SYNTHESIS OF SILVER-DOPED ZINC OXIDE PHOTOCATALYST VIA SOLVOTHERMAL METHOD FOR DEGRADATION OF 4-CHLOROPHENOL

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By

NUR SYAFIQA HAZIRAH BINTI RAZALI

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

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A humble dedication to my beloved parents;

Razali bin Jily and Dyg Korina binti Abg Mansor,

Family and friends for their unfaltering sacrifices and unwavering love

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

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4-chlorophenol is the one of priority pollutants that must be treated from the environment due to their toxicity and resistant to conventional treatment. Photocatalytic degradation is an advanced oxidation method which has proven to destroy persistent pollutants from water. The photocatalytic activity of ZnO for removal of water pollutant has been well established. In this work, the effect of silver doping on ZnO was studied and its photocatalytic activity on 4-chlorophenol was investigated.

Undoped ZnO and silver doped ZnO (Ag-ZnO) photocatalyst were synthesised under mild solvothermal method at 150°C for 3 hours with further calcination at 300°C, with silver concentrations of 0.2, 0.6, 1.0, 1.5 and 2.0 mol%. The synthesised products were characterized by X-ray diffractions (XRD), Field emission- scanning electron microscopy (FESEM), Energy dispersive Xray (EDX) and UV-VIS-NIR spectroscopy. All samples exhibited hexagonal wurtzite ZnO structure with metallic Ag exists interstitially on the ZnO lattice. There was no significant difference in band gap energy of ZnO and Ag-ZnO, which showed that the band gap energy of all samples were 3.15 eV, which is under UV range. The morphologies of the samples were irregular and rod-like shape with crystallite size in range of 70-90 nm. The BET surface area increase in surface area from undoped ZnO (6.54 m^2g^{-1}) to 1% Ag-ZnO (9.20 m^2g^{-1}) and decrease with higher loading of Ag.

Photocatalytic activities of ZnO and Ag-ZnO were investigated by suspension of the photocatalysts in 4-chlorophenol solution under irradiation of UV light and visible light. The result showed that the degradation of 4CP only occurred under UV light irradiation. 0.6% Ag-ZnO photocatalyst showed the highest degradation of 4-chlorophenol than undoped ZnO and Ag-ZnO with other percentage loading. Various basic operational parameters including catalyst amount, initial pH, and initial concentration of 4-Chlorophenol have been investigated. The highest amount of 0.6%

Ag-ZnO for the degradation of 4CP is 0.8g. The highest initial concentration of 4CP is 20 ppm, which showed the highest reaction kinetic rate with pseudo-first order reaction. The effect of pH on decomposition of 4CP was found to be influenced by 4CP adsorption and the change of molecular form of 4CP to anionic form. The reusability test of 0.6% Ag-ZnO has been investigated and there is no significant loss of Ag-ZnO and its photocatalytic activity indicates that Ag-ZnO is a stable photocatalysts.

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

SINTESIS FOTO-PEMANGKIN PERAK-TERDOP ZINK OKSIDA MELALUI KAEDAH SOLVOTERMAL UNTUK PENGURAIAN 4-KLOROFENOL

Oleh

NUR SYAFIQA HAZIRAH BINTI RAZALI

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Sebatian 4-klorofenol merupakan bahan pencemar utama yang perlu dirawat daripada alam sekitar disebabkan oleh kadar toksik yang tinggi dan keampuhan terhadap rawatan secara konvensional. Penguraian secara pemangkinan foto merupakan kaedah pengoksidaan termaju yang telah terbukti keberkesanannya untuk menyingkirkan bahan-bahan tercemar di dalam air. Peranan zink oksida dalam penguraian bahan tercemar melalui proses pemangkinan foto adalah diiktiraf umum. Dalam kajian ini, kesan mengedopkan perak pada ZnO dan aktiviti pemangkinan foto ke atas penguraian 4-klorofenol telah dikaji.

Fotomangkin zink oksida dan perak terdop zink oksida (Ag-ZnO) telah disintesis di bawah kaedah solvotermal pada suhu 150 °C selama 3 jam dengan proses pengkalsinan pada suhu 300 °C , dengan kepekatan perak 0.2 , 0.6 , 1.0 , 1.5 dan 2.0 mol % . Produk yang disintesis telah dicirikan oleh pembelauan sinar-X (XRD) , medan pengimbas mikroskop elektron (FESEM), tenaga serakan Xray (EDX) dan UV-VIS-NIR spektroskopi . Semua sampel menunjukkan struktur wurzit heksagon ZnO dengan logam Ag wujud di celahan pada kekisi ZnO itu. Tiada perbezaan yang ketara dalam ruang tenaga daripada ZnO dan Ag-ZnO, iaitu ruang tenaga daripada semua sampel ialah 3.15 eV, iaitu berada di ultra-ungu. Morfologi sampel adalah bentuk yang tidak teratur dan rod dengan saiz hablur dalam julat 70-90 nm. Kawasan peningkatan permukaan BET di kawasan permukaan dari ZnO tulen (6.54 m^2g^{-1}) ke 1 % Ag-ZnO (9.20 m^2g^{-1}) dan berkurangan dengan muatan Ag yang lebih tinggi.

Aktiviti pemangkinan foto ZnO dan Ag-ZnO telah disiasat dengan menguji fotomangkin di dalam larutan 4-klorofenol di bawah sinaran cahaya UV dan cahaya yang boleh dilihat. Hasilnya menunjukkan bahawa penguraian 4-klorofenol hanya berlaku di bawah sinaran cahaya UV. 0.6% Ag-ZnO fotomangkin menunjukkan penguraian 4-klorofenol tertinggi berbanding daripada ZnO tulen dan Ag-ZnO dengan peratusan muatan Ag yang lain. Pelbagai parameter termasuk jumlah pemangkin, pH awal, dan kepekatan awal 4-klorofenol telah dikaji. Jumlah tertinggi dos 0.6% Ag-ZnO untuk penguraian 4-klorofenol adalah 0.8g. Kepekatan awal 4-klorofenol yang tertinggi adalah 20 ppm, dengan tindakbalas kinetik tertib pseudo-pertama. Kesan pH ke atas penguraian 4-klorofenol didapati dipengaruhi oleh penjerapan 4-klorofenol dan perubahan bentuk molekul 4-klorofenol kepada anionik. Ujian kebolehgunaan 0.6% Ag-ZnO telah disiasat dan tidak ada penurunan besar terhadap aktiviti pemangkinan foro 0.6% Ag-ZnO jelas menunjukkan bahawa Ag-ZnO adalah fotomangkin yang stabil.

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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:

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LIST OF ABBREVIATIONS

4CP	4-chlorophenol
AAS	Atomic Absorption Spectrometer
AOP	Advanced Oxidation Process
BET	*Brunauer-Emmett-Teller*
CB	Conduction band
DOE	Department of Environment, Malaysia
DMS	Diluted Magnetic Semiconductor
EDX	Energy Dispersive X-ray
EPA	Environmental Protection Agency
FESEM	Field Emission Scanning Electron Microscopy
GAC	Granular Activated Carbon
MB	Methylene blue
MO	Methyl Orange
PAC	Powdered Activated Carbon
PZC	Point of Zero Charge
UV	Ultra-violet
UV-VIS-NIR	Ultra-violet Visible Near Infra-Red
VB	Valence Band
XRD	X-ray Diffraction

LIST OF SYMBOLS

e-	electron
h^+	hole
p/p^0	Relative pressure
E_g	Band gap energy
$[\ ]_0$	Initial concentration of
[ ]	Concentration of
e^-_{cb}	Conduction band electron

CHAPTER 1

INTRODUCTION

1.1 Background of study

In recent years, minimization of human and environmental exposure to hazardous pollutant is one of the important challenges in the chemical industry (Silva, *et al.*, 2009). Industrial wastes, sewage and a wide array of synthetic chemicals, affect considerable parts of water resources. The elimination of toxic chemicals from wastewater is presently one of the most important aspects of pollution control. It causes problems to the classical biological treatment. A wide range of organic compounds are detected in high organic wastewater. Some of these compound both synthetic organic chemical as well as naturally occurring substances, also pose severe problem in biological treatment (Singh, *et. al*, 2013).

Contamination of fresh water by phenol and its derivatives due to their extensive applications has become a serious global problem. Special attention has been given to the treatment of wastewater containing phenolic compound and its derivatives, such as chlorophenols. Chlorophenols constitute a group of a serious environmental pollutant that must be eliminated. Chlorophenols can be found in surface of water, soil and industrial water. 4-chlorophenol (4CP) has direct relevance to water remediation due to its solubility and severity of hazard to both terrestrial and aquatic life (Gaya *et. al*, 2009). 4CP has been listed as a toxic or priority pollutant by both US Environmental Protection Agency and European Commission. Besides, the removal or treatment of phenolic compound become as important environmental concern in Malaysia as less than 1mg/L of phenol is required for wastewater discharge, enacted by the Department of Environment (DOE) Malaysia in the Environmental Quality Act 1979 (Sewage and Effluent). However, 4CP is still widely used in industrial manufacturing process such as pesticide, herbicides, paint and pharmaceutical industries (Bertelli and Selli, 2006).

Generally, there are several conventional methods available for phenolic compounds removal such as the Fenton technology, catalytic wet oxidation, hydrogen peroxide (Jia, *et al*., 2012) and photolytic oxidation method (Kılıç and Çınar, 2008). However, these conventional methods are expensive and not environmental friendly. In addition, they are also challenging due to the stability and high solubility of 4CP in water (Bertelli and Selli, 2006). Photolytic oxidation process has proven to efficiently remove many pollutants in wastewater but highly toxic products are generated during UV treatment of wastewater (Kılıç and Çınar, 2008). To overcome these problems, these methods should be replaced with other method without any bad effects to the environment and safety issues.

Advanced Oxidation Process (AOP) is the latest technology employed by the photogeneration of highly oxidizing radical species to effect the destruction of persistent pollutants. Recently, heterogeneous photocatalytic AOPs received a lot of attention among the researchers due to their non-selectivity property (Gaya *et al*., 2009). It also can completely remove organic pollutants from wastewater by transforming the toxic products to other organic compounds and finally into the formation of benign compounds (Bertelli and Selli, 2006). Besides, photocatalysis using semiconductor photocatalyst provide mineralization of wide range of pollutants under mild reaction condition by employing light irradiation to activate the process (Satuf *et al*., 2008).

Last three decades, there are many semiconductor photocatalysts such as TiO_2, ZnO, CdS, ZrO, WO_3 and SnO_2 have been used for wastewater treatments under AOPs (Neppolian *et al*., 2007). Titanium dioxide (TiO_2) is widely used in industry due to its physical and chemical stability and high efficiency in removing hazardous pollutants.
In this study, zinc oxide (ZnO) has been chosen as photocatalyst because of its high catalytic performance, non-toxic chemical and its photocatalytic activity is comparable to TiO_2, which has same reaction of photogeneration mechanism, so it is considered as a qualified alternative of TiO_2 (Gaya *et al*., 2009). It also has high chemical and thermal stability, wide band gap (3.2 eV at room temperature) and a large exciton binding energy (60 meV) (Ghazi *et al*., 2011). Theoretically, the efficiency of the photocatalytic degradation depends on the photogeneration of electron and holes from the semiconductor (Jia, *et al*., 2012). When semiconductor is irradiated with a suitable radiation source, electron-hole pairs are generated. The electrons are promoted from valence band to conduction band and the holes form in valence band. The electrons converted adsorbed O_2 to highly active superoxide radicals and holes will oxidise the organic molecules. Both of holes and electrons induce a complex series of reaction which can completely degrade the organic pollutants (Welderfael, *et al*., 2013; Yıldırım *et al*., 2013).

However, the low efficiency of the performance under irradiation in visible region and rapid recombination of electron and holes are two limitations of ZnO as heterogeneous photocatalyst. Recombination of electrons and holes can reduce efficiency of photocatalytic activity of ZnO. To overcome these problems, few studies have been done to suppress electron hole recombination on the surface and broaden the absorption spectrum and increase the photocatalytic activity of ZnO (Welderfael, *et al*., 2013).

Modification of ZnO semiconductors with metals has become a special interest in heterogeneous photocatalysis study. Previously, ZnO doped with various metal dopants have been investigated to improve the segregation of electron and holes (Jia, *et al.,* 2012). Combination of semiconductor substrate and metal clusters has been proven to improve photocatalytic activity by trapping the photoinduced charge carriers besides increasing the charge-transfer process (Height, *et al*., 2006; Wang, *et al*., 2004). There are some efforts have been done on enhancement of the photocatalytic activity such as transition metal doping, semiconductor combination or modification with noble metals. Among these methods, modification of semiconductor with noble metal is the most promising method in improving the photocatalytic activity of semiconductors. So, doping ZnO with various noble metals such as gold, silver (Ag) and palladium could enhance its photocatalytic activity (Yıldırım *et al*., 2013).

This research focused on the synthesis of Ag doped ZnO (Ag-ZnO) via solvothermal method. This is because, Ag is much cheaper and easily available compared to other noble metal such as gold and platinum. In previous research, Ag nanoparticles show unique activities in catalytic, chemical and biological sensing (Chin, *et al*., 2011). In the photochemical reaction, Ag particles can trap the photogenerated electron from ZnO and form the holes to create hydroxyl radicals to react with organic molecules. Crystal defects and oxygen vacancies are also the most important of surface properties for improvement the photocatalytic activities of semiconductor particles. In addition, higher light scattering of Ag can enhance the photocatalytic performance of ZnO semiconductor (Yıldırım *et al*., 2013).

In this research, ZnO and Ag-ZnO with various percentage loadings of Ag were synthesized via solvothermal method, which is an excellent method to synthesize various type of nanoparticles. This method is well capable for producing nanostructure materials due to low cost, mild reaction condition and low growth temperature. It is also a simple route to control the size and morphology of synthesized particles by manipulating the reaction condition (Parvin, *et al*, 2012; Rashad *et al*., 2014). Besides, the effect of percentage loading of Ag on size and morphology of the ZnO also had been explored.

Reactions in aqueous phase can be complex due to the additional variable (e.g. mass loading of photocatalyst, concentration of pollutant and pH) that must be accounted for and carefully controlled. Therefore, these parameters were also investigated in order to simulate the condition of photodegradation of 4CP by Ag-ZnO in aqueous solution.

1.2 Problem statement

Recently, ZnO has been widely used as photocatalyst especially in photodegradation of phenolic compound such as 4CP. However, photocatalytic activity of ZnO is limited due to fast recombination of photogenerated electron-hole pairs. To overcome this problem, the modification of ZnO should be extensively studied to improve the segregation of electron and holes so their recombination can be suppressed.

In this work, silver metal was chosen as a dopant to improve the photocatalytic activity of ZnO. Although some works on Ag doped ZnO have been reported in previous studies but most of synthesis preparations were using the conventional methods such as co-precipitation, impregnation and thermal evaporation (Chauhan, *et al*., 2012; Welderfael, *et al*., 2013; Yıldırım *et al*., 2013) which require high temperature and high operational cost. Thus, in this study solvothermal method was chosen to synthesise Ag-ZnO. There were only few projects involved with Ag doped ZnO synthesised via solvothermal methods, which were using ethylene glycol and ethanol as solvents and polyvinyl pyrolidone (PVP) as template (Yiamsawas *et al*., 2009). The use of polymer templates in synthesis is unfavourable because polymer templates are expensive and must be separated from the products. However, synthesis of Ag doped ZnO using isopropanol has not been reported.

In addition, the study of photocatalytic activity of Ag doped ZnO in degradation of phenolic compounds such as 4CP is still lacking. Most of the previous reports used dye as model contaminants such as methylene blue (Chauhan, *et al*., 2012; Wang *et al*., 2004), methyl orange (Jia, *et al.*, 2012; Yıldırım *et al*., 2013), brilliant blue dye (Parvin, *et al*, 2012) and active red 88 (AR88) (Behnajady, *et al*., 2009). In this work, the efficiency of Ag-ZnO in the photodegradation of 4CP was studied by using synthetic 4CP solution as modal pollutant to simulate the actual wastewater containing the said pollutant.

1.3 Objectives

The main objectives of this research are:

1. To synthesize the ZnO and Ag-ZnO photocatalysts via solvothermal method and characterize their physico-chemical properties.
2. To investigate the photocatalytic activity of Ag-ZnO for the degradation of 4CP.
3. To study the effect of the basic operational parameters of photodegradation such as mass loading of photocatalysts, initial concentration of pollutant and initial pH.

1.4 Scope of research

In this research, ZnO and Ag-ZnO photocatalysts were synthesised via solvothermal method. For synthesis of Ag-ZnO, different loading of Ag were used (Ag: 0.2%, 0.6%, 1.0%, 1.5% and 2%). The physico-chemical properties of the prepared photocatalysts were characterized using the field emission-scanning electron microscope (FESEM), x-ray diffractometer (XRD), *Brunauer–Emmett–Teller* (*BET)* surface area analyser, energy dispersive x-ray (EDX) and the ultraviolet-visible near infrared (UV-VIS-NIR) spectrophotometers.

The photocatalytic activity of ZnO and Ag-ZnO photocatalyst were evaluated via photodegradation of 4CP. The 4CP solution was prepared synthetically by dilution of pure 4CP into several concentrations. The progress of the degradation was monitored by determining the residual concentration of pollutant using the UV-VIS spectrophotometer. Basic parameters were also investigated such as the mass loading of photocatalyst, pH of solution and the initial concentration of 4CP. The stability of the photocatalyst was also investigated in reusability test. However, the investigation of the photocatalytic activity of Ag-ZnO was only limited to synthetic 4CP solution due to the small yield of the photocatalyst produced via solvothermal method in laboratory scale. So, the study of photocatalytic activity of Ag-ZnO in actual wastewater could not be investigated.

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