MAGNETICALLY RECOVERABLE BIOSYNTHESISED GOLD NANOPARTICLES AS CATALYSTS FOR OXIDATION OF BENZYL ALCOHOL AND REDUCTION OF 4-NITROPHENOL

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For my beloved husband, children, parents and family, thank you for everything

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ABSTRACT

In recent years, gold nanoparticles (AuNPs) have received considerable attention owing to their unique properties which are promising in diverse fields and applications such as biomedical science and catalysis. AuNPs has been considered as the catalyst of choice for numerous organic reactions. Vast numbers of chemical, physical and biological strategies have been employed to synthesise AuNPs. Among these approaches, the biological method employing plant extract is gaining attention as it is simple and environmentally friendly. In this research, a green biosynthetic approach for the preparation of AuNPs using aqueous leaf extract of *Polygonum minus* as reducing and stabilising agent is described. The reduction of Au(III) ions to elemental Au occurred rapidly and it was completed within 20 min at room temperature as monitored by ultraviolet-visible (UV-Vis) spectroscopy. High resolution transmission electron microscopy/energy-dispersive X-ray (HRTEM/ EDX) and X-ray diffraction (XRD) analytical data indicated that the nanoparticles were in fcc crystalline shape, mostly icosahedral and nearly monodispersed with an average size of 23 ± 5.1 nm. Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetry (CV) analyses of the AuNPs and the leaf extract revealed that the oxidised (quinone) form of quercetin and myricetin were presumably the main stabilising agents in the formation of stable nanoparticles. The biosynthesised AuNPs showed good catalytic activity, with a turnover frequency (TOF) of 85.2 h^{-1} for the oxidation of benzyl alcohol and a normalised rate constant, K_{nor} of 0.06 s^{-1} $mmol^{-1}$ in the reduction of 4-nitrophenol. The same bioreduction process was employed in the preparation of AuNPs catalysts supported on highly branched metformin-functionalised silica-coated magnetite (Fe_3O_4-SiO_2-Met). The structural, surface and magnetic properties of the support material (Fe_3O_4-SiO_2-Met) was investigated by FTIR, XRD, HRTEM/EDX, elemental carbon-hydrogen-nitrogen (CHN), thermogravimetry (TGA) and vibrating sample magnetometry (VSM) analyses. The XRD, HRTEM/EDX, X-ray photoelectron spectroscopy (XPS) and atomic absorption spectroscopy (AAS) analytical data revealed that AuNPs with smaller average sizes (6.1 ± 2.2 nm and 16.2 ± 8.3 nm) were well-dispersed on the Fe_3O_4-SiO_2-Met support. Under optimum benzyl alcohol oxidation reaction conditions, 0.3% Au/Fe_3O_4-SiO_2-Met catalyst displayed an enhanced catalytic performance as compared to the unsupported AuNPs, with a TOF improvement factor of 2.5. Meanwhile, the catalytic performance of the 6% Au/Fe_3O_4-SiO_2-Met catalyst showed enhancement with an increase in the normalised rate constant, K_{nor} value by a factor of 8.8 as compared to the unsupported AuNPs under an optimised 4-nitrophenol reduction reaction conditions. The supported AuNPs catalyst could be easily recovered magnetically and reused for at least four times and three times in the oxidation and reduction reactions, respectively, without significant loss of activity.

ABSTRAK

Dalam beberapa tahun kebelakangan ini, nanopartikel emas (AuNPs) telah mendapat perhatian disebabkan oleh sifat-sifat uniknya yang menjanjikan dalam pelbagai bidang dan penggunaan, misalnya sains bioperubatan dan pemangkinan. AuNPs telah dianggap sebagai mangkin pilihan bagi pelbagai tindak balas organik. Banyak strategi kimia, fizik dan biologi telah digunakan untuk mensintesis AuNPs. Antara pendekatan ini, kaedah biologi yang menggunakan ekstrak tumbuhan telah mendapat perhatian kerana ia mudah dan mesra alam sekitar. Kajian ini menghuraikan pendekatan biosintesis hijau bagi penyediaan AuNPs menggunakan ekstrak akueus daun *Polygonum minus* sebagai agen penurunan dan agen penstabilan. Penurunan ion Au(III) kepada unsur Au telah berlaku dengan cepat dan ia selesai dalam masa 20 minit pada suhu bilik sebagaimana yang dipantau menggunakan spektroskopi ultra ungu-cahaya nampak (UV-Vis). Data mikroskopi elektron penghantaran resolusi tinggi/serakan tenaga sinar-X (HRTEM/EDX) dan pembelauan sinar-X (XRD) menunjukkan nanopartikel adalah berbentuk hablur fcc, kebanyakannya ikosahedral dan hampir mono-tersebar dengan saiz purata 23 ± 5.1 nm. Analisis spektroskopi inframerah transformasi Fourier (FTIR) dan voltammetri berkitar (CV) bagi AuNPs dan ekstrak daun menunjukkan bahawa bentuk teroksida (kuinon) bagi kuersetin dan mirisetin dianggap sebagai agen penstabilan yang utama dalam pembentukan nanopartikel yang stabil. AuNPs yang telah dibiosintesis menunjukkan aktiviti pemangkinan yang baik, dengan frekuensi pusingan balik (TOF) 85.2 j^{-1} bagi pengoksidaan benzil alkohol dan pemalar kadar dinormalkan, K_{nor} 0.06 s^{-1} $mmol^{-1}$ dalam penurunan 4-nitrofenol. Proses biopenurunan yang sama telah digunakan dalam penyediaan mangkin AuNPs disokong magnetit bersalut silika berkefungsian metformin (Fe_3O_4-SiO_2-Met) yang sangat bercabang. Sifat struktur, permukaan dan kemagnetan bahan penyokong (Fe_3O_4-SiO_2-Met) telah dikaji menggunakan analisis FTIR, XRD, HRTEM/EDX, penentuan unsur karbon-hidrogen-nitrogen (CHN), termogravimetri (TGA) dan magnetometri sampel bergetar (VSM). Data XRD, HRTEM/EDX, spektroskopi fotoelektron sinar-X (XPS) dan spektroskopi serapan atom (AAS) menunjukkan AuNPs yang bersaiz lebih kecil (6.1 ± 2.2 nm and 16.2 ± 8.3 nm) telah tersebar dengan seragam pada penyokong Fe_3O_4-SiO_2-Met. Di bawah keadaan tindak balas pengoksidaan benzil alkohol yang optimum, mangkin 0.3% Au/Fe_3O_4-SiO_2-Met telah memaparkan peningkatan prestasi pemangkinan berbanding dengan AuNPs tanpa penyokong, dengan peningkatan TOF 2.5 kali ganda. Sementara itu, prestasi pemangkinan mangkin 6% Au/Fe_3O_4-SiO_2-Met menunjukkan peningkatan dengan kenaikan nilai pemalar kadar dinormalkan, K_{nor} 8.8 kali ganda berbanding dengan AuNPs tanpa penyokong di bawah keadaan tindak balas penurunan 4-nitrofenol yang optimum. Mangkin AuNPs berpenyokong boleh diperoleh semula dengan mudah secara magnetik dan boleh digunakan semula sekurang-kurangnya masing-masing empat kali dan tiga kali bagi tindak balas pengoksidaan dan penurunan, tanpa pengurangan aktivti yang ketara.

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LIST OF ABBREVIATIONS

AAS	-	atomic absorption spectroscopy
APTES	-	(3-aminopropyl)-triethoxysilane
AuNPs	-	gold nanoparticles
CC	-	cyanuric chloride
CHN	-	carbon-hydrogen-nitrogen
CV	-	cyclic voltammetry
CVD	-	chemical vapour deposition
DIPEA	-	*N,N*-diisopropylethylamine
EDX	-	energy-dispersive X-ray
EXAFS	-	extended X-ray absorption fine structure
fcc	-	face-centred cubic
FFT	-	fast fourier transform
FRAP	-	ferric reducing antioxidant power
FTIR	-	fourier transform infrared
GAE		gallic acid equivalent
GC-FID	-	gas chromatography-flame ionization detector
HRTEM	-	high resolution transmission electron microscopy
JCPDS	-	The Joint Committee on Powder Diffraction Standards
KBSI	-	Korea Basic Science Institute
Met	-	metformin
NCIM	-	National Collection of Industrial Microorganisms
RT	-	room temperature
SPR	-	surface plasmon resonance

TAE	-	tannic acid equivalent
TBHP	-	*tert*-butyl hydroperoxide
TEOS	-	tetraethyl orthosilicate
TGA	-	thermogravimetric analysis
THF	-	tetrahydrofuran
TOF	-	turnover frequency
TON	-	turnover number
TPC	-	total phenolic content
UKM	-	Universiti Kebangsaan Malaysia
UV-Vis	-	ultraviolet-visible spectroscopy
VSM	-	vibrating sample magnetometer
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray powder diffraction

LIST OF SYMBOLS

%	-	percent
% w/v	-	percent weight per volume
°C	-	degree Celcius
°C min^{-1}	-	degree Celcius per minute
µm	-	micrometer
µmol	-	micromole
2θ	-	Bragg angle
Å	-	Ångström
cm	-	centimeter
cm^{-1}	-	frequency
emu g^{-1}	-	magnetic moment per gram
eV	-	electronvolt
g	-	gram
h	-	hour(s)
h^{-1}	-	per hour
K_a	-	rate constant
K_{nor}	-	normalised rate constant
keV	-	kiloelectronvolt
kOe	-	kiloOersted
kV	-	kilovolt
M	-	Molarity
M_s	-	saturation magnetisation
m	-	meter

$M\Omega \cdot cm$	-	conductivity
mA	-	miliampere
mg	-	milligram
min	-	minute(s)
mL	-	milliliter
mm	-	millimeter
mM	-	millimolar
mmol	-	millimole
mVs^{-1}	-	millivolt per second
nm	-	nanometer
°	-	degree angle
ppm	-	part per million
rpm	-	revolutions per minute
s	-	second(s)
s^{-1}	-	per second
s^{-1} $mmol^{-1}$	-	per second per milimole
V	-	volt
wt%	-	weight percent
λ	-	wavelength
λ_{max}	-	wavelength maxima

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Gold (Au) is known to be highly resistant towards oxidation and corrosion as compared to other metals and is traditionally regarded as chemically inert and catalytically inactive (Housecroft and Sharpe, 2008). However, when the size of Au is reduced to nanometres, the catalytic properties of Au are revealed. Bond et al (1973) first reported the hydrogenation of olefins using supported Au nanocatalysts. More than a decade later, Haruta et al (1987) discovered the surprising activity of Au nanoparticles (AuNPs) with diameters of less than 10 nm in promoting the low-temperature oxidation of CO. Since then, many findings on the catalytic properties of AuNPs have been published. Currently, AuNPs is considered the catalyst of choice for organic reactions such as oxidation of CO, alcohols and alkenes, hydrogenation of unsaturated carbonyls and nitro group, alkyne activation and C−C coupling reactions (Takale, Bao and Yamamoto, 2014; Hutchings, 2018; Zhao and Jin, 2018).

AuNPs can be synthesised by using a variety of physical and chemical methods. Although the existing methods have successfully produced well-defined and pure AuNPs, the processes are expensive, require high energy, involve the use of hazardous chemicals and generate by-products that are potentially harmful to the environment (Thakkar, Mhatre and Parikh, 2010; Alex and Tiwari, 2015; Santhoshkumar, Rajeshkumar and Kumar, 2017; Zada et al, 2018).

Recently, the utilisation of biological systems has appeared as a novel and reliable method for the synthesis of AuNPs due to growing demand to develop eco-friendly processes in nanomaterials syntheses. Organisms such as bacteria, fungi, yeast, algae and plants have been employed in the AuNPs syntheses. Among these,

plants have more advantages compared to other organisms since the biosynthesis using plants is eco-friendly, simple, non-toxic, inexpensive, easily scalable, faster reaction rate and produce more stable and various morphologies of AuNPs (Iravani, 2011; Noruzi, 2015; Singh et al, 2016). Besides, plant extracts contain biomolecules such as flavonoids, terpenoids, alkaloids, and polyphenols that may act as reducing and stabilising agents in the formation of AuNPs (Mittal, Chisti and Banerjee, 2013; Jeevanandam, Chan and Danquah, 2016).

Generally, AuNPs are not stable and tend to form larger particles to minimise its high surface energy, which contributed by its high surface-to-volume ratio properties. When synthesised colloidal AuNPs are used directly as a catalyst in the liquid phase, the activity will decrease with time due to the agglomeration of AuNPs (Panigrahi et al, 2007). Moreover, the very small AuNPs are difficult to be separated from the reaction mixture by traditional filtration techniques (Karimi, Mansouri and Mirzaei, 2015). Therefore, AuNPs have been dispersed onto a solid support to protect it from agglomeration and make it easily separated and possibly reuse.

1.2 Problem Statements

Traditionally, AuNPs can be successfully synthesised via physical and chemical methods. However, the physical methods such as laser ablation, laser pyrolysis and ultrasonic fields, that require expensive high technology device and high pressure and temperature are not energy-efficient (Tangeysh et al, 2013; Bouhadoun et al, 2015; Okitsu et al, 2001). Meanwhile, chemicals such as sodium borohydride, hydroxylamine hydrochloride and tetrakis(hydroxymethyl)phosphonium chloride being used as reducing and stabilising agents are hazardous, not eco-friendly and may contribute to the toxicity issue and potentially harmful to the environment (Iwamoto et al, 2005; Haiss et al, 2007; Zhang et al, 2013). These problems can be principally minimised by using the proposed biological synthesis method in the preparation of AuNPs.

Recently, the biological synthesis method employing plant extracts has appeared as a non-toxic, simple, eco-friendly and rapid method for the synthesis of AuNPs. Moreover, this biosynthesis method is suitable for large-scale production due to its low cost and is readily conducted at room temperature and pressure (Iravani, 2011; Noruzi, 2015; Singh et al, 2016). Hence, in this research, a biosynthesis method employing *Polygonum minus* aqueous leaf extract has been studied. Aqueous leaf extract of *Polygonum minus* has been reported to have the highest total phenolic content (TPC) which is 44.35 mg/ 100 g fresh weight, tannic acid equivalent (TAE) and 55.5 mg/ g extract, gallic acid equivalent (GAE). It also has the highest reducing power with the ferric reducing antioxidant power (FRAP) values of 849.33 mmol GAE/ g extract among several herbs in Malaysia (Huda-Faujan et al, 2007; Qader et al, 2011). Phenolic compounds such as flavonoids quercetin and myricetin were identified in the aqueous leaf extract of *Polygonum minus* have great potential as reducing and stabilising agents in the preparation of AuNPs (Miean and Mohamed, 2001).

AuNPs have been immobilised on various solid supports such as carbon, silica, metal oxides and zeolites to ease the catalyst recovery and enhance the catalyst stability (Bond and Thompson, 1999). However, the use of these traditional inorganic supports requires time and energy-consuming workup procedures such as filtration and centrifugation to recover the supported AuNPs catalysts. In order to conquer this problem, the utilisation of magnetic nanoparticles as catalyst support has emerged as a viable alternative as their paramagnetic and insoluble nature enables easy and efficient catalyst recovery (Karimi et al, 2015). In this research, magnetite (Fe_3O_4) nanoparticles were used as the catalyst support as it could facilitate the dispersion of AuNPs as well as can be easily recovered and separated from the reaction mixture by using an external magnetic field.

Generally, the Fe_3O_4 nanoparticles are coated with a silica (SiO_2) shell to form a core-shell Fe_3O_4-SiO_2 structure to improve the dispersity, chemical stability and thermal stability of the catalyst support. However, the surface of SiO_2 is not suitable for the deposition of AuNPs due to weak interactions between AuNPs and the support, which resulted in low metal loading. Furthermore, the AuNPs tend to

agglomerate and form larger particles, which leads to loss of catalytic activity. Hence, the AuNPs has to be stabilised to prevent agglomeration. With the aim of addressing this problem, the ligands with metal affinity groups, such as amino ($-NH_2$) group has been post-grafted onto the surface of SiO_2 to stabilise and disperse the AuNPs (Oliveira, Kiyohara and Rossi 2010; Oliveira et al, 2011). In this study, the highly branched metformin-functionalised silica-coated magnetite (Fe_3O_4-SiO_2-Met) has been synthesised as catalyst support. Metformin (Met), a polydentate biguanide derivative, contains $-NH_2$ groups that anchored the AuNPs onto the solid support via electrostatic interaction and therefore can control the particle size, circumvent agglomeration, increase stability and dispersion of AuNPs

Benzaldehyde with a characteristic almond-like odour is the second most important aromatic molecule after vanillin used in the perfumery, cosmetics, pharmaceutical, dyestuff, food and agrochemical industries (Pina, Falletta and Rossi, 2008; Santra et al, 2016). Commercially, benzaldehyde is synthesised via hydrolysis of benzal chloride and the air oxidation of toluene (Kroschwitz, 2004). However, the benzaldehyde produced is contaminated with chlorine in the first process, and the latter provides poor selectivity of benzaldehyde. Recently, catalytic liquid-phase oxidation of benzyl alcohol to benzaldehyde is practically a preferred reaction as it provides chlorine-free and high selectivity of benzaldehyde, which is required in perfumery and pharmaceutical industries (Ndolomingo and Meijboom, 2017). Commonly, oxidation of alcohols has been carried out with a stoichiometric amount of metal-based oxidants, notably chromium(VI) and permanganate reagents (Hudlický, 1990). However, these oxidants have a disadvantage of generating a large amount of toxic heavy metal waste, thus, cause severe environmental problems. Hence, in this study, a non-toxic and environmentally benign oxidant, *tert*-butyl hydroperoxide (TBHP) was used in the liquid-phase oxidation of benzyl alcohol to benzaldehyde in conjunction with biosynthesised AuNPs catalysts.

4-Nitrophenol is a common organic pollutant that exists in industrial and agricultural effluents. It possesses high toxicity, suspected carcinogens and is listed in the 58^{th} position out of the 129 priority pollutants by the United States Environmental Protection Agency (2014). Usually, the removal of 4-nitrophenol by

physicochemical treatment and biological method are difficult due to the high stability and biorefractory characteristics of 4-nitrophenol. Thus, the development of a method for efficient removal of 4-nitrophenol is important for public health and can help to restore impacted environments. On the other hand, 4-aminophenol is an important intermediate to produce pharmaceuticals substances, photographic materials and rubber materials (Gkizis, Stratakis and Lykakis, 2013). Generally, 4-aminophenol can be synthesised via catalytic reduction of 4-nitrophenol. However, the process requires extreme reaction condition such as high temperature, high hydrogen pressure and use of organic solvents (Vaidya, Kulkarni and Chaudhari, 2003; Du et al, 2004). In order to overcome this problem, an effective catalytic reduction of 4-nitrophenol to 4-aminophenol in aqueous solution and under mild condition by using biosynthesised AuNPs as a catalyst and clean reductant, hydrazine hydrate have been carried out in this study.

1.3 Objectives of the Research

The objectives of the research are:

(i) To synthesise AuNPs using *Polygonum minus* aqueous leaf extract as reducing and stabilising agents.

(ii) To immobilise the biosynthesised AuNPs onto highly branched metformin-functionalised silica-coated magnetite support.

(iii) To evaluate the performance of the biosynthesised AuNPs and supported biosynthesised AuNPs catalysts in the oxidation of benzyl alcohol and reduction of 4-nitrophenol.

1.4 Scope of the Research

This research focused on the preparation of AuNPs using aqueous leaf extract of *Polygonum minus* as reducing and stabilising agents with varying parameters namely, the reaction time, volume and pH of leaf extract to obtain the optimum

reaction parameters. Then, the AuNPs supported on metformin-functionalised silica-coated magnetite materials (Au/Fe_3O_4-SiO_2-Met) were prepared by using a similar biosynthesis method. The catalytic activity of the biosynthesised AuNPs and Au/Fe_3O_4-SiO_2-Met have been tested in the liquid-phase oxidation of benzyl alcohol to benzaldehyde using TBHP as oxidant and the reduction of 4-nitrophenol to 4-aminophenol using hydrazine hydrate as reductant. The samples were characterised by an analytical technique such as UV-Vis, FTIR, XRD, HRTEM/EDX, XPS, VSM, TGA, CV, AAS, CHN and GC-FID. The research outline is illustrated in **Figure 1.1**.

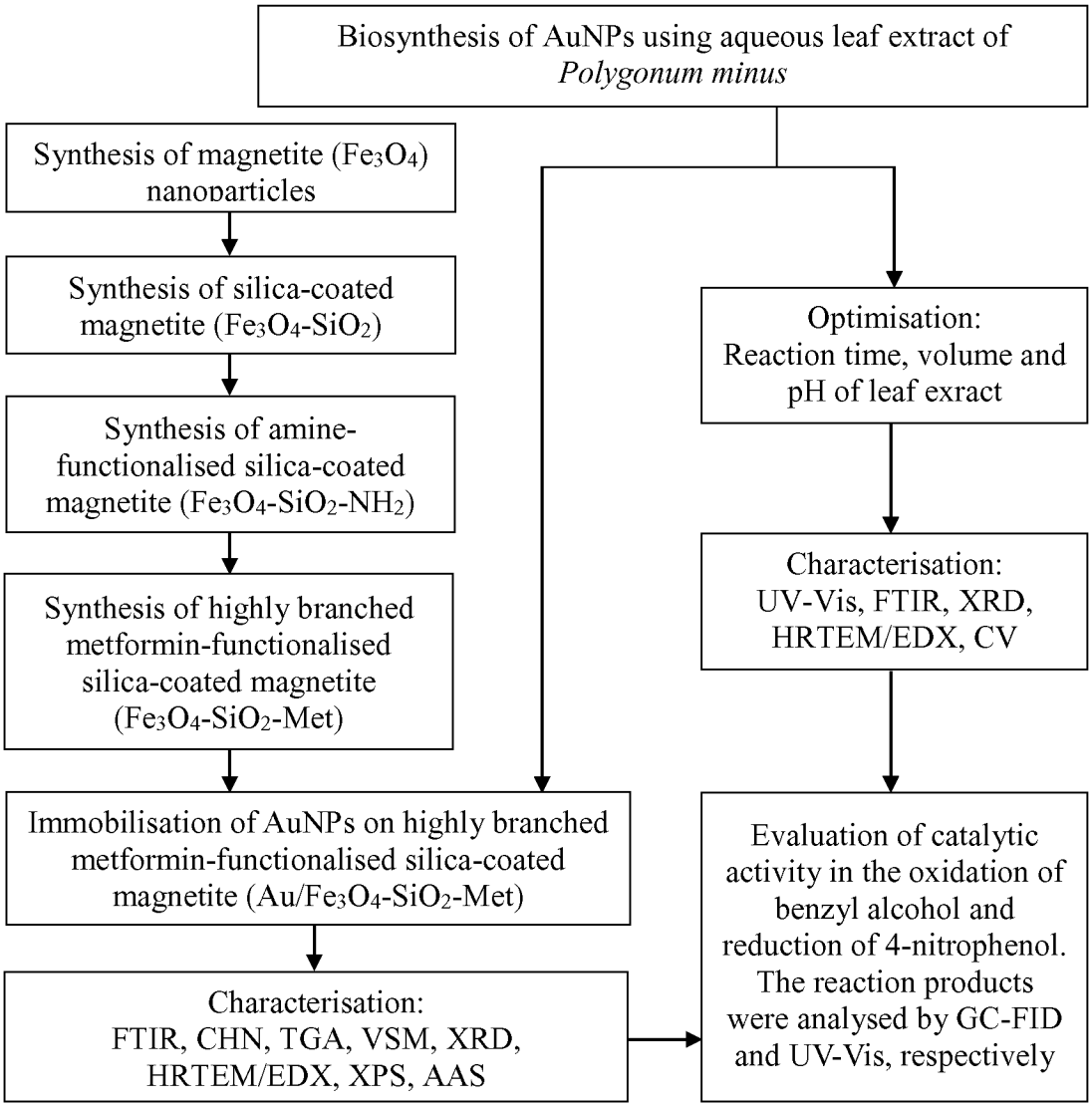

Figure 1.1 Research flow-chart outline

1.5 Significance of the Research

The biosynthesis method using aqueous leaf extract of locally available *Polygonum minus* plant employed in this research is an eco-friendly, simple, non-toxic and rapid process. Furthermore, this approach is significant in the preparation of large-scale metal nanoparticles due to its low cost, easily scalable and readily conducted at room temperature and pressure thus can avoid the use of hazardous and toxic chemicals. The magnetically recoverable magnetic support used in the catalyst design can be considered a green technology since it is efficient, fast, consumes low energy and avoid the use of solvents. Moreover, the magnetic separation can facilitate the catalyst recovery in the recycling process and thus, enhance the catalyst reusability. The magnetically separable biosynthesised AuNPs catalyst in this research could be a promising catalyst in the chemical industries, especially in the alcohol oxidation process and the removal of nitroarenes pollutants from wastewater. Besides, this research may be useful in developing a green oxidation and reduction processes by employing clean oxidant and reductant, utilising eco-friendly biosynthesised catalyst as well as demonstrating the efficient catalyst separation and recovery techniques.

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Appendix L

List of publication, conferences and patent

1. Suhaila Borhamdin, Mustaffa Shamsuddin and Abdolhamid Alizadeh. (2016). Biostabilised Icosahedral Gold Nanoparticles: Synthesis, Cyclic Voltammetric Studies and Catalytic Activity Towards 4-Nitrophenol Reduction. *Journal of Experimental Nanoscience*. 11(7), 518-530. https://doi.org/10.1080/17458080.2015.1090021 (Q2, IF: 2.482)

2. Suhaila Borhamdin, Mustaffa Shamsuddin and Abdolhamid Alizadeh. Biomediated Synthesis of Icosahedral Gold Nanoparticle using *Polygonum minus* Leaf Extract and Its Catalytic Activity for 4-Nitrophenol Reduction. (2014). *Paper presented at the 18th Malaysian International Chemical Congress (18MICC)*. November 3-5. PWTC, Kuala Lumpur.

3. Suhaila Borhamdin, Mustaffa Shamsuddin and Abdolhamid Alizadeh. Gold Clusters on Thiol-Functionalized Fe_3O_4@SiO_2 Nanoparticles: A Novel Bioreduced Catalyst for Oxidation of Benzyl Alcohol. (2014). *Paper presented at the Twelfth Regional Annual Fundamental Science Symposium (12th RAFSS)*. September 8-10. Persada Johor International Convention Centre, Johor Bahru, Johor.

4. Suhaila Borhamdin, Mustaffa Shamsuddin and Jon Efendi. Biosynthesis of Gold Nanoparticles Using Leaf Extract of *Polygonum Minus*. (2013). *Paper presented at the 4th International Conference for Young Chemists (4th ICYC)*. January 30 - February 1. Bayview Hotel, Georgetown, Penang.

5. Suhaila Borhamdin and Mustaffa Shamsuddin. Method of Preparing "Green" Gold Nanoparticles Using *Polygonum minus* Aqueous Leaf Extract. Malaysian Patent file no: PI 2014700170. (2014).