

**PHOTODEGRADATION OF METHYLENE BLUE USING COPPER OXIDE
PREPARED BY HYDROTHERMAL METHOD**

ENGKU MOHAMAD HAFZANURUDIN BIN ENGKU YUNUS

UNIVERSITI SAINS MALAYSIA

2018

**PHOTODEGRADATION OF METHYLENE BLUE USING COPPER OXIDE
PREPARED BY HYDROTHERMAL METHOD**

by

ENGKU MOHAMAD HAFZANURUDIN BIN ENGKU YUNUS

*Thesis submitted in partial fulfilment of the requirement
for the degree of Bachelor of Chemical Engineering*

June 2018

ACKNOWLEDGEMENT

First and foremost, I would like to convey my sincere gratitude to my supervisor, Dr. Noorashrina A. Hamid for her precious encouragement, guidance and generous support throughout this work.

I would also extend my gratitude towards all the MSc and PhD students for their kindness cooperation and helping hands in guiding me carrying out the lab experiment. They are willing to sacrifice their time in guiding and helping me throughout the experiment besides sharing their valuable knowledge.

Apart from that, I would also like to thank all SCE staffs for their kindness cooperation and helping hands. Indeed, their willingness in sharing ideas, knowledge and skills are deeply appreciated. I would like to express my deepest gratitude to my beloved parents, Engku Yunus Bin Tuan Derahman and Tuan Ruhani Binti Ku Jusoh for their continuous love and support.

Once again, I would like to thank all the people, including those whom I might have missed out and my friends who have helped me to the accomplishment of this project. Thank you very much.

Engku Mohamad Hafzanurudin Bin Engku Yunus

June 2018

TABLE OF CONTENTS

ACKNOWLEDGEMENT	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
LIST OF SYMBOLS	vii
LIST OF ABBREVIATION	viii
ABSTRAK	ix
ABSTRACT	x
CHAPTER ONE	1
INTRODUCTION	1
1.1 Problem Statement	4
1.2 Research Objective	4
1.3 Scope of Work	5
CHAPTER TWO	6
LITERATURE REVIEW	6
2.1 Implementation and Consequence of Methylene Blue	6
2.2 Method of Dye Removal	7
2.3 Photocatalytic Performance Copper Oxide Nanostructure	11
2.4 Main Active Species in Photocatalytic Experiment	12
2.5 Route for Producing Copper Oxide Nanostructure	13
CHAPTER THREE	19

MATERIALS AND METHODOLOGY	19
3.1 Introduction	19
3.2 Materials and Chemicals	21
3.3 Equipment and Instrumentation	21
3.4 Apparatus	22
3.5 Copper Oxide preparation	23
CHAPTER FOUR	29
RESULT AND DISCUSSION	29
4.1 Scanning Electron Microscope (SEM)	29
4.2 X-Ray Diffraction	33
4.3 UV-Vis	35
4.4 Brunauer Emmett Teller (BET)	39
CHAPTER FIVE	40
CONCLUSION AND RECOMMENDATIONS	40
5.1 Conclusion	40
5.2 Recommendations	41
REFERENCES	42

LIST OF TABLES

Table 3.1: Materials and Usage	21
Table 3.2: Equipment and Instrumentation.....	21
Table 3.3: Apparatus and Usage	22
Table 4.1: BET Test Results	39

LIST OF FIGURES

Figure 2.1 : Photocatalytic Performance of Catalyst (Tju et al., 2017)	12
Figure 2.2: Degradation Efficiency over Time (Tju et al., 2017).....	13
Figure 2.3: Growth Mechanism of Crystal during Hydrothermal Process (Jiang et al., 2014).....	14
Figure 3.1: Process Flow Experiment.....	20
Figure 4.1: SEM image for Sample Prepared by Hydrothermal Process at Temperature 110 °C and 134 °C.....	30
Figure 4.2: SEM image for Sample Prepared by Hydrothermal with NaOH Dosage 1 M and 0.5 M.....	32
Figure 4.3: XRD pattern for CuO nanostructure (from the standard card JCPDS 72-0629) (Jia et al., 2009).....	34
Figure 4.4: XRD pattern of CuO nanosphere synthesized by hydrothermal process	34
Figure 4.5: Effect of Different Concentration of Copper Acetate and Urea Towards .Photodegradation of Methylene Blue	36
Figure 4.6: Effect of Different Temperature towards Photodegradation of Methylene Blue	37
Figure 4.7: Effect of Addition of NaOH Towards Photodegradation of Methylene Blue	38

LIST OF SYMBOLS

	Symbol	Unit
a	BET equation constant	-
C	BET constant	-
C_e	Equilibrium concentration of adsorbate	mg L^{-1}
C_o	Highest initial adsorbate concentration	mg L^{-1}
n	Amount of gas adsorbed	molg^{-1}
n_m	Monolayer capacity	-
P	Solvent partial pressure in the gas phase	Torr
N_A	Avogadro Number	mol^{-1}
P_o	Saturated solvent vapor pressure	Torr
S_{BET}	BET specific surface area	m^2g^{-1}

LIST OF ABBREVIATION

AOP	Advanced Oxidation Process
BET	Brunauer Emmett Teller
CF	Coagulation/Flocculation
CO	Chemical Oxidation
COD	Chemical Oxygen Demand
FCZ	Ferum Copper Zinc Composite
FZ	Ferum Zinc Composite
MB	Methylene Blue
MH	Microwave-Assisted Hydrothermal
MO	Methyl Orange
NF	Nanofiltration
NS	Nanostructure
OH	Reactive Hydroxyl Radicals
PAC	Poly-Aluminium Chloride
PCB	Polychlorinated Biphenyls
PDDA	Poly-Diallyldimethylammonium Chloride
PEG-400	Polyethylene Glycol
PEI	Polyetherimide
Rh-B	Rhodamine-B
Rhodamine 6G	R6g
RO	Reverse Osmosis
SEM	Scanning Electron Microscope
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
UF	Ultrafiltration
UV	Ultraviolet
UV-Vis	Ultraviolet–Visible Spectroscopy
XRD	X-Ray Powder Diffraction

FOTODEGRADASI METILENA BIRU MENGGUNAKAN KUPRUM OKSIDA DISEDIAKAN MELALUI KAEDAH HIDROTHERMAL

ABSTRAK

Methylene Blue (MB) telah digunakan dalam banyak industri secara meluas. Pelaksanaan MB tanpa rawatan boleh mengakibatkan banyak kesan negatif kepada kehidupan akuatik. Manusia juga tidak terkecuali untuk terdedah dengan kesan negatif MB yang tidak dirawat kerana manusia memerlukan air untuk hidup. Cara termudah untuk rawatan MB adalah fotodegradasi yang menggunakan cahaya matahari yang merupakan sumber semulajadi untuk mengoksidakan MB. Kajian terus dengan mensintesis pemangkin tembaga oksida (CuO) untuk photodegradation MB menggunakan proses hidroterma yang merupakan cara yang mencukupi untuk mendapatkan kristal yang diingini dengan keadaan ringan, morfologi yang dikawal, pengagregatan yang rendah dan kristalografi yang tinggi. Proses hidrotermal diubah dengan suhu, kepekatan prekursor dan penambahan NaOH. Selepas itu, sampel akan menjalani pencirian yang mengimbas mikroskop elektron (SEM), X-Ray Diffraction (XRD), spectroscopy yang dapat dilihat Ultraviolet (UV-VIS) dan Brunauer Emmett Teller (BET). Hasil daripada eksperimen menerangi saiz struktur yang lebih besar apabila peningkatan kepekatan. Crystallinity juga dipertingkatkan apabila peningkatan suhu dan penambahan NaOH menjadi prekursor telah menghasilkan kesan besar kepada CuO morfologi, fasa dan prestasi penyingkiran. Parameter optimum proses hidroterma untuk mempunyai peratusan penyingkiran pewarna yang luar biasa ialah 0.05 M acetate tembaga dan urea, 134 °C dan penambahan 1 M NaOH.

**PHOTODEGRADATION OF METHYLENE BLUE USING COPPER OXIDE
PREPARED BY HYDROTHERMAL METHOD**

ABSTRACT

Methylene Blue (MB) has been used in many industries widely. The discharging of MB without treatment may lead to many negative effects to aquatic life. Humans are also no exception to be exposed to the negative effects of untreated MB because they need water to live. The easiest way for MB treatment is photodegradation that used sunlight that is natural source to oxidize the MB. Study continued with synthesizing Copper Oxide (CuO) catalyst for MB photodegradation using hydrothermal process that is adequate ways to obtain desirable crystals with mild condition, controllable morphology, low aggregation and high crystallinity. Hydrothermal process was varied with temperature, concentration of precursor and addition of NaOH. After that, the sample will undergo characterization which scanning electron microscope (SEM), X-Ray Diffraction (XRD), Ultraviolet-visible spectroscopy (UV-VIS) and Brunauer Emmett Teller (BET). Result from experiment illuminate size of structure bigger when concentration increase. Crystallinity also enhanced when temperature increase and addition of NaOH to precursor had produce big impact to CuO morphologies, phase and removal performance. The optimum parameter of hydrothermal process to have magnificent dye removal percentage is 0.05 M of copper acetate and urea, 134 °C and addition of 1 M of NaOH.

CHAPTER ONE

INTRODUCTION

Methylene Blue (MB) are commonly used in textiles industries during dyeing process. Large amount of waste produced which contain high concentration of chemical and colour. Improper treatment could cause big negative impact on environment. Generally, dyeing process was used in textile, dyestuff, paper and plastic industries to colour their product while consuming substantial volume of water. Colour was the first contaminant that can be observed and need to be removed before discharging of wastewater. With the presence of dye with very small amount which was even less than 1ppm, the colour was highly visible and affects the aesthetic merit, water transparency and gas solubility of water. Then, the pollution of dye potential was primarily prompted the concern about their possible toxicity and carcinogens (Banat et al., 1996).

There were multiple ways founded to remove the dyes which consist of chemical method, physical treatment and biological treatment (Robinson et al., 2001). Example of chemical method is oxidative process that used hydrogen peroxide (H_2O_2) as oxidizing agent. However, H_2O_2 need to be activated by ultraviolet (Marechal, 1997). Photochemical also being used to degrade dyes to H_2O and CO_2 by using UV treatment in presence of H_2O_2 . Degradation is caused by the presence of high concentration of hydroxyl radicals. Additional by-products such as halides, metals, inorganic acids, organic aldehydes and organic acid also produced depending on initial materials and the extent of decolourisation treatment (Yang, 1998). Dye also can be removed by using electrochemical destruction technique. The breakdown metabolites are generally not hazardous, and it was safe leaving into waterways. However, relatively high flowrates for dye removal and cost of electricity was comparable to the price of chemicals (Ogutveren, 1994).

Physical treatment commonly used to remove dye is adsorption and membrane filtration. Decolourisation during adsorption process was caused by adsorption and ion exchange which affected by many physio-chemical factors such dye adsorbent interaction, adsorbent surface area, particle size, temperature, pH and contact time (Kumar, 1998). Meanwhile, membrane filtration process of removing dye has the ability to clarify, concentrate and able to separate dye continuously from effluent (Mishra, 1993). This process also has high resistance to temperature and adverse to chemical environment and microbial attack. Then, it was suitable for water recycling within textile dye plant with low concentration of dye because concentrated residue lead to disposal problems (Robinson et al., 2001).

Lastly for biological treatment for removing dye, decolourisation by white rot fungi and adsorption by living/dead microbial biomass were used. White rot fungi were organisms that were able to degrade lignin which was structural polymer in woody plant (Barr, 1994). The most widely studied white rot fungus was Phanerochaete Chrysosporium which capable to degrade dioxins, polychlorinated biphenyls (PCB) and other chloro organics. Kirby (1999) shown that Phanerochaete Chrysosporium had the ability to decolourise artificial textile effluent as high to 99% throughout 7 days. Then, adsorption of living/dead microbial biomass was obtained by accumulation of chemicals by microbial mass that have been termed biosorption. Depending on dye and the species of micro-organism used, capacities and binding rate would be different (Polman, 1996).

Studies also showed that degradation of dyes was seen as a cost effective method to remove the pollutant from environment (Banat et al., 1996). Oxidation processes have been taking interest to remove methylene blue (MB) from solution. It is because highly reactive hydroxyl radicals (OH) were generated that leads into oxidative degradation of organics (Li et al., 2017). Many types of metal oxide nanoparticles have been produced such as TiO₂, Fe₃O₄, SnO₂ and CuO to provide oxidative degradation of various types of organic dyes such as methylene blue (MB), methylene orange (MO) and Rhodamine 6G (R6G) in wastewater. Copper Oxide (CuO) was commonly chosen among others because it has environmental stability, high catalysis efficiency and low cost materials (Li et al., 2017). CuO is a p-type semiconductor with a narrow band gap of 1.2 eV and can be used in catalysis, semiconductors, batteries and gas sensors. Multiple studies have been done to synthesize various CuO nanostructures with morphologies that can be controlled.

Chemical properties and physical properties of CuO nanostructure highly depend on its size and shape (Jia et al., 2009). CuO nanostructure can exist in the form of nanotubes (Sun et al., 2012), nanowires (Zhu et al., 2010) and nanospheres (Jia et al., 2009). Then, CuO can also be prepared in multiple ways, which include the solid state method, sol-gel method and hydrothermal method. For the solid state method, reactants are mixed and heated up at the required temperature (Sohrabnezhad and Valipour, 2013). For the sol-gel method, reactants are mixed and stirred vigorously and then cooled down to obtain the gel (Zeng et al., 2017). Then, for the hydrothermal method, the reactants are mixed and then heated at a constant temperature for a set time inside a Teflon-lined stainless steel autoclave and cooled down naturally at room temperature (Jiang et al., 2014).

1.1 Problem Statement

CuO nanostructure properties such as size, morphology and specific surface area are highly dependent on preparation method. Hydrothermal process was commonly used to synthesis CuO nanostructure because it was easy to manipulate, scalable production, well defined size and shape and low cost (Jiang et al., 2014). Jia et al. (2009) stated that CuO exhibit uniformity in size and shape which consist uniform nanoneedles. The size can be controlled with change the reactant concentration. Then, newer study Jiang et al. (2014) stated that well CuO nanosheet were synthesized at low temperature when in a large quantity using hydrothermal method. The morphology of CuO can be changed by adjusting concentration, precipitant and temperature. With all the information obtained, further study was continued using CuO and urea as reactant with changing parameter of concentration of reactant, temperature and precipitant to observe the effectiveness of CuO obtained using hydrothermal method. However, the effect of CuO prepared with different concentration of reactant, temperature and addition of surfactant toward photodegradation of MB has not yet done so far. Thus, this research is focusing to study the latter parameter and to observe the performance of CuO to remove methylene blue by degradation process.

1.2 Research Objective

- i. To investigate effects of reaction concentration as well as hydrothermal temperature towards and nanostructure CuO
- ii. To study the effect of NaOH to nanostructure CuO
- iii. To determine the efficiency methylene blue degradation using fabricated nanostructure CuO

1.3 Scope of Work

The scopes of the research were presented to achieve the three outlined objectives above:

- i. Copper Oxide (CuO) nanostructure (NS) was chosen as main catalyst for this experiment. The CuO NS will be synthesized by using hydrothermal method with variation of concentration and temperature. Sample of experiment will be characterized using XRD and SEM
- ii. With the optimum sample obtained from optimum concentration of reactant and temperature during hydrothermal process, further study will be carried out using sodium hydroxide (NaOH) as precipitant. Variation amount of precipitant will be added. Sample of experiment will be characterized using XRD, SEM and BET
- iii. For the final objective, the most optimum CuO NS will be studied its efficiency towards degradation of methylene blue using UV-Vis Spectrometer.

CHAPTER TWO

LITERATURE REVIEW

2.1 Implementation and Consequence of Methylene Blue

Coloured chemical has been stated by Tao et al. (2015) and Rafatullah et al. (2010), that it has been used by textile, leather, paper, plastics, etc., to colour their product and uses high volume of water. Annually, it is estimated more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff produced. Methylene blue is commonly used to dye cotton, wood and silk to produce eye catching products. Ghosh and Bhattacharyya (2002) added that water pollutions in industries that involve organic dye have high possible harmful effects and affect the aesthetical colour of water. It is stated that the methylene blue has multiple harmful effects although it is not strongly perilous. Accidentally ingesting MB will cause a burning sensation and may lead to nausea, diarrhoea, vomiting and gastritis. If people inhale MB, they can feel short period of rapid or difficult breathing. The effects of MB can become more severe with a large dose, that it can cause abdominal and chest pain, profuse sweating, mental confusion, painful micturition and methemoglobinemia. Also, Houas et al. (2001) stated that the release of coloured wastewater in the ecosystem can cause non-aesthetic pollution, eutrophication in aquatic life.

2.2 Method of Dye Removal

There are two components of dye, which are dye chromosphere and dye auxochrome. The chromosphere structure which have double bond (C=C), will oscillate to absorb light and produce visible colour when exposed to light. Methods of removal for these dyes consist of three types, which are physical method, chemical method and biological method.

Physical Method

The physical method consists of adsorption, coagulation/flocculation (CF) and membrane separation. The adsorption method is popular and effective method, but the activated carbon is not cheap. The adsorption efficiency also reduces drastically after regeneration and reactivation, which is up to 10-15 % reduction of adsorbent. Galán et al. (2013) stated that the activated carbon is an efficient adsorbent for different types of dyes, but it has regeneration limit and unfavourable cost. For economically practicable application of the adsorption method, some researchers used a low-cost adsorbent material such as peat, bentonite clay, fly ash and polymeric resins. Other than that, there are also scientists who studied to try biotic resources like wheat residue, treated ginger waster, ground nut shell charcoal, date stones and potato plant waste for the decolourisation of textile wastewater. These applications had been restricted due to the dumping problem, sludge generation and expensive adsorbent. From Gupta et al. (2016), adsorbents method should be applied only when there is low concentration of pollution, low cost of adsorbent and easily regenerated.

Besides that, the coagulation/flocculation (CF) has been widely used for the dye removal because it has low capital cost and easy operation. Coagulation is a process to destabilize the dye inside the wastewater to form agglomerates and floc. Flocculation, on the other

hand, is a process of destabilizing the suspended particles and bringing the aggregated flocs to form larger agglomerates that can settle down to the bottom through gravity force. For coagulation process, charge neutralization usually become initial requirement. Liang et al. (2014) studied to select proper coagulant and selecting suitable flocculant. It is founded that PAC is the most favourable coagulant to remove dyes due to the charge neutralization and promoted formation of flocs. PDDA is recognized as the most proper flocculant because it can create synergetic effects with PAC that can enhance dye removal. Good flocculant also has high growth rate of flocs and minimize breakdown of aggregates.

Besides, the dye also can be separated using pressure driven membrane technology such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). UF is proven to be able to separate high molecular weight molecule and insoluble dyes from water. Then, RO has the highest efficiency compared to NF and UF. However, it requires high pressure that can prevent its wide application. NF has higher efficiency than UF but lower than RO. It was introduced in early 1980s, with low operating pressure and low capital and operating cost. Most of NF membranes use negative charged flat-sheet composite membranes that have high fouling tendency due to the foulants that are usually positive charged. Further research continues with NF spiral wound membranes that have higher surface area per unit volume. Shao et al. (2013) studied NF membrane further with new thin-film composite NF hollow fibre membrane by interfacial polymerization on inner surface of polyetherimide (PEI) hollow fibre supports that can remove 90 % of dyes.

Chemical Method

Chemical method is also called oxidation method, consists of two methods which are advanced oxidation process (AOP) and chemical oxidation (CO). Both processes can degrade toxic initial, byproduct chemical, dyes and pesticides under ambient condition. For AOP, these processes involve hydroxyl radicals which act as a powerful oxidizing agent produced in adequate amounts. Most dyes reacts with hydroxyl radicals with high rate reaction constant (Asghar et al., 2015). The hydroxyl radicals also can oxidize many types of complex organic and inorganic chemicals present in the textile discharged water. AOP process also includes photocatalytic oxidation which uses sunlight for activation of semiconductor catalyst and Fenton chemistry that involved Fe^{3+} and H_2O_2 . Complex organic pollutant can be removed effectively using Fenton's reagent that is resistant to biological degradation.

Chemical oxidation involves oxidizing agents such as O_3 and H_2O_2 that can form strong non-selective hydroxyl radicals at high pH value. The hydroxyl radicals that are produced has high oxidation potential that can actively break down the conjugated double bonds of dye chromophores as effective as other functional group. The following generation of smaller non-chromophoric molecules reduces the colour of effluent (Tehrani-Bagha et al., 2010). Chemical oxidation which also called ozonation has lower degradation rate of dye as compared to AOP method because it produces lower amount of hydroxyl radicals. It also has severe disadvantage of forming toxic byproduct due to ozone usage. However, ozonation can be done in gaseous state which does not raise the volume of wastewater and not produces sludge.

Biological Method

For biological method, only dissolved matter in wastewater can be removed. The ratio of organic load/dye and microorganism load, temperature and oxygen concentration highly affect the process effectiveness. Biological textile waste treatment can be divided into aerobic and anaerobic method. Aerobic treatment will use microbes to treat the waste with the presence of oxygen while for anaerobic treatment occur in absence of oxygen. The mix of anaerobic and vigorous technique is ordinarily executed in genuine practice which utilizes an anaerobic procedure to treat material wastewater of chemical oxygen demand (COD), trailed by the utilization of high-impact cleaning treatment to treat the subsequent material wastewater of low COD (Hunton and Wang, 2011).

Along these lines, anaerobic treatment brings about the age of methanogenic bio-gas having some calorific value. Some portion of the vitality produced by its burning at that point can be utilized for aerobic cleaning step. In these biological treatment, microorganisms adjust to material colors and new strong strains become normally out of survival prerequisite, which at that point change over a few colors into less perilous structures. In this framework, the biodegradation system for headstrong colors depends on the stroke of the compounds, for example, laccase, lignin peroxidase, NADH-DCIP reductase, tyrosinase, hexane oxidase and aminopyrine N-demethylase (Solís et al., 2012).

2.3 Photocatalytic Performance Copper Oxide Nanostructure

Copper oxide had been researched to be used as advanced materials to catalyst efficiently. From Tju et al. (2017), they had conducted a research about photocatalytic performance of CuO using Methylene Blue (MB) as an organic sample. After being tested under visible light irradiation, MB with catalyst had been kept in the dark for 30min to reach adsorption and desorption equilibrium.

From the Figure 2.1, we can see the difference of photocatalytic performance comparing FZ and FCZ. FZ is a catalyst from the combination of $\text{Fe}_3\text{O}_4/\text{ZnO}$ while FCZ is the same catalyst with addition of CuO. Degradation of MB was increased when there was addition of CuO. The experiment was further continued to find the optimum catalyst dosage. From 0.01 g to 0.03 g of catalyst, the degradation efficiency increased due to increased number of active sites that can lead to increase of formation of oxygen species.

From Xia et al. (2016), when subjected to light, the catalyst will be excited on nanocrystal surface and generate electron hole in the catalyst. It is also called polarization of catalyst. Under polarization of catalyst, the plasmon excited electrons move and accumulate on the surface of catalyst nanocrystal and will act as reservoir for photogenerated electrons from catalyst and promote charge separation. Hence, improve the survived holes on surface of catalyst and promote the charge separation.

After that, photocatalytic reaction also included transportation of adsorbate molecule over catalyst surface. Under light penetration, the adsorbate on the surface of catalyst reacted with photogenerated active species that can promote oxidation of adsorbate. It was also stated that when the initial concentration of methylene blue increased, the degradation efficiency decreased due to the blocking of light by dye

molecule. From Tao et al. (2015), both high dosage and low dosage of catalyst can lead into problem. Hence, the optimum dosage need to be studied.

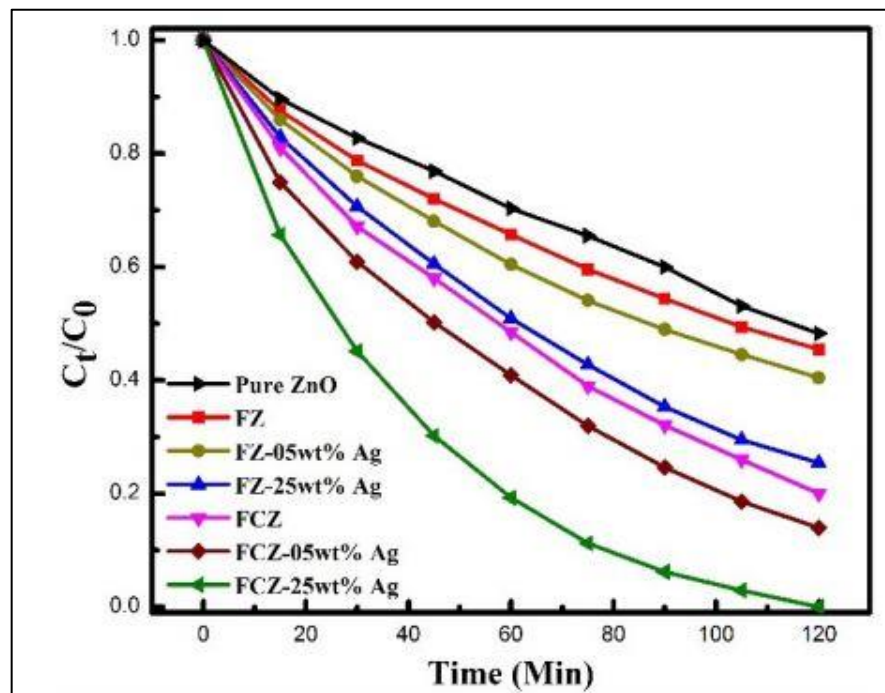


Figure 2.1 : Photocatalytic Performance of Catalyst (Tju et al., 2017)

2.4 Main Active Species in Photocatalytic Experiment

For further studies, Tju et al. (2017) controlled the experiment by adding small amount of trapping agent. Sodium sulphate, di-ammonium oxalate and tert-butyl alcohol were used to trap electron, OH and holes inside the catalyst. Result from Figure 2.2 shows that degradation efficiency of MB decreases clearly when adding hole scavenger (di-ammonium oxalate). It can be concluded that main active species in the photocatalytic experiment of catalyst nanostructure were holes, OH ion and electron.

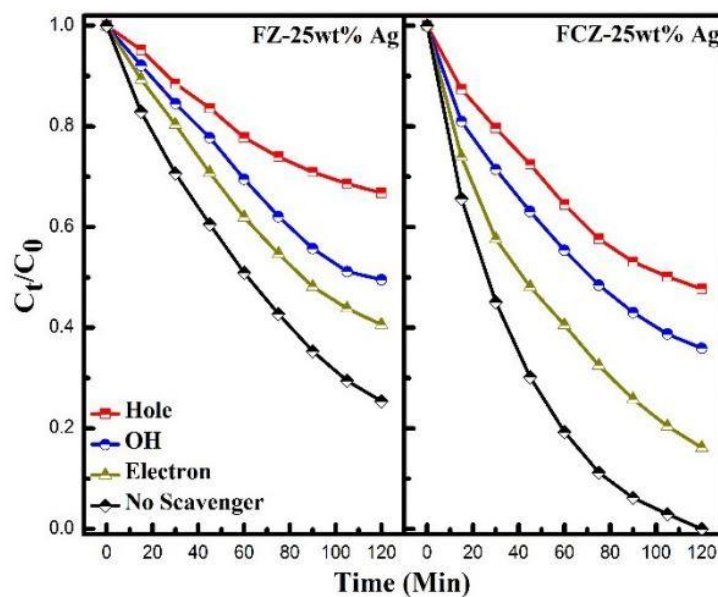


Figure 2.2: Degradation Efficiency over Time (Tju et al., 2017)

2.5 Route for Producing Copper Oxide Nanostructure

Hydrothermal Process Synthesizing Copper Oxide

From Jiang et al. (2014), hydrothermal reaction was an adequate way to obtain desirable crystals with mild condition, controllable morphology, low aggregation and high crystallinity. Temperature and pressure during hydrothermal process have explicit effects on microstructure of the product. While, Jia et al. (2009) said that CuO nanosphere can be obtained by directly adding copper acetate to the urea solution followed with hydrothermal process. Then, the amount of CuO nanosphere and microspheres depends on decomposition and formation rate at different temperature. Result of experiment shows that surface of CuO microspheres and nanospheres was smoother than previous research. It was proven that hydrothermal reaction was efficient and can yield CuO nanospheres and microspheres as high as ~90%. Then, Yang et al. (2013) claimed that hydrothermal process was easy to manipulate, scalable production, well defined size and shape and low cost.

From Jiang et al. (2014), the primary stages of hydrothermal process were dissolution of copper acetate and NaOH in water at room temperature lead to hydrolysis reaction of chemical. Figure 2.3 explained the formation of copper oxide process through hydrothermal. The heating of reactant will make the interplanar H-bonds breaks and speed up dehydration process. After bond breaking, $\text{Cu}(\text{OH})_2$ which was orthorhombic structure will rapidly into monoclinic structure of CuO nanoplates. Consequently, growth process can be continued on crystallographic planes of high atomic densities and improved thermodynamically favourable. The electron density of the ligands by steric impediment can varied the observed morphologies.

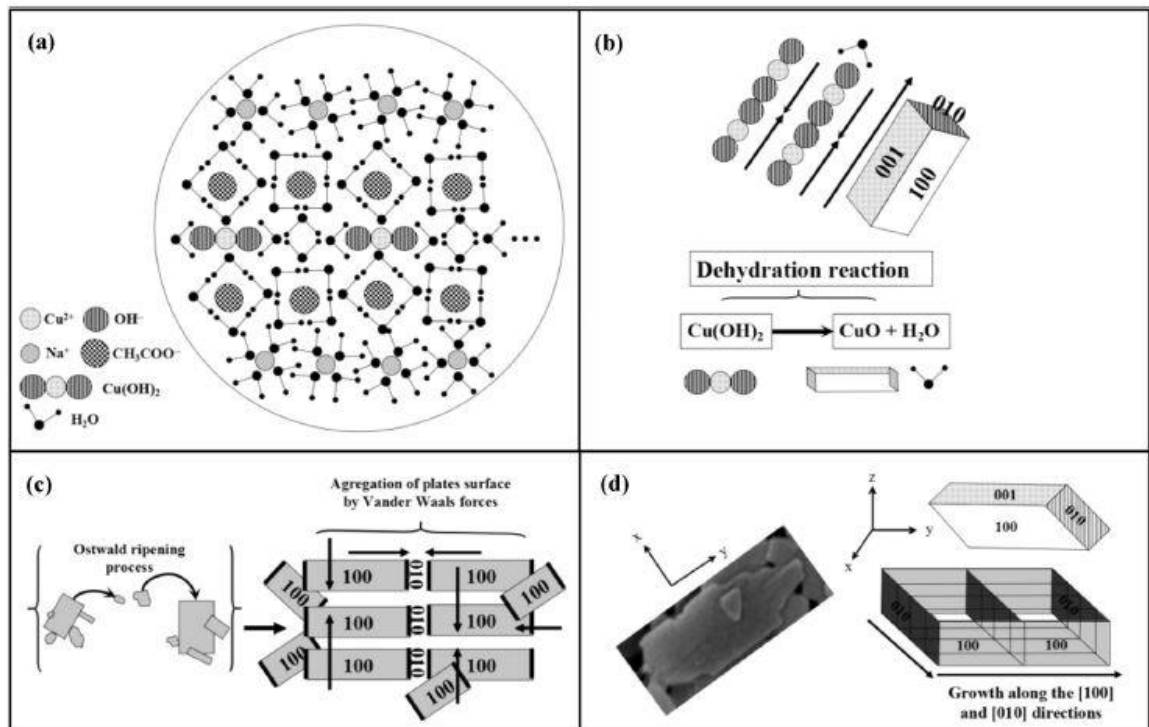


Figure 2.3: Growth Mechanism of Crystal during Hydrothermal Process (Jiang et al., 2014)

The growth of CuO nanocrystal can be explained by Ostwald ripening process (Hua Chun, 2007), which describing growth of larger crystal from smaller crystals because smaller has higher solubility than larger crystal. Colloidal particles formed in the

solution media and many chemical equilibria exist between solid and liquid interfaces. Then, the growth of nutrient across the bulk solution were changing because of the non-uniformity of crystal. Liu and Zeng (2005) stated, complete dissolution small crystal will happen when homogenization of concentration gradient as result the growth of large crystal. Ostwald process involves matter relocation of interior space for crystallite aggregates. Hence, the cavity will be generated in a location where crystallites were smaller and less compact during Ostwald process. However, at some cases, large crystallites can be essentially immobile while the smaller ones were mass relocation through solid-solution-solid process.

The results of the experiment by Jiang et al. (2014) had showed that with increasing copper acetate concentration, the nanostructure of copper oxide largely changed. The morphology of copper oxide obtained at low concentration of copper acetate was flower like structure. However, the structure changed into dispersed plum like structure. Jia et al. (2009) uncovered that the size of CuO sphere can be facilely and selectively controlled from several hundred nanometres to a few micrometres just by adjusting the concentration of reactant

When there were additional of sodium hydroxide as capping agent, Jiang et al. (2014) obtained the CuO with surfactant have sharper and narrower structure showing that there were better crystallinity on addition of surfactant. Hence, NaOH had played an important work to decide the morphology CuO nanostructure because OH⁻ largely related to the structure of nanocrystals. When Cu²⁺ or OH⁻ was not enough to form fin CuO nuclei spontaneously in aqueous complex solution, CuO nanocrystals would grow along with the surface of first seeds to use less energy that will formed tufted structure rather scattered crystals. Yang et al. (2013) had used low molecular weight polyethylene glycol (PEG-400) as surfactant that plays role as an inducer for formation of nuclei and directing

the growth metal oxide crystals through kinetic and selective adsorption in the surface of particles. PEG also helps to control the growth rates of crystallographic facets.

During the process temperature changed, Jiang et al. (2014) founded raising temperature at a certain temperature range can improve the crystallinity of nanocrystalline of nanocrystal. Jia et al. (2009) said that CuO sphere structure was stable at room temperature because extra ring pattern was still not observed after 10 minutes irradiation. However, due to local heating under SEM eletro-beam irradiation, the nanoparticles aggregated and coursen into solid nanosphere. Highly pure CuO can be obtained from one step reaction with low temperature without using templates and unfriendly ammonia. Yang et al. (2013) also stated that another important parameter that affects the phase transition from Cu(OH)₂ to CuO by thermos-dehydration was precipitation temperature.

Reaction time was also varied during hydrothermal process. Jiang et al. (2014) stated when the reaction time were extended, the higher and narrower diffraction peaks. It was indicated that reaction time had slight impact on the structure of CuO nanocrystal.

According to Yang et al. (2013), urea was used during precipitation process to decomposed into NH₃ and CO₂ at elevated temperature. Ammonia produced will be used for ammonia corrosion process under hydrothermal condition to evolve solid CuO microsphere into hollow CuO microsphere. Ammonia also can promote the partial dissolution of CuO nanoparticles in the synthetic system. Final size and shape of nanoparticles can be affected by the dissolve species that serve as growth unit for re-crystallization. Štengl et al. (2003) said pH of solution will be increased due to degradation of urea in synchrony with active release of OH⁻ and CO₃²⁻. The study shows that urea will be fully decomposed at temperature up to 80-85°C.

Sol-Gel Process Synthesizing Copper Oxide

Sol-gel chemistry is the preparation of inorganic polymers or ceramic from solution through changing of liquid to sol and then to gel. Nazeer et al. (2017) stated that sol gel consists of two stages of sol and gel formation. There are multiple parameters that could be controlled in sol gel method such as rate of solution formation, gel formation condition, type of catalyst, time of gel formation, changing of initial reactant and gel physical processing. Sol-gel chemistry is the preparation of inorganic polymers or ceramic from solution through changing of liquid to sol and then to gel. Danks (2015) said that there will be additional citric acid to form complex compound with zinc citrate. After that, the solution will be added with ethylene glycol to form a polymerization. The main usage of citric acid is to form complex compound nitrate.

Widiarti et al. (2017) described that during processing, the gel will be washed with distilled water and dried to temperature 120 °C to constant weight. The experiment continued with calcination at 500 °C for 4 hours to eliminate the organic compound and intermediate molecule. From XRD analysis, it was founded that CuO was composited on ZnO. After synthesizing, the particle size decreases because of the long aging process which is 48 hours. CuO-ZnO that synthesized were formed by CuO covered surface of ZnO, hence the composite followed the size of CuO. Surface morphologies 25 % CuO-ZnO have uniform shape and size. Large cluster was also not founded because of the low degree of agglomeration.

Solid State Synthesizing Copper Oxide

From Kumaresan (Jan 2015), solid state method used for synthesized Copper oxide by grounded together copper chloride and sodium hydroxide by adding surfactant. Furthermore, the salt will be annealed at 350 °C and 800 °C. It is obtained that crystalline size increases with the increases of annealed temperature. Result shows from SEM that at temperature 350 °C, CuO obtained in nanosphere structure while for sample at 800 °C have pebble shape nanoparticles. It shows that sample at higher annealing temperature is better. The study continues for photocatalysis of prepared CuO using degradation of Rhodamine-B (Rh-B) under visible-light. It is stated that the catalysis properties are affected by surface area of catalyst. Result shows that 350 °C annealed sample have better catalysis performance because it has bigger surface area.

One step solid state from Wang et al. (2001) was experimented in air room temperature within a short period. It was copper chloride and NaOH with additional PEG-400. Then, ethanol was used to remove PEG-400 after washing. Data acquired from XRD analysis have matched consistently with JCPSS showing highly pure CuO. Using TEM, nanorods structure has been observed because PEG-400 helps to form chain structure.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 Introduction

For this chapter, materials and method will be explained briefly about the experiment of research study on Figure 3.1. First, material, chemical and equipment needed to be identified before conducting experiment. Synthesizing of copper oxide are started with addition of urea and copper acetate into autoclave to make sure the bond is breaking down using hydrothermal process. Then, continue with characterization of sample using X-ray Powder Diffraction (XRD) analysis and Scanning Electron Microscope to identify the optimum parameter of hydrothermal process to obtain good sample of copper oxide. After that, the sample will undergo Brunauer Emmett Teller (BET) to determine total pore area. Lastly, the sample prepared will tested its catalytic performance on photodegradation of methylene blue using UV-Vis.

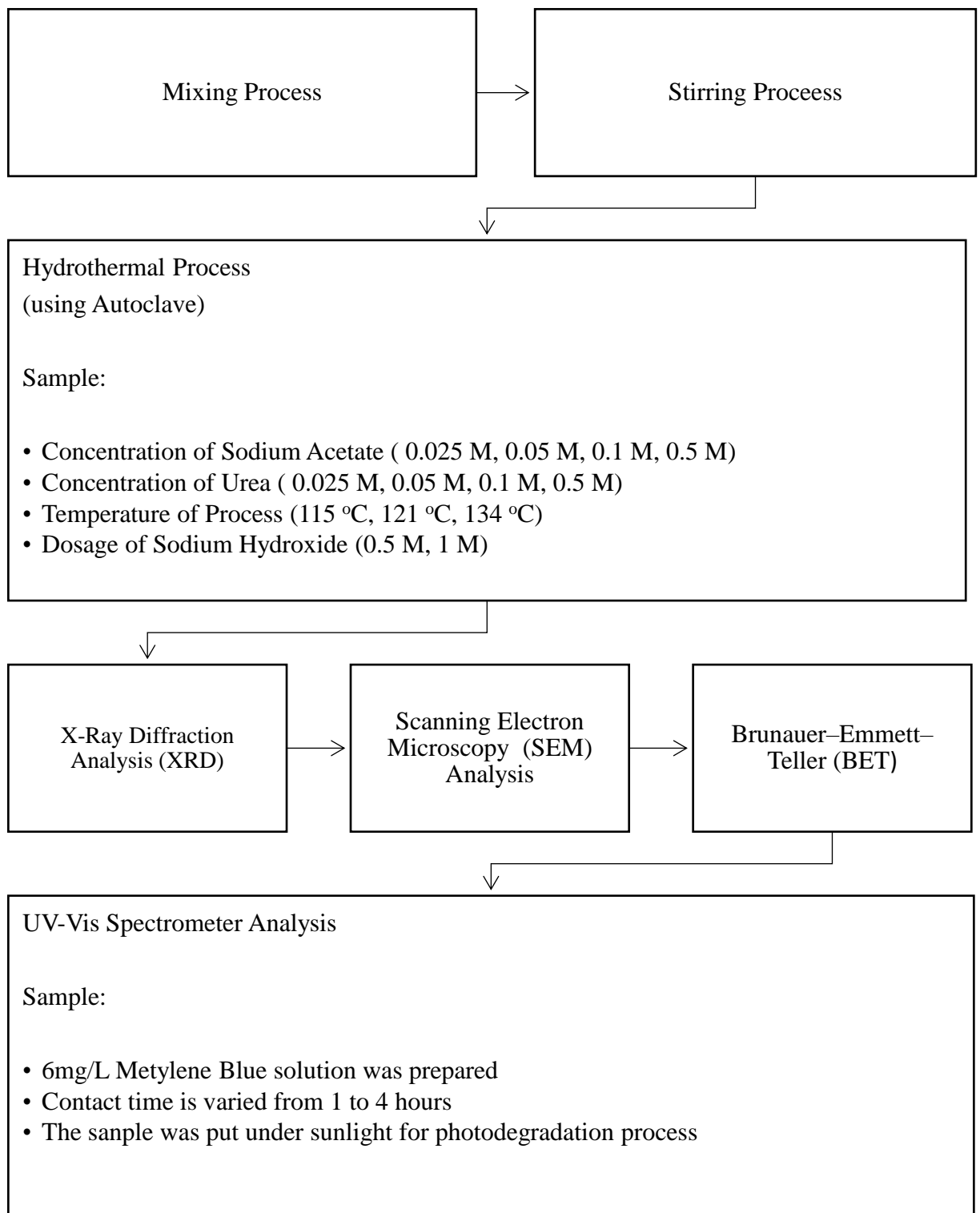


Figure 3.1: Process Flow Experiment

3.2 Materials and Chemicals

All chemical reagent such as copper acetate, ethanol, urea and sodium hydroxide were analytical grade and not purified after purchased. Copper acetate, urea and sodium hydroxide were purchased in solid form where it need to dissolve into deionized water for future use. While, ethanol was purchased in liquid form. Table 3.1 shows the list of chemical and its usage.

Table 3.1: Materials and Usage

Chemical/Material	Chemical Formula	Usage
Copper Acetate	$\text{Cu}(\text{CH}_3\text{COO})_2$	Raw Material
Urea	$\text{CH}_4\text{N}_2\text{O}$	Binder/Catalyst
Sodium Hydroxide	NaOH	Surfactant
Ethanol	$\text{C}_2\text{H}_6\text{O}$	Washer
Deionized Water	H_2O	Solvent/Hydrolyzer

3.3 Equipment and Instrumentation

Table 3.2: Equipment and Instrumentation

Equipment	Model	Usage
Scanning Electron Microscope (SEM)	-	To analyse the morphologies of the sample at suitable magnification
X-ray (XRD)	Diffraction -	To identify the phase of the crystal
UV-Vis Spectrometer	-	To check effectiveness of MB degradation using CuO

Centrifuge Machine	Eppendorf 5702	Centrifuge	To allow the crystal inside the solution to sediment
Electronic Stirrer	IKA KS 4000i control		To stir the sample for better mixing
Autoclave	Heuer		To allow hydrothermal process
Oven	Memmet		To dry the sample
Analytical Balance	Shimadzu		To weight the sample
Filter Paper	-		To filter the sample after centrifuge
Aluminium Foil	-		To cover the solution of urea and copper acetate during hydrothermal process to control the removal of vapor from solution

3.4 Apparatus

Table 3.3: Apparatus and Usage

Apparatus	Usage
Beaker	-To become the vase for solution of reactant
Centrifuge Tube	-Build in container for centrifuge machine
Petri Dish	-Place where formed CuO put into for drying process
Spatula	-To scrape off hard CuO nanocrystal on filter paper after dryer -To add and remove amount of reactant during weighing process

3.5 Copper Oxide preparation

To make sure the process proceeds smoothly, all the availability of equipment, apparatus and materials need to be checked out before running the experiment. All the step will be repeated with different concentration of copper acetate (0.025 M, 0.05 M, 0.1 M, 0.5 M) and urea (0.025 M, 0.05 M, 0.1 M, 0.5 M), temperature (115 °C, 121 °C, 134 °C) and addition of sodium hydroxide (NaOH) with different concentration (0.5 M, 1 M).

3.5.1 Calculating the Required Mass

For the first experiment, 0.025 M of urea and 0.025 M of copper acetate need to be used.

By using equation,

$$\text{Molarity} = \frac{\text{mol}}{\text{volume}} \quad (3.1)$$

Where,

$$0.025M = \frac{0.025\text{mol}}{L} = \frac{0.000025\text{mol}}{\text{mL}}$$

After that, multiply with the set volume to get the required mol

$$\frac{0.000025\text{mol}}{\text{mL}} \times 50\text{mL} = 0.00125\text{mol}$$

Multiply the mol of reactant with molecular weight of reactant

$$\text{Mass of urea required} = 0.00125\text{mol} \times \frac{60.06\text{g}}{\text{mol}} = 0.075\text{g}$$

$$\text{Mass of copper acetate required} = 0.00125\text{mol} \times \frac{181.63\text{g}}{\text{mol}} = 0.23\text{g}$$

Additionally, this method also can be used to prepared NaOH solution from solid state.

3.5.1 Weighing the Reactant

First, put all the material and apparatus near to weigh balance. Then put small beaker into weight balance and press “Tare” button and wait till the number on weight balance display turn to 0. Then, slowly put urea into the beaker until reading reach the requirement. After that, repeat the same process using bigger beaker to measure the mass of copper acetate into solution.

3.5.2 Mixing the Reactant

Put urea into copper acetate beaker. Rinse the reactant with deionized water slowly to make sure all the compressed copper acetate breaks down. After that, put the sample into electronic stirrer and set into 150 rpm and wait till the reactant completely mixed that can be indicated with the blue colour become paler.

3.5.3 Hydrothermal Process

Next, put the sample and into autoclave and set the machine into “program 2” that already set up with 115 °C and 30 minutes of sterilizing. Wait until the process stop and the machine cold down because sample can only be taken at temperature below 100°C.

3.5.4 Centrifuge Process

The sample will be cold down at room temperature and appearing precipitate can be observed. Sample will be put into centrifuge tube for further separation of solid from liquid using sedimentation process. Centrifugation process may take 20-30 minutes with 400 rpm.