UNIVERSITI PUTRA MALAYSIA

PHOTODEGRADATION OF METHYL ORANGE USING COPPER OXIDE DOPED ZINC OXIDE UNDER ULTRAVIOLET LIGHT IRRADIATION

SITI NUR SURHAYANI BINTI JEFRI

FS 2018 47

PHOTODEGRADATION OF METHYL ORANGE USING COPPER OXIDE DOPED ZINC OXIDE UNDER ULTRAVIOLET LIGHT IRRADIATION

By

SITI NUR SURHAYANI BINTI JEFRI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PHOTODEGRADATION OF METHYL ORANGE USING COPPER OXIDE DOPED ZINC OXIDE UNDER ULTRAVIOLET LIGHT IRRADIATION

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October 2017

Chairman : Associate Professor Abdul Halim bin Abdullah, PhD
Faculty : Science

Copper oxide doped zinc oxide photocatalyst was synthesized by sonochemistry method using $Zn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ as precursor and two different precipitation agents NaOH and NH_4OH. The precipitate was washed, dried and calcined at 400°C for 3 hr. The product was characterized by X-ray diffractometry (XRD), UV- Vis NIR Spectrophotometer, field emission scanning electron microscopy (FE-SEM), Transmission Electron Microscope (TEM) and surface area (BET method) . XRD result showed the sonicated ZnO produced by NaOH as precipitation agent has bigger crystallite size, 61.1 nm and the surface area was 4.43 nm2/g . After doping with CuO, the crystallite size decreased to 19.4 nm and the surface area increased to 8.2 nm2/g. The band gap energy of ZnO and CuO doped ZnO was 3.3 eV respectively. Majority of the particles were about 13.0 nm as obtained from the particle size distribution histrogram After doping with CuO, the particle size decreased to 10.8 nm. The efficiency of the photocatalyst was examined by photodegrading Methylene Orange (MO). The effects of photodegradation parameters such as photocatalyst mass loading, MO initial concentration and MO initial pH examined. The experiments were evaluated by photodegradation of methyl orange under UV light irradiation for 4 hours. Photocatalytic activities showed that the highest removal was when the 0.6g of 0.8% CuO doped ZnO used in 5ppm MO with pH 6.8 which is the percentage removal was 54.1%. Experimental design methodology also applied using response surface methodology (RSM). The multivariate experimental design was employed to develop a quadratic model as a functional relationship between the mg/g per of MO and three experimental factors (mass loading, MO initial concentration and MO initial pH). The highest removal of MO approached 12.8 mg/g when the 0.2g of 0.8% CuO doped ZnO used in 5ppm MO with pH 5.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

FOTODEGRADASI METIL OREN MENGGUNAKAN KUPRUM OKSIDA DIDOP ZINK OKSIDA DI BAWAH RADIASI SINAR ULTRAVIOLET

Oleh

SITI NUR SURHAYANI BINTI JEFRI

Oktober 2017

Pengerusi : Profesor Madya Abdul Halim bin Abdullah, PhD
Fakulti : Sains

Kuprum oksida didop dengan zink oksida disintesis melalui kaedah sonokimia dengan menggunakan $Zn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2.3H_2O$ sebagai bahan asas dan dua ejen pemendakan iaitu NaOH dan NH_4OH. Mendakan itu dibilas, dikeringkan dan dibakar pada suhu untuk 3 jam. Produk tersebut dianalisis menggunakan X-ray diffractometer (XRD), UV-Vis NIR Spectrophotometer, field emission scanning electron microscopy (FE-SEM), Transmission Electron Microscope (TEM) dan luas permukaan (kaedah BET). Keputusan XRD menunjukkan ZnO yang didedahkan dengan gelombang ultrasonik dan menggunakan NaOH sebagai ejen pemendakan mempunyai saiz kristal yang lebih besar, 61.1 nm dan luas permukaannya adalah 4.43 nm2/g . Selepas didop dengan CuO, saiz kristal menurun kepada 19.4 nm dan luas permukaan meningkat kepada 8.2 nm2/g. Tenaga band gap bagi ZnO dan ZnO yang didop CuO adalah 3.3 eV masing- masing. Melalui histogram pengagihan saiz partikel, saiz partikel bagi ZnO adalah 13.0 nm dan selepas didop dengan CuO, saiz partikel menurun kepada 10.8 nm. Keberkesanan pemangkin cahaya diuji menggunakan Metil Oren (MO). Efek parameter seperti berat pemangkin cahaya, kepekatan awal MO dan pH awal MO turut diuji. Eksperimen itu diuji di bawah sinaran UV selama 4 jam. Keputusan aktiviti pemangkinan cahaya paling tinggi adalah 54.1% dan dikesan apabila 0.6g 0.8% CuO didop ZnO digunakan di dalam 5ppm MO dengan pH 6.8. Kaedah merangka eksperimen juga digunakan melalui response surface methodology (RSM). Beberapa variasi eksperimen dirangka untuk mewujudkan model kuadratik sebagai hubungan berfungsi antara mg/g MO bersama tiga faktor eksperimen (berat pemangkin, kepekatan awal MO dan pH awal MO). Penyingkiran tertinggi adalah 12.8 mg/g apabila 0.2g of 0.8% CuO didop ZnO di dalam 5ppm MO dengan pH 5.

ACKNOWLEDGEMENTS

Alhamdulillah all the praises to Allah SWT finally i made it to the end. Thank you to my supervisor Assoc. Prof. Dr. Abdul Halim bin Abdullah for being patient and guiding me throughout my research. I would like to express my appreciation to my co-supervisors Dr. Ernee Noryana for giving me guidance and opinion to improve my research.

To all laboratory assistants from Faculty of Science, ITMA and Institute Bioscience for assisting me on handling equipments. Many thanks to my research group Afini,Syafiqah, Muhammad, Izsdihar, Zul, Nisa and Marylin for helping me a lot. To my lab mates Yati, Ain, Zida, Izzah, Hidayat and other for giving me motivation to keep on track.

Last but not least, to my husband Fauzan Shafieq,who giving me full of support and encouragement to finish my master, my children Fayyadh, Maryam and 'Aisyah for giving me strength, My parents and my siblings who keep giving me their magical words and everyone who contribute in this project.

I certify that a Thesis Examination Committee has met on 27 October 2017 to conduct the final examination of Siti Nur Surhayani binti Jefri on her thesis entitled "Photodegradation of Methyl Orange Using Copper Oxide Doped Zinc Oxide Under Ultraviolet Light Irradiation" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller surface area measurements
Eg	Band gap energy
FT-IR	Fourier Transform-Infra Red
FWHM	Full width at half maximum
JCPDS	Joint Committee of Powder Diffraction Standards
MO	Methyl orange
SEM	Scanning electron microscope
TEM	Transmission electron microscope
UV	Ultraviolet
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Water is important for all living things especially for human health and for the conservancy of the environment. However, according to United Nations (UN) for every ten persons in the world, about four do not have opportunity to the water sources and about two lack the sources of getting safe drinking water. Most of them are children, who die from illnesses due to insufficient water source and sanitation. Low water quality and poor hygiene are causing negative effects to the safety of foods and lifestyles.Water related disasters like tsunamis, storms and floods also contribute to problems such as hunger and malnutrition to poor countries.

About one billion people still have a restriction to get safe water and more than 2.5 billion people are having difficulties to get an adequate sanitation.Estimations have been made that by 2025 about more than half of the population will be facing this problem. Water inflation will be take place by 2030 in some developing countries, affecting 50% of the population (Kulshreshtha,1998).

Textiles industry is one of the leading contributors to the problem, as they are using a large amount of water in producing their products (Allegre et al.,2006).Every year there are about 80,000 tonne of reactive dyes generated and used for cotton colouring, but only a few of these are environmentally tolerant dyes. These intolerance dyes will be producing wastes which are extremely coloured,with high salts concentration (Hessel et al.,2007) . Hence, the removal of these the dyes is necessary since the color will highly pollute the quality of water (Crini,2006) and almost all of the dyes are justified as toxic and carcinogenic (Crini,2006; Mittal et al.,2007; Chen et al.,2010).

Methyl orange (MO) is one of dyes which has been widely utilised in textile, printing, paper, food and pharmaceutical industries and research laboratories (Mittal et al.,2007).It is an acidic dyes and has a mutagenic properties (Mittal et al.,2007; Chen et al.,2010). According to US OSHA, permissible exposure level is 5mg/m3. The elements of the dyes are also highly-resistant towards decay due to their stability to the light and oxidation (Chen et al.,2010).There are various techniques to get rid of the dye elements from water such as physical, chemical and biological methods (Crini,2006; Chen et al.,2010).This includes physical methods such as coagulation, adsorption on activated carbon, and reverse osmosis. Unfortunately, these methods are difficult to destroy, and required post-treatments of the materials (Perez et al.,2006).

Advanced Oxidation Processes (AOPs) is another technique for the degrading of dyes and other organics in wastewater and effluents. This technique involves either UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of pollutants.AOPs technique is largely available, inexpensive, non- toxic and leads to

total mineralization of organic chemicals to CO_2, water and mineral acids (Akyol et al.,2004). Many studies are carried out towards creating new catalyst purposely to remove these kinds of pollutants from polluted water (Perez et al.,2006).One of the semiconductor photocatalysts that had been studied widely is Titanium dioxide (TiO2)). TiO_2 is believed to be the greatest photocatalyst and it owns the capability to treat water (Kusvuran et al.,2005). Nevertheless, using TiO_2 is uneconomic for a massive scale of remediation, so that the research is still undergoing in the direction of seeking other photocatalyst besides TiO_2 (Kansal et al.,2007). Many studies have been done to investigate the photocatalytic activity of various semiconductors like SnO_2, ZrO_2, CdS and ZnO (Lizama et al.,2002; Neppolian et al.,2002; Akyol et al.,2004; Lathasree et al.,2004). In 2002, Lizama reported that the photocatalytic degradation of Reactive Blue 19 (RB-19) in aqueous solutions by using ZnO was more successful than TiO_2 (Lizama et al.,2002). Daneshvar reported that zinc oxide (ZnO) is the best option to TiO_2 for the photodegradation of Acid Red 14, because the degradation mechanism is similar to TiO2 (Daneshvar et al.,2003). The greatest benefit of ZnO is the absorption ability. It can absorb more fraction of solar range than TiO_2 (Sakthivel et al.,2003).

Doping the CuO will modify the ZnO photoluminescent (PL) transitions by forming an impurity levels (Garces et al.,2002). Besides, CuO with the energy level 0.17eV, acts as an receiver in ZnO (Kanai,1991).

1.2 Scope of Study

In this study, a preparation of of ZnO as undoped and doped with various percentage of CuO via co-precipitation method in the presence of NaOH and NH_4OH as precipitation agent. The introduction of ultrasonic power also will be introduced. The prepared photocatalyst was used as catalyst in photodegradation of methyl orange as organic dyes. The influences of parameters are studied to accomplish the degradation efficiency of dyes near 100%.

1.3 Objective

In this research, the main objectives are

- To synthesize ZnO using co-precipitation method with different co-precipitation agents and methods.
- To synthesize and characterize CuO doped ZnO using co-precipitation method with different ratios of CuO.
- To investigate the photodegradation activity and reaction of CuO doped ZnO with methyl orange as a pollutant under UV light irradiation

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