SYNTHESIS OF FLOWER-LIKE TITANIA NANOPARTICLES FOR PHOTOCATALYTIC DECOLOURIZATION OF METHYLENE BLUE

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Specially dedicated to my lovely Father and Mother,
Mustapha bin Abdullah and Salina binti Aziz,
Thank you Dad for always be my hero and Mom will forever remain my life's biggest inspiration,
&
To my beloved siblings and fiancé,
Thank you for always making me smile and supporting me through all those tough times.

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ABSTRACT

In recent times, industrial dye effluent has produced adverse effects towards human health and the environment, majorly due to its high level of toxicity. Among the various techniques for treatment of the dye effluents, photocatalytic decolourization proves to be highly promising owing to its safety, low energy consumption and high efficiency. Titanium dioxide (TiO_2) is the most well-known photocatalyst. However, due to its large band-gap and agglomeration tendency, a lot of researches such as modification of its morphology have been reported in attempt to resolve this problem. In this study, the flower-like titanium dioxide nanoparticle (FTN) photocatalyst was prepared under different concentrations (2M-4M) of hydrochloric acid (HCl) via hydrothermal method and subsequently tested for decolourization of methylene blue (MB). The properties of the catalysts were characterized using x-ray diffraction, field emission scanning electron microscope, Fourier transform infrared, electron spin resonance, ultraviolet-visible spectrophotometer diffuse reflectance spectroscopy and nitrogen adsorption-desorption. The increase in HCl concentration was observed to result in more enhancement of the pure crystalline rutile TiO_2 with the more open structure of its individual nanospindle. The highest distribution of hydroxyl group, oxygen vacancy and Ti^{3+} surface defect was observed for the catalyst synthesized using 3M HCl concentration, thereby increasing its potential use in visible light irradiation. The photocatalytic activity of the catalysts towards decolourization of 10 mg L^{-1} MB at pH 11 with 0.25 g L^{-1} catalyst after 1 hour 30 minute under visible light irradiation was in the following order: FTN-3M (98%) > FTN-4M (92%) > FTN-2M (86%). The kinetics study specified that decolourization of MB followed the pseudo first order Langmuir-Hinshelwood model. The regeneration study showed that the catalyst remained stable after 5 cycles. Lastly, the synthesized catalyst has displayed remarkable performance (above 80%) in decolourization of simulated dyes which consist of rhodamine B, MB, methyl orange and congo red, and has potential use as catalyst for wastewater treatment in textile industry.

ABSTRAK

Sejak kebelakangan ini, sisa buangan pencelup industri menghasilkan kesan buruk terhadap kesihatan manusia dan alam sekitar, terutamanya disebabkan oleh ketoksikan yang tinggi. Di antara pelbagai teknik bagi perawatan sisa buangan pencelup, penyahwarnaan fotobermangkin terbukti amat berpotensi oleh sebab keselamatannya, pengunaan tenaga yang rendah dan tinggi keberkesanannya. Titanium dioksida (TiO_2) adalah fotomangkin yang amat dikenali. Namun begitu, oleh kerana kelemahannya pada jalur-jurang yang besar dan kecenderungan untuk bergumpal, pelbagai kajian seperti modifikasi terhadap morfologi telah dilaporkan dalam usaha untuk menyelesaikan masalah ini. Dalam kajian ini, fotomangkin nanozarah TiO_2 berupa bunga (FTN) telah disediakan dengan berbeza kepekatan (2M-4M) asid hidroklorik (HCl) melalui kaedah hidroterma dan seterusnya diuji untuk penyahwarnaan metilena biru (MB). Sifat-sifat fizikokimia mangkin telah dicirikan mengunakan pembelauan sinar-x, mikroskop elektron pengimbas pancaran medan, spektroskopi inframerah transformasi Fourier, resonans putaran elektron, spektroskopi pantulan serakan spektrofotometer cahaya nampak-ultraungu dan penjerapan-penyahjerapan nitrogen. Kenaikan kepekatan HCl telah diperhatikan menyebabkan peningkatan habluran rutil TiO_2 tulen dengan struktur yang semakin terbuka daripada individu nanospindel. Bilangan tertinggi kumpulan hidroksil, permukaan kekosongan oksigen dan kecacatan tapak Ti^{3+} telah diperhatikan bagi sintesis mangkin yang menggunakan kepekatan 3M HCl, dengan itu meningkatkan potensi penggunaannya dalam penyinaran cahaya nampak. Aktiviti fotobermangkin bagi mangkin terhadap penyahwarnaan 10 mg L^{-1} MB pada pH 11 dengan 0.25 g L^{-1} mangkin selepas 1 jam 30 minit di bawah sinaran cahaya nampak adalah dalam turutan berikut: FTN-3M (98%) > FTN-4M (92%) > FTN-2M (86%). Kajian kinetik menunjukkan bahawa penyahwarnaan MB mengikut model tertib pertama pseudo Langmuir-Hinshelwood. Kajian kebolehgunaan semula menunjukkan mangkin kekal stabil selepas 5 kali kitaran. Akhir sekali, mangkin yang telah disintesis menunjukkan prestasi yang unggul (lebih daripada 80%) dalam penyahwarnaan pencelup simulasi yang terdiri daripada rodamina B, MB, metil jingga dan kongo merah, dan berpotensi sebagai mangkin untuk rawatan air sisa dalam industri tekstil.

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LIST OF ABBREVIATIONS

Ag - Argentum

AOP - Advance oxidation process

B-TiO_2 - Bulk defect TiO_2

CB - Conduction band

Co - Cobalt

CR - Congo red

ESR - Electron spin resonance

FESEM - Field emission scanning electron microscope

Fe_2O_3 - Iron (III) oxide

Fe_3O_4 - Iron (II,III) oxide

F-TiO_2 - Fluorine doped TiO_2

FTN - Flowerlike titania nanoparticles

FTIR - Fourier transform infrared

HCl - Hydrochloric acid

HF - Hydrofluoric acid

HNO_3 - Nitric acid

KBr - Potassium bromide

MB - Methylene blue

MO - Methyl orange

MSN - Mesoporous silica nanoparticles

MTN - Mesoporous titania nanoparticles

$NaBH_4$ - Sodium borohydride

NaCl - Sodium chloride

NH_4Cl - Ammonium chloride

NH_4OH - Ammonium hydroxide

RhB - Rhodamine B

S-B-TiO_2 - Surface and bulk defect TiO_2

SEM - Scanning electron microscope

SiO_2 - Silicon dioxide

S-TiO_2 - Surface defect TiO_2

TBOT - Tetrabutyl titanate

TiF_4 - Titanium tetrafluoride

TiO_2 - Titanium dioxide

TSD - Ti^{3+} surface defect

UV-vis/DRS - UV-visible spectrophotometer/ Diffuse Reflectance Spectroscopy

UV - Ultraviolet

VB - Valance band

VL - Visible light

V_o - Oxygen vacancy

XRD - X-ray diffraction

LIST OF SYMBOLS

α - Alpha

β - Beta

° - Degree

% - Percentage

θ - Theta

λ - Wavelength

℃ - Degree Celsius

cm - Centimetre

eV - Electron Volt

g - Gram

$g\ L^{-1}$ - Gram per litre

h - Hour

K - Kelvin

M - Molar

W - Watt

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Dye industry is one of the most important economic sectors that contribute to other related industries such as textile, printing, paint and coating, cosmetic, food industry and medicine. (Jaganathan *et al.*, 2014; Vaiman *et al*., 2016). About 100,000 commercially available dyes with $7x10^5$ tons of dyestuff are produced annually (Khataee *et al.*, 2010). Additionally, the synthetic origin and complex aromatic structures of dyes make them stable and difficult to be biodecolourized (Srinivasan and Viraraghavan, 2010). Dyes can be classified into two types depending on its sources which are natural and synthetic, while the latter is more preferred due to its attractive colour texture, low cost and tuneable applications (Holme, 2006; Murmann *et al*., 2001).

Synthetic dyes are man-made dyes which consists of a vast chromophoric group such as azo, nitro, thiazine and rhodamine. Specific wavelengths are absorbed by a specific type of chromosphere resulting in the emission of a specific colour which is then named as methylene blue, methyl orange, congo red and so on. Among them, methylene blue (MB) is widely used in dyeing of textile material, paper, plastic and medical application due to its good absorption capabilities onto solid (Chongrak *et al.*, 1998; Shanmugam, 2005). However, MB has its own drawbacks for instance, it gives harmful effects to human health such as rapid heart rate, vomiting, cyanosis, jaundice and tissue necrosis in humans (El-Ashtoukhy *et al.*, 2015). There are some recent reports which stated that MB can also cause Central Nervous System (CNS) toxicity with only a dose of 1 mg kg^{-1} (Gillman *et al.*, 2011).

The massive dye industry with vast and uncontrollable productions contributes to the abundant productions of dye effluent. Direct or indirect discharge of a highly toxic effluent into the nearby watercourses can give many negative effects on the environment, health and public complain (Noel *et al.*, 2015). Therefore, various wastewater treatment has been used for the purification of dye effluents such as adsorption, membrane filtration, ion exchange, ozonation and electrochemical destruction (Robinson *et al.*, 2001; Karim *et al.*, 2014). Nevertheless, there are several disadvantages of the aforementioned techniques that requires extra expenditure on operation, unable to treat various types of dyes and productions of sludge and secondary pollutant. (Harrelkas *et al.*, 2009; Zhang *et al.*, 2012; Jaafar *et al.*, 2015b).

In order to overcome the shortcomings mentioned, the recent technology has shifted to the green approach of photocatalytic reaction using heterogeneous catalysts which is cost-effective, stable, recyclable, produce a non-harmful end product and capable to mineralise the organic compounds (Tian *et al.*, 2012; Jalil *et al.*, 2013). This alternative wastewater treatment is also called an advance oxidation process (AOP) due to the removal of toxic organic pollutant by the superoxide anion and hydroxyl radicals which are generated from the photocatalyst (García-Muñoz *et al.*, 2016; Jusoh *et al.*, 2014). This heterogeneous photocatalyst which consist of various types of semiconductor such as TiO_2, Fe_2O_3, ZnO and ZrO_2 have made progress, owing to its capabilities to generate electron-hole pairs under light irradiation (Jusoh *et al.*, 2013; Jusoh *et al.*, 2015c; Jaafar *et al.*, 2015a; Sinhamahapatra *et al.*, 2016).

Titanium dioxide or titania (TiO_2) has been established as an active photocatalyst since it was first discovered in 1972 (Fujishima *et al.*, 1972). Thereafter, extensive discoveries on the photocatalytic performance of TiO_2 have been done due to its economic, inert and high chemical and photocorrosion stability. TiO_2 consists of three types of polymorphs which are anatase, rutile and brookite. Among these, rutile

TiO_2 is the most thermodynamically stable phases at any temperature, pressure and even in the strongly acidic or basic condition, and has been extensively applied in batteries and dye-sensitised solar cells (Ge *et al.*, 2011; Kumar *et al.*, 2014). Although it receives less attention in photocatalytic reaction compared to anatase, yet in certain condition rutile TiO_2 can be a potential candidate due to its high refractive index and good light scattering efficiency by modifying its morphology, metal ion doping or addition of mesoporous support (Kumar *et al*., 2014). There are several parameters that influence the photocatalytic performance of TiO_2 such as crystallinity, particle distribution, porosity, band gap, surface area and surface hydroxyl density (Ahmed *et al.*, 2011b).

Furthermore, the designing architecture of TiO_2 has been extensively developed within the research area starting from a simple into a complex morphology aiming the active catalyst under visible light irradiation. There are several types of TiO_2 morphological modification such as synthesis of nanorod, nanocube, nanosphere, flower-like, mesoporous and microsphere (Diebold, 2003). However, an active bare flower-like TiO_2 nanostructured (FTN) catalyst under visible light is still in less number of researches. This flower-like structure may provide better light utilization efficiency and more adsorption sites of pollutant thereby resulting in a good photocatalytic reaction (Guo *et al.*, 2014). Thus, the objective of this study is focused on the synthesis and characterization of flower-like TiO_2 using a simple acid hydrothermal method and to investigate its performance in photodecolourization of MB. The kinetics and mechanism of the photodecolourization process were also performed.

1.2 Problem Statement and Hypothesis

TiO_2 is a well-known photocatalyst for the decomposition of organic contaminants due to its excellent photoactivity than other metal oxide semiconductor (Hashimoto *et al.*, 2005). Although anatase TiO_2 is an active photocatalyst compared to other TiO_2 polymorph, it still has several drawbacks such as wide band gap (3.2 eV), fast electron-hole recombination rate and easy to agglomerate which hinders the catalyst active sites, thus reducing its photocatalytic performance (Zhang *et al.*, 2014). The limitation of light-response range allows the catalyst to be active only under UV light irradiation thus requires more energy consumption. Therefore, the advantage in low band gap energy (3.0 eV), high refractive index, thermodynamically stable and good light scattering efficiency of rutile TiO_2 may contribute to an improved photocatalyst under visible light irradiation (Kumar *et al.*, 2014).

Structural design of TiO_2 photocatalyst from basic to hierarchical structure have been extensively studied due to its widespread potential applications in many aspects such as solar cells, catalysis, lithium-ion batteries and drug delivery (Lin *et al.*, 2014; Jaafar *et al.*, 2015; Liu *et al.*, 2016; Wang *et al.*, 2015). However, the synthesis method of complex TiO_2 morphology is still facing a great challenge with several methods being implemented to solve the problem such as chemically induced self-assembly, chemical etching and template-assisted (Gao *et al.*, 2015). Among them, template-assisted is the most commonly used, however, this method involved quite complicated steps such as coating, etching and calcination, as well as difficulty in controlling and obtaining the uniform samples (Jia *et al.*, 2015). Therefore, a free-template method is desired. This method requires in monitoring the pH condition of the solution. Acidic solution such as HCl can form a rutile TiO_2 due to increase in number of H^+ ions in the reaction solution will increase the number of OH_2^+ ligands forming a stable linear TiO_2 (Lai *et al.*, 2014). While, Cl^- ions have a weaker affinity towards Ti atoms resulting in epitaxial growth of 1D rutile TiO_2 (Zhou *et al.*, 2012). In order to form a well-defined flower-like structure with a multiple 1D rutile extended from center, an optimum HCl concentration is needed. Thus, it is hypothesised that the use of HCl with an optimum concentration will form a well-defined flower-like structure of rutile TiO_2.

A basic structure or a single constituent TiO_2 nanostructure is the lack of necessary properties and tend to agglomerate in the photocatalytic wastewater system (Li *et al.*, 2015b). Many efforts focusing on increasing the catalyst surface area have been done, yet, further increased in surface area by decreasing the particle size to certain nanosize may activate an attractive Van der Waals force, thus resulting in agglomeration (Jusoh *et al.*, 2013; Jaafar *et al.*, 2015b; Gao *et al.*, 2015). Therefore, flower-like structure is a promising morphology on improving the photocatalytic activity due to its unique structure which can enhance the light harvesting from the multiple reflection of light on the surface of the extended nanorod structure (Jusoh *et al.*, 2013; Yu *et al.*, 2009). Furthermore, the open structure of each individual nanorod extended from the center may provide more exposed and assessable active side which are limited in other structure. Hence, in this study it is hypothesised that the synthesis of flower-like TiO_2 nanoparticle (FTN) catalysts can successfully enhance the photoactivity on decolourization of MB which is capable to be activated under visible light under shorter reaction time.

1.3 Objective of the Study

The aims of this study are:

1. To synthesise and characterise the flower-like titania nanoparticle (FTN) catalysts.
2. To evaluate the photodecolourization of MB by the FTN catalysts.
3. To determine the kinetics and mechanism of the photodecolourization as well as the capability of the system for simulated wastewater treatment.

1.4 Scope of the Study

The scope of this study are:

1. Synthesis and characterization of physicochemical properties of flower-like TiO_2 nanostructured (FTN).
   FTN was prepared using an acid hydrothermal process by varying the concentration of hydrochloric acid (2M, 3M and 4M). All of the catalysts were characterised by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), nitrogen (N_2) adsorption-desorption, Field Emission Scanning Electron Microscope (FESEM), electron spin resonance (ESR), and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis/DRS).

2. Evaluation of the photodecolourization of MB.
   Photocatalytic testing of the synthesised catalysts on decolourization of MB was conducted under various parameters such as pH (3-11), catalyst dosage (0-0.375 g L^{-1}) and initial concentrations (10-70 mg L^{-1}). The choice for the selection of pH, catalyst dosage and concentration levels is based on reported literature (Jusoh *et al.*, 2015b; Jusoh *et al*., 2013; Jaafar *et al.*, 2012; Jalil *et al.*, 2013; Jalil *et al.*, 2015; Hassan *et al.*, 2015; Sahoo *et al.*, 2012).

3. Study on kinetics and mechanism of photodecolourization of MB as well as application on simulated wastewater treatment.
   The kinetics expression modelling was described based on the pseudo-first order-Langmuir-Hinshelwood models in order to find the appropriate proposed reaction mechanism for photocatalytic decolourization. A simulated wastewater treatment was prepared using MB, MO, CR and RhB.

1.5 Significant of Study

This study was conducted to synthesise FTN based catalysts for photodecolourization of MB. A detail investigation on physicochemical properties of the catalysts as well as the photocatalytic activity was also conducted. The TiO_2 have been commonly applied as a photocatalyst concerning its outstanding photoactivity in removal of organic pollutant. Nonetheless, it has narrow light-response range, rapid electron-hole recombination rate and difficulty in handling process, giving the limitation on its application under visible light irradiation. In recent approach, a modification on TiO_2 morphology can improve its own drawbacks and results in a fascinating photocatalytic activity.

The preparation method is a critical part in modifying the TiO_2 morphology. There are several studies on various morphological modifications of TiO_2 had been done to further improve its photocatalytic performance, however, the detail discussion on the catalyst properties related to the structure is still limited. Among the other morphological structures, the flower-like TiO_2 synthesised by the acid hydrothermal method is able to lower the band gap, improve the efficiency of light utilization and provide more surface contact between pollutant and the catalyst. Hence, it was hypothesised that the synthesis of TiO_2 flower-like structure using a simple acid hydrothermal method was expected to enhance the photocatalytic decolourization of MB and this study will give an advantage for the knowledge transfer and improve the efficiency of the wastewater treatment.

1.6 Thesis Outline

This thesis was divided into five chapters. In chapter 1, general introduction is given about the use of dye in various area of industries, types of synthetic dye and the risk of the dye effluent especially MB dye towards the environmental and human health. Several wastewater treatment for decolourization of MB were also mentioned. Besides that, the potential of FTN as a photocatalyst for removal of MB were highlighted. The problem statements of the current research were stated to clarify the objectives of the present study. The scopes of study covers the research work to meet the objectives. The significance of research was also clearly mentioned.

Chapter 2 or literature review covers the details on previous studies in order to get the better understanding in synthesis, characterization and photoactivity efficiency of FTN catalyst.

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

Chapter 4 focuses on results and discussion which are divided into three parts, (i) physicochemical properties of catalysts (ii) photocatalytic activity of the catalyst and (iii) potential of catalyst on photodecolourization of simulated dye wastewater.

Finally, the conclusion about the study and the future studies were simplified in the last chapter which is chapter 5.

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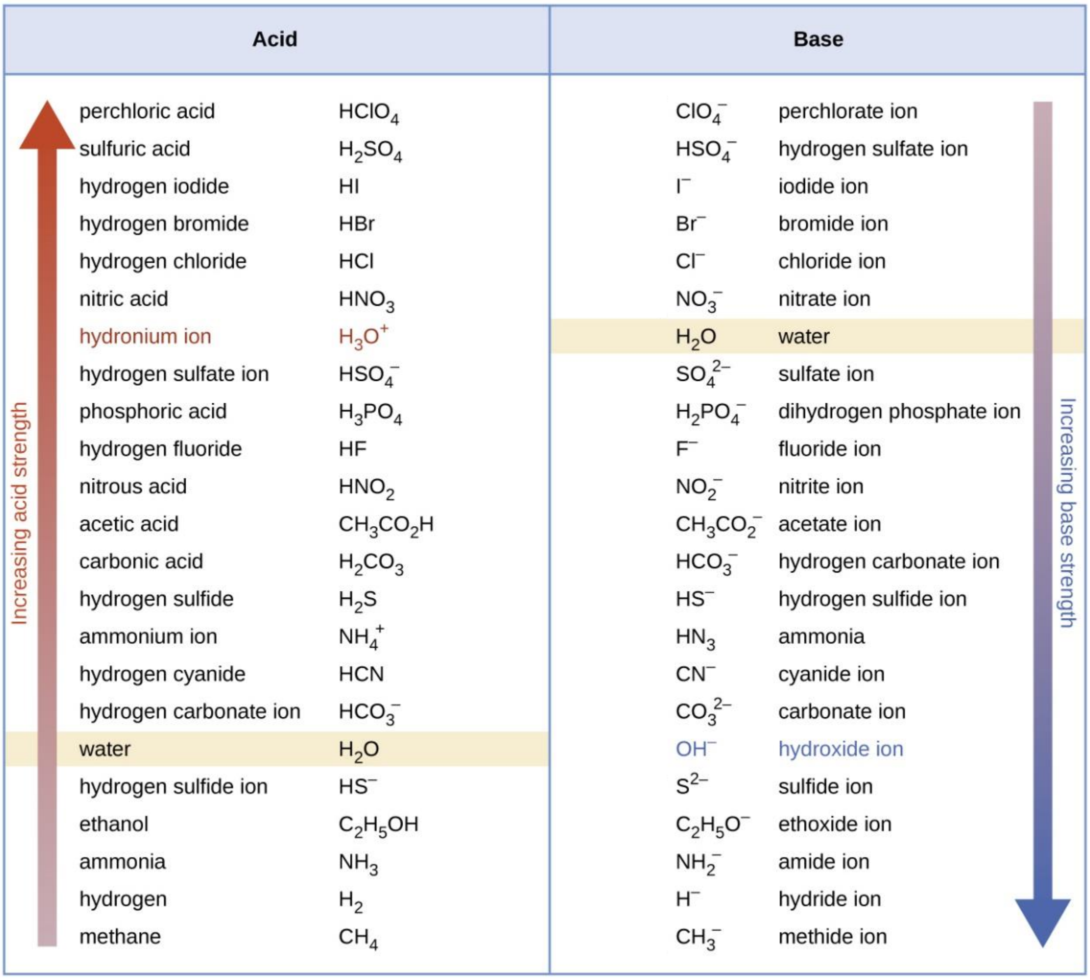
APPENDIX A

Acid-base strength chart



Increasing acid strength

Acid		Base	
perchloric acid	$HClO_4$	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4	HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI	I^-	iodide ion
hydrogen bromide	HBr	Br^-	bromide ion
hydrogen chloride	HCl	Cl^-	chloride ion
nitric acid	HNO_3	NO_3^-	nitrate ion
hydronium ion	H_3O^+	H_2O	water
hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4	$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF	F^-	fluoride ion
nitrous acid	HNO_2	NO_2^-	nitrite ion
acetic acid	CH_3CO_2H	$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3	HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S	HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+	HN_3	ammonia
hydrogen cyanide	HCN	CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	carbonate ion
water	H_2O	OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	S^{2-}	sulfide ion
ethanol	C_2H_5OH	$C_2H_5O^-$	ethoxide ion
ammonia	NH_3	NH_2^-	amide ion
hydrogen	H_2	H^-	hydride ion
methane	CH_4	CH_3^-	methide ion

Increasing base strength

APPENDIX B

Calculation particle size of FTN using Scherrer's formula

By taking 2θ = 25.32°, the particle size of the catalyst can be estimated as follows,

$$\tau = \frac{k\lambda}{\beta \cos\theta}$$

where τ is particle size, λ is the wavelength of X-ray radiation (Cu K_α = 0.154 nm), *k* is shape factor (*k* = 0.9), β is the line width at half maximum height in radian and θ is the angular position of the peak maximum in radian.

$$\beta = \frac{\left(0.34^\circ \times \pi\right)}{180^\circ} = 5.9341 \times 10^{-3} rad$$

$$\theta = \frac{\left(27.5^\circ \times \pi\right)}{180^\circ} = 0.47997 rad$$

$$\tau = \frac{0.9 \times 0.154}{5.9341 \times 10^{-3} \cos\left(0.47997\right)} = 26.33nm \approx 26nm$$

Thus, the crystallite size of FTN-3M was 26 nm at 2θ = 27.5°

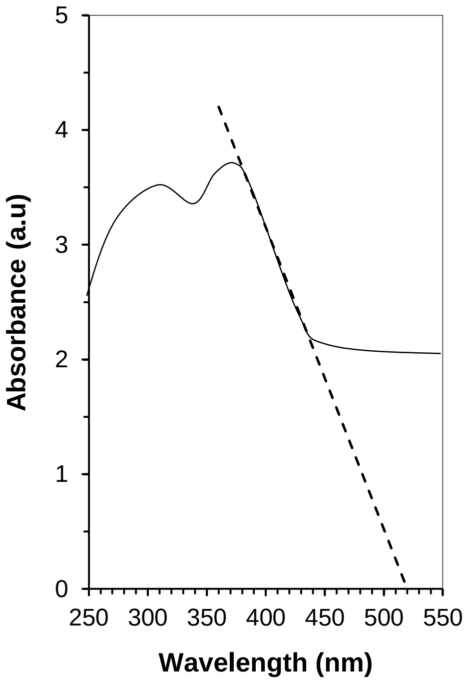
APPENDIX C

Calculation of band gap

The band gap of the catalysts were calculated by using the following equation:

$$E = \frac{hc}{\lambda} = \frac{1240 eV \cdot nm}{\lambda}$$

where *E* is the band gap energy, *h* is Planck's constant $\left(6.626 \times 10^{-34} J \cdot s\right)$, *c* is speed of light $\left(2.988 \times 10^{8} m/s\right)$ and λ is the wavelength obtained from the extrapolation of straight line as shown in the figure of UV-vis/DRS spectra.



λ = 520 nm

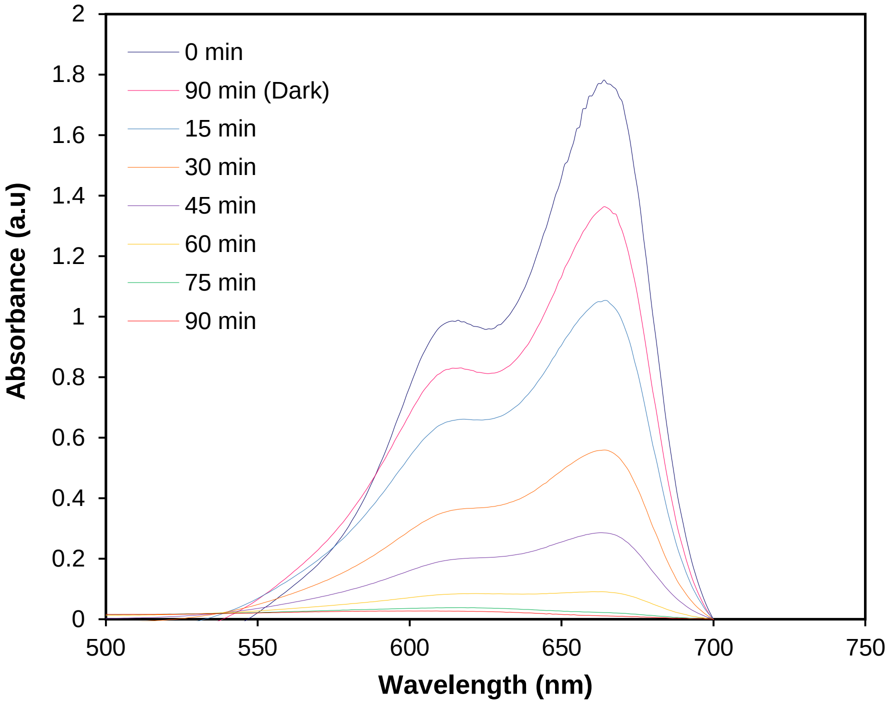
E = 1240 eV · nm / 520 nm

= 2.38 eV

Thus, the band gap of FTN-3M was 2.38 eV

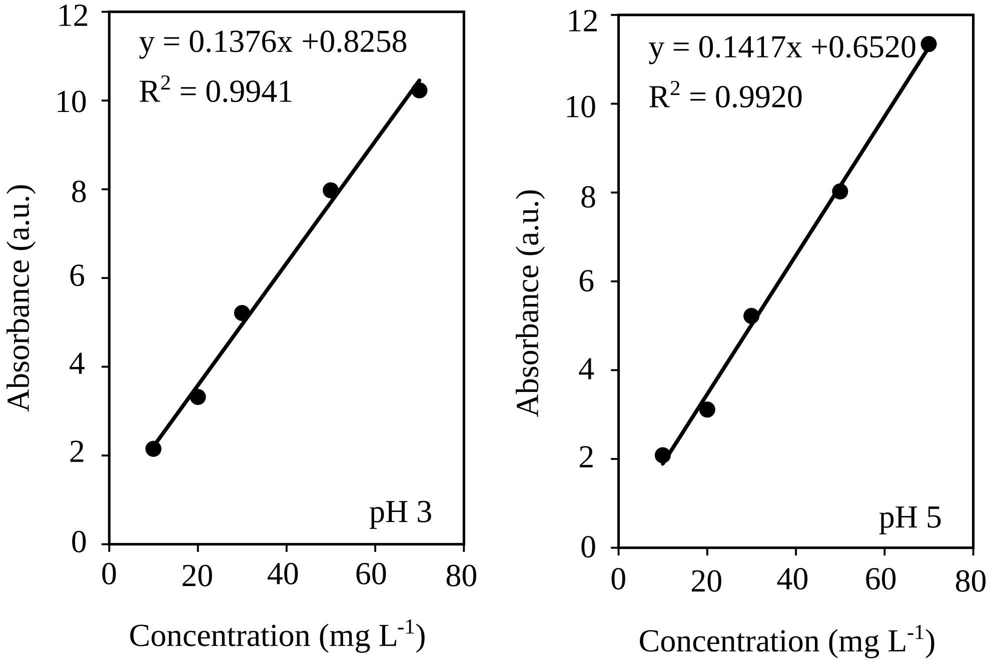
APPENDIX D

Raw data of MB decolourization profile for FTN-3M

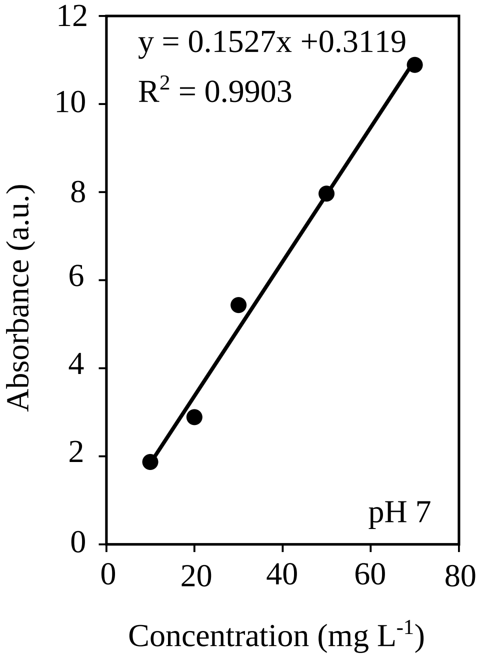


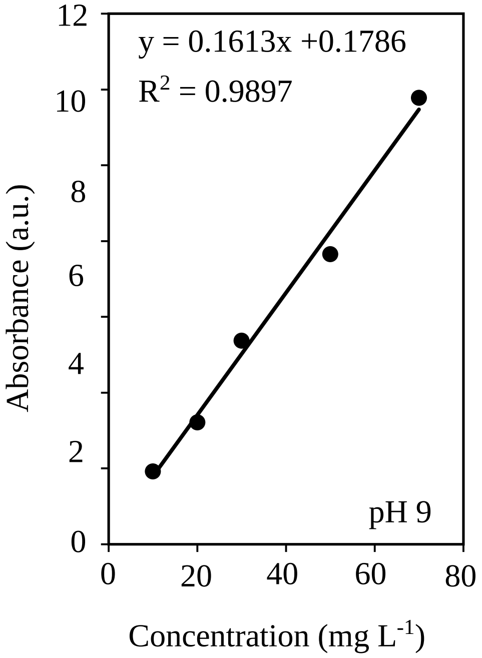
APPENDIX E

Standard calibration curve

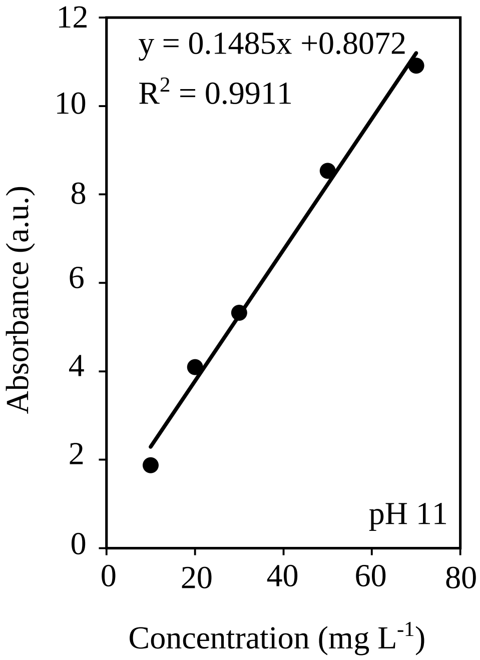


Standard Calibration Curve (Continued)



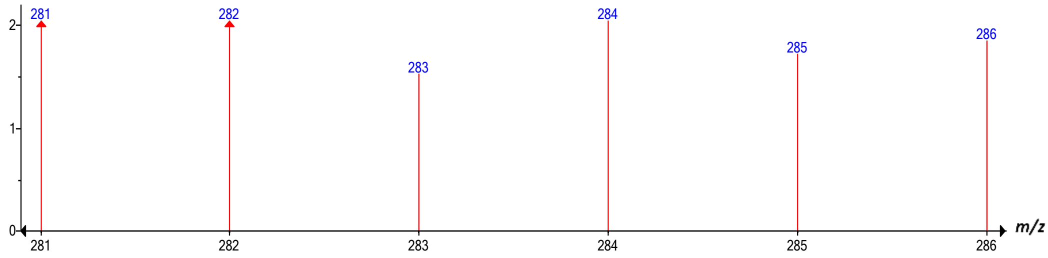


Standard Calibration Curve (Continued)

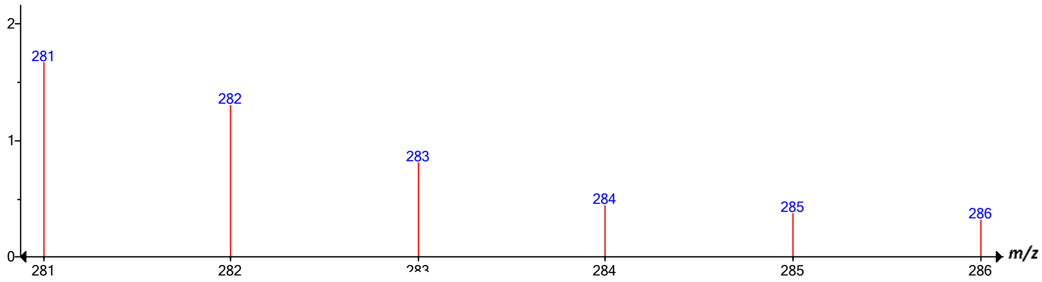


APPENDIX F

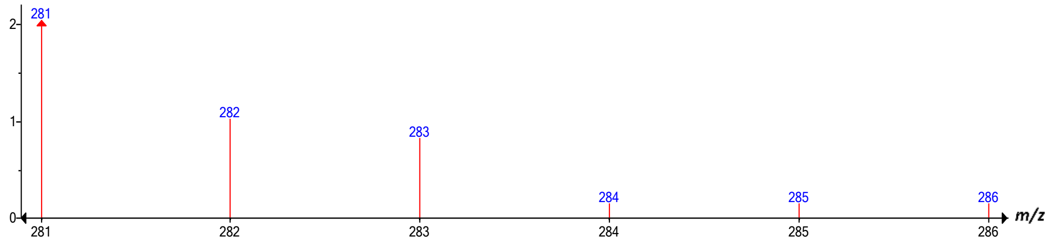
Mass spectra of MB (m/z 284) along the photocatalytic testing starting from blank to 45 min of the photoreaction



+ Scan (20.166-20.300 min, 19 Scans) MB blank.D



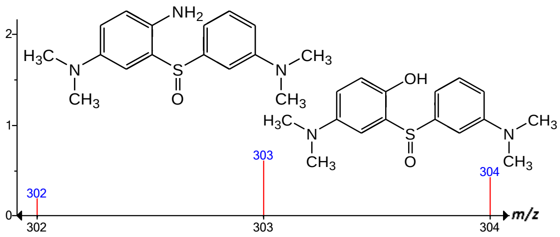
+ Scan (20.148-20.201 min, 8 Scans) 15min



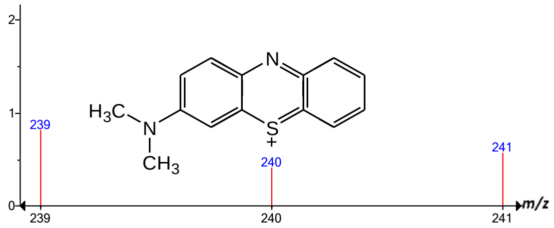
+ Scan (20.979-21.031 min, 8 Scans) 45min

APPENDIX G

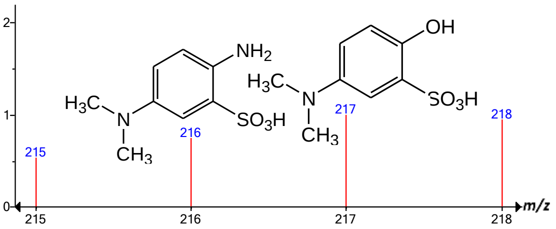
Mass spectra of MB's intermediate product from 15 min to 90 min under visible light irradiation



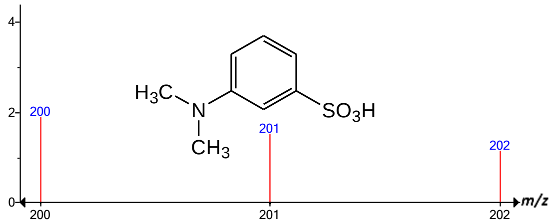
+ Scan (12.569-12.599 min, 5 Scans) 15min



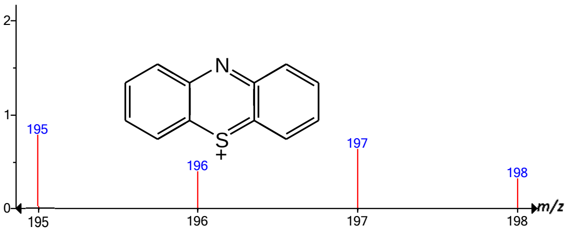
+ Scan (20.148-20.201 min, 8 Scans) 15min



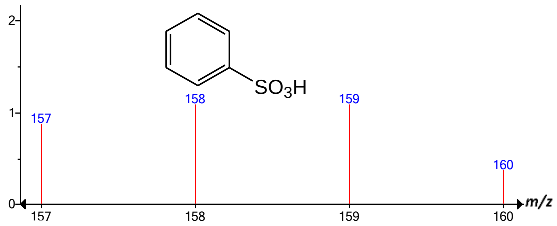
+ Scan (9.726-9.763 min, 6 Scans) 15min



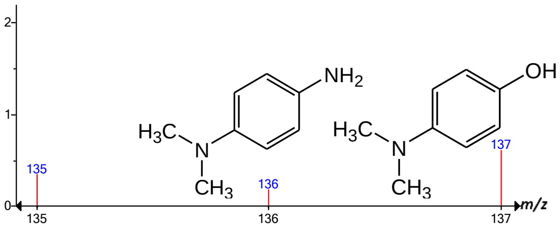
+ Scan (9.726-9.763 min, 6 Scans) 15min



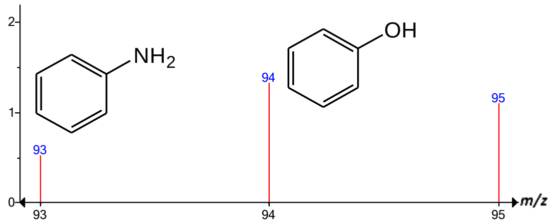
+ Scan (21.720-21.742 min, 4 Scans) 45min



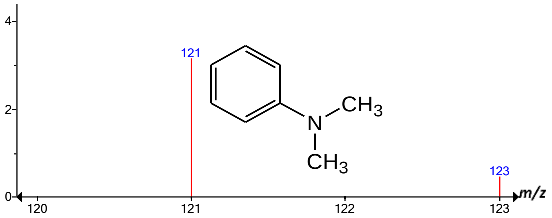
+ Scan (10.908-10.953 min, 7 Scans) 45min



+ Scan (2.902-2.925 min, 4 Scans) 75min



+ Scan (5.775-5.835 min, 9 Scans) 75min



+ Scan (6.000-6.067 min, 10 Scans) 90min