BIOSYNTHESIS OF SILVER NANOPARTICLES-EGGSHELL NANOCOMPOSITE USING *Garcinia mangostana L*. LEAF EXTRACT AND ITS APPLICATION FOR THE REDUCTION OF 4-NITROPHENOL

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A dissertation submitted in fulfilment of the
requirements for the award of the degree of
Master of Science

Faculty of Science
Universiti Teknologi Malaysia

AUGUST 2020

ACKNOWLEDGEMENT

Along my M.Sc. journey, there are many wonderful people whom I am grateful for. Firstly, I would like to give my most sincere thanks to my supervisor, Prof. Dr. Mustaffa Shamsuddin for giving me this golden opportunity to be his student, for his supervision, endless efforts in guidance, encouragement, patience, knowledge and understanding throughout the course of my project. I am very thankful for his invaluable advice and detailed direction to make this journey a success.

I would like to express my deepest appreciation to the technical staff from Department of Chemistry, University Teknologi Malaysia (UTM), Mr. Amin and Mr. Fuad, from Department of Physics, University Teknologi Malaysia (UTM), Ms. Zaza and from University Laboratory Management Centre (PPMU), for their technical support in handling instrument and assistance in sample analysis.

To my fellow lab mates, Dr. Suhaila Borhamdin, Ms. Atieya Abdul Hadi and Mr. Omar, I wish to say thanks a lot for all the help and opinions. Their kindness are which I can't repay with thanks.

Lastly, I would like to express my special thanks to my parents, Mr. Mohd Tubillah and Mdm. Wan Rosnani for their countless support. Also, special thanks to my family members. For all of you, thank you from the bottom of my heart.

ABSTRACT

In recent years, metal nanoparticles have attracted wide attention due to their attractive properties and interesting applications. In particular, the catalytic properties of silver nanoparticles (Ag NPs) are of interest to many researchers because of their high reactivity. This study reported the synthesis of Ag NPs using *Garcinia mangostana L*. leaf extract as reducing and stabilizing agent. The biosynthesized Ag NPs were then immobilized on the surface of eggshell powder. The formation of Ag NPs were confirmed by the presence of absorption peak at 450 nm and the bioreduction reaction was completed within 4 h as monitored by ultraviolet-violet (UV-Vis) spectroscopy. The Fourier transform infrared spectroscopy (FTIR) analysis on the *Garcinia mangostana L*. leaf extract revealed the presence of -OH functional groups that were involved in the reduction and stabilizing of Ag NPs. Energy dispersive X-ray (EDX) analysis on the AgNPs/eggshell nanocomposite showed the presence of Ag peaks that indicated the successful immobilization of Ag on the eggshell powder. The X-ray diffraction (XRD) analytical data on the nanocomposite showed a series of diffraction peaks that are consistent with crystalline $CaCO_3$ from the eggshell and metallic Ag. From TEM images, Ag NPs were mostly of spherical shape with a mean diameter of 14.6 nm. The synthesised AgNPs/eggshell nanocomposite was tested as catalyst for the reduction of 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride at room temperature. The highest activity was observed for the AgNPs/eggshell nanocomposite with Ag loading of 6 wt% and 4-nitrophenol with concentration of 0.03 mM. Under these optimum conditions, the 4-nitrophenol reduction showed good reproducibility where the average rate of reaction is 0.1478 min^{-1} while the average percentage of reduction calculated is 98.49%. From the recyclability test, the AgNPs/eggshell nanocomposite gave a slight decreased in catalytic activity within three catalytic cycles due to mass loss.

ABSTRAK

Beberapa tahun kebelakangan ini, nanopartikel logam telah mendapat perhatian kerana sifat dan aplikasinya yang menarik. Khususnya, sifat pemangkinan nanopartikel perak (Ag NPs) telah menarik minat ramai penyelidik kerana kereaktifannya yang tinggi. Kajian ini melaporkan sintesis Ag NPs dengan menggunakan ekstrak daun *Garcinia mangostana L.* sebagai agen penurunan dan agen penstabilan. Ag NPs yang telah disintesis itu kemudian dipegunkan pada permukaan serbuk kulit telur. Pembentukan Ag NPs telah disahkan dengan kehadiran puncak penyerapan pada 450 nm dan tindak balas biopenurunan itu selesai dalam masa 4 jam sebagaimana yang dipantau menggunakan spektroskopi ultra ungu-cahaya nampak (UV-Vis). Analisis spektroskopi inframerah transformasi Fourier (FTIR) ke atas ekstrak daun *Garcinia mangostana L.* menunjukkan kehadiran kumpulan berfungsi -OH yang terlibat dalam penurunan dan penstabilan Ag NPs. Analisis serakan tenaga sinar-X (EDX) bagi nanokomposit AgNPs/kulit telur menunjukkan kehadiran puncak Ag yang membuktikan Ag berjaya dipegunkan pada permukaan serbuk kulit telur. Data analisis pembelauan sinar-X (XRD) bagi nanokomposit menunjukkan satu siri puncak pembelauan yang konsisten dengan hablur $CaCO_3$ dari kulit telur dan logam Ag. Dari imej TEM, kebanyakan Ag NPs berbentuk sfera dengan purata diameter 14.6 nm. Nanokomposit AgNPs/kulit telur yang telah disintesis itu kemudiannya diuji sebagai pemangkin untuk penurunan 4-nitrofenol kepada 4-aminofenol dengan kehadiran natrium borohidrida pada suhu bilik. Aktiviti tertinggi diperhatikan untuk nanokomposit AgNPs/kulit telur dengan muatan Ag sebanyak 6 wt% pada kepekatan 4-nitropenol 0.03 mM. Di bawah keadaan optimum ini, penurunan 4-nitrofenol menunjukkan kebolehulangan yang baik dengan kadar tindak balas purata 0.1478 min^{-1} manakala peratusan pengurangan purata yang dikira adalah 98.49%. Daripada ujian kitar semula, nanokomposit AgNPs/kulit telur menunjukkan sedikit pengurangan dalam aktiviti pemangkinan dalam tiga kitaran mangkin disebabkan kehilangan jisim.

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LIST OF ABBREVIATIONS

AgNPs	-	silver nanoparticles
EDX	-	Energy Dispersive X-Ray
fcc	-	face centered cubic
vs	-	Versus
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
NPs	-	nanoparticles
TG-DTA	-	Thermogravimetric-differential Thermal Analysis
SPR	-	surface plasmon resonance
BET	-	Brunauer-Emmett-Teller
TEM	-	Transmission Electron Microscopy
UV-Vis	-	Ultraviolet Visible
XRD	-	Powder X-ray Diffraction

LIST OF SYMBOLS

µm	-	Micrometre
^{o}C	-	degree Celsius
Å	-	Armstrong
cm^{-1}	-	per centimetre
g	-	gram
kV	-	kilo volt
mA	-	milli Ampere
mM	-	milli Molar
nm	-	nanometer
rpm	-	revolution per minute

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nanoscience is a multidisciplinary field that involve the design and engineering of functional systems at the molecular scale. It is a field of applied science focused on the synthesis, characterization and application of materials and devices on the nanoscale. In general, nanoscience can be defined as the art and science of manipulating matter at the nanoscale to create new and unique materials. Nanoscaled materials are usually categorized as materials having structured components with at least one dimension less than 100 nm (Sithara *et al*, 2017).

Nanoparticles are of great interest owing to their extremely small size and high surface to volume ratio, which alter their physical and chemical properties compared to bulk of the same chemical composition (Nakkala *et al*, 2018). In recent years, metal nanoparticles have received considerable attention because of their attractive properties and interesting applications. They are widely used in various fields including sensors, catalysts, electronics and drug delivery (Rasheed *et al*, 2018; Chouhan *et al*, 2017). Among them, silver nanoparticles (Ag NPs) are being studied extensively for their potential in catalysts, antibacterial agents, biological diagnostics and electronics (Zhang *et al*, 2019; Beyene *et al*, 2017). In particular, the catalytic properties of Ag NPs are of interest to many researchers because of their high reactivity.

Currently, the synthetic approaches for Ag NPs are categorized into physical, chemical, and biological green syntheses. The disadvantages of the physical and chemical syntheses are high energy requirement, difficult set-up and usage of hazardous chemicals (Ravichandran *et al*, 2011; Karthik *et al*, 2017). Meanwhile, the biological synthesis of Ag NPs by using plant extract has attracted wide attention because it is simple, cost-effective and greener synthesis method. The bioactive molecules such as polyphenols and flavonoids that are naturally present in the plant extract could act as a reducing and stabilizing agent in the formation of Ag NPs (Jean *et al*, 2012; Arya *et al*, 2019).

Nanosized particles has propensity to agglomerate due to their higher surface energy as compared to their bulk (Wang *et al*, 2017; Sudhakar and Soni *et al*, 2018). Colloidal Ag NPs when used directly as catalyst in the liquid phase will show a decrease in its activity with time due to agglomeration (Nasrollahzadeh *et al*, 2020). In addition, the very small size of Ag NPs are very difficult to be separated from the reaction mixture by traditional filtration methods. Therefore, immobilization of Ag NPs onto a solid support have attracted a lot of attention to avoid it from agglomeration and allow ease of separation.

Eggshell is a solid bio-waste produced from food processing industries. Most of the eggshell waste is commonly disposed in landfills because it was traditionally useless. The chemical constituent of eggshell consists of calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) (Nagabhushana *et al*, 2017; Wei *et al*, 2009). The high content of calcium carbonate ($CaCO_3$) in the eggshell waste and the abundance of eggshell waste resources make it a great low-cost material for metal catalyst support.

Mangosteen (*Garcinia mangostana L.*) as a medicinal plant is useful in the treatment of diarrhoea, infections of the skin, inflammation and fever (Pandey *et al*, 2015). Previous studies showed the extracts of *Garcinia mangostana L.* from all parts of the plant contain secondary metabolites such as xanthones. In particular, there were studies on the structure of xanthones found in the leaf extracts of *Garcinia mangostana L.* (Kao *et al*, 2018; Jose *et al*, 2008). Thus, these xanthones, tannins and flavonoids have antioxidant activity that could act as reducing agent as well as capping agent in the formation of Ag NPs.

In this study, an environmentally friendly approach for the preparation of the Ag NPs onto eggshell powder using *Garcinia mangostana L*. leaf extract as reducing and stabilizing agents was reported. The performance of the AgNPs/eggshell nanocomposite as catalyst for the 4-nitrophenol to 4-aminophenol in aqueous media at ambient temperature was investigated.

1.2 Problem Statement

Traditionally, Ag NPs have been successfully synthesized through physical and chemical methods. The physical method such as laser photoreduction requires high temperature and pressure and high technology equipment (Courrol *et al*, 2018). Meanwhile, the chemical methods usually involves usage of toxic and hazardous chemicals as reductant or solvents (Younis *et al*, 2019). These disadvantages may be overcome by using the proposed biosynthesis method in the synthesis of Ag NPs.

Biological method using plant extracts is an alternative way to synthesize Ag NPs. The biological method has appeared to be simple, environmentally friendly and non-toxic and is readily conducted at ambient conditions. In this study, a biological method using leaf extract of *Garcinia mangostana L*. has been explored as a reducing and capping agent in the synthesis of Ag NPs. Biomolecules such as xanthones and polyols are reported to be present in the *Garcinia mangostana L*. leaf extract and have potential to act as reducing and stabilizing agents in the synthesis of Ag NPs (Pierson *et al*, 2012; Alsultan *et al*, 2017).

Due to their high surface area to volume ratio, Ag NPs can greatly enhance the catalytic performance (Zhang *et al*, 2018). However, agglomeration and difficulties in their separation from the reaction mixtures are some of the downsides of Ag NPs. In order to prevent agglomeration and overcome the problem of their recovery, immobilizing Ag NPs on a solid support is needed. Immobilization helps to reduce agglomeration, increase stability and facilitate the separation and recovery (Das *et al*, 2019). Several inorganic supports such as SiO_2, TiO_2 and Fe_3O_4 have been employed to prevent agglomeration and aid in the catalyst separation (Veisi *et al*, 2019; Liu *et al*, 2019). Although these compounds are good support, there are difficulties in their preparation.

Bio-waste such as eggshell powder seems to be suitable to be used for Ag NPs immobilization due to its abundance and low cost. Eggshell is usually discarded as it is considered as waste. It comes from food industries and has been disposed about hundreds of thousands of tonnes worldwide (Laca *et al*, 2017). In this study, eggshell waste is applied as a solid support for Ag NPs. It is beneficial to make good use of the eggshell waste because it is easily available biomaterial with good chemical and thermal stability and low toxicity. Moreover, its inertness and porous structure make eggshell waste a good option as a support for Ag NPs (Dash *et al*, 2018).

The United States Environmental Protection Agency stated that nitroaromatic compounds such as 4-nitrophenol is a priority pollutant because it is toxic and resists biodegradation (Ai and Jiang, 2013; Veisi *et al*, 2019). Nitroaromatic compounds found in wastewaters come from manufacture of drugs, pesticides and dyes (Rajegaonkar *et al*, 2018; Alhokbany *et al*, 2019). Therefore, it is necessary to find the effective methods to remove these pollutants from wastewater. Reduction process in the presence of metal nanoparticles and sodium borohydride ($NaBH_4$) is a technique for the removal of nitroaromatic compounds such as 4-nitrophenol. In this study, a catalytic reduction of 4-nitrophenol to 4-aminophenol in aqueous solution by using the synthesized catalyst, AgNPs/eggshell nanocomposite was carried out.

1.3 Objectives of Study

The objectives of this study are:

i. To synthesize Ag NPs using *Garcinia mangostana L.* leaf extract as reducing and stabilizing agents.

ii. To immobilize and characterize the biosynthesized Ag NPs onto eggshell powder.

iii. To evaluate the catalytic performance of the biosynthesized AgNPs/eggshell nanocomposite in the reduction of 4-nitrophenol.

1.4 Scope of Study

This study focused on the green synthesis of the AgNPs/eggshell nanocomposite by using leaf extract of *Garcinia mangostana L.* as a reducing and stabilizing agent followed with the investigation of its catalytic activity in the reduction of 4-nitrophenol with the presence of sodium borohydride at room temperature. The green synthesis of the Ag NPs was carried out by addition of *Garcinia mangostana L.* leaf extract (1 mL) into $AgNO_3$ solution (3 mL; 1 mM) to investigate the ability of leaf extract in reducing metal ions. The formation of Ag NPs was preliminarily monitored by UV-Vis spectroscopy. The immobilization of the Ag NPs on eggshell powder support was carried out by adding $AgNO_3$ solution (50 mL) to eggshell powder (1 g). Then, the eggshell powder with immobilized Ag^+ ions were added into of *Garcinia mangostana L.* leaf extract (100 mL) to obtain AgNPs/eggshell nanocomposite. The AgNPs/eggshell nanocomposite were then characterized by FTIR spectroscopy, XRD, EDX and TEM analyses. The evaluation of catalytic activity of AgNPs/eggshell nanocomposite on the reduction of 4-nitrophenol was carried out in a quartz cuvette and the reaction process was monitored by the UV-Vis spectroscopy. Freshly prepared sodium borohydride solution (300 μL; 100 mM) was added into 4-nitrophenol solution (3 mL; 0.05 mM). The color change was observed, and the time taken for the intensity of the peak at 400 nm to decrease and disappear was noted. The reproducibility and recyclability of the AgNPs/eggshell nanocomposite as a catalyst were investigated in this study.

1.5 Significance of Study

This study employed a green method to prepare Ag NPs using abundant and locally available plant. The use of *Garcinia mangostana L*. leaf extract as a reducing agent as well as stabilizing agent in this study is an eco-friendly, simple and toxic free method. In addition, this study also showed that the application of environmentally benign bio-waste as an alternative method for immobilization of metal nanoparticles. Utilization of eggshell powder as a valuable catalyst support not only provide a cost-effective and environmentally friendly way of recycling the solid biomass eggshell waste thus significantly reducing its environmental effects. In this study, the eco-friendly biosynthesized AgNPs/eggshell nanocomposite acted as an effective catalyst to reduce nitrophenols and its derivatives that are considered as intractable pollutants in industrial wastewater.

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