which are large surface area, high surface acidity, abundant surface hydroxyl, ability to improve light harvesting and could prevent electron-hole recombination that is favourable for increasing photodegradation performance (Kapridaki et al., 2014; Wang et al., 2014). Besides, mesoporous silica (MS) has become the focus of study due to its high surface area, highly uniform pore distribution, tuneable pore size and unique hosting (Karim et al., 2012). However, morphological properties of the catalyst also play a role and require modifications to improve its effectiveness.

With regards to all the factors, herein, this study has reported the synthesis and characterisation of fibrous silica titania (FST) with different molar ratios of toluene and water. The performance of FST towards photodegradation of IBP and other pollutants were evaluated using the best reaction condition.

1.2 Problem Statement and Hypothesis

A well-known semiconductor, which is TiO_2 nanoparticle has several drawbacks as mentioned in previous section. Many researchers have focused on modifying TiO_2 by incorporating it with porous supports including silica, which is effective to increase surface area and can prevent the aggregation of titania particles (Dong et al., 2015). In previous studies, the nanostructured TiO_2 or TiO_2 supported on high surface area supports has been synthesised to enhance surface area and particle size (Singh et al., 2016). Besides, it has been reported that the incorporation of SiO_2 with TiO_2 can be effective in preventing charge recombination in dye-sensitised solar cell (Dong et al., 2015). The synthesis of Ti-containing materials with enhanced accessibility to the reactive sites with large pores including mesoporous silica (MS) has been also developed (Ke et al., 2007). Even though, the modification had improved the properties of TiO_2 supported on porous material, the interaction between pollutant and catalyst seemed to be decreased. Thus, the synthesised TiO_2 incorporated with porous SiO_2 has poor accessible to active sites due to the high possibility of pores clogging which partially collapse after thermal treatment.

Recently, fibrous structure has attracted much attention in improving the performance due to its unique structure, which has high surface area and accessibility of active sites (Polshettiwar et al., 2010). Moreover, this structure has open pore channels and adjustable pore sizes that can be altered by synthesis parameters such as amount of surfactant, stirring and heating time. In the previous study, fibrous structure doped with TiO_2 which has been synthesised by Atomic layer deposited (ALD) method was used in the degradation of methylene blue. However, this catalyst has several limitations, which are its poor accessibility of light due to pore clogging and limited Ti loading (Singh et al., 2016). Thus, this study aimed at reporting the synthesis of fibrous silica titania (FST) by hydrothermal method with tuneable molar ratio of toluene and water and their applications in photodegradation of ibuprofen and other pollutants. It is expected that FST catalyst would have high surface area, more accessible active sites, better light harvesting and reusability that can enhance the photocatalytic performance.

1.3 Objective of Study

The objectives of this study are:

I. To synthesis the fibrous silica titania (FST) photocatalysts using hydrothermal method and characterise the physicochemical properties.

II. To evaluate the photoactivity of the catalysts on degradation of ibuprofen (IBP) and various pollutants.

III. To examine the stability of the FST, kinetics and proposed mechanism of the photodegradation of IBP.

IV. To optimise the photodegradation of IBP using Response Surface Methodology (RSM).

1.4 Scope of Study

The scopes of this study are:

I. Synthesis and characterisation of physicochemical properties on fibrous silica titania (FST).
The catalysts were prepared using hydrothermal method by varying toluene and water molar ratio (7:1, 6:1 and 5:1). The catalysts were characterised by X-ray diffraction (XRD), UV-visible spectrophotometer/Diffuse Reflectance Spectroscopy (UV-vis/DRS), N_2 adsorption-desorption, Field Emission Spectroscopy (FESEM), Transmission Emission Spectroscopy (TEM), Fourier Transform Infrared (FTIR) and Electron Spinning Resonance (ESR).

II. Evaluation of photodegradation.
Photocatalytic activity of the catalysts on degradation of IBP was conducted under different molar ratio of toluene and water, light condition and various parameters such as pH (3-9), catalyst dosage (0-0.625 g L^{-1}) and initial concentrations (10-100 mg L^{-1}). FST was also tested for different types of pollutant including aspirin (ASP), paracetamol (PAR) and BPA (bisphenol A) with 10 mg L^{-1} of initial concentration.

III. Study on the stability of the FST, kinetics and proposed mechanism of the photodegradation of IBP.
The stability test was conducted by repeating the reaction for five times. The kinetics expression modelling was described based on Langmuir-Hinshelwood models and the proposed mechanism of the photodegradation of IBP was confirmed using gas chromatography-mass spectrometry (GCMS).

IV. Optimisation using response surface methodology (RSM).
Response surface methodology (RSM) using central composite design (CCD) was employed to optimise the conditions of photodegradation using the high potential catalyst under three parameters included in this part, which were pH (5-9), catalyst dosage (0.25-0.5 g L^{-1}) and initial concentration (5-15 mg L^{-1}) of IBP.

1.5 Significance of Study

In the recent approach, the modification of TiO_2 photocatalyst was seen to improve its own drawbacks mentioned in the previous section and photocatalytic performance. This study was conducted to synthesis FST by varying toluene and water molar ratio to improve the efficiency in photodegradation. The preparation method plays a crucial part in the modification of catalyst to obtain the desired morphology either in a simple or complex ways. Currently, TiO_2 supported with dendrimeric morphology has not been widely practiced in photodegradation of pharmaceutical compound. FST is one of the new modifications in photocatalysis to obtain superior properties such as increased surface area, high accessibility of active site and better light harvesting. These properties can be obtained by FST due to its unique structure, which is spherical with cockscomb-like structure and having an alternate silica and titania framework. Thus, the FST is expected to have higher photocatalytic performance compared to commercial TiO_2.

1.6 Study Outline

This study is divided into five chapters. Chapter 1 addresses the general introduction on the pharmaceuticals wastewater in various areas of industries, types of PhACs that are commonly used and the threat of the PhACs effluent towards the environmental and human health. Several wastewater treatments to remove PhACs are also mentioned. Besides, the potential of FST with different molar ratio of toluene and water as a photocatalysts for degradation of IBP are highlighted. The problem statement and objectives of the present study were stated. The scopes of study are explained covering the research work to achieve the objectives. The significance of study is also clearly elucidated.

Chapter 2 or literature review covers the details on previous studies to improve understanding in synthesis, characterisation and photoactivity efficiency of modified catalyst supported with dendrimeric morphology.

Meanwhile, chapter 3 or methodology describes the materials and chemicals used, catalyst preparation, characterisation and photocatalytic reaction including the experimental setup and analysis calculation.

Chapter 4 focuses on results and discussion which involved the details about characterisation and photocatalytic activity of IBP as well as others targeted pollutants in simulated wastewater. Finally, the conclusion about this study is simplified in the chapter 5.

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