PREPARATION OF LEAD, COPPER AND MERCURY ADSORBENT FROM SAGO WASTE: EFFECT OF ADSORBENT pH

ANGELINE ANAK GOWBEI

This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours (Resource Chemistry)

Faculty of Resource Science and Technology
University Malaysia Sarawak
(2008)

DECLARATION

No portion of work referred to in this dissertation has been submitted in support of an application for another degree of quantification of this or any university or institution of higher learning.

Angeline anak Gowbei
Program of Resource Chemistry
Faculty of Resource Science and Technology
University Malaysia Sarawak

ACKNOWLEDGEMENTS

First of all, I would like to express my greatest gratitude to my supervisor, Mdm. Rafeah Wahi and my co-supervisor, Ms. Azaima Razali for their continuous guidance, encouragement, advice and support. Without their help and guidance, I might not be able to complete this project.

I would also like to take this opportunity to thank my friend, lab mates and the lab assistants for helping and assist me to find the solution if any problem occur during the lab work.

Not forgetting my parents, my brothers and my sisters for their love, understanding, encouragement, and continuous support through the period when the project was carried out.

Last but not least, I would like to thank all the staff of the Department of chemistry and administration staff for their help and support and also those who have helped me towards the success of this project.

TABLE OF CONTENTS

REFERENCES

APPENDIX

LIST OF FIGURES

LIST OF TABLES

Preparation of Lead, Copper and Mercury Adsorbent from Sago Waste

Angeline anak Gowbei

Resource Chemistry Program
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

Sago processing waste, which is both a waste and a pollutant, were used to adsorb lead, mercury and copper ions from solution. The effects of adsorbent's pH and types of sago wastes on the sorption process were examined. The most effective pH range for adsorbent was found to be 4.5 to 6 for mercury for both wastes. pH 4.5 was found to be effective for the removal of lead by coarse waste but the removal of lead by fine waste was very poor. For copper removal, the sorption was found to be poor for both type of activated carbon prepared. Sago coarse waste in this study found to be a better adsorbent compared to sago fine waste because it could adsorb two types of metal, which were Pb and Hg out of the three metals in this study whereas fine waste adsorbent could only adsorb Hg out of the three metal.

Key words : Activated Carbon ; coarse waste ; fine waste ; lead ; copper; mercury

ABSTRAK

Bahan buangan sagu yang di perolehi dari kilang pemprosesan tepung sagu di gunakan sebagai bahan penjerapan bagi ion plumbum, merkuri dan kuprum dalam larutan berair. Proses penjerapan ini di kaji dari segi pH pada permukaan bahan penjerap dan juga dua jenis bahan buangan dari dua peringkat pemprosesan sagu yang berlainan telah di gunakan untuk di bandingkan keberkesanan mereka dalam proses penjerapan terhadap logam-logam berat yang di kaji. pH yang paling berkesan dalam proses penjerapan bagi logam merkuri adalah dalam lingkungan pH4.5 ke pH6 bagi kedua-dua jenis bahan buangan, pH 4.5 bagi logam plumbum untuk bahan buangan bersaiz besar sahaja dan proses penjerapan bagi logam kuprum adalah sangat lemah bagi kedua-dua jenis bahan buangan. Bahan buangan sagu yang bersaiz besar merupakan bahan penjerap yang lebih baik jika di bandingkan dengan bahan buangan bersaiz kecil. Ini adalah kerana, karbon teraktif yang disediakan dari bahan buangan bersaiz besar ini dapat menjerap dua jenis logam-logam berat iaitu plumbum dan merkuri daripada tiga jenis logam-logam berat dengan berkesannya dan bagi karbon teraktif bahan buangan sagu bersaiz kecil, hanya merkuri sahaja yang di jerap dengan sangat berkesan.

Kata kunci : Karbon teraktif; bahan buangan bersaiz besar; bahan buangan bersaiz kecil; plumbum; kuprum; merkuri

CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metals pollution has become a major issue throughout many countries because the contents of heavy metals in potable waters and wastewaters often exceed allowable limits. The effluents from industrial processes represent one of the most important sources of heavy metal pollution. If these discharges are emitted without treatment, they may have an adverse impact on the environment and consequently on human health. Heavy metals are continuously released into the aquatic environment from natural processes such as volcanic activity and weathering of rocks (Serpone *et al*, 1988).

In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial wastewaters prior to discharge into natural waters. This has led to the introduction of more strict legislation to control water pollution, such as the Environmental Quality (Scheduled Wastes) Regulation 1989 in Malaysia (Yeoh and Chong, 1991), which will probably affect metal-related industries.

This effect is likely to be even more pronounced for small and medium-scale industries where profit is small and expertise on wastewater treatment is unlikely to be available.

Conventional methods, for example, ion exchange, chemical precipitation, ultra filtration, or electrochemical depositions do not seem to be economically feasible for such industries because of their relatively high costs. The disadvantages of those processes often include the production of toxic sludge that is difficult for further disposal or the high operational cost arising from the consumption of chemicals or electricity. As an alternative, selective adsorption technology has received increasing attention in recent years due to its simplicity, high-efficiency and low-cost in the removal of heavy metal ions from aqueous solutions (Hu *et al*., 2005; Pan *et al*., 2006; Liu *et al*., 2006).

Adsorption has advantages over other methods. The design is simple, and it is sludge-free and can involve low investment in terms of both the initial cost and land (Viraraghaven and Dronamraju, 1993). Activated carbon (AC) has been recognized as a highly effective adsorbent for the treatment of heavy metals in wastewater (Reed and Arunachalam, 1994).

In this study, a material relevant to the situation in Malaysia, sago processing waste, was chosen. Malaysia exports 25 000 to 30 000 t of sago flour annually and the residues from its production tend to be discharged to rivers. These residues, which are largely composed of celluloses and lignins (Vikineswary *et al*., 1994), are, therefore, both a waste and a pollutant. Their chemical composition suggests that they could have some potential as an adsorbent.

In this study, the AC will be prepared using sago mill waste with NaOH as the chemical activating agent and physico-chemical properties of AC will be investigated. Adsorptive removal of Pb, Cu and Hg from aqueous solution onto AC prepared from sago mill waste will be studied under varying conditions of pH and type of waste to assess the kinetic and equilibrium parameters.

The sago waste will be taken from two different stages of sago processing and the adsorption capacities for AC from these wastes will be compared. The sampling location will be at Sago mill located in Mukah, Sarawak.

1.2 Statement of Problem

Preparation of activated carbon by removing lead, copper and mercury has been done on various types of lignocellulosic material mainly from agricultural by-products and sago waste also included in the previous studies. However, the studies regarding the sago waste in producing activated carbon is mostly from one stage of the sago processing which is from the pulping stage (coarse waste). The study on sago waste from sago extraction process stage (fine waste) mostly used as a substrate in fermentation process. Hence this study would be undertaken to compare the efficiency of the two types of sago waste from different stages of sago processing.

1.3 Objectives

The objectives of this study were:

i) To generate the activated carbon from two types of sago waste in terms of different adsorbent pH.

ii) To compare the chemical properties and adsorption capacity of coarse and fine sago wastes for different pH of adsorbent.

iii) To investigate the adsorption efficiency of activated carbon produced, on Pb, Cu and Hg.

CHAPTER 2
LITERATURE REVIEW

2.1 Heavy Metal

Heavy metals are toxic elements and these metals have been shown to cause environmental problems. (Ariffin, 1998). If the concentrations of heavy metals exceed allowable limits they can pose health hazards. These types of metals are stable elements in which they cannot be metabolized by the body and these metals are also bio-accumulative (Kadirvelu *et al.*,2000) are known to be accumulative within biological systems so there is still a potential for long-term contamination even when the concentration of metals does not exceed these limits. (Quek *et al*, 1998).

The essential toxicity of the metal compounds is characteristic of the metal, modified by the degree to which a specific compound reaches specific tissues. All metals are toxic if present in an organism in excess, but some metals are else essential trace element, taken up actively by the organism (Ariffin, 1998).

Heavy metal ions are commonly found in industrial effluents and some of them may contain heavy metal ions at high concentrations (Dabrowski *et al.*, 2004; Hunsom *et al.*, 2005). For example, in the manufacture of printed circuit boards (PCBs) in the electronic industry, the etching of the laminated copper layer and the stripping of the lead resist generated spent etching solution, stripping solution and rinsing solution and formed a large quantity of wastewater containing both copper and lead ions (Edwards et al., 1995; Scott *et al*., 1997; Lee *et al*., 2003; Naseem *et al*., 2005).

2.1.1 Lead

Lead commonly released from road travel, accounting for at least 90% of the total metals in road runoff. Lead is one of the heavy metals with the greatest potential hazard due to their high toxicity, so they deserve special consideration (Lodeiro *et al*, 2006) Lead is ubiquitous in the environment and is hazardous at high levels. It is a general metabolic poison and enzyme inhibitor (Li *et al.,* 2002), causes toxicity to the neuronal system, and affects the function of brain cells (Ho *et al*., 2001). There is a growing need to prepare activated carbon from cheaper and locally available waste materials. Several researchers have used different activated carbons prepared from agriculture wastes such as oil palm shells (Kassim *et al.*, 2004), coir pith carbon (Kadirvelu and Namasivayam, 2000a), peanut husks (Ricordel *et al*., 2001), olive pulp (Galiatsatou *et al*., 2002) and charcoal (Mishra and Chaudhary, 1994) for the removal of lead. P-DETA was also found to adsorb lead ions significantly. P-DETA is the adsorbent which was prepared by amination of the micro beads synthesized from glycidyl methacrylate and trimethylolpropane trimethacrylate co- polymerization (Changkun *et al*., 2007).

2.1.2 Copper

About half of the copper contribution to the environment from urbanization is from automobiles. Motor oil also tends to accumulate metals as it comes into contact with surrounding parts as the engine runs, so oil leaks become another pathway by which metals enter the environment.

EPA has found copper to potentially cause the following health effects when people are exposed to it at levels above the Action Level. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Use of water that exceeds the Action Level over many years could cause liver or kidney damage (Igwe and Abia, 2005). Commonly adopted methods to remove copper from industrial wastewaters include P-DETA which was found to adsorb copper ions significantly (Changkun *et al*., 2007).

2.1.3 Mercury

Mercury is considered one of the most harmful metals found in the environment (Knock and Hemphil, 1976). Hence, it is necessary to remove Hg (II) from wastewaters before they are discharged into the environment. The three most common forms of mercury (elemental, inorganic and methyl mercury) can all produce adverse health effects at sufficiently high doses. Mercury can damage human health because it is toxic to the nervous system, the brain and spinal cord particularly the developing nervous system of a fetus or young child.

Commonly adopted methods to remove mercury from industrial wastewaters include sulfide precipitation, ion exchange, alum and iron coagulation, activated carbon adsorption, electro deposition, and various biological processes (Kadirvelu *et al.*, 2003).

2.2 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid, forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptive are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. Among the developed technologies (e.g., ion exchange, filtration, coagulation and adsorption), however, adsorption has been shown to be the most effective one (Li *et al*., 2007)

2.3 Adsorbents

The adsorbents usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameter between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small micropore diameter, which results in higher exposed surface area and hence high capacity of adsorption. The adsorbents must also have a distinct macropore structure which enables fast transport of the gaseous vapours

The adsorbent can be used to recover agriculturally desirable metals in chelated form from contaminated water. The liquid form of the adsorbent can be used to wash solids to remove contaminants (US Patent, 1999). In the selective adsorption technology, adsorbents with proper functional groups play the vital role in the adsorption performance. Materials carrying iminodiacetic, thiol or amine functional groups have been shown for their prospective applications and performances (Höll *et al*., 1991;

Vilensky *et al.*, 2002; Yan and Bai, 2002; Deng *et al.*, 2003). In particularly, adsorbents with nitrogen-containing functional groups have been widely explored because these functional groups have been found to be one of the most effective functionalities in the adsorption or removal of heavy metal ions (Yoshitake *et al.*, 2002; Jeon and Höll, 2003; Atia *et al.*, 2003; Takafuji *et al.*, 2004; Nastasović *et al.*, 2004; Deng and Bai, 2004; Li and Bai, 2005). Research attention has also been paid to the adsorption selectivity of heavy metal ions on these functional adsorbents (Warshawsky *et al.*, 2000; Kiefer and Höll, 2001; Stöhr *et al.*, 2001; Li *et al.*, 2002; Pavan *et al.*, 2003; Lam *et al.*, 2006a; Hudson *et al.*, 2006).

2.4 Activated carbon

Activated carbons can be produced from a large variety of raw materials, basically by two methods: Physical or chemical activation or a combination of both of them. The physical activation method involves carbonization of the raw material and the subsequent activation at high temperature in a carbon dioxide or steam atmosphere. The chemical activation method involves the carbonization of the raw material previously impregnated with a chemical agent.

Activated Carbons are highly porous, amorphous solids consisting of microcrystallites with a graphite lattice. They are low cost adsorbent and non polar and one of their main characteristic is that they are combustible. In order to better understand the adsorption process mechanism, it is very important to know the distribution and concentration of functional groups present on the carbon surface. Lactonic groups are present in high concentration in activated carbon, followed by carbonyl, carboxyl basic and phenolic groups (Kadirvelu *et al.*,2003).

The use of activated carbon for the removal of undesirable odours was first recorded more than 200 years ago (Ahmedna *et al*., 1997). This includes the activated carbons used in raw sugar decolourisation. Activated carbons made from agricultural by-products (lignocellulosic material) are potential substitutes for commercial activated carbons currently used in raw sugar decolourisation. Almost any lignocellulosic material can be converted to an activated carbon (Ahmedna *et al*., 1997).

2.5 Sago waste

The largest sago-growing areas in Malaysia are to be found in the state of Sarawak, which is now the world's biggest exporter of sago. In Sarawak, sago palms are inexpensive and grow well in swampy areas that are in urgent need of economic development. (Pushpamalar *et al*, 2006). Sago waste is produced as a by-product from the production of sago starch (Doelle, 1998). Sago waste produced from the sago palm is one of the cheapest, biodegradable and most readily available of all renewable natural polymers existing in Malaysia. Cellulose is an abundant naturally occurring macromolecular material in sago waste (Pushpamalar *et al*., 2006 and is a light fluffy material generated in the preparation process of sago made up of cellulose, hemi-cellulose and lignin (Namasivayam and Periasamy, 1993; Kadirvelu, 1998). The utilization of this material for activated carbon synthesis may give a solution to solid waste management in the sago industry and in other industries, which require the removal of pollutants (Kadirvelu *et al.*, 2004). Sago carbon which can be prepared from sago processing waste, which is both a waste and a pollutant, was used to adsorb lead and copper ions from solution. (Namasivayam and Periasamy, 1993) and also reported to be effective adsorbent for the removal of Hg (II) from aqueous solutions (Kadirvelu *et al.*, 2004). Figure below shows the sago processing steps.

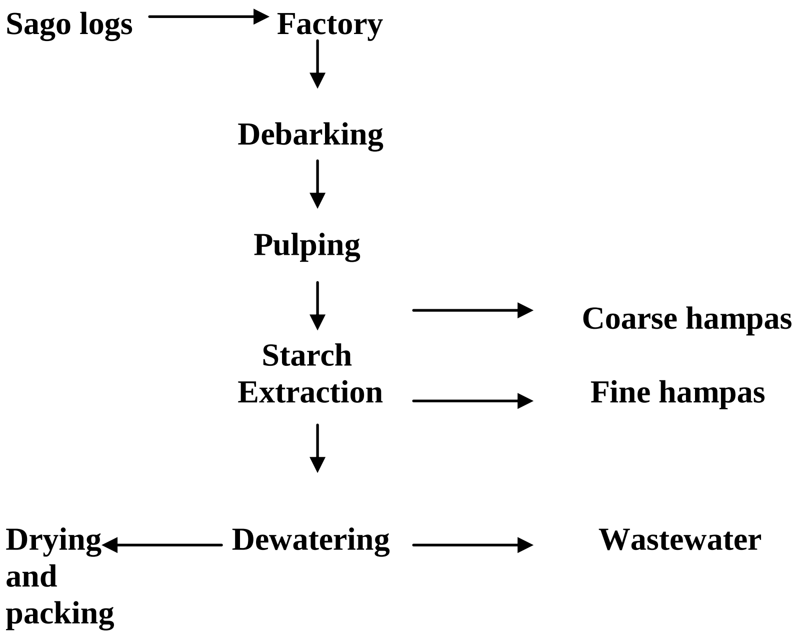

Figure 2.1: Schematic flow diagram for sago processing

(adapted from Yean and Lan, 1993)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The sampling location was at Mukah, Sarawak. Sago wastes was obtain from two different stages of sago processing which the first waste sample was the coarse waste and the second waste sample was the fine waste which both were from the sago extraction processing stage. The chemicals used in this study were 5M NaOH and 5M HCl.

3.2 Preparation of Adsorbent

The sago waste was carbonized at 400^{o}C for 30 minutes in tube furnace (Malik *et al.*,2007). During this process, nitrogen gas with the flow rate at 150Nml/min was flowed into the system to provide an inert atmosphere (Aik and Jia, 1998). The carbonized sago waste then impregmented with 5M NaOH for 2 hours with constant stirring at 60 ^{o}C and NaOH/ char ratio was 3:1. After the impregnation process, the samples have been dried at 105°C for 24 hours. The NaOH serves as the chemical activating agent. Sago waste were then undergo carbonization once again under the temperature of 700^{o}C for 1 hour and at this stage, again the nitrogen gas was flowed into the system in the flow rate of 150 Nml/min to provide an inert atmosphere.

After the heat treatment, a washing process has been carried out using first a 5 M HCl solution, followed by distilled water. In the first washing, the mineral matter was removed, and chlorine ions were eliminated with the distilled water (M. A. Lillo-Ródenas *et al.* 2001).

3.3 Adsorbent characterization

The specific surface area of the adsorbent was determined by the method described by Shoemaker and Garland (1967). 500mg of adsorbent was placed in BOD bottles containing 50ml of 0.05, 0.10 and 0.15 M acetic acid; a control was also prepared without adsorbent. They were tightly closed and agitated for 1 h at 150 rpm. The samples were filtered and the filtrated was titrated with standard NaOH solution to find out the remaining concentration of acetic acid (C). The concentration of acetic acid remaining in each case (C) was divided by the number of moles of acetic acid (N) adsorbed per gram of the adsorbent to get the ratio C/N. The slope of the linear plot of C/N vs. C yielded Nm value(i.e., Nm= 1/ slope). By substituting the Nm value in the following equation, surface area, A (m2/g), was calculated:

$A = Nm \times No \times \sigma \times 10^{-20}$

Where

No- Avogadro number

Nm- Number of moles per gram required to form monolayer

σ- molecular cross section area given in square Angstron ($21^{o}A$) for acetic acid.

Surface Morphology of activated carbon were determined by using Scanning Electron Microscopy (SEM).

The functional groups of activated carbon were examined by using Fourier-Transform Infrared Spectroscopy (FT-IR KBr plate).

3.4 Elemental Analysis

Elemental analysis of C, H, N in the activated carbon were carried out on a C,H,N elemental analyzer (Kadirvelu *et al*, 2003).

3.5 Proximate Analysis

Moisture content of the adsorbent was gained by the different in weight before and after drying in oven at 105^{o}C overnight (Hernandez *et al*., 2006)

The ash content of the extracted activated carbon was obtained after ignition in furnace at 800^{o}C.

Quantity of volatile matters was gained by decomposition at 850^{o}C for 7 minutes (Aik and Jia, 1998).

3.6 Batch adsorption studies

A stock solution of 1000 mg /l of Hg (II) was prepared by dissolving 1.3540 g of $HgCl_2$ in doubly distilled water acidified with 5 ml of concentrated HNO_3 to prevent hydrolysis and diluting to 1000 ml (Kadirvelu *et al.*, 2003). Stock solutions (1000 mg/l) of lead and copper was prepared from lead nitrate and hydrated copper sulphate. These were then diluted with distilled water to obtain the solutions used in the adsorption experiments (Quek *et al.*, 1998).

All the experiments were carried out on a shaker set at 150±5 r·min-1 and the temperature maintained at 25±5°C using capped conical flasks (250 ml). In all sets of experiments, fixed amounts of adsorbent were thoroughly mixed with the metal ion solution (100 ml) having the desired initial concentration. After shaking the flasks for

24 h, the reaction mixtures were filtered through filter paper (No. 1) and the concentration of metal ion in the filtrate was analyzed (Quek *et al.*, 1998). The metal ions concentrations in the filtrate were determined using Flame Atomic Absorption Spectrometer [FAAS].

All the experiments were replicated. Two different controls were performed. The control without adsorbent was to determine if the wall of the conical flask will adsorb metal ions. The control without metal ions (distilled water were used instead of metal solution) were to estimate any leaching from adsorbents during the study period. The metal ion concentration was measured by atomic absorption spectrophotometry using an air-acetylene flame and single element hollow cathode lamps. Lead absorbances were measured at 217.0 nm and those for copper at 324.7 nm and Mercury at 253.65nm. (Kadirvelu *et al*., 2003)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Properties of raw sago waste

4.1.1 Fourier-Transform Infrared Spectroscopy

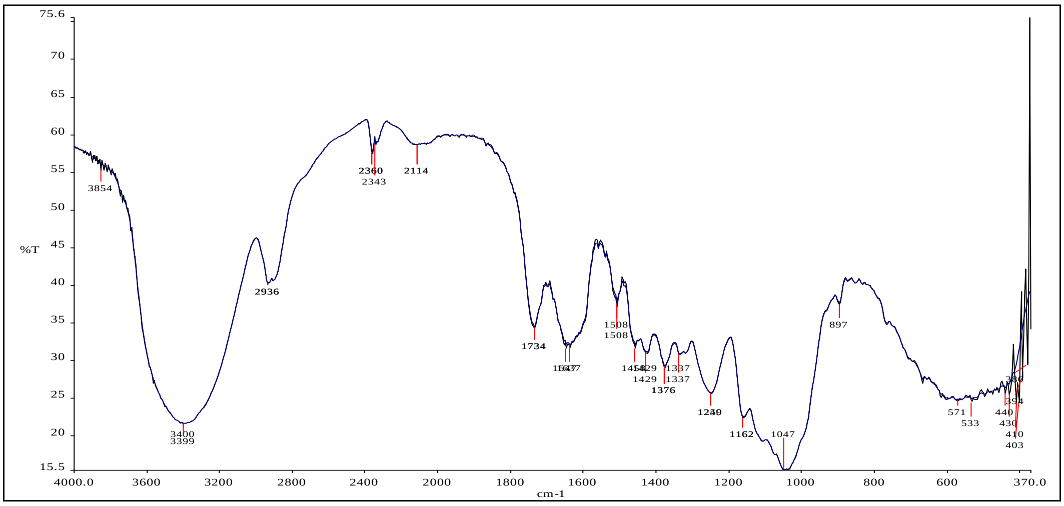

Figure 4.1 : Coarse waste FT-IR spectrum

The functional groups detected in the coarse waste were summarized in the table below:

Table 4.1: Coarse waste functional group

Group	Frequency (cm-1)
O-H (Intermolecular H bonds)	3400
O-H (chelate compound)	2936
C=O stretching vibration in ketones	2360
C=C-H (terminal)	2114
C=O stretching vibration	1734
C=O stretching vibration(conjugated)	1607
C=O bending vibration in amide	1508
CH_2 (bending vibration)	1450
CH_3 (bending vibration)	1429

CH_3 (bending vibration)	1376
O-H bending vibration out of plane	1337
C-O stretching vibration in carboxylic acid	1298
C-N stretching vibration in amines	1162
S=O stretching vibration	1047
$C=CH_2$	897

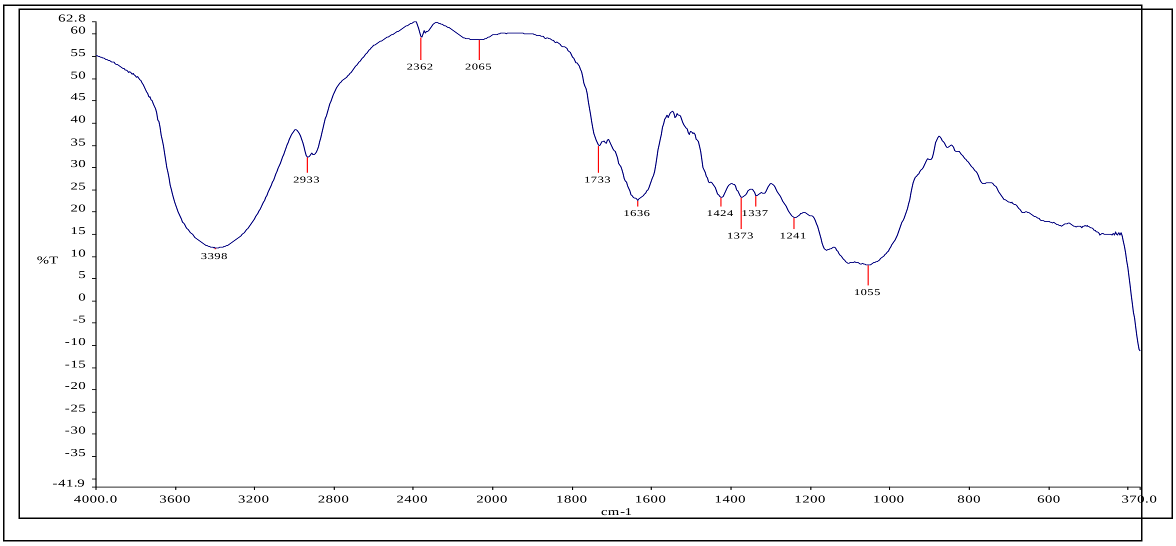

Figure 4.2: Fine waste FT-IR spectrum

The functional groups detected in the fine waste were summarized in the table below:

Table 4.2: Functional groups of fine waste

Group	Frequency (cm^{-}1)
O-H stretching(intermolecular H)	3398
CH_2 stretching Vibration	2933
C=O stretching vibration in ketones	2362
C-C=-C-C=-CH	2065
C=O Stretching Vibrations	1733
C=C conjugated	1636
CH_2 bending vibration	1424
CH_3 bending vibration	1373