UNIVERSITI PUTRA MALAYSIA

VISIBLE-LIGHT PHOTODEGRADATION OF NITROBENZENE BY MICROWAVE SYNTHESIZED ZnO AND ITS NANOCOMPOSITES Ag/ZnO and Cu/ZnO

HAUWA ALIYU SIDI

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By

HAUWA ALIYU SIDI

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

December 2014

DEDICATIONS

I dedicate this work of mine to my beloved husband Sirajo Lawan Bichi and my late father Alhaji Aliyu Sidi and my beloved mother Hajiya Fatima Muhammad Yusuf. May the mercy of Allah be upon us all. Your support and courage is what made me what I am today. Thank you.

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

VISIBLE-LIGHT PHOTODEGRADATION OF NITROBENZENE BY MICROWAVE SYNTHESIZED ZnO AND ITS NANOCOMPOSITES Ag/ZnO AND Cu/ZnO

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Chairman: Associate. Professor. Dr. Abdul Halim Abdullah, Ph.D.
Faculty: Science

ZnO and Ag/ZnO was successfully synthesized using the microwave extraction irradiation at low temperature of 90^{o}C and power of 120 Watt while Cu/ZnO was produced at 240 Watt after 15 minutes. The synthesized nanopowders were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM) and X-ray Fluorescence (XRF). The band gaps energy of the nanocomposites were from absorption data obtained from UV-Vis-NIR spectroscopy. All the samples indicated the synthesized nanocomposites showed hexagonal ZnO structure. The average crystallite sizes of the composites estimated using Scherrer's equation was found to be less than 100 nm which is smaller than the actual particle sizes in the images obtained from transmission electron microscopy (TEM) analysis which were found to be below 200 nm with rod-like particle and this is true since in the actual sense crystallite size are expected to be small than particle size because it is group of crystallite particles that composes the crystalline material forming particle. The elemental composition of the samples were confirmed through EDX and XRF analysis. The photodegradation efficiency of the synthesized nanocomposites was evaluated by employing nitrobenzene as a model organic pollutant. Adsorption study was carried out in order to establish the adsorption-desorption equilibrium. And the maximum adsorption time was found to be 45 minutes with maximum catalyst load of 0.25 g for ZnO and Cu/ZnO and 0.5 g for Ag/ZnO. The efficiency of all the MW-synthesized nanocomposites was found to be higher than the commercial ZnO. Ag/ZnO was found to have the highest efficiency of 96.47% after 2 hours of photodegradation and adsorption process.

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

FOTODEGRADISI NITROBENZENA DIBAWAH CAHAYA NAMPAK OLEH ZnO DAN NANOKOMPOSITNYA Ag/ZnO DAN Cu/ZnO YANG DISINTESIS DENGAN GELOMBANG MIKRO

Oleh

HAUWA ALIYU SIDI

Disember, 2014

Pengerusi: Prof. Madya. Dr. Abdul Halim Abdullah, Ph.D.
Fakulti: Sains

ZnO dan Ag/ZnO telah berjaya di sintesis menggunakan sinaran gelombang mikro pada suhu rendah iaitu 90^{o}C dan kuasa sebanyak 120 watt manakala Cu/ZnO pada 240 Watt selama 15 minit. Serbuk bersaiz nano yang telah di sintesis dikaji menggunakan Pembelauan sinar-X (XRD), Mikroskopi Transmisi Elektron (TEM), Mikroskopi Medan Pancaran-Imbasan Elektron (FESEM) dan Pendafluor Sinar-X (XRF). Luang tenaga nanokomposit berdasarkan data daripada spektroskopi UV-Vis-NIR . Semua sampel menunjukkan ZnO berstruktur heksagonal. Purata saiz kristal nanokomposit yang dianggarkan berdasarkan persamaan Scherrer di dapati berada di dalam julat yang sama dengan imej daripada analisis TEM, iaitu dibawah 200 nm dengan partikel berbentuk rod. Komposisi elemen bagi sampel disahkan melalui analisis EDX dan XRF. Keberkesanan fotodegradasi nanokomposit yang di sintesis telah dinilai menggunakan nitrobenzena sebagai bahan pencemaran organik.
Kajian penjerapan telah jalan bagi mencapai keseimbangan penjerapan - penyahjerapan. Masa penjerapan tertinggi adalah 45 minit dengan maksimum jisim 0.25 g bagi ZnO dan Cu/ZnO dan 0.5 g bagi Ag/ZnO.
Nanokomposit yang di sintesis menggunakan gelombang mikro didapati lebih berkesan daripada ZnO. Keberkesanan Ag/ZnO iaitu sebanyak 96.47% selepas 2 jam proses fotodegradasi dan penjerapan.

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I certify that a Thesis Examination Committee has met on 8 December 2014 to conduct the final examination of Hauwa Sidi Aliyu on her thesis entitled "Visible-Light Photodegradation of Nitrobenzene by Microwave-Synthesized ZnO and its Nanocomposites of Ag/ZnO And Cu/ZnO" 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.

Members of the Thesis Examination Committee were as follows:

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Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkarnain b Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Anita Ramli, PhD
Associate Professor
Fundamental and Applied Sciences Department
Univeriti Teknologi Petronas
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 February 2015

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Master of Science**.

The members of the Supervisory Committee were as follows:

Abdul Halim Abdullah, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairperson)

Zulkifly Abbas, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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Committee:____________________

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LIST OF ABBREVIATIONS

Ag	Silver metal
AOPs	Advance Oxidation Processes
Au	Gold metal
AZ1-AZ8	Ag/ZnO samples prepared at different condition
BET	Brunauer-Emmett-Teller
CB	Conduction Band
Cu	Copper metal
CZ1-CZ8	Cu/ZnO samples prepared at different condition
Ebg	Energy band gap
Ecb	Conduction energy band
Ecg	Energy band gap
EDTA	Ethylene diammine tetraacetic acid (Disodium salt)
eV	Electron volt
Evb	Valence energy band gap
	Surface Photo-voltage Spectroscopy
HMT	Hexamethylenetetramine
mL	milliliter
MW	Microwave
NB	Nitrobenzene
NO	Nitrogen oxide
nm	Nanometer
O_2	Oxygen
PCA	Photo-catalytic Activity
Pd	Lead metal
SPS	Surface Photo-voltage Spectroscopy
STP	Standard temperature and pressure
TEM	Surface Photo-voltage Spectroscopy
Tempt	Temperature
TiO_2	Surface Photo-voltage Spectroscopy
Uv-light	Ultra violet light
Va	Pore volume
$V_{meso+micro}$	Volume of adsorbed gas at STP
Vm	Volume of adsorbed gas at STP to produce an apparent monolayer in a sample
XRD	Surface Photo-voltage Spectroscopy
XRF	X-ray fluorescence spectroscopy
λ	wavelength

CHAPTER 1

INTRODUCTION

Industries are the major source of waste water pollutants and these has globally drawn the attention of scientist due to the need for vital environmental, clean and friendly processes. Waste water can be harmful to both underground and surface sources of water and even to the environment as a whole (Kavitha and Palanivelu, 2005; Pardeshi and Patil, 2008). Fig. 1.1 illustrates the coagulation method for the treatment of extracted polluted underground water.

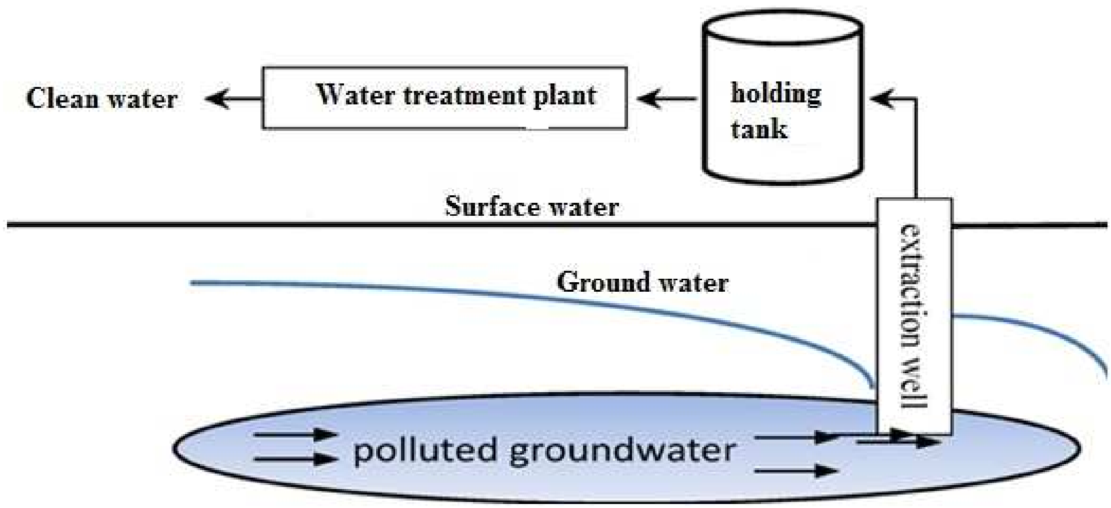

Figure 1.1: Schematic Diagram for the Treatment of Polluted Extracted Underground Water

Nitrobenzene [NB] aqueous, a poisonous aromatic organic waste water pollutant with bitter almond odor that is pale yellow in appearance, sometimes called oil of MIRBANE mostly used as aniline precursor chemical in the manufacture of textiles, pesticides,rubber materials pharmaceutical and cosmetics, is considered to be highly toxic organic pollutant that is easily absorbed in to the human body when inhaled or contacted through skin and causes sickness such as, headache, general body weakness, vertigo and sometimes vomiting (Thou-Jen et al., 2012). Due to this reason, nitrobenzene [NB] was choosen as the model organic pollutant in the present study. Hence the effective removal of this organic waste water pollutants is recently becoming both economic and environmental problem (Flox et al., 2007; Guyer, 1998). Therefore, different methods both physical and chemical processes have been developed in order to remove these pollutants such as; coagulation method, precipitation, ultra filtration, air stripping, adsorption using light activated carbon, UV-irradiated degradation and reverse osmosis. However, only UV-irradiated degradation was found to degrade NB with optimum efficiency of nitrobenzene residue as low as 8.8% achieved which is still considered insufficient and highly expensive. While all the other aforementioned existing water treatment processes and pollutant removal methods have a major drawback in the sense that they only end up transforming the pollutants into different phase instead of destroying them completely, and eventually may lead to more severe pollution (secondary pollution). Therefore it becomes necessary to develop methods of treatments that can lead to the complete destruction of the pollutants from industrial discharged waste water (Zhang and Zeng, 2012).

The utilization of advanced oxidation processes (AOPs) for the complete degradation (mineralization) of organic pollutants in waste water is of great interest in the recent years. The AOPs are mainly based on generation of species which are highly reactive such as the hydroxyl radicals capable of non-selectively oxidizing wide range of organic pollutants rapidly. Homogenous AOPs is found to face some limitations such as; environmental, economic and technical drawback, and this has lead to development of heterogeneous-based semiconductor photocatalysis and is currently considered to be most promising technique for the treatment of waste water and other processes of remediation. System of Photocatalysis involving combination of semiconductors and oxidants such as light are example of advanced oxidation processes (AOPs). Among these systems heterogeneous photocatalysis has gained considerable attention from scientists owing to its destructive ability in the elimination of most organic pollutants during waste water treatment (Fox and Dulay, 1993). On this basis, semiconductor photocatalysts have widely been used in various areas of environmental protection processes due to its unique property in the ability to decompose harmful organic pollutants into water, carbon dioxide and mineral acids which are non-harmful.

In photo-generated catalysis, the photo-catalytic activity (PCA) of the semiconductor highly relies on its electron-hole pair production capability, thus, creating free radicals (e.g. hydroxyl radical ^{-}OH) which can further undergo secondary reactions. Advanced oxidation process application was made possible after electrolysis of water was discovered using titanium dioxide. There are different ways advanced oxidation process (AOP) can be conducted without using TiO_2 as semiconductor and UV-light as light source for photo-degradation. Since the photo-catalytic activity relies on hydroxyl radical production capability of the semiconductor. The employment of nanocomposites photo-catalyst in the photodegradation of organic waste water pollutant has gained considerable interest in the recent years (Lai et al., 2010; Dunnil et al., 2009). Though various semiconductor photo-catalysts have been used, ZnO nanomaterial has received much attention due to its chemical and thermal stability, non-toxicity, high catalytic efficiency and low cost (Wojtoniszak et al., 2012). One of the major advantages of ZnO over other semiconductor nanocomposites is its ability to absorb great portion of solar spectrum, thus, able to remove many organic pollutants in an aqueous solution under visible light irradiation (Sakthivel et al., 2003; Pardeshi and Patil, 2008; Dindar and Icil, 2010).

However, the rapid recombination of photo-excited electron-hole pairs formed during photocatalytic processes limits the photo-catalytic efficiency of ZnO. Though recombination has faster kinetics than redox reaction, but it greatly reduces the quantum efficiency of photo-catalysis. Significant efforts have been made to retard the recombination of the photo-excited electron-hole pairs and enhance photo-catalysis by coupling the photocatalyst with other materials such as semi-conductors (Yong and Jung, 2011), metals (Kundu et al., 2011; Zhang and Zeng, 2012) carbon nanotubes (Ahmmad et al., 2008). One of the metals found having positive and great influence on the activity of ZnO nanoparticle is silver (Ag), and is achieved through the inhibition of charge recombination processes and capturing of the photo-induced charge carriers (Chang et al., 2009; Donkova et al., 2011). Silver Ag being very expensive metal used for coupling ZnO, hence the need for substitute with low cost metal of similar property and activity as silver. Another metals of interest is copper (Cu) being in the same group with silver, has been studied and applied for various reactions. Copper (Cu), is one of the metals of interest due to the fact that it is the same group with Ag and it is known that elements of the same group tend to have similar properties. Hence Cu metal has been widely used as catalyst for many reactions. Copper can enhance the photo-catalytic activity of ZnO due to the fact that it exhibit two oxidation states Cu^{+} and Cu^{2+} on the surface of ZnO. Cu^{+} can react with H_2O_2 on the surface of ZnO in order to generate the required ^{-}OH radical. There were little reports made on the photo-catalytic activity of Cu-coupled ZnO (Jongnavakit et al., 2012).

There has been no report on the use of microwave irradiation for the preparation of Cu coupled nanocomposite. Several methods have been reported for the preparation of metal/ZnO nanocomposites such as chemical bath deposition, hydrothermal method, photo reduction method, sol-gel method, non-ionic polymer assisted thermolysis (Pall and Sharan, 2002; Wang et al., 2007; Lu et al., 2008; Wang et al., 2011) and so on. However, most of these methods are limited to research purposes because of either the use of toxic reagents, high temperature, high pressure, expensive equipments or long reaction period. Thus, a fast, simple and more effective route for the preparation of metal/ZnO nanocomposites is still required to meet economic and industrial needs.

1.1 Micro-wave Oven Radiation

Micro-wave oven radiation technique has become an effective tool in synthetic removal of organic waste water pollutants in the field of photo-catalysis due to molecule collision created during friction, the microwave irradiation generates energy for heating and nucleation becomes accelerated (Alammar and Mudrig, 2009). The temperature of the reactant solution and its concentration gradient can be eliminated thus; a uniform nucleation can be achieved (Kathalingam et al., 2011). The microwave irradiation known to be a "non-conventional reaction condition" has been used to destroy large percentage of chemical compounds and materials and also accelerate reaction processes in different areas of chemistry and technology (Thou-Jen et al., 2012).

Microwave-based synthetic route is considered as one of the methods that is quick, energy saving, green and easy for production of nanoparticles in large scale. Microwave preparation method is considered as an energy-efficient, low-cost, eco-friendly, hygienic, rapid and a novel route and also very convenient heating method that leads to high production yield within short reaction period (Mohajerani et al., 2008; Fazhe et al., 2009).

1.2 Nanocomposite in Photocatalysis

In trying to enhance advanced oxidation processes, nanotechnology is considered as an alternative option in solving technical problems facing the effective removal of waste water in developing countries as reported by (Hillie and Hlophe, 2007). In order to increase removal efficiency rate with better cost/benefit ratio, nanocomposite materials can be used as catalyst/photocatalyst or part of the catalyst/photocatalyst in heterogeneous advance oxidation processes AOPs (Savage and Diallo, 2005; Doria et al., 2013). GDNP 2006 in a comparison between conventional and nano-based water technologies pointed out that the commonly used materials in nano-based technologies are mainly; titanium dioxide nanoparticle, nanoscale titanium dioxide photocatalyst, nanoscale zero valent ion and nanostructured iron oxide adsorbent. But due to the low cost and availability of zinc oxide and absorbs larger portion (fraction) of the solar radiation with ability to efficiently produce hydrogen peroxide (H_2O_2) makes it to be considered as suitable material for contaminant destructive technology and a nanocatalyst in heterogeneous AOPs.

1.3 Statement of the Problem

The rapid recombination of photo-excited electron-hole pairs generated during photocatalytic processes limits the photo-degradation efficiency of ZnO. Excessive loading of silver particles would shield UV-light adsorption, and thus, decrease the photon utilizing efficiency. Several methods have been reported on the preparation of Ag/ZnO and Cu/ZnO nanocomposites such as hydrothermal method (Lu et al., 2008), chemical bath deposition (Wang et al., 2011), sol-gel method (Lu et al., 2008), photo reduction method (Dindar and Icil, 2010), and so on.

However, most of these methods are limited to research work purposes due to the use of high temperature, toxic reagent, high pressure, long reaction time or expensive equipments. Thus, a simple, fast and more effective route is needed for the preparation of Ag/ZnO and Cu/ZnO nanocomposites for the treatment of organic waste water pollutants in order to meet both economic and industrial needs.However, no study has been conducted on organic waste water pollutant using Ag/ZnO and Cu/ZnO under visible-light irradiation. This work tends to look at the photo-degradation of

Ag/ZnO and Cu/ZnO nanocomposite photo-catalysts under visible-light irradiation. The effect of some variables such as; concentration of the organic pollutants, photocatalyst loading and pH on photo-degradation efficiency were studied. In addition the photo-products were investigated using total organic carbon content (TOC) measurements from TOC-VCSN Shimadzu.

1.4 Objectives

In general the main objective of this work is: Improve and enhance the photocatalytic performance of the ZnO by coupling it with Ag and Cu. The specific research objectives are:

- To synthesize ZnO and its nanocomposites Cu/ZnO and Ag/ZnO using microwave [MW] irradiation method by optimizing operational conditions such as temperature, power and time,
- To characterize the MW synthesized ZnO and its nanocomposites Cu/ZnO and Ag/ZnO using various solid state characterization techniques such as XRD, TEM, BET, XRF, FESEM, UV-Vis-NIR,
- To evaluate the photo-catalytic performance of the nanocomposites, by measuring removal ability of nitrobenzene by the synthesized ZnO and its nanocomposites Cu/ZnO and Ag/ZnO under visible light irradiation.
- To optimize the photodegradation efficiency of nitrobenzene by the prepared catalysts taking into consideration pH, maximum catalyst load and maximum pollutant concentration.

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