SYNTHESIS, SORPTION-BIOREDUCTION AND CATALYTIC ACTIVITY OF GOLD ON THIOCTIC ACID FUNCTIONALISED SILICA COATED MAGNETITE NANOPARTICLES

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ABSTRACT

Gold (Au) is a precious metal that has low toxicity but has vast applications and high market prices. There is an increasing interest in the catalytic application of Au due to its unique properties. However, the global resources of Au are quite limited, thus recovery of Au from waste solution is a challenging and important task. Hence, this research focuses on the adsorption of Au(III) ions on a thiol based adsorbent and its subsequent bio-reduction to Au(0). Thioctic acid functionalised silica coated magnetite nanoparticles (RS-SR-NH-SiO_2-Fe_3O_4) has been synthesised and its ability for the recovery of Au(III) from aqueous solutions was assessed at different parameters. The results of the adsorption thermodynamics and kinetics showed that this magnetic adsorbent has good adsorption capacity for Au(III) and the best interpretation of the experimental data was given by the Langmuir isotherm model. The results showed that the adsorption kinetics followed a pseudo-second-order rate equation with maximum adsorption capacity for Au(III) as 285.71 mg g^{-1} at 45°C. The thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ were −13.56 kJ mol^{-1}, −24.33 kJ mol^{-1}, and −36.18 J $K^{-1}mol^{-1}$, respectively. The adsorption was a chemisorption process with activation energy of 11.58 kJ mol^{-1}. In the next step, the adsorbed Au(III) ions were reduced into Au(0) using *Phaleria macrocarpa* (Scheff.) Boerl fruit aqueous extract. The performance of the biosynthesised Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 catalysts were evaluated by using 4-nitrophenol reduction and styrene epoxidation. Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 catalyst showed a good catalytic performance in the reduction of 4-nitrophenol into 4-aminophenol in the presence of $NaBH_4$ as the hydrogen source. The effect of three different parameters, namely volume of $NaBH_4$, concentration of 4-nitrophenol and amount of catalyst were investigated. Under optimal conditions (0.5 mL $NaBH_4$, 0.05 mM 4-nitrophenol and 2 mg Au-RS-SR-NH-SiO_2-Fe_3O_4), the conversion of 4-nitrophenol were found to be 96% after 60 min. Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 catalyst also showed high reusability as the catalytic activity remained excellent after five successive runs. Meanwhile, the effects of amount of base, reactant to oxidant mole ratio, catalyst amount, solvent volume, temperature and time on the catalytic epoxidation of styrene by Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 catalyst were also investigated. Response surface methodology (RSM) demonstrated the ability to predict the conditions that favour high percentage conversion of styrene. Under the proposed optimised conditions, considering all variables in the model range, namely TBHP molar ratio of 4 and run for 6 h at 80°C, a high percentage conversion of styrene of 61.8% was attained. This catalyst could be easily recovered magnetically and reused for at least four times with satisfactory conversion. Leaching of Au from the RS-SR-NH-SiO_2-Fe_3O_4 surface was extremely small and can be considered negligible. This study showed that RS-SR-NH-SiO_2-Fe_3O_4 acted as dual functional material with excellent properties as adsorbent for the recovery of Au and as support for Au catalyst for the reduction 4-nitrophenol and epoxidation of styrene.

ABSTRAK

Emas (Au) adalah logam berharga yang mempunyai ketoksikan yang rendah tetapi mempunyai aplikasi yang luas dan harga pasaran yang tinggi. Terdapat peningkatan minat dalam penggunaan Au sebagai mangkin kerana sifatnya yang unik. Walau bagaimana pun, sumber Au global agak terhad, dengan itu perolehan semula Au daripada sisa cecair adalah satu tugas yang mencabar dan penting. Oleh itu, kajian ini memberi tumpuan kepada penjerapan ion Au(III) pada penjerap berasaskan tiol dan seterusnya bio-penurunannya kepada Au(0). Nanopartikel magnetit bersalut silika berkefungsian asid tioktik (RS-SR-NH-SiO_2-Fe_3O_4) telah disintesis dan kebolehannya untuk perolehan semula Au(III) daripada larutan akueus telah dinilai pada parameter yang berbeza. Keputusan penjerapan termodinamik dan kinetik menunjukkan bahawa penjerap magnetik ini mempunyai kapasiti penjerapan yang baik bagi Au(III) dan interpretasi terbaik data eksperimen diberikan oleh model isoterma Langmuir. Keputusan menunjukkan kinetik penjerapan mengikuti persamaan kadar pseudo-tertib kedua dengan kapasiti penjerapan maksima bagi Au(III) 285.71 mg/g pada 45°C. Parameter termodinamik $\Delta G°$, $\Delta H°$, dan $\Delta S°$ ialah masing-masing -13.56 kJ mol^{-1}, -24.33 kJ mol^{-1}, dan -36.18 J K^{-1} mol^{-1}. Penjerapan adalah proses pengkimierapan dengan tenaga pengaktifan 11.58 kJ mol^{-1}. Dalam langkah seterusnya, ion Au(III) yang terjerap telah diturunkan kepada Au(0) menggunakan ekstrak akueus buah *Phaleria macrocarpa* (Scheff.) Boerl. Prestasi biosintesis mangkin Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 telah dinilai dengan menggunakan penurunan 4-nitrofenol dan pengepoksidaan stirena. Mangkin Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 menunjukkan prestasi pemangkinan yang baik dalam penurunan 4-nitrofenol menjadi 4-aminofenol dengan kehadiran $NaBH_4$ sebagai sumber hidrogen. Kesan tiga parameter yang berbeza, iaitu isipadu $NaBH_4$, kepekatan 4-nitrofenol dan jumlah mangkin telah dikaji. Di bawah keadaan optimum (0.5 mL $NaBH_4$, 0.05 mM 4-nitrofenol dan 2 mg Au-RS-SR-NH-SiO_2-Fe_3O_4), didapati penurunan 4-nitrofenol adalah sebanyak 96% selepas 60 minit. Mangkin Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 juga menunjukkan kebolehgunaan semula yang tinggi kerana aktiviti pemangkinan kekal cemerlang selepas lima kali penggunaan berturut-turut. Sementara itu, kesan jumlah alkali, nisbah mol reaktan terhadap pengoksida, jumlah mangkin, isipadu pelarut, suhu dan masa pengepoksidaan bermangkin stirena oleh mangkin Au(0)-RS-SR-NH-SiO_2-Fe_3O_4 juga dikaji. Kaedah permukaan gerak balas (RSM) menunjukkan keupayaan untuk meramal keadaan yang memihak kepada peratusan penukaran stirena yang tinggi. Di bawah keadaan optimum yang dicadangkan, dengan mengambil kira semua pembolehubah dalam julat model iaitu nisbah molar TBHP 4 dan dijalankan selama 6 jam pada 80°C, peratus tinggi penukaran stirena telah dicapai sebanyak 61.8%. Mangkin ini boleh diperoleh semula secara magnetik dengan mudah dan digunakan semula sekurang-kurangnya empat kali dengan penukaran yang memuaskan. Larut-lesapan Au dari permukaan RS-SR-NH-SiO_2-Fe_3O_4 adalah sangat kecil dan boleh diabaikan. Kajian ini menunjukkan bahawa RS-SR-NH-SiO_2-Fe_3O_4 bertindak sebagai bahan dwi-fungsi dengan sifat sebagai penjerap yang sangat baik untuk perolehan semula Au dan sebagai sokongan bagi mangkin Au untuk penurunan 4-nitrofenol dan pengepoksidaan stirena.

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LIST OF ABBREVIATIONS

α-Fe_2O_3	-	Hematite
$\Delta G°$	-	Gibbs free energy
$\Delta H°$	-	Enthalphy
$\Delta S°$	-	Entrophy
3-MPTMS	-	3-mercaptopropyltrimethoxysilane
Au	-	Gold
AAS	-	Atomic Absorption spectrometer
APTES	-	Aminopropyltriethoxysilane
BBD	-	Box–Behnken design
CIL	-	Carbon-in-leach
CIP	-	Carbon-in-pulp
DCC	-	N,N'-dicyclohexylcarbodiimide
DCM	-	Dichloromethane
DMF	-	Dimethylformamide
E_a	-	Activation energy
EDTA	-	Ethylenediaminetetraacetic acid
EtOH	-	Ethanol
$FeCl_2.4H_2O$	-	Iron(II) chloride tetrahydrate
$FeCl_3.6H_2O$	-	Iron(III) chloride hexahydrate
FTIR	-	Fourier Transform Infrared
GC-FID	-	Gas chromatography-flame ionization detector
H_2O_2	-	Hydrogen peroxide
$HAuCl_4$	-	Tertahydrochloroauric acid
HCl	-	Hydrochloric acid
HRTEM	-	High-resolution transmission electron microscopy
HSAB	-	Hard–soft acids bases
KBr	-	Potassium bromide
KBSI	-	Korea Basic Science Institute

$MgAl_2O_4$	-	Magnesium aluminate
Mn_2O_3	-	Manganese(III) oxide
Ms	-	Magnetic saturation
N_2	-	Nitrogen gas
$NaBH_4$	-	Sodium borohydride
NaCl	-	Sodium chloride
$NaHCO_3$	-	Sodium bicarbonate
NaOH	-	Sodium hydroxide
NaOH	-	Sodium hydroxide
NH_2-SiO_2-Fe_3O_4	-	Amine functionalized silica coated magnetite nanoparticles
NH_4OH	-	Ammonium hydroxide
NHS	-	N-hydroxysuccinimide
O_2	-	Molecular oxygen
pH_{pz}	-	pH of point zero charge
RSM	-	Response surface methodology
RSM	-	Response surface methodology
RS–SR–NH–SiO_2–Fe_3O_4	-	Thioctic acid functionalised silica coated magnetic
RT	-	Room temperature
SDS	-	Sodium dodecyl sulfate
TBHP	-	Tert-butyl hydroperoxide
TEOS	-	Tetraethyl orthosilicate
TOF	-	Turnover frequency
TON	-	Turnover number
VSM	-	Vibrating sample magnetometer
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction
XRF	-	X-ray fluorescence

.

LIST OF SYMBOLS

%	-	Percent
°C	-	Degree celcius
2θ	-	Bragg's angle
A	-	Arrhenius constant
Å	-	Amstrong
C_{ads}	-	Concentration of ions adsorbed
C_{des}	-	Concentration in desorption solution
C_e	-	Equilibrium concentration
C_{liquid}	-	Concentration of ions at equilibrium (mg/L)
cm^{-1}	-	Frequency
cm^2	-	Area
C_o	-	Initial concentration
C_{solid}	-	Concentration at equilibrium
C_t	-	Concentration at time interval
Cu Kα	-	X-ray diffraction from copper energy levels
E_a	-	Activation energy
emu/g	-	Magnetic moment per gram
eV	-	Electronvolt
g	-	Gram
h	-	Hour
K	-	Kelvin
k	-	Kinetic reaction rate constants
kJ mol^{-1}	-	Energy per amount
k_1	-	Pseudo-first order rate constant
k_2	-	Pseudo-second order rate constant
K_c	-	Equilibrium constant of the adsorption process
K_{eq}	-	Equilibrium constant
K_F	-	Freundlich adsorption isotherm constants
K_L	-	Langmuir equilibrium constant
kOe	-	Kilooersted

kV	-	Kilovolt
L	-	Liter
m	-	Meter
M	-	Molarity
mA	-	Miliampere
mg	-	Miligram
mg/L	-	Concentration
min	-	Minute
mL	-	Mililiter
mM	-	Milimolar
mmol	-	Milimole
MΩ·cm	-	Conductivity
nm	-	Nanometer
q_e	-	Equilibrium contact time
q_m	-	Maximum amount of ions adsorbed per unit weight of adsorbent at equilibrium
q_t,	-	Amount of uptake at any time
R	-	Gas constant
R^2	-	Correlation coefficients
rpm	-	Revolution per minute
T	-	Absolute temperature (K)
t	-	Contact time
T	-	Absolute temperature
v	-	Volume
w	-	Mass
w/v	-	Weight per volume
wt %	-	Weight percentage
λ_{max}	-	Maximum absorption peak
μm	-	Micrometer

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Gold (Au) has been known to human for more than 5000 years and it has been considered as a precious element throughout history and societies. Owing to its rarity, malleability, ductility, vivid colour, nontoxic properties, and inertness in air or water, Au is considered a symbol of fortune to its owner and it has been used in coinage, jewellery and ornaments, and other art works (Wang *et al.*, 2012). Meanwhile, in this modern era, Au is widely use in industrial and economic activities such as medical fields and biomedical research, catalytic, and electric and electronic components (Baba, 1987; Cui and Zhang, 2008; Syed, 2012).

Due to the wide uses of Au in various applications, the demand of Au has increased rapidly. However, Au existence in nature is at very low level and it is predicted that the natural sources of Au will be exhausted by the end of 2030 (Moyer, 2010). Thus, due to an increasing demand for Au, it is a great interest to recover Au from aqueous and waste solution.

Many studies have been carried out to recover Au(III) ions from aqueous solution. For example, pyrometallurgical and hydrometallurgical processes have been used to recover Au from wastewater (Jacobsen, 2005). However, the hydrometallurgical methods, including adsorption, solvent extraction, ion exchange, and cementation, have been utilised more often than the pyrometallurgical process (Das, 2010; Syed, 2012). In particular, adsorption process has gained the most interest among the researchers and applied in the industrial processes due to its simple equipment, low cost, ease of operation, and high efficiency even at low metal ion

concentration (Singh and Tiwari, 1997; Ramesh *et al.*, 2008; Tabakci and Yilmaz, 2008).

Several adsorbents for Au adsorption had been reported, including natural biosorbents, such as algae (Umali *et al.*, 2006; Mata *et al.*, 2009) and bacteria and yeasts (Tsuruta, 2004), as well as synthetic materials, for example, resins, mesoporous adsorbents, and activated carbon (Soylak *et al.*, 2000; Elci *et al.*, 2007; Tuzen *et al.*, 2008; Syed, 2012). Among these adsorbents, biosorbents are considered as a promising technology for the recovery of Au(III) ions, and have been used for the recovery of Au(III) ions from real wastewater (Das, 2010). However, some of these adsorbents suffer from difficulty in its separation, long equilibrium time, and regeneration (Das, 2010). For the complicated structure of biosorbents, the adsorption mechanism for Au(III) ions could not be explained clearly.

The area of Au catalysis has taken a giant leap forward in the past decade. The initial breakthrough of catalysis by Au was made 30 years ago by Hutchings (1985) and Haruta *et al.* (1987) as they proved that Au can be an excellent catalyst in contrast to the existing perception that it was unlike other precious metals. One key early paper was the observation by Sermon *et al.* (1979) which reported that Au could be an effective hydrogenation catalyst for butadiene. Since then, many studies had been carried out using Au as catalyst (Hutchings, 1985; Bond and Thompson, 2000; Hutchings, 2008; Wojcieszak *et al.*, 2016; Megías-Sayago *et al.*, 2017; Philip *et al.*, 2017; Simakova *et al.*, 2017) and now Au nanoparticles are recognised as a hot area for research (Amdouni *et al.*, 2018; Hosseini *et al.*, 2018; Umamaheswari *et al.*, 2018).

Colloidal Au nanoparticles was extensively studied in aerobic oxidation of alcohols (Tsunoyama *et al.*, 2005; Tsunoyama *et al.*, 2009), 1,2-diols (Mertens *et al.*, 2005), and CO (Iizuka *et al.*, 1999; Sanchez-Castillo *et al.*, 2004), as well as nitrophenol reduction (Hayakawa *et al.*, 2003; Rashid and Mandal, 2008; Biondi *et al.*, 2011) and carbon–carbon coupling (Tsunoyama *et al.*, 2004). The advantage of this colloidal Au nanoparticles in the catalytic reaction is it can act as both homogeneous and heterogeneous catalyst simultaneously (Wong, 2017). This Au nanoparticles can be seen as a bridge between homogeneous and heterogeneous catalysis because it can

react actively as the homogeneous catalyst and can be separated and recycled into the next reaction like the heterogeneous catalyst (Wong, 2017). However, due to its ultra-small size, this colloidal nanoparticle suffers from major limitations as it requires filtration techniques that may often lead to the loss of the catalyst.

Hence, in this research, thioctic acid functionalised silica coated magnetite nanoparticles was designed with the capability to function as an adsorbent in the recovery of Au(III) ions from dilute aqueous solution and subsequently the immobilised gold be used as catalyst in the reduction of 4-nitrophenol and epoxidation of styrene.

To the best of our knowledge, there is yet a study which reported on the dual function of thioctic acid functionalised silica coated magnetite nanoparticles as an absorbent and also as support for Au catalyst.

1.2 Problem Statement

The demand for Au in recent years is significantly increasing and thus it increases the demand for mining capacities. However, the global resources of Au are quite limited, which bring serious problems with regards to the supply of Au, economical, and environmental issues. Mining Au requires high cost and only a small amount of product is obtained as they are typically found in ores at very low concentrations of below 10 gram/tonne (Hageluken *et al.*, 2009). Moreover, mining process can result in a high emission of greenhouse gases and loss of land and biodiversity. Therefore, a critical approach such as recovery and recycling Au from waste solution can help in slowing down the depletion of natural resource and the price of Au can be kept lower.

Recovery of Au in dilute solution becomes a great interest and many techniques have been established to recover Au such as ion exchange, precipitation, solvent extraction, and biosorption. However, these techniques have several disadvantages

and difficulties. For example, the recovery of Au ions from chloride solution using solvent extraction consumes a lot of organic solvents that are toxic, flammable, and volatile, leading to numerous environmental problems. Hence, a technique that is more environmentally friendly, efficient, and safe should be used in the recovery of Au(III) ions in dilute solution.

Many materials have been used such as activated carbon, natural biosorbent, and mesoporous sorbent for the recovery of Au in solutions. However, these adsorbents require additional techniques such as filtration or centrifugation for its recovery and reusability which leads to the possibility of losing the adsorbent during this process. Thus, by designing a magnetic adsorbent with magnetite as its core, the used adsorbent can be easily recovered using an external magnetic field.

4-Nitrophenol and its derivatives is widely used in manufacturing industries of pharmaceutical (Shen *et al.*, 2017), synthetic dyestuff, herbicide, and insecticide (Seo *et al.*, 2017). The high concentration of 4-nitrophenol released in water downstream can substantially damage the ecosystem as it is one of the most toxic and refractory pollutants (Zhang *et al.*, 2014). Meanwhile, the product of 4-nitrophenol reduction which is 4-aminophenol is less poisonous and has various applications as corrosion inhibitor, drying agent, and an important precursor for the manufacture of analgesic and antipyretic drugs (Zhao *et al.*, 2015). Thus, the reduction of 4-nitrophenol to 4-aminophenol possesses great implication in the pollution abatement and resources regeneration.

Meanwhile, the conventional production of styrene oxide is by the epoxidation of styrene, using stoichiometric amounts of chlorohydrin or peracid as an oxidizing agent (Nepak and Srinivas, 2016). However, peracids are hazardous to handle, very expensive, nonselective towards epoxidation, and its usage may lead to the formation of many undesirable products (Dumbre *et al.*, 2014). Hence, a green oxidant which is a far more reactive form of oxygen species such as H_2O_2 or TBHP is necessary to produce the epoxides.

1.3 Objectives of the Study

The aims of this study are:

1. To synthesise and examine the physicochemical properties of thioctic acid functionalised silica coated magnetic (RS–SR–NH–SiO_2–Fe_3O_4) nanoparticles.
2. To assess the Au adsorption, desorption, reusability characteristics of the RS–SR–NH–SiO_2–Fe_3O_4 and investigate the equilibrium isotherm, kinetics, and thermodynamics of the adsorption.
3. To reduce the immobilised Au(III)–RS–SR–NH–SiO_2–Fe_3O_4 into Au(0)–RS–SR–NH–SiO_2–Fe_3O_4 using *Phaleria macrocarpa* (Scheff.) Boerl fruits extract.
4. To evaluate the catalytic activity of Au(0)–RS–SR–NH–SiO_2–Fe_3O_4 in the reduction of 4-nitrophenol and epoxidation of styrene.

1.4 Scope of the Study

This research focused on the synthesis of thioctic acid surface functionalised silica coated magnetite nanoparticles as an adsorbent and as a support for a catalytic reaction. The assessment of the adsorbent on the adsorption Au(III) ions and reusability characteristics were done with the optimisation of several parameters namely pH, ionic strength, adsorbent dosage, concentration of Au(III) ions, temperature, and contact time. The reusability of the adsorbent was also investigated with different concentrations of the desorption agent. Later, the obtained Au(III) ions on the surface of thioctic acid functionalised silica coated magnetite (Au(III)–RS–SR–NH–SiO_2–Fe_3O_4) were reduced using *Phaleria macrocarpa* extract to Au–RS–SR–NH–SiO_2–Fe_3O_4 and tested for catalytic reaction of reduction of 4-nitrophenol and epoxidation of styrene. Box–Behnken design (BBD) model from response surface methodology (RSM) was used for the optimisation process. The sample were characterised using FTIR, HRTEM, XRD, XRF, VSM, zeta potential, XPS, AAS, and GC-FID. The research outline is illustrated in **Figure 1.1**.

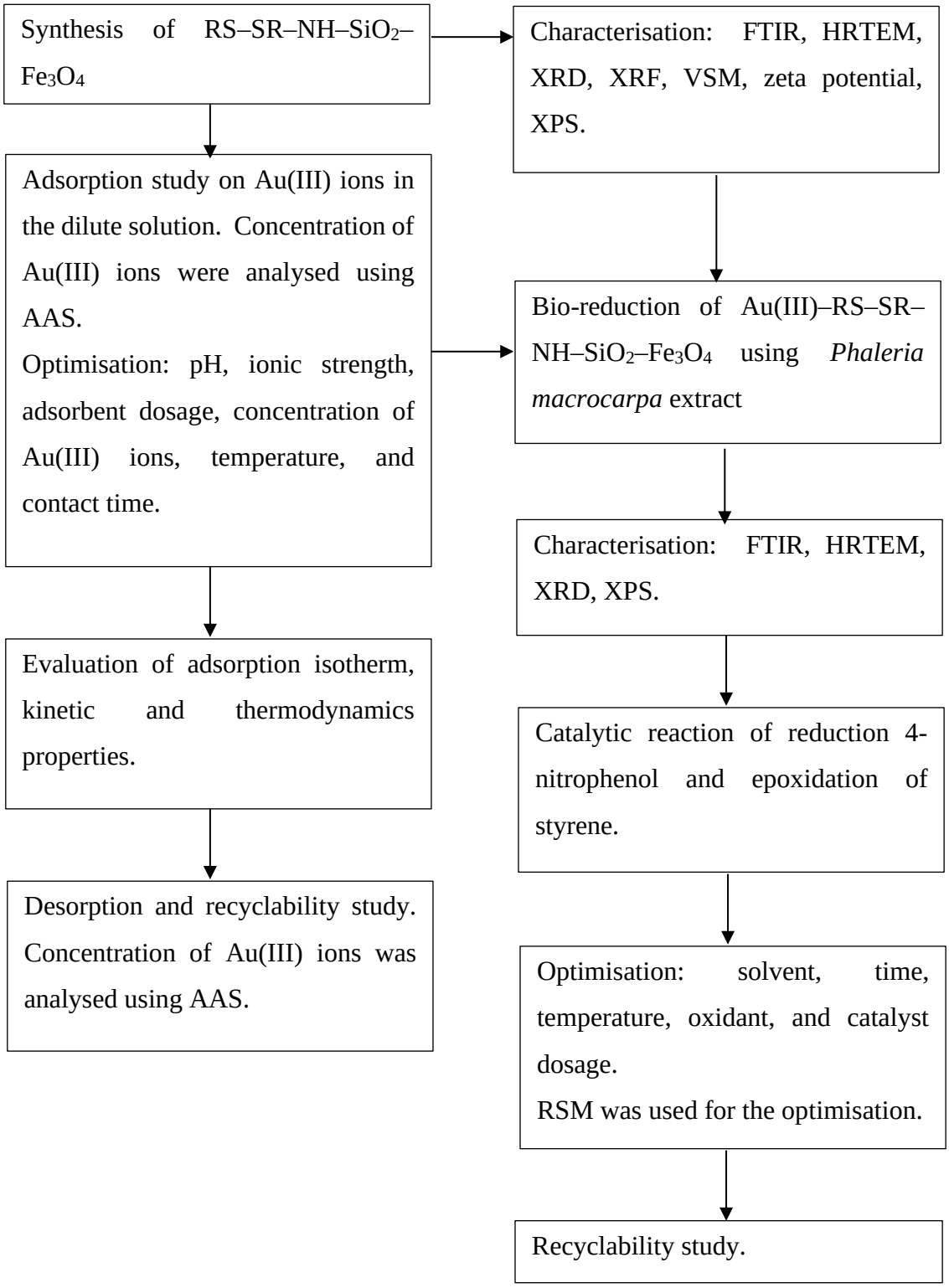

Figure 1.1 Research outline

1.5 Significance of the Study

In this research, a novel thioctic acid functionalised silica coated magnetite nanoparticles was used for the recovery of Au(III) ions in dilute solution. The use of magnetic material offers many advantages over conventional materials in terms of recovery and recycling process as it can be simply and efficiently recovered from the reaction media with the use of an external magnet. Meanwhile, according to hard–soft acid–base theory, thiol ligands have a high affinity towards Au ions. Thus, in this study thioctic acid was grafted onto the surface of silica coated magnetite nanoparticles to enhance the recovery of Au ions from dilute solutions.

In addition, this study was the first one that explored the dual functionalities of thioctic acid functionalised silica coated magnetite nanoparticles as an adsorbent and also as a support for Au catalyst. In addition, this research employs a simple and environmentally-friendly biosynthesis for Au NPs on the supports by using a locally available plant, *Phaleria macrocarpa* fruit extract. Moreover, the use of green oxidant in catalytic reaction and the application of response surface methodology approach for catalytic optimisation give advantages as it is more cost effective and environmentally friendly.

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LIST OF PUBLICATIONS

Journal with impact factor:

1. A. Razak, N.F., Shamsuddin, M., Lee, S.W., (2018). Adsorption kinetics and thermodynamics studies of gold(III) ions using thioctic acid functionalized silica coated magnetite nanoparticles. *Chemical Engineering Research and Design*, *130,* 18–28. https://doi.org/10.1016/j.cherd.2017.12.004. (Q2, IF: 3.073)
2. A. Razak, N.F., Shamsuddin, M., (2020). Catalytic reduction of 4-nitrophenol over biostabilized gold nanoparticles supported onto thioctic acid functionalized silica coated magnetite nanoparticles and optimization using response surface methodology. *Inorganic and Nano-Metal Chemistry.* https://doi.org/10.1080/24701556.2020.1720724. (Q4, IF: 0.685)

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1. A. Razak, N.F., Shamsuddin, M., (2016). Adsorption of gold(III) from aqueous solution using thioctic acid functionalized silica coated magnetite nanoparticles adsorbents. In *29th Malaysian Analytical Chemistry Symposium (SKAM 29).*