Removal of Mercury as Heavy Metal from Aqueous Solution Using 'Rambai' Leaves (*Baccaurea Motleyana*) as a Novel Adsorbent

by

Amir Farid B. Azman (6873)

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Removal of Mercury as Heavy Metal from Aqueous Solution Using 'Rambai' Leaves (*Baccaurea Motleyana*) as a Novel Adsorbent

by

Amir Farid B. Azman (6873)

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Associate Professor Dr. Saikat Maitra)

Assoc. Prof Dr Saikat Maitra
Associate Professor
Cemical Engineering Department
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Amir Farid B. Azman

ACKNOWLEDGEMENTS

First and foremost, deepest regards are dedicated to the author's supervisors, Prof. Dr. Binay Kanti Dutta and Assoc. Prof. Dr. Saikat Maitra. The author has received endless guidance and support from them throughout the project period, especially in understanding the adsorption concepts and the research aspects of the project.

The author would also like to thank Universiti Teknologi PETRONAS and PRSB for the opportunity to use their analysis equipments. Not forgetting the laboratory technicians who have assisted the author in operating laboratory equipments and led him to work in the safest, fastest most efficient working environment, the author would like to specially thank Mr. Yusof, Mr. Firdaus, Mr. Omar and their other colleagues. Without these individuals, the project would not be as successful, effective and as convenient as it is. The author would also like to thank the coordinator Mr. Tazli and other lecturers specifically from Chemical Engineering Department of UTP, for all the assistance, knowledge and suggestions.

Lastly, with love the author would like to thank family members and friends for their moral support, encouragement and inspirations throughout the period of the project and throughout the author's life. Thank you.

With Utmost Gratitude,

……………………

Amir Farid B. Azman
Undergraduate of Chemical Engineering Faculty
Universiti Teknologi PETRONAS

TABLE OF CONTENTS

CERTIFICATION i

ACKNOWLEDGEMENTS ii

ABSTRACT iii

TABLE OF CONTENT vi

LIST OF FIGURES ix

LIST OF TABLES x

LIST OF ABBREVIATIONS xi

CHAPTER 1: INTRODUCTION 1

- 1.1 Background Study 1
- 1.2 Problem Statement 1
  - 1.2.1 Problem Identification 1
  - 1.2.2 Significance of Project 2
- 1.3 Objectives and Scope of Study 2
  - 1.3.1 The Relevancy of Project 2
  - 1.3.2 Scope of Study 3
- 1.4 Feasibility of the Project 4

CHAPTER 2: LITERATURE REVIEW 4

- 2.1 Mercury 5
  - 2.1.1 Description of Mercury 5
  - 2.1.2 Sources of Mercury Exposure 6
    - 2.1.2.1 Drinking Contaminated Water 6
    - 2.1.2.2 Toxicity of Eating Contaminated Fish 7
    - 2.1.2.3 Mercury Toxicity from Dental Fillings 8
    - 2.1.2.4 Mercury Toxicity from Vaccinations containing Thimerosal 8
  - 2.1.3 Effect of Mercury 9
    - 2.1.3.1 Health Effects 9
    - 2.1.3.2 Environmental Effects 10
- 2.2 Adsorption 11

2.2.1 Factors that Influences Adsorption Testing.................. 12
2.2.1.1 Characteristics of Adsorbate........................ 12
2.2.1.3 Characteristics of Adsorbent........................ 13
2.2.1.3 Characteristics of Solutions......................... 13
2.3 Effect of Initial Concentration....................................14
2.4 Effect of pH..15
2.5 Effect of Adsorbent Dosage....................................... 15

CHAPTER 3: METHODOLOGY.. 17
3.1 Methodology...17
3.2 Experimental Procedure.. 18
3.2.1 Safety Hazard Analysis....................................... 18
3.2.2 Preparation of Adsorbent.................................... 19
3.2.3 Adsorbent Characterization..................................20
3.2.4 Sorption Procedure.. 20
3.2.5 Analysis.. 24

CHAPTER 4: RESULTS AND DISCUSSIONS............................... 26
4.1 Adsorption Characterization................................... 26
4.1.1 Textural Characterization.................................... 26
4.1.2 FTIR Analysis..28
4.1.3 Decomposition Kinetic Using TGA..........................30
4.2 Adsorption Equilibrium Study.................................. 33
4.3 Effect of Initial Concentration....................................34
4.4 Effect of Initial Contact Time......................................36
4.5 Effect of pH..36
4.6 Effect of Adsorbent Dosage....................................... 38
4.7 Reproducilibity.. 38
4.8 Adsorption Isotherm...39
4.8.1 Langmuir Isotherm... 39
4.8.2 Freundlich Isotherm... 42
4.9 Adsorption Kinetics..43
4.9.1 Bangham's Kinetic..44

4.9.2 Pseudo-first-order Model.. 45
4.9.3 Pseudo-second-order Model...................................... 47
4.9.4 Intra-particle Diffusion Study.................................. 49
4.10 Comparison with other Adsorbents................................. 51
CHAPTER 5: CONCLUSION AND RECOMMENDATION...................... 52
5.1 Conclusions.. 52
5.2 Recommendations.. 53
REFERENCES.. 54
APPENDIX I: PROJECT GANTT CHART...................................... 56
APPENDIX II: SAFETY HAZARD ANALYSIS.................................. 57
APPENDIX III: OTHER EXPERIMENTAL RESULTS............................. 59
APPENDIX IV: EQUIPMENTS DETAILS...................................... 63

LIST OF FIGURES

Figure 2.1: pH Scale.......... 15

Figure 3.1: Flowchart of the Experimental Procedure.......... 17

Figure 3.2a: Raw/Fresh 'Rambai' Leaves.......... 19

Figure 3.2b: 'Rambai' Leaves are dried in the Oven.......... 19

Figure 3.2c: 'Rambai' Leaves after Drying.......... 19

Figure 3.2d: 'Rambai' Leaves after Cut into Small Pieces.......... 19

Figure 3.3a: FTIR.......... 20

Figure 3.3b: TGA.......... 20

Figure 3.3c: SEM.......... 20

Figure 3.4a: Samples are agitated at 160 rpm.......... 25

Figure 3.4b: Samples are Filtered and Ready to be Analyzed.......... 25

Figure 3.4c: AAS.......... 25

Figure 3.4d: CVAFS.......... 25

Figure 4.1: SEM Images.......... 26

Figure 4.2: SEM with EDX Analysis.......... 27

Figure 4.3: Absorption Peaks resulted from the FTIR Analysis on the Adsorbent 28

Figure 4.4: 'Rambai' Leaves Decomposition at a Heating Rate of 10°C/min...... 30

Figure 4.5: TGA Kinetics.......... 31

Figure 4.6: log ø vs. 1/T 32

Figure 4.7: Extraction of Hg (II) and Cd (II) vs. Time (hrs).......... 33

Figure 4.8: Hg (II) Extracted (%) vs. Initial Concentration (ppb).......... 34

Figure 4.9: Cd (II) Extracted (%) vs. Initial Concentration (ppm).......... 35

Figure 4.10: Hg (II) Extracted (%) vs. Initial Contact Time (min).......... 36

Figure 4.11: Hg (II) Extracted (%) vs. pH Value.......... 37

Figure 4.12: Hg (II) Extracted (%) vs. Adsorbent Dosage (g).......... 38

Figure 4.13: Reproducibility Determination Considering 2 Trials.......... 39

Figure 4.14: Langmuir Isotherm Plot.......... 41

Figure 4.15: Freundlich Isotherm Plot.......... 42

Figure 4.16: Bangham's Model Plot.......... 45

Figure 4.17: Pseudo-first-Order Model Plot.. 46
Figure 4.18: Pseudo-second-order Model Plot.. 48
Figure 4.19: Intra-particle Diffusion Model Plot....................................... 50

LIST OF TABLES

Table 2.1: Principal of Adsorption..11
Table 2.2: Parameters which Effect Adsorption.. 12
Table 3.1: Hazard Analysis of Experimented Substances............................... 18
Table 3.2: Summary of Isotherm Experiments for Hg (II).............................. 21
Table 3.3: Summary of Kinetic Experiments Considering 4 Parameters for Hg (II) for Determination of Equilibration Time.................................... 22
Table 3.4: Summary of Experiments for Cd (II).. 23
Table 4.1: Adsorbent Compositions.. 27
Table 4.2: Figure 4.3 Interpretation.. 29
Table 4.3: Corresponding Temperature for Each Different Heating Rates at Different Constant.. 32
Table 4.4: Langmuir Isotherm Parameters... 41
Table 4.5: Freundlich Isotherm Parameters.. 43
Table 4.6: Bangham's Model Parameters.. 45
Table 4.7: Pseudo-first-order Model Parameters.. 46
Table 4.8: Pseudo-second-order Model Parameters..................................... 48
Table 4.9: Intra-particle Diffusion Model Parameters.................................. 50
Table 4.10: Comparison of 'Rambai' Leaves with Some Reported Sorbents for Mercury... 51

LIST OF ABBREVIATIONS

Hg - Mercury

Cd - Cadmium

FTIR - Fourier Transform Infrared Spectroscopy

SEM - Scanning Electron Spectroscopy

SEM EDX - Scanning Electron Spectroscopy Energy Dispersive X-rays

TGA - Thermal Gravimetric Analyzer

CVAFS - Cold Vapor Atomic Fluorescent Spectroscopy

AAS - Atomic Adsorption Spectrophotometer.

NaOH - Sodium Hydroxide

$Cd(NO_3)2$ - Cadmium Nitrate

$HgCl_2$ - Mercury (II) Chloride

HNO_3 - Nitric Acid

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Water used in industries creates a wastewater that has a potential hazard for our environment because of various contaminants such as heavy metals being introduced into soil and water resources. In this study or research project, removal of heavy metals from aqueous solutions using novel adsorbents will be investigated. The metal of interests is mercury. Current methods of heavy metals removal include precipitation, ion exchange, membrane and reverse osmosis and adsorption. Whereby adsorption being the best method to date, utilizes activated carbon as the adsorbent of which are commonly used in the industries even though known to be quite expensive. Thus, this project aims to find a cost effective solution to removing mercury via adsorption using 'rambai' leaves as the adsorbent. Apart from being an unused agricultural product, making it economically justified or cheap, it is also abundantly available in Malaysia. Moreover, stories are told by villagers or people in Lubuk Mandi, Kelantan that 'rambai' leaves to be the reason that miners there are less affected to the mercury exposure during their mining activities.

1.2 Problem Statement

1.2.1 Problem Identification

The contamination of environment and specifically water by virtue of toxic heavy metals implicated from human technological activities has for years posted a global challenge. Heavy metals are major pollutants in marine, ground, and air and even treated wastewaters. Industrial wastes constitutes the major source of various kinds of metal pollution in natural waters, The release of large quantities of heavy metals into the natural environment, for example, irrigation of agricultural fields by sewage has resulted in a number of environmental problems and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health. Moreover, the current use of activated carbon as the practical and common adsorbent used in the industries requires researchers to come up with other alternatives that are cheaper, easily available and more effective. Considering these requirements, agricultural products or wastes are the appropriate sector to be looked into.

1.2.2 Significance of Project

In recent times, adsorption is being commonly used to remove impurities from aqueous solution, in this case, mercury from water. It is a process that occurs when gas or liquid solute accumulates on the surface of a solid (adsorbent), forming a molecular or atomic film (the adsorbate).

To evaluate the adsorption capabilities of the 'rambai' leaves for heavy metal of mercury, an observation of the metals concentration after adsorption will be noted. A reduction in concentration implies or proves that 'rambai' leaves can be used to remove or reduce the mercury content in aqueous solution.

Furthermore, utilization of 'rambai' leaves as adsorbent is a novel effort of creating or maximizing the use of agricultural wastes. The research paper would be able to determine the feasibility of using 'rambai' leave as adsorbent for removal of mercury.

1.3 Objective and Scope of Study

1.3.1 The Relevancy of the Project

The project aims to find solutions in optimizing removal of heavy metal of interest which is mercury, in aqueous solution using a novel adsorbent in the form of 'rambai' leaves. The specific objectives of the project are:

i) To determine and measure the adsorption potential of ‘rambai’ leaves.
ii) To remove mercury from aqueous solution
iii) To study the efficiency of mercury removal based on various parameters.
iv) To get the optimum condition for adsorption to occur by plotting the trends.

1.3.2 Scope of Study

In an effort to use a novel adsorbent for the removal of heavy metals, the agricultural sectors are the best and appropriate area in terms of its availability and low costs. An extensive research on literatures or journals of the past researches on the topics is emphasized in order to grasps the full understanding of the project as well as producing a reliable and efficient research.

Basically the removal of mercury from aqueous solution will be studied. Observations of mercury concentrations before and after adsorption by utilizing Cold Vapor Atomic Fluorescent Spectroscopy (CVAFS) as the analysis tool will help to quantify the amount thus proving the effectiveness of the ‘rambai’ leaves.

From there on, analysis of parameters are done to improve the level of efficiency of ‘rambai’ leaves. This research will be compared to the existing adsorption capabilities of activated carbon. Furthermore, other heavy metal such as Cadmium would also be investigated. The research is a bench scale experimental type consists of isotherm experiment and kinetic experiments of which effect of initial concentration, initial contact time, pH and amount of absorbent dosage will be investigated. These parameters will be varied accordingly and trending done to determine the optimum parameters for the most effective removal of mercury.

1.4 Feasibility of the Project

Considering the scope of the project as mention above and the time frame given, the project is very much feasible. Refer to Appendix I for detailed activities carried out in accordance to the scheduled timeline.

CHAPTER 2
LITERATURE REVIEW

2.1 Mercury

2.1.1 Description of Mercury

According to the Agency of Toxic Substances and Disease Registry (ATSDR), "Mercury is a naturally occurring metal which has several forms. The metallic mercury is a shiny, silver-white, odorless liquid. If heated, it is a colorless, odorless gas. Mercury combines with other elements, such as chlorine, sulfur, or oxygen, to form inorganic mercury compounds or 'salts.' Most inorganic mercury compounds are white powders or crystals. Mercury also combines with carbon to make organic mercury compounds. The most common organic mercury compound is methyl mercury. Methyl mercury is produced mainly by small organisms in the water and soil, but more mercury in the environment can increase the levels of methyl mercury that these small organisms make [1].

Toxicity caused by excessive mercury exposure is now becoming recognized as a widespread environmental problem and is continuing to attract a great deal of public attention. The dangers of mercury toxicity, as with other heavy metals, has been known for some time, but it is only in recent years that the extent of the problem, and the sources of the health risk associated with these toxicities, especially mercury toxicity have become apparent. It has become so prevalent that it could be seen as a major public health concern. Heavy metal toxicity or poisoning arises when the body accumulates an excessive amount of a heavy metal, such as mercury, lead, arsenic, cadmium, aluminum or nickel which places the individual at risk for serious illness. These heavy metals play no known biological role in the human body, unlike with some elements such as selenium, which is an effective antioxidant, iron, which is required by blood cells, and copper, which is an integral part of many enzymes. Since they are not useful to the organism, and because the body has storage sites for them, these heavy metals can accumulate in tissues over time and cause serious health problems. Toxicity from mercury, in common with the other heavy metals, arises from environmental contamination and also from some unexpected sources as we shall see below. With mercury, it is the nature of the environmental sources that are particularly worrying in the context of nutrition [2].

2.1.2 Sources of Mercury Exposure

Main Sources of mercury toxicity/poisoning:

- Drinking contaminated water
- Eating fish contaminated with mercury
- Leaching of mercury from badly fitting dental fillings.
- From vaccinations containing thimerosal.

2.1.2.1 Drinking Contaminated Water

It has been estimated that the ordinary American is exposed to tap water containing heavy metals at levels exceeding the safe upper limit. With lead, for example, it is estimated that 40 million Americans drink water containing levels exceeding the safe limit set by the EPA. The lead contamination comes mainly from lead plumbing in older homes and soldered joints in copper pipes. Mercury from environmental contamination (derived mainly from coal-fired power plants and medical and municipal incinerators) eventually enter our water system through soil, rivers, streams and lakes.

The form of mercury hazardous in drinking water is the inorganic form, which can easily be converted to the organic form, methyl mercury, by bacterial action present in soil and water environments. As discussed below this is the form that eventually enters our food chain. The maximum level of mercury in drinking water permitted by the EPA is 2 parts per billion. Although levels of mercury in tap water are generally within this limit, there have been reports of mercury exceeding the EPA safe limit in several areas of the country, most notably from well sources. In New Jersey, for example, a survey found 265 out of 2,239 wells with high mercury levels [2].

2.1.2.2 Toxicity from Eating Contaminated Fish

This is one of the main sources of mercury poisoning and one which is attracting a great deal of recent attention. The FDA is coming under increasing pressure from environmental groups to warn the public of the dangers of eating tuna because it contains enough mercury to damage a developing fetus. At least three states, Washington, New Jersey and Minnesota, have recommended pregnant women to limit tuna consumption to 1 1/2 can per week, and in Canada and advisory were issued warning women of childbearing age and children to limit consumption of shark, swordfish and fresh tuna to one meal per month.

The FDA since 2001 had already advised pregnant women, women who may become pregnant and small children to avoid eating four types of fish: shark, swordfish, king mackerel and tilefish. However, tuna was not on the list of fish to avoid and the FDA recommendations that up to 12 ounces or 2 1/2 cans of tuna per week is safe to eat is being challenged by the environment working group. It is important to note that not all fish are considered risky in the context of mercury contamination. Fish is high in omega-3 polyunsaturated fatty acids, which is known to be beneficial to cardiovascular health. Therefore, rather than avoid all fish, it is more prudent to find good substitutes for the risky fish. There are many types of fish available and farm raised fish is one option. Only trace amounts of mercury, 40-100 times below the safe limit were found in common commercially produced fish [2].

2.1.2.3 Mercury Toxicity from Dental Fillings

Dental amalgams or "silver fillings" contains about 50% mercury along with silver, tin, copper and zinc. Mercury tends to leach from the amalgam with release of mercury vapor so over time there is a real risk of a toxic load to the body posing a real health risk. Toxicity from dental amalgams has been the subject of debate for many years. The simple fact alone that mercury is highly toxic to the human body and that mercury release from amalgam readily occurs (some studies show 10 micrograms per day released per amalgam) should sound an alarm. Yet, despite the dangers that exist from the use of a highly toxic material in dental fillings, the fact remains that an estimated 92 % of US dentists use mercury almagams.

In April, 2003 a Swedish evaluation of the use of mercury in dental practice effectively concluded that amalgam posed unacceptable risk. The expert in charge of the evaluation was quoted as saying that "amalgam as soon as possible should be banned in the whole of the European Union". In the US, a bill was introduced in 2002 to ban mercury use in dental amalgam from the year 2006 [6].

2.1.2.4 Mercury Toxicity from Vaccinations containing Thimerosal

This is one of the most topical issues on mercury toxicity. It is one that is steadily gaining public awareness ever since the link between autism and vaccinations was first proposed. A little known fact before public awareness campaigns started is the fact that the preservative, thimerosal usually added to vaccines contain mercury. In 1999, the Centers for Disease Control and prevention (CDC) called for the removal of mercury from vaccines. Paradoxically, the CDC still continues to recommend the measles, mumps and rubella vaccine. Young children are particularly sensitive to mercury toxicity and statistics have shown that since the introduction of thimerosal in vaccines in 1990 there has been a 10-fold increase in the incidence of autism. Many parents also report the onset of autistic behavior in their children within days of a vaccination.

Strikingly, 40 % of parents of autistic children are said to believe that vaccines cause the disease. The effect of mercury on the central nervous system is well documented. Excessive prenatal exposure leads to delayed developmental functions including delayed walking, delayed speech development and hearing impairment. The level of mercury exposure in vaccines has been put at 125-times the safe recommended limit by the Environmental Agency. A recent study also reports a strong correlation between the relative risk of autism and heart arrests and the dose of mercury contained in childhood vaccines. In contrast to such evidence, The Institute of Medicine has recently found no association between measles, mumps and rubella vaccine and autism [2].

2.1.3 Effects of Mercury

2.1.3.1 Health Effects

Pure elemental mercury is a cumulative heavy-metal poison that is moderately absorbed through the skin, poorly absorbed through the gastrointestinal tract, and readily absorbed as vapor through the lungs. The element is strongly toxic when absorbed as vapor from the respiratory tract, but it is considerably less so when exposure occurs via other routes. Elemental mercury often passes through the GI tract without being absorbed; in the past mercury was used for mechanical relief of intestinal obstructions. Compounds of mercury tend to be much more toxic than the element itself, and organic compounds of mercury are often extremely toxic. Mercury damages the central nervous system, endocrine system, kidneys, and other organs, and adversely affects the mouth, gums, and teeth. Exposure over long periods of time or heavy exposure to mercury vapor can result in brain damage and ultimately death. Mercury and its compounds are particularly toxic to fetuses and infants. Women who have been exposed to mercury in pregnancy have given birth to children with serious birth defects. Some of the toxic effects of mercury are reversible. However, heavy or prolonged exposure can do irreversible damage, particularly in fetuses, infants, and young children. Mercury exposure in very young children can have severe neurological consequences, preventing nerve sheaths from forming properly. Mercury poisoning in the young is suspected as a possible cause of autistic behaviour [3].

2.1.3.2 Environmental Effects

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Mono-methyl mercury causes damage to the brain and the central nervous system, while fetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children. Mercury is a global pollutant with complex and unusual chemical and physical properties. The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural bodies of water.

World-wide mining of the metal leads to indirect discharges into the atmosphere. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps and thermometers). It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry. Concern over mercury in the environment arises from the extremely toxic forms in which mercury can occur. Mercury is mostly present in the atmosphere in a relatively un-reactive form as a gaseous element. The long atmospheric lifetime (of the order of 1 year) of its gaseous form means the emission, transport and deposition of mercury is a global issue. Natural biological processes can cause methylated forms of mercury to form which bio-accumulate over a million-fold and concentrate in living organisms, especially fish. These forms of mercury: mono-methyl mercury and di-methyl mercury are highly toxic, causing neuro-toxicological disorders. The main pathway for mercury to humans is through the food chain and not by inhalation.

The main sources of mercury emissions in the UK are from the manufacture of chlorine in mercury cells, non-ferrous metal production, coal combustion and crematoria. UK emissions of mercury are uncertain and it is estimated that the range is from 13 to 36 tonnes per year (DERA). Emissions are estimated to have declined by around ¾'s between 1970-1998 (NAEI), mainly due to improved controls on mercury cells and their replacement, and the fall in coal use. Whilst there has been a decline in the level of European emissions of mercury, emissions from outside of Europe have started to increase – increasing the level of ambient concentrations in the continent [4].

2.2 Adsorption

Adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate [5]. In this project, the adsorbent is the 'rambai leaves' while cadmium and mercury refers to the adsorbate. The most common categorization of adsorption is when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate) [6].

There are 2 principles types of adsorption and there are chemical and physical. Table 2.1 below shows the descriptions of the 2 types:

Table 2.1: Principal of Adsorption

Types	**Adsorption Descriptions**
Chemical	Involves a reaction between the adsorbate and the adsorbent causing a change in the chemical form of the adsorbate.
Physical	Results from the action of Van Der Waals forces, which are comprised of both London Dispersion forces and Classical Electrostatic forces.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column [6].

A number of parameters specific to a given system will affect adsorption for adsorbate and adsorbent as well as the system properties as described in the table below.

Table 2.2: Parameters which affects Adsorption

Adsorbate	**Adsorbent**	**System**
▪ Concentration ▪ Molecular Weight ▪ Molecular Size ▪ Steric form of configuration ▪ The nature of background of competitive adsorbates ▪ Molecular polarity	▪ Surface area ▪ Physical size and form of adsorbent particles ▪ The physicochemical nature of the surface ▪ Availability of that surface to adsorbate molecules or ions	▪ pH ▪ Presence of other competing adsorbate compounds ▪ Temperature

2.2.1 Factors that Influence Adsorption Testing

As stated in table 4, there are a few factors that influence the adsorption testing and there are the characteristics of adsorbate, characteristics of adsorbent and characteristics of the solution or the system.

2.2.1.1 Characteristics of Adsorbate

1. Molecular size is important for 2 reason:
   a) Solubility: As size increases, solubility increases
   b) Surface area: if the molecular size is too large, it cannot penetrate pores or pathways within the adsorbent

2. Molecular form:

   Molecular forms such as ionic or neutral state, branched isomer or straight chain affects the solubility of the adsorbate and the determination of the energy of adsorption, for example, the force with which the particular molecule is held on the adsorbent [5].

2.2.1.2 Characteristics of Adsorbent

1. Chemical properties:

   The degree of ionization of the surface of the adsorbent, the types of functional groups which are present on the adsorbent and the degree to which these properties may be changed by contact with the solution.

2. Physical properties:

   Granules or particles or very fine powdered adsorbent will influence surface area and size and distribution of pores in the particles thus direly affect adsorption performance [5].

2.2.1.3 Characteristic of Solutions

1. pH:

   Some adsorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and therefore solubility and adsorption capacity.

2. Temperature of solution has 2 major effects:
   a) Rate of adsorption increases with higher temperatures due to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent.
   b) Solubility and adsorption are inversely related; as temperature affects solubility it will therefore affect the extent of adsorption.

3. Presence of competing adsorbate compounds:

The presence of materials with a particularly high affinity for the adsorbent will tend to displace from the adsorbent materials of lesser affinity [5].

The evaluation of adsorption activities in this study is focused on mercury as adsorbate. Since the utilization of 'rambai' leaves which is an agricultural waste and as novel adsorbent, this research attempts to determine the feasibility of using the 'rambai' leaves for mercury extraction.

2.3 Effect of Initial Concentration

Based on a research paper entitled sorption of lead ions from aqueous solution by chickpea leaves, stems and fruit peelings, it is noted that there is an effect on the adsorption when initial concentrations are varied.

It suggested that a gradual increase in Pb(II) ion removal (leaves, 50.21-81.30%; stems, 48.35-80.10%; and fruit peelings, 1.25-53.26%) occurred when the initial adsorbate concentration was increased over the range 50-200ppm, followed by a decrease (81.30-75.6%; stems, 80.10-73.1%; fruit peelings, 53.26-49.83%) when the initial adsorbate concentration was increased over the range 200-250 ppm. At the same adsorbent dose and contact time, a drop occurred in the percentage removal at higher initial Pb(II) ion concentration whereas, at lower concentration, sufficient adsorption were available for the sorption of such metal ions. However, at higher concentrations, the numbers of metal ions present in solution were relatively greater than the availability of adsorption sites [7]. In conclusion, the percentage removal of various metals ion concentration and decreases as the initial concentration increases.

2.4 Effect of pH

pH is the measure of the acidity or alkalinity of a solution. In pure water at 25 °C, the concentration of H^+ equals the concentration of hydroxide ions (OH^-). This is defined as "neutral" and corresponds to a pH level of 7.0. Solutions in which the concentration of H^+ exceeds that of OH^- has a pH value lower than 7.0 and are known as acids. Solutions in which OH^- exceeds H^+ have a pH value greater than 7.0 and are known as bases [7]. Theoretically, since mercury has a positively charged ion, they must thus prefer to adsorb on negatively charged surfaces. To enhance adsorption capacity, the surface of 'rambai' leaves should be negatively charged to attract the positively charged cation mercury from solution. Therefore, in general adsorption is more favorable as pH increases.

The effect of pH (over the range of 4.0-9.0) on the binding of Pb(II) ions onto chickpea leaves, stems and fruit peelings shows that the percentage adsorption increased as the pH values of the aqueous solution increased and attained a maximum value at pH 6.0 [7].

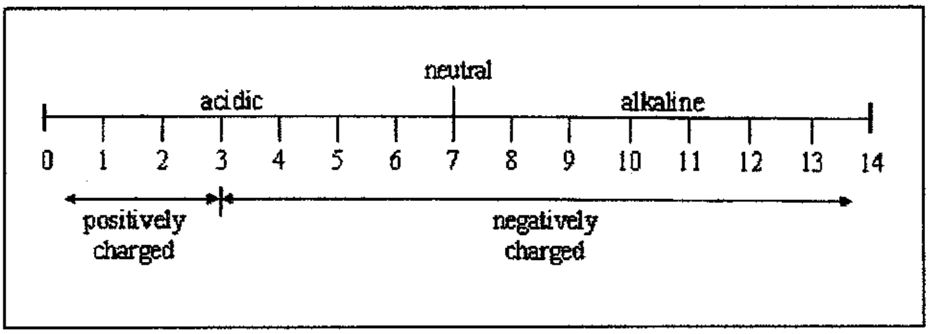


Figure 2.1: pH Scale

2.5 Effect of Adsorbent Dose

Referring to research paper entitled sorption of lead ions from aqueous solution by chickpea leaves, stems and fruit peelings, different amounts of adsorbents (varying over the range 0.05-0.4 g/100 ml solution) with the same initial concentration of adsorbate (200ppm) have been used to optimize the necessary amount of adsorbent under the conditions prescribed (temperature, 30°C; agitation speed, 150 rpm; pH, 6.0) to obtain a maximum adsorption capacity (81.3%, 80.1% and 53.26% for leaves, stems and fruit peelings, respectively) was achieved when 0.3 g/100 ml of each of the various types of adsorbent studies was utilized. The percentage removal first increased and then decreased as the initial adsorbent concentration increased. The decrease in Pb(II) ion uptake capacity with increasing adsorbent dose (>0.3 g / 100 ml) may be due to the formation of clusters of adsorbent particles on the surface giving rise to decrease in surface area and hence a decrease in uptake capacity [7].

CHAPTER 3

METHODOLOGY

3.1 Methodology

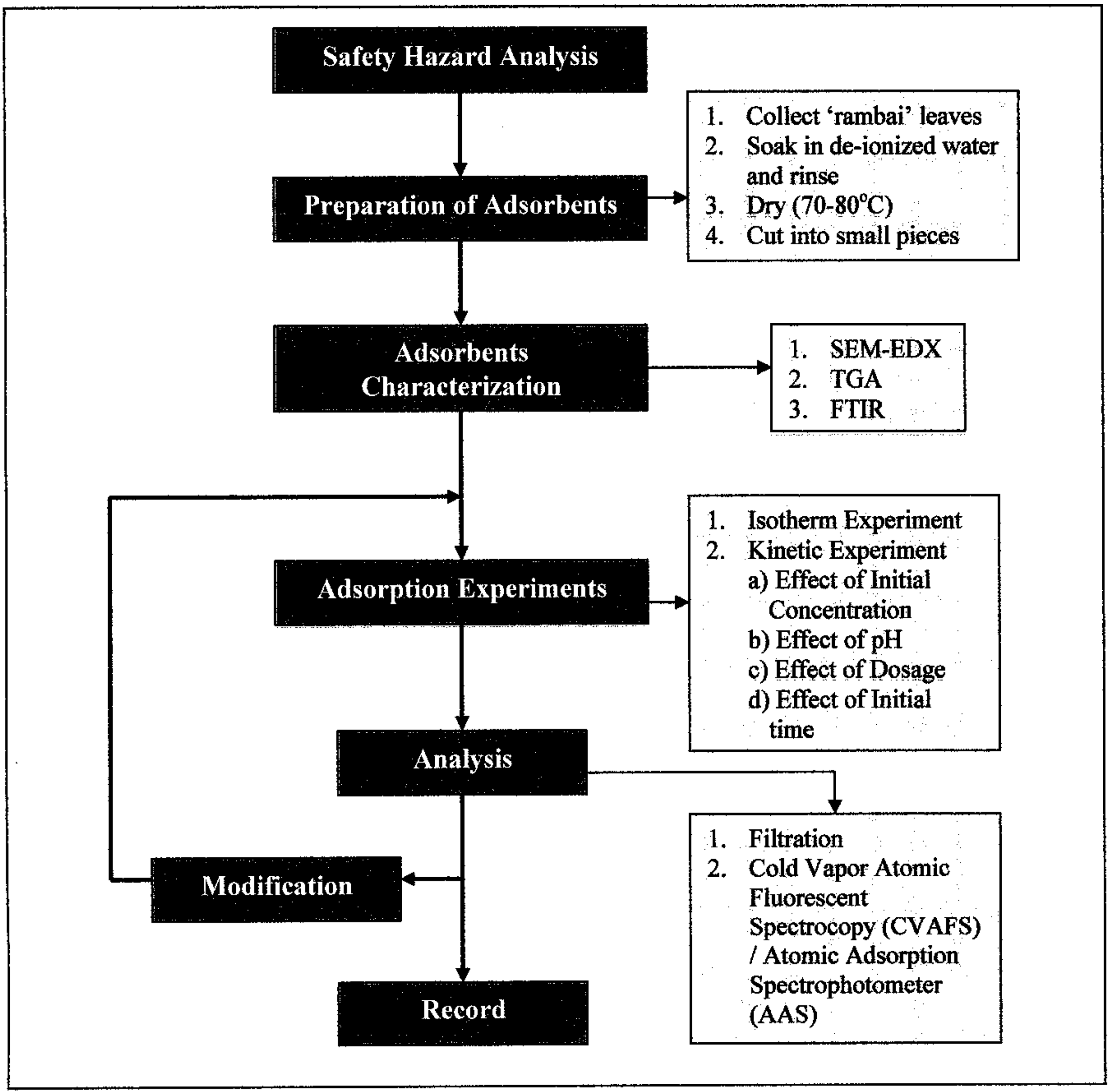


Figure 3.1: Flowchart of the Experimental Procedure

3.2 Experimental Procedure

Figure 3.1 basically represent the experimental procedure in general for the research project. Initially, before conducting the actual experiment, safety hazard analysis of the substances and apparatus used are emphasized, purely for safety purposes. Then preparations of adsorbent are done followed by the isotherm and kinetic experiments which will be discussed in detail later. Then, analyses of samples with the utilization of atomic adsorption spectrophotometer are conducted to determine the concentration of metals after adsorption. After necessary modification based on the consistency of results obtained, data are recorded for further discussions and future reference.

3.2.1 Safety Hazard Analysis

Before every experiment a safety hazard analysis on the apparatus, laboratory environment and the substances used were done[1]. Table 3.1 shows the hazards description for every substance.

Table 3.1: Hazard Analysis of Experimented Substances

No.	**Substance**	**Hazards**					
							
1	$HgCl_2$	X		X		X	X
2	$Cd(NO_3)_2$	X				X	X
3	HNO_3			X			
4	NaOH			X			

---

[1] Appendix II – Safety Hazard Analysis

3.2.2 Preparation of Adsorbents

The raw material ('rambai' leaves) required for the preparation if adsorbents were collected from Kuala Lumpur, Malaysia. It is first soaked and rinsed in de-ionized water at room temperature of 24°C-26°C for 1-2 hours till clean or colourless. It was then dried in oven for a few hours (4-5 hours) at temperature of 80°C. Finally, it is cut to small pieces ready to be used as an adsorbent. Figure 3.2 displays the activities conducted for the preparation of the adsorbent.

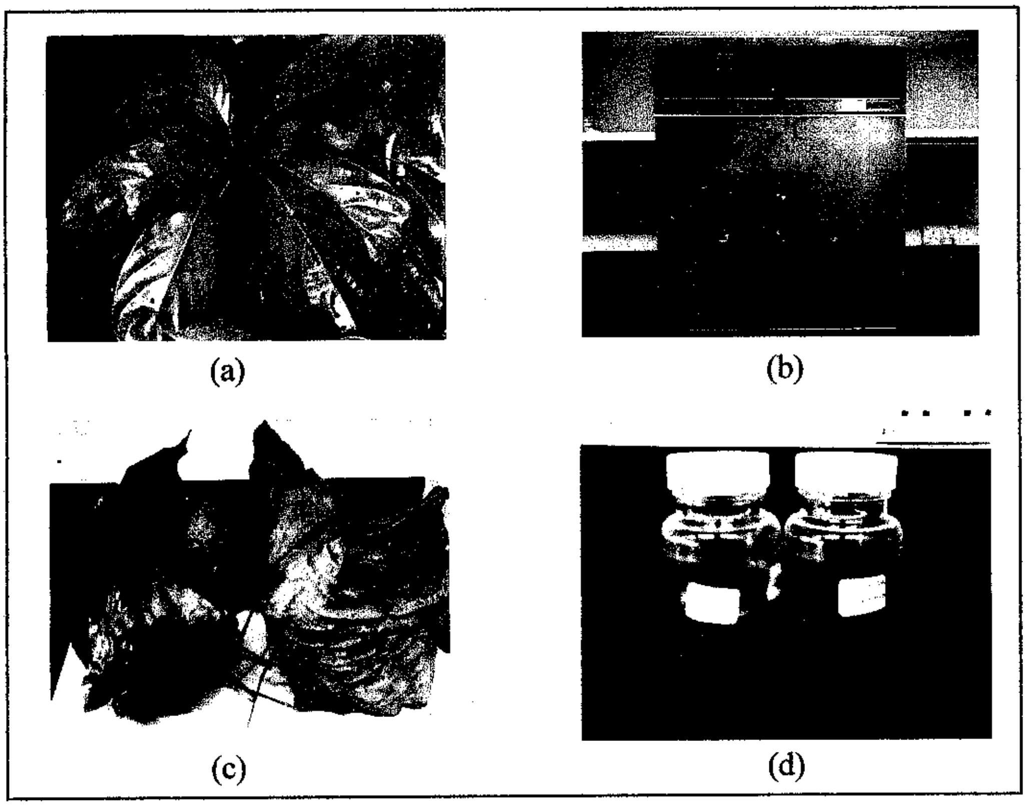


Figure 3.2: a) Raw/Fresh 'Rambai' Leaves, b) 'Rambai' Leaves are dried in the Oven, c) 'Rambai' Leaves after Drying, d) 'Rambai' Leaves after Cut into Small Pieces

3.2.3 Adsorbent Characterization

In order to understand the adsorbent or 'rambai' leaves's properties that influence the adsorption phenomena, its characterization is investigated. For that, a few equipments are utilized in the form of Scanning Electron Microscope (SEM), Fourier Transformation Infrared (FTIR), and also Thermal Gravimetric Analyzer (TGA). Figure 3.3 shows the equipments used.

(a) (b) (c)

Figure 3.3: a) FTIR, b) TGA, c) SEM

3.2.4 Sorption Procedure

To prepare 1000mg/litre Hg (II) or 1000ppm mercury concentration, 0.1354 g of mercuric chloride ($HgCl_2$) is dissolved in a mixture of 75 mL water and 20 mL of NHO_3 (sp.gr 1.42) and dilute to 100 mL with water. The samples are diluted further to the desired concentrations with de-ionized water. Sample bottles containing solutions with different concentrations of Hg (II) ions (5, 20, 40, 60, 90, 120, and 500 ppb) and 0.05, 0.10, 0.15 and 0.2g of adsorbent were used for such studies, with the pH values of ranging from 3 to 8 using diluted aqueous solutions of NaOH and HNO_3. The samples containing the adsorbate and adsorbent are agitated in a shaker at room temperature at fixed speed of 160 rpm for different contact times.

Initially, to determine the time for the sorption to reach equilibrium, the samples with Hg (II) concentrations of 60 and 120 ppb are agitated for 1 to 7 hours, whereby samples are taken during each hours respectively. After period of equilibrium are known, the rest of concentrations are done at that specified time only. These isotherm experiments are conducted with pH value of 4 and adsorbent amount of 0.1 g at room temperature. In order to observe and investigate the reproducibility of the experimental conduct and results, some experiments are repeated. Table 3.2 below summarizes the isotherm experiments of which to determine time of equilibrium and kinetic experiments (refer to Table 3.3) to be conducted with the specified parameters that have been prepared for Hg (II). The kinetic experiments consider the study of the effect of 4 parameters, which are, initial concentration, pH, initial contact time and adsorbent dosage.

Table 3.2: Summary of Isotherm Experiments for Hg (II) for Determination of Equilibration Time

Sample	**Initial Concentration, Co (ppb)**	**Amount of Adsorbate Solution, V (L)**	**Weight of Adsorbent, W (g)**	**pH**	**Contact Time (hours)**
1	60	0.05	0.1002	4	1
2	60	0.05	0.1002	4	2
3	60	0.05	0.1002	4	3
4	60	0.05	0.1002	4	4
5	60	0.05	0.1002	4	5
6	60	0.05	0.1002	4	6
7	60	0.05	0.1002	4	7
8	120	0.05	0.1005	4	1
9	120	0.05	0.1005	4	2
10	120	0.05	0.1005	4	3
11	120	0.05	0.1000	4	4
12	120	0.05	0.1000	4	5
13	120	0.05	0.1000	4	6
14	120	0.05	0.1000	4	7

Table 3.3: Summary of Kinetic Experiments Considering 4 Parameters for Hg (II)

Sample	Initial Concentration, Co (ppb)	Amount of Adsorbate Solution, V (L)	Weight of Adsorbent, W (g)	pH	Contact Time (min/hrs)	Trial
1	5	0.05	0.1003	4	2 min	1
2	5	0.05	0.1003	4	4 min	1
3	5	0.05	0.1003	4	10 min	1
4	5	0.05	0.1003	4	20 min	1
5	5	0.05	0.1003	4	40 min	1
6	5	0.05	0.1004	4	2 min	2
7	5	0.05	0.1004	4	4 min	2
8	5	0.05	0.1004	4	10 min	2
9	5	0.05	0.1004	4	20 min	2
10	5	0.05	0.1004	4	40 min	2
11	20	0.05	0.1002	4	2 min	1
12	20	0.05	0.1002	4	4 min	1
13	20	0.05	0.1002	4	10 min	1
14	20	0.05	0.1002	4	20 min	1
15	20	0.05	0.1002	4	40 min	1
16	20	0.05	0.1000	4	2 min	2
17	20	0.05	0.1000	4	4 min	2
18	20	0.05	0.1000	4	10 min	2
19	20	0.05	0.1000	4	20 min	2
20	20	0.05	0.1000	4	40 min	2
21	60	0.05	0.1010	4	2 min	1
22	60	0.05	0.1010	4	4 min	1
23	60	0.05	0.1010	4	10 min	1
24	60	0.05	0.1010	4	20 min	1
25	60	0.05	0.1010	4	40 min	1
26	60	0.05	0.1002	4	2 min	2
27	60	0.05	0.1002	4	4 min	2
28	60	0.05	0.1002	4	10 min	2
29	60	0.05	0.1002	4	20 min	2
30	60	0.05	0.1002	4	40 min	2
31	40	0.05	0.0500	4	5 hours	1
32	40	0.05	0.1504	4	5 hours	1
33	40	0.05	0.2001	4	5 hours	1
34	40	0.05	0.0504	4	5 hours	2
35	40	0.05	0.1500	4	5 hours	2
36	40	0.05	0.2000	4	5 hours	2
37	40	0.05	0.1011	3	5 hours	1

38	40	0.05	0.1003	4	5 hours	1
39	40	0.05	0.1002	5	5 hours	1
40	40	0.05	0.1007	6	5 hours	1
41	40	0.05	0.1005	7	5 hours	1
42	40	0.05	0.1012	8	5 hours	1
43	5	0.05	0.1004	4	5 hours	1
44	20	0.05	0.1005	4	5 hours	1
45	40	0.05	0.1001	4	5 hours	1
46	90	0.05	0.1002	4	5 hours	1
47	500	0.05	0.1002	4	5 hours	1

Additional experiments are also conducted to determine the adsorbent adsorption capabilities with other heavy metal Cadmium, Cd (II). This batch of experiments are conducted to the extent of determining the equilibrium time and effect of initial concentration. Table 3.4 specify more specifically the parameters used.

Table 3.4: Summary of Experiments for Cd (II)

Sample	**Initial Concentration, Co (ppm)**	**Amount of Adsorbate Solution, V (L)**	**Weight of Adsorbent, W (g)**	**pH**	**Contact Time (hours)**
1	20	0.05	0.1001	4	1
2	20	0.05	0.1008	4	2
3	20	0.05	0.1001	4	3
4	20	0.05	0.1005	4	4
5	20	0.05	0.1001	4	5
6	20	0.05	0.1004	4	6
7	20	0.05	0.1001	4	7
8	5	0.05	0.1010	4	5
9	10	0.05	0.1003	4	5
10	20	0.05	0.1004	4	5
11	30	0.05	0.1004	4	5
12	40	0.05	0.1009	4	5
13	50	0.05	0.1010	4	5

As observed, the initial concentration for Hg (II) and Cd (II) solution are specified in terms of ppb and ppm respectively. This is because the respective concentrations units are used in the industries for these specific heavy metals. For that, no direct comparison can be made between both heavy metals in terms of quantitative amount adsorb.

3.2.5 Analysis

The solid adsorbent are separated from the adsorbate solutions by filtration using filter syringe (filter wattmen nylon 0.45 dm), with the supernatant liquid being analyzed for its residual concentration of Hg (II) and Cd (II) ions via Cold Vapor Atomic Fluorescent Spectroscopy, CVAFS and Atomic Adsorption Spectrophotometer, AAS respectively. For consistency and reproducibility determination, duplicate runs of experiments are conducted. The metal ion concentration retained by the adsorbent phase is calculated using equation:

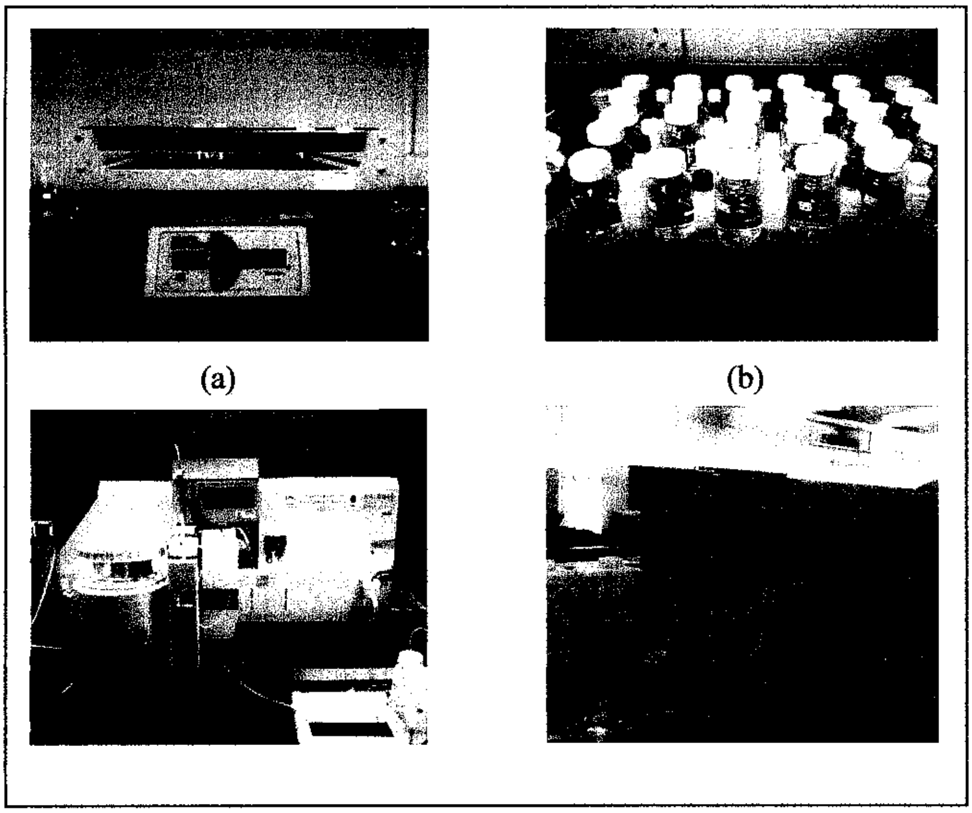
$$Q_e = (C_0 - C_e)\, V / W \qquad (1)$$

Where Q_e is the amount of metal ions sorbed per unit mass of adsorbent (mg/g), C_0 is the initial concentration of adsorbate (mg/l), C_e is the equilibrium concentration of the adsorbate (mg/l), V is the volume of the sample (L) and W is the weight of the adsorbent (g) employed [5].

The adsorption efficiency was calculated as follow:

$$\text{Adsorption (\%)} = (A_o - A)/A_o \times 100 \qquad (2)$$

Where A_o and A are the initial and final adsorbance of the solution, respectively.



(a) (b)

(c) (d)

Figure 3.4: a) Samples are agitated at 160 rpm, b) Samples after Filtered and Ready to be analyzed, c) AAS, d) CVAFS

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Adsorbent Characterization

4.1.1 Textural Characterization

SEM images of the 'rambai' leaves (Baccaurea Motleyana) are presented here. It is quite obvious from the obtained SEM images (Figure 4.1) that the surface is fairly porous in its structure. It is also noted that, acids are responsible to provide protons upon ionization in aqueous solutions which in turn can further open the pores of the adsorbent which increases the surface area, resulting to higher adsorption capacity. Thus, by reducing the pH of the aqueous solution, the solution will become more acidic and theoretically will increase the adsorption capacity. This will be discussed later in the chapter.

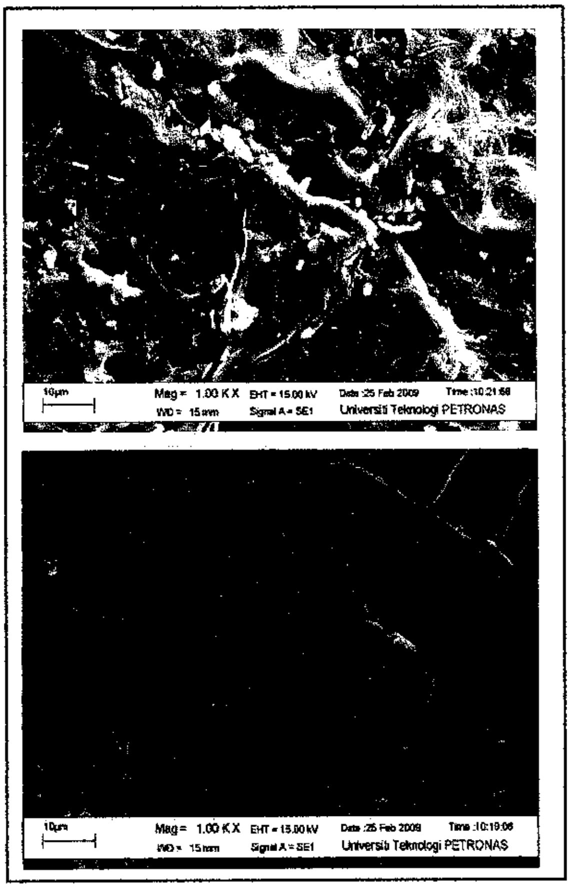


Figure 4.1: SEM Images

SEM with EDX (Energy Dispersive X-ray Spectroscopy) is also conducted to determine the adsorbent compositions. Figure 4.2 and Table 4.1 shows the specific compositions, whereby it is observed that as expected the components of carbon, C and oxygen, O is dominant with 65 atomic % and 31.3 atomic % respectively, since the adsorbent is an organic material.

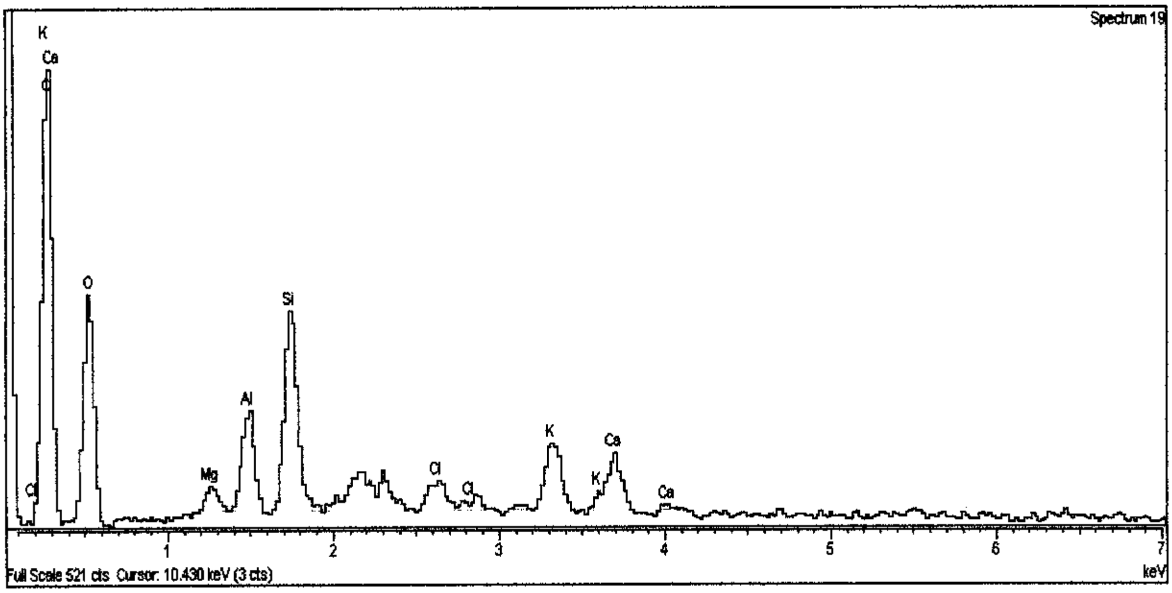


Figure 4.2: SEM with EDX Analysis

Table 4.1: Adsorbent Compositions

Element	**Weight, %**	**Atomic, %**
C	56.76	65.48
O K	36.14	31.3
Mg K	0.46	0.26
Al K	1.43	0.73
Si K	2.68	1.32
Cl K	0.45	0.17
K K	1.18	0.42
Ca K	0.91	0.31
Totals	100	100

4.1.2 FTIR Analysis

FTIR analysis is a technique used to identify chemical compounds based on how infrared radiation is adsorbed by the compounds chemical bond. Figure 4.3 shows the absorption peaks for atomic bonds and functional group that can be found on the adsorbent, 'rambai' leaves. Table 4.2, which is tabulated based on Figure 4.3, shows the functional groups as well as its vibration mode that is available on the adsorbent.

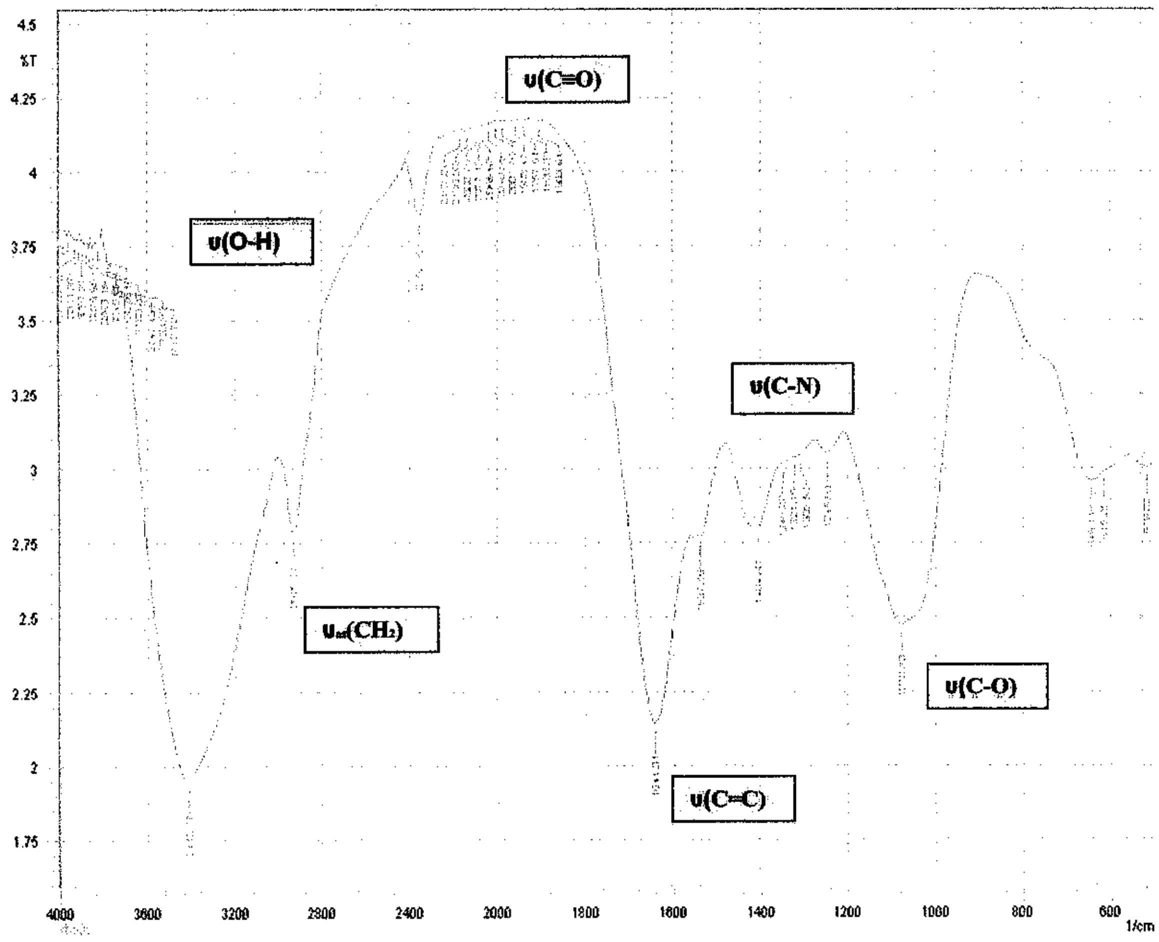


Figure 4.3: Absorption Peaks resulted from the FTIR Analysis on the Adsorbent

Table 4.2: Figure 4.3 Interpretation

Peak (cm-1)	Interpretation		
	Functional Group / Compounds	**Formula**	**Vibration Mode**
3500-2800	Hydroxyl	O-H	Stretching
2955-2922	Methylene	CH_2	Antisymmetrical Stretching
1100-1060	Primary Alcohol	C-O	Stretching
2170-1900	Carbonyl	C≡O	Stretching
1350-1310	Secondary Amides	C-N	Stretching
1641	Cyclic	C=C	Stretching

When Hg (II) is present in the adsorptive solution, referring from the FTIR analysis above, taking an example specifically the hydroxyl functional group, the following surface complex may be formed:

$$2C_xOH^+ + Hg^{2+} \rightarrow (C_xO)_2 Hg^{2+} + 2H^+$$

This surface complex among others that might be formed would enhance the chemisorptions of mercury on the surface of the adsorbent and result in an increased in adsorption capacity.

4.1.3 Decomposition Kinetics Using TGA

The TGA kinetics approach is based on the Flynn & Wall method which requires at least three determinations at different linear heating rates, where in this case, 10°C/min, 15°C/min and 20°C/min are conducted. Figure 4.4 displayed are the TGA result generated on the 'rambai' leave at an applied heating rate of 10°C/min. The plot shows the percent mass a function of sample temperature. A single well-defined weight loss event is obtained with the onset temperature of 258.004 °C. As the heating rate is increased, the onset of decomposition is pushed to lower temperatures, reflecting the time, temperature dependency of the decomposition reaction. Similarly, as the heating rate is decreased, the onset temperature is moved to increasingly higher temperature. This is shown in Figure 4.5 for the 'rambai' leave at heating rates of 10, 15 and 20°C/min. Refer to Appendix III for the other single graphs/curves generated by TGA.

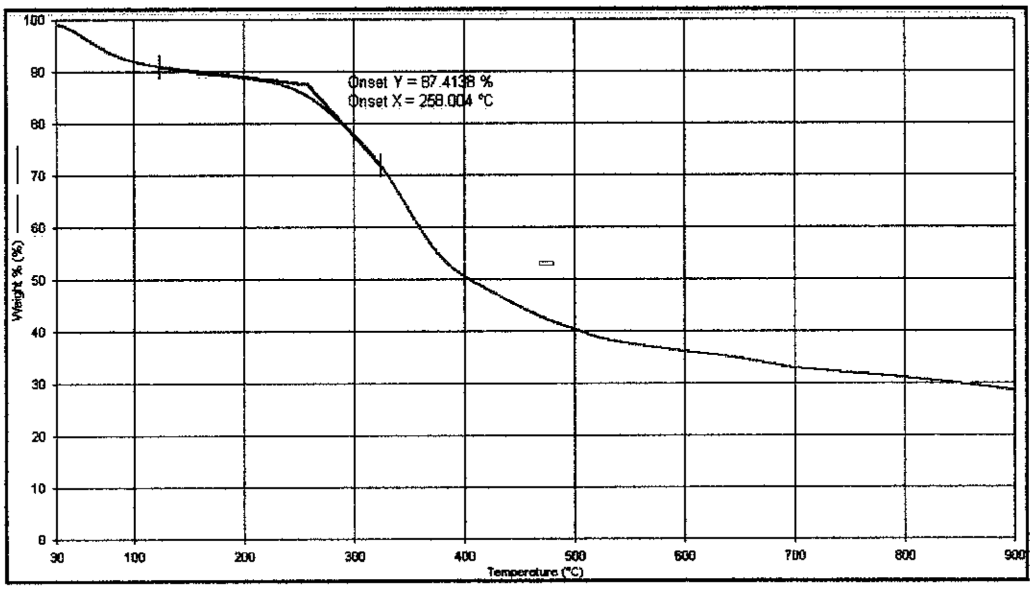


Figure 4.4: Rambai Leaves Decomposition at a Heating Rate of 10°C/min

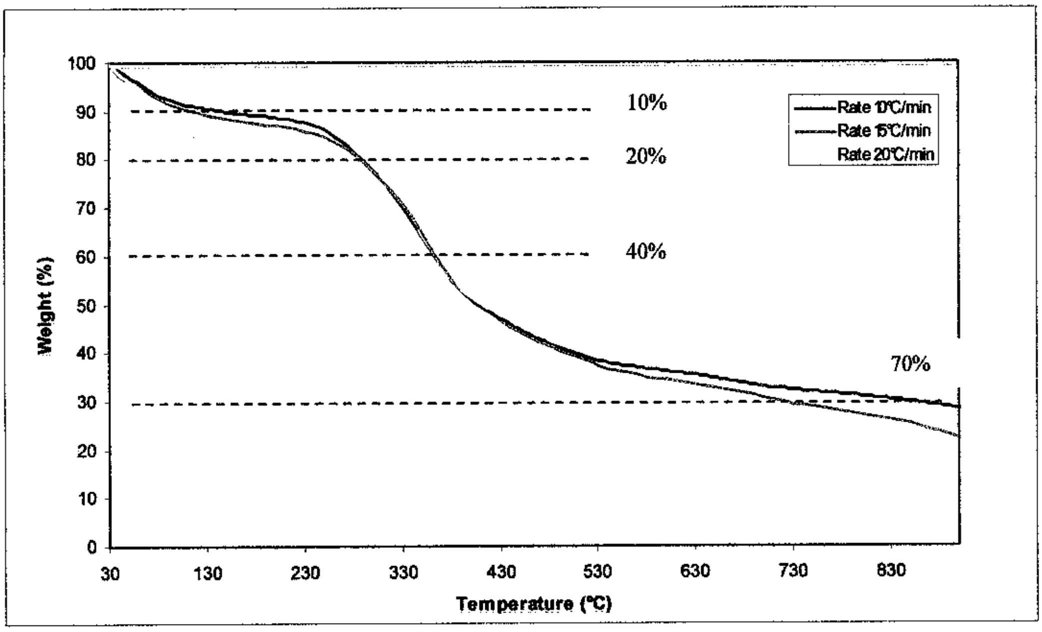


Figure 4.5: TGA Kinetics

The approach assumes the basic Arrhenius equation [8],

$$(d\alpha/dt) = A \exp(-Ea/RT)(1-\alpha)^n \tag{3}$$

Where α is the fraction composition, t is the time(s), (dα/dt) is the rate of mass loss, Z is the pre-exponential factor (1/second), Ea is the activation energy (J/mole, R is the gas constant (8.314 J/mole K) and n is the reaction order (dimensionless). Under the application of a constant heating rate, ø, and assuming a first order reaction (n=1), the rate expression becomes:

$$d\alpha/(1-\alpha) = (A/ø)\exp(-Ea/RT)dT \tag{4}$$

As observed in Figure 4.5, a constant decomposition level is selected and the corresponding temperature is determined for each different heating rate. In this case 10, 15 and 20% decomposition level is used. Refer to Table 4.3 for the corresponding temperature value. The measured values of temperature and TGA heating rate are then used to calculate the activation energy by plotting log ø vs. 1/T (Figure 4.6).

Table 4.3: Corresponding Temperature for each Different Heating Rates at Different Constant Decomposition Level

Decomposition Level	**Heating Rates, ø (°C/min)**	**Temperature, T (°C)**	**log ø**	**1/T**
10%	10	150	1.00	0.00667
	15	110	1.18	0.00909
	20	90	1.30	0.01111
15%	10	260	1.00	0.00385
	15	240	1.18	0.00417
	20	230	1.30	0.00435
20%	10	290	1.00	0.00345
	15	280	1.18	0.00357
	20	275	1.30	0.00364

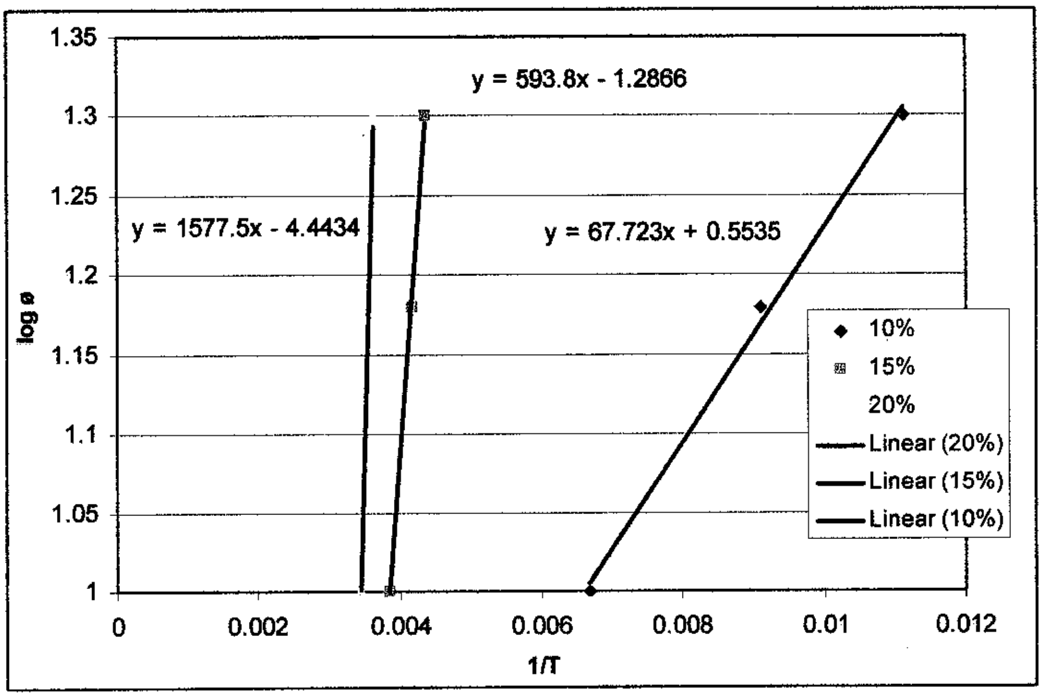


Figure 4.6: log ø vs. 1/T

The activation energy is assessed to be 67.7, 593.8 and 1577.5kJ/mole at the 10, 15 and 20% conversion level. The change in the decomposition kinetics is due to factors such as anti-oxidants.

4.2 Adsorption Equilibrium Study

The effect of agitation time on the extraction/adsorption of metal ions is considered to be of significant importance to study the extracting behavior of sorbent. Figure 4.7 shows equilibrium adsorption times of 60 ppb Hg (II) and 20 ppm Cd (II) with pH of 4, volume of 5 mL, and adsorbent dosage of 0.1 g and conducted at room temperature (24-25 °C).

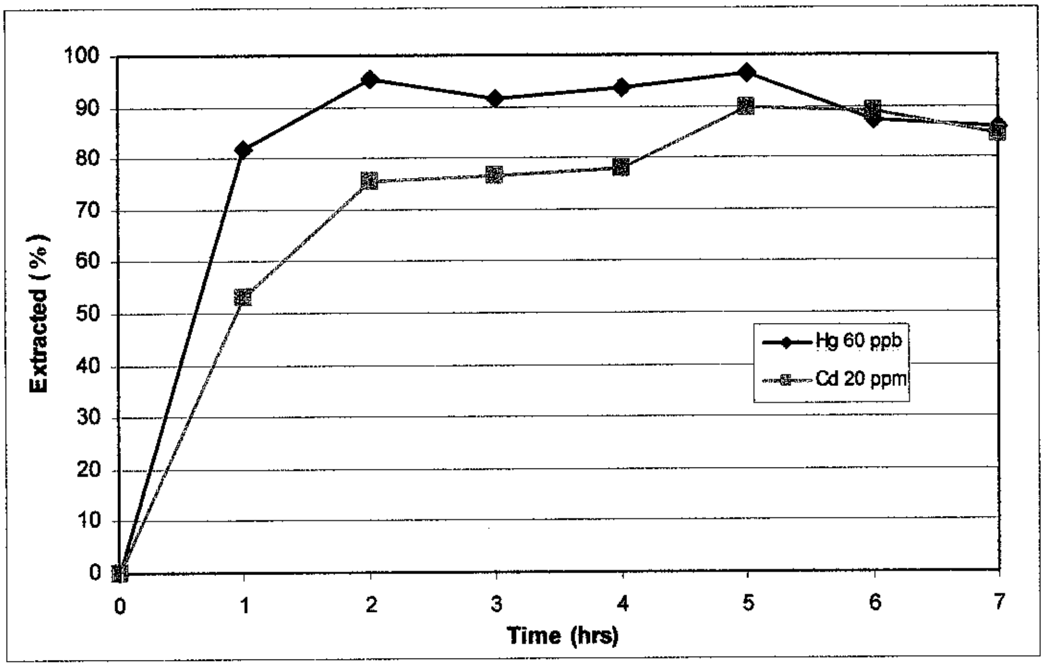


Figure 4.7: Extraction of Hg (II) and Cd (II) vs. Time (hrs)

It is observed that for both solution of Cd (II) and Hg (II), it is evident that adsorption which was very rapid initially become slower with lapse of time. For Hg (II), 81.65% of total extraction took place after 1 hour, while 53% extraction for Cd (II) in the first hour. At the initial stage, the process of adsorption was fast due to the availability of abundant free sites near the surface where the approach of the metal ions faced less hindrance. With the lapse of time and decrease in the availability of active sites near the surface, the metal ions had to diffuse into the pores of the adsorbent ('rambai' leave) through the interconnected pores and channels. It can be safely considered that the adsorption process reaches equilibrium after 5 hours as observed in Figure 4.7, where the optimum adsorptions are 96.67% and 90% for Hg (II) and Cd (II) respectively. In terms of amount of metal ions adsorbed per unit mass of adsorbent, Q_e, for 60 ppb of Hg (II), 28.94µg/g is adsorbed while 4.955 mg/g amount of Cd (II) ions removed with initial concentration of 20 ppm. Refer to Appendix III for the results calculated in terms of amount of metal ions adsorbed per unit mass of adsorbent.

4.3 Effect of Initial Concentration

The effect of Hg (II) concentration on its sorption was examined over concentration ranging from 5 ppb to 120 ppb as presented in Figure 4.8. Importantly the other parameters are kept constant including the contact time of 5 hours (Refer to Table 3.3).

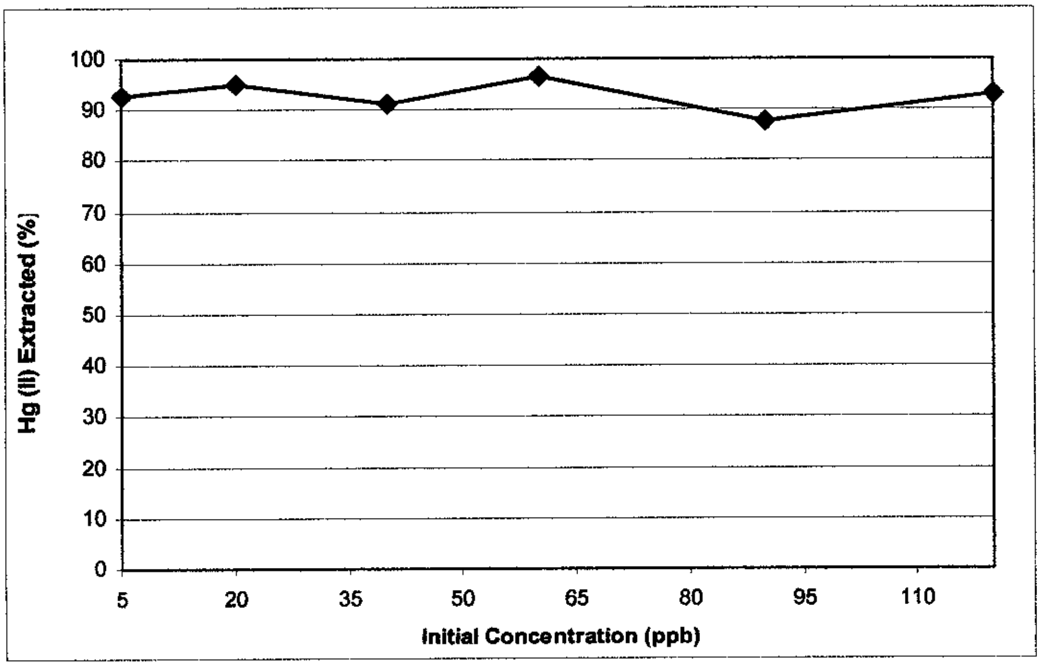


Figure 4.8: Hg (II) Extracted (%) vs. Initial Concentration (ppb)

It can be observed that the % Hg (II) extracted does not particularly affected by the increase of initial Hg (II) concentration as the extracted Hg (II), maintains about 90% throughout the concentration change. This is expected since the Hg (II) concentration is measured in ppb, which is small thus concentration ranging from 5-120 ppb does not have a significant influence on the extraction capacity. However, the variation of initial concentration on the extraction of Cd (II) as can be observed in Figure 4.9. This is obvious since the concentrations are measured in ppm, which is higher.

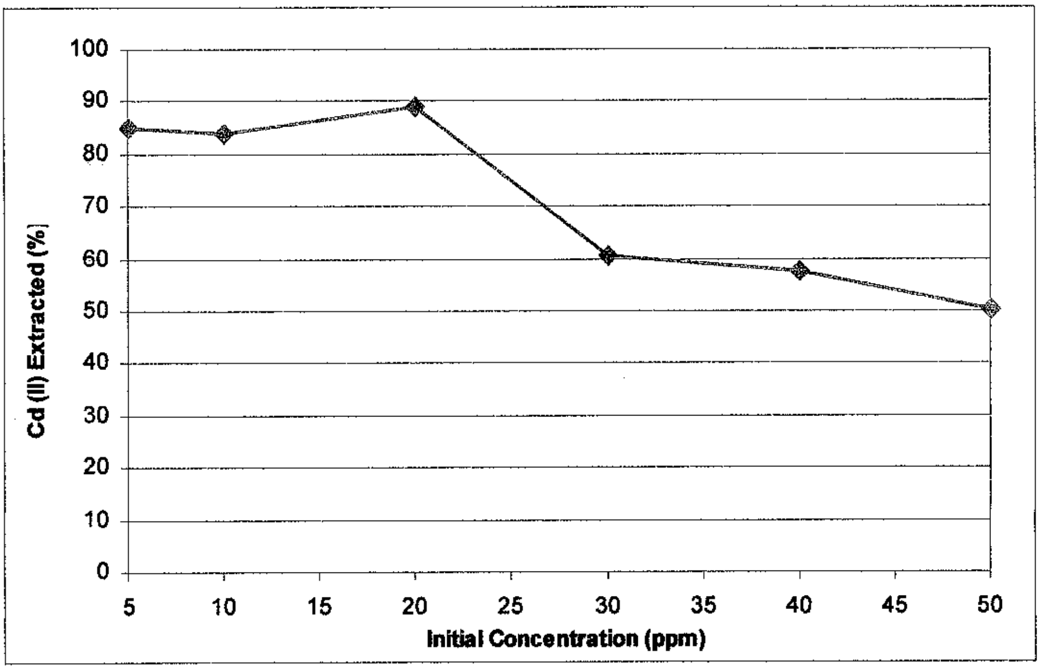


Figure 4.9: Cd (II) Extracted (%) vs. Initial Concentration (ppm)

Figure 4.9 indicates that the removal percentage decreases with the increase in initial Cd (II) concentration. With the same adsorbent dosage, pH and contact time, there is a drop in removal percentage when initial Cd (II) concentration is high. This is due to the fact that with lower initial Cd (II) concentrations, sufficient adsorption sites are available for the sorption of the metal ions. However, at higher concentrations the number of Cd (II) ions is relatively more as compared to the available adsorption sites. Hence, the percentage removal of Cd (II) depends on the initial Cd (II) concentration and decreases with increase in initial Cd (II) concentrations.

4.4 Effect of Initial Contact Time

Figure 4.10 elaborates that the Hg (II) extracted very rapidly when contacted with the adsorbent. It is observed that after 4 minutes the extraction/adsorption can occur up to 65.1%, 90.83% and 91.75% for 5, 20 and 60 ppb initial Hg (II) concentrations respectively. Moreover, it can also be noted at the initial period of contact time, ranging from 0-40 minutes, the effect of initial concentration is obvious as compared to that after 5 hours of contact time, as can be observed in Figure 4.8. Increase in the initial concentration will result to an increase in the adsorption capacity.

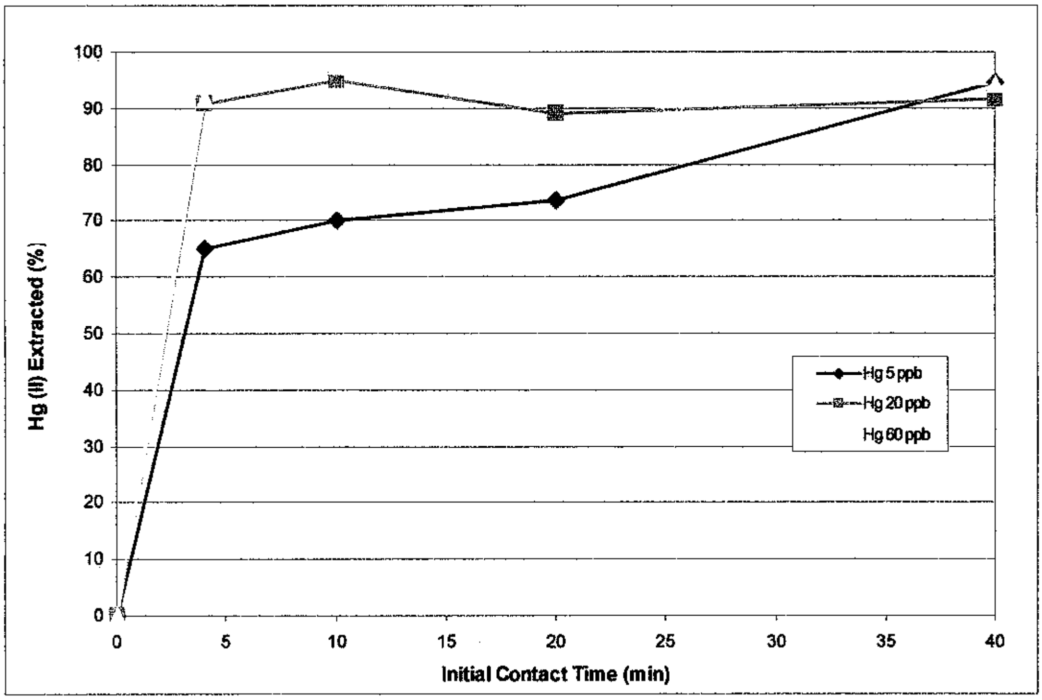


Figure 4.10: Hg (II) Extracted (%) vs. Initial Contact Time (min)

4.5 Effect of pH

pH values ranging from 3-8 are considered to study the effect of pH to towards the adsorption capacity of the adsorbent with other parameters kept constant. It can be noted from Figure 4.11 that higher adsorption % is observed for pH value of 3 and 4.

Referring to Figure 2.1, the pH scale, the lower the pH value the more positively charged and thus more acidic. Even though the Hg (II) is positively charged, the pH measurements are that of the solution or adsorbate and not the adsorbent, and thus attraction phenomena of different charges cannot be considered. However, the positively charged adsorbate solution results in it being more acidic, and as mentioned previously, acid will further open the pores of the adsorbent resulting to an increase in adsorption capacity. Furthermore, even though declining trend is observed, the adsorption is still high with the lowest at pH of 6 still have 80.655% adsorption capability.

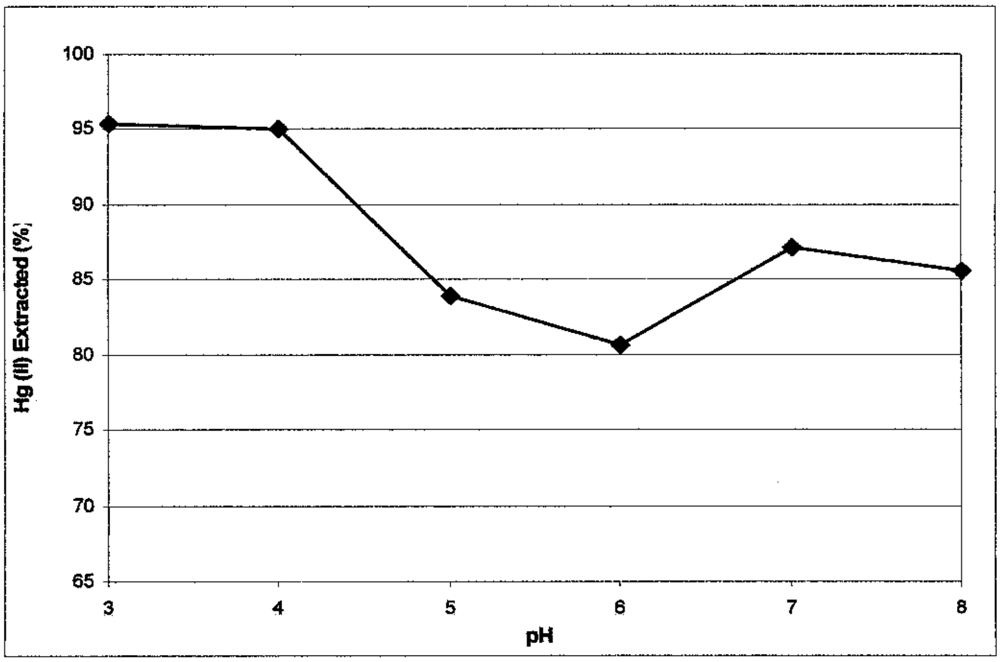


Figure 4.11: Hg (II) Extracted (%) vs. pH Value

4.6 Effect of Adsorbent Dosage

Four different adsorbent dosages of 0.05g, 0.1g, 0.15g and 2.0g are utilized to study its effect on the adsorption capacity of the adsorbent ('rambai' leave). Figure 4.12 indicates a decline after reaching optimum amount of 015 g adsorbent with 92.54% removal. This decrease in removal percentage with increase in the dosage of the adsorbent can be attributed to the formation of clusters of 'rambai' leaves particles resulting in decreased surface area.

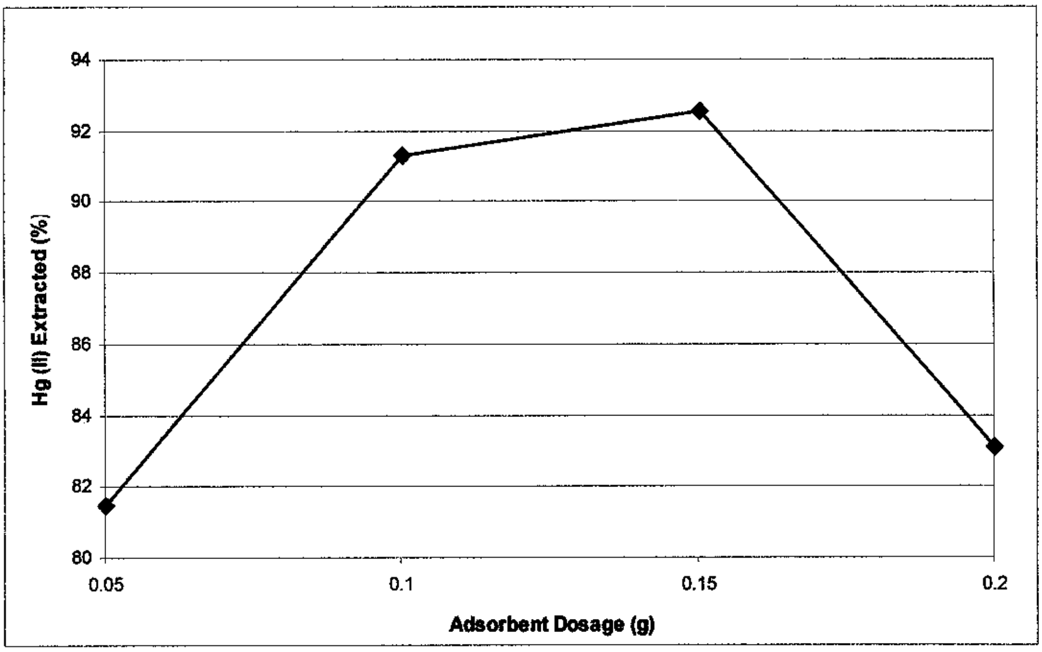


Figure 4.12: Hg (II) Extracted (%) vs. Adsorbent Dosage (g)

4.7 Reproducibility

The experiments are conducted in 2 trials to investigate the reproducibility of the results obtained. As can be observed in Figure 4.13, it can be concluded that the results obtained are reliable as it is fairly reproducible (Note: One outlier for Hg 5ppb Trial 2 sample can be neglected).

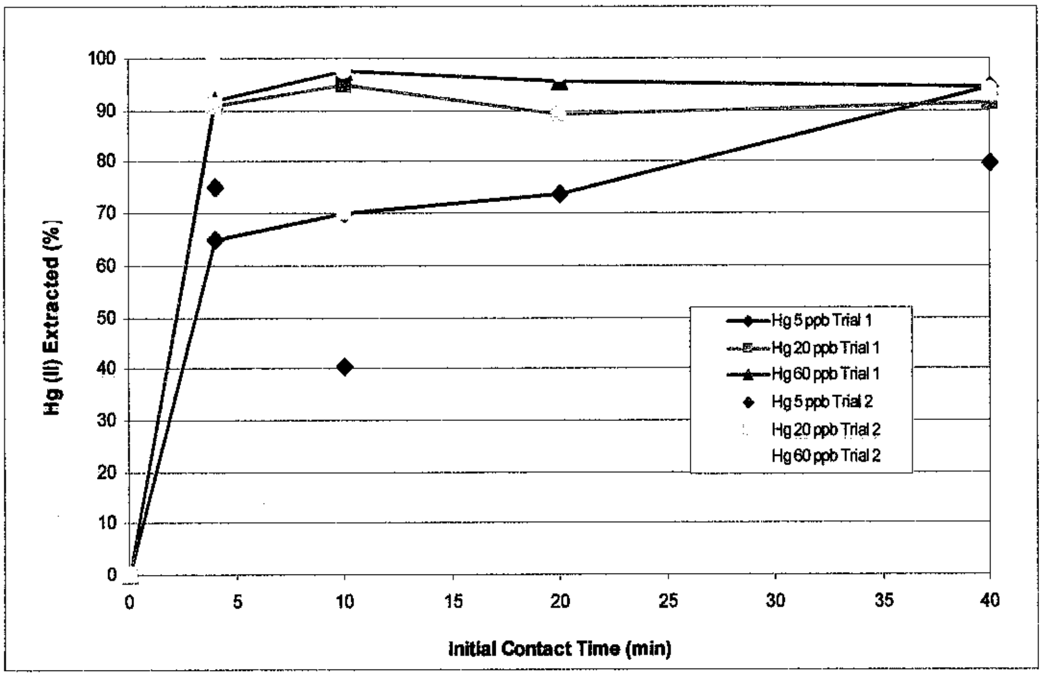


Figure 4.13: Reproducibility Determination Considering 2 Trials

4.8 Adsorption Isotherm

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The Langmuir and Freudlich isotherms are the equations most frequently used to represent the data on adsorption from solution. Langmuir and Freundlich isotherms are represented by the following equations [9]:

$$C_e/Q_e = \alpha_L C_e/ K_L + 1/K_L \quad (5)$$

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (6)$$

4.8.1 Langmuir Isotherm

Langmuir model is the simplest theoritical model for monolayer adsorption onto a surface with finite number of identical sites. It is originally developed to represent chemisorption on a set of distinct, localized adsorption sites. Langmuir has developed a theoritical equilibrium isotherm relating the amount of gas adsorbed on a surface due to the pressure of the gas. The equation is applicable to homogeneous adsorption where adsorption process has equal activation energy, based on the following assumptions [9]:

i) Molecules are adsorbed at a fixed number of well-defined localized sites
ii) Each sites can hold one adsorbate molecule
iii) All sites are energetically equivalent
iv) There is no interaction between molecules adsorbed on neighbouring sites

The general Langmuir equation is as follow:

$$Q_e = K_L C_e/(1+ \alpha_L C_e) \qquad (7)$$

When linearized, Eq. (3) becomes Eq. (1). K_L and α_L are the equilibrium constants of Langmuir equation. Plotting C_e/Q_e against C_e as in Figure 4.14, yields a straight line with slope, α_L/K_L and intercept $1/K_L$. The ratio α_L/ K_L indicates the theoritical monolayer saturation capacity, Q_o. Figure 4.14 represent the Langmuir Isotherm plot and Table 4.4 illustrate the Langmuir isotherm parameters obtained.

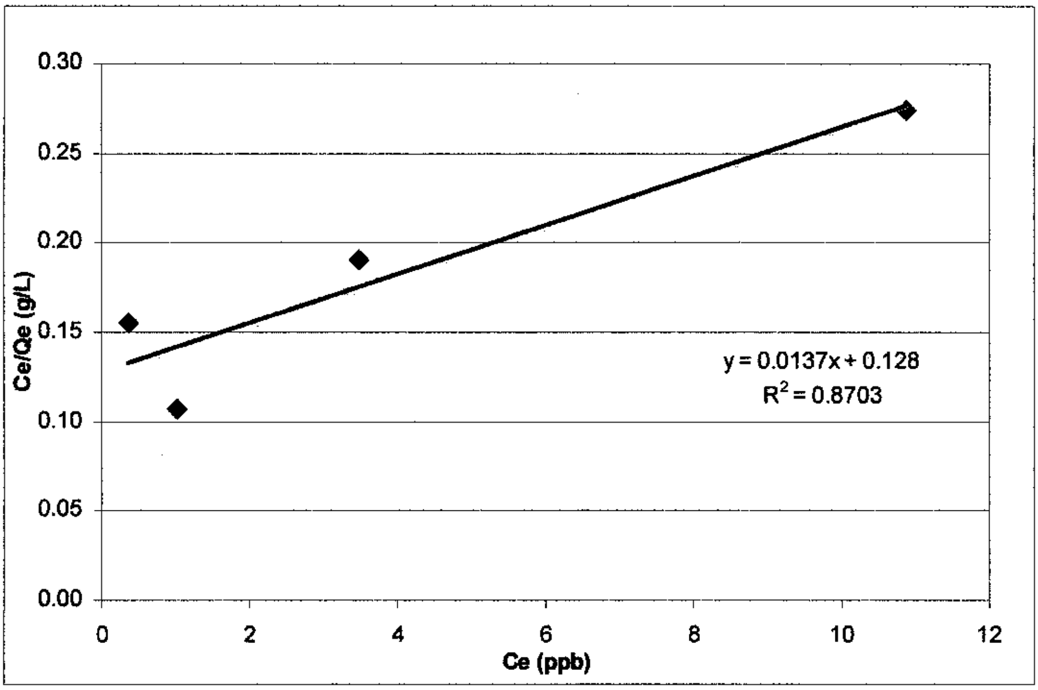


Figure 4.14: Langmuir Isotherm Plot

Table 4.4: Langmuir Isotherm Parameters

Langmuir Parameters	**Value**
Slope, α_L / K_L	0.0137
K_L / α_L	72.9927
y-intercept, $1/ K_L$	0.128
K_L	7.8370
R^2	0.8703

4.8.2 Freundlich Isotherm

Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption. The model is given as [9],

$$Q_e = K_F C_e^{1/n} \tag{8}$$

If the concentration of solute in the solution at equilibrium, C_e, is raised to the power of 1/n, with the amount of solute adsorbed being Q_e, then $C_e^{1/n}/ Q_e$ are constant at a given temperature. K_F indicates relative indicator of adsorption capacity, while the dimensionless, 1/n, is indicative of the energy or intensity of the reaction and suggests the favoribility and capacity of the adsorbent/adsorbate system. According to the theory, n>1 represents favorable adsorption conditions. Eq. (8) is linearized into logarithmic form for data fitting and parameter evaluation to become as Eq. (6). Figure 4.15 represent the Freundlich Isotherm plot.

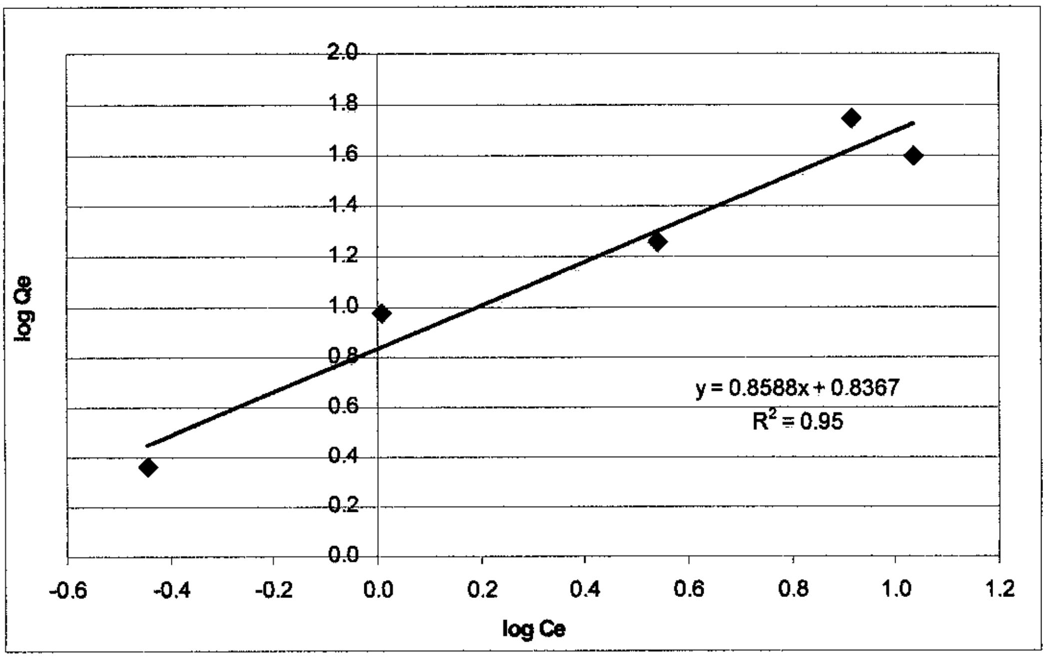


Figure 4.15: Freundlich Isotherm Plot

Table 4.5: Freundlich Isotherm Parameters

Freundlich Parameters	**Value**
Slope, 1/n	0.8588
n	1.1644
y-intercept, log K_F	0.8367
K_F	6.8670
R^2	0.9500

Since the calculated correlation coefficients are consistent and closer to unity for Freundlich Isotherm model than the Langmuir Isotherm, therefore, the adsorption isotherm could well be explained and approximated more favorably by Freundlich Isotherm model for 'rambai' leaves adsorbent

4.9 Adsorption Kinetics

The prediction of kinetics is necessary for the design of sorption systems. Chemical kinetics explain how fast the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of sorption process depends on physico-chemical characteristics of the adsorbent and system conditions like temperature, pressure, etc. Measurement of sorption rate constants is an important physico-chemical parameter to evaluate the basic qualities of a good adsorbent such as time required for the adsorbent to remove particular metals/compounds, efficacy of the sorbent, etc. [7].

In batch adsorption processes the adsorbate molecules diffuse into the interior of the porous adsorbent. It was investigated that the adsorption of Hg (II) ions from aqueous solution is a linear phase for 15 minutes (noted that the concentration is in ppb), while the adsorption of Cd (II) ions is a linear phase for 300 minutes (noted that the concentration is in ppm). This behaviour can be attributed to the utilization of available adsorbing sites on the surface of the adsorbent. After this phase, sorption of Hg (II) and Cd (II) was almost ignorable. This might attributed to extremely slow diffusion of metal ions from the surface film into the micro pores which are the least accessible sites for adsorption. In order to observe the sorption process of Hg (II) ions, on 'rambai' leaves adsorbent, four kinetic models were implemented, which includes, Bangham, pseudo-first-order, pseudo-second-order, and intra-particle diffusion.

4.9.1 Bangham's Equation

The rate constant, K_r for the sorption of Hg (II) were calculated using the simplest form of Bangham Equation [7]:

$$dQ/dt = Q_t/mt \qquad (9)$$

The intergral form can be written as:

$$Q_t = K_r t^{1/m} \qquad (10)$$

Assessment of the rate constants is possible by simple linear transformation of the equation:

$$\log Q_t = \log K_r + (1/m) \log t \qquad (11)$$

As can be observed from Figure 4.16, the linearity obtained plot indicates the applicability of the (1/m)th order kinetics for the system under observation. The adsorption rates constant was calculated from the intercept and slopes of the straight lines and are reported in Table 4.6.

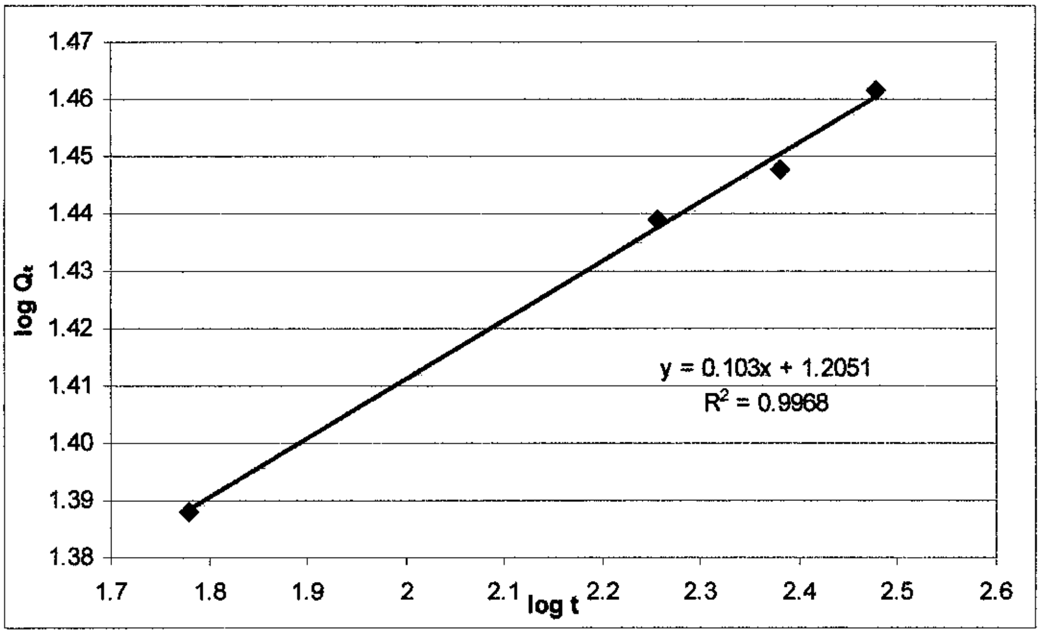


Figure 4.16: Bangham's Model Plot

Table 4.6: Bangham's Model Parameters

Bangham's Parameter	**Value**
Slope, 1/m	0.103
y-intercept, log K_r	1.2051
Rate Constant, K_r (mg/g min)	16.036
R^2	0.9968

4.9.2 Pseudo-first-order Model

The pseudo-first-order equation can be written as:

$$dQ_t /dt = K_f (Q_e - Q_t) \qquad (12)$$

Where Q_t (mg/g) is the amount of adsorbate adsorbed at time t, Q_e (mg/g) the adsorption capacity in equilibrium, K_f (min^{-1}) is the rate constant for pseudo-first-order model and t (min) is the time. After definite integration by applying the initial conditions $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, the equation becomes:

$$\log (Q_e - Q_t) = \log Q_e - K_f t/2.303 \qquad (13)$$

Adsorption rate constant, K_f and adsorption capacity, Q_e for the adsorption of Hg (II) ions by 'rambai' leave adsorbent were calculated from the slope and intercept of the plots of log $(Q_e - Q_t)$ vs. t as displayed in Figure 4.17 and the parameters are reported in Table 4.7.

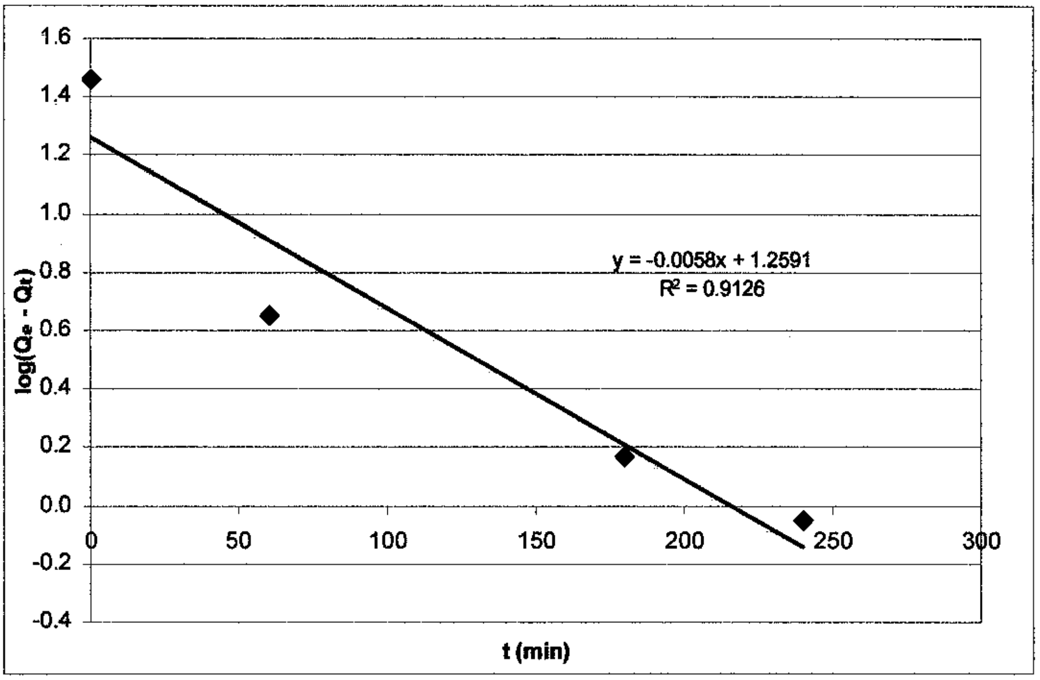


Figure 4.17: Pseudo-first-order Model Plot

Table 4.7: Pseudo-first-order Model Parameters

Pseudo-First-Order Parameter	**Values**
Slope, $K_f/2.303$	0.0058
y-intercept, log Q_e	1.2591
Q_e (mg/g)	18.159
Rate Constant, K_f (min^{-1})	0.0134
R^2	0.9126

4.9.3 Pseudo-second-order Model

The pseudo-second-order model can be presented in the following form [7]:

$$dQ_t/dt = K_s(Q_e - Q_t)^2 \tag{14}$$

Where, K_s is the rate constant of the Pseudo-second-order model (g/mg min). Definite integration of Equation 14 for boundary conditions $Q_t = 0$ when $t = 0$ and $Q_t = Q_t$ at $t = t$, the following form of equation can be obtained:

$$t/Q_t = 1/(K_sQ_e^2) + (1/Q_e)t \tag{15}$$

The initial sorption rate constant, h (mg/g min), at $t = 0$ can be defined as [7]:

$$h = K_sQ_e^2 \tag{16}$$

The initial sorption rate, h, the equilibrium adsorption capacity, Q_e and the pseudo-order rate constants K_s were obtained from the slope and intercept of the plots of t/Q_t vs. t as displayed in Figure 4.18, while its parameters values are reported in Table 4.8.

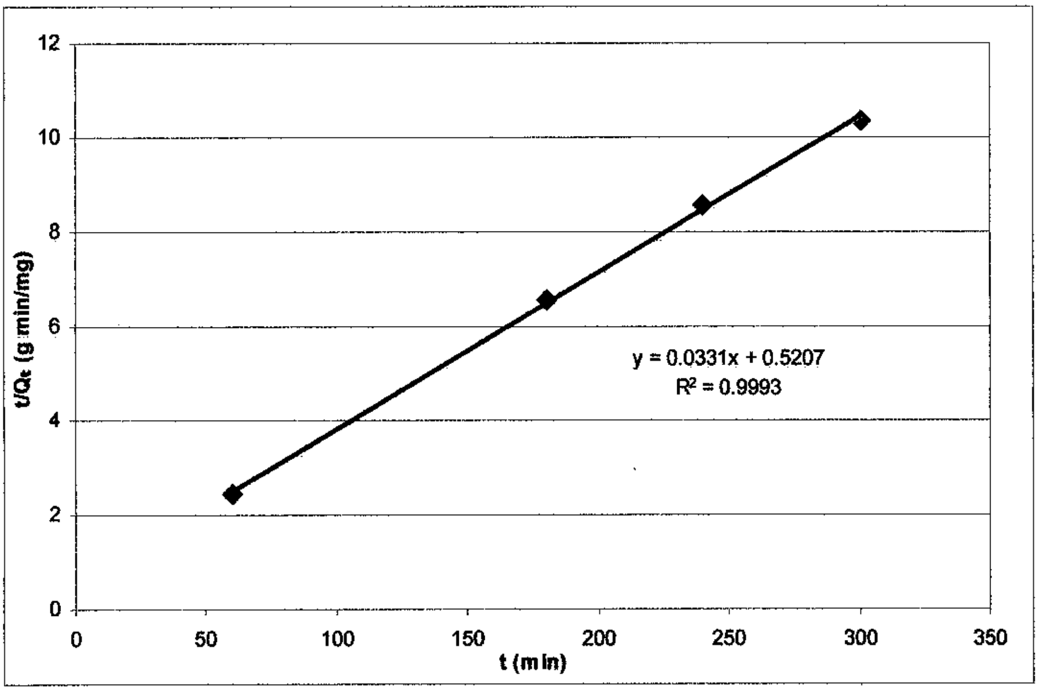


Figure 4.18: Pseudo-second-order Model Plot

Table 4.8: Pseudo-second-order Model Parameters

Pseudo-Second-Order Parameter	**Values**
Slope, $1/Q_e$	0.0331
Q_e (mg/g)	30.2115
y-intercept, $1/(K_sQ_e^2)$	0.5207
Rate Constant, K_s(mg/g min)	0.0021
R^2	0.9993
h (mg/g min)	1.9205

Since the calculated correlation coefficients are consistent and closer to unity for pseudo-second-order kinetics model than the others, therefore, the adsorption kinetics could well be explained and approximated more favorably by pseudo-second-order kinetic model for 'rambai' leaves adsorbent.

4.9.4 Intra-particle Diffusion Study

An empirically functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Webere Morris plot, rather than with the contact time, t [7]:

$$Q_t = K_{id}t^{1/2} + C \tag{17}$$

Where, K_{id} is the intra-particle diffusion rate constant. According to Equation 17, a plot of Q_t vs. $t^{1/2}$ should be a straight line with slope K_{id} and intercept C when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea of the thickness of boundary layer i.e., the larger the intercept the greater will be the boundary layer effect. Figure 4.19 displays the plot of mass of Hg (II) ion adsorbed per unit mass of adsorbent Q_t versus $t^{1/2}$ is presented. The deviation of straight lines from the origin can be attributed to the difference in rate of mass transfer in the initial and final stages of adsorption. The value of K_{id} as obtained from the slopes of straight lines is listed in Table 4.9. Intra-particle diffusion is responsible to consumes more time due to very slow diffusion of the adsorbates from the surface film into the micro pores, which are least accessible sites of adsorption.

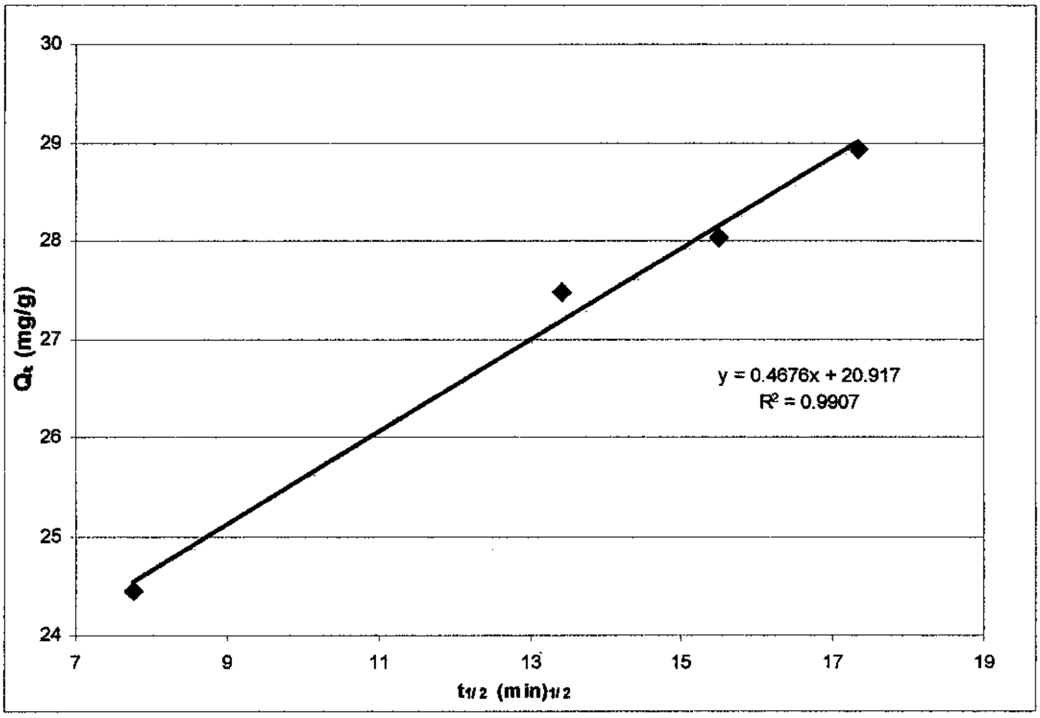


Figure 4.19: Intra-particle Diffusion Model Plot

Table 4.9: Intra-particle Diffusion Model Parameters

Intra-Particle Diffusion Parameter	**Values**
Slope, K_{id}	0.4676
y-intercept, C (thickness of boundary layer)	20.917
R^2	0.9907

4.10 Comparison between with Other Adsorbents

Even though sorbents reported in the literature for adsorption of mercury, as shown in Table 4.10 respectively, can effectively achieve concentration reduction, there is scope for improvement [10]. The 'rambai' leaves described in this research work shows fast exchange kinetic as well as proven to be effective in metals removal. In addition, this adsorbent is an agricultural waste, thus are low cost, easy and simple to prepare.

Table 4.10: Comparison of 'Rambai' Leave with Some Reported Sorbents for Mercury

Adsorbents	**Removal of Mercury (wt%)**
Treated Granular Activated Carbon	99.6
Treated Sawdust	99.5
Weathered Coal	98.1
'Rambai' Leave (Dried)	96.7
Polymerised Sawdust	95.0
Carbon Aerogel	94.8
Granular Activated Carbon	76
Sawdust	68.3
Mustard Husk	56.2

As observed in Table 4.10, the 'rambai' leave removal capability is comparable to most of the adsorbents currently available.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Mercury like any other heavy metals poses a significant danger to humans as well as the environment. The main contributors of mercury to our environment are from the industries, thus it is necessary to find mercury removal techniques that not only effective but also cost effective. For that, agricultural wastes can be considered as an alternative adsorbents.

The removal of Hg (II) ions from aqueous solution may be achieved through the use of low-cost adsorbents which are abundantly available. 'Rambai' leave which are readily available agricultural wastes in Malaysia, have been investigated as adsorbent materials for the removal of Hg (II) ions from aqueous solution. The result obtained showed a very desirable result and can be optimized by optimizing the pH of the system and the adsorbent dosage. It is observed that the optimum pH condition is 3 and 4 with 95% adsorption while the optimum adsorbent amount is 0.15 g with 92.54% adsorption. The Freundlich adsorption isotherm was found to be more desirable model while pseudo-second-order model is the best kinetic model for Hg (II) adsorption by 'rambai' leaves. The research also found that 'rambai' leaves is very effective in removal of Cd (II). Thus, it can be concluded that 'rambai' leaves may be utilized successfully for the treatment of industrial effluents containing Hg (II) and Cd (II).

5.2 Recommendations

There are few additional improvements and recommendation that can be made experimental wise to further establish the effectiveness of 'rambai' leave as an adsorbent in the future. There are:

1) Consider other parameters such as particle size, higher concentrations (ppm for Hg (II) ions), temperatures, flow rates, and effect of co-existing heavy metals.
2) Conduct more analysis on the Cd (II), to find the optimum conditions
3) Establish kinetic and lifetime estimates associated with 'rambai' leave using the PerkinElmer TGA Decomposition Kinetics Software.
4) Consider drying at different temperatures, during adsorbent preparation.

REFERENCE

1. http://cerhr.niehs.nih.gov/common/mercury.html
2. http://www.balanceyournutrition.com/In_Focus_mercury_toxicity.htm
3. http://www.jamaicaobserver.com/lifestyle/html/20070324T230000-0500_120798_OBS_HEAVY_METAL_POISONING__PART_II_HEALTH_EFFECTS_OF_MERCURY.asp
4. http://www.lenntech.com/heavy-metals.htm
5. Frank L.Slejko, *Adsorption Technology: A Step by Step Approach to Process Evaluation and Application*, 1-8, 37-40, 42, 46-51, 55-65
6. http://en.wikipedia.org/wiki/Adsorption
7. Muhammad Nadeem, I.B. Tan, M.R.U Haq, S.A Shahid, S.S Shah and G. McKay, *Sorption of Lead Ions from Aqueous Solution by Chickpea Leaves, Stems and Fruit Peelings*, Adsorption Science and Technology, 2006, Volume 24 Number 3.
8. W.J Sichina, *Characterizing Polymer Lifetimes Using TGA Decomposition Kinetics*, Thermal Analysis Application Note, PerkinElmer Instruments.
9. M.A. Abdullah, L. Chiang, M. Nadeem, *Comparative Evaluation of Adsorption Kinetics and Isotherms of a Natural Product Removal by Amberlite Polymeric Adsorbents*, Chemical Engineering Journal, 2008.
10. Ajay Kumar Meena, G.K Mishra, Satish Kumar and Chitra Rajagopal, *Low-Cost Adsorbents for the Removal of Mercury (II) from Aqueous Solution – A Comparative Study*, Defence Science Journal, Vol. 54, No. 4, October 2004.

Other References

- Muhammad Nadeem, A. Mahmood, S.A Shahid, S.S Shah, A.M Khalid, G. McKay, *Sorption of Lead from Aqueous Solution by Chemically Modified Carbon Adsorbent*, Journal of Hazardous Materials 2006.
- M. Nadeem, M. Shabbir, M.A Abdullah, S.S Shah, G. McKay, *Sorption of Cadmium from Aqueous Solution by Surfactant-Modified Carbon Adsorbents*, Journal of Hazardous Materials

- Amir Hossein Mahvi, Dariush Naghipour, Forugh Vaei and Shahrokh Nazmar, *Teawaste as an Adsorbent for Heavy Metal Removal from Industrial Wastewaters*, American Journal of Applied Sciences, 2005.
- Aslam Khan, Farzana Mahmood, M. Younas Khkhar, Shujaat Ahmed, *Functionalized Sol-Gel Material for Extraction of Mercury (II)*, Reactive & Functional Polymer ScienceDirect, 2006.
- Frank L.Slejko, *Adsorption Technology: A Step by Step Approach to Process Evaluation and Application*, 1-8, 37-40, 42, 46-51, 55-65
- Helmut Gunzler, Hans-Ulrich Gremlich, *IR Spectroscopy, An Introduction*, Wiley-Vch, 2002.
- S. Sauerbrunn, P. Gill, *Decomposition Kinetics Using TGA*, TA Instruments, Thermal Analysis
- D. M. Fox, J. W. Gilman, H. C. De Long and P.C Trulove, *TGA Decomposition Kinetics of 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate and the Thermal Effects of Contaminants,* Naval Research Laboratory Chemistry Division, Washington DC 20375.
- A. Rezaee, J. Derayat, S. B. Mortazavi, Y. Yamini and M.T Jafarzadeh, *Removal of Mercury from chor-alkali Industry Wastewater using Acetobacter xylinum Cellulose*, American Journal of Environmental Sciences 1 (2): 102-105, 2005.

APPENDIX I - PROJECT GANTT CHART

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1	**Selection of Project Topic**	▨	▨																												
2	**Preliminary Research Work**		▨	▨	▨	▨																									
3	**Safety Hazard Analysis**				▨	▨	▨	▨	▨	▨	▨																				
4	**Apparatus and Chemical Setup**				▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨																
5	**Experimental Work**																														
	Adsorbent Preparation											▨	▨	▨	▨	▨	▨	▨													
	Chemical Preparation											▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨									
	Experiments											▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨									
	Sample Analysis														▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨						
	Adsorbent Characterization																					▨	▨	▨	▨	▨	▨				
7	**Data Analysis/Record**														▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
8	**Dissertation**																										▨	▨	▨		
9	**Final Oral Presentation**																														▨

▨ Timeline

APPENDIX II

SAFETY HAZARD ANALYSIS

Parameters	Possible hazards	Consequences	Solutions
Working with hazardous chemicals	1. Handling chemicals with insufficient accessories (eg. safety gloves, safety shoes, lab coat, etc.)		1. Safety sheet for chemicals posted folder by the lab station to refer to when handling hazardous chemicals
Handling heated glassware	1. Severe burn		1. Handle glassware with leather gloves working with equipment during an experiment
Protective shield	1. Running an experiment without closing the protective shield	1. An accident (eg. explosion) caused by the experiment is not contained to the lab station.	1. Close the protective shield for the lab station while not working with the experiment. 2. When working with an experiment, open the shield so that the exposure of the experiment is minimized

Working with chemicals:

Always refer to Material Safety Data Sheet (MSDS) of the chemicals.

Hazard Symbols	Description	Hazard Symbols	Description
	Irritant		Toxic
	Harmful		Very Toxic
	Corrosive		Explosive

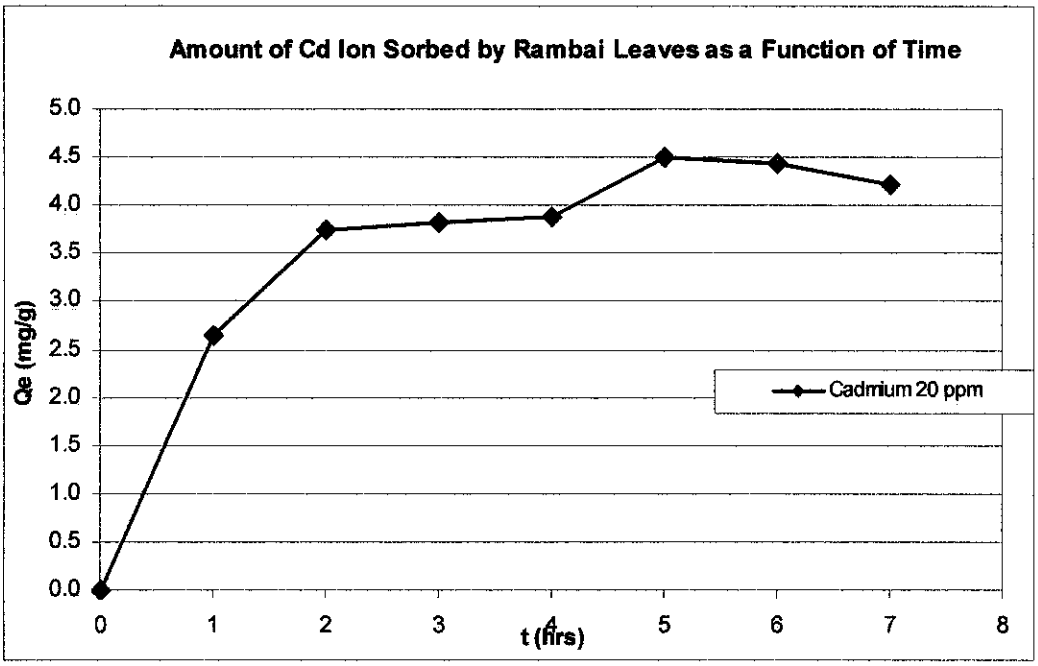
	Highly Flammable		Oxidizing Agent
	Extremely Flammable		Dangerous to the Environment

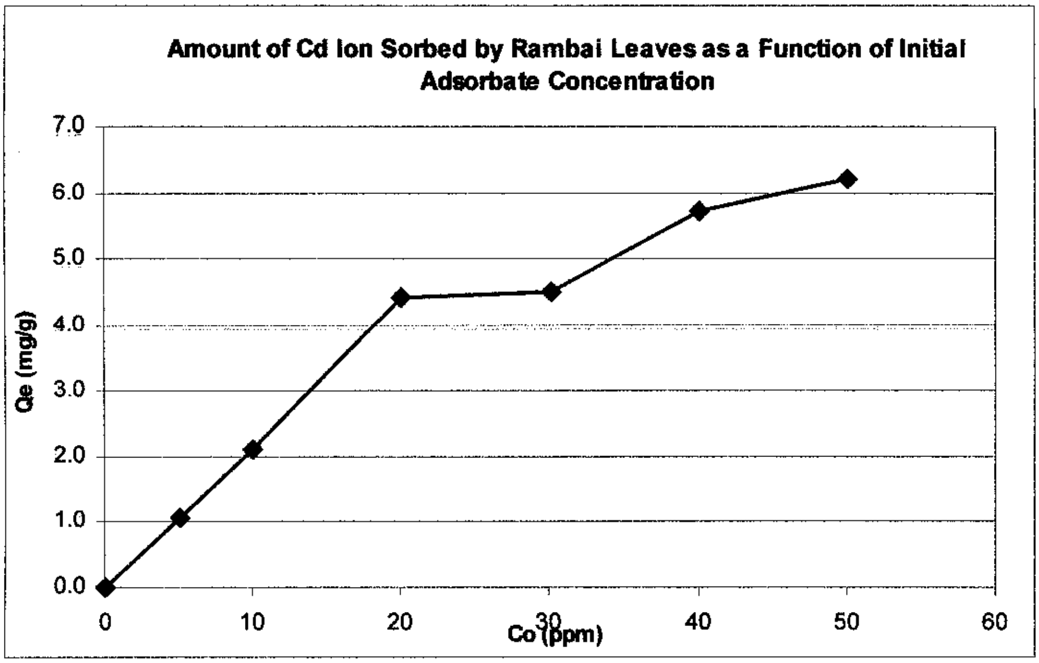
Working with glass apparatus:

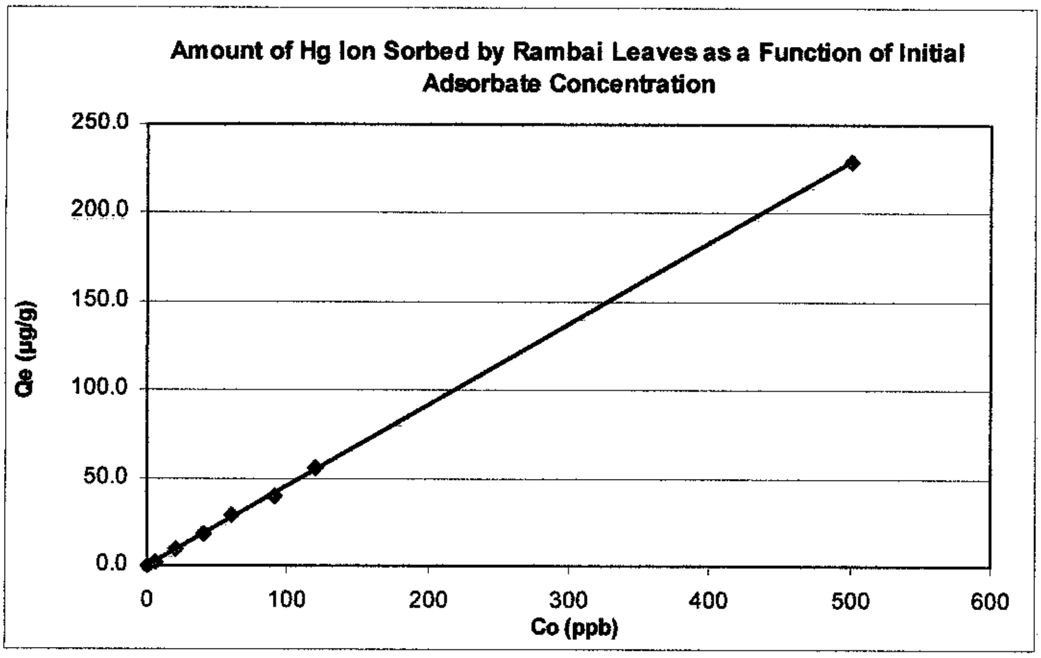
Possible hazards	Consequences	Solutions / Safety Measures
1. Shatter glass equipment	1. Chemical spillage a. Harmful chemicals exposed to atmosphere b. Slippery floor 2. Exposure to sharp glass fragments leading to personal injuries	1. Use bucket when transporting glass apparatus. 2. Wear leather gloves to disconnect glass apparatus attaching to one to another. If it is not possible, use hot water. 3. All stacking glass apparatus must be aligned to avoid tension /stress to the apparatus. 4. Use plastic apparatus if possible. 5. Do not catch falling glass apparatus to avoid injuries. 6. Always check the set-up of the experiment before using.
1. Improper disposal of shattered glass	1. Perforate disposal container (eg. plastic bag) 2. Shattered glass in unmarked container may cause personal injury to disposal personnel.	1. Dispose broken glasses into proper glass waste container.

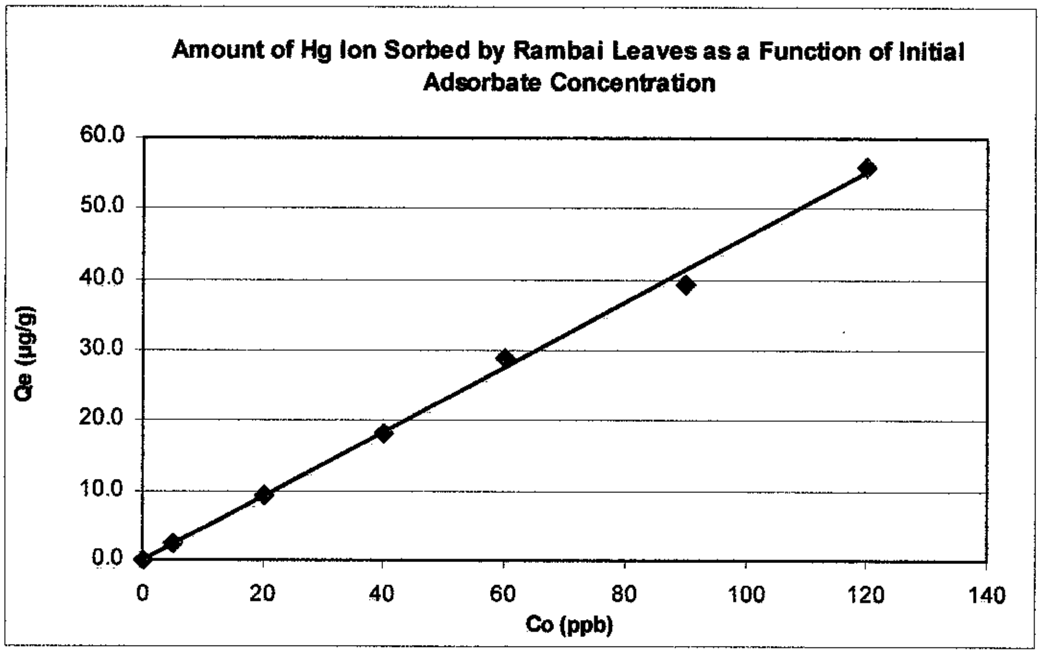
APPENDIX III

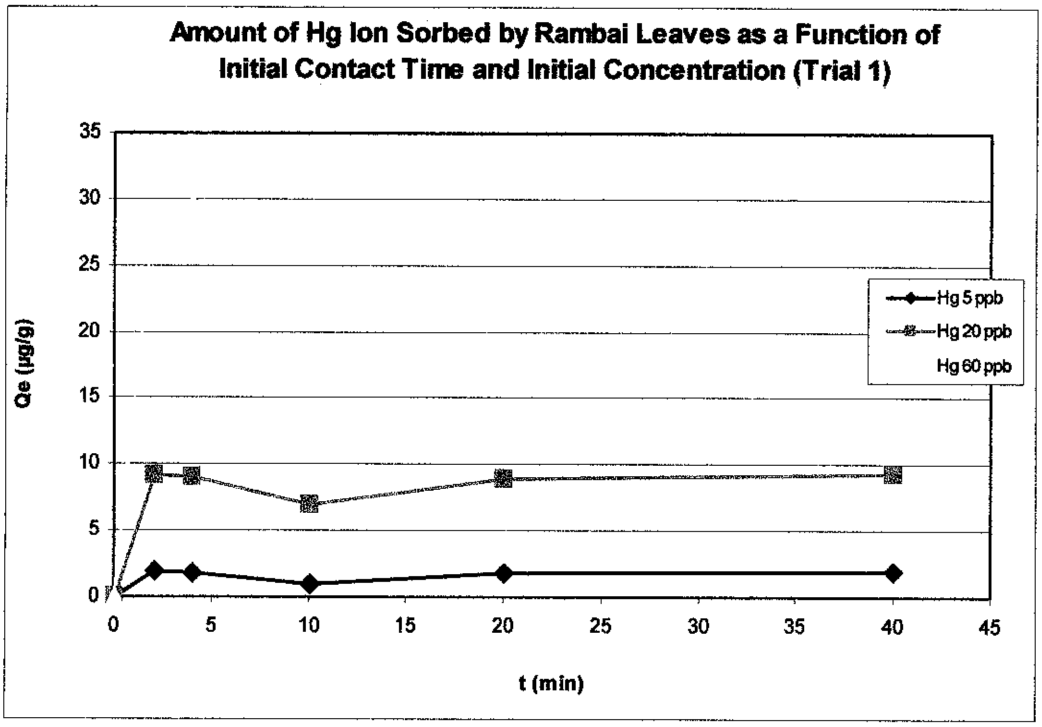
OTHER EXPERIMENTAL RESULTS

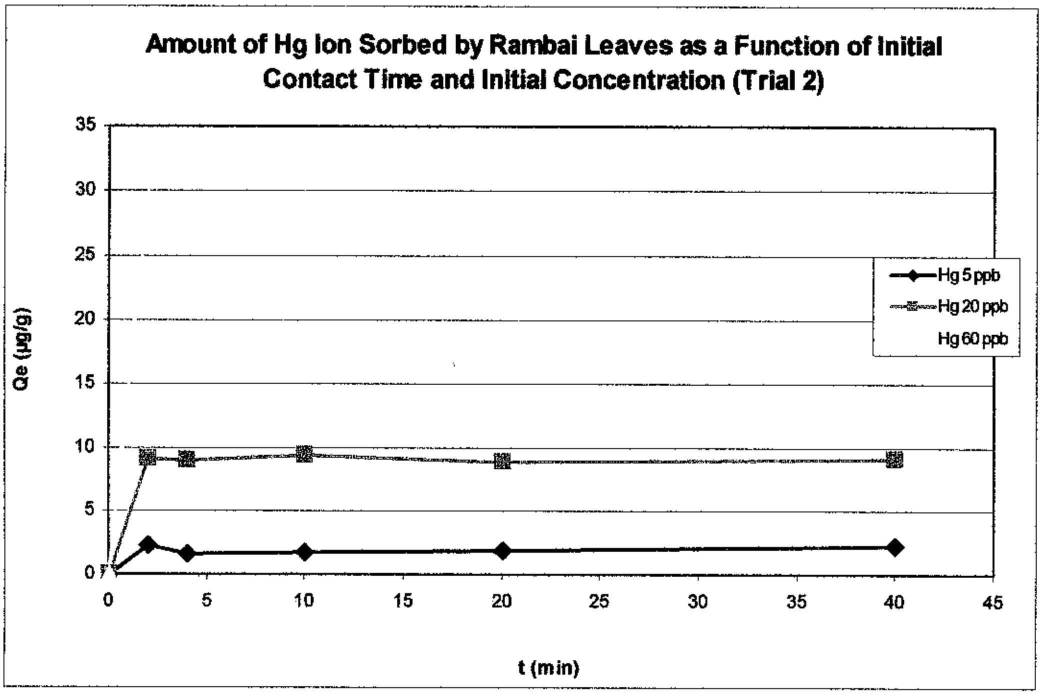




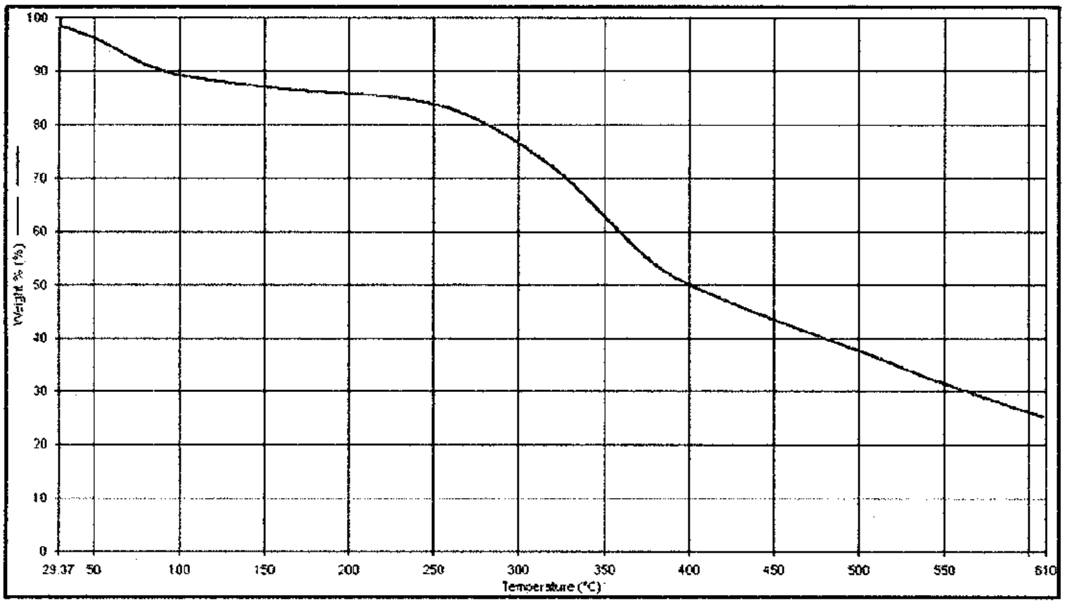

Amount of Hg Ion Sorbed by Rambai Leaves as a Function of Initial Adsorbate Concentration
Qe (µg/g)
250.0
200.0
150.0
100.0
50.0
0.0
0
100
200
300
400
500
600
Co (ppb)


Amount of Hg Ion Sorbed by Rambai Leaves as a Function of Initial Adsorbate Concentration
Qe (µg/g)
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
20
40
60
80
100
120
140
Co (ppb)

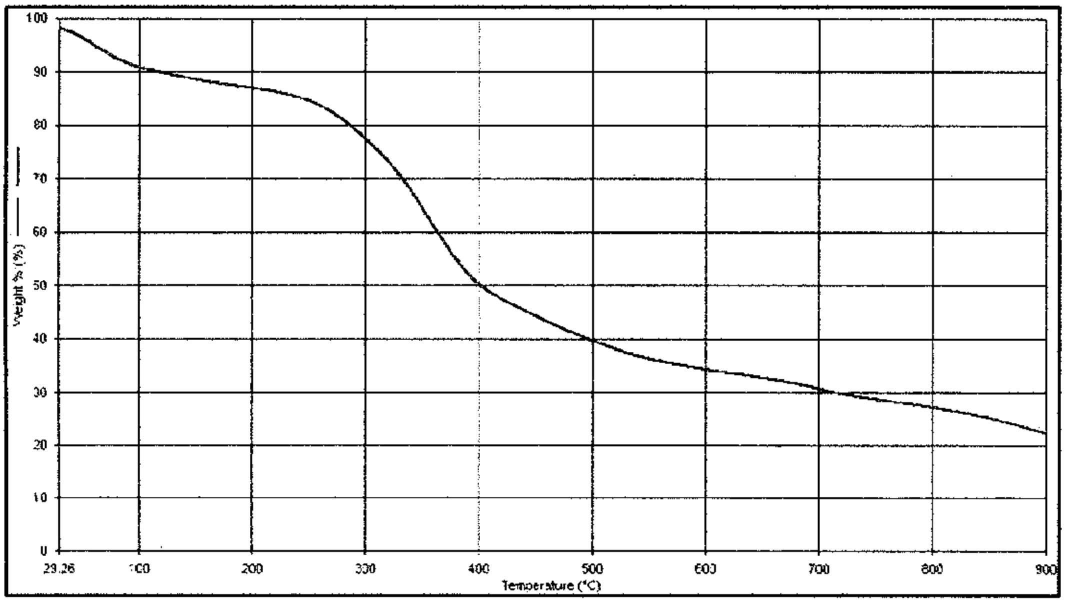

Amount of Hg Ion Sorbed by Rambai Leaves as a Function of Initial Contact Time and Initial Concentration (Trial 1)


Amount of Hg Ion Sorbed by Rambai Leaves as a Function of Initial Contact Time and Initial Concentration (Trial 2)

Rate = 15°C/min



Rate = 20°C/min



APPENDIX IV

EQUIPMENTS DETAILS

Reference:

- http://www.dt.navy.mil/sur-str-mat/fun-mat/fir-pro-sea/the-gra-ana/index.html,
- http://www.dt.navy.mil/sur-str-mat/fun-mat/fir-pro-sea/the-gra-ana/index.html,
- http://en.wikipedia.org/wiki/Scanning_electron_microscope
- www.lpdlabservices.co.uk/analytical_techniques/sem/index.php
- http://en.wikipedia.org/wiki/Fourier_transform_spectroscopy

1) SEM-EDX

SEM-EDX is the name of the energy-dispersive X-ray spectroscopy analysis conducted by means of SEM. It allows determining the chemical composition of a specimen, for instance soot particles formed in the combustion of Diesel engines or biomass, as well as its morphology and structure. The information on particle composition and morphology is extremely useful for understanding the expected life of components like a gas turbine fed though gasification of biomass or a diesel particulate filter and quality of air.

Principle

An SEM is essentially a high magnification microscope, which uses a focussed scanned electron beam to produce images of the sample, both top-down and, with the necessary sample preparation, cross-sections. The primary electron beam interacts with the sample in a number of key ways:-

- Primary electrons generate low energy secondary electrons, which tend to emphasise the topographic nature of the specimen
- Primary electrons can be backscattered which produces images with a high degree of atomic number (Z) contrast

- Ionized atoms can relax by electron shell-to-shell transitions, which lead to either X-ray emission or Auger electron ejection. The X-rays emitted are characteristic of the elements in the top few μm of the sample.

Applications

The SEM instrument has many applications across different industry sectors. The extremely high magnification images together with localised chemical information mean the instrument is capable of solving a great deal of common industrial issues such as particle analysis, defect identification materials and metallurgical problems. LPD Lab Services has extensive experience in using SEM/EDX in the following industrial sectors; electronics and semiconductor, pharmaceutical, petrochemicals, plastics and polymers etc.

Range of materials:-

- Metals, Glass and Ceramics
- Semiconductors
- Plastics
- Powders and Dust
- Fibres (Textile, glass, asbestos, natural)

Range of applications:-

- Classification of materials
- Failure and defect analysis
- Examination of surface morphology (including stereo imaging)
- Analysis and identification of surface and airborne contamination
- Powder morphology, particle size and analysis
- Cleaning problems and chemical etching
- Welding and joining technology
- Paints and coating failures
- Identification and elimination of corrosion and oxidization problems.

Examples Applications / Case Studies

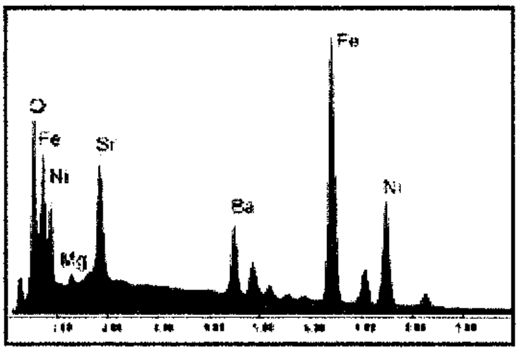
Image Magnification, Measurement and Resolution: The image is of the surface of a metal stamper used to imprint the information onto a compact disc during manufacture. The image was taken at a magnification of X 40,000 on the SEM. The photograph illustrates the shape and structure of individual bits of information. The height, roughness and steepness of the sidewalls of the information are all critical to the manufacture of a good disc, as is the separation between adjacent tracks. The second image is of a fracture section through a pellet made of tungsten powder that has been sintered and then sputter coated with an alloy of osmium and ruthenium.

The output from both the secondary electron and backscatter detectors has been mixed together on the SEM to highlight the sputtered layer on the surface of the pellet. This enables accurate measurement of the thickness of the sputtered layer and shows the growth structure through the layer. The thickness of the layer was measured at 640 nm.

Analysis of Thin Films:

EDX analysis was carried out on a thin evaporated layer on top of a nickel / iron alloy.

The layer contained a mixture of barium, strontium and oxygen, with a small amount of magnesium. The thickness of the layer was calculated to be ~ 38 nm.



2) CVAFS

Cold vapour atomic fluorescence spectroscopy, sometimes referred to by the acronym CVAFS, is a subset of the analytical technique known as atomic fluorescence spectroscopy (AFS). Used in the measurement of trace amounts of volatile heavy metals such as mercury, cold vapour AFS makes use of the unique characteristic of mercury that allows vapour measurement at room temperature. Free mercury atoms in a carrier gas are excited by a collimated ultraviolet light source at 253.7 nm. The excited atoms re-radiate their absorbed energy (fluoresce) at this same wavelength. Unlike the directional excitation source, the fluorescence is omni-directional and may thus be detected using a photomultiplier tube or UV photodiode. The technique differs from the more conventional atomic absorption (AA) technique in that it is more sensitive, more selective, and is linear over a wide range of concentrations. However, any molecular species present in the carrier gas will quench the fluorescence signal and for this reason, the technique is most commonly used with an inert carrier gas such as argon.

Gold coated traps may be used to collect mercury in ambient air or other media. The traps are then heated, releasing the mercury from the gold while passing argon through the cartridge. This pre-concentrates the mercury, increasing sensitivity, and also transfers the mercury into an inert gas.

A number of companies have commercialized mercury Detection via CVAFS and produced transportable analysers capable of measuring mercury in ambient air. These devices can measure levels in the low parts per quadrillion range. (10-15)

Various analytical methods approved by the United States Environmental Protection Agency are in common use. US EPA Methods 245.7 and EPA Method 1631, are commonly used methods for mercury measurement in waters and industrial effluents using CVAFS.

3) FTIR

Infrared spectroscopy (IR spectroscopy) is the subset of spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify compounds or investigate sample composition. Infrared spectroscopy correlation tables are tabulated in the literature.

Background and Theory

The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400-10 cm^{-1} (1000–30 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 4000-400 cm^{-1} (30–1.4 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately 14000-4000 cm^{-1} (1.4–0.8 μm) can excite overtone or harmonic vibrations. The names and classifications of these subregions are merely conventions. They are neither strict divisions nor based on exact molecular or electromagnetic properties.

Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes). These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole. In particular, in the Born-Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

Simple diatomic molecules have only one bond, which may stretch. More complex molecules have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups. For example, the atoms in a CH_2 group, commonly found in organic compounds can vibrate in six different ways: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting:

The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures.

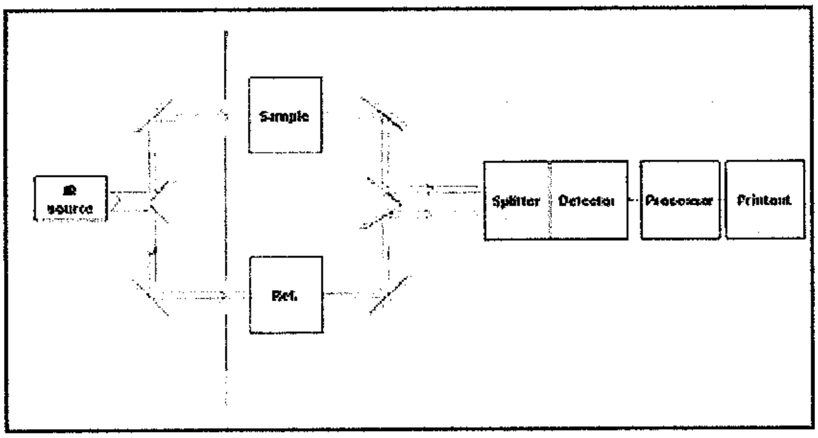
Sample preparation

Gaseous samples require little preparation beyond purification, but a sample cell with a long pathlength (typically 5-10 cm) is normally needed, as gases show relatively weak absorbances. Liquid samples can be sandwiched between two plates of a high purity salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and will not introduce any lines onto the spectra. Some salt plates are highly soluble in water, so the sample and washing reagents must be anhydrous (without water).

Solid samples can be prepared in four major ways. The first is to crush the sample with a mulling agent (usually nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is applied onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.

The third technique is the Cast Film technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis. The final method is to use microtomy to cut a thin (20-100 micrometre) film from a solid sample. This is one of the most important ways of analysing failed plastic products for example because the integrity of the solid is preserved. It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

Typical method



Typical apparatus

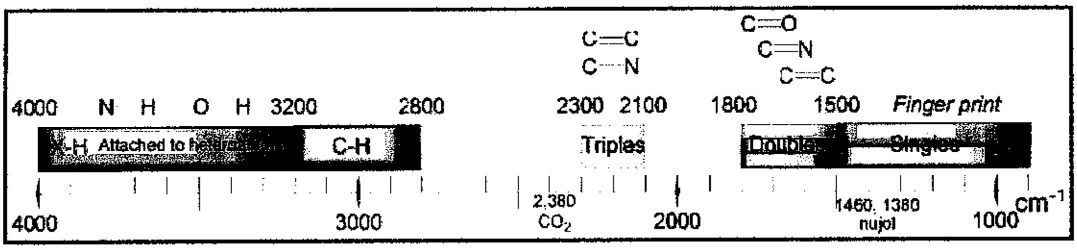
A beam of infrared light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in. The beams are both reflected back towards a detector, however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.

A reference is used for two reasons:

- This prevents fluctuations in the output of the source affecting the data
- This allows the effects of the solvent to be cancelled out (the reference is usually a pure form of the solvent the sample is in)

Summary of absorptions of bonds in organic molecules

Infrared Spectroscopy Correlation Table Wavenumbers listed in cm^{-1}.



Uses and applications

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. It is of especial use in forensic analysis in both criminal and civil cases, enabling identification of polymer degradation for example. It is perhaps the most widely used method of applied spectroscopy.

The instruments are now small, and can be transported, even for use in field trials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage. By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research instruments can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Techniques have been developed to assess the quality of tea-leaves using infrared spectroscopy. This will mean that highly trained experts (also called 'noses') can be used more sparingly, at a significant cost saving. Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc. In physical and analytical chemistry, infrared spectroscopy ("IR spectroscopy") is a technique used to identify chemical compounds based on how infrared radiation is absorbed by the compounds' chemical bonds. This article is an IR spectroscopy correlation table that lists some general absorption peaks for common types of atomic bonds and functional groups. Note that this information is unreferenced, and may not be accurate.

4) TGA

Thermal gravimetric analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and de-convolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Analyzer

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection. A method known as hi-res TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified. Several modern TGA devices can vent burn-off to a Fourier-transform infrared spectrophotometer to analyze composition.