SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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REDUCTIVE LEACHING OF SYNTHETIC MANGANESE ORE USING BAMBOO SAWDUST AS REDUCING AGENT: A COMPARISON BETWEEN DIRECT HYDROLYSIS-LEACHING PROCESS AND SIMULTANEOUS HYDROLYSIS-LEACHING PROCESS

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation titled **"Reductive Leaching of Synthetic Manganese Ore using Bamboo Sawdust as Reducing Agent: A comparison between direct hydrolysis-leaching process and simultaneous hydrolysis-leaching process"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other title of this for any other examining body or University.

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LIST OF SYMBOLS AND ABBREVIATIONS

BSD	Bamboo Sawdust
DOE	Design of Experiment
SEM	Scanning Electron Microscope
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
FRIM	Forest Research Institute of Malaysia
FESEM	Field Emission Scanning Electron Microscope
ANOVA	Analysis of Variance
LOI	Loss on Ignition
mL	Milliletre
M	Molar
rpm	Rotation per Minute
g	Gram
cm	Centimeter
µm	Micronmeter
%	Percent
°C	Degree Celsius

PELARUT LESAPAN PENURUNAN BIJIH SINTETIK MANGAN MENGGUNAKAN SERBUK BULUH SEBAGAI AGEN PENURUNAN: PERBANDNGAN ANTARA PROSES HIDROLISIS-PELARUT LESAPAN LANGSUNG DAN PROSES HIDROLISIS-PELARUT LESAPAN SERENTAK

ABSTRAK

Kajian ini dilakukan untuk menyiasat kesan kepekatan asid sulfurik dan kelajuan pengaduk terhadap pelarut lesapan penurunan bijih sintetik mangan menggunakan serbuk buluh sebagai agen penurunan, dengan membandingkan proses hidrolisis-pelarut lesapan langsung dan proses hidrolisis-pelarut lesapan serentak. Sebelum eksperimen dilakukan, penyediaan sampel dan analisi pencirian dijalankan untuk memahami penghabluran, morfologi permukaan, taburan saiz zarah and kandungan abu sampel serbuk buluh. Keputusan daripada analisis pencirian mencadangkan bahawa serbuk buluh sesuai untuk dijadikan agen penurunan dalam proses pelarut lesapan penurunan. Kerja eksperimen ini dilaksanakan mengikut reka bentuk faktorial penuh $2^3 + 1$. Tiga faktor yang diuji dalam kajian ini adalan kepekatan asid sulfurik, kelajuan pengaduk dan jenis proses. Agen penurunan bentuk cecair diperolehi daripada proses hidrolisis, perolehan mangan ditentukan dengan menggunakan titratan isipadu EDTA dengan thymolphthalexone sebagai indikator. Berdasarkan model statistik yang dijana oleh ANOVA, kepekatan asid sulfurik (X_1) merupakan kesan paling ketara terhadap pelarut lesapan penurunan sintetik mangan menggunakan serbuk buluh sebagai agen penurunan diikuti dengan kelajuan pengaduk (X_2). Kajian ini juga menunjukkan bahawa perbezaan jenis proses tidak memberi kesan besar terhadap pelarut lesapan penurunan bijih sintetik Mangan secara keseluruhan. Dengan itu, lebih kurang 99% perolehan mangan boleh didapati dari bijih mangan sintetik dengan menggunakan serbuk buluh sebagai agen penurunan dalam keadaan optimum 4 M kepekatan asid sulfurik, 400 rpm kelajuan pengaduk, 100°C suhu tindak balas, 6 jam masa tindak balas, 10% ketumpatan pulpa dan -75 μm saiz zarah.

REDUCTIVE LEACHING OF SYNTHETIC MANGANESE ORE USING BAMBOO SAWDUST AS REDUCTIVE AGENT: A COMPARISON BETWEEN DIRECT HYDROLYSIS-LEACHING PROCESS AND SIMULTANEOUS HYDROLYSIS-LEACHING PROCESS

ABSTRACT

This research was carried out to investigate the effects of concentration of sulfuric acid and stirring speed on the reductive leaching of synthetic manganese ore using bamboo sawdust as reducing agent, comparing the direct hydrolysis-leaching process and simultaneous hydrolysis-leaching process. Prior to the experimental work, sample preparation and characterisation analysis were carried out to understand the crystallinity, surface morphology, particle size distribution and ash content of the BSD sample. The results obtained from the characterisation studies further suggests that BSD is a good carbohydrate source and suitable to be used as a reducing agent in the reductive leaching process. The experimental work is based on the full factorial design using $2^3 + 1$. The three variables in the reductive leaching experiment are concentration of sulfuric acid, stirring speed and hydrolysis-leaching method. Reducing sugars in solution form is obtained from the hydrolysis process. The manganese recovery was estimated volumetrically by EDTA titration using thymolphthalexone indicator. Based on the statistical model generated from the ANOVA, it was found that concentration of sulfuric acid (X_1) has the most significant effect of the reductive leaching of synthetic manganese ore in terms of recovery followed by the stirring speed (X_2). This study also shows that different hydrolysis-leaching method does not have a significant effect on the overall reductive leaching of synthetic manganese ore. Approximately 99% of manganese can be recovered from synthetic manganese ore using BSD as reducing agent under the optimum conditions of 4 M concentration of sulfuric acid, 400 rpm stirring speed, 100°C reaction temperature, 6 hours reaction time, 10% pulp density and -75 μm particle size.

CHAPTER 1

INTRODUCTION

1.1 Significance of Work

Manganese is essential in several industries such as dry cell batteries, fine chemicals, fertilizers, preparation of dietary additives as well as the most widely known iron and steel production. Thus many attempts of hydrometallurgical treatment has been carried out on low grade to medium grade manganese ores and also synthetic manganese ore in the recent years due to the depletion of high grade manganese ores in the 21st century (Ismail et al., 2016, Su et al., 2008, Hariprasad et al., 2007, Furlani et al., 2006, Pagnanelli et al., 2004, Sahoo et al., 2001).

The most well-known hydrometallurgical process for the extraction of manganese is the dissolution of manganese dioxide (occurs in nature mostly as pyrolusite, MnO_2) in an acid media such as H_2SO_4 with the utilization of a reducing agent. However, since some reducing agents employed such as SO_2, may be harmful to the environment, researchers have been investigating an environmental friendly alternative that is to use carbohydrates from agricultural biomass as reducing sugar. Carbohydrates are inexpensive non-hazardous reducing agents that may be used under mild acidic conditions. It can be found in abundance and often used in it its pure form or in industrial wastes (Furlani et al., 2006, Trifoni et al., 2001).

In previous works, several different carbohydrates, both in solution and in powders, have been investigated as reducing sugars in the leaching of manganese ores. Among the agricultural biomass that has been used includes bamboo sawdust, cane molasses, whey, rice husks, corncob, cornstalks, and wheat stalks (Zhang et al., 2013b, Furlani et al., 2009, Su et al., 2008, Hariprasad et al., 2007, Furlani et al., 2006, Beolchini et al., 2001, Trifoni et al., 2001, Veglio et al., 2000, Trifoni et al., 2000).

1.2 Problem Statements

As the demand for manganese rises with the depletion of natural manganese ores, the use of synthetic Manganese ores will be more notable. In the past decade, there have been hardly any new revolutionary studies on the extraction of manganese from synthetic manganese and low grade manganese ore via reductive leaching using carbohydrates as reducing agent.

Previous works regarding the hydrolysis process of bamboo sawdust has been carried out where the operating conditions have been optimized by studying the effect of factors such as concentration of acid media, particle size, temperature, stirring speed and time (Zahir, 2016, Ghazali, 2016). The use of bamboo sawdust as a reductant in Manganese extraction has also been studied in terms of its kinetic modeling and characterization studies (Ismail et al., 2016, Ismail et al., 2015, Ismail et al., 2013).

The recovery of manganese from the reductive leaching of Manganese ore using reducing sugars have shown to be above 90% in most cases (Tian et al., 2010, Su et al., 2008, Hariprasad et al., 2007, Ismail et al., 2004). However, although the optimum conditions on manganese recovery was demonstrated from previous researchers, little attention has been made to the percent yield of produced reducing sugar during the leaching process, hence the mechanism of BSD dissolution in sulfuric acid is still questionable.

Apart from that, there are two approaches to using agricultural biomass for the reductive leaching of manganese ore. One is to extract the reducing sugars via hydrolysis process then use the reducing sugar in solution for the leaching process (direct hydrolysis-leaching process) while the other is to add the carbohydrates in powder form into the leaching system where hydrolysis and leaching will occur simultaneously (simultaneous hydrolysis-leaching process).

The present work studies the extraction of manganese from the reductive leaching of synthetic manganese ore using bamboo sawdust (BSD). A comparison on the both approaches of using BSD in reductive leaching is carried out and the manganese recovery from both approaches were analyzed statistically by ANOVA.

1.3 Objectives

i. To study the effects of sulfuric acid concentration and stirring speed on the synthetic manganese extraction using bamboo sawdust as reducing agent with direct hydrolysis-leaching process.
ii. To study the effects of sulfuric acid concentration and stirring speed on the synthetic manganese extraction using bamboo sawdust as reducing agent with simultaneous hydrolysis-leaching process.
iii. To compare the two approaches of using bamboo sawdust for the reductive leaching of manganese from synthetic manganese ore.

1.4 Scope of Study

The present study is solely experimental laboratory work. Prior to the experimental procedures, thorough sample preparation and characterization studies were carried out to prep the samples as well as to further understand the characteristics of the raw sample. The sample preparations carried out includes size reduction and characterization whereas several relevant analysis were performed for characterization studies.

The first experimental work done was to hydrolyze the bamboo sawdust in order to obtain reducing sugars in solution form. Next the reductive leaching of synthetic manganese ore employing the two different approached of biomass as reducing sugars is performed. The DOE used in this research is full factorial of 2^3 + 1 center point. A total of 5 hydrolysis experiments and 10 leaching experiments were completed. Once the experimental work is done, the recovery of the Manganese was estimated volumetrically by EDTA titration. The results from the two approaches were compared.

1.5 Thesis Organization

The framework of this thesis is made up of five main chapters - introduction, literature review, methodology, results and discussion, finishing off with conclusion and recommendation. Chapter 1 outlines the introduction of this research work which covers a general idea of this research, a survey of problem statements from past researches, the objectives of this research and also the overall scope of work that has been done. In Chapter 2, several articles and journals related to this research were studied and reviewed to learn about the present knowledge which includes substantive findings, in addition to theoretical and methodological contributions. Literature review is crucial in a thesis to enhance our understanding as well as to avoid redundant testing and analysis.

For Chapter 3, as the title Methodology suggests, basically explains the materials and methodologies involved in this research work. The entire process flow and experimental procedures that the raw BSD undergoes up till the reductive leaching of synthetic manganese ore and the determination of its recovery via EDTA titration are well explained in this chapter. Results and discussion are presented in Chapter 4. Results from the experimental work is interpreted and explained, in which doubts and questions regarding the research is clarified. Discussions and arguments are made in this chapter and supporting statements will be used to back up the research results whenever possible. Lastly, Chapter 5 portrays an overview of this research plus concludes the findings and significant results of this research work. It also states whether the objective of this research is accomplished or otherwise. Moreover, recommendations for future studies is suggested at the end of the chapter to improvise and ease related further studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides an insight on the work related to the hydrolysis of BSD, and the reductive leaching of Manganese ore in general, organized thematically. The topics discussed will include current knowledge and substantive findings, including theoretical and methodological contributions.

The topics included in the literature review of hydrolysis of BSD are an overview of the agricultural biomass, its characteristics and also research background on the hydrolysis process for reducing sugar production. A good understanding of the species of bamboo used and its characteristics is fundamental in the study of producing reducing sugar through dissolution in acid media. Apart from that, there are also various methods of hydrolysis process in which have improvised and evolved over the years.

Reductive leaching is a well-known hydrometallurgical process that has been widely used in the mineral processing industry. Studies on reductive acid leaching of Manganese ore using carbohydrates as reducing sugars has been ongoing since the beginning of the 21^{st} century, although at a rather sedate pace. The reductive leaching of Manganese ore can be done using other reducing agents such as sulfur dioxide. However due to its negative effects to the environment, researchers have been opting more environmental friendly options in hydrometallurgical processes (Ali et al., 2016, Xie et al., 2013, Tian et al., 2010).

Chapter 2 will provide both summary and synthesis of the important information of the sources used and referred to, that lead to the study of extraction of Manganese from synthetic Manganese ore using BSD as reducing agent using the two possible approaches.

2.2 Bamboo Sawdust

Bamboo belongs to the Gramineae family and Bambuseae subfamily and is widely distributed around the world, especially economical and significant in Asia. *Gigantochloa Scortechinii* (commonly known as buluh semantan) is the most abundant bamboo and most easily available resources to supplement local wood found in Peninsular Malaysia and the rest of the world (Hisham et al., 2006). Bamboo is one of the most rapidly growing plants, and because of modern processing techniques, bamboo can be used for multipurpose. In this research, *Gigantochloa Scortechinii* will be used in the form of sawdust during experimental work.

Bamboos vary considerably in size, depending on their species, locality and vigor of the clump. On the other hand, attributes such as stem size and cell wall thickness influences the range of their usage. 3-year-old culm of *Gigantochloa Scortechinii* is found to have the longest mean internode length. Based on its physical characteristics, 3-year-old culms are better in terms of its length, internode length, diameter breast height as well as its circumference. Thus, the usage of culm is much preferred at this age (Mohamed et al., 2011).

Bamboo is a lignocellulosic biomass, as with wood, the chemical composition of bamboo includes cellulose, hemicellulose, lignin, and a small amount of extract and ash. Cellulose is the primary constituent in any biomass to produce oligosaccharides (cellotetraose, cellotriose, and cellobiose), and monomeric sugars (glucose and fructose). Hemicellulose is the secondary most abundant polymer in biomass to produce pentose sugars (xylose, arabinose) and hexoses (galactose, glucose and mannose) (Mohan et al., 2015).

Physical, chemical or physiochemical pretreatment is employed to break down the hemicellulose and lignin structure in order to improve the enzymatic hydrolysis rate. These pretreatment approaches includes steam explosion, diluted acid and lime (Li et al., 2012). In 2012, Binod discovered that pretreating cotton stalk with sodium hydroxide was effective in deriving fermentable sugars (Binod et al., 2012).

In a characterization study done by Ismail et al., detailed bamboo sawdust constituents were analysed and the cellulose, hemicellulose and lignin content were determined. The results obtained exhibited a wide size range distribution with 1.86 span value and approximately 100 µm geometric mean diameter. The dominant composition of the BSD were cellulose (38.96%), hemicellulose (26.95%) and lignin (25.86%). A smooth fibrous surface with multiple aligned bundles were observed from the morphology characteristics by SEM. The assessable crystalline index of cellulose was found to be 56.12% (Ismail et al., 2013). In a sequential study on the leached residue characterization of manganese-bamboo sawdust blend, it was reported that the crystallinity of BSD residue has decreased from 56.12% to 52.65% (Ismail et al., 2015). A decrease in the percent crystallinity indicates that degradation of BSD has occurred.

2.3 Manganese Ore

Manganese, one of the most significant ferrous metals, is a black and brittle element used in the metallurgical applications as an alloying addition, particularly in cast iron and steel production. It is utilised as an alloy with nonferrous metals such as aluminium and copper while on the other hand no metallurgical applications of manganese includes soft ferrite magnets used in electronics, battery cathodes, water treatment chemicals, micronutrients found in fertilizers and animal feed, as well as a colorant for bricks and ceramics. Although manganese is the 12th most abundant element in the earth's crust, it is not found free in nature. manganese deposits occur on all land area, deep ocean floors, on lake bottoms and other marine locations. The two general types of economically significant manganese deposits are marine chemical sediments and secondary enrichment deposits (Corathers, 2005).

Due to its sulfur-fixing, alloying and deoxidising properties, manganese is essential to steel and iron production. Steelmaking, including ironmaking component has accounted to 85-90% of the total domestic manganese demand. With its various uses, including its utilization as a key component in aluminium alloys and in dry cell batteries, the level and nature of manganese is expected to remain constant in the near term. As of now, there are no innovations or practical technologies for the replacement of manganese with other materials or for using domestic deposits or other accumulations to reduce the dependence on manganese ore (Corathers, 2013).

One of the major applications of Manganese that dates from 1893 is steelmaking, when manganese was reported to improve malleability of ferrous articles. In 1856, Robert Forester Mushet discovered that steel could be mass produced by the Bessemer process, provided that there was addition of manganese (Williams, 1980). Since then, manganese has been an essential element in the commercial production of almost all steels. Following that discovery, bulk manganese ferroalloy industry was established and by 1870, cheap ferromanganese containing 75% or more manganese was available (Corathers, 2010).

Current research and technology done on manganese includes advanced materials, electrochemistry of manganese oxides, lithium manganese oxides, biology, and environment and toxicology (Gray and Luan, 2002, Bowden et al., 2002, Doyle and Arora, 2001, Nelson et al., 2002). According to Corathers, the domestic and global demand trend for manganese is expected to follow closely to that of steel production. Although the growth rates for certain non-metallurgical components of manganese demand may be higher than steel production, for instance batteries, this scenario will only have a minor effect on the overall manganese demand (Corathers, 2009).

2.4 Hydrolysis Process

Hydrolysis is a pretreatment process to extract sugar monomers from lignocellulosic biomass. Plants containing sugar and starch can be easily converted into sugars and pretreatment is a crucial step in the process. Pretreatment removes hemicellulose, reduces cellulose crystallinity, increases porosity of the materials and improves the digestibility of the lignocellulosic materials. Apart from that, pretreatment must meet the following requirements: (1) improve the formation of sugars or the ability to subsequently form sugars by enzymatic hydrolysis; (2) avoid the degradation or loss of carbohydrate; (3) avoid the formation of byproducts inhibitory to the subsequent processes; and (4) be cost effective (Sun and Cheng, 2002).

Since cost is a deciding factor in pretreatment processes, H_2SO_4 at concentrations below 4 wt % has been of most interest to researchers as it is effective and inexpensive. Dilute H_2SO_4 is mixed with biomass to hydrolyze hemicellulose to xylose and other sugars and then continues to breakdown xylose to form furfural. The dilute H_2SO_4 effectively removes and recovers most of the hemicellulose as dissolved sugars, and glucose yields from cellulose increase with hemicellulose removal to almost 100% for complete hemicellulose hydrolysis. Hemicellulose is removed when H_2SO_4 is added where it enhances the digestibility of cellulose in the residual solids (Mosier et al., 2005).

Concentrated acids such as sulfuric acid and hydrochloric acid have been used to treat lignocellulosic materials. Diluted acid hydrolysis has been successfully developed for the pretreatment of lignocellulosic materials. The dilute H_2SO_4 pretreatment can achieve high reaction rates and significantly improve cellulose hydrolysis (Esteghlalian et al., 1997). Recent development of dilute acid hydrolysis processes aims to use less severe conditions and to achieve high xylan and xylose conversion yields. This is necessary to achieve favorable overall process economics because xylan accounts for up to a third of the total carbohydrates in various lignocellulosic biomass (Hinman et al., 1992). The two primary types of dilute acid pretreatment processes are high temperature

(>160°C) with continuous-flow process for low solid loading (5-10%) (Converse et al., 1989, Brennan et al., 1986) and low temperature (<160°C) with batch process for high solids loading (10-40%) (Esteghlalian et al., 1997, Cahela et al., 1983).

The most studied acid in acid pretreatment of lignocellulosic materials is diluted H_2SO_4 and it is reported to have high hydrolysis yields. Other acids that have been tested are hydrochloric acid, phosphoric acid and nitric acid (Mosier et al., 2005). A recent study by Yat et al. reported the dilute acid pretreatment of four timber species (aspen, balsam fir, basswood and red maple) and switchgrass using dilute H_2SO_4 for 50 g of dry biomass/L. Xylose formation and degradation at different reaction temperatures (160-190°C), sulfuric acid concentrations (0.25-1.0% w/v), and particle sizes (28-10/20 mesh) in a glassed lines 1-L well-mixed batch reactor were studied. Both temperature and acid concentration influenced the reaction rates for the generation of xylose from hemicellulose and the generation of furfural from xylose strongly (Yat et al., 2008).

As stated by Ghazali in his research, the most significant factor that influences the hydrolysis of bamboo sawdust is the size of bamboo sawdust, followed by hydrolysis temperature and mass of bamboo sawdust. White the factor that showed the least effect on the hydrolysis system is the concentration of H_2SO_4 (Ghazali, 2016). However, the research done by Zahir mentions that the acid concentration of H_2SO_4 showed significant influence in the hydrolysis of bamboo sawdust as opposed to the speed rotation of the stirrer (Zahir, 2016).

Dilute acid hydrolysis is the more favorable method of pretreatment for industrial applications and it has been researched for pretreating wide range of lignocellulosic materials. Percolation, plug flow, shrinking-bed, batch and counter current reactors are some of the different types of reactors used for the pretreatment of lignocellulosic biomass (Taherzadeh and Karimi, 2008). The advantages of this method are solubilizing hemicellulose, mainly xylan, but also converting solubilized hemicellulose to fermentable sugars (Saha et al., 2005). Anyhow, dilute acid hydrolysis generates lower degradation products than concentrated acid pretreatments.

The key factors to consider for an effective pretreatment of lignocellulosic biomass are high yields for multiple crops, sites ages, harvesting times; highly digestible pretreated solid; no significant sugar degradation; minimum amount of toxic components; biomass size reduction not required; operation in reasonable and moderate cost reactors; non-production of solid-waste residues; effectiveness at low moisture content; obtaining high sugar concentration; fermentation compatibility; lignin recover; and minimum heat and power requirements (Alvira et al., 2010).

Even though dilute acid hydrolysis is said to be able to achieve excellent hemicellulose sugar yields and highly digestible cellulose, the equipment configurations and the high ratio of water to solids employed in flow-through systems require significant energy for pretreatment and recovery. Despite significantly improving cellulose hydrolysis, it usually cost much more than physiochemical pretreatment processes such as steam explosion or AFEX (Kumar et al., 2009). Dilute acid pretreatment is also known to have a negative effect on the enzymatic hydrolysis of biomass as reported by Selig et al. where the formation of spherical droplets on the surface of residual corn stover following dilute acid pretreatment at high temperature (Selig et al., 2007).

Thus it is extremely important to carefully examine the appropriate dilute acid pretreatment of lignocellulosic materials. The prime advantages of acid hydrolysis is that it hydrolyzes hemicellulose to xylose and other sugars and it alters the lignin structure. However, it has been shown that materials subjected to acid hydrolysis can be harder to ferment because of the presence of toxic substances (Galbe and Zacchi, 2007). Apart from that, acid pretreatment in general requires costly materials for construction, high pressures, neutralization, and conditioning of hydrolysate prior to biological steps, slow cellulose digestion by enzymes, and nonproductive binding of enzymes to lignin (Wyman et al., 2005). Significant research works done since the 21st century on the production of sugars from agricultural biomass is tabulated in Table 2-1.

Table 2-1 Research background on the production of sugars from agricultural biomass

Journal Title	**Research Sample**	**Operating Conditions**	**Results**
Hydrolysis of bamboo cellulose and cellulose characteristics by Streptomyces griseoaurantiacus (Chu et al., 2012)	Bamboo powder	H_2SO_4 concentration: 0.2 M Temperature: 100°C Reaction time: 1 hour	Maximum yield of 8.67 g/L reducing sugar was obtained.
Dilute acid pretreatment of bamboo for fermentable sugar production (Leenakul and Tippayawong, 2010)	Bamboo (*Dendrocalamus asper)*	H_2SO_4 concentration: 1.2% Temperature: 120°C Reaction time: 60 minutes	Maximum yield of 85 mg/g fermentable sugar was obtained.
Enzymatic hydrolysis and fermentation of pretreated cashew apple bagasse with alkali and diluted sulfuric acid for bioethanol production (Rocha et al., 2009)	Cashew apple bagasse	H_2SO_4 concentration: Diluted (not specified) Temperature: 121°C Reaction time: 15 minutes	Ethanol achieved a high 0.47 g/g glucose in fermentation test.
Conversion of olive tree biomass into fermentable sugars by diluted acid pretreatment and enzymatic saccharification (Cara et al., 2008)	Olive tree biomass	H_2SO_4 concentration: 1.4% Temperature: 210°C Reaction time: N/A	Olive tree biomass resulted in 76.5% hydrolysis yield of fermentable sugars.
Diluted acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol (Saha et al., 2005)	Wheat Straw	H_2SO_4 concentration: 0.75% v/v Temperature: 121°C Reaction time: 1 hour	Saccharification yield as high as 74%.

2.5 Reductive Leaching of Manganese ore

Reductive leaching is a well-known hydrometallurgical process, for the extraction of minerals from its ore, in an acid media by using reducing agent. The main focus of this study is the reductive leaching of manganese ore. Manganese ores can be treated either by reduction-roasting followed by acid leaching or directly by reductive leaching using different kinds of reducing agents and acids. A reducing agent is necessary to reduce Mn(IV) to soluble Mn(II) in the leaching of manganiferous ores containing tetravalent manganese because they are stable in acid or alkaline oxidizing conditions. In aqueous reduction of manganese ore, several reducing agents can be use such as SO_2 (Naik et al., 2000), $FeSO_4$ (Das et al., 1982), sucrose (Veglio and Toro, 1994), charcoal (Das et al., 1989), coal and lignite (Hancock, 1986), pyrite (Parida et al., 1990) etc.

In the study of reductive leaching of manganese oxide ore in aqueous methanol-sulfuric acid medium, Momade found that the conditions for optimum manganese extraction are determined by the methanol and sulfuric acid concentrations as well as the reaction time. It was reported that manganese extraction of about 98% was reached at 160°C with a methanol dosage of 40 vol% at 0.3 M sulfuric acid within a period of 2 hours. In general, satisfactory results were obtained during autoclave digestion at temperatures between 150 and 170°C with a reaction mixture containing 20-40 vol% methanol at relatively low sulfuric acid concentrations between 0.1 and 0.2 M (Momade and Momade, 1999).

The use of SO_2 as a reducing agent in the leaching of manganese ore is encouraged by its rapid rate of reaction, low temperature operation, ease of purifying leach liquors and elimination of barren solution disposal problems. In a study done on the aqueous SO_2 leaching on Nishikhal Manganese ore, it was found that 95% of manganese can be extracted from -150 μm ore with twice the stoichiometric quantity of SO_2 required for the dissolution of manganese in 15 minutes. The effect of variables on extraction of manganese were independent of each other within the range of variables chosen for the experiment and the quantity of SO_2 present in the solution is the controlling factor in the extraction of manganese (Naik et al., 2000).

In recent studies, researchers have been focusing on organic reductants for the reductive leaching of manganese ore such as oxalic acid, glucose, sucrose and lactose. The focus on alternative reductants instead of the traditional reductants as mentioned above is because some reducing agents such as SO_2 may be harmful to the environment if not controlled and regulated. Organic reductants in the reductive leaching of manganese ores has been reported to be efficient and simple under mild temperature conditions (<90°) (Hariprasad et al., 2009), however the commercial applications of this technique is limited due to the cost of reductant and high consumption rate (Tian et al., 2010).

In the reductive leaching of manganese dioxide ore, oxalic acid can also be used as a reducing agent. Leaching of manganese ore to produce microorganisms using oxalic acid as reducing agent has been reported by Stone (Stone, 1987). In the research done by Sahoo, it is shown that manganese can be extracted from low grade ore using oxalic acid as reductant at approximately 85°C in sulfuric acid medium where the oxalic acid concentration has the strongest influence on the extraction of Manganese followed by reaction temperature and sulfuric acid concentration (Sahoo et al., 2001).

Agricultural biomass are inexpensive and effective reducing agents used to reduce manganese ore with a degree of reduction of more than 95% at temperatures below 450°C. The types of biomass studied in recent years includes sawdust, cane molasses, corncob, cornstalks, rice husks, wheat stalks, bagasse, bamboo and shredded paper (Zhang et al., 2013a). These low cost, renewable and non-hazardous alternative reductants have attracted much attention in the recent years in order to extract manganese ore efficiently and economically and also taking into consideration the environment (Xie et al., 2013).

In a study on the reductive leaching of manganiferous ores by glucose and H_2SO_4 on the effect of alcohol, two different process sequences were proposed: manganiferous ore acid leaching by using glucose in an alcohol-modified media and aqueous acid leaching of the manganiferous ore by using glucose and successive add titin of the alcohol to the leach liquor. Although the manganese concentration gained after 6 hours of treatment, with methyl alcohol concentration and glucose, are very similar to those obtained in the test performed with both alcohol and glucose and only with glucose, the kinetics of manganese dissolution in the presence of glucose and methyl alcohol are faster compared to the tests performed with only methyl alcohol (Trifoni et al., 2001).

In another study on the usage of glucose as reductant, the oxidation of glucose during the reductive leaching of pure MnO_2 and manganese ore in sulfuric acid at 90°C was investigated. The aim of the study was to identify the organic derivatives of glucose during the leaching of manganese ores. In order to achieve a better comprehension and control on the leaching process, a thorough understanding of carbohydrates degradation is required. The glucose degradation in this research occurs at high temperature of 90°C in acid solution containing 0.3 g of glucose in 2% concentrated sulfuric acid in a Duboff Shaker. The organic derivatives were monitored by HPLD and the chromatographic patterns of the leached solutions showed that formic acid was the major compound formed. Minor quatites of glycolic, glycerin and traces of gluconic acids were also found (Furlani et al., 2006).

The purification of liquor leached solutions obtained from low-grade manganese ores leached by carbohydrates in sulfuric medium were studied by Pagnanelli et al. The aim of the research was to develop a combined technology approach for the production og high quality manganese sulfate solutions from low grade manganese ores where the

$MnSO_4$ liquor leach is obtained by reductive leaching using glucose as reducing agent. In the acid reductive leaching of low grade Manganese ore using glucose as reductant, high purity of $MnSO_4$ solutions were obtained. This leaching process can be considered environmental friendly as it uses non-hazardous materials, including industrial waste as a reducing agent, operating in a relatively mild conditions (Pagnanelli et al., 2004).

In a kinetic study on a manganiferous ore leaching in diluted nitric acid using sucrose as reducing agent, it is reported that a shrinking core model with variable activation energy was found to successfully fit experimental data of manganese extraction yields vs leaching time. A physical confirmation of the complex reactions that take place during the manganese leaching and the different reactivity and accessibility of the mineralogical forms present in the ores are found in this model. Appropriate kinetic study on leaching is crucial in designing an efficient hydrometallurgical process operations. Identification of the controlling reaction step(s), studies on the influence of the main operating conditions on the metal extraction yield and the development of a mathematical model that predicts experimental leaching data are fundamental in designing the correct process (Beolchini et al., 2001).

Apart from glucose and sucrose, lactose has also been studied as a reductant in the leaching of Manganiferous ores. A study carried out by Veglio et al. investigated the use of lactose and whey as reducing agents for the acid leaching of Manganiferous ores at 70°C. The researchers simulated the possible use of the byproducts of cheese industries as reducing agents for metal extractions, using lactose to simulate the whey behavior. The results of the study showed that similar Manganese extraction yields obtained by using both lactose and whey. Thus it is possible to use lactose in order to simulate the whey behavior during the leaching process (Veglio et al., 2000).

Corncobs is one of the more favorable biomass in the study of reductive leaching of manganese ore using carbohydrates as reductants. According to Tian et al., the leaching efficiency of manganese reached 92.8% under the optimum condition which was determined for 10g of manganese dioxide ore as corncob amount of 3 g, ore size of 75 μm, sulfuric acid concentration of 1.9 mol/L, leaching temperature of 85°C for 60 minutes (Tian et al., 2010). A similar study by Ali et al. reported that manganese extraction of 92.48% was achieved for a leaching time of 60 minutes at 90°C using 1.9 mol/dm^3 H_2SO_4 concentration and 4g of corncob (Ali et al., 2016). This method provided a good leaching yield while demonstrating that corncob is a low cost, renewable, and non-hazardous reducing agent.

Cane molasses has also been investigated as a reductant in the reductive leaching of low grade manganese ore in H_2SO_4. Cane molasses is a byproduct of sugar manufacture and generally contains 25-35% cane sugar, 15-25% invert sugar and 9-11% colloidal materials. In a study carried out by Su et al., the effect of concentration of cane molasses and acid, leaching temperature and reaction time were investigated for the reductive leaching of low grade manganese ore using cane molasses as a reducing agent. 97% leaching efficiency of manganese was achieve under the optimum condition of 1.9 mol/L H_2SO_4 and 60.0 g/L came molasses for 120 minutes at 90°C while using particle sizes smaller than 0.147 nm (Su et al., 2008).

In a comparative study on acid leaching of low grade manganese ore using some industrial waste as reductants, sawdust $(C_6H_{10}O_5)_n$ with -1 mm particle size or lactose $(C_{12}H_{22}O_{11})$ with 98% purity are considered industrial wastes and used as reducing agent. The study shows that low grade manganese ore could be successfully treated by direct sulfuric acid leaching using either lactose or sawdust as reducing agent. Both sawdust and lactose have been proven to be effective reducing agents and the maximum manganese recovery of 92.5% with sawdust as reductant was achieve at -100 mesh particle size, 90°C leaching temperature, 90 minutes reaction time, 30% acid concentration, 1.5 acid/MnO_2 stoichiometric ratio, 0.5 g/g sawdust/ore weight ratio, and 700 rpm agitation rate. On the other hand the maximum recovery of manganese is 90.5%

with lactose as reductant with optimum conditions of -100 mesh particle size, 90°C leaching temperature, 120 minutes reaction time, 20% acid concentration, and 1.8 acid/MnO_2 stoichiometric ratio (Ismail et al., 2004).

A research done by Hariprasad et al., studied the effects of pulp density, amount of acid, leaching temperature, particle size of ore and amount of sawdust in the leaching of manganese ore using sawdust as reductant. Manganese extraction from low grade manganese ore, manganese nodule and Mn-nodule leach residues were tested and the recovery was approximately 98% under the following conditions: 8 hours leaching time, 5% H_2SO_4 (v/v), 10% pulp density, 90°C and 5% sawdust (w/w), i.e. 0.5 g/g ore. As stated by Hariprasad and his co researchers, sawdust is a potential reducing agent for manganese ores of various grades based on sand or in sea. The response of reductive leaching using sawdust as reductant was good even for high silica containing ore. Regardless of manganese content, approximately 98% manganese can be extracted within 4 to 8 hours by maintaining the leaching temperature at 90°C and varying sawdust and H_2SO_4 (Hariprasad et al., 2007).

Another research done by Hariprasad and his co researchers utilized waste cellulosic as a reductant in the reductive leaching of medium grade manganese ore. In the study to investigate the effectiveness of lignocellulosic base wastes such as used newspaper as a reductant, low grade and medium grade siliceous manganese ore containing 15.83% and 38.22% Mn was leached in sulfuric acid medium using shredded newspaper as reducing agent. It was reported that high manganese extraction of 93.1% was obtained under the following conditions: 10% pulp density, 8 hours leaching time, 5% (v/v) sulfuric acid, leaching temperature of 90°C and reductant to ore ratio of 0.5. The leach solution was enriched through recycling, purification and evaporation to obtain ($MnSO_4 \cdot H_2O$) of high purity (Hariprasad et al., 2009).

The study on bamboo sawdust as a reducing agent for the reductive leaching of low grade manganese ore in acidic medium (H_2SO_4) and the dissolution kinetics has been investigated by Ismail et al.. In the research, the effects of variables such as temperature, sulfuric acid concentration, and bamboo loading were investigated using Response Surface Methodology (RSM) based on a Central Composite Design. It was found that the most significant parameter on the leaching of low grade manganese ore is temperature, followed by sulfuric acid concentration and bamboo loading. In order the achieve 99% manganese extraction, the optimum conditions are leaching temperature of 100°C, 2.2 M sulfuric acid concentration and 8.3 g bamboo loading (Ismail et al., 2016).

Zhang et al. studied the mechanisms of biomass reduction on low grade manganese dioxide ores by investigating the reaction temperature, reaction time, biomass/ore ratio, composition of biomass, nitrogen flow rate, and particle size of raw materials on the manganese recovery degree. It was reported that the degree of reduction increased significantly with the increase in reaction temperature, reaction time, and biomass/ore ratio and decreasing particle sizes of biomass and amount of air. MnO_2 in the ore was found to reduce stepwise via Mn_3O_4 and MnO. It was also found that the reduction process of manganese dioxide ore involved 3 steps in general: (1) the biomass decomposed to released reductive volatiles, (2) the volatiles were absorbed onto the surface of the manganese ore particles, and (3) the manganese ore reacted with the gaseous reductive substances. The findings also showed that biomass/ore ratio had a strong effect on the reduction mechanism (Zhang et al., 2013a).

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter focuses on the details of the raw materials used, chemicals used, sample preparation technique, experimental design, experimental set-up, experimental procedure as well as the relevant characterization processes associated with this research. The raw materials used in this experiments includes bamboo sawdust and synthetic manganese ore. Prior to the experimental works, the raw materials are required to undergo the necessary sample preparation procedures and raw material characterization processes.

In addition to that, the experimental parameters and design of experiment using Minitab 16 will also be discussed. The experimental procedures involved in this research includes hydrolysis process where reducing sugar is produced from BSD, leaching process where reductive leaching of synthetic Manganese ore takes place with aid of reducing sugar produced from the hydrolysis process, and also a simultaneous hydrolysis and leaching process where the hydrolysis of BSD and reductive leaching of Manganese ore is carried out at the same time in the same reaction flask.

Liquors collected at time intervals during the course of the experiment and also leached liquors from the reductive leaching process are estimated volumetrically by EDTA titration using thymolphthalexone indicator. BSD residues from the hydrolysis process are to undergo another series of product characterization analysis. The results from the experimental work are then analyzed using Minitab 16. The overall work flow of this research work is shown in Figure 3-1.

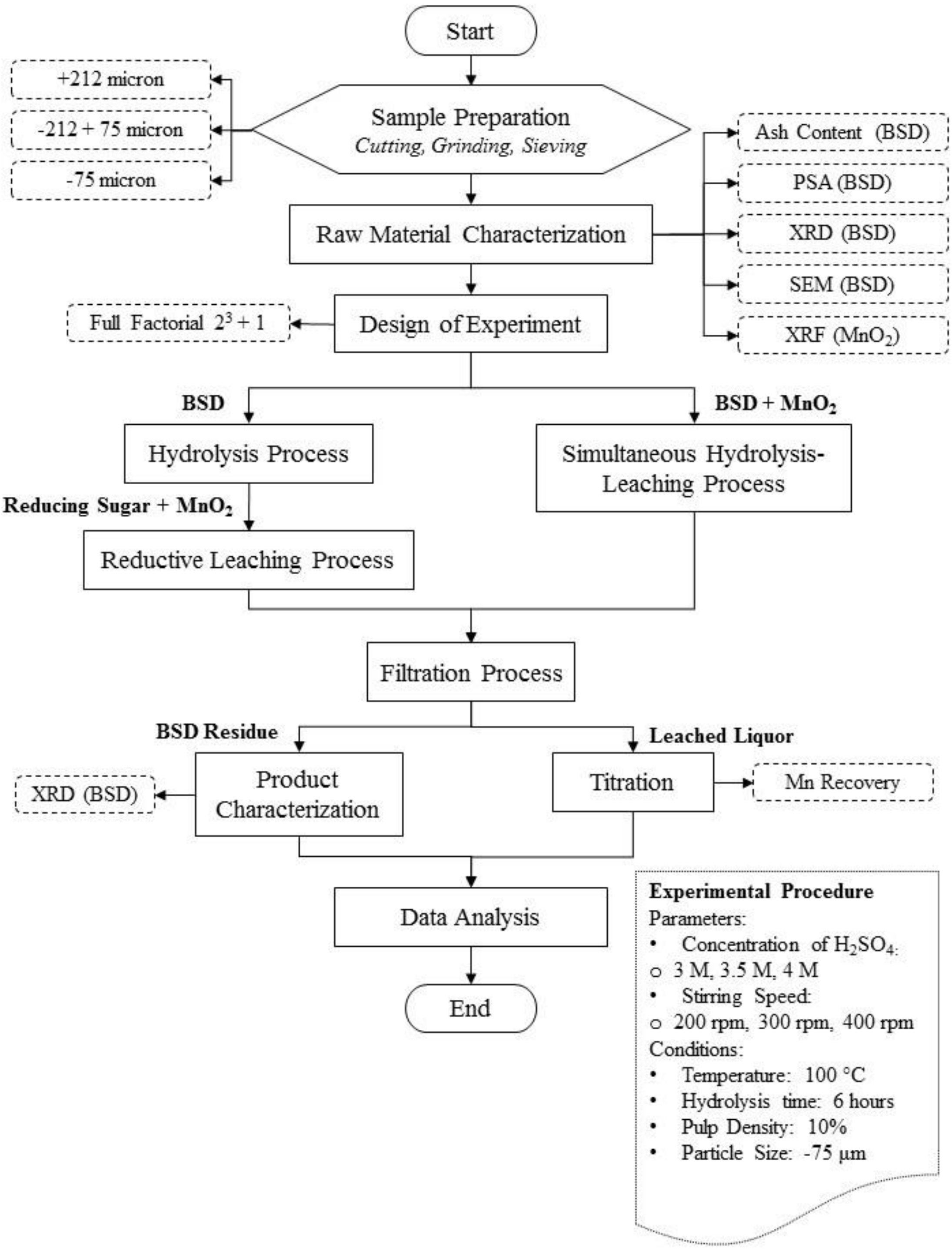

Figure 3-1 Overall work flow of experimental procedure

3.2 Raw Materials

The raw materials utilized in this research are BSD which is used as a reducing agent for the reductive leaching of SMO.

3.2.1 Bamboo Sawdust (BSD)

The species of bamboo used for this research is called *Gigantochloa Scortechinii.* Approximately 5 kg of fresh bamboo was collected from the Forest Research Institute of Malaysia (FRIM), Selangor. The bamboo sample required for this research consist of a mixture of nodes and internodes. Sample preparation process of bamboo will be further discussed in Chapter 3.4 Sample Preparation, the weight of the BSD amount to 1000 g. The BSD will undergo the hydrolysis process to extract reducing sugars which will be used as reductants for the reductive leaching process.

3.2.2 Synthetic Manganese (SM)

The SM used was produced by Acros Oganics at -10 mesh and 99% purity. Further size reduction has been done to reduce the particle size to -75 μm for x-ray fluorescence analysis (XRF) and leaching process. Elemental analysis from the XRF analysis carried out by using RX 300 XRF spectrometer by Rigaku shows that several elements were dominantly present in the ore, mainly Manganese (34.33%), Iron (0.048%) and Silica (0.024%). Other traces of elements present in the SM include alumina, sulfur, chlorine potassium, calcium, chromium, nickel, copper and selenium.

3.3 Chemicals

The main chemicals used in the experimental work are sulfuric acid, H_2SO_4, and nitric acid, HNO_3. H_2SO_4 is used during the hydrolysis process, leaching process and simultaneous hydrolysis-leaching process.

18 M of H_2SO_4 was supplied by MERCK and dilution is necessary to obtain the required concentration which is 3 M, 3.5 M, and 4 M, for the experimental work. As for HNO_3, the concentration provided is 12 M and the required concentration is 1% and 10%. It is used to wash and rinse the lab apparatus before any experimental work commences. Apart from that, HNO_3 also acts as a medium to preserve the leached liquor and to avoid any precipitation of metal before sending the leached liquor for the titration process.

The titration process involves more chemicals used, namely triethanolamine ($C_6H_{15}NO_3$), hydroxyl ammonium chloride ($HONH_2 \cdot HCl$), concentrated ammonia (NH_3), thymolphthalexone indicator ($C_{28}H_{30}O_4$) and EDTA ($C_{10}H_{16}N_2O_8$). The role of $C_6H_{15}NO_3$ is a masking agent to avoid interference from Fe cations, $HONH_2 \cdot HCl$ prevents the oxidation of Mn (II) ions, NH_3 acts as a buffer solution to attain a pH of 10-12, thymolphthalexone is the indicator used during the titration process and EDTA is the titrant which also acts as a chelating agent. The details of all chemicals used are shown in Table 3-1.

Table 3-1 Chemicals used in this research work

Chemicals	Molecular Formula	Actual Concentration	Supplier	Purity
Sulfuric acid	H_2SO_4	2 M, 3 M, 4 M	Merck 64271	95-97%
Nitric acid	HNO_3	1%, 10%	Merck 64271	65%
Triethanolamine	$C_6H_{15}NO_3$	20%	Merck 108377	99%
Hydroxyl Ammonium Chloride	$HONH_2 \bullet HCl$	10%	Merck 104676	99%
Ammonia	NH_3	25%	Merck 105432	25%
Thymolphthalexone	$C_{28}H_{30}O_4$	N/A	Fluka 33933	N/A
EDTA	$C_{10}H_{16}N_2O_8$	0.045 M	Merck 108418	99%