CERTIFICATION OF APPROVAL

Removal of Heavy Metals Using Fish Scales

by

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ABSTRACT

The selection of activated carbon has always preceded other adsorbents as the material is the most versatile adsorbent in industry. However, the trend nowadays is aimed at diversifying the origin of adsorbent most of which comes from micro organisms and biomass product. This project is aimed to study the feasibility of using fish scale as industrial adsorbent to remove heavy metal from its aqueous solution. The adsorptive nature of three types of metals namely Copper (Cu), Nickel (Ni) and Lead (Pb) on fish scale are studied independently.

These objectives were achieved via batch experiment whereby a set of metal solution is added with the fish scales and the adsorption test was carried out. The fish scales were first washed with deionized water and further grinded into powdered form (<500μm). Fish scales activation was not implemented in this study. The effects of initial metal concentration and temperature were studied in the adsorption test. The effect of initial metal concentration was studied at 10ppm, 30ppm and 50ppm while the effect of temperature was studied at 20°C, 30°C, 40°C and 50°C. Atomic Absorption Spectrophotometer (A.A.S) was used to determine the concentration of the identified metal in the particular solution. Fourier Transform Infrared Spectrophotometer (FTIR) was used to determine the functional group of the fish scales.

Batch experiments and isotherm kinetics studies were carried out to investigate the effect of contact time, initial concentration of the adsorbate, particle size and temperature. It was noted that an increase in the metal concentration and temperature and a reduction in particle size resulted in an increase in the metal uptake per unit weight of adsorbent. For temperature effect, however the trend increases up to a maximum temperature then decreases. The maximum temperature depends on the type of heavy metal and they differ from one another.

Langmuir and Freundlich adsorption isotherms were applied to calculate the thermodynamics properties of the adsorption process. The feasibility and

spontaneous nature of adsorption process is well confirmed from the negative values of $-\Delta G^{o}$. The positive values of enthalpy change (ΔH^{o}) further suggest the endothermic nature, while positive ΔS^{o} values reflect the affinity of the adsorbent materials towards lead and also as an indication that the disorder of the adsorption process increases. The FTIR analysis showed that there are a lot of functional group that exist on the surface of the fish scales; hydroxyl, carbonyl, carboxyl, amides, amines, and esters.

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ABBREVIATIONS AND NOMENCLATURES

Cu = Copper

Ni = Nickel

Pb = Lead

V = Volume of metal-bearing solution contacted with the sorbent. [L]

C_i = Initial concentration of the metal in the solution [mg/L]

C_f = Equilibrium concentration of the metal in the solution [mg/L]

S = Amount of added sorbent on dry basis. [g]

q_{eq} = Equilibrium metal uptake (mg/g)

B = Langmuir isotherm constant

K, n = Freundlich isotherm constant

ΔG^o = Gibbs Free Energy (J/mol)

ΔH^o = Enthalpy (kJ/mol)

ΔS^o = Entropy (J/mol)

AAS = Atomic Absorption Spectrophotometer

FTIR = Fourier Transform Infrared Spectrophotometer

BET = Brunauer, Emmett and Teller Test Method

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF WORK

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain [13].

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down. (metabolized) [13].

One of the many technologies of heavy metals removal is via sorption. In this study, the main type of sorption mechanism that is involved is adsorption. Adsorption is a process of using solids to remove substances from either gaseous or liquid solution. From the early days of using bone char for decolorization of sugar solutions and other foods, to the later implementation of activated carbon for removing a wide range of organic compounds, the adsorption phenomenon has become a useful tool for both purification and separation [8].

The process of 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. Physical adsorption is caused mainly by van der Waals and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized by surface properties mainly specific surface area [13]. Below shows a diagram of the mechanism of how the heavy metals could be transported to our body.

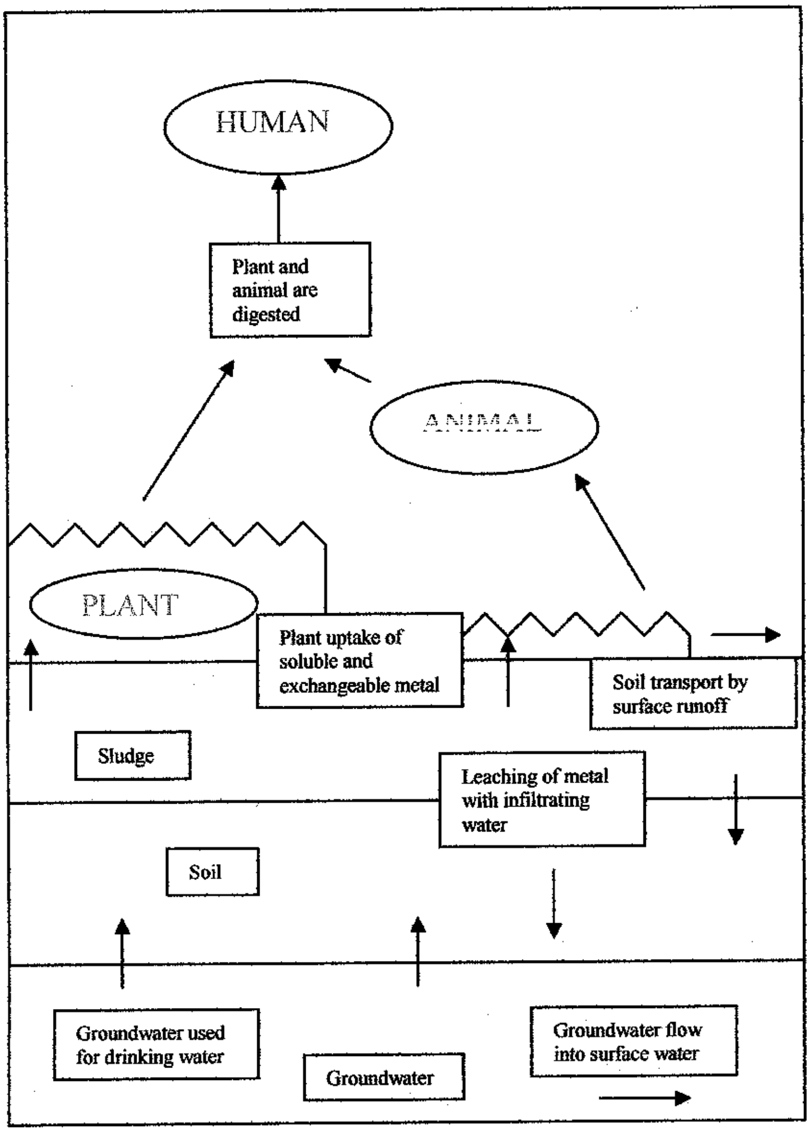

Figure 1.1: Transport of Heavy Metals to Human Body

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Activated carbon has been long recognized as one of the most versatile adsorbents to be used for the effective removal of low concentrations of organic substances from solution. Most modern water treatment plants use powdered activated carbon for control of tastes and odors of biological or industrial origin in batch processes. Alternative adsorbents are gaining popularity as most carbonaceous materials needs to undergo two major processes before it can be used as activated carbon; carbonization followed by activation. Carbonization (pyrolysis) is mainly a heating process in the absence of air to temperature usually below 600^0C. The following process which is treating the chars with oxidizing agents such as steam, carbon dioxide, or oxygen at elevated temperatures, 800^0C – 900^0C is called activation [8]. In spite a rather complex preparation, the usage of activated carbon also requires high capital and regeneration cost.

The use of by-product from biomass would be the most ideal alternative adsorbents since these materials are not fully utilized in industry and often regarded as waste. Feathers, animal bone, crab shell and fish scale are some examples of by-product from biomass. In this research, fish scale was used as a possible alternative to remove heavy metals from aqueous solution.

1.2.2 Significance of the Project

The technology of biosorption (adsorption using biomass) is relatively new in the industry. However early research have shown success using materials of biological origin for the removal of heavy metals. For example; Aksu and Kutsal used the biomass *Chlorella vulgaris* for the removal of lead ions from wastewater. Baldry and Dean used *Escherichia coli* to adsorp copper ions from aqueous solution. With the completion of this project, it is hoped that another possible adsorbent be utilized in the industry which is fish scale. This research could be used as a platform for better understanding of the potential of fish scale as industrial adsorbent.

1.3. OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objective

The objectives of the project are as follows;

1. To study the characterization of fish scales to further understand the process of adsorption of heavy metals using fish scale.
2. To conduct experimental test to the determine the adsorption capacity of three identified metal ions (copper, nickel, lead) using fish scale
3. To determine the effect of temperature and initial metal concentration on the adsorption capacity

1.3.2 Scope of Study

This project would cover the determination of adsorptive capacity of fish scale towards three types of heavy metals (copper, nickel, and lead). There are many parameters or factors that needed to be studied in this particular project. The experiments of the removal of heavy metals will be done in batch process. Operating parameters such as temperature and initial metal concentration will also be manipulated to determine the effect of each in the process of heavy metals removal. Apart from that, the effect of particle size of the fish scales would also be incorporated in the research.

A research will also be done to study the characterization of the fish scale. Physical characteristics such as specific surface area and pore size distribution will be studied to improve the understanding of the adsorption process of heavy metals. As with all biomass products, the metal uptake by these materials was attributed to their constituents of carbohydrates, proteins, and lignin which contains functional groups such as carboxyl, hydroxyl and amine groups that are responsible for the metal sorption. A further study of this matter is also planned on commencing.

CHAPTER 2

LITERATURE REVIEW / THEORY

2.1 THEORY

2.1.1 Heavy Metals

In the research, three heavy metals were identified (Copper Cu, Nickel Ni and Lead Pb). Each heavy metal and its associated effects to both the environment and humans are discussed.

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth [13].

Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains [13].

In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing fetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system [13]. Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead. In the general non-smoking, adult population the major exposure pathway is from food and water [13].

2.1.2 Adsorption

An adsorption phenomenon is present in most natural physical, biological and chemical systems. This process of adsorption involves the separation of one substance, called adsorbate, from one phase to be accumulated or concentrated at the surface of another, called adsorbent. This is different from absorption where in the process of absorption, the solute would form a 'solution' with the absorbent.

The overall adsorption process consists of a series of steps. When the fluid is mixed together with the adsorbent particles, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then, the solute diffuses inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface of the adsorbent. The adsorption process would usually occur as a mono-layer on the surface of the fine pores. Four principal types of adsorption exist; exchange, physical, chemical, and specific could be identified, depending upon the attractive force that exists between the adsorbate and the adsorbent [8]. Exchange adsorption involves an electrostatic attachment of ionic species to sites of opposite charge at the surface of the adsorbent. Physical adsorption results from the effect of Van der Waals forces, which are made up from both London dispersion forces and the electrostatic forces.

Chemical adsorption involves a reaction that would occur between the adsorbate and adsorbent. This would result in a change in the chemical form of the adsorbate. The resulting chemical adsorption force is usually that are derived from the physical Van der Waals forces. Lastly, the attachment of adsorbate molecules at functional groups on adsorbent surfaces can also result from specific interactions that do not result in adsorbate transformation. These specific adsorptions exhibit a range of binding energies ranging from adsorbidity values commonly associated with physical adsorption to the higher energies associated with chemisorption.

The extent of adsorption would depend heavily by the solvophobicity of the compound, which is its 'dislike' for, or insolubility in the solvent phase [8]. The greater is the insolubility of the adsorbate in the solvent, the greater is the tendency for the adsorbate to be adsorbed from the solvent onto the adsorbent. Bonding between the adsorbate and the solvent must firstly be broken in order for the adsorption process to be continued. The greater the solubility of the compound, the stronger is the bond, and hence the lower is the extent of adsorption.

Another factor that would also influence the extent of adsorption is the affinity of the adsorbate for the surface of the adsorbent. If the affinity of adsorbate to the adsorbent is stronger than the bond that exists between adsorbate and its solvent, the adsorption process would occur.

A number of parameters specific to the adsorption system will affect the adsorption process. For the adsorbate, they include concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration and the nature of background or competitive adsorbates [8]. For the adsorbent, the most important factors that would determine the extent of adsorption process would include surface area, the physicochemical nature of the surface, the availability of that surface to adsorbate molecules and the physical size and form of the adsorbent particles [8]. System parameters such as temperature and pH can also influence the adsorption process to the extent that they effect changes in any one or more of the parameters mentioned above.

The main study was done to understand the different factors that affect adsorption. Since the adsorption process results in a concentration of solutes at the surface, it is obvious that the surface area is one of the many important factors. The adsorption capacity generally is proportional to the specific surface area [8, 9]. However pore structure should also be noted since micropores that are not accessible by the solute may contribute a major portion of the specific surface area. Therefore it is reasonably to expect that the solute will readily penetrate into pores that only have certain diameter. In other words, the surface area accessible to the sorbate will be influenced by its molecular size, and only those pores that are accessible to the sorbate will contribute to the effective surface area [9].

Another factor that affects adsorption is the particle size as well. The surface area of nonporous adsorbents increases considerably with a decrease in particle size [9]. Consequently, the adsorptive capacity should increase with reduction in particle diameter. Hence, in the experiment the recommended shape for the fish scale adsorbent to be is in powdered form.

In this study, two operating parameters were manipulated; temperature and also initial metal concentration. The increase of the initial concentration induced an increase in the slope of the curves of metal uptake versus time. The saturation of the adsorbent used was achieved more rapidly at higher influent concentrations [7]. As for temperature, the increase in temperature would result in an increase in adsorption capacity as well. This increment can be explained by the dissociation of some compounds available at the surface of the fish scale which respond to metal adsorption thus providing more sites for metal adsorption [9].

2.1.3. Biosorption

Biosorption is the removal or recovery of free metal ions from a solution by biosorbent. The biosorbent, unlike mono functional ion exchange resins, contains variety of functional sites including carboxyl, imidazole, sulphydryl, amino, phosphate, sulphate, thioether, phenol, carbonyl, amide and hydroxyl moieties [18].

It has long been recognised that many biological materials would accumulate metals. Much of the past researches emphasis have been on the investigation of the utilisation of various microorganism for metal adsorption. However, there is a growing indication that various plant and animal body parts can also be used to accumulate metals (e.g animal bone, bird's feathers). The utilization of microorganisms as the adsorbent is generally attractive, due to the fact that it grows rapidly, is relatively inexpensive to generate and has been demonstrated to have adsorption capacities that are comparable to various other adsorbents.

Biosorption have similar applications to conventional water treatment processes such as ion exchange or activated carbon in wastewater industries. The major advantages offered by biosorbents compared to other methods are the higher percent removal at low-metal-contaminant levels. So, the biological materials could effectively treat lower concentration influents and reach a lower level of effluent concentration. Biosorbents are also more selective for transition and heavy metals, thus making it a better alternative to other adsorbents currently available to the market.

When choosing the biomass for metal biosorption, its origin is a major factor to be taken into account. Biomass can come from (i) industrial wastes which should be obtained free of charge; (ii) organisms easily available in large amounts in nature; and (iii) organisms of quick growth, especially cultivated or propagated for biosorption purposes [19]. Cost effectiveness is the main attraction of metal biosorption, and it should be kept that way. Not only could microbial biomass be used directly, but biosorbents derived from animal/plant should be most low-priced for economical metal-removal process applications.

2.1.4. Mechanisms of Biosorption

Biosorption mechanisms are mainly the same to that of adsorption. Although a generalization of the mechanisms could be drawn, the effective biosorption mechanism is highly dependent on the type of biomass that was being used, the type of metal utilised and the operating conditions of the experiments. Biosorbents mainly has the same materials at the surface area of the biosorbent which is complex protein. The cell walls and internal materials within the biomass offer particularly abundant sites for the adsorption of metal ions [18]. Biological components have large amount of polysaccharides, proteins and lipids that are replete with metal binding functional groups including carboxyl, hydroxyl, sulfate, phosphate and amino groups [18].

Due to the fact that so many potential binding sites exist, it is difficult to identify clearly those that are specifically responsible for the primary binding of metals to cellular components. It can be shown that the fish scales in fact do have a lot of functional group at its surface sites.

2.1.5. Components in Fish Scale

The type of fish scales in this study is 'ikan jenahak' or *Lutjanus argentimaculatus* a.k.a. mangrove jack [17]. The Mangrove Jack is greenish brown to reddish. Juveniles have pale bars on the sides of the body and one or two blue lines on the cheeks. This species has an emarginate caudal fin and scale rows on the back that are roughly parallel to the lateral line. It grows up to 1.2 m in length. Juveniles usually live in mangrove estuaries and freshwater streams. Adults live on deeper offshore reefs down to depths of at least 100 m. The Mangrove Jack live in tropical and some warm temperate marine waters of the Indo-West and Central Pacific.

There are many different types of scales; the Mangrove Jack has the cycloid and ctenoid type [17]. Cycloid and ctenoid scales are found in the majority of bony fishes. The anterior part of each scale is usually overlapped by the posterior portion of the scale in front. This arrangement of imbricate (overlapping) scales gives the fish greater flexibility. Ctenoid scales have a variously developed spiny posterior margin meaning comb, and refers to the comb-like ctenii on the margin of the scale [17]. Cycloid scales have a smooth posterior margin lacking ctenii. The word 'cycloid' comes from the Greek 'cyclo', meaning circle.

Cycloid and ctenoid scales consist of two main regions, a surface bony layer, composed of an organic framework impregnated largely with calcium based salts, and a deeper fibrous layer composed mainly of collagen [14]. Collagen is a family of highly characteristic fibrous proteins found in all multicellular animals which are the most abundant proteins found in mammals, constituting 25% of the total protein mass [14]. The characteristic feature of a typical protein molecule is its long, stiff, triple-stranded helical structure in which three collagen polypeptide chains (called α chains) are wound around each other forming a rope-like super helix. Collagen is extremely rich in the amino acids proline and glycine. Further studies on the active group of the collagen are recommended to further understand the adsorption process.

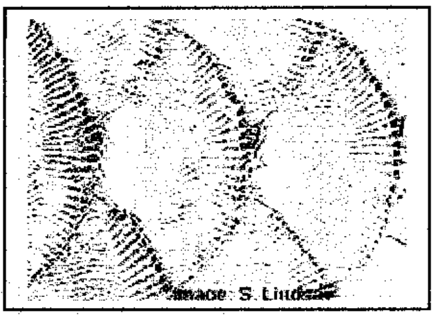

Figure 2.1: Ctenoid scales of *Lutjanus argentimaculatus*

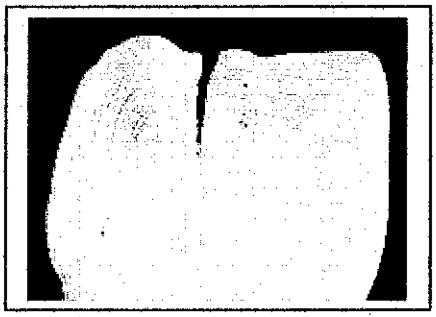

Figure 2.2: Cycloid scales of barramundi

2.1.6. Atomic Absorption Spectrometer

The atomic absorption spectrometry uses absorption of light of intrinsic wavelengths by atoms. All atoms are classified into those having low energies and those having high energies. The state having low energies is called the ground state and the state having high energies is called the excited state. The difference between energies in the ground state and in the excited state is fixed by the element and wavelength of light to be absorbed. Atomic absorption spectrometry uses the hallow cathode lamp (HCL). The HCL gives off light characteristic to the elemental wavelength being measured. Thus, the light absorbed measures the atomic density.

The principle mentioned above can be applied to light absorption of 'Free Atoms'. A free atom means an atom not combined with other atoms. However, elements in the sample to be analysed are not in the free state and are combined with other elements invariably to make a so-called molecule. For example, sodium in the seawater mainly combines with chlorine to form NaCl molecule. Absorption cannot be done on samples in the molecule state, because molecules do not absorb light.

The combination must be cut off by some means to free the atoms. This is called atomisation. The most popular method of atomization is dissociation by heat. Samples are heated to a high temperature so that molecules are converted into free atoms. For example; a sample of calcium chloride is tested. In the burner, the sample is atomised by a nebulizer at first. Then, big water drops are discharged into the drain, and only fine mist is mixed with fuel, and oxidant in the atomizer chamber and sent to the flame. When they get in the flame, the mist evaporates instantaneously and fine particles of calcium chloride are dissolved by heat and free calcium atoms and chloride atoms are produced.

If the beam of light at wavelength 422.7nm (Ca) is introduced through this part of the flame, atomic absorption and thus the concentration of the atom can be measured. Many combinations of various gases have been tested as the flame for atomisation. In the consideration of analysis sensitivity, safety, easy use, cost and other points, there are four standard flames used, air-acetylene, nitrous oxide-acetylene, air-hydrogen and argon-hydrogen. These flames are used for each element depending on the temperature and gas characteristics [19].

2.2. LITERATURE REVIEW

Many literature reviews can be found about the usage of biomass product as adsorbents for heavy metals. A few of the examples are animal bones, hair, and feathers. These adsorbents are all keratin based biomass waste, sharing the same characteristic as fish scale. These literature reviews could be a base platform for the study of fish scale as adsorbents. Apart from collagen based biomass, some researchers also utilized macro organisms such as algae.

Animal bones are found to be effective in the adsorption of zinc from aqueous solution. Batch experiments were carried out to investigate the effect of contact time, initial concentration of the adsorbate, particle size, temperature, pH, and addition of salt (NaCl) on this adsorption process [1].

It was noted that an increase in the zinc concentration, temperature, and initial pH of the metal solution resulted in an increase in the metal uptake per unit weight of the sorbent. The decrease in the particle size of the sorbent resulted in an increase in the metal uptake per unit weight of the sorbent. The concentration of salt in the metal solution showed significant influence on the zinc ion sorption by the sorbent. Desorption process was also carried out by using different types of acids and it was found that H_2SO_4 is the most effective desorbent [1].

The removal of lead ions from industrial waste water by different types of natural materials such as animal bone powder, activated carbon, Nile rose plant powder, commercial carbon and ceramics was studied [2]. The adsorption process was affected by various parameters such as contact time, pH and concentration of lead solution. The uptake percent of lead increased by increasing pH value. The uptake percent of lead is increased by decreasing the concentration of lead at constant pH. There was no removal of lead by ceramics.

Another experiment was done to study the effect of initial metal concentration on the copper uptake using animal bones. Column experiments were conducted at 25, 50, 100, 150 and 200 mg/l Cu^{2+} concentrations. The breakthrough data for different initial concentrations of Cu^{2+} showed that the increase of the initial concentration induced an increase in the slope of the metal uptake versus time curves. The saturation of the adsorbent used was achieved more rapidly at higher influent concentrations. At the lowest concentration of Cu ions, the saturation and retention time of the biosorbent bed were higher.

Aside from biomass waste such as animal bone, microorganisms such as algae are proven to be able to adsorb heavy metals as well. The ability of four different algae (three brown and one red) to adsorb Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+} ions was investigated [3]. The metal uptake was dependent on the type of biosorbent, with different accumulation affinities towards the tested elements. The extent of uptake of the different metals with the tested algae was assessed under different conditions such as pH, time of algal residence in solution with the metal, and concentration of algal biomass.

In processing carbonaceous materials into activated carbon, one of the major processes that it needs to undergo is the activation process. The activation process depends on the type of carbonaceous materials; however digestion with acid is the most common. Acid digestion on the adsorption capacity Cu^{2+} and Ni^{2+} by *Chlorella vulgaris* was studied [4]. The influence of HCl pretreatment (0.1 mM) on sorption of Cu^{2+} and Ni^{2+} by *Chlorella vulgaris* was tested using single and binary metal solutions. The optimal initial pH for sorption was 3.5 for Cu^{2+} and 5.5 for Ni^{2+}. The kinetic constant q_e (metal sorption at equilibrium) for sorption of test metals from single and binary metal solutions was increased after pretreatment of the biomass with HCl. The Langmuir adsorption isotherm was developed for describing the various results for metal sorption. In single metal solution, acid pretreatment enhanced q_{max} for Cu^{2+} and Ni^{2+} sorption by approximately 70% and 65%, respectively.

The kinetics and mechanism of lead biosorption by powderized *Rhizopus oligosporus* was studied to determine the mechanism of adsorption [5]. The experimental results shows that the optimum biomass concentration and initial solution pH for lead sorption at initial lead concentrations ranging from 50±200 mg/l was obtained at 0.5 g/l and pH 5, respectively. In term of the ratio of initial lead concentration to biomass concentration ratio, the highest lead adsorption was obtained at 750 mg/g which gave the maximum lead uptake capacity of 126 mg/g.

The experimental data of lead sorption by *R. oligosporus* fitted well to the Langmuir sorption isotherm model, indicating that the sorption was similar to that for an ion-exchange resin. This means that the sorption is a single layer metal adsorption that occurred as a molecular surface coverage [5]. This assumption was confirmed by the examination of lead sorption using transmission electron microscope and energy dispersive X-ray analysis, which showed that during sorption most of the lead was adsorbed on the surface of cell.

A preliminary study on the removal of cadmium by nonmetabolizing live biomass of *Rhizopus oligosporus* from aqueous solution was also presented. The equilibrium of the process was in all cases well described by the Langmuir sorption isotherm, suggesting that the process was a chemical, equilibrated and saturable mechanism which reflected the predominantly site-specific mechanism on the cell surface.

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1. EXPERIMENTAL PROCEDURE

3.1.1. Fish Scale Treatment

1. Fish scales were collected from Pasar Tronoh.

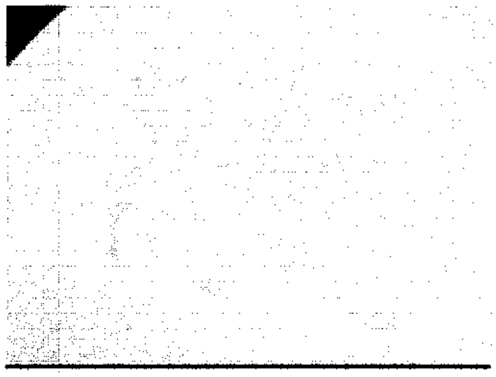

Figure 3.1: Untreated fish scales

2. The scales were cleaned with deionized water for several times and dried. Further drying process was achieved by drying the scales in oven at 120°C for approximately 4 hours.
3. The dried scales were then blended into small particles (<500μm).

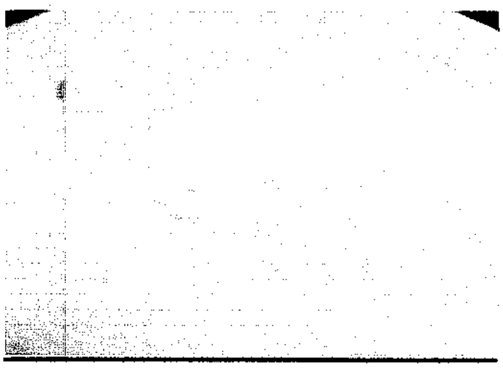

Figure 3.2: Grinded fish scales (<500μm)

3.1.2. Batch Sorption Experiments

1. 20mg/L of Cu, Ni, and Pb solution were prepared.
2. 2.5g of powdered fish scales were poured into 400ml of metal solution.
3. The adsorption process was stopped at 15 minutes for the first beaker, 30 for the second, 45 for the third, 60 for the fourth, 90 for the fifth, and 120 for the last reading for filtration.
4. The solution containing the fish scale was filtered and metal ion concentrations were determined using A.A.S test.
5. To study the effect of temperature, sorption tests were carried out in a temperature water bath controlled at 20, 30, 40 and 50°C.
6. The effect of initial metal concentration (10ppm, 30ppm and 50ppm) on the sorption of heavy metals was investigated by preparing metal ion solution adjusted at different initial metal concentration via dilution.
7. The particle size effect was studied by using different sizes of fish scales (untreated, grinded <500μm).

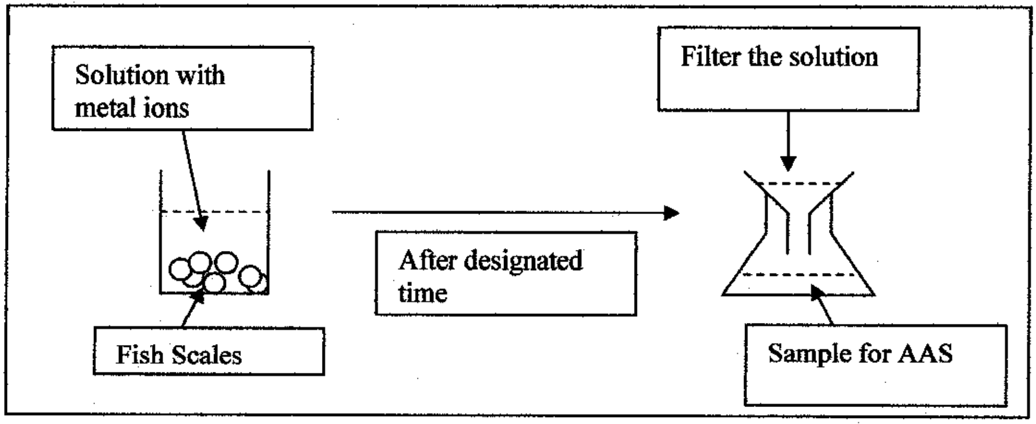

Figure 3.3: Procedure for batch adsorption test

The metal uptake capacity of fish scales would be evaluated using the formula

$$\text{Metal uptake, q} = V[L]x\frac{(C_i - C_f)[mg/L]}{S[g]} \qquad \text{(Equation 1)}$$

V = Volume of metal-bearing solution contacted with the sorbent.

C_I & C_f = Initial and equilibrium concentration of the metal in the solution

S = Amount of added sorbent on dry basis.

The metal uptake could also be analysed by calculating the metal uptake rate as defined by the equation,

$$\text{Percentage adsorbed} = \frac{C_i - C_f}{C_i} \times 100\% \qquad \text{(Equation 2)}$$

3.1.3. Atomic Absorption Spectrophotometer

1. 3 sets of standard solution were prepared whereby the range depends upon the type of element of interest. For example; copper (1ppm, 2ppm, and 4ppm).
2. The standard solutions along with the samples to be determined were poured inside the tube.
3. Using the computer, respective tubes were assigned with their respective numbering. For standard solution, the respective metal concentration was assigned.
4. The Atomic Absorption Spectrophotometer equipment was run.

The atomic absorption spectrophotometer (AAS) is an analytical method based on the absorption of UV or visible light by gaseous atoms. The sample becomes atomized by injecting a solution into a flame or by heating a dried sample in an energized graphite pipe. As source of light, a hollow-cathode lamp (HCL) is used to determine the contained element. These element's atoms in the flame absorb precisely the wavelength sent by the source of light. The absorption is proportional to the concentration. The light produced by the HCL is spectrally divided in the monochromator, and only the resonance line is passed trough the exit slit. [16]

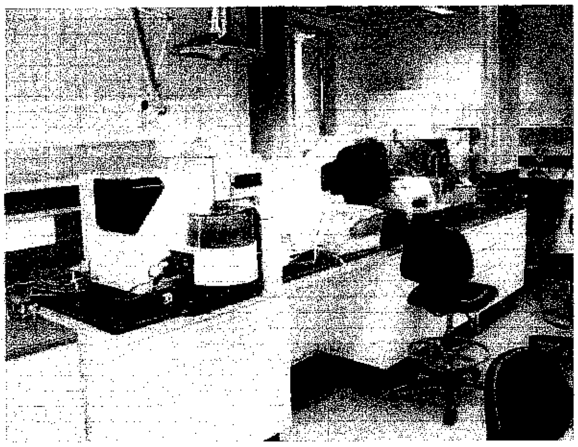

Figure 3.4: Atomic Absorption Spectrophotometer setup

3.1.4. Fourier Transform Infrared Spectrophotometer

Infrared (IR) spectroscopy was the instrumental method most often used for structure determination of numerous organic compounds. IR is very useful in such that it can identify the presence of certain functional groups within a molecule. Infrared radiation comprises the portion of the electromagnetic spectrum between microwaves and visible light. The fraction of the infrared region of most use for structure determination lies between 2.5 x 10^{-6}m and 16 x 10^{-6}m in wavelength. When a molecule absorbs a photon of infrared radiation, its energy increases and this increased energy is associated with bond vibrations, especially one involving the stretching and bending of bonds. Most common functional group absorbs infrared energy at characteristic frequencies in the infrared spectrum. The presence of a peak at a particular frequency can be used to determine whether an unknown molecule contains a certain functional group [21].

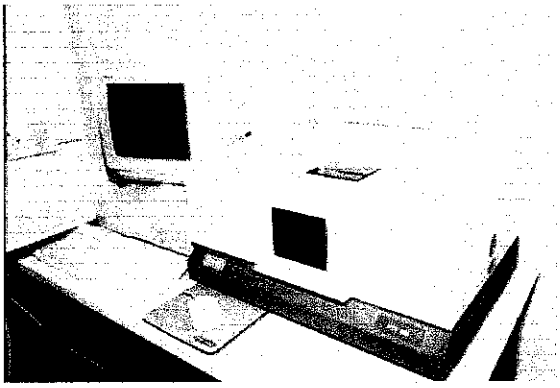

Figure 3.5: Fourier Transform Infrared Spectrophotometer setup

3.1.5. Adsorption Isotherm

Sorption data of heavy metals by fish scales can be correlated with Langmuir and Freundlich isotherm model

$$\frac{1}{q} = \frac{1}{Qo} + \frac{1}{bQo} \text{x} \frac{1}{C} \qquad \text{(Langmuir equation)}$$

$$\log q = \log K + \frac{1}{n} \log C \qquad \text{(Freundlich equation)}$$

whereby q = equilibrium metal uptake (mg/g)

Q_o = metal uptake (mg/g)

C = final concentration (ppm)

b, K, and n = isotherm constant

1. The correlation of the sorption data was plotted using Langmuir and Freundlich isotherm model.
2. Isotherm constants were determined form the plot.
3. Thermodynamics properties of the adsorption process was calculated using the following formula;

ΔG^o = -RT ln b (Gibbs free energy)

$\Delta H^o = -R\left(\frac{T2T1}{T2-T1}\right)\ln\left(\frac{b2}{b1}\right)$ (Enthalpy)

$\Delta S^o = (\Delta H^o - \Delta G^o) / T$ (Entropy)

3.2. TOOLS

Major equipment that is needed in this study is Atomic Absorption Spectrophotometer (A.A.S) and Fourier Transform Infrared Spectrophotometer (FTIR). Other apparatus for example beaker, stirring rod, water bath, chiller, filter funnel, thermometer and others are some normal equipments that are needed as well. Computer software such as Microsoft Word and Excel would also be of help in producing the final dissertation and plotting various data trends.

CHAPTER 4

RESULTS AND DISCUSSION

After the experiments, all the results were tabulated as shown in Appendix 1. After the calculations using Equation 1 and 2, all the results could be shown graphically as follows. In this section, the findings would be explained in great details, offering the possible reasons and explanations to the trends observed. It is important to note that the scales were not chemically activated and the results found from this study could be used as the base performance of fish scales in adsorbing heavy metals.

4.1. PARTICLE SIZE EFFECT

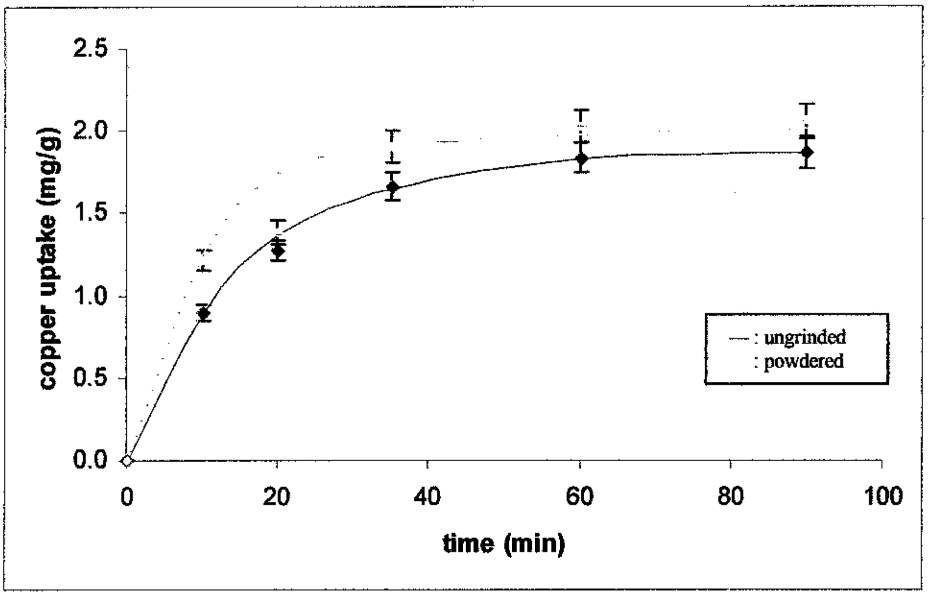

Figure 4.1: Copper uptake (mg/g) by fish scales as a function of time

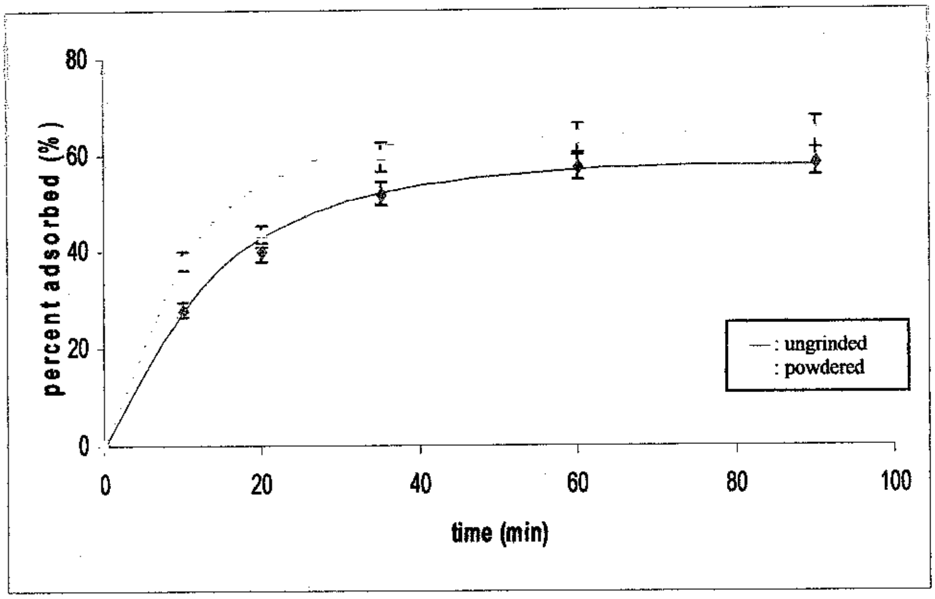

Figure 4.2: Percent removal of copper by fish scales as a function of time

From the particle size effect experiment data (Figure 4.1, 4.2), the maximum capacity of copper uptake up until 90 minutes for both untreated and grinded adsorption is approximately 1.69mg/g and 2.07mg/g which is equivalent to 59% and 65% adsorbed respectively. The increase in copper uptake is approximately 22% by a percent reduction of size of 97.5% from 2cm to 500μm. Adsorption capacity generally is proportional to the specific surface area. And surface area can be enhanced via reducing the diameter of the particles of the adsorbent [9].

For particle size effect experiment, whereby we use the untreated dried fish scales which is approximately 2cm in diameter where else in the other experiment powdered form of fish scales are used instead which is approximately <500μm in size. By having more contact of surface area per the same unit mass by reduction in particle size, we increased the adsorption site for adsorption to occur. For larger particles, the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption [11].

4.2. TEMPERATURE EFFECT

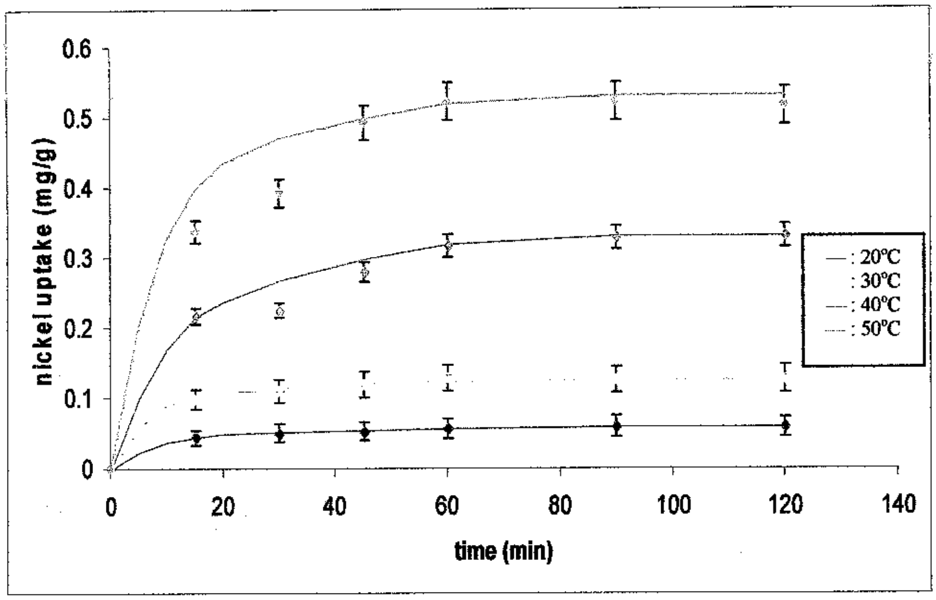

Figure 4.3: Nickel uptake (mg/g) by fish scales as a function of time

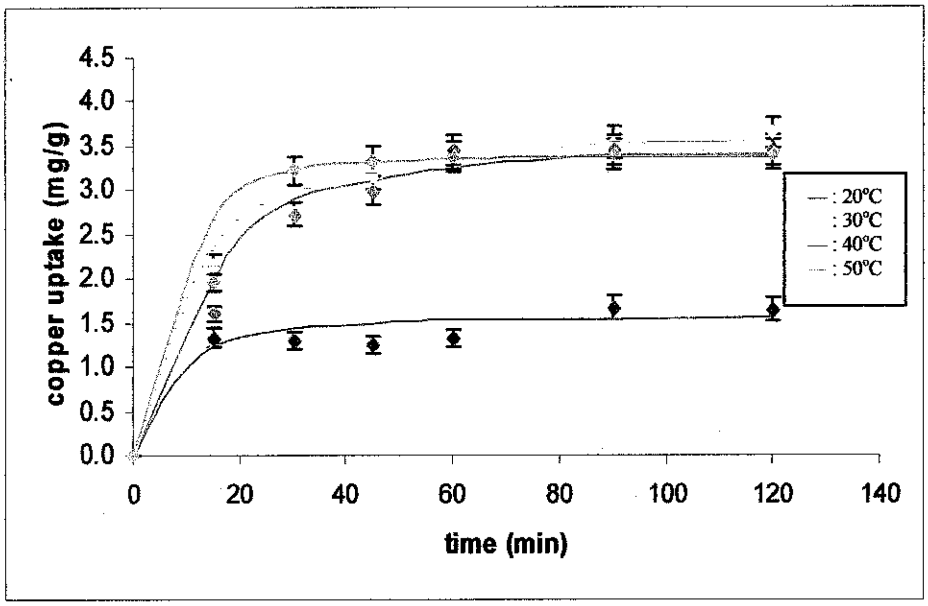

Figure 4.4: Copper uptake (mg/g) by fish scales as a function of time

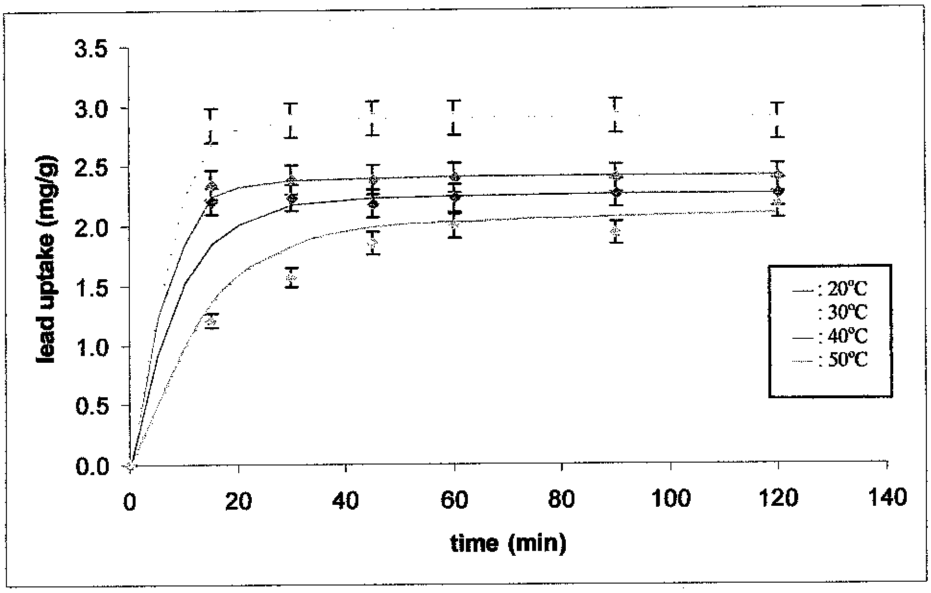

Figure 4.5: Lead uptake (mg/g) by fish scales as a function of time

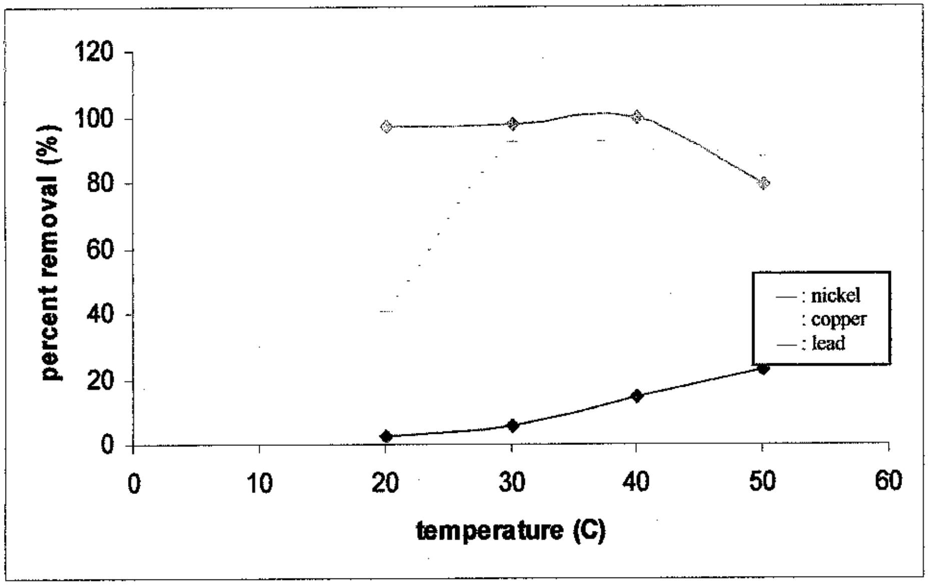

Figure 4.6: Percent removal of heavy metals by fish scales as a function of temperature

The effect of temperature was also studied by ranging the temperature from 20°C, 30°C, 40°C, and 50°C by using chiller and water bath. And as for temperature effect, the general trending is that the percent removal will increase as we increase the temperature up to a maximum temperature before the metal uptake starts to decrease. As for lead, the maximum temperature, for adsorption is at 40°C (99.79% removal) and lowest at 50°C (79.11%) For copper, the maximum temperature for adsorption is 30°C (92.3% removal) while 20°C being the lowest (40.51%). For nickel the maximum is at 50°C (22.85% removal) lowest at 20°C (2.57% removal). The general increase in metal uptake with temperature may be due to the dissociation of certain compound on the surface area thus yielding more adsorption sites. The increase in temperature could also enhance the rate of intraparticle diffusion of adsorbate, and probably due to the change in the sizes of the pore.

Up to a certain maximum temperature, the forward process which is adsorption dominates. However, further increment in the temperature would result in the reverse reaction which is desorption since adsorption is a highly reversible process and highly dependent on operating parameters such as temperature. This theory can be seen from the result whereby the maximum temperature for copper is 30°C, lead at 40°C and nickel at 50°C. Further increment in temperature after the maximum temperature is reached would yield a lower metal uptake value which indicates the following phenomenon to occur.

4.3. INITIAL CONCENTRATION EFFECT

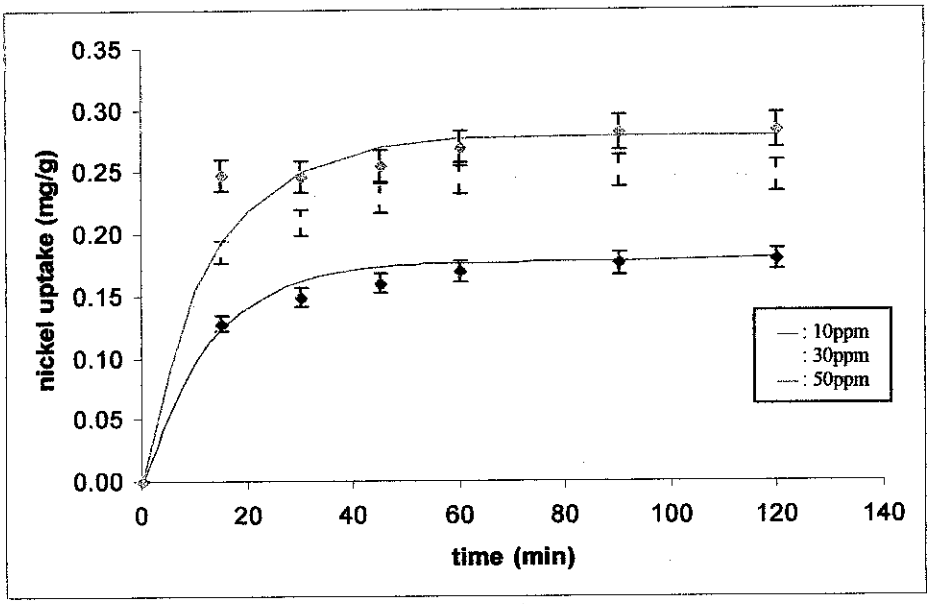

Figure 4.7: Nickel uptake (mg/g) by fish scales as a function of time

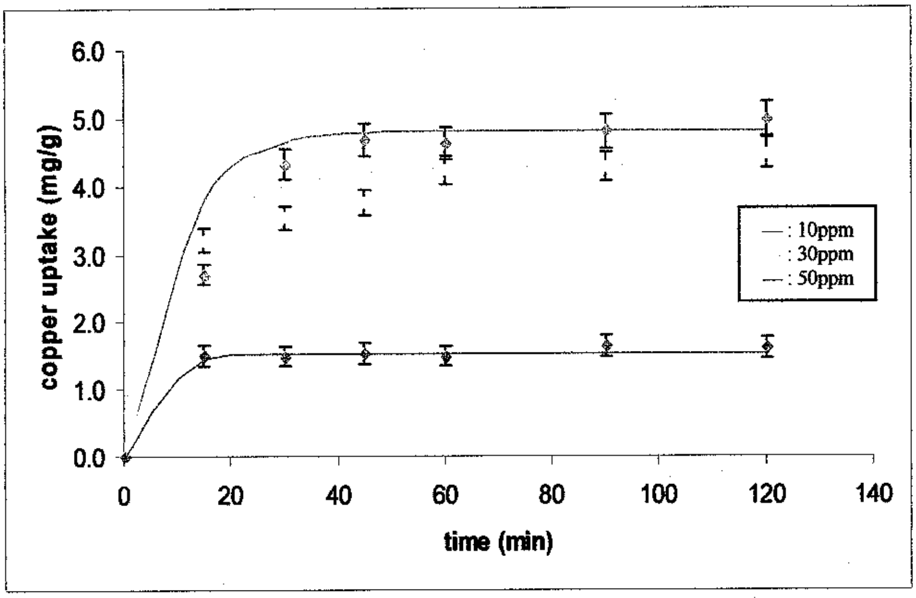

Figure 4.8: Copper uptake (mg/g) by fish scales as a function of time

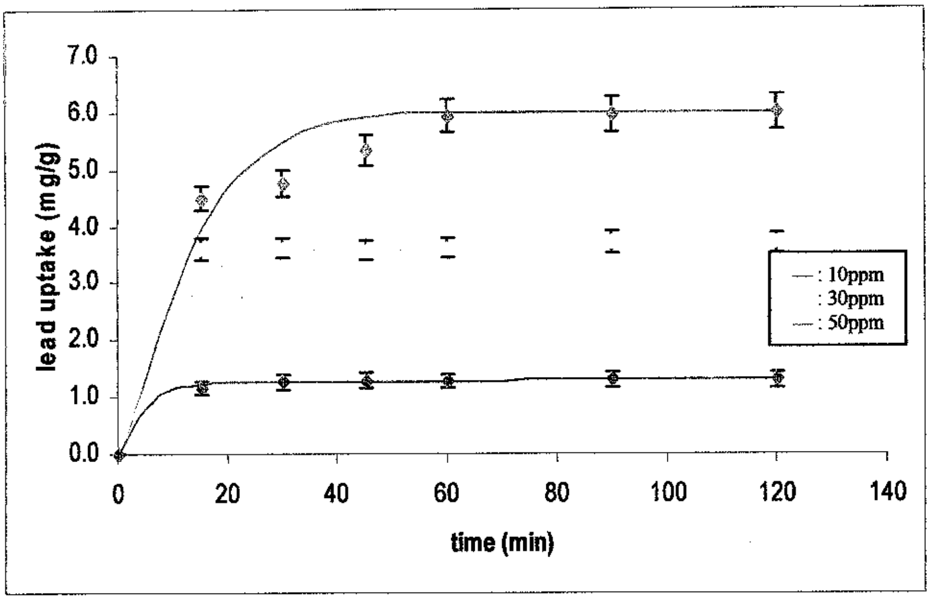

Figure 4.9: Lead uptake (mg/g) by fish scales as a function of time

From Figures 4.7, 4.8 and 4.9, increasing initial metal concentration will result in an increasing trend of equilibrium metal uptake. For lead the equilibrium uptake is 1.3024mg/g (10ppm), 3.608mg/g (30ppm) and 5.9904mg/g (50ppm). For copper the equilibrium uptake is 1.6096mg/g (10ppm), 4.4704mg/g (30ppm) and 4.9728mg/g (50ppm). For nickel the equilibrium uptake is 0.1792mg/g (10ppm), 0.2464mg/g (30ppm), and 0.2832mg/g (50ppm). . As the initial concentration is increased, the amount of metal ions that surround a particular unit of adsorbent would also increase. Hence, this would result in a greater extent of adsorption. The abundance of the metal ions resulted in a greater adsorption capacity. Simply stated, as there are more ions in the metal solution, more adsorption could occur.

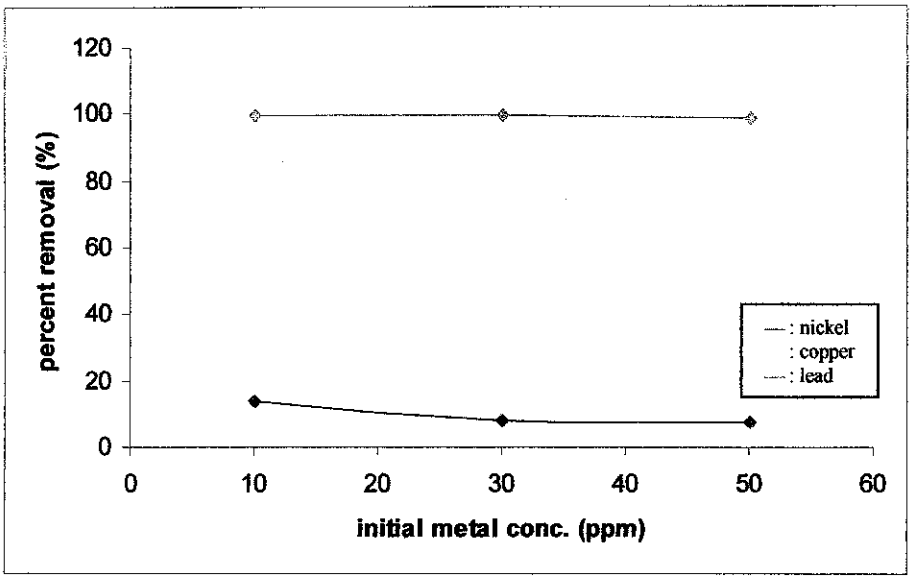

Figure 4.10: Percent removal of heavy metals by fish scales as a function of initial metal concentration

However the percent removal shows a decreasing trend as depicted in Figure 4.10. Percent removal for lead decreases from 99.5%, 99.4% to 98.6% as we increase the initial concentration from 10ppm, 30ppm to 50ppm. Percent removal for copper decreases from 87.0%, 78.4 to 58.8% respectively with increasing initial concentration. And for nickel the percent removal decreases form 14.1%, 8.32% to 7.38%. The decrease in percentage of adsorption indicates that the extent of adsorption does not increase linearly with the initial concentration of metal ions. There would come a point where the increase in initial ion concentration would not increase the extent of adsorption, i.e. when all the adsorption sites are occupied. Apart from that, the extent of competitive nature of the metal ions itself resulted in the decreasing trend of percent removal. All ions are fighting for the same active adsorption site for adsorption to occur. As more ions are available, the extent of competitive nature increases.

All the data in the metal uptake results as a function of time possess the same shape of curve. The sorption rate of metal was very rapid during the initial stages of the sorption process (0 to 20 min). After a very rapid sorption, metal uptake capacity (q) increased slowly with time. It is stipulated that the increase in the metal uptake over time is negligible after 120 minutes (if existed) since the assumption made was that the equilibrium metal uptake was obtained under the 120 minutes time limit. The equilibrium value of lead specific uptake (q_{eq}) by activated carbon from coconut shell [11] was studied and the curve reached equilibrium at 120 minutes.

This type of biosorption is typical for sorption of metals involving metabolically inert biomass, where metal removal from solution is due to purely to physico-chemical interaction between biomass and metal in solution. Two step processes, physical and chemical sorptions, normally occurred during metal sorption. The physical sorption is relatively a fast adsorption step. The rapid increase in metal uptake during the initial stages of metal sorption (0 to 20 min) by powdered fish scales are dominated by physical adsorption which can be categorized as extracellular sorption or surface binding [5].

The second step of metal sorption is a chemical sorption or chemisorption. This step of sorption needs relatively high energy to adsorb metals into the cell interior (intracellular) and the rate is very slow. The second phase of metal sorption (>20 min) which was very much slower than the first sorption phase is dominated by chemical sorption. The chemical sorption or intracellular sorption is a more metabolic process than the physical sorption [5].

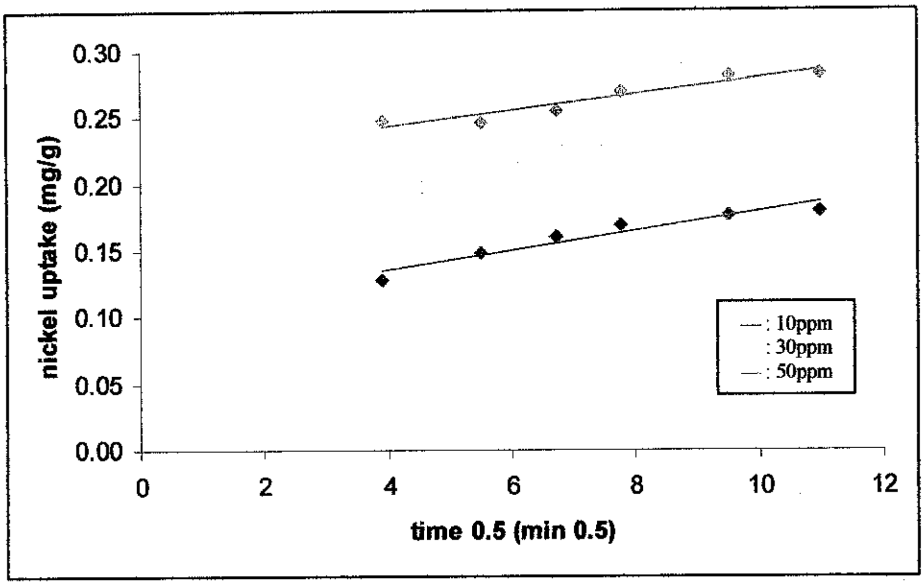

Figure 4.11: Nickel uptake (mg/g) by fish scales against the square root of time

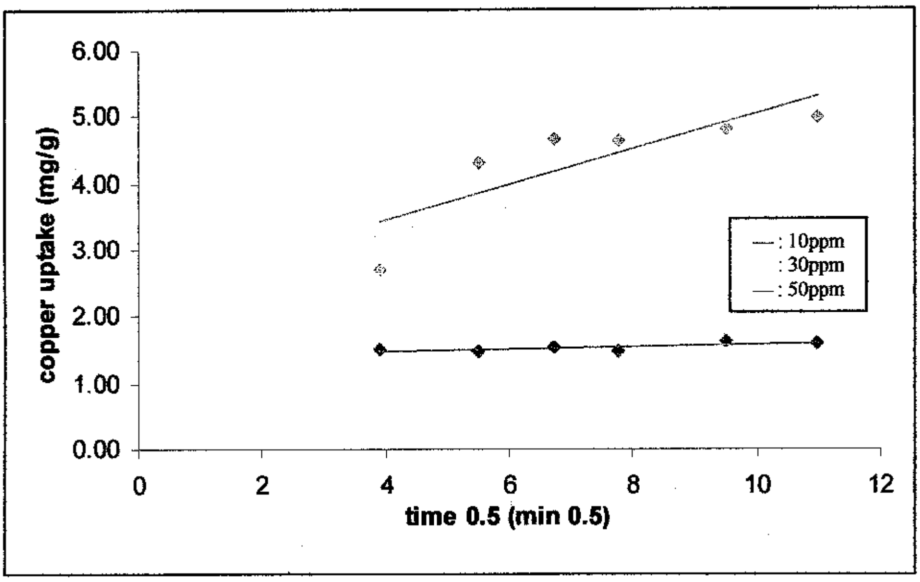

Figure 4.12: Copper uptake (mg/g) by fish scales against the square root of time

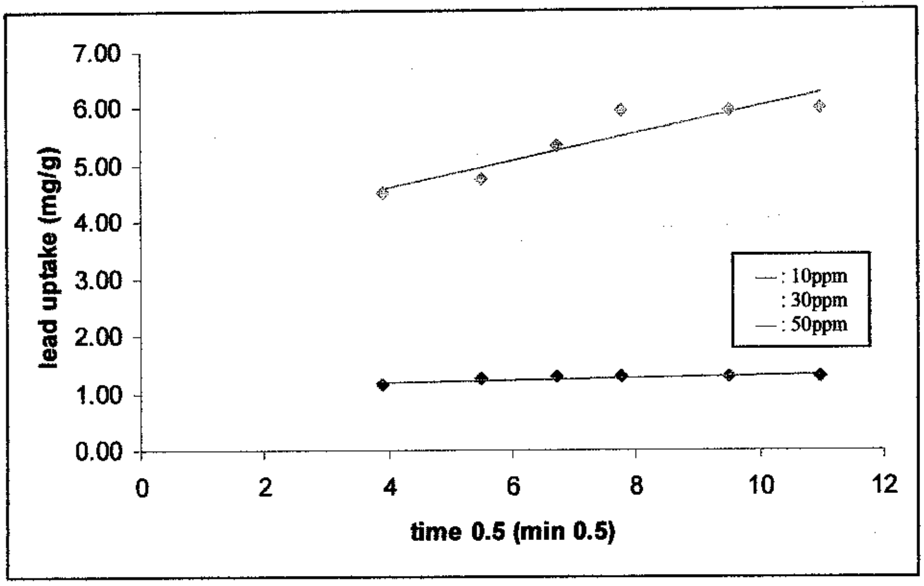

Figure 4.13: Lead uptake (mg/g) by fish scales against the square root of time

From Figures 4.11, 4.12 and 4.13, it could be seen that the plots of metal uptake against the square root of time could be fitted into a straight line. These linear correlations indicate that intrapore diffusion was involved in the sorption process, but it is not the controlling step, because the lines do not pass through the origin. This also gives the reason as to why Lead ions, which have the largest atomic radii among the three ions also showed the greatest extent of adsorption. As the intrapore diffusion is not the controlling step in this adsorption process, the atomic radii of a particular ion is not the prime factor in estimating the extent of adsorption of the ion.

From all the graphs plotted for the metal adsorption process, it could be seen that fish scales are able to adsorb the metal ions tested in this experiment, with preference to Lead (Pb), Copper (Cu) and lastly Nickel (Ni). This trend is apparent with the reference to Figures 4.6 and 4.10. This trend is also consistent with the observations obtained from various other studies where the adsorption of metal ions onto various types of adsorbents also showed that the adsorption of Lead would generally be the greatest among the three, followed by Copper and lastly Nickel.

A mean of explaining the observed trend is possible by using the Irving-Williams theory. The descending order of divalent metal-ion complexes stabilities formed regardless of the nature of complexing nature is as follows:

$$Pb > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg$$

The relative affinity of the adsorbent for free metal ions will increase with the tendency of the ions to enter the inner-space of the adsorbent, which would be related to the ionic radii [8]. However, for the transition metal, the single factor of ionic radii is not enough to fully explain the metal uptake of transition metals. There are other factors that also contribute to metal uptake such as the solvent used, stereochemistry and electronic configuration.

Different biomass types would exhibit different capabilities of binding Lead and Copper. These differences are due to the dissimilar structures and composition of the biomass cell walls that holds the distinctive ligands for metal binding. Generally, it is stipulated that the adsorption of metal ions onto fish scales are largely affected by the amount of protons that are present in the metal atoms. As Lead has the biggest number of atomic number (82) and hence the number of proton in the atoms, it would then have the largest extent of attraction to the adsorption sites. This is followed by the atomic number of Copper that is 29 and lastly Nickel, which is 28.

Apart from the proton inside the nucleus itself, we should also look at the electron configuration of the atom. Higher atomic radii resulted in increase of polarizabilty. The ease with which the charge distribution in a molecule can be distorted by an external electric field is called polarizability. In general, larger molecules tend to have greater polarizabilities because they have a greater number of electrons and their electrons are farther from the nuclei [9]. Because molecular size and mass generally parallel each other, dispersion forces tend to increase in strength with increasing molecular weight.

As the size increases, the energy level also increases hence the ease of polarizibility also increases. The most outer electron is 'free' in the sense of lower energy required to form bonds with the adsorption surface area. For lead of atomic number of 82 (electron configuration; 2:8:18:32:18:4), for copper atomic number of 29 (2:8:18:1) and for nickel 28 (2:8:16:2). Even though the energy level for copper and nickel is the same (4) but copper has only one outer electron, so the adsorption capacity is expected to be higher than nickel.

4.4. ADSORPTION ISOTHERM

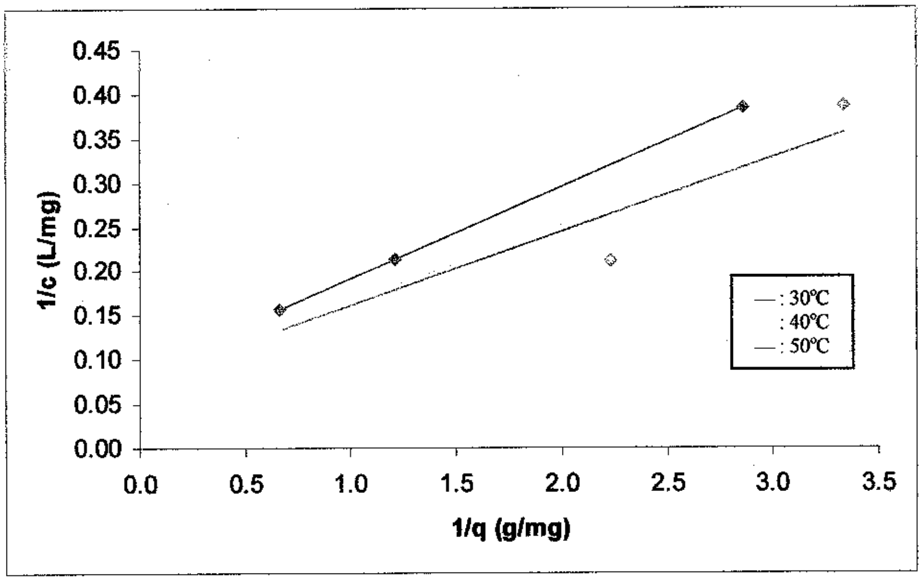

Figure 4.14: Langmuir isotherm for lead

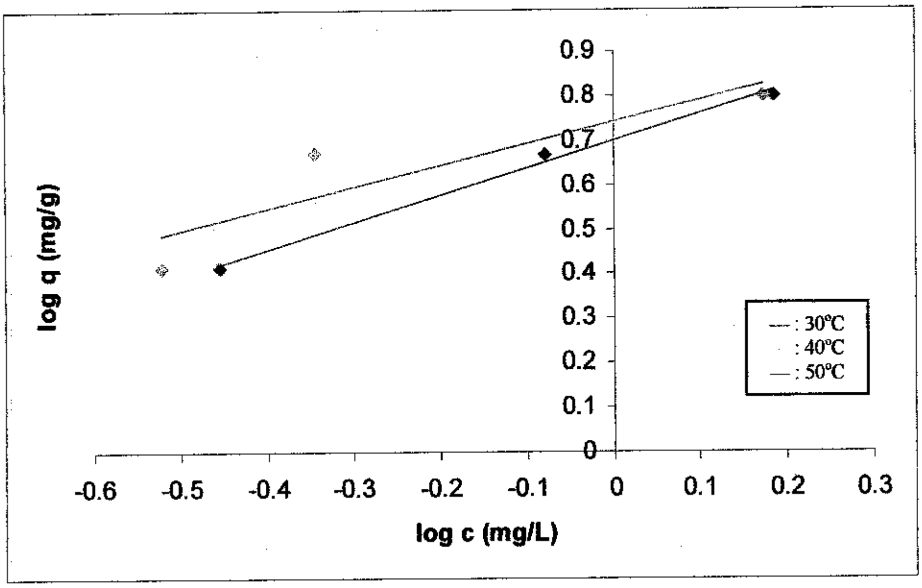

Figure 4.15: Freundlich isotherm for lead

Table 4.1: Thermodynamics properties of adsorption of lead by fish scales

Adsorbent	-ΔG° (J/mol)			ΔH° (kJ/mol)	ΔS° (J/mol)
	30°C	40°C	50°C		
Fish scales	328.37	337.11	59.19	8.809	27.089

In each case, the feasibility and spontaneous nature of adsorption process is well confirmed from the negative values of -ΔG°. It is also observed that in each case, -ΔG° value decreases with the increasing temperature from 30°C to 40°C, indicating thereby greater adsorption at higher temperature. However the metal uptake reduces at temperature of 50°C as indicated by the high -ΔG° (59.19J/mol) value at 50°C. The positive values of enthalpy change (ΔH°) further suggest the endothermic nature, while positive ΔS° values reflect the affinity of the adsorbent materials towards lead and also as an indication that the disorder of the adsorption process increases.

4.5. FTIR ANALYSIS

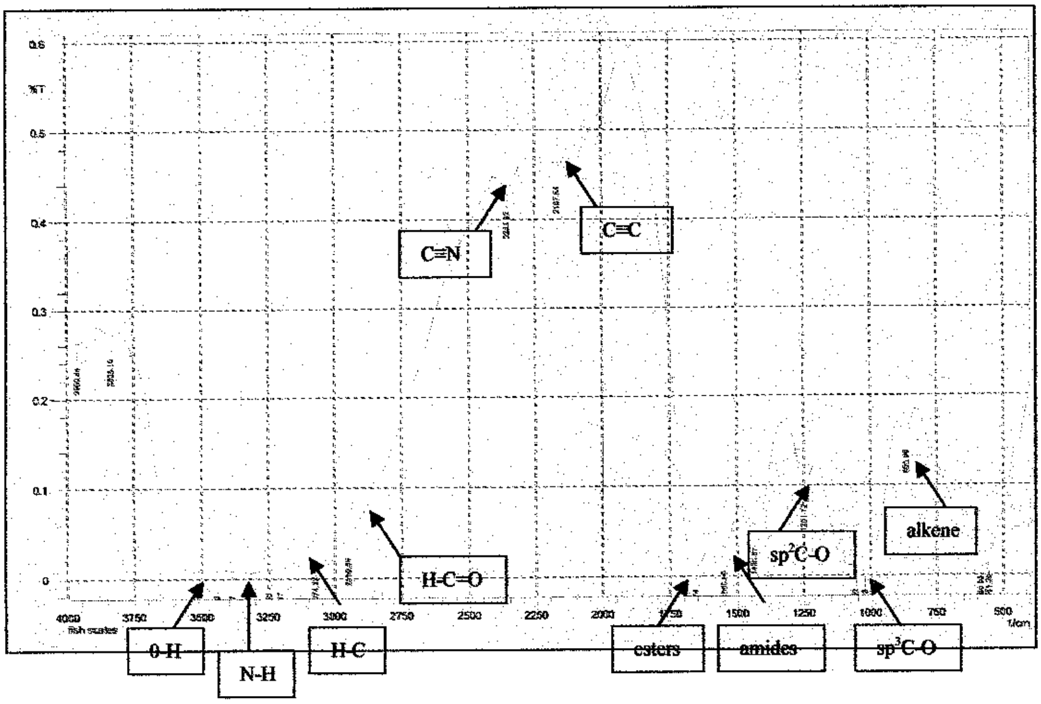

Figure 4.16: Percent transmittance as a function of wavelength

Infrared spectrum of an organic compound usually contains a number of peaks, frequently only the peak associated with the functional group is assigned. The group of peaks around 3000cm^{-1} is mostly observable in most organic molecules, because it is in the region that absorption due to carbon-hydrogen stretching occurs. This region mostly contains hydroxyl in the range of 3200-3600, carbonyl in the 3000 region, N-H in the 3350-3500, and H-C=O in the 2750-3000 region [10].

The region of an infrared from 1400 to 625cm^{-1} is where the variations from compound to compound are the greatest. This part of the spectrum is called the fingerprint region, because no two chemical compounds have the same exact pattern of peaks, just as no two persons have identical fingerprint patterns. The peaks in the fingerprint region are often difficult to assign, but the pattern they form can be useful when comparing the IR spectrum of a sample to that of a reference compound in the same way that criminals are identified by fingerprint comparisons [10].

CHAPTER 5

CONCLUSION

Biotechnology has become one of the great importance in the industry. Utilization on various biosorbents are focused and investigated all around the world. Although much effort had been exerted in this field, the existing information on available biomass and its application as adsorbents is still inadequate. Studies done on alternative adsorbents from biomass such as fish scales will prove to be a key area of scientific application in the future decades. From the results and discussion, the following conclusions are made;

1. From the studies done, it was found that fish scales indeed have the potential to be one of the prime adsorbents for heavy metals removal.
2. Adsorptions of Lead ions are the greatest, followed by Copper and lastly Nickel.
3. The adsorption process was usually quick, achieving more than 50% of the final uptake value in less than 5 minutes. This is important to determine the practicality of using fish scales as the adsorbent in the commercial scale.
4. The rapid increase in metal uptake during the initial stages of metal sorption (0 to 15 min) by powdered fish scales are dominated by physical adsorption which can be categorized as extracellular sorption or surface binding.
5. The slower rate of metal uptake signifies the chemisorption process. This step of sorption needs relatively high energy to adsorb metals into the cell interior (intracellular).
6. By having more contact of surface area per the same unit mass by reduction in particle size, we increased the adsorption site for adsorption to occur.
7. As the initial metal concentration is increased, the amount of metal ions that surround a particular unit of adsorbent would also increase. Hence, this would result in a greater extent of adsorption.
8. The general increase in metal uptake with temperature may be due to the dissociation of certain compound on the surface area thus yielding more

adsorption sites. The increase in temperature could also enhance the rate of intraparticle diffusion of adsorbate, and probably due to the change in the sizes of the pore.

9. The Gibbs free energy reflects the spontaneous nature and feasibility of the adsorption process. The more negative the value of Gibbs free energy is, the greater extent is the adsorption towards fish scales is.
10. The positive values of enthalpy change (ΔH^o) further suggest the endothermic nature of adsorption.
11. Positive ΔS^o values reflect the affinity of the adsorbent materials towards lead and also as an indication that the disorder of the adsorption process increases.
12. Despite the fish scale's ability to adsorb heavy metals, however, when compared to the performance of activated carbon, fish scales are found to be still marginally lacking in terms of its uptake.
13. The functional groups that exists in '*lutjanus argentimaculatus*' are abundant; some of which hydroxyl, amines, amides, carboxyl, carbonyl and esters.

More studies especially in the areas of fish scales preparation and activation needs to be conducted in order to fully harness its potential as a heavy metal adsorbent. With the completion of this study, it is hoped that a new perspective towards fish scales could be found, where this biomass waste would be looked upon as a potential prime adsorbent for wastewater in the near future

As a comparison with other types of adsorbent, the following cost analysis was estimated;

Adsorbent	Fish scales	C240 resin	GAC
Cost	RM0.15/g	RM350/25g	RM350/200g

Copper uptake of 10ppm solution @ room temperature	1.5mg/g	5mg/g	5mg/g
Raw material cost to remove 1g of copper	RM100	RM2800	RM350

*The cost analysis was based on the estimated cost of fish scales whereby the raw fish scales which are available in the market is considered free.

*The RM0.15 is the utility cost associated with the treatment of the fish scales which is the washing, drying and grinding.

CHAPTER 6

RECOMMENDATIONS

From the study, it was found that fish scales could adsorb heavy metals. However, there are still many aspects and areas in the utilization of fish scales as heavy metals adsorbent that must be studied to a greater extent. Here, some of the studies that could be conducted in the future would be recommended. These studies would greatly help to elevate the potential of utilizing fish scales as the heavy metals adsorbent in the future.

1. The study of single metal adsorption of other metals

By conducting this study, the adsorption characteristics for other metals and contaminants would also be able to be determined. Thus, by conducting these single metal adsorption studies, the extent of adsorption behaviour for these metals could also be predicted in an actual multi component wastewater.

2. A binary metal solution and continuous experiment.

Binary metal and continuous adsorption experiments needed to be conducted. In binary metal solution, the extent of adsorption of each metal can be determined. A continuous experiment of the adsorption by fish scales should also be conducted to determine the saturation loading of the fish scales.

3. Study of adsorption when other process parameters are varied.

In this study, the extent of adsorption for metals with a varying time, initial concentration and temperature was examined. Apart from these two parameters, other process parameters could also be used to determine their effect on the adsorption process such as pH of the metal solution. This is also very important information to be obtained if fish scales are to be used as commercial adsorbents.

4. The effect of different preparation methods on the adsorption process.

In the experiments conducted in this study, the fish scales used were only cleaned, dried and grinded. No methods of chemical activation were used to increase the adsorption capacity of the scales. This is to provide the basic information about the adsorption capacity of fish scales. From here, different methods of preparation could be utilized to increase its capacity. A few of the methods that could be studied further are by activation using acid or base, heating at high temperature etc.

5. Further characterization of the fish scales

Physical as well as chemical characterization studies are important in determining the effectiveness of typical adsorbents. Though literature review and FTIR analysis has been done about the composition of the scales, more could be done in this type of study such as BET test with the focus of providing more information about the adsorption mechanism on fish scales. With a better knowledge in this area of study, a better and more effective adsorption process could be done, with a more accurate explanations to all the observations made from the results.

6. More accurate experimental procedure

During the experiment, the initial concentration of the metal solution for each set of time data is held constant as we use only one origin. However over time as we filter the solution, some portion of the fish scales and also the solution itself are gone. Hence the ratio of volume (ml) / adsorbent added (g) has changed. The assumption made was that the amount of volume filtered and amount of adsorbent are proportional for each time of filtration so that makes the ratio of volume (ml) / adsorbent added (g) a constant. However, this clearly is not the case.

CHAPTER 7

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CHAPTER 7

APPENDICES

APPENDIX A – EXPERIMENTAL PROCEDURE

Calculation of preparing the 20ppm heavy metals solution

20ppm Cu^{2+}

Ratio of Cu^{2+} ions in copper (II) chloride dihydrate salts

$$= \frac{\text{MW of } Cu^{2+}}{\text{MW of Cu salts}}$$

$$= \frac{63.546}{170.48}$$

$= 0.373\text{g of } Cu^{2+}/\text{g of salts}$

Since preparing 20ppm Cu2+ ions needs a small amount of salts, 500ppm was prepared instead of a 20ppm and then diluted with water.

Amount in grams needed

$$= \frac{0.5\text{g of salts}}{0.373\text{g of } Cu^{2+}/\text{g of salts}}$$

= **1.34g of Cu salts**

Dilution process

$M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1}$$

= 20ppm (1L)/ 500ppm

= 40ml of the 500ppm solution

The same calculation was repeated for the next two solutions;

20ppm Ni^{2+}

Ratio of Ni^{2+} ions in nickel (II) nitrate hexahydrate salts

$$= \frac{\text{MW of } Ni^{2+}}{\text{MW of Ni salts}}$$

$$= \frac{58.69}{290.81}$$

= 0.202g of Ni^{2+}/g of salts

Amount in grams needed

$$= \frac{0.5\text{g of salts}}{0.202\text{g of } Ni^{2+}\text{/g of salts}}$$

= **2.4775g of Ni salts**

Dilution process

$M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1}$$

= 20ppm (1L)/ 500ppm

= 40ml of the 500ppm solution

20ppm Pb^{2+}

Ratio of Cu^{2+} ions in lead (II) nitrate salts

$$= \frac{\text{MW of } Pb^{2+}}{\text{MW of Pb salts}}$$

$$= \frac{207.19}{331.20}$$

= 0.62557g of Pb^{2+}/g of salts

Amount in grams needed

= 0.5g of salts

0.62557g of Pb^{2+}/g of salts

= **<u>0.7993g of Pb salts</u>**

Dilution process

$M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1}$$

= 20ppm (1L)/ 500ppm

= 40ml of the 500ppm solution

APPENDIX B – CONCENTRATION DATA

Table 7.1: Concentration data for particle size effect on copper

Time (min)	Concentration (ppm)	
	Untreated scales	Grinded scales
0	20.00	20.00
10	14.40	12.42
20	12.02	11.36
35	9.61	8.07
60	8.51	7.34
90	8.32	7.11

Table 7.2: Concentration data for temperature effect on copper

Time (min)	Concentration (ppm)			
	20°C	30°C	40°C	50°C
0	25.45	24.67	23.92	24.72
15	17.15	11.20	13.90	12.43
30	17.36	7.60	6.90	4.61
45	17.62	4.90	5.20	3.91
60	17.21	3.62	2.42	3.56
90	15.00	2.60	2.31	3.48
120	15.14	1.90	2.36	3.41

Table 7.3: Concentration data for temperature effect on nickel

Time (min)	Concentration (ppm)			
	20°C	30°C	40°C	50°C
0	12.97	14.41	14.09	14.09
15	13.73	13.89	12.74	11.98
30	13.69	13.82	12.69	11.64
45	13.68	13.76	12.34	11.01
60	13.65	13.70	12.11	10.83

90	13.63	13.72	12.04	10.83
120	13.64	13.71	12.03	10.87

Table 7.4: Concentration data for temperature effect on lead

Time (min)	Concentration (ppm)			
	20°C	30°C	40°C	50°C
0	15.34	14.2	14.2	17.09
15	0.28	0.43	0.38	9.58
30	0.03	0.17	0.24	7.32
45	0.03	0.10	0.54	5.49
60	-0.06	0.09	0.27	4.60
90	-0.03	0.03	0.04	4.98
120	-0.02	0.37	0.03	3.57

Table 7.5: Concentration data for initial concentration effect on copper

Time (min)	Concentration (ppm)		
	10ppm	30ppm	50ppm
0	11.56	35.63	52.89
15	2.17	15.56	35.96
30	2.26	13.56	25.89
45	1.97	12.20	23.68
60	2.23	9.19	23.97
90	1.36	8.85	22.90
120	1.50	7.69	21.81

Table 7.6: Concentration data for initial concentration effect on nickel

Time (min)	Concentration (ppm)		
	10ppm	30ppm	50ppm
0	7.94	18.05	24.00
15	7.14	17.34	22.45
30	7.01	17.19	22.46

45	6.94	17.07	22.41
60	6.88	16.97	22.32
90	6.84	16.93	22.24
120	6.82	16.96	22.23

Table 7.7: Concentration data for initial concentration effect on lead

Time (min)	Concentration (ppm)		
	10ppm	30ppm	50ppm
0	8.22	22.69	37.99
15	0.96	0.23	9.84
30	0.35	0.14	8.18
45	0.16	0.37	4.60
60	0.22	0.09	0.91
90	0.06	0.16	0.75
120	0.08	0.14	0.55

Table 7.8: Concentration data for adsorption isotherm

Conc. (ppm)		Time (min)	
20ppm	30°C	15.83	-0.37
	40°C	15.83	-0.46
	50°C	15.83	-0.045
30ppm	30°C	29.09	-0.43
	40°C	29.09	-0.44
	50°C	29.09	-0.44
50ppm	30°C	39.07	-0.39
	40°C	39.07	-0.08
	50°C	39.07	-0.4

APPENDIX C – DATA MANIPULATION

Sample calculation of metal uptake data and percent removal data

Example; Metal uptake, q $= V[L]x\dfrac{(C_i - C_f)[mg/L]}{S[g]}$

$= 400\text{ml x } \dfrac{20-7.11ppm}{2.5g}$

$= 2.0624\text{mg/g}$

Percent removal $= \dfrac{C_i - C_f}{C_i} \times 100\%$

$= \dfrac{20-7.11ppm}{20ppm} x100\%$

$= 64.45\%$

All the concentration data are calculated and tabulated as follows;

Table 7.9: Metal uptake and percent removal data for particle size effect on copper

Treatment	Untreated		Grinded	
Time (min)	uptake (mg/g)	percent removal (%)	uptake (mg/g)	percent removal (%)
0	0	0	0	0
10	0.896	28	1.2128	37.9
20	1.2768	39.9	1.3824	43.2
35	1.6624	51.95	1.9088	59.65
60	1.8384	57.45	2.0256	63.3
90	1.8688	58.4	2.0624	64.45

Table 7.10: Metal uptake data for temperature effect on copper

Temp. (°C)	20		30		40		50	
Time (min)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)
0	0	0	0	0	0	0	0	0
15	8.30	1.3280	13.47	2.1552	10.02	1.6032	12.29	1.9664
30	8.09	1.2944	17.07	2.7312	17.02	2.7232	20.11	3.2176
45	7.83	1.2528	19.77	3.1632	18.72	2.9952	20.81	3.3296
60	8.24	1.3184	21.05	3.368	21.50	3.440	21.16	3.3856
90	10.45	1.6720	22.07	3.5312	21.61	3.4576	21.24	3.3984
120	10.31	1.6496	22.77	3.6432	21.56	3.4496	21.31	3.4096

Table 7.11: Metal uptake data for temperature effect on nickel

Temp. (°C)	20		30		40		50	
Time (min)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)
0	0	0	0	0	0	0	0	0
15	0.27	0.0432	0.61	0.0976	1.35	0.216	2.11	0.3376
30	0.31	0.0496	0.68	0.1088	1.4	0.224	2.45	0.392
45	0.32	0.0512	0.74	0.1184	1.75	0.28	3.08	0.4928
60	0.35	0.056	0.8	0.128	1.98	0.3168	3.26	0.5216
90	0.37	0.0592	0.78	0.1248	2.05	0.328	3.26	0.5216
120	0.36	0.0576	0.79	0.1264	2.06	0.3296	3.22	0.5152

Table 7.12: Metal uptake data for temperature effect on lead

Temp. (°C)	20		30		40		50	
Time (min)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)

0	0	0	0	0	0	0	0	0
15	14.64	2.3424	17.77	2.8432	13.82	2.2112	7.51	1.2016
30	14.89	2.3824	18.03	2.8848	13.96	2.2336	9.77	1.5632
45	14.89	2.3824	18.1	2.896	13.66	2.1856	11.6	1.856
60	14.98	2.3968	18.11	2.8976	13.93	2.2288	12.49	1.9984
90	14.95	2.392	18.17	2.9072	14.16	2.2656	12.11	1.9376
120	14.94	2.3904	17.83	2.8528	14.17	2.2672	13.52	2.1632

Table 7.13: Metal uptake data for initial concentration effect on copper

Initial conc. (ppm)	10		30		50	
Time (min)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)
0	0	0	0	0	0	0
15	9.39	1.5024	20.07	3.2112	16.93	2.7088
30	9.3	1.488	22.07	3.5312	27	4.32
45	9.59	1.5344	23.43	3.7488	29.21	4.6736
60	9.33	1.4928	26.44	4.2304	28.92	4.6272
90	10.2	1.632	26.78	4.2848	29.99	4.7984
120	10.06	1.6096	27.94	4.4704	31.08	4.9728

Table 7.14: Metal uptake data for initial concentration effect on nickel

Initial conc. (ppm)	10		30		50	
Time (min)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)	$C_i - C_f$ (ppm)	uptake (mg/g)
0	0	0	0	0	0	0
15	0.8	0.128	1.16	0.1856	1.55	0.248
30	0.93	0.1488	1.31	0.2096	1.54	0.2464
45	1	0.16	1.43	0.2288	1.59	0.2544
60	1.06	0.1696	1.53	0.2448	1.68	0.2688

90	1.1	0.176	1.57	0.2512	1.76	0.2816
120	1.12	0.1792	1.54	0.2464	1.77	0.2832

Table 7.15: Metal uptake data for initial concentration effect on lead

Initial conc. (ppm)	10		30		50	
Time (min)	C_i - C_f (ppm)	uptake (mg/g)	C_i - C_f (ppm)	uptake (mg/g)	C_i - C_f (ppm)	uptake (mg/g)
0	0	0	0	0	0	0
15	7.26	1.1616	22.46	3.5936	28.15	4.504
30	7.87	1.2592	22.55	3.608	29.81	4.7696
45	8.06	1.2896	22.32	3.5712	33.39	5.3424
60	8	1.28	22.6	3.616	37.08	5.9328
90	8.16	1.3056	22.53	3.712	37.24	5.9584
120	8.14	1.3024	22.55	3.699	37.44	5.9904

Table 7.16: Percent removal data for temperature effect

Heavy Metals	Temp (°C)	Percent removal (%)
Nickel	20	2.57
	30	5.45
	40	14.62
	50	22.85
Copper	20	40.51
	30	92.3
	40	90
	50	89
Lead	20	97
	30	98
	40	99.79
	50	79.11

Table 7.17: Percent removal data for initial concentration effect

Heavy Metals	Initial conc. (ppm)	Percent removal (%)
Nickel	10	14.1
	30	8.32
	50	7.38
Copper	10	87
	30	78.4
	50	58.8
Lead	10	99.5
	30	99.4
	50	98.6

Table 7.18: Data of final concentration and equilibrium uptake

	C	Q	1/c	1/q	log c	log q
30°C	0.30	2.592	3.333333	0.385802	-0.52288	0.413635
	0.45	4.728	2.222222	0.211506	-0.34679	0.674677
	1.48	6.3232	0.675676	0.158148	0.170262	0.800937
40°C	0.32	2.6016	3.125	0.384379	-0.49485	0.415241
	0.47	4.7248	2.12766	0.211649	-0.3279	0.674383
	1.49	6.3216	0.671141	0.158188	0.173186	0.800827
50°C	0.35	2.5952	2.857143	0.385327	-0.45593	0.414171
	0.83	4.6672	1.204819	0.214261	-0.08092	0.669056
	1.53	6.3152	0.653595	0.158348	0.184691	0.800387

Table 7.19: Data of Langmuir isotherm constant

$1/bQ_o$	$1/Q_o$	Q_o	K	B
0.1031	0.0905	11.04972	1.139227	0.877789
0.0881	0.0774	12.9199	1.138243	0.878547

0.0824	0.0806	12.40695	1.022333	0.978155

Calculation of determining the thermodynamics properties

-ΔG° (30°C) = -RT ln b

= -8.314 (303) ln 0.877789

= -328.37J/mol

-ΔG° (40°C) = -RT ln b

= -8.314 (313) ln 0.878547

= -337.11J/mol

-ΔG° (50°C) = -RT ln b

= -8.314 (323) ln 0.978155

= -59.19J/mol

ΔH° (30°C → 50°C) $= -R\left(\frac{T2T1}{T2-T1}\right) \ln\left(\frac{b2}{b1}\right)$

$= -8.314\left(\frac{323x303}{323-303}\right) \ln\left(\frac{0.978155}{0.877789}\right)$

= 8.809kJ/mol

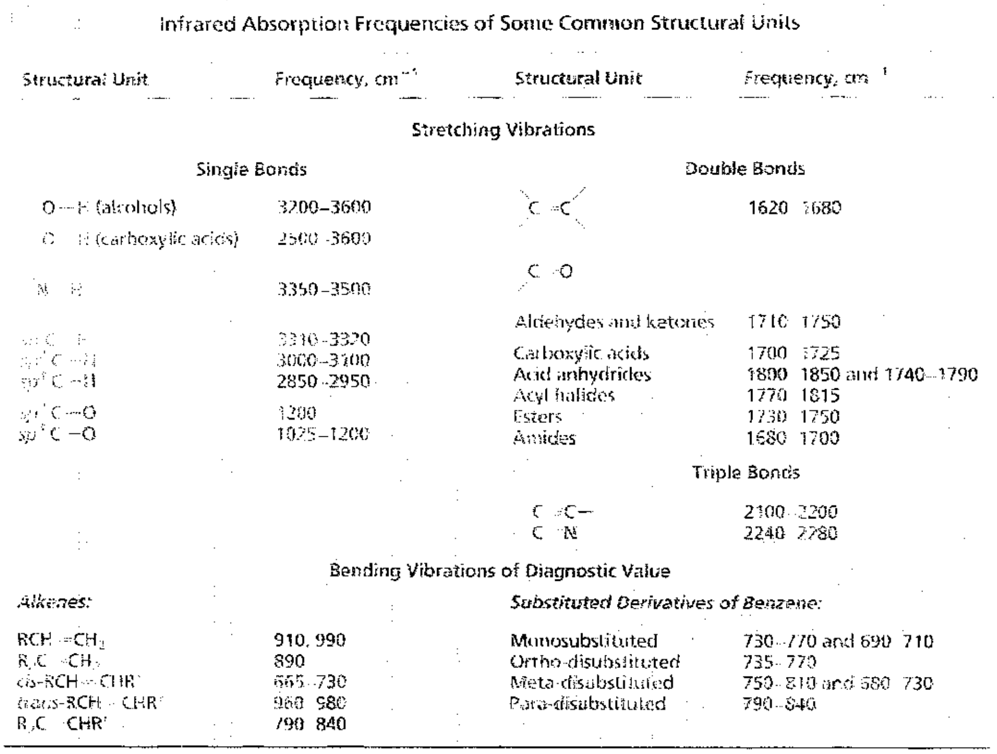
ΔS° (50°C) = (ΔH° - ΔG°) / T

= (8.809 – 0.05919) / 323

= 27.089J/mol

APPENDIX D – FTIR ANALYSIS

Figure 7.20: List of common structural unit as a function of wavelength



Infrared Absorption Frequencies of Some Common Structural Units

Structural Unit	Frequency, cm^{-1}	Structural Unit	Frequency, cm^{-1}
Stretching Vibrations			
Single Bonds		Double Bonds	
O—H (alcohols)	3200–3600	$\mathrm{C{=}C}$	1620–1680
O—H (carboxylic acids)	2500–3600		
N—H	3350–3500	$\mathrm{C{=}O}$	
		Aldehydes and ketones	1710–1750
sp C—H	3310–3320	Carboxylic acids	1700–1725
sp^2 C—H	3000–3100	Acid anhydrides	1800–1850 and 1740–1790
sp^3 C—H	2850–2950	Acyl halides	1770–1815
sp^2 C—O	1200	Esters	1730–1750
sp^3 C—O	1025–1200	Amides	1680–1700
		Triple Bonds	
		$\mathrm{C{\equiv}C{-}}$	2100–2200
		$\mathrm{C{\equiv}N}$	2240–2280
Bending Vibrations of Diagnostic Value			
Alkenes:		*Substituted Derivatives of Benzene:*	
$\mathrm{RCH{=}CH_2}$	910, 990	Monosubstituted	730–770 and 690–710
$\mathrm{R_2C{=}CH_2}$	890	Ortho-disubstituted	735–770
cis-$\mathrm{RCH{=}CHR'}$	665–730	Meta-disubstituted	750–810 and 680–730
trans-$\mathrm{RCH{=}CHR'}$	960–980	Para-disubstituted	790–840
$\mathrm{R_2C{=}CHR'}$	790–840		