CHITOSAN SUPPORTED BIOSYNTHESIZED GOLD NANOPARTICLES AS CATALYST FOR OXIDATION AND REDUCTION REACTIONS

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To my beloved Mother, Father and Family.....
Thank you for everything

and to someone special......

Sami Ahmed, Ahmed & Duha

Thank you for waiting all this while

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ABSTRACT

For many years, gold was considered as an inert catalyst. However, gold nanoparticles (AuNPs) are now attracting significant attention as they show different chemical and physical properties depending on size and shape. AuNPs have been recognised as an active and effective catalyst for organic transformations. Currently, there is a growing need to develop environmentally benign metal nanoparticle synthesis process that does not use any toxic chemicals. In this regard, biological approach for metal nanoparticle synthesis using microorganisms, enzymes, plants or plant extracts have been applied as possible eco-friendly alternatives to chemical and physical methods. In this research, an environmental friendly method for the synthesis and stabilization of AuNPs by the reduction of aqueous $AuCl_4^-$ ions using leaf extract of *Psidium guajava* is reported. The optimized parameters for the formation of AuNPs are 10 mL of 1 mM Au(III) ions, 1 mL of 1% leaf extract at pH 6 and at 30 minutes reaction time. UV-Vis spectroscopic analysis of the reaction mixture confirmed the successful reduction of Au(III) ions to Au(0). Transmission electron microscopic (TEM) analysis revealed a dominant spherical morphology of the AuNPs with average size of 7.6 nm. X-ray diffraction (XRD) analysis of the purified gold nanoparticles showed five Bragg reflection peaks at 2θ of 38.42 Å, 44.45 Å, 64.71 Å, 77.61 Å and 81.87 Å corresponding to the (111), (200), (220), (311) and (222) lattice planes respectively that could be indexed to the face centred cubic (fcc) structure of gold. Fourier transform infrared (FTIR) spectroscopic analysis on the purified AuNPs revealed the presence of surface adsorbed biomolecules during the preparation. A chitosan supported AuNPs heterogeneous catalyst has been synthesised and characterized by various physicochemical techniques such as UV-Vis spectroscopy, XRD, TEM analysis, FTIR spectroscopic analysis and X-ray photoelectron spectroscopy (XPS). The catalytic performance of the chitosan supported AuNPs was examined in two types of organic reactions. The catalyst showed excellent catalytic activity in oxidation reaction with complete conversion of benzyl alcohol with 97% selectivity to benzaldehyde at $80^{\circ}C$ after 6 hours. The catalyst could be recycled at least four times without significant loss in the conversion. Catalytic activity of the chistosan-GLA/AuNPs was also tested for the reduction of 4-nitrophenol to 4-aminophenol using an excess of *Psidium guajava* leaf extract as a reducing agent instead of $NaBH_4$ complete reduction of 4-nitrophenol occurred within 15 minutes at room temperature.

ABSTRAK

Selama ini, aurum dianggap sebagai mangkin yang lengai. Walau bagaimanapun, nanopartikel aurum (AuNPs) kini menjadi tumpuan disebabkan sifat kimia dan fizik yang tunjukkan itu berbeza-beza bergantung kepada saiz dan bentuk. AuNPs telah diiktiraf mangkin yang aktif dan efektif bagi transformasi organik. Kini, terdapat keperluan untuk membangunkan proses sintesis nanopartikel logam yang mesra alam tanpa menggunakan sebarang bahan kimia toksik. Dalam hal ini, pendekatan biologi dalam sintesis nanopartikel logam menggunakan mikroorganisma, enzim, tumbuhan dan ekstrak tumbuhan merupakan kaedah mesra alam yang mungkin sebagai alternatif kepada kaedah kimia dan fizik. Dalam penyelidikan ini, satu kaedah yang mesra alam bagi sintesis dan penstabilan AuNPs melalui penurunan ion $AuCl_4^-$ akueus menggunakan ekstrak daun *Psidium guajava* dilaporkan. Parameter optimum bagi pembentukan AuNPs adalah 10 mL, 1 mM ion Au(III), 1 mL 1% ekstrak daun pada pH 6 dan 30 minit masa tindak balas. Analisis spektroskopi UV-Vis ke atas campuran tindak balas mengesahkan penurunan Au(III) kepada Au(0). Analisis mikroskop elektron penghantaran (TEM) menunjukkan AuNPs dalam morfologi sfera yang dominan dengan purata saiz 7.6 nm. Analisis pembelauan sinar-X (XRD) menunjukkan kehadiran lima puncak pantulan Bragg pada nilai 2θ 38.42 Å, 44.45 Å, 64.71 Å, 77.61 Å dan 81.87 Å masing-masing sepadan dengan satah kekisi (111), (200), (220), (311) dan (222) satah kekisi yang diindeks kepada struktur kubus berpusat muka (fcc) aurum. Analisis spektroskopi inframerah transformasi Fourier (FTIR), ke atas AuNPs menunjukkan kewujudan biomolekul terjerap permukaan semasa pembentukan. Mangkin heterogen AuNPs berpenyokong kitosan telah disintesis dan dicirikan melalui pelbagai teknik fizikokimia. Seperti analisis spektroskopi UV-Vis, analisis spektroskopi inframerah transformasi Fourier (FTIR), analisis pembelauan sinar-X (XRD), analisis mikroskop elektron penghantaran (TEM) dan spektroskopi fotoelektron sinar -X (XPS). Prestasi AuNPs berpenyokong kitosan sebagai mangkin telah diuji dalam dua jenis tindak balas organik. Aktiviti pemangkinan yang sangat baik ditunjukkan dalam tindak balas pengoksidaan benzil alkohol dengan penukaran lengkap dan 97% kepilihan kepada benzaldehid pada 80°C setelah 6 jam. Mangkin itu boleh dikitar semula sekurang-kurangnya empat kali tanpa pengurangan penukaran yang ketara. Aktiviti pemangkinan kitosan-GLA/AuNPs juga diuji dalam tindak balas penurunan 4-nitrofenol kepada 4-aminofenol menggunakan lebihan ekstrak daun *Psidium guajava* sebagai agen penurun menggantikan $NaBH_4$. Penurunan lengkap 4-nitrofenol berlaku dalam masa 15 minit pada suhu bilik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

^{1}H NMR	_	Proton Nuclear Magnetic Resonance
AAS	_	Atomic Absorption Spectroscopy
BET	_	Brunauer, Emmet, Teller
C-H	_	Carbon –Hydrogen
CHN	_	Carbon –Hydrogen-Nitrogen
CDCl$_3$	_	Deuterated Chloroform
Eq	_	Equation
EDX	_	Energy Dispersive X-Ray Microscopy
XRD	_	X-Ray Diffraction
FESEM	_	Field Emission Scanning Electron Microscopy
HR-TEM	_	High-resolution transmission electron microscopy
FID	_	Flame Ionization Detector
GC	_	Gas Chromatography
FTIR	_	Fourier Transform Infrared
AuNPs	_	Gold Nanoparticles
Chi	_	Chitosan
GLA	_	Glutaraldehyde
HCl	_	Hydrochloric acid
NaOH	_	Sodium Hydroxide
TG-DTA	_	Thermogravimetric/Differential Thermal Analyzer
TON	_	Turnover numbers
BzOH	_	Benzyl alcohol
BzH	_	Benzaldehyde
BzA	_	Benzoic Acid

4-NP _ 4-Nitrophenol

4-AP _ 4-Aminophenol

LIST OF SYMBOLS

nm _ nanometer
ppm _ Part per million
g _ gram
° C _ degree Celsius
cm^{-1} _ Frequency
min^{-1} _ per minit
Cu Kα _ X-ray diffraction from copper energy levels
λ_{max} _ maximum wave length
θ _ theta
° _ degree angle
mA _ miliampere
mL _ millilitre
mg _ milligram
% _ percentage
Kv _ kilovolt
mmol/g _ milimole per gram
M _ molarity
h _ hours
min _ minutes
d _ inter planer spacing
J_{HH} _ coupling condtant
W/V _ weight per volume
δ _ chemical shift
ν _ wave number
A _ Integrated peak area

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Research in transition-metal nanoparticles (NPs) has attracted strong interest due to their significant physical and chemical properties, which leads to their wide applications in different scientific and technological fields, including catalysis, optics, electronics, and biotechnology (Cao *et al.,* 2001). Gold nanoparticles have been considered as important area of research due to their unique and intense plasmon resonance in the visible range and their application in biomedical sciences. In catalysis area, transition metal nanoparticles such as Au, Pd, Pt and Rh have attracted remarkable interest particularly in alcohol oxidations (Mallat and Baiker, 2004; Ferri *et al.,* 2006; Hosokawa *et al.,* 2009). Supported gold nanoparticles have been studied extensively as catalysts for a wide range of oxidation reactions including low-temperature CO oxidation, alkene epoxidation, aldehyde oxidation, and aerobic oxidation of alcohols in both gas- and liquid-phase under relatively mild conditions (Hutchings *et al.,* 2006). Au based catalyst have been particularly studied because of the excellent catalytic performance in which it has shown high activity and selectivity in the liquid phase oxidation of benzyl alcohol to benzaldehyde (Li *et al.,* 2006; Zahmakran and Özkar, 2010; Chen *et al.,* 2010).

Nitroaromatic compounds are widely used in the manufacturing of dyes, pharmaceuticals, pigments, plastics, pesticides and industrial solvents (Herrera-Melián *et al.,* 2012; Narayanan and Sakthivel, 2011). These compounds have been `classified as the most pollutants that can produce in the industrial wastewater.

4-Nitrophenol has been listed by the US Environmental Protection Agency (EPA) as one of the top organic pollutant (Lai *et al.,* 2011; Li *et al.,* 2012). Recently, the role of metal nanoparticles in the field of catalysis opens a new horizon. AuNPs serve as an effective catalyst in the reduction of various pollutants like 4-NP, the most common organic pollutant. So much attention has been given to develop an efficient methodology for the conversion of 4-NP. The use of supported metal nanoparticles as catalysts for 4-nitrophenol reduction, in presence of an excess of $NaBH_4$ has been reported. Regarding to this problem of using such hazardous chemical, *Psidium guajava* leaf extract in this research has been used instead of $NaBH_4$ as green and nontoxic reducing agent.

During the last decade different methods have been widely used to synthesize nanoparticles with different sizes and shapes. Several chemical methods were recognized to synthesize AuNPs and in most cases, the used reducing and sablizing agents were toxic in nature. However, with the growth of these new methods, the concern for environmental contaminations is also heightened as theses chemical procedures involved in the synthesis of metal nanoparticles produce a large amount of hazardous chemical as by products. Since AuNPs were using in many biological and medical applications (Huang, 2006), it is necessary to avoid toxic chemical methods and to devolpe eco-friendly green methods to synthesize AuNPs. Thus, this ‘green chemistry’ that uses biological organisms such as microorganisms, plant biomass or plant extract could be an alternative to common chemical and physical methods for the production of nanoparticless in a clean, non-toxic, ecologically sound and environment-friendly manner.

Green synthesis employing plant extract as reducing agent provides advancement over chemical and physical method as it is cost effective due to low cost for extract prepration , environment friendly, easily scaled up for large scale synthesis and avoid the use of toxic chemicals. Biomolecules as reductants are found to have an important advantage over their counterparts as protecting agents (Huang *et al.,* 2007). Surface complexation of nanogold with this biomolcules such as poly phenols, amino acids and proteins is an emerging field of research. *Psidium guajava* is a type of plants which is cultivated in many parts of Malaysia and other subtropical countries because of its pleasant tasting fruit (Perez *et al.,* 2008). *Psidium guajava* leaves have been used traditionally for the treatment of many diseases worldwide (Abdelrahim *et al.,* 2002). They have been reported to possess anti-oxidant properties due to the presence of high phenolic contents. This type of chemical constituents has great potential to be used as reducing agents in the preparation of metal nanoparticles.

Supported AuNPs on metal oxides, polymers or activated carbon, have attracted a lot of attention during the last decade especially in the oxidation of alcohols because of their high activity, selectivity and lower percentage of metal leaching compared to their classical noble metal counterpart (Hashmi and Hutchings, 2007). Chitosan is a biopolymer that has good potential to be used as support material for metal nanoparticles. Due to the presence of large numbers of amine and hydroxyl groups on its chain it has high ability for metal ions adsorption, dyes and proteins (Chiou and Li, 2002). Both the hydroxyl and amine groups present in the raw chitosan flakes can be chemically or physically modified (Yang and Yuan, 2001) to enhance its adsorption capacities and mechanical strength.

1.2 Catalysis

The “catalysis” concept was introduced by Berzelius in 1836 to describe a new thing that is able of promoting the occurrence of a chemical reaction by a “catalytic contact”. According to him, the substance that is added to the reaction to accelerate the rate of the reaction without being consumed or produced at the end of the reaction (Farnetti *et al.,* 2009). The chemical substance that is added to accelerate the rate of chemical reaction to reach the equilibrium stage without being expanded in the reaction is named as catalyst.

The catalyst could speed up the rate of a chemical reaction by lowering the activation energy of the reaction pathway in order to provide easier access to the transition state for the substrate. The catalyst does not allow for thermodynamically forbidden reactions to occur, it only enables reactions to occur at higher rates until equilibrium is reached.

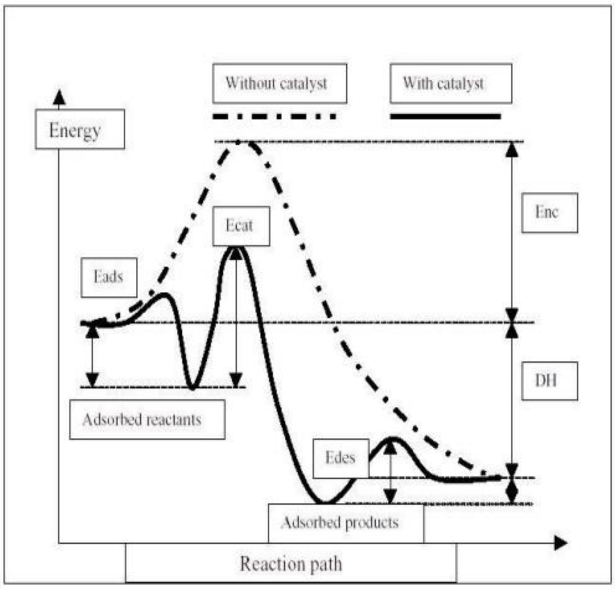
Catalysts are significant to the chemical industry, with over 90 % of all the artificial chemicals using catalysts. Catalysis is one of the scientific disciplines in which even small advances, when based on research, may have an outstanding impact on society. Due to the vast levels of marketable applications, growth in catalysis can have a positive economic impact as well as a profound environmental impact, more specifically; on the automotive and power production industries which are the sectors that stand to benefit most directly from breakthroughs that are predicted to take place in the field of catalysis in the foreseeable future.

1.3 Catalyst

By definition catalyst is a material that speeds up the rate to reach equilibrium in a chemical reaction without being involved in the reaction (Schuth *et al.,* 1997). A catalyst also is a substance that when added in a chemical reaction, accelerates the attainment of the chemical equilibrium between the reactants and the products without influencing the thermodynamic equilibrium of the process. Frequently catalysts are not involved through the reaction and could be found unaffected after the reaction completes. In reality, catalysts are submitted to a slow transformation with use, causing a general reduction of the activity and/or selectivity. The first main difference among catalysts relaies on their nature in relation to the reactants. Different types of catalysts have been used in a variety of reactions and, some of them include organometallic catalyst, biocatalyst, electrocatalyst and organocatalyst. (Seayad, 2005). Organometallic catalysts are playing an important role in asymmetric synthesis reactions where, in the most of these catalysts are single molecules containing N, C, O, P and S. Biocatalysts which are natural catalysts such as lipases and enzymes are used in different types of organic reactions such as trans esterifications, ammoniolysis, and epoxidation reactions. Electrocatalysts are metal-containing catalysts found in fuel cells and are used to accelerate the rate of oxygen reduction or fuel oxidation as these types of catalysts are composed of Pt and

Pd.(Richardson, 1998). Organocatalyst are also composed of metals but here the metal is inserted into an organic framework.

The main impact of a catalyst is also to decelerate the reaction that permits the activation of energies of different reaction steps in order to, accelerate another reaction to reach the desired equilibrium. As illustrated in Figure 2.1, it shows how the activation energy of the reaction path is lowered to allow the transition state to be reached move easily before forming the combined product of reactants 1 and 2. The overall change in energy is the same whether the catalyst is present or not. At the end of the reaction, the catalyst can be recovered unchanged, as it does not react and only facilitates the reaction of the substrates. The figure also shows the cyclic nature of a catalytic reaction, where once the product has desorbed, and more reactants are free to adsorb on to the catalyst again and continue the reaction (John, 2010).



Activation energies

E_{ads}-for adsorption

E_{cat}-for surface reaction

E_{des}-for desorption

E_{nc}-for activation energy without catalyst

DH-total heat of reaction

Figure 1.1 Reaction profile for a chemical reaction with and without catalyst Source (Campanati *et al*., 2003)

A good synthesized catalyst must possess three main requirements: being that it must exhibit high activity or conversion in a reaction. The second is that it must show good selectivity of a desired product, as it may be difficult to separate out the side-products. The final requirement is that the catalyst must show good durability without deterioration or loss of activity under reaction conditions.

1.3.1 Classification of Catalysts

Catalysts generally can be classified into two main classes, namely, homogeneous and heterogeneous catalysts. In homogeneous system the catalyst and substrate are found to be in the same phase, usually the liquid phase. In this system the catalyst is dissolved in a solvent which can also be the reactant or the product itself. A homogeneous catalyst shows advantageous in obtaining higher selectivity in some reactions particularly in the synthesis of optically active compounds. In the exothermic reactions, it makes it easier to control the temperature, and this type of catalyst can be further applied to different types of organic reactions in hydrogenation, isomerization, carbonylation ,oxidation and alkene metathesis as well as cross-coupling, through which most of the catalyst molecules are involved in the catalytic reaction.

Meanwhile, in heterogenous catalysis, the reactants and catalyst exist in different phases (heterogeneous or heterogenized catalyst). Most commonly, solid catalysts are used with the reactants in either gas or liquid form. In principle, the catalyzed reaction takes place at the phase interface that is on the catalyst surface. However, homogeneous catalysts have their own disadvantages in which they are difficult to separate from the reaction media as, there is possibility of contamination of the products by the catalysts themselves while the treatment of toxic liquid waste that is obtained after the separation and the recycling of catalyst expensive (Beller *et al.*, 1996)

Therefore there is a need to find a way to develop the catalysis research area not only to obtain the higher activity and selectivity but also to get the novel catalytic properties including significantly improved reactivites, selectivities and ease of separation and the higher recyclability of the catalyst. These properties have been reported for nanoparticle (NPs) catalysts as compared to their bulk counterparts. Many experimental studies on the nanocatalysts have focused on the correlated catalytic activity with the particle size. While a particle size is an important consideration, many other factors such as geometry, composition, oxidation state, and chemical/physical environment can play a significant role in setting the NPs reactivity. The focus of this thesis will be on the synthesis of supported AuNPs catalyst and its application in oxidation reactions of alcohols and reduction of 4-nitrophenol and the means by which they are characterized.

1.4 Metal Nanoparticles

Metal nanoparticles refer to metal having at least dimension that varies between 1-100 nm. Due to their high surface-to-volume ratio, surface energy, spatial confinement and reduced imperfections, metal nanoparticles have characteristics such as physical, chemical, electronic, electrical, mechanical, magnetic, thermal, and biological properties that different from the bulk materials (Narayanan *et al.,* 2011). Nanomaterials have achieved significant consideration due to their potential applications in drug delivery, sensing, imaging and chemotherapy in recent period. Particularly for drug delivery, polymeric nanoparticles, dendrimers, liposomes and metal nanoparticles are being widely explored. Nanoparticles have a unique optical and electronic property that greatly depends on the size and shape of nanoparticles as an effect of quantum confinement of electrons**.** For example, AuNPs in solution have a remarkable colour which is due to the red shift of the plasmon band to visible frequencies, unlike that for bulk metals where the plasmon absorption is in the UV region.

Different types of metal NPs with different shapes, sizes and composition can be easily synthesized through either the chemical, physical or biological synthesis (Kimling *et al*., 2006). The common method that was used for the metal NPs synthesis was the chemical reduction method by reducing the metal salt using a reducing agent such as sodium citrate commonly known as the Tukevich method (Turkevich *et al*., 1951), in which they used toxic and hazardous materials such as Sodium Borohydrate ($NaBH_4$) or Hydraizine as reducing agent. From this point there is a new concern towards green chemistry and other friendly and green alternative reducing agents. In this research the synthesis of the AuNPs was carried out using the *Psidium guajava* leaf extract as the reducing and stabilizing agent.

1.5 Nanoparticles Catalyst

Due to the high surface-to-volume ratio, urface energy, spatial confinement and reduced imperfections of metal nanoparticles they show different properties such as physical, chemical, electronic, electrical, mechanical, magnetic, thermal, optical and biological compared to thier bulk partener material (Narayanan *et al.,* 2011).
The use of metal NPs in catalysis dates back to the 19th century which it was used in photography and hydrogen peroxide decomposition. Metal nanoparticles as catalyst show advantages that they are easy to remove from the reaction media and the recyclability of the catalyst itself is high as compared to the bulk catalyst systems due to higher amount of surface area to the volume ratio. Usually homogeneous catalysts need large amounts of solvents to separate the catalyst from the products which lead to the production of too much waste. Further more if the catalyst could be easally separated from the product The larger amount of surface area to volume ratio that the metal NPs posses results in higher active sites and it is thus found to exhibit a higher catalytic activity and selectivity

The transition metal nanoparticles are based on clusters or colloids containing from ten to a number of thousands of metal atoms varying in sizes from 1-100 nm. The particles with smaller size have shown to be catalytically active with growing activity when the size of the cluster is decreasing. For example the turnover rates for the 2 nm particles could be about 8 times higher than that of the particles with a size of 12 nm turnover (Grass *et al*., 2008). Particles with smaller sizes have a higher surface atom (larger surface-to-volume ratio) than larger particles, thus resulting in a higher amount of surface disorder and yielding more surface limited active sites (Figure 2.2).

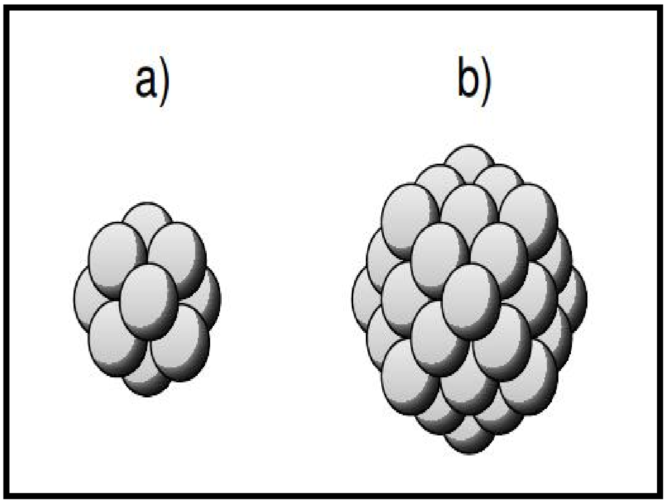


Figure 1.2 Metal nanosized clusters; small nanoparticles (a) have a higher percentage of surface atoms than larger particles (b) resulting in higher amount of surface defects yielding more surface limited active sites. Source (Eriksson, 2013)

For example, gold as a metal shows unusual characteristics as it has no catalytic activity in the form of large particles, where it shows high activity is when it is present in nanosized form (Guczi, 2004). It was reported by Jamwal and co-workers (2011) that palladium nanoparticles supported cellulose was a highly efficient heterogeneous catalyst for Suzuki coupling between aryl bromides and phenyl boronic acid in water and aerobic oxidation of benzyl alcohols. Recoverable ruthenium nanocatalyst prepared by Jacinto *et al*. (2009) converted aryl and alkyl alcohol to aldehydes under mild conditions with negligible metal leaching.

One of the main problems for using metal NPs as catalyst is the lack of longer stability in which they tend to aggregate, as the small particles have shown to have higher surface energies due to their higher surface areas, hence when an aggregation occurs it tend to increase the metal to a bigger size which then decreases the percentage of the surface atoms that make the energy of specific system to decreased. To overcome this problem there are two pathways, the first way is to add a ligand to act as stabilizing agents for the NPs which have shown to increase the stability, and the second way is to find a solid support to immobilize the metal NPs to the support surface which increase the life span or the recyclability of the catalyst. In this research AuNPs has been supported by chitosan-GLA beads as biopolymer support in order to increased their stability and avoid the metal leaching problems.

1.6 Problem statement

Many homogeneous systems able to catalyse liquid phase oxidation have been used successfully, resulting in high product yields (Storhoff *et al.,* 2002). However, the uses of homogeneous catalysts still have major problems in separating, recycling of the catalysts and the product purity which leads to production of excessive amounts of waste. In a small scale synthesis these problems are solved by purification using chromatography accompanied by the loss of the catalysts, but in industrial applications, the costs of the catalyst materials are also importance. The problems discussed could be principally minimized by developing heterogeneous catalytic systems employing metal nanoparticles catalyst, in which they show advantages due to the large surface area they possess, easy removal and regeneration of the catalytic species.

Oxidation reactions of benzyl alcohol are one of the most important transformations of functional groups in organic synthesis reactions, due to the production of benzaldehyde (BzH), which is very important chemical that is used as starting material in different industrial and laboratory manufacturing (Sheldon *et al.,* 2001; Mallat and Baiker, 2004). Usually, several oxidizing agents such as ammonium permanganate, chromium trioxide (Behera and Parida, 2012) and different organic solvents been used to complete the oxidation transformation. However, these types of oxygen donors have dangerous drawbacks as they have many associated toxicity problems and they are also expensive (Sheldon *et al.,* 2001). Organic solvents such as benzene, acetonitrile chloroform, and xylene are widely applied for alcohol oxidation (Zhang *et al.,* 2011), their major problem is their toxicity and volatility. Thus with the ever increasing environmental concerns, our attempt is to develop efficient and green catalytic procedures, utilizing green oxidants, such as hydrogen peroxide or oxygen. H_2O_2 has been selected as an oxidant because it is widely available, cheap, safe and overall it produces only water by-product. Employing clean solvents by using water leads to large industrial significance and also environmental meaning (Mallat and Baiker, 2004).

Large numbers of heterogeneous catalysts have been prepared and have been employed successfully for the oxidation of benzyl alcohols to benzaldehydes (Vinod *et al*., 2011; Layek *et al.,* 2011). Most of these types of heterogeneous catalysts are based on silicas which show several advantages such as high stability (both in thermal and chemical), fine accessibility, and thier organic groups can be strongly anchored to the surface to offer catalytic centres. However, there are some drawbacks such as limitation of stability in the aqueous media, especially the basic types and are non-degradable. Due to these disadvantages there is a need to find other types of support for the heterogeneous catalyst. In this work, chitosan as biopolymer was selected to support AuNPs which offers many advantages. It is available in nature, non-toxic compared to organic polymers, easy to modify either Physicaly or chemically modification and easy degradation at the end of the life cycle which leads to application of clean and green chemistry.

Catalysis using Au has attracted great interest (Hashmi and Hutchings, 2006) and different strategies have been used for the preparation of Au supported catalysts. Different chemical techniques have been traditionally used for depositing AuNPs on support materials which include co-precipitation, impregnation, deposition–precipitation and ion exchange. However, "greener" and cost-effective approaches are still needed for Au catalysts preparation. The production of Au catalysts normally involves toxic and expensive hazardous chemicals via using either chemical or physical methods (Corti *et al.,* 2005). It has becomes necessary to find other alternatives such as biological methods since this route is cost-effective and eco-friendly. Nevertheless, to date there are only some reports that focus on the production of Au nano-catalysts by using biological method. Hence, a biosynthetic reduction method employing *Psidium guajava* leaf extract as reducing and capping or protecting agent that supporting the stabilization of biosynthesized AuNPs was used here due to the higher phenolic content of the laef extract as a simple, green and eco-friendly alternative method (Mohanpuria *et al.,* 2008).

AuNPs catalyst show high efficiency especially in the reduction of various types of pollutant such as 4-nitrophenol, which is classified as one of the dangerous organic pollutant that is produces as industrial and agricultural waste. The 4-nitrophenol is used as building unit for many dyes, pesticides and it breaks down in water and soil surface leading to higher toxicity problems in nature towards human, animals and plants. Therefore critical health problems and hazards to human being can appear in drinking water or eating foods grown in soil contaminated with 4-nitrophenol. Hence much consideration has been given to find an efficient method for the reduction of 4-nitrophenol. $NaBH_4$ is commonly used in 4-nitrophenol reduction but it is known to be hazardous and toxic. In this work, an attempt to find a safe and green method for the reduction of 4-nitrophenol to 4-amino phenol using the green synthesised AuNPs supported on chitosan beads catalyst in presence of *Psidium guajava* leaf extract as an alternative to $NaBH_4$ was investigated.

1.7 Objective of Research

(i) To synthesize AuNPs by using *Psidium guajava* aqueous leaf extract.

(ii) To immobilize and reduce Au(III) ions onto the cross-linked chitosan beads.

(iii) To characterize the synthesized AuNPs and supported AuNPs catalyst by using UV-Vis spectrophotometer, XRD, HR-TEM, FTIR, FSEM-EDX, XPS, AAS, TG-DTA and BET surface area analysis.

(iv) To evaluate the catalytic activity of the chitosan supported AuNPs catalyst in oxidation reaction of benzyl alcohol, primary and secondary alcohols and reduction of 4-nitrophenol.

1.8 Scope of Research

This research involved a simple method for AuNPs synthesis by using aqueous leaf extract of *Psidium guajava*. The leaves are known to have high phenolic contents which may be responsible for the reduction of Au(III) ion to AuNPs.Various parameters have been optimized such as volume of leaf extract, pH, metal ion concentration and reaction temperature to get the optimum reaction conditions. For the heterogenization purpose, chitosan was selected as a new, low cost and environmental friendly support material for AuNPs due to its higher binding to metal nanoparticles.

The synthesized chitosan supported AuNPs catalyst was characterized with different techniques namely UV-Vis spectrophotometer, elemental analysis CHN/O, FTIR, XRD, FESEM-EDX, XPS, HR-TEM, BET surface area analysis and TGA-DTA and AAS. These techniques determine AuNPs and the supported catalyst morphology, thermal stability, surface area and Au loading in the synthesized catalyst.

The performance of chitosan supported AuNPs catalyst was evaluated in two types of organic reaction, firstly oxidation reaction of benzyl alcohol and secondly the reduction of 4-nitrophenol to 4-aminophenol. For the oxidation reactions benzyl alcohol (BzOH) has been selected as model reaction, and several parameters has been varied such as Au loading in the catalyst, reaction time, reaction temperature (28°C, 40°C, 60°C, 80°C and 100°C), the molar ratio of hydrogen peroxide to benzyl alcohol and catalyst weight. The conversion of benzaldehyde product was determined using GC chromatogram and characterized by using FTIR spectroscopy and ^{1}H NMR. The optimized condition was applied in other types of oxidation reaction of primary and secondary alcohols. For the reduction of 4-nitrophenol the leaf extract was used instead of using $NaBH_4$ which promise for a new green chemistry methodology.

1.9 Significance of Research

This research applies one of the green chemistry approaches by synthesizing AuNPs using *Psidium guajava* aqueous leaf extract as reducing and satbilizing agent to avoid using toxic chemical and hazardous. The use of biosynthesized AuNPs supported onto chitosan beads as catalyst conforms to the environmentally and friendly processes.The catalyst was readily recovered by centrifugation. The catalyst showed high activity and be recycled four times. The reduction of 4-nitrophenol to 4-amino phenol using Au nanocatalyst was conducted at room temperature using the leaf extract instead of using $NaBH_4$ and the reaction was completed within15 minutes.

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