PULLULAN BASED ZINC OXIDE AND POLYANILINE NANOCOMPOSITES FOR PHOTODEGRADATION OF RHODAMINE B

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To my family, especially my mother, Hafsah Sulaiman, for all her help, love and sacrifice in helping me achieving my dream.

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ABSTRACT

Water pollution has been plaguing the world ever since the industrial revolution. One of the main water pollutants is dyes and they pose adverse effect on mankind and aquatic life. This pollutant can be removed through an emerging alternative technique; the advanced oxidation process (AOPs). Photocatalysis, one of popular AOPs, utilizes semiconductor catalyst to degrade the dyes. Zinc oxide (ZnO) is a promising material for this process. In this study, pullulan-based zinc oxide nanoparticles (ZnO NPs), polyaniline/pullulan composites (PANI/Pul Cs) and zinc oxide-polyaniline/pullulan nanocomposites (nZPP NCs) were synthesized. The catalysts were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectrophotometer (UV-Vis), transmission electron microscopy (TEM), surface area and pore analyser and thermogravimetric analysis (TGA). In this study pullulan served as capping agent for the production of ZnO NPs and PANI/Pul Cs. For the synthesis of ZnO NPs, the effects of calcination conditions, temperature and time, on the properties of ZnO NPs were studied. The crystallinity and particle size of ZnO NPs increased proportionally with calcination temperature. Concerning calcination time, significant increase of particle size was observed when the time was increased to two hours. TEM results showed that the particles size of synthesized ZnO NPs ranged from 28 to 127 nm. All the catalysts were subjected to photodegradation of rhodamine B (RhB) dye. ZnO NPs produced with calcination conditions of 400 °C for 1 hour showed the best activity with degradation rate of 0.0801 min^{-1}. Then, composites PANI/Pul were synthesized with variation of aniline to pullulan mass ratio. The impact of mass ratio variation on the properties PANI/Pul Cs was compared. In the presence of pullulan, the crystallinity of PANI/Pul Cs improved. Besides, the particle morphology also became more consistent rod-like shape in the presence of pullulan with aniline to pullulan mass ratio of 1:3. All the synthesized PANI/Pul Cs were subjected to photodegradation of RhB and the results showed that the best activity was exhibited by the PANI/Pul C synthesized with 1:3 aniline to pullulan mass ratio with degradation rate of 0.0086 min^{-1}. Then nZPP NCs were synthesized using ZnO NPs produced with calcination conditions of 400 °C for 1 hour and PANI/Pul C with 1:3 aniline to pullulan mass ratio. The weight per cent of PANI/Pul C in nZPP NCs were varied as two, six and 10 per cent. With the addition of PANI/Pul C on ZnO NPs, the crystallinity of ZnO NPs was not disturbed. The nZPP NCs catalyst activity was optimized by using response surface methodology (RSM) with the variable being weight per cent of PANI/Pul C, catalyst dosage and pH with the response being degradation rate. The results showed that the most suitable model was quadratic with the optimum degradation rate obtained was 0.2319 min^{-1} with six weight per cent of PANI/Pul C, catalyst dose of 0.7 g/L and initial pH of 8. Lastly, the optimized catalyst was tested with simulated dye wastewater which was created by mixing five dyes together. The results showed that complete decolourization was achieved in 180 minutes.

ABSTRAK

Pencemaran air telah melanda dunia sejak revolusi industri. Salah satu bahan pencemar utama adalah pewarna dan ia memberi kesan yang buruk kepada manusia dan hidupan akuatik. Bahan pencemar ini dapat dihapuskan melalui teknik alternatif yang muncul; proses pengoksidaan termaju (AOP). Fotokatalisis, salah satu AOP yang terkenal, menggunakan pemangkin semikonductor untuk degradasi pewarna. Zink oksida (ZnO) adalah bahan yang mempunyai harapan untuk proses ini. Dalam kajian ini, nanozarah ZnO berasaskan pullulan (ZnO NPs), komposit polyanilin/pullulan (PANI/Pul Cs) dan nanokomposit zink oksida- polyanilin/ pullulan (nZPP NCs) telah disintesis. Pemangkin telah dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektrofotometer cahaya-nampak ultraungu (UV-Vis), mikroskopi pancaran elektron (TEM), luas permukaan dan penganalisis liang dan analisis termogravimetrik (TGA). Dalam kajian ini, pullulan berfungsi sebagai agen penutup untuk penghasilan ZnO NPs dan PANI/Pul Cs. Untuk sintesis ZnO NPs, kesan keadaan kalsinasi iaitu suhu dan masa, terhadap sifat ZnO NPs telah dipelajari. Penghabluran dan ukuran zarah ZnO meningkat secara berkadar dengan suhu kalsinasi. Dari segi masa kalsinasi, peningkatan saiz zarah yang ketara diperhatikan apabila masa dinaikkan menjadi dua jam. Hasil TEM menunjukkan bahawa ukuran partikel ZnO NPs yang telah disintesis berkisar antara 28 hingga 127 nm. Semua pemangkin telah diuji pada fotodegradasi pewarna rhodamine B (RhB). ZnO NPs yang telah dihasilkan dengan keadaan kalsinasi 400 °C selama 1 jam menunjukkan aktiviti terbaik dengan kadar degradasi 0.0801 min-1. Kemudian, komposit PANI/Pul Cs telah disintesis dengan variasi nisbah jisim anilin dan pullulan. Kesan variasi nisbah jisim pada sifat PANI/Pul Cs telah dibandingkan. Dengan adanya pullulan, kristaliniti PANI/Pul Cs bertambah baik. Selain itu, morfologi zarah juga menjadi bentuk batang yang lebih konsisten dengan nisbah anilin kepada pullulan 1:3. Semua PANI/Pul Cs yang dihasilkan telah diuji terhadap fotodegradasi RhB dan hasilnya menunjukkan bahawa aktiviti terbaik dipamerkan oleh Pul/PANI C yang telah disintesis dengan nisbah jisim analin dan pullulan 1:3 dengan kadar degradasi 0.0086 min-1. Kemudian, nZPP NCs telah disintesis menggunakan ZnO NPs yang dihasilkan dengan keadaan kalsinasi 400 °C selama 1 jam dan PANI/Pul C dengan nisbah jisim analin dan pullulan 1:3. Peratusan berat Pul/PANI C pada nZPP NCs divariasi seperti 2, 6 dan 10 peratus. Dengan penambahan PANI/Pul C pada ZnO NPs, kristaliniti ZnO NPs tidak terganggu. Aktiviti pemangkin nZPP NCs telah dioptimumkan dengan kaedah respon permukaan (RSM) dengan pemboleh ubah adalah peratusan berat PANI/Pul C, dos pemangkin dan pH dengan respon dikaji adalah kadar degradasi. Hasil kajian menunjukkan bahawa model yang paling sesuai adalah kuadratic dengan kadar degradasi optimum diperoleh adalah 0.2319 min-1 dengan enam peratus berat PANI/Pul C, dos pemangkin 0.7 g/L dan pH 8. Akhir sekali, pemangkin yang telah dioptimumkan telah diuji dengan air sisa pewarna simulasi yang telah dihasilkan dengan mencampurkan lima pewarna bersama. Keputusan menunjukkan bahawa penyahwarnaan lengkap telah dicapai dalam 180 minit.

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LIST OF ABBREVIATIONS

10ZPP	-	10 wt % 13PP loaded on Z4
11PP	-	Weight ratio aniline to pullulan 1:1
13PP	-	Weight ratio aniline to pullulan 1:3
15PP	-	Weight ratio aniline to pullulan 1:5
2FI	-	Two factorials
2ZPP	-	2 wt % 13PP loaded on Z4
6ZPP	-	6 wt % 13PP loaded on Z4
AFM	-	Atomic force microscopy
Ag-ZnO NCs	-	Silver-zinc oxide nanocomposites
ANOVA	-	Analysis of variance
AOPs	-	Advanced oxidation processes
ATR	-	Attenuated total reflectance
Au/ZnO	-	Gold on zinc oxide
BET	-	Brunauer-Emmett-Teller
BJH	-	Barett-Joyner-Halenda
BQ	-	Para-benzoquinone
CB	-	Conduction band
CCD	-	Central composite design
CI	-	Colour index
CuxO/ZnO	-	Copper oxide-zinc oxide
CV	-	Crystal violet
DMSO	-	Dimethyl sulfoxide
EDS	-	Energy dispersive X-ray spectroscopy
EDTA	-	Disodium ethylenediaminetetraacetic acid
FDA	-	US food and drug administration
FTIR	-	Fourier transform infrared spectroscopy
G	-	Graphene
GO	-	Graphene oxide
GRAS	-	Generally recognised as safe

HOMO	-	Highest occupied molecular orbital
IPA	-	Isopropanol
ITO	-	Indium tin oxide substrate
LC-MS	-	Liquid chromatography mass spectrometry
LUMO	-	Lowest unoccupied molecular orbital
MB	-	Methylene blue
MO	-	Methyl orange
MR	-	Methyl red
NCs	-	Nanocomposites
NPs	-	Nanoparticles
nZPP NCs	-	Zinc oxide-pullulan/polyaniline nanocomposites
OVAT	-	One-variable-at-a-time
PANI	-	Polyaniline
PANI	-	Weight ratio aniline to pullulan 1:0
PANI/Pul Cs	-	Polyaniline/pullulan composites
PPy	-	Polypyrrole
PZC	-	Point zero charge
rGO	-	Reduced graphene oxide
RhB	-	Rhodamine B
RSM	-	Response surface methodology
S.D	-	Standard deviation
STM	-	Scanning tunnelling microscopy
SWCNTs	-	Single walled carbon nanotubes
TEM	-	Transmission electron microscopy
TGA	-	Thermogravimetric analysis
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet-visible spectrophotometer
VB	-	Valence band
XRD	-	X-Ray diffraction
Z4	-	Calcination conditions of 400 °C, 1 hour
Z4-2h	-	Calcination conditions of 400 °C, 2 hours
Z4-4h	-	Calcination conditions of 400 °C, 4 hours

Z4-8h	-	Calcination conditions of 400 °C, 8 hours
Z5	-	Calcination conditions of 500 °C, 1 hour
Z6	-	Calcination conditions of 600 °C, 1 hour
Z7	-	Calcination conditions of 700 °C, 1 hour
ZnO-PPy	-	Zinc oxide-polypyrrole

LIST OF SYMBOLS

A	-	Constant
%	-	Percent
C	-	Concentration
D	-	Crystallite size
Eg	-	Band gap energy
eV	-	Electron volt
h	-	Planck's constant light frequency
k	-	Pseudo-first order rate constant
R^2	-	Correlation coefficient
t	-	Time
wt	-	Weight
α	-	Absorption coefficient
β	-	Full width at half maximum
θ	-	Diffraction angle
λ	-	X-ray wavelength of radiation
π	-	Pi

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Water pollution is one of the biggest problems plaguing everybody around the world. It is known that clean water is essential for survival of mankind. However, with industrial revolution, it is nearly impossible to obtain clean water straight from its source. The majority of wastewater from the industries were insufficiently treated and released to the water bodies thus potentially contaminate and pollute the clean water source. One of the main contributors to water pollution is textile industry and the dyes being the major pollutant. Statistic shows that 450000 ton of organic dyes produced annually and more that 11 % of it is lost in the effluents during manufacture and application process [1]. It is also one of the most water-consuming industrial sectors where it released approximately 115-175 kg/ton of finished product of wastewater [2]. The presence of trace amount of dyes in effluent is highly visible and undesirable. It causes adverse effect to both aquatic life and human health as some of these dyes are toxic, mutagenic and carcinogenic [3, 4]. Once the dyes enter the water, they are difficult to remove. Furthermore, their complex aromatic structure and the synthetic origin makes them more stable thus harder to degrade [5].

In a typical process of textile wastewater treatment, biological process followed by chemical coagulation is employed Although this treatment unit's processes are effective in removing dyes, it is high in cost as it requires specific equipment and high energy. Furthermore, generation of large amount of by-product lead to the problem of safe disposal [4, 6]. Due to these issues, the focus of textile wastewater treatment has been shifted towards advanced oxidation processes (AOPs). This process involves the generation and the use of hydroxyl radical as strong oxidant to destroy the compounds until all the constituents degraded or mineralized to carbon dioxide and water [6, 7]. The generation of hydroxyl radical can proceed through two main pathways which are nonphotochemical and photochemical process. Between these two, photochemical process gained more attention, as it is more economical. In this process, there are three main methods to generate the hydroxyl radical which are ultraviolet (UV) irradiation in presence of hydrogen peroxide, Fenton reagents in presence of light and heterogeneous semiconductor photocatalysis. Among these, heterogeneous semiconductor photocatalysis is the most popular method due to its safe and detoxification nature to the environment [8]. It employed photocatalysts such as titanium dioxide (TiO_2), iron oxide (Fe_3O_4), zinc oxide (ZnO), copper oxide (CuO) and cadmiun sulphide (CdS) in the treatment of dyes wastewater.

In the field of photocatalysis, ZnO has emerged as the leading candidate and this is due to its properties such as direct and wide band gap (3.37 eV) in the near UV spectral region, strong oxidation ability and good photocatalytic property [9, 10]. It also possesses excellent electrical, mechanical and optical properties similar to TiO_2. Furthermore, the production of ZnO is more economical compared to TiO_2. However, ZnO still possess several disadvantages such as limited light absorption in the visible light region due to wide band gap energy and fast recombination of photogenerated charges which lead to low photocatalytic efficiency. Improvement can be done on ZnO to overcome these problems by producing nanoscale ZnO thus increasing the surface area, metal and/or non-metal doping, coupling with another semiconductor, surface modification and others [9-11].

Nanotechnology has garnered a lot of attention around the world across many fields. It is defined as a field of research that involved in the development of very small materials which is within nanometer range [12]. Nanomaterials are unique as they display different properties compared to their bulk counterpart. Due to their small size, they have a greater relative surface area which resulted in enhancement of several properties [13, 14]. To obtain nanomaterials, there are two main approaches which are “top-down” and “bottom-up” approach. In “top-down” approach, it involves breakage of large material to nanomaterials. However, this method generate particles with wide size distribution and variation of morphologies [15]. “Bottom-up” approach is much more common in nanomaterials synthesis and it involves the growth of nanoparticles from single atom [12]. This approach give rise to a better nanomaterial in terms of shape and size which is useful in the targeted applications. In both approaches, there are three main synthesis techniques in obtaining nanomaterials which are physical, chemical and green synthesis method. With the increasing concern of environmental pollution, the synthesis process has been more focus towards green synthesis which is also known as biosynthesis [16]. In general, biosynthesis makes use of environmentally friendly, non-toxic and safe reagent. The overall cost of synthesis process also reduced as no additional chemical is needed. Furthermore, the overall experimental process is relatively mild which can save energy.

The properties of ZnO NPs can be controlled by manipulating the synthesis parameters such calcination conditions. The two main phenomena that effect the ZnO NPs properties, especially its particle size, are Ostwald ripening and quantum confinement effect. Ostwald ripening referring to the growth particles through the diffusion of smaller particles and this process may be enhanced by reaction temperature [17]. Due to small particles size, quantum confinement effect can occur. This process referring to the confinement of electron within the nanoparticle size which resulted to the generation of different properties compared the materials bulk counterpart [18]. Therefore, by controlling the synthesis parameters, ZnO NPs with desirable characteristic as photocatalyst can be generated. Other than developing ZnO nanoparticles (ZnO NPs), improvement can be done by coupling it with other materials. Through this coupling, the overall catalyst properties such as better light absorption, suppression of photoinduced electron-hole pair recombination and increase of charge separation can be achieved. One of the materials that is suitable to be coupled with ZnO is conducting polymer. Conductive polymer provide extra advantages over normal polymer as it can match its band structure with the photocatalyst thus reducing the recombination of photogenerated electron-hole pairs [19]. Besides that, with the presence of conducting polymer, the process of recollection of photocatalyst for reusability will be easier compared to collecting pure ZnO NPs.

Although there has been a lot of effort in the research of determining the suitable catalyst for photocatalytic degradation of dyes in wastewater, there are still some issues that are still unclear. There is still lack of report on utilization of composites consisting of ZnO NPs and conducting polymer for dyes treatment. Herein, we report the preparation of ZnO NPs and conducting polymer polyaniline (PANI) in the presence of biopolymer pullulan. The produced ZnO NPs and PANI were tested for photodegradation of rhodamine B dye. The best ZnO NPs and PANI were used to produce nanocomposites (NCs) consisting of both ZnO NPs and PANI. The NCs photocatalytic activity was optimized via response surface methodology (RSM) and the optimized sample was used to determine its potential as photocatalyst for treatment of textile wastewater by testing it against simulated dye wastewater.

1.2 Problem Statement

In the last decades, worldwide textile industry has made a great impact on the market economics. However, due to the rapid expansion of this industry, the negative impact to the environment also increases especially towards the water and its sources. Textile industry uses large number of chemicals and dyes in each step of processing. Therefore, its discharge contains a lot of dangerous chemical substances, especially dyes. Without treatment, this discharge will cause harm to the environment and even human health as well. Hence, the treatment for textile effluent is necessary to protect the environment and human.

The current conventional wastewater treatment process relies on several treatment stages which consist of physical, chemical or biological approaches. Physical approach involves the usage of adsorbent, filtration and gravity sedimentation while chemical approach includes the use of chemicals to cause coagulation for removal of inorganic dissolved trace metals and removal of bacteria through usage of chlorine or ozone. Aerobic and anaerobic treatments are some of biological approach used to treat the wastewater [6, 20]. All these treatment approaches are effective to treat the wastewater but the high fabrication and maintenance cost make these treatments uneconomical [5]. Therefore, alternative treatment method that is much more economical is highly needed.

In recent years, AOPs have been receiving a lot of attention due to their potential to remove the pollutants. This process is able to degrade the pollutants without generating secondary pollution. One of the materials that has been utilized as photocatalyst is TiO_2 but it has the tendency to agglomerate and uneconomical for large scale production. Due to this, ZnO has been gaining interest to replace TiO_2. However, ZnO has large band gap and high recombination rate of photoinduced electron-hole pairs which lead to lower photocatalytic activity. Therefore, improvement on ZnO to increase its photocatalytic activity is needed.

The main improvement on ZnO to increase its photocatalytic activity is by producing ZnO NPs. Typical method to produce ZnO NPs is through chemical synthesis. Although the properties of chemically synthesized ZnO NPs is promising, the chemical used in the synthesis process normally will cause toxicity to the environments. Therefore, green synthesis emerged as an alternative way in producing ZnO NPs. Green synthesis utilizes natural products such as plants extract, microorganism and biopolymer as mediator and the overall synthesis process is environmentally friendly, simple, fast and cost effective.

It is known that ZnO NPs on its own has a very good photocatalytic activity. However, it has large band gap and high recombination rate. Its photocatalytic activity can be further improved by coupling it with other materials. Conducting polymer emerged as one of the coupling materials which can improve the ZnO NPs photocatalytic properties. Furthermore, through this coupling, the process of recollection for recyclability will be easier.

1.3 Objectives

The main objective of this study is to develop pullulan-based zinc oxide nanoparticles (ZnO NPs), polyaniline/pullulan composites (PANI/Pul Cs) and zinc oxide-polyaniline/pullulan nanocomposites (nZPP NCs) for the purpose of photocatalyst in dye degradation application. This objective can be divided into several specific objectives as follow:

(a) To synthesize ZnO NPs, PANI/Pul Cs and nZPP NCs at various experimental conditions

(b) To characterize and evaluate the physico-chemical properties of synthesized ZnO NPs, PANI/Pul Cs and nZPP NCs

(c) To determine the photocatalytic activity of ZnO NPs, PANI/Pul Cs and nZPP NCs using rhodamine B dye

(d) To optimize the photodegradation of rhodamine B over nZPP NCs by response surface methodology (RSM) and evaluate its potential on photodegradation of simulated dye wastewater.

1.4 Scope of study

In order to achieve all the objectives of this research, the scopes of study comprise the main task corresponding to the objectives are as follow:

(a) The synthesis of ZnO NPs was carried out via sol-gel method with pullulan as the capping agent. The effect of calcination conditions, temperature (400, 500, 600 and 700 °C) and time (1,2,4 and 8 hours) on the properties of synthesized ZnO NPs were studied. The synthesis of PANI/Pul Cs were carried out through oxidative polymerization of aniline monomer in the presence of pullulan. The mass ratio of aniline to pullulan was varied as 1:0, 1:1, 1:3 and 1:5. A series of nZPP NCs was fabricated through chemisorption process between ZnO NPs and PANI/Pul C. The weight percent of PANI/Pul C were varied as 2, 6 and 10 wt % in comparison to ZnO NPs.

(b) All the synthesized samples were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectrophotometer (UV-Vis), transmission electron microscopy (TEM), surface area and pore analyser and thermogravimetric analysis (TGA) techniques. The impact of synthesis parameters variation on the properties of produced materials was evaluated based on the result of characterizations.

(c) The photocatalytic activity of ZnO NPs, PANI/Pul Cs and nZPP NCs were evaluated using Rhodamine B (RhB) dye. For ZnO NPs, all the catalysts produced at different calcination conditions were tested for their photocatalytic activity through degradation of RhB. The photocatalytic conditions used were 0.2 g/L catalyst dosage, 10 ppm dye concentration and pH remain unchanged (pH 5). Similarly, with PANI/Pul Cs, all the catalysts produced were tested for their photocatalytic activity against degradation of RhB. The photocatalytic conditions used were 0.5 g/L catalyst dosage, 10 ppm dye concentration and pH remain unchanged (pH 5). The ZnO NPs and PANI/Pul Cs with the best photocatalytic activity respectively were selected for the fabrication of nZPP NCs. All the synthesized nZPP NCs were subjected to photodegradation of RhB with experimental conditions of 0.2 g/L catalysts dosage, 10 ppm dye concentration and solution pH remain unchanged (pH 5).

(d) The optimum catalyst and condition for photodegradation of RhB over nZPP NCs was identified by RSM experiment using central composite design (CCD) develop by Statistica 13.0 Statsoft. The parameters including weight percent of PANI/Pul C (2 – 10 wt %), pH (5 – 11) and catalyst dosage (0.2-1.2 g/L). The performance of the catalysts was evaluated by analysing the response which is the degradation rate of RhB. The model was then validated and the optimize sample was obtained from the model generated. The optimized sample was then subjected to two other several photocatalytic testing such as reusability test and determination of active radical species. Then the optimized sample was used for degradation of simulated dye wastewater which was created by combining five dyes such as RhB, methyl orange (MO), methyl red (MR), methylene blue (MB) and crystal violet (CV).

1.5 Significance of research

Water pollution is a major environmental issue and with the additional problem of water scarcity, the recovery of wastewater and its treatment is one of the main ways to overcome the matters. AOPs, especially photocatalysis emerged as the alternative treatment method to water pollution. With the recent focus towards clean and green process, green synthesis emerged as a preferable method in the production of materials. This work reported on the usage of pullulan in the production of ZnO NPs and PANI/Pul Cs, which has never been reported before. For ZnO NPs, green synthesis technique was employed with pullulan as the capping agent. With the implementation of green synthesis process, the adverse effect towards the environment can be minimized as the usage of toxic chemical reagents was avoided. Furthermore, this work also studied the impact of calcination conditions, temperature and time, on the properties of ZnO NPs and their activity towards degradation of RhB. For PANI/Pul Cs, it was produced via oxidative polymerization in the presence of pullulan. It was found that the presence of pullulan improved the overall properties of PANI/Pul Cs towards the degradation of RhB. Nanocomposites consists of the synthesized ZnO NPs and PANI/Pul Cs (nZPP NCs) were then produced via chemisorption process. To the best of our knowledge, this synthesized nanocomposite has not been reported before. Furthermore, there are still lacking of research on utilization of conducting polymer as composites materials for photocatalyst. Overall, it will be a good contribution to knowledge to study about the utilization of pullulan in the production of ZnO NPs and PANI/Pul Cs and the fabrication of nZPP NCs as photocatalyst for dye degradation.

1.6 Thesis outline

This thesis consists of five chapters. Chapter 1 is introduction to the thesis which includes the background of research to give the main idea of this study. The problems and issues that can be addressed by this research is explained in the next section. Then the research objectives are stated followed by scope of study that will be conducted to fulfill the objectives. Finally, the significant of research is also covered in this chapter.

The second chapter is about the literature reviews. This chapter elaborates on nanotechnology and methods to produce nanomaterials with the focus being towards ZnO NPs, ZnO NCs and conductive polymer PANI, the current issues of water pollution, dyes as the pollutants, treatment methods and optimization process.

Chapter 3 describes the detail experimental methodology and the materials and chemicals reagent used in this study. A research methodology flowchart is also included to provide a general overview of the research.

Chapter 4 is about the results and discussion of the experimental works. This chapter is divided into six parts. First is regarding the fabrication of ZnO NPs and their photocatalytic activity followed by the fabrication of PANI/Pul Cs and their photocatalytic activity. Third is about the fabrication of nZPP NCs and their photocatalytic activity. Then the optimization of RhB degradation rate with nZPP NCs by response surface methodology (RSM) followed by the evaluation of photocatalyst reusability, photocatalytic degradation mechanism and proposed degradation pathway. The final part is the photodegradation of simulated dye wastewater with optimized catalyst.

The final chapter, Chapter 5 is the conclusion drawn from the study. The recommendation for future study is also proposed.

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LIST OF PUBLICATIONS

Web of Science Indexed Journals

1. **EDM Isa**, K Shameli, HJ Ch’ng, NWC Jusoh and R Hazan. (2021) Photocatalytic Degradation of Selected Pharmaceuticals using Green Fabricated Zinc Oxide Nanoparticles. *Advanced Powder Technology*, 32 (7), 2398-2409. (**Q1, IF: 4.833**)

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Non-indexed Journals

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