ELECTRO–SYNTHESIS OF COPPER OXIDE SUPPORTED ON MULTI–WALL CARBON NANOTUBES CATALYST FOR PHOTODEGRADATION OF *p*–CHLOROANILINE

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Specially dedicated to my husband and princess,

(Mohd Azzizul bin Chamingan and Kayyisah Nur Ameenah)

'Thank you for always standing next to me and waiting for me patiently'

To Abah, Ibu, Ayah, and Mak,

(Khusnun Yahya, Noraini Bahran, Chamingan Bahari, and Rohani Ibrahim)

'Thank you for always being there; your endless love, faith and encouragement never fail to strengthen me'

&

To my beloved siblings, family and family-in-laws

'Thank you for your endless love and encouragement during my hard time'

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ABSTRACT

Recently, the discharge of *p*-chloroaniline (PCA) into the environment has gained much concern due to the toxicity and danger that PCA poses to the aquatic and human life. Photocatalytic degradation is one of the promising techniques to degrade organic pollutants as it is safe and economical for solving environmental problems. In this study, an electrochemical method was used to load copper oxide (CuO) nanoparticles (1-90 wt%) onto multi-wall carbon nanotubes (MWCNT). The catalysts were characterized by X-ray diffraction, nitrogen adsorption-desorption, electron spin resonance, Raman spectroscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The effect of CuO loading on the photodegradation of PCA under ultraviolet (UV) and visible (VIS) light irradiation system was investigated. Under UV light, a low amount of CuO was sufficient to provide a synergistic effect with MWCNT in the system. However, a higher loading of CuO was required to shift the adsorption spectrum toward the VIS light region. The degradation of PCA over the CuO/MWCNT catalysts under UV light was in the following order: 3 wt% CuO/MWCNT (96%) > 1 wt% CuO/MWCNT (82%) > 5 wt% CuO/MWCNT (76%), while under VIS light was 50 wt% CuO/MWCNT (97%) > 10 wt% CuO/MWCNT (92%) 90 wt% CuO/MWCNT (82%). It is presumed that the C–N moieties of PCA were chemisorbed on the catalyst prior to photodegradation. Studies on the effect of scavengers showed that hole (h^+) was the main active species under the UV system, and electron (e^-) for the VIS system. Under the UV system, based on the highest occupied molecular orbital (HUMO) and the lowest unoccupied molecular orbital (LUMO) potentials of both CuO and MWCNT, the electron (e^-)–hole (h^+) transfer occurred between their conduction band (CB) and valence band (VB) that reduced the e^-–h^+ recombination and enhanced the degradation as compared to bare CuO photocatalyst. On the other hand, surface defects and oxygen vacancies lowered the band gap energy of the catalyst and allowed for more excitation of e^- under VIS light to produce hydroxyl radicals for enhanced degradation of PCA. The Langmuir–Hinshelwood model verified the transformation of first to zero order kinetics model under the UV system upon the increasing initial concentration of PCA, and vice versa for the VIS system. This supported the fact that the higher energy of UV light urged the h^+ to directly react with the PCA at VB and resulted in the transition from kinetic control to mass transfer limitation by increasing PCA molecules while the opposite shift occurred under the lesser energy of VIS light. Optimization using response surface methodology gave the highest degradation of PCA at the optimum condition of 11.02 mg L^{-1} using 0.45 g L^{-1} 50 wt% CuO/MWCNT at pH 7.26. The obtained condition was reasonably close to the predicted value with 0.26% error. Remarkable mineralization results of PCA were attained by total organic carbon (89.1%) and biological oxygen demand (50.7%). Reusability studies showed that the catalysts were still stable even after five cycles. It is believed that the CuO/MWCNT catalyst has a great potential to degrade various types of organic pollutants for wastewater treatment.

ABSTRAK

Kebelakangan ini, pelepasan *p*-kloroanilin (PCA) ke alam sekitar menimbulkan kebimbangan kerana ketoksikan dan kesan bahaya PCA ke atas hidupan akuatik dan manusia. Degradasi fotobermangkin ialah salah satu daripada teknik yang berpotensi dalam mendegradasi pencemar organik kerana ia selamat dan jimat bagi menyelesaikan masalah alam sekitar. Kajian ini menggunakan kaedah elektrokimia untuk endapan nanozarah CuO (1-90 % berat) pada nanotiub karbon dinding berlapis (MWCNT). Mangkin dicirikan melalui pembelauan sinar–X, penyerapan-nyahjerapan nitrogen, resonan putaran elektron, spektroskopi Raman, mikroskopi transmisi-elektron, spektroskopi inframerah jelmaan Fourier dan spektroskopi fotoelektron sinar–X. Kesan endapan CuO ke atas fotodegradasi PCA di bawah sistem penyinaran cahaya sinar ultralembayung (UV) dan sinar tampak (VIS) dikaji. Di bawah sinar UV, hanya sedikit jumlah CuO diperlukan bagi membekalkan kesan sinergistik dengan MWCNT di dalam sistem. Namun, endapan CuO yang lebih banyak diperlukan untuk mengalihkan spektrum penyerapan ke arah rantau cahaya VIS. Degradasi PCA oleh mangkin CuO/MWCNT di bawah cahaya UV adalah seperti aturan berikut: 3 % berat CuO/MWCNT (96%) > 1 % berat CuO/MWCNT (82%) > 5 % berat CuO/MWCNT (76%), manakala di bawah VIS 50 % berat CuO/MWCNT (97%) > 10 % berat CuO/MWCNT (92%) > 90 % berat CuO/MWCNT (82%). Anggapan bahawa moiti C–N PCA diserapkimia di atas mangkin sebelum fotodegradasi. Kajian ke atas kesan penghapus-sisa menunjukkan lubang (h^+) merupakan spesies aktif utama di bawah sistem UV dan elektron (e^-) bagi sistem VIS. Di bawah sistem UV, berdasarkan potensi penghunian orbital molekul tertinggi dan tidak penghunian orbital molekul terendah bagi kedua-dua CuO dan MWCNT, pemindahan elektron (e^-)–lubang (h^+) berlaku di antara jalur pengaliran (CB) dan jalur valens (VB) yang menurunkan kombinasi semula e^-–h^+ dan meningkatkan degradasi berbanding fotomangkin CuO terdedah. Walau bagaimanapun, kecacatan permukaan dan kekosongan oksigen merendahkan tenaga jurang jalur mangkin dan membenarkan lebih banyak pengujaan e^- di bawah cahaya VIS bagi menghasilkan radikal hidroksil untuk mempertingkatkan degradasi PCA. Model Langmuir-Hinshelwood mengesahkan transformasi model kinetik dari tertib pertama hingga tertib sifar di bawah sistem UV melalui peningkatan kepekatan awal PCA, dan sebaliknya bagi sistem VIS. Ini menyokong kenyataan bahawa lebih tinggi tenaga cahaya UV mendesak h^+ untuk bertindakbalas secara terus dengan PCA pada VB dan menyebabkan peralihan daripada kawalan kinetik kepada pembatasan pindah jisim dengan meningkatkan molekul PCA, manakala peralihan bertentangan diperoleh di bawah tenaga VIS yang kurang. Pengoptimuman menggunakan metodologi permukaan gerak balas menyebabkan degradasi tertinggi PCA dalam keadaan optima 11.02 mg L^{-1} menggunakan 0.45 g L^{-1} 50 % berat CuO/MWCNT pada pH 7.26. Keadaan yang diperoleh hampir dengan nilai jangkaan dengan ralat 0.26%. Hasil penghabluran PCA yang luar biasa diperolehi melalui jumlah karbon organik (89.1%) dan keperluan oksigen biologi (50.7%). Kajian kebolehgunaan semula menunjukkan mangkin masih stabil selepas lima kitaran. Mangkin CuO/MWCNT menunjukkan keupayaan besar bagi mengdegradasi pelbagai jenis pencemar organik bagi perawatan air sisa.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	-	Activated Carbon
AOP	-	Advanced Oxidation Process
BJH	-	Barret, Joyner, and Halenda
CB	-	Conduction Band
CH_4	-	Methane
ClBz	-	Chlorobenzene
ClPh	-	Chlorophenol
CNT	-	Carbon Nanotubes
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
COD	-	Chemical Oxygen Demand
CuO	-	Copper Oxide
CdS	-	Cadmium Sulfide
DMF	-	Dimethylformamide
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
Fe_XO_X	-	Iron Oxide
FTIR	-	Fourrier Transform Infra-Red
GO	-	Graphene Oxide
H_2O	-	Water
HCl	-	Hydrochloric Acid
MWCNT	-	Multi-walled Carbon Nanotubes
NaOH	-	Sodium Hydroxide
NLDFT	-	Non-Local Density Functional Theory
O_2	-	Oxygen

PCA	-	*p*-chloroaniline
RSM	-	Response Surface Methodology
SnO_2	-	Tin Dioxide
SWCNT	-	Single-walled Carbon Nanotubes
TEAP	-	Tetraethylammonium Perchlorate
TEM	-	Transmission Electron Microscopy
TiO_2	-	Titanium Oxide
TOC	-	Total Organic Compound
UV	-	Ultra violet
VB	-	Valence Band
VL	-	Visible Light
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction
ZnO	-	Zinc Oxide
ZrO_2	-	Zirconia Oxide

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Chlorinated *p*-Chloroaniline (PCA) is widely used as an intermediate of reaction during a variety of chemical manufacture, including agricultural chemicals, plastic, azo dyes and pigments, production of synthetic organic chemicals and polymers like polyurethanes, rubber additives, pharmaceuticals, cosmetic products, pesticides and herbicides, and drugs (Hussain *et al*., 2012). The widespread use of these compounds has resulted in their ubiquity in industrial effluents, sludge, and agriculture soils. As one of the persistent organic pollutants (POPs) and being widely distributed in the environment, PCA is a priority toxic pollutant listed in US EPA and EU legislation and imposes a serious risk on public health and the environment (Zhang *et al*., 2010; Liang *et al*., 2013). Several technologies such as biodegradation (Zhang *et al*., 2010; Hongsawat &Vangnai, 2011), radiochemical methods (Sanchez *et al*., 2001), and adsorption (Bakhaeva *et al*., 2001) have been developed to degrade this compound. However, their applications are limited due to high cost and time-consuming use, as well as production of secondary wastes of some persistent organic pollutants such as aniline derivative.

Over the past three decades, advanced oxidation processes (AOPs) have gained increasing attention as promising benign environmental processes for the elimination of organic or inorganic contaminants in water and wastewater (Selvarajan *et al.*, 2017). This process involves simultaneous use of more than one oxidation process to accelerate the production of reactive hydroxyl free radicals. However, incomplete mineralization and non-selective target pollutants, as well as inappropriate operating conditions have prompted their combination with other AOPs such as photocatalysis, the addition of H_2O_2 or membrane technologies (Gil *et al.* 2017). In fact, heterogeneous photocatalytic degradation under ultraviolet (UV) or visible (VIS) light irradiation is a popular and an economical process that converts the pollutants to less harmful final products, which are carbon dioxide and water (Derikvandi & Nezamzadeh-Ejhieh, 2017). Besides, its capability to destruct pollutants at ambient temperature and pressure also becomes the reason for the researchers to increase their focus on this area.

Among the catalysts used, TiO_2 is the most popular one but fast electron–hole recombination always suppresses its efficiency. Hybridization of TiO_2 with other nanometal oxides such as ZnO, Fe_2O_3, CuO, ZrO_2, CdS, and SnO_2 as well as supporting TiO_2 on several mesoporous materials such as silica, zeolite and alumina have been among the efforts to lower the band gap, as well as to suppress the fast electron –hole recombination rate. In the past few decades, the explorations of various suitable photocatalysts for the removal of organic pollutants from wastewater have been done using various types of photocatalyst (Jalil *et al*., 2007; Ma *et al*., 2008; Jalil *et al*., 2013; Jusoh *et al.*, 2014). However, their relatively low activity and low efficiency under VIS light irradiation limited their practical use in water treatment.

CuO is one of the important narrow band gap semiconductors, which acts under VIS light driven. However, CuO can only absorb a small amount of solar spectrum in the UV region, which results in low photocatalytic efficiency (Pandiyarajan *et al*., 2017). To enhance the efficiency, many studies have been performed to modify this metal oxide. Generally, there are several ways to improve the photocatalytic activity of such semiconductor: (i) increasing the surface area of metal oxide by synthesizing

nanosized materials, (ii) adding a support such as silica, alumina, zeolite, CNT, etc., (iii) creating a defect structure, and (iv) adding other metals or semiconductors. On the other hand, in term of safety, the maximum contaminant limit threshold for CuO was 1.3 mg/L. Although there is a limit, considerable amount of the CuO usage needs to be controlled appropriately.

In parallel with the first techniques, electrochemical method has been reported to have many advantages, particularly in the synthesis of nanoparticles materials. Previously, some literature reported a simple in situ electrochemical method for preparing various metal nanoparticle such as a-Fe_2O_3, CuO, and ZnO supported on zeolites and silica (Jaafar *et al.*, 2012; Jalil *et al.*, 2013; Jusoh *et al.*, 2015). Besides the formation of metallic nanoparticles, metal ions incorporated in the supports were also discovered during electrolysis, resulting in photocatalysts with high potential for efficient decolorization of various dyes.

Recently, carbon materials, particularly multi-walled carbon nanotubes (MWCNT), have also been used as excellent catalyst supports for various semiconductor photocatalysts due to their interesting features: (1) MWCNT have a large specific surface area, generally > 150 m^2/g (Peigney et al., 2001). Heterogeneous catalysis degradation of aqueous pollutants is best modeled by the Langmuir–Hinshelwood mechanism, which requires the adsorption of chemicals before the chemicals are degraded on the catalyst. The large specific surface area is helpful for the adsorption of pollutants. It should be noted that the specific surface area of MWCNT is smaller than that of AC, so the following merits of MWCNT are more important; (2) MWCNT could be easily functionalized with carbonyl and hydroxyl moieties via acid treatment, and these groups could be further modified to improve the adsorption affinity toward some specific chemicals, leading to “selective degradation” processes, like degradation of pollutants over benign species, and highly-toxic pollutants over low-toxic pollutants; (3) the uniform porous structure of MWCNT reduces the mass-transfer limitations of reactants from solution to active sites on the catalyst; (4) MWCNT have good thermal stability and resistance to acidic and basic media thus could be used in severe conditions (Ana *et al.*, 2011; Dong *et al.*, 2006).

The loading of MWCNT onto metal oxides such as ZnO, TiO_2, Fe_3O_4, and Al_2O_3 is also able to alter the physicochemical properties of the catalysts and enhance the photocatalytic degradation of organic pollutants. However, information on the most important aspects addressing the behavior of individual metal ions in or on MWCNT, particularly in possible chemical interactions between both, is still lacking and is of interest. Other than that, the investigations generally focus on the low MWCNT amounts, which is below 20% (Ahmed *et* al., 2008). The high cost and dark color of MWCNT are most probably the main constraints to use high amounts of MWCNT photocatalyst. Nevertheless, due to the high demand of MWCNT, particularly for other commercial applications, a large scale production using various synthetic methods has been developed, and a cost-effective production from wastes has become a popular route nowadays (Bazargan & McKay, 2012). A large-scale production is defined as the production of 10,000 tons of MWCNT per annum (See & Harris, 2007).

Herein, the study report a synthesis of various loadings of CuO supported onto MWCNT nanoparticles via electrolysis method. The physicochemical properties of the catalysts were investigated and the performance on photocatalytic degradation of PCA were tested under both UV and VIS light irradiation. The optimization process was also carried out using response surface methodology (RSM). The kinetic studies, the proposed structure of the catalyst, and the mechanism of degradation are also discussed. The mineralization, biodegradability, stability test, and other potential application of the catalyst were also performed. In fact, there have been only a few reports on the degradation of PCA via basic AOPs, including the use of ozone, photoinduced iron (III), and persulfate-activated with zero-valent iron (Sanchez *et al.*, 2002; Mailhot *et al*., 2004; Liang *et al*., 2013). The outcomes from this report are believed to lead to the design of superior CNT-based catalysts for various applications.

1.2 Problem Statement and Hypothesis

In the last two decades the interest for water health protection greatly increased, also due to the increasing amount of pollutants introduced into the environment. Particular interest is devoted to PCA because of their recently recognised toxicity associated to their ubiquitous discharge. PCA was indentified as the principal raw materials presents in effluents derived from several chemical manufacture such rubber, dyes and pigmens, pharmaceuticals and drugs industries. It is detected in high concentration in these wastewaters. It is highly toxic to aquatic life and US Environmental Protection Agency (US EPA) has suggested an ambient limit in water of 262 mg/L, based on health effects (Sarasa *et* al. 2002).

Several techniques have been developed to remove PCA from the wastewater. Last few decades, photocatalysis has been a hot topic in the degradation of organic pollutant due to their safe in operation, easy to handle, and environmental friendly. Generally, metal oxide such as TiO_2, CdS, ZnO, ZrO, WO_3 and Fe_2O_3 were used as semiconductor and act as a catalyst during the photocatalysis. However, it has their own drawbacks such as higher electron-hole recombination and lower efficiency of degradation percentage under VL irradiation. This is most probably due to the higher band gap of the semiconductor and the agglomeration of the metal oxide itself increased the electron-hole recombination. In addition, the semiconductor itself was less active under VL irradiation due to higher band gap.

Previously, many researcher have move forward to use narrow band semiconductor such as CuO (1.7 eV). However, CuO can only absorb a small amount of solar spectrum in the UV region, which resulted in low photocatalytic efficiency. Most recently, researchers used semiconductor oxide and support catalyst to overcome the problems. To date, MWCNT had been use as excellent support material due to several reasons such as high surface area, high thermal stability and resistance to acidic and alkaline media. It also has been shown that coupling of semiconductor oxides and support can reduce their band gap, extend their absorption range to visible light region,

and consequently, achieve a higher photocatalytic activity under VIS light irradiation. Unfortunately, detailed studies on metal-support interaction and influence of the defect site are still lacking. Therefore, it is desirable to explore the structure of the synthesized catalysts, study the interaction between metal and support material as well as the formation of the defect sites which play significant roles in enhancing the photocatalytic efficiency.

In this study, it is hypothesized that the synthesis of copper oxide nanoparticles supported onto the MWCNT by electrochemical method gives a great advantage as a facile synthesis route. The introduction of CuO species onto the MWCNT is believed to lead to a synergistic effect between them which was anticipated to improve the photocatalytic activity. It is also expected to form an active site, Cu–O–C bond, surface defect, and oxygen vacancies which will enhance the photocatalytic activity under both UV and VIS light irradiation system.

1.3 Objective of Study

The objectives of this study are:

I. To synthesize and characterize the CuO supported onto MWCNT (CuO/MWCNT) photocatalysts.
II. To evaluate the performance of the catalysts on the photodegradation of PCA
III. To optimize the photocatalytic degradation by RSM.
IV. To study the kinetics, mechanism of degradation, mineralization, biodegradability and stability of the catalyst toward degradation of PCA.

1.4 Scope of Study

The scopes of this study are:

I. Synthesis and characterization of CuO/MWCNT photocatalysts.

CuO supported on the carbon nanotubes were synthesized by electrochemical method under metal loadings of 1, 3, 5, 10, 50, and 90 wt %. The catalysts were characterized using X-ray diffraction (XRD), nitrogen (N_2) adsorption–desorption, electron spin resonance (ESR), Raman spectroscopy, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).

II. Performance of catalysts on the photodegradation of *p*-chloroaniline in aqueous solution.

The screening process was conducted based on literature parameters to determine the optimum conditions including effect of pH of the solution (pH 3–11), initial concentration of PCA (10–100 mg L^{-1}), catalyst dosage (0.125–0.625 g L^{-1}), and metal oxide loading. The lower range of CuO loadings (1–3 wt%) were tested under UV light irradiation, while the higher range of CuO loadings (10–90 wt%) were tested under VIS light irradiation.

III. Optimization of the photocatalytic degradation by response surface methodology (RSM).

Optimization of the photocatalytic degradation of PCA over the best 50 wt% CuO/MWCNT was performed using central composite design (CCD) by

response surface methodology (RSM) developed by Statistica 6.0 StatSoft. The factors affecting the photoactivity of catalyst included pH of solution (pH 3, 5, 7, 9, and 11), catalyst dosage (0.125, 0.250, 0.375, 0.5, and 0.625 g L^{-1}), initial PCA concentration (5, 10, and 15 mg L^{-1}) and metal oxide weight loading (10, 50, and 90 wt %). These parameters were chosen based on the results of preliminary studies that have been conducted.

IV. Study the kinetics, mechanism of degradation, mineralization, biodegradability and stability of the catalyst toward degradation of PCA.

The kinetic expression were described based on Langmuir–Hinshelwood kinetic model over the best catalyst for both UV and VIS light irradiation system. The mechanism of photocatalytic degradation of PCA over the catalysts were proposed by running out the effect of scavenger experiment to determine the important species such as photogenerated holes (h^+), electrons (e^-), and hydroxyl radicals (•OH) by using several scavengers (sodium oxalate, potassium peroxydisulfate, and sodium bicarbonate). Then, mechanism of the photocatalytic degradation of PCA were proposed. The mineralization and biodegradability studies were carried out by Total Organic Compoung (TOC) and Biological Oxygen Demand (BOD_5), respectively over the best catalyst. Lastly, the stability was done by running five repetitions of the experiment under similar condition by using the best catalyst.

1.5 Significance of Study

This study was conducted to synthesize MWCNT-based photocatalyst for photocatalytic degradation of organic pollutants. In recent approaches, this carbon material has been used to mitigate the support effect. Due to the one-dimensional nanostructure and high specific surface area of MWCNT, various inorganic

nanoparticles such as metals, metal oxides, and semiconducting nanoparticles were attached on the MWCNT surface to obtain nanotube/nanoparticle hybrid materials with useful properties.

Among the various types of semiconductors, the CuO nanoparticles experienced intensive advances due to their outstanding features such as low cost, narrow band gap, good chemical and thermal stability, and excellent optical properties. It was hypothesized that the synthesis of copper oxide nanoparticles loaded onto MWCNT will be achieved by electrochemical method. As a result, the combination of metal oxides and MWCNT will form an active site, Cu–O–C bond, surface defect, and oxygen vacancies, which enhance the photocatalytic activity under both UV and VIS light irradiation system. The catalyst is believed to show high potential in wastewater treatment. Additionally, this study may contribute for the knowledge in wastewater technology.

1.6 Thesis Outline

The thesis is divided into five chapters. In Chapter 1, a general introduction is given about the environmental effects of organic pollutants such *p*-chloroaniline. Several methods for PCA removal are also mentioned. Besides that, the potential of metal oxides supported on MWCNT as photocatalysts for degradation of PCA are highlighted. The problem statement of the current research is stated to give the main objectives of the present study, while the scopes of study cover the research work to meet these objectives.

Chapter 2, which is literature review, covers detailed information regarding chlorinated compounds in wastewater, technologies of PCA removal, photocatalytic degradation process, as well as the studies on CuO, and CNT-based photocatalyst.

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