BIOSYNTHESIS OF COPPER(II) OXIDE NANOPARTICLES USING *Murraya koenigii* LEAF EXTRACT AND THEIR CATALYTIC ACTIVITY IN THE REDUCTION OF NITROAROMATIC COMPOUNDS

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DEDICATION

Thank you Allah and Rasulullah....

For my supervisor, beloved husband, family, parents and friends – with love

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ABSTRACT

The applications of copper-based nanoparticles have generated a great deal of interest in the field of catalysis. The natural abundance of copper and its relatively low cost make copper-based nanoparticles a viable alternative to catalysts made from expensive precious metals, such as platinum and palladium. In this study, a rapid, simple and green method was developed for the synthesis of copper oxide nanoparticles (CuO NPs) using *Murraya koenigii* leaves aqueous extract as reducing and stabilising agent. The antioxidant activity of the *Murraya koenigii* leaves extract was determined using ferric reducing antioxidant potential (FRAP) assay. During the bioreduction, several parameters were optimized, namely the volume of leaf extract, pH, reaction temperature and reaction time. The optimum conditions obtained for the biosynthesis were 3 mL of leaf extract, pH 11, room temperature and reaction time of 50 minutes. The biosynthesised CuO NPs were characterized using ultraviolet-visible (UV-Vis) spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). The UV-Vis absorption spectrum confirmed the formation of CuO NPs with the appearance of a surface plasmon resonance band at λ_{max} 634-670 nm. Meanwhile, the FTIR spectroscopic analysis of CuO NPs showed the presence of surface adsorbed biomolecules from the leaf extract that acted as the reducing and stabilizing agents. XRD analysis displayed a series of diffraction peaks that are consistent with monoclinic structure of copper(II) oxide, CuO (JCPDS No. 45-0937). HRTEM images revealed that the CuO NPs were mostly spherical with a mean diameter of 8.4 nm. In the presence of sodium borohydride, $NaBH_4$, the biosynthesized CuO NPs demonstrated good catalytic activity in the reduction of nitroaromatic compounds. The reduction of 4-nitrophenol to 4-aminophenol showed 98% conversion and was maintained for three cycles, indicating no significant loss of catalytic activity. The reaction followed a pseudo-first-order kinetics with a rate constant value of 4.3×10^{-3} s^{-1}. The product of the catalytic reaction was isolated and purified. The purified product was characterized using nuclear magnetic resonance (NMR) and FTIR spectroscopic techniques. The catalytic reduction of other nitroaromatic compounds with various substituents, namely, nitrobenzene, 4-nitrotoluene, 4-nitrobenzaldehyde, 4-nitroaniline, 2-methyl-4-nitrophenol, 2-nitrotoluene and 3-nitrotoluene was also investigated. Nitroaromatic compounds with electron donating group exhibited higher reaction rates compared to nitroaromatic compounds with electron withdrawing group.

ABSTRAK

Penggunaan nanopartikel berasaskan kuprum telah menimbulkan minat yang mendalam dalam bidang pemangkinan. Kelimpahan semulajadi kuprum yang tinggi dan kosnya yang relatif rendah, telah menjadikan nanopartikel berasaskan kuprum sebagai satu alternatif berdaya maju berbanding mangkin yang diperbuat daripada logam bernilai yang mahal seperti platinum dan paladium. Dalam kajian ini, satu kaedah yang cepat, ringkas dan hijau telah dibangunkan bagi sintesis nanopartikel kuprum oksida (CuO NPs) menggunakan ekstrak akueus daun *Murraya koenigii* sebagai ejen penurun dan penstabil. Aktiviti antioksida dalam ekstrak akueus daun *Murraya koenigii* telah diukur menggunakan cerakin potensi penurunan antioksidan ferik (FRAP). Semasa bio-penurunan, beberapa parameter dioptimumkan, iaitu isipadu ekstrak daun, pH, suhu tindak balas dan masa tindak balas. Keadaan optimum untuk biosintesis ini ialah 3 mL ekstrak daun, pH 11, suhu bilik dan masa tindak balas 50 minit. CuO NPs yang dibiosintesis telah dicirikan menggunakan spektroskopi ultra ungu-cahaya nampak (UV-Vis), spektroskopi inframerah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), dan mikroskopi elektron penghantaran resolusi tinggi (HRTEM). Spektrum penyerapan UV-Vis mengesahkan pembentukan CuO NPs dengan kemunculan jalur resonans plasmon permukaan pada λ_{maks} 634-670 nm. Sementara itu, analisis spektroskopi FTIR terhadap CuO NPs mengesahkan kewujudan biomolekul daripada ekstrak daun yang terjerap pada permukaan yang bertindak sebagai agen penurunan dan penstabilan. Analisis XRD menunjukkan siri puncak pembelauan yang konsisten dengan struktur monoklinik kuprum(II) oksida, CuO (JCPDS No. 45-0937). Imej HRTEM mendedahkan bahawa kebanyakan CuO NPs adalah berbentuk sfera dengan diameter purata 8.4 nm. Dengan kehadiran natrium borohidrida, $NaBH_4$, CuO NPs yang telah dibiosintesis menunjukkan aktiviti pemangkinan yang baik dalam penurunan sebatian aromatik nitro. Penurunan 4-nitrofenol kepada 4-aminofenol menunjukkan 98% penukaran dan dapat dikekalkan sebanyak tiga kali kitaran tanpa menunjukkan penurunan aktiviti pemangkinan yang ketara. Tindak balas adalah mengikut kinetik tertib pertama pseudo dengan nilai pemalar kadar 4.3×10^{-3} s^{-1}. Hasil tindak balas bermangkin telah diasingkan dan ditulenkan. Hasil yang ditulenkan telah dicirikan menggunakan teknik spektroskopi resonans magnetik nuklear (NMR) dan FTIR. Penurunan pelbagai terbitan sebatian aromatik nitro yang lain, iaitu nitrobenzena, 4-nitrotoluena, 4-nitrobenzaldehid, 4-nitroanilina, 2-metil-4-nitrofenol, 2-nitrotoluena dan 3-nitrotoluena juga dikaji. Sebatian aromatik nitro dengan kumpulan penderma elektron mempamerkan kadar tindak balas yang lebih tinggi berbanding sebatian aromatik nitro dengan kumpulan penarik elektron.

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LIST OF ABBREVIATIONS

^{1}H NMR	-	Proton nuclear magnetic resonance
4AP	-	4-aminophenol
4NP	-	4-aminophenol
CTAB	-	cetyltrimethylammonium bromide
CuNPs	-	copper nanoparticles
CuO NPs	-	copper oxide nanoparticles
DMSO	-	dimethyl sulfoxide
DPPH	-	2,2-diphenyl-1-picrylhydrazyl
EDG	-	electron-donating groups
EWG	-	electron-withdrawing groups
FRAP	-	Ferric Reducing Antioxidant Potential
FTIR	-	Fourier transform infrared spectroscopy
HEBM	-	High-energy ball milling
HRTEM	-	high-resolution transmission electron microscope
IGC	-	inert gas condensation
LCMS	-	Liquid chromatography mass spectrometry
MNPs	-	metal nanoparticles
PLAL	-	Pulsed laser ablation in liquid
PVA	-	polyvinyl alcohol
TLC	-	thin layer chromatography
TPC	-	total phenolic content
TPTZ	-	2,4, 6-tripyridyl-s-triazine
XRD	-	X-ray diffraction

LIST OF SYMBOLS

%	-	percent
°C	-	degree Celcius
Å	-	Ångström
%w/v	-	percent weight per volume
2θ	-	Bragg angle
cm	-	centimeter
Cu Kα	-	X-ray diffraction from copper energy levels
g	-	gram
h	-	hour
M	-	Molarity
mg	-	milligram
°	-	degree angle
ppm	-	part per million
rpm	-	revolutions per minute
λ_{max}	-	wavelength maxima
R^2	-	coefficient of determination
δ	-	chemical shift
J	-	coupling constant

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Currently nanomaterials are being used in various fields of physics, chemistry, biology, medicine and engineering (Mandal and Ganguly, 2011; Pavlovic *et al.*, 2013). The major advantage of nanomaterials is that their properties changes drastically from bulk material such as lower melting points, higher specific surface areas, specific optical properties, mechanical strengths, and specific magnetizations (Horikoshi and Serpone, 2013). The optical properties of metal nanoparticles for example, changes significantly due to their varied size dependent interactions with light, a property termed as surface plasmon resonance (SPR). The properties of nanoparticles could be easily altered by varying their size and shape (M. Singh *et al.,* 2016). Metals such as gold, platinum, palladium, silver, and copper are widely reported as excellent examples of catalyst on organic reactions (Wang and Gu, 2015a). Metal nanoparticles catalyst offers high catalytic efficiency due to their larger surface area to volume ratio. Consequently, this maximizes the reaction rates and minimizes consumption of the catalyst. Copper was reported as a highly efficient catalyst for facile and economical synthesis of many organic reactions such as reduction of nitroaromatic compounds (Pi *et al.,* 2018). Recently, much research has focused on the utilization of copper nanoparticles as catalyst compared to other precious metals due to their earth abundance and inexpensive.

The use of copper nanoparticles, CuNPs, is restricted by Cu's inherent instability under atmospheric conditions, which makes it prone to oxidation. The susceptibility of CuNPs to undergo oxidation allows the formation of copper oxide nanoparticles, CuO NPs, during the synthesis under atmospheric conditions. Similar to CuNPs, CuO NPs also have various potential applications for solar energy

(Wanninayake *et al.*, 2015; Masudy-Panah *et al.*, 2016; Sonthila *et al.*, 2017), gas sensors (Wang *et al.*, 2016) , water treatment (Peternela *et al.*, 2017), and act as good catalyst in chemical reactions (Anaraki-ardakani and Zaki, 2015; Iniyavan *et al.*, 2015; Tanna *et al.*, 2016) .

There are two approaches for the synthesis of metallic nanoparticles, namely "bottom-up" approach and "top-down" approach. Top-down method refers to the size reduction of macroscopic starting materials to nanosize using physical methods such as ball milling and pyrolysis. A major drawback of the "top-down" approach is the difficulty of adjusting the uniformly particle size as well as shape (Khandelwal and Joshi, 2018). Meanwhile, the "bottom-up" strategy involves basic building blocks such as atoms or molecules arrange into large nanostructures using chemical or physical forces (Su and Chang, 2017). The commonly used procedures employed wet chemicals because of their simplicity and easily scale up for high volume production. Nevertheless, these procedures have several drawbacks such as involve the use of toxic chemicals and generation of hazardous by-products.

Currently, due to the increased concern on the environmental issues, greener routes that utilize biological sources such as microorganism and plants have received considerable attention. Biogenic synthesis of metal nanoparticles reduces the environmental issues compared with some of the physicochemical methods and can be used to large scale production of nanoparticles with well-defined size and morphology (Malik *et al.*, 2014). Among the organisms, plants seem to be the best candidates and they are suitable for large scale biosynthesis of nanoparticles with various shapes and sizes. The biomolecules present in the plants extract include various water soluble metabolites such as alkaloids, polyphenols, flavonoids and terpenoids may act both as reducing and stabilizing agents in the synthesis of nanoparticles.

Murraya koenigii is one of the locally grown plants that has been investigated and identified to have high content of biomolecules such as flavonoids and phenolic compounds (Salomi and Manimekalai, 2016). These biomolecules give *Murraya koenigii* the great potential as antioxidant and thus making it suitable to be used in biosynthesis of metal nanoparticles. To the best of our knowledge, there have been no reports on the synthesis of CuO NPs using *Murraya koenigii* aqueous extract.

Nitroaromatic compounds such as nitrobenzene, nitrophenol, nitrotoluene and nitrobenzoate are common industrial nitrogen-containing aromatic organic compounds that are commonly used in the manufacturing of pharmaceuticals, plastics, dyes and fertilisers (Higson, 1992; Ju *et al.*, 2010). For example, *o*-vinylnitrobenzenes are used in the production of indoles, which are active components of several drugs and agrochemicals (Glotz *et al.*, 2017).

The formation of nitro aromatic amines through the reduction of nitroarenes also represents a fundamental transformation. This is because of aromatic amines are considered to be important intermediates and essential building blocks that are frequently used in industrial synthesis of dyes, pharmaceutical products, agricultural chemicals, surfactants and polymers (Freeman, 2011; Peter and John, 2012; Pereira *et al.*, 2013). The importance of nitro aromatic amine compounds in a wide range of applications has resulted in the development of many effective protocols to improve the catalytic reduction of nitroaromatic compounds to amino compounds.

1.2 Problem Statement

Copper oxide nanoparticles (CuO NPs) are synthesized through different techniques and methods including precipitation, sonochemical route, sol-gel, hydrothermal approach, chemical bath deposition, and chemical reduction. These methods have many disadvantages due to the difficulty of scale up the process, high energy consumption and using hazardous chemicals. For example, preparation via chemical reduction involve the hazardous reducing agent such as hydrazine hydrate, N_2H_4 and stabilizers such as cetyltrimethylammonium bromide (CTAB) and polyvinyl alcohol (PVA) are required to prevent the nanoparticles from agglomeration and precipitating out. These reducing agents and stabilizers used are toxic and potentially hazardous to human and environment. Physical methods of synthesis such as laser ablation method and ball milling may provide an alternative route for synthesis of metal nanoparticles that are free from unwanted chemical toxicity. Nevertheless, these methods require sophisticated and high-cost equipment as well as require high-energy consumption that may lead to increase in cost.

Recently, the biosynthetic method employing plant extract has appeared as a green, simple and viable method for the synthesis of metallic nanoparticles due to a growing demand to develop eco-friendly and energy efficient processes in nanoparticles synthesis (Iravani, 2011). The existence of biomolecule such as flavonoid and polyphenols in plants can potentially act as reducing and stabilizing agent in the synthesis of metal nanoparticles (P. Singh *et al.*, 2016). A phytochemical screening of *Murraya koenigii* showed a high content of flavonoid (quercetin, catechin, epicatechin, naringin, rutin, myricetin) and phenolic compounds (gallic acid) levels in its extract (Ghasemzadeh *et al.*, 2014). Moreover, *Murraya koenigii* has been reported to possess high antioxidant activity in 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging and high value of total phenolic content (TPC) (Patterson and Verghese, 2015). Thus, *Murraya koenigii* leaf extract has great potential to be used as reducing and stabilising agents in the preparation of CuO NPs.

Aromatic nitro-compounds are the organic pollutants present in industrial and agricultural wastewaters as these compounds are used mainly to prepare dyes, pesticides, explosives, plasticizers and herbicides. Especially, 4-nitrophenol pollutes water and is a significant threat to the environment and public health, as it is highly toxic and carcinogenic in nature. In contrast, 4-aminophenol is an industrially important raw material, which has been widely used as the intermediate for the manufacture of many analgesic and antipyretic drugs. Traditionally, the reduction from nitro to amino can be carried out by various transition metal-catalysed hydrogenations, which is considered one of the most important and challenging tasks in synthetic organic chemistry. Although various metal catalysts such as Au and Pd, have been effectively used to reduce nitro-compounds, a successful catalyst system with high reaction rate, low dosage of catalyst and excellent yields has not been achieved. Additionally, in most cases, hydrogenating agents like $LiAlH_4$ or $LiBH_4$ were employed with the use of hazardous organic solvents like THF, DMF, *etc* (Souza *et al.*, 2016). and in some cases, the reaction temperature was very high. Thus, the development of a heterogeneous catalyst for the selective hydrogenation of nitroaromatic to aromatic amines in the aqueous phase under mild conditions is highly demanded.

In the past few decades, attention has drawn to the use of earth abundant copper as organic transformation catalyst. Thus, utilization of copper-based catalyst in nitroaromatic compound reduction reaction is promising since copper is low toxicity and easily available metals. By using $NaBH_4$ as the source of hydrogen, the dehydrogenation of $NaBH_4$ in water can be effectively catalyzed by transition metals such as copper without employing hazardous organic solvents, which is not sustainable for green production.

1.3 Objectives of the study

The objectives of this study are:

(a) To synthesize and optimize the bioreduction process of copper(II) oxide nanoparticles using *Murraya koenigii* aqueous leaf extract.

(b) To characterize the biosynthesised copper(II) oxide nanoparticles.

(c) To evaluate the catalytic activity of the biosynthesized copper(II) oxide nanoparticles in the reduction of nitroaromatic compounds.

1.4 Scope of the Study

This research is focused on the biosynthesis of CuO NPs by using aqueous leaf extracts of *Murraya koenigii* as both reducing and stabilizing agent. The synthesis of CuO NPs was optimized using several parameters namely, the volume of *Murraya koenigii* leaf extract (1, 2, 3, 4 mL), pH (5.4, 8, 9, 10, 11), temperature (26°C, 60°C, 80°C) and the reaction time (until saturation). The formation of the CuO NPs was monitored using UV-Vis spectroscopy. The biosynthesised CuO NPs were then characterized by FTIR spectrocopy, XRD and HRTEM analyses. The catalytic activity of the biosynthesised CuO NPs has been tested towards the reduction of several nitroaromatic compounds (4-nitrophenol, 2-methyl-4-nitrophenol, nitrobenzene, 4-nitroaniline, 4-nitrobenzaldehyde, 4-nitrotoluene, 3-nitrotoluene, 2-nitrotoluene) to their corresponding aminoaromatic compounds in aqueous phase using sodium borohydride as the reductant. The catalytic reduction reactions were monitored using UV-Vis spectroscopy. The product of the catalytic reduction reaction of 4-nitrophenol was isolated and structurally characterized using FTIR and ^{1}H NMR spectroscopic analyses.

1.5 Significance of the study

The biosynthesis method using leaf extract of *Murraya koenigii* proposed in this research is promising as its laboratory approach and working procedures are simple. In addition, the bioreduction is green, viable and eco-friendly in CuO NPs syntheses and eliminates the use of hazardous and toxic chemicals. Furthermore, this approach is significant due to its low cost, easily scalable and readily conducted at room temperature. This biosynthetic methodology will make it possible to develop other copper-based nanoparticles with specific properties tailored to application in fine chemicals industry especially in organic transformations.

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