RAW MATERIAL CHARACTERIZATION AND REDUCTIVE LEACHING OF LOW GRADE MANGANESE ORE WITH BAMBOO SAWDUST IN SULPHURIC ACID

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by

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
BSD	Bamboo Sawdust
BSE	Back Scattered Electron
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatography
LGMO	Low Grade Manganese Ore
LOI	Loss on Ignition
PSA	Particle Size Analysis
SMO	Synthetic Manganese Ore
VMD	Volume Moment Diameter
V_d	Volume Diameter
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

LIST OF SYMBOLS

^{O}C	Degree Celsius
Al	Alumina
C	Carbon
D_{90}	Volume diameter (90 % sample)
D_{50}	Volume diameter (50 % sample)
D_{10}	Volume diameter (10 % sample)
Fe	Iron
Fe_2SO_4	Iron sulphate
G	Goethite
H_2O	Water
H_2SO_4	Sulphuric acid
HNO_3	Nitric acid
K_a	Weight of sample after heated and cooled (ash content)
K_c	Weight of crucible and lid (ash content)
K_s	Weight of sample and crucible (ash content)
L_a	Weight of sample after heated and cooled (loss on ignition)

L_c	Weight of crucible and lid (loss on ignition)
L_s	Weight of sample and crucible (loss on ignition)
M	Molar
min	Minute
Mn	Manganese
O	Oxygen
P	Pyrolusite
Q	Quartz
R	Rutile
Si	Silicon
W_a	Weight of amorphous content
X	Amount found by Rietveld Refinement
Y	Weight of rutile

PENCIRIAN BAHAN MENTAH DAN PELARUTLESAPAN PENURUNAN BIJIH MANGAN BERGRED RENDAH MENGGUNAKAN HABUK BULUH DALAM ASID SULFURIK

ABSTRAK

Kajian ini menggunakan dua jenis bahan mentah iaitu bijih mangan sinetik dan bijih mangan bergred rendah. Pencirian bahan mentah ditentukan melalui kajian morfologi dan penentuan fasa mineral. Keputusan menunujukkan bijih mangan sinetik bergred tinggi dengan 34.32 %Mn dan bijih mangan yang digunakan adalah bergred rendah dengan 15.26 %Mn. Bijih mangan sinetik mengandungi pyrolusite dan bijih mangan bergred rendah mengandungi fasa pyrolusite, goetit dan kuarza. Pelarutlesapan penurunan bijih mangan sintetik dan bijih mangan bergred rendah dijalankan menggunakan habuk buluh sebagai agen penurunan dalam sulfurik asid. Pelarutlesapan bijih mangan sintetik digunakan sebagai kajian kawalan untuk bijih mangan bergred rendah. Pelarutlesapan dijalankan selama 360 minit. Maksimum pengekstratan mangan dan kesan kepekatan sulfurik asid (2.5 M – 4.0 M) dan suhu (70 ^{o}C – 100 ^{o}C) terhadap pengekstratan mangan telah dikaji. Keputusan menunjukkan maksimum pengekstratan mangan sebanyak 96.14 % dan 75.40 % dicapai menggunakan 4.0 M kepekatan sulfurik asid pada 100 ^{o}C untuk bijih mangan sintetik dan bijih mangan bergred rendah. Gula habuk buluh dan penguraian glukosa juga telah dikenalpasti. Habuk buluh mengandungi selulosa (56.11 %) dan hemiselulosa (28.6 %) terurai kepada glukosa sebagai gula utama. Sistem pelarutlesapan mengandungi (15-20) % glukosa. Glukosa yang terhasil digunakan untuk penurunan bijih. Tindak balas perantaraan dimana glukosa juga terurai kepada asid organik. Asid organik utama yang terbentuk adalah asid formik (<0.005 ppm).

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ABSTRACT

This research used two types of raw materials which are synthetic manganese ore and low grade manganese ore. The characterization analysis of raw materials was determined via morphological study and phase identification. The results showed synthetic manganese ore is high grade with 34.32 % Mn and the manganese ore is of low grade with 15.26 % Mn. The phase present in synthetic manganese ore is pyrolusite and the low grade manganese ore contains the pyrolusite, goethite and quartz phases. The reductive leaching of synthetic manganese ore and low grade manganese ore were conducted using bamboo sawdust as a reducing agent in sulphuric acid. Synthetic manganese ore was leached acted as a control experiment for the manganese ore. Leaching was conducted for 360 minute. Maximum manganese extraction and the effects of sulphuric acid concentration (2.5 M – 4.0 M) and temperature (70 ^{o}C – 100 ^{o}C) on manganese extraction were also determined. The results indicated maximum manganese extractions of 96.14 % and 75.48 % were achieved using 4.0 M sulphuric acid concentration at 100 ^{o}C for the synthetic manganese ore and low grade manganese ore. The sugar identification of bamboo sawdust and glucose degradation was also determined. Bamboo sawdust which contain cellulose (56.11 %) and hemicellulose (28.6 %) was degraded into glucose as the major sugar. The glucose present in the leaching system was (15-20) %. The glucose produced was used to reduce the Mn ores and degraded into organic acid. The major organic acid formed was formic acid (<0.005 ppm).

CHAPTER ONE
INTRODUCTION

1.1 Background of research

Manganese predominantly forms a compound of combination with other elements. This includes iron (e.g: bixbiyite and jacobsite) and oxide (e.g: pyrolusite and manganite). The most common manganese (Mn) occurs as pyrolusite with Mn (IV) ion (Ali et al., 2016; Dan et al., 2016; Ding et al., 2016)

However, pyrolusite with higher valences has limited economical value (Ali et al., 2016). This is due to the natural occurring pyrolusite containing impurities such as iron (Fe) and silicon (Si). High purity of Mn is significant due to the production of goods such as battery required purified Mn. Pyrolusite is reduced to lower valence so that it can be commercialized. As time passes, high grade Mn ore is depleted whereas Mn demand increase (Dan et al., 2016; Feng et al., 2016).

The major Mn consumption is in steel production (Abdullah et al., 2016). High quality of steel is developed by alloying with Mn. Almost all metallic items required proper amount of Mn (Alaoui et al., 2016). The Mn usage in dry cell battery goes well as well as steelmaking. The production of battery consumes 1.31 million tons (Dan et al., 2016). This battery is used in daily life which is in toys, cameras, remote control and watches. Mn also strategically used in fertilizers, dyes, medicines and chemical reagents (Dan et al., 2016; Wang et al., 2017;[a] Zhang et al., 2018).

Mn is known as the 4th most highest consumed metal in the world (Alaoui et al., 2016). The largest producer and consumer is China with 14 million tons consumption in a year (Dan et al., 2016; Wang et al., 2017). Together with the positive progression of Mn, Malaysia has showed its competition towards Mn production. Mn resources in Malaysia are located at several states which are Johor, Kelantan, Pahang and Terengganu. Some Mn mines in Malaysia include Pertama Ferroalloys Sdn. Bhd., OUS Mining in Pahang, OM Holding LTD which is currently built smelter in Sarawak and Sakura Ferroalloys Sdn. Bhd. in Sarawak. The diversity of Mn investors are due to Mn consumption trend in the world is predicted will strike further in the future (Dan et al., 2016).

The boost consumption from society however is worsen by depletion of rhodochrosite (Mn carbonate ore) thus makes pyrolusite roles significant in replacing $MnCO_3$ (Dan et al., 2016; [a]Zhang et al., 2018). Therefore, low grade pyrolusite ore is exploited to occupy this boost demand (Ali et al., 2016; [e]Ismail et al., 2016; Wang et al., 2017). Low Grade Manganese Ore (LGMO) has a complex structure which often forms inclusion with iron, silica and alumina.

The conventional process to extract Mn ore includes pyrometallurgy which is reduction roasting. Despite the excellent extraction, reduction roasting generates high dust emission which develop pollutants, high investment and cost (Dan et al., 2016; Deng et al., 2018; [a]Zhang et al., 2018). Leaching of LGMO is seen as satisfying with high Mn extraction. Yet, pyrolusite is insoluble in water. It is easily dissolved in acid with the aid of reducing agent (Ding et al., 2016; Feng et al., 2016; [a]Zhang et al., 2018). Therefore, previous worked reported the reducing agent used to reduce Mn (IV) such as organic reductants which was simple sugars for example glucose (Biswas et al., 2015; Furlani et al., 2006; Pagnanelli et al., 2004) and sucrose (Wang et al., 2017), potassium oxalate (Alaoui et al., 2016), corncob (Ali et al., 2016), sawdust (Feng et al., 2016) and EDTA ([a]Zhang et al., 2018).

In this work, Mn ore was obtained in Pahang region. The ore was collected at iron mine in Sungai Temau located in Kuala Lipis district. The mine is 35 km from northeast Selinsing and 45 km from northwest Penjom. The mine is located between

Selinsing and Penjom which is labelled as 3 and 4 on the map shown in Figure 1.1. Based on the geological setting, the ore is expected to be calcareous or argillaceous. The extraction of the ore is a complex process due to ore association with impurities. In this work, Mn extraction from Malaysian Low Grade Manganese Ore (LGMO) is determined using bamboo sawdust (BSD) as a reducing agent in sulphuric acid for commercial used.

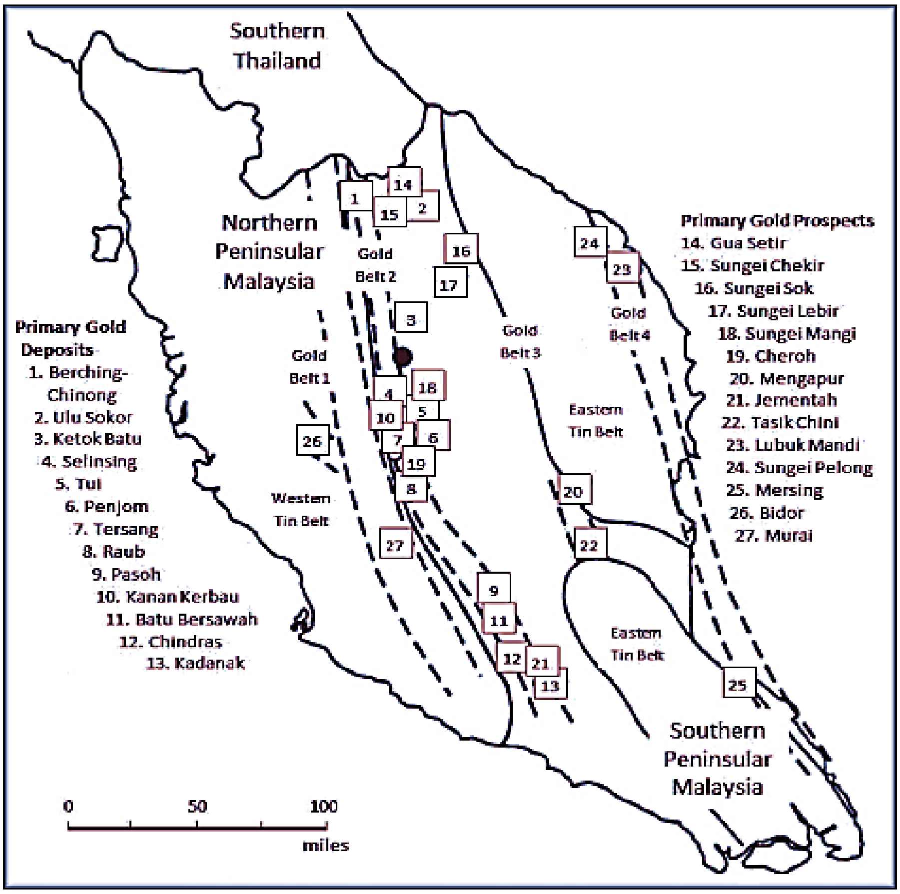

Figure 1.1: Tin and gold belts of Peninsular Malaysia (Ariffin, 2015)

This works utilized complete hydrometallurgy process to extract the LGMO using BSD as a reducing agent in H_2SO_4. This alternative method is seen as a low cost and low pollutant due to less temperature needed compared to pyrometallurgy. The biomass usage is seen to solve global warming issue (Feng et al., 2016). The specialty of this work is that bamboo is easily available particularly in Asia. More than half portion of aggregate bamboo resources is in Asia (Mohan et al., 2015). In Malaysia itself, there is an abundant resource of bamboo in almost all states. Malaysian widely harvests bamboo for construction and clothing. Hence, the usage of green BSD biomass in Malaysia as a reducing agent is an interesting solution to extract LGMO without harming environment.

1.2 Problem statements

The manganese ores used in this work are synthetic manganese ore (SMO) and low grade manganese ore (LGMO). The characterization of raw materials (SMO and LGMO) is needed to study the morphology, identify the elemental content and phases present. The ore inclusion with impurities such as Si and Fe is able to be determined when characterization analysis is conducted. The grade of each ore either high or low grade is determined during characterization analysis. The characterization analysis of each ore is also different due to its location and behavior. Therefore, the characterization analysis for SMO and LGMO is needed in this work.

This research used bamboo sawdust (BSD) as a reducing agent. Almost all characterization of bamboo was made for bamboo composite, cellulose fiber and pulp production (Cao et al., 2014; Zakikhani et al., 2014; [b]Zhang et al., 2014). Only few researchers made a characterization of BSD for leaching purpose (Abdullah et al,, 2012). However, the work does not includes the BSD structure breakage when react with acid. The study of structure breakage is important to determine the morphology of BSD when react with acid. As leaching consists of several steps which include hydrolysis of BSD, the structure breakage during hydrolysis itself hardly found in the leaching system. The structure breakage study of BSD can be carried out using part of BSD analysis such as analysis of hemicellulose, cellulose and holocellulose content. The previous work still does not conduct this structure breakage study of BSD. Thus, incomplete characterization of BSD suggests this work to characterize BSD as a reducing agent in reductive leaching of LGMO in sulphuric acid.

Leaching reaction occurred in sulphuric acid (H_2SO_4). Mn (IV) is highly soluble in acidic reducing environment (Ding et al., 2016; [a]Zhang et al., 2018). The idea of correlation between acid concentration and Mn reduction is important so that the enhancement of Mn extraction is determined. Study on the effect of temperature in Mn extraction is also needed to determine the temperature to obtain maximum Mn extraction. Hence, this work is designed to determine the effect of H_2SO_4 concentration and temperature on Mn extraction in the leaching system using BSD as a reducing agent.

Hydrolysis of BSD is thought to be a complex process as cellulose is crystalline and hemicellulose is an amorphous. The crystalline material is difficult to hydrolyze compared to an amorphous. The hydrolysis process will degrade BSD and convert into reducing sugars. Theoretically, cellulose and hemicellulose have a great tendency to degrade into glucose (Van der Weijden et al., 2002; Furlani et al., 2006). However, as the BSD structure is complex, the conversion reaction to glucose is unknown. No research work have identified the BSD degradation. Hence, this research also aims to identify BSD degradation into reducing sugars.

BSD degradation occurred through a complex network reaction. BSD is degraded into reducing sugars such as glucose. At the same time, the glucose produced is degraded into organic acid such as formic acid. This reaction will affect Mn (IV) reduction. As the glucose produced is degraded into organic acid thus the role as a reducing sugar is interrupted. Hence, the chemical pathway of glucose degradation is important. However, no research work was found to study the degradation of glucose from BSD into organic acid. Furlani et al., (2006) in his work studied the degradation of glucose into organic acid but he directly used glucose to conduct the analysis. Whereas this work used BSD degradation into glucose as a source to study glucose degradation into organic acid.

1.3 Objectives

The objectives of this work are:

i) To conduct characterization study on the synthetic manganese ore (SMO) and low grade manganese ore (LGMO) such as particle size analysis, morphological study and phase identification.

ii) To characterize the reducing agent used which is bamboo sawdust (BSD) such as identification of holocellulose, cellulose, hemicellulose and lignin content in BSD.

iii) To determine maximum Mn extraction of reductive leaching of SMO and LGMO using BSD as a reducing agent in sulphuric acid medium.

iv) To study the effect of parameters such as sulphuric acid concentration and temperature on Mn extraction.

v) To identify BSD degradation into reducing sugars and glucose degradation into organic acid using High Performance Liquid Chromatography (HPLC).

1.4 Scope of Study

This work used two types of raw materials which were synthetic manganese ore (SMO) and low grade manganese ore (LGMO). The SMO was of high grade and