CHARACTERIZATION STUDY OF CHITOSAN AS METAL IONS REMOVAL

By

MIRZA BINTI MOHD ZAID

Dissertation submitted in partial fulfillment
of the requirements for the
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Universiti Teknologi Petronas
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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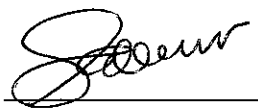
Approved by,



(Ms. Asna Mohd Zain)

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TRONOH, PERAK

July 2005

CERTIFICATION OF ORIGINALITY

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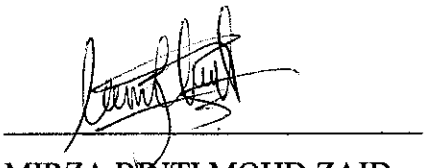

MIRZA BINTI MOHD ZAID

ABSTRACT

Removal of certain metal ions from wastewater by using biopolymers is proved to be a great alternative at the moment. Chitosan is one of the best examples in removing heavy metal ions. Its high amino content has been found to possess good sorptive capacities for many heavy metal ions through complexion of heavy metal ions with the amine group in chitosan. Chitosan indicates a family of deacetylated chitins. Chitin ((1-4)-linked 2-acetamido-2-deoxy-β-D-glucan) is widely distributed among invertebrates. Chitin is extracted from crab shells through demineralization and deproteination process. Chitosan is obtained by deacetylation of chitin in concentrated sodium hydroxide (NaOH). The efficiency of metal ions removal using chitosan is tested against oily wastewater. The presence of metal ions in sample solution is measured using Flame Atomic Absorption Spectrometry (FAAS). The weight percentage of chitin extracted from crab shells powder is 45.51 wt %. The weight percentage of chitosan yield from the deacetylation process is 69.94 wt %. The study of the influence of dose of chitosan and effect of contact time gives the expected result. As the dose of chitosan added to the sample oily wastewater increases, the percentage removal of metal ions also increases. The percentage removal of zinc, lead and iron at optimum dose of chitosan added is 89.08%, 84.00%, and 61.36% accordingly. Increasing the contact time also results in increases of percentage removal of metal ions. The percentage removal of zinc, lead, and iron at optimum contact time is 93.70%, 78.85%, and 65.58% accordingly. From the results obtained, the selectivity of chitosan to metal ions decreased in order $Zn^{2+} > Pb^{2+} > Fe^{2+}$.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

One of the earliest applications of chitosan was for chelating harmful metal ions, such as copper, lead, mercury, and uranium, from wastewater. Chitosan is a polysaccharide obtained by deacetylating chitin, which is the major constituent of the exoskeleton of crustaceous water animals. Polysaccharides are one such class of biopolymers, comprising of simple monosaccharide (sugar) molecules connected by ether type linkages to give high molecular weight polymers. Biopolymer is a term commonly used to refer to polymers biologically synthesized by nature.

Among the polysaccharide, cellulose and chitin are the two most abundant biopolymers in the biosphere. The structure of chitin, chitosan, and cellulose is shown in Figure 1.1.

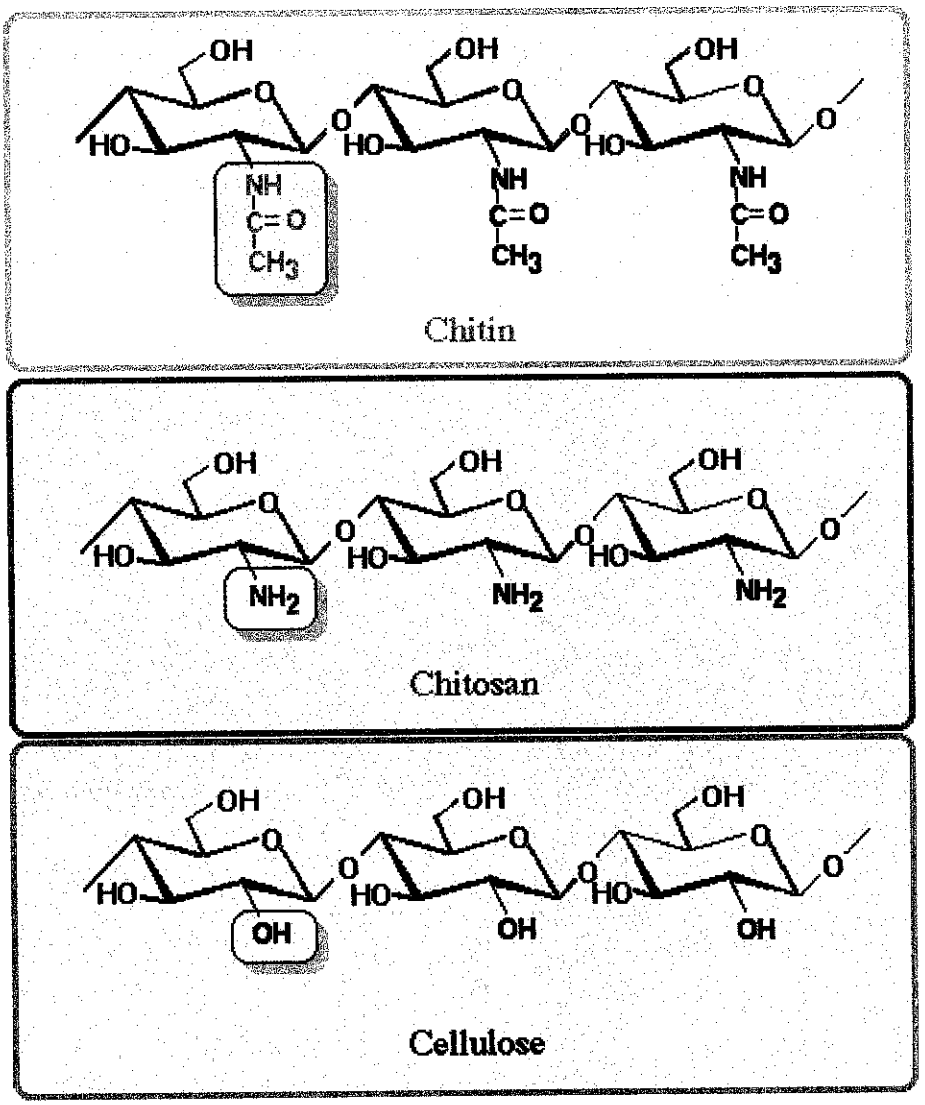


Figure 1.1 Structure of chitin, chitosan, and cellulose.

According to Khor (2001), the first explicit account of chitin was in 1811, attributed to the Frenchman, Braconnot, Professor of Natural History, Director of the Botanical Garden and member of the Academy in Sciences of Nancy, France. Braconnot described and named the alkali-resistant fraction from isolates of some higher fungi "Fungine". In 1823, Odier found a material with the same general properties as fungine in the cuticle of beetles and designated it "chitin" after the Greek word "chiton" that denotes "coat of mail" in reference to the cuticle.

Chitin is widely distributed both in the animal and plant kingdom (Khor, 2001). Chitin can be found in mushrooms, yeasts, and the hard outer shells of insects and crustaceans (Goosen, 1997). Crab shells are the main sources of chitin because this latter can be found in big quantities.

Crabs are invertebrates, animals without a backbone. They have an exoskeleton which is also called a carapace, an outer shell that both protects them from predators and provides support. These crustaceans have ten jointed legs, two of which have large, grasping claws. These claws also called pincers or chelipeds. They have a flattened body, two feelers or antennae, and two eyes located at the ends of stalks. Crabs are divided into several parts as tabulated below in Table 1.1 and pictured in Figure 1.2.

Table 1.1 Descriptions of body parts of crabs.

Crabs part	Description
Antennae	Two sensory organs (feelers) located towards the front of the crab.
Carapace	The hard, protective outer shell of the crab. The carapace is made of chitin.
Cheliped	One of two big claws used for defense and food handling.
Eyestalk	The two compound eyes are located on eyestalks.
Mouth	The mouth is located at the front of the crab, near base of the eyestalks and the antennae.
Walking legs	Four pairs of long, jointed legs used for locomotion (walking).

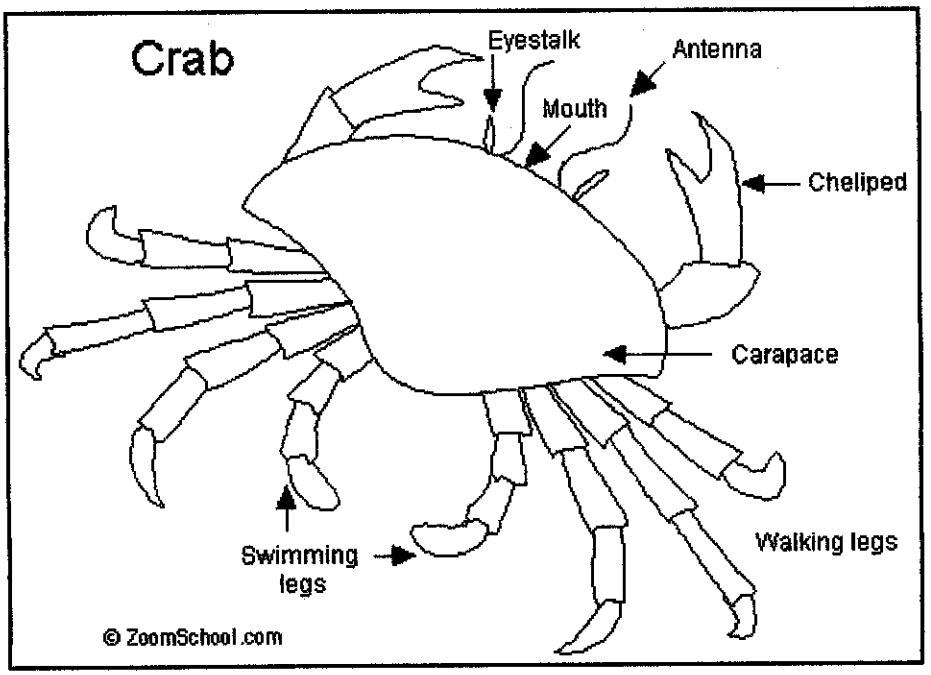


Figure 1.2 The external anatomy diagram of a crab.

According to Khor (2001), the differentiation between chitin and chitosan is to consider their respective acetyl content. When the number of acetamido groups is more than 50% (more commonly 70-90%) the biopolymer is term chitin. In chitin terminology, the number of acetamido groups is termed the degree of acetylation. On the other hand, when the degree of deacetylation or the amino groups is predominant, the biopolymer is termed chitosan.

1.2 Problem Statement

Most of heavy metals are toxic and not biodegradable, accumulation and distribution of these metals to our environments occur which is of concern to the public. They must be removed from the polluted streams in order to meet increasingly stringent environment quality standards.

In recent years, considerable attention has been devoted to the development of innovative techniques for reducing heavy metals in aqueous systems to acceptable levels. For treatment of such metal-bearing effluents, chemical precipitations, electrodeposition, ion exchange, membrane, and adsorption have been applied. Of these methods, chemical precipitation is known to be the most economic but is ineffective for dilute solutions. Ion exchange and reverse osmosis are generally effective, but they have high maintenance and operation costs and subject to fouling. Adsorption is the promising alternatives for this purpose, especially using low-cost adsorbent like clay materials, agricultural wastes, and seafood processing wastes (Juang and Shao, 2002).

1.3 Objectives and Scope of Study

The objectives of this final year research project are (i) to deacetylate chitosan from chitin that extracted from crab shells and (ii) to study its efficiency in removal of metals ion in oily wastewater.

Extraction of chitin from crab shells is conducted experimentally so as the deacetylation process of chitin to obtain chitosan. The purified chitosan is tested against oily wastewater from industrial waste to study its efficiency in removal of metal ions. The measurement of the metal ions is done using Flame Atomic Absorption Spectrometry (FAAS). The procedures for the experiments indicate above will be discussed further in the methodology section.

CHAPTER 2
LITERATURE REVIEW

According to Nomanbhay and Palanisamy (2005), at least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health. Recently, an increasing interest has been focused on removing Pb^{2+} ions from drinking water due to its supreme toxicity to our health. Drinking those that contain Pb^{2+} ions for long term, even if in a very low concentration, could lead to a wide range of spectrum health problem, such as nausea, convulsions, coma, renal failure, cancer and subtle effects on metabolism and intelligence (Li et al., 2005).

Different approaches to remove Pb^{2+} ions from wastewater, including chemical precipitation, ion exchange, reverse osmosis and adsorption, have been reported (Li et al., 2005). One of which, adsorption method, is simple and cost-effective, thus has been widely used. Li et al. (2005) reported that various adsorbents such as activated carbon, iron oxides, filamentous fungal biomass and natural condensed tannin have been explored and the results are promising.

According to Nomanbhay and Palanisamy (2005), a wide range of physical and chemical processes is available for the removal of Cr (VI) from wastewater, such as electro-chemical precipitation, ultra filtration, ion exchange and reverse osmosis. A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique for such a purpose. However, it is not economically appealing because of high operational cost. Adsorption using commercial activated carbon (CAC) can remove heavy metals from wastewater, such as Cd, Ni, Cr, and Cu. However, CAC remains an expensive material for heavy metal removal.

Juang and Shao (2002) reported that chitosan is a known adsorbent for metals such Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}, VO^{2+}, and UO_2^{2+} because its amino groups ($-NH_2$) can serve as coordination sites. In particular, chitosan, because of its high amino content, has been found to possess good sorptive capacities for many heavy metal ions through complexion of heavy metal ions with the amine group in chitosan (Yan and Bai, 2005). Other applications of chitosan are tabulated in Appendix A (Table A.1).

In adsorption process one or more components of a gas or liquid streams are adsorbed on the surface of a solid adsorbent and a separation is accomplished (Geankoplis, 2003). In adsorption process, molecules or atoms or ions in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or held there by weak intermolecular forces (Seader and Henley, 1998). The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. Figure 2.1 shows the mechanism of adsorption process.

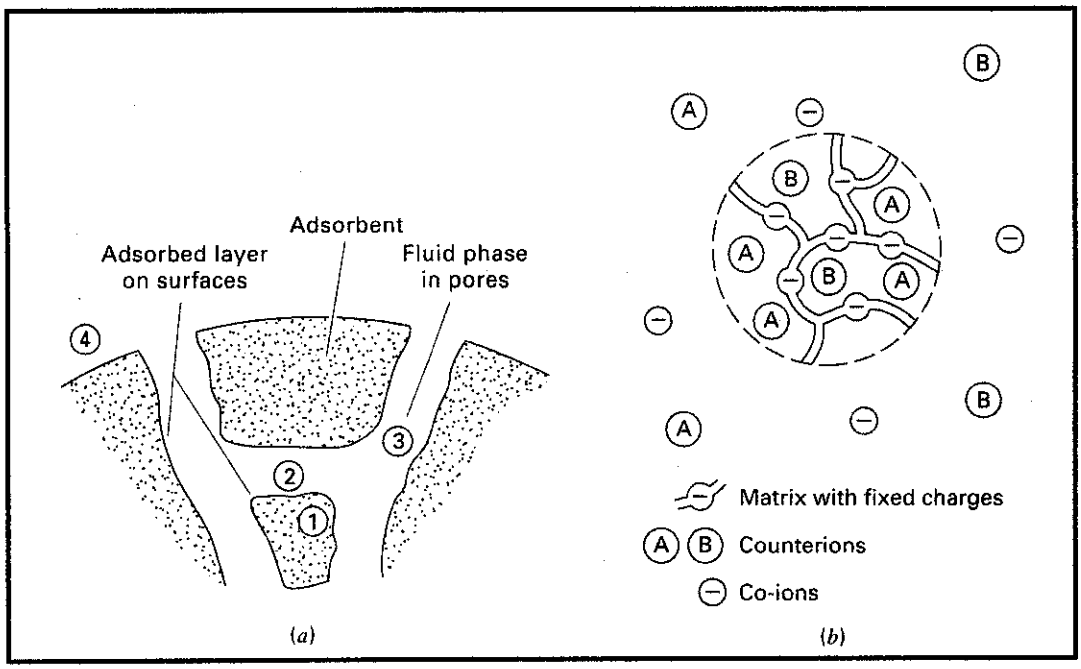


Figure 2.1 Sorption operations with solid-particle sorbents. (a) Adsorption. (b) Ion exchange.

Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion concentrations. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Nomanbhay and Palanisamy, 2005).

According to Nomanbhay and Palanisamy (2005), among the many other low cost absorbents identified, chitosan has the highest sorption capacity for several metal ions. Chitin (2-acetamido-2-deoxy-b-D-glucose-(N-acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps. Worldwide, the solid waste from processing of shellfish, crabs, shrimps and krill constitutes large amount of chitinaceous waste. Chitosan (2-acetamido-2-deoxy-b-D-glucose-(N-acetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution as shown in Figure 2.2.

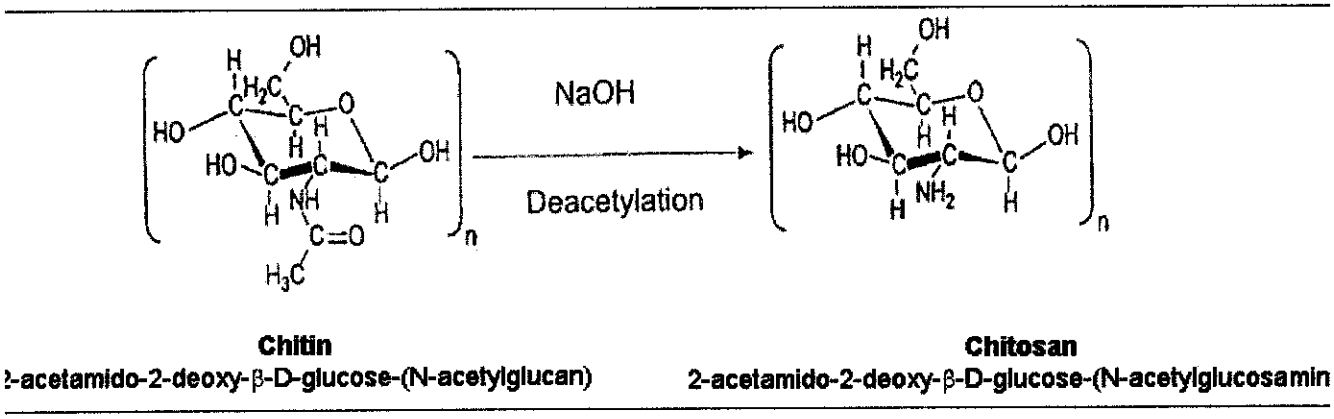


Figure 2.2 Conversion of chitin to chitosan by deacetylation.

The term chitosan does not refer to a uniquely defined compound. It merely refers to a family of copolymers with various fractions of acetylated units. Chitosan is found in nature, to a lesser extent than chitin. It was reported that chitosan and chitin are contained in cell walls of fungi (Goosen, 1997).

According to Nomanbhay and Palanisamy (2005), chitosan chelates five to six time greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin. The biosorbent material, chitosan, is slightly soluble at low pH and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions. In addition, the active binding sites of chitosan are not readily available for sorption. Transport of the metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications.

It has been proposed to define chitosan and chitin as soluble or insoluble in 0.1 M acetic acid respectively. According to Khor (2001), instant differentiation between chitin and chitosan can be attained from their solubility and nitrogen content. Chitin is soluble in 5% Lithium chloride/N, N-Dimethylacetamide solvent [LiCl/DMAc] and insoluble in aqueous acetic acid while the converse is true of chitosan. The nitrogen content in purified samples is less than 7% for chitin and more than 7% for chitosan.

The adsorption of heavy metals with raw and chemically modified chitosan has been widely studied. For example, Yang and Zall (1984) and Huang et al. (1996) found that the selectivity decreases in the order $Cu^{2+} > Cr^{3+} = Cd^{2+} > Pb^{2+} >> Zn^{2+}$ and $Cu^{2+} = Hg^{2+} >> Pb^{2+} = Cd^{2+} > Ni^{2+}$, respectively using raw chitosan (Juang and Shao, 2002).

CHAPTER 3
METHODOLOGY

Through out the project, three experiments have been done to obtain the chitosan. The experiments were (i) preparation of crab shells powder, (ii) extraction of chitin, (iii) deacetylation of chitin to chitosan.

3.1 Preparation of Crab Shells Powder

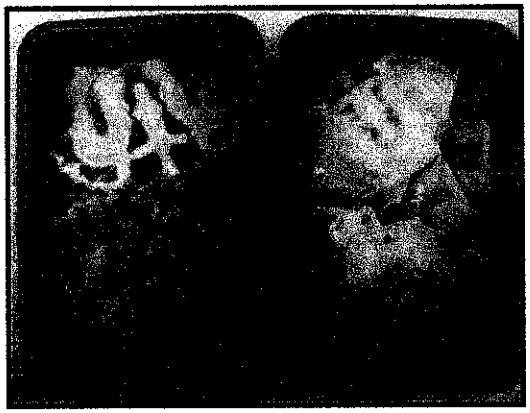
The initial interest of this project is to obtain the crab shells powder. Therefore, 2.1 kilograms (kg) of crabs is bought from Giant Hypermarket at Ipoh. The crabs is put in the container and washed down with waters to remove any dirt and sludge. All the flesh is removed from its shell. The carapace and crab legs are washed again with water to remove any remaining flesh and are placed in the separated container. The removal of flesh from the chelipeds was quite difficult. Hammer is used to break the chelipeds apart before the flesh can be taken out. The chelipeds is washed again to remove any remaining flesh attach to it and is placed in the container.

The crab shells consist of carapace, legs, and chelipeds as shown in Figure 3.1 is dried under the sun to remove unpleasant odor. In enhance, drying under the sun makes the shells more brittle. Thus, it can help the grinding process later on. The sun drying process took up until four days due to the bad weather. The crab shells after sun drying is weighted.

(a)

(b)

(c)



(d)

(e)

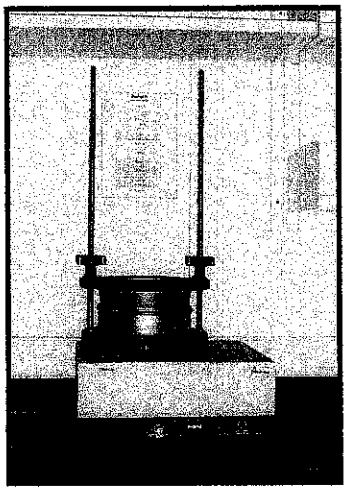
(f)

Figure 3.1 Preparation of crab shells. (a) 2.1 kg of crabs (Ketam Harimau) (b) Crabs is washed down with water. (c) Fleshes. (d) Carapace. (e) Crab legs. (f) Chelipeds.

The shells are crushed into smaller pieces for the sake of grinding. The shells then, are grinded using lab blender to obtain the crab shells powder. The weight of crab shells powder is recorded.

The crab shells powder is sieved using sieves and shakers model Retsch as200. The crab shells powder is sieved for 5 minutes with the amplitude of 70 to obtain the fine powder within the range of 1 mm and below. The weight of fine powder obtained is weighted. The fine powder can increase the surface area thus increases the rate of reaction. After sieving process completed, the fine powder of the crab shells is placed in the oven at 120 °C for 2 hours. Figure 3.2 shows lab equipments used for preparation of crab shells powder.

(a)



(b)

(c)

Figure 3.2 Lab equipments used for preparation of crab shells powder. (a) Lab blender. (b) Sieves and shakers. (c) Oven.

Heating process purposely made the powder become more brittle and to prevent organic decomposition. The weight of the crab shells powder after being heated is recorded. Figure 3.3 shows crab shells powder prepared from crab shells.

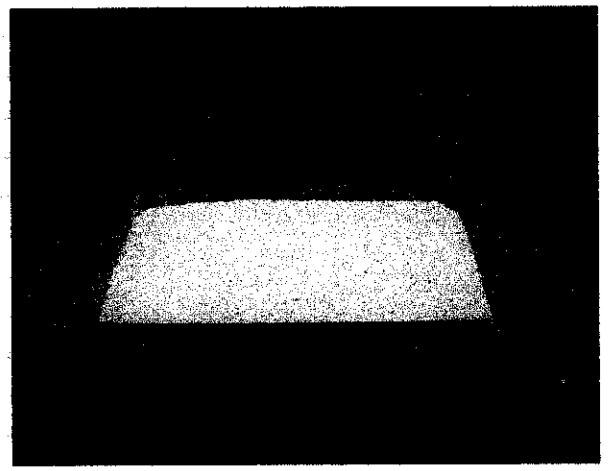


Figure 3.3 Crab shells powder.

3.2 Extraction of Chitin using Broussignac Method

The dry shells of crabs contain 20-40% chitin, 30-40% of recoverable proteins and 20-30% of calcium carbonate. This experiment consists of Demineralization and Deproteination process in order to remove calcium carbonate and protein respectively.

In deproteination, covalent chemical bonds have to be destroyed between the chitin-protein complex to form free radicals. Free radicals are active sites of molecules which in presence will enhance the growing of molecular chains of biopolymers.

3.2.1 Demineralization Process

A solution of 1.5M of hydrochloric acid (HCl) has to be prepared first. Since there is only HCl with 36% concentration that is available in the lab, a dilution need to be made.

The dilution formula is equated in Equation 3.1.

$$M_1 V_1 = M_2 V_2 \tag{3.1}$$

where M_1 is the molarity of concentrated solution, M_2 is the molarity of dilute solution, V_1 is the volume of concentrated solution needed, and V_2 is the volume of dilute solution.

Molarity of a solution is defined as the number of moles solute, n in liter of solution, V as shown in Equation 3.2.

$$M = \frac{n}{V} \tag{3.2}$$

Whereas number of moles solute is obtained using Equation 3.3.

$$n = \frac{Mass}{MW} \tag{3.3}$$

Here MW is the molecular weight of the solute.

The density, m is defined as the amount of mass in a unit volume of the substance as shown in Equation 3.4.

$$m = \frac{Mass}{Volume} \tag{3.4}$$

Substituting Equation 3.2, Equation 3.3, and Equation 3.4 yields Equation 3.5. With the density of HCL 36% is m_1 = 1.19 kg/l as stated at the bottle, the density of 1.5 M HCl, m_2 can be calculated.

m_2 = Molarity x molecular weight (MW) of HCl (3.5)

= 1.5 M x 36.46 g/mol

= 1.5 mol/l x 36.46 g/mol

= 54.69 g/l

= 0.05469 kg/l.

Thus, we can calculate the volume for dilution, V_1 by equating Equation 3.1 and Equation 3.5. V_2 is the volume of dilute solution which is 0.5 liter.

$m_1 V_1 = m_2 V_2$ (3.6)

(1.19 kg/l) V_1 = (0.05469 kg/l) (0.5 l)

V_1 = 0.02298 l

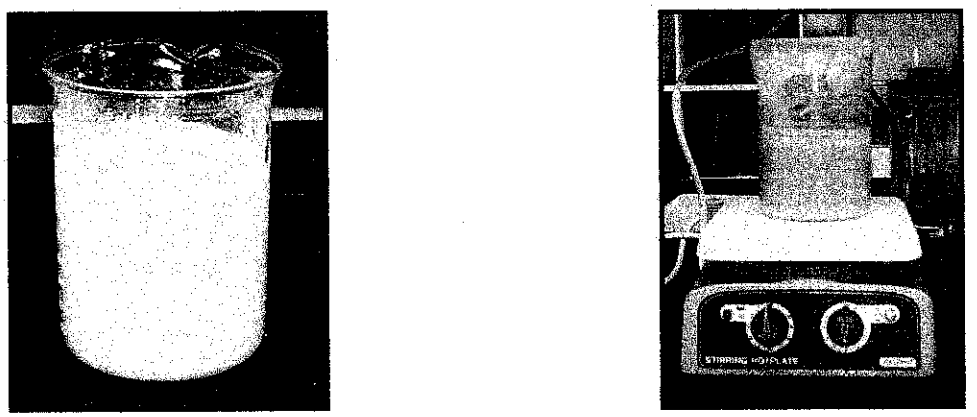
V_1 = 22.9790 ml

Thus, from Equation 3.6, 22.9790 ml of HCl 36% is put in the volumetric flask of 500 ml and is top up with the distilled water.

Procedure of demineralization:

- 20 ml of 1.5 M of hydrochloric acid was added per gram of crab shells powder. The $CaCO_3$ in the crab shells powder will be decomposed as the HCl was reacted with the $CaCO_3$.

- The mixture was kept for 2 days with a constant stirring, in order to make sure all the crab shells had been reacted with the hydrochloric acid. Most of the solution will be decanted off at the end. Figure 3.4 illustrates the demineralization process.



(a) (b)

Figure 3.4 Demineralization process. (a) 1.5 M HCl + 25 g crab shells powder. (b) The mixture is kept for constant stirring.

3.2.2 Deproteination Process

A solution of 1.2 M of sodium hydroxide (NaOH) has to be prepared first. Concentration of NaOH, M = 1.2 M and the volume of solution to be prepared, V = 0.5 liter, l.

Substituting Equation 3.2 into Equation 3.3 yields Equation 3.7. Mass of NaOH pellet required can be calculated.

$$m = M \times V \times MW \tag{3.7}$$

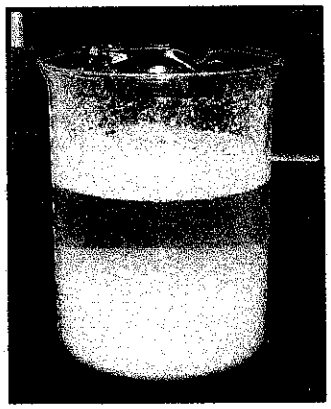
$$m = 1.2mol/l \times 0.5l \times 40g/mol$$

$$m = 24g$$

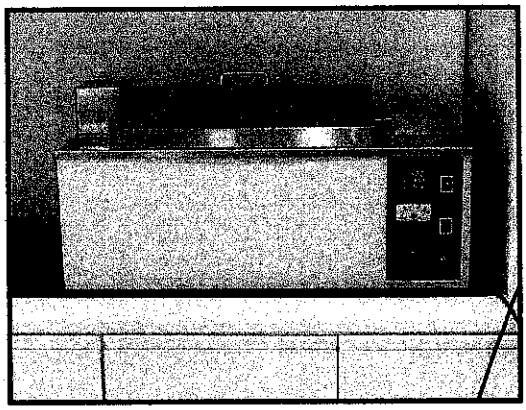
Therefore, 24 grams of NaOH pellet is used to prepare 500 ml of 1.2 M NaOH solution.

Procedure in deproteination:

- 20 ml of 1.2M NaOH was added per gram of crab shells powder.
- The mixture was heated at 90 °C in water bath for 1 hour.
- Next the mixture was left to react for 1 day at room temperature with constant stirring process.
- After 1 day, the powdery residue was collected using Buchner funnel and washed using distilled water before it can be dried up using acetone.
- The sample then was left for overnight to stabilize it. The chitin obtained was measured and recorded. The deproteination process is illustrated in Figure 3.5.



(a)



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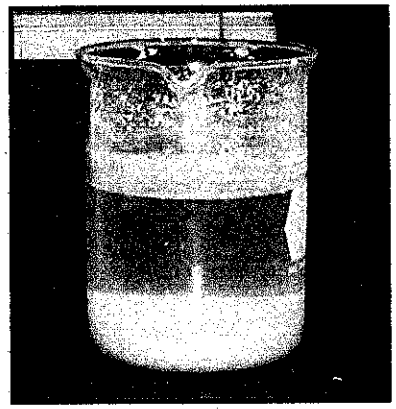

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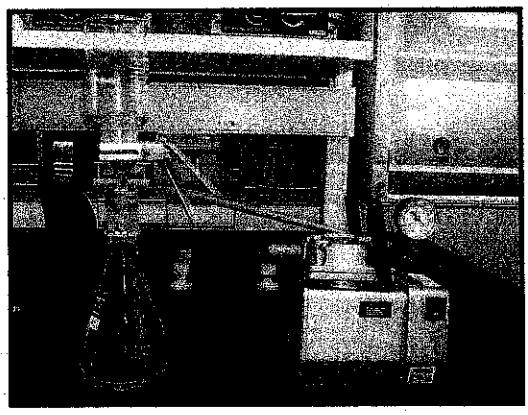

(d)

(e)

Figure 3.5 Deproteination process. (a) 1.2 M NaOH + 25 g decalcified crab shells powder. (b) The mixture was heated in water bath for 1 hour at 90 °C. (c) The mixture after 1 day. (d) The powdery residue was collected using Buchner funnel. (e) Chitin.

3.3 Deacetylation of Chitin to Chitosan using Method of Alimunar and Zainuddin

The deacetylation of chitin to chitosan is usually achieved by treating chitin with 50% NaOH at 95 °C for 3 hours, cooling down decanting off the NaOH and washing with water until neutral pH. Finally the chitosan is extracted with 2% acetic acid solution, filtered and precipitated in distilled water to give purified chitosan that is dried and stored.

3.3.1 Deacetylation Process

- 50% NaOH solution was prepared by mixing 50 g of NaOH pellets in 100 ml of distilled water.
- The solution prepared then is heated in the water bath at 95 °C for 3 hours. A 50 ml of concentrated solution was added per gram of chitin and left for 3 days at room temperature.
- The mixture is chilled and diluted with distilled water until the pH is neutralized.
- The mixture then is extracted with 2% acetic acid, filtered and precipitated in distilled water to obtain purified chitosan.
- The powdery residue is collected using Buchner funnel and dried out using acetone wash (Figure 3.6).

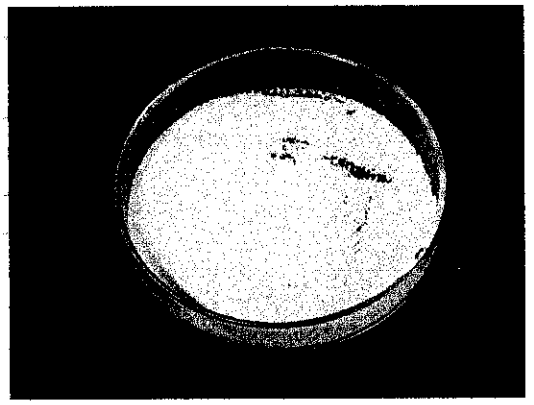

Figure 3.6 Chitosan.

Chitosan obtained from the experiment will be tested against oily wastewater to study its efficiency in removal metal ions. The oily wastewater from the oil separator equipment is collected from Optimal Olefin at Kerteh, Terengganu. The measurement of metal ions presence in oily wastewater is done using Flame Atomic Absorption Spectrometry (FAAS). The FAAS principle is described in Appendix B.

3.4 Oily Wastewater

In the petrochemical industry, quench water system is used in ethylene and other olefin manufacturing operations where the untreated process water used may contain mixtures of heavy, middle, and light hydrocarbons. The oil-water mixture comes out from the bottom of quench tower and is routed to oil-water separator. Oil-water separator separates heavy oil and oily wastewater. Heavy oil is routed to heavy oil tank. The oily wastewater sample is taken at the bottom outlet of oil-water separator. Figure 3.7 shows the manometer-type oil-water separator.

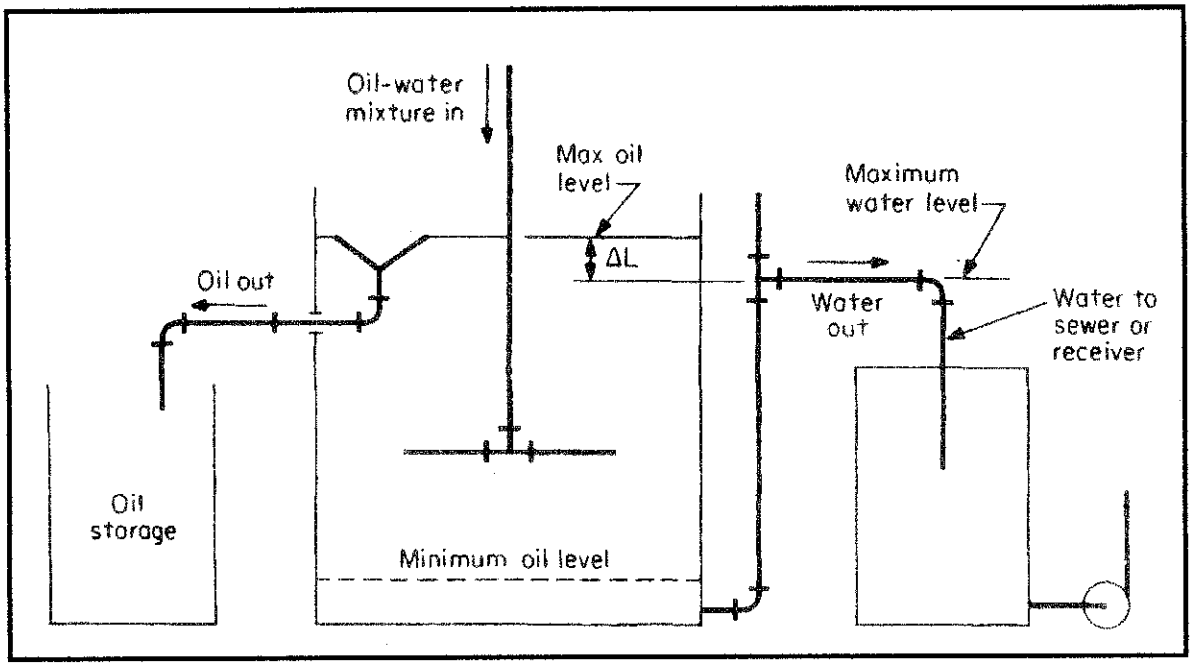

Figure 3.7 Manometer-type oil-water separator ΔL based on the difference between specific gravity of oil and specific gravity of water.

3.4.1 Procedures of Metal Ions Analysis for Oily Wastewater Sample

The oily wastewater is tested using FAAS to measure the metal ions contained in the sample solution. The standard solution for metal ion to be tested; Fe^{2+}, Zn^{2+}, and Pb^{2+} are prepared by dilution method. The concentrations of the standard solution used for Fe^{2+} are 1 ppm, 2 ppm, and 4 ppm. The concentrations used for standard solution of Zn^{2+} are 0.2 ppm, 0.4 ppm, and 0.8 ppm whereas for Pb^{2+} are 4 ppm, 8 ppm, and 16 ppm. 20 ml of standard solution prepared is used in the measurement of selected metal ions presence using FAAS.

The APDC (ammonium pyrrolidine thiocarbamate)-MIBK (methyl isobutyl ketone) method used to treat sample solution consists of neutralization, formation of complex (chelating), extraction, fractioning, and measurement steps.

Procedures of sample solution preparation;

- 100 ml of sample solution is put into a flask and 2 or 3 drops of bromphenol blue solution 0.1% is added.
- For neutralization steps, the solution is transferred into 200 ml beaker and 100 ml of ammonia water is added until the solution becomes purple.
- 25 ml of saturated ammonia solution is added to the mixture.
- For chelating step, the mixture is transferred into a separating funnel. 1 to 5 ml of 1% aqueous solution of APDC is added.
- Extraction step is achieved by adding10 ml of MIBK and shake vigorously for 2 minutes for mixing.
- After the solution is separated into two phases, the upper phase (MIBK phase) is put into a beaker and the lower phase (water phase) is discarded. This is the fractioning step.
- The sample solution is placed in test tubes provided.
- All of the standard solution and samples solution were placed in the FAAS test tubes holder and recorded accordingly.

- The FAAS ran in an automatic mode to measure the selected metal ion presence (Figure 3.8).

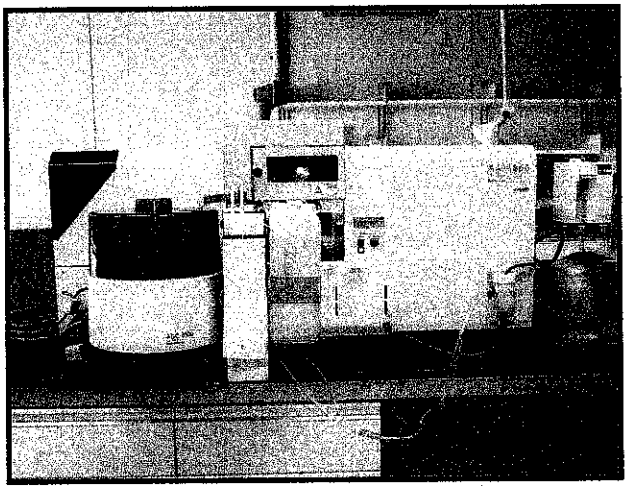

Figure 3.8 FAAS equipment.

3.5 Study of Metal Ions Removal Efficiency

The next step of this final year researched project is to study the influence of dose and effect of contact time. The dependence of metal ions sorption on dose is studied by varying the amount of chitosan, whereas the effect of contact time is studied by varying the contact time of mixed chitosan with sample oily wastewater. The experimental data is shown in Appendix C (Table C.1).

3.5.1 Influence of Dose

- 3 samples of 30 ml oily wastewater sample are prepared in 150 ml beaker.
- 0.20 g, 0.50g, and 1.00g of chitosan are added in each beaker respectively.
- The samples are placed under continuous stirring at room temperature for 2 hours of reaction at agitation speed of 60 rpm.
- The mixture is extracted with APDC-MIBK method and measured using FAAS.
- The result is tabulated and the graph of removal efficiency against the dose of chitosan added is plotted.

3.5.2 Effect of Contact Time

- 3 samples of 30 ml oily wastewater sample are prepared in 150 ml beaker.
- 1.00g of chitosan added into each beaker.
- Each of the samples is placed under continuous stirring at room temperature for 2 hours, 4 hours, and 8 hours respectively at agitation speed of 60 rpm.
- The mixture is extracted with APDC-MIBK method and measured using FAAS.
- The result is tabulated and the graph of removal efficiency against contact time is plotted.

3.6 List of Equipment Used for the Experiment

- Beaker.
- Buchner funnel.
- Volumetric flask.
- Petri dish.
- Filter paper.
- Lab blender.
- Oven.
- Sieves and shakers.
- Flame Atomic Absorption Spectrometry (FAAS).

CHAPTER 4
RESULTS AND DISCUSSION

The experimental results throughout the project are discussed in detail in this chapter. The effect of dose and contact time of chitosan to the removal of metal ions in oily wastewater is studied.

4.1 Chitin and Chitosan Extracted from Crab Shells Powder

The crab shells powder obtains from 2.1 kg of crabs being dried, grinded, sieved, and heated is 269.09 g. Table 4.1 indicates the weight in grams for each steps.

Table 4.1 Total weight of crab shells powder.

Parameter	Weight (g)
Weight of crabs	2100.00
Weight of crab shells after sun drying	385.66
Weight of crab shells powder after grinded	342.01
Weight of crab shells powder after sieved	332.12
Weight of crab shells powder after heated	269.09

The first batch of chitin is extracted using 75 g of crab shells powder. Due to the limited equipment and time constraint, only 3 batches of chitin are extracted from crab shells powder. From 3 batches of chitin extracted, only 2 batches of chitosan are obtained due to the same matters.

The crab shells powder undergo the demineralization and deproteination process to obtain the chitin. Demineralization or Decalcification is the removal of minerals, primarily calcium carbonate ($CaCO_3$).

This process involves the decomposition of $CaCO_3$ to calcium chloride ($CaCl_2$), carbon dioxide (CO_2), and water (H_2O) as shown in Equation 4.1.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad (4.1)$$

This process is accomplished by adding crab shells powder into 1.5 M of Hydrochloric acid (HCl) solution. During the demineralization process, the mixture turned to cloudy residue with formation of foam as shown in Figure 3.4 (a). The foams were slightly decreasing in continuous stirring. This is believed to be the production of calcium salt, CaCl and CO_2 released.

According to Khor (2001), proteins as well as other organic impurities are removed by an alkali treatment. Pigments, primarily carotenoids are removed by extraction with ethanol or acetone after the demineralization process.

In the deproteination process, a white precipitates observed settling at the bottom surface of the beaker as shown in Figure 3.5 (c). The mixture seems to be heterogeneously mixed. In other words, the powder added is not dissolves in the sodium hydroxide (NaOH) solution.

Table 4.2 shows the weight percentage of chitin and chitosan obtained throughout the experiments.

Table 4.2 Weight percentage of chitin and chitosan obtained.

Stages	Crab shells powder	Chitin	Chitosan
Weight (g)	75.00	34.13	23.87
Wt %	-	45.51	69.94

The weight percentage of chitin extracted from 75.00 g of crab shells powder is 45.51%. The yield of chitosan from the deacetylation process of chitin is 69.94 weight percent (wt %) which is agree with the theoretical value of optimum amount of chitosan that can be extracted from the source of chitin is 70%.

Chitin and chitosan obtained is dissolved in 0.1 M acetic acid. From the observation, chitosan is soluble in 0.1 M acetic acid whereas chitin is not. Thus, it is confirmed that the chitin and chitosan are produced from the experiments that has been carried out.

4.2 Metal Ions in Oily Wastewater

The initial concentration of three selected metal ions in sample oily wastewater collected from Optimal Olefin at Kerteh, Terengganu is shown in Table 4.3.

Table 4.3 Initial concentration of metal ions in oily wastewater.

Metal Ions	Concentration of untreated oily wastewater (ppm)
Fe^{2+}	8.10
Zn^{2+}	2.38
Pb^{2+}	0.52

The highest concentration is iron (Fe^{2+}) that account for 8.10 ppm and followed by 2.38 ppm of zinc (Zn^{2+}) and 0.52 ppm of lead (Pb^{2+}). These three selected metal ions are studied in this final year research project.

4.3 Influence of Dose

The dependence of metal ions sorption on dose was studied by varying the amount of chitosan added to the sample oily wastewater. The result is expressed as the removal efficiency *(E)* of the chitosan on iron, zinc, and lead. The removal efficiency *(E)* is defined as in Equation 4.2.

$$E(\%) = \frac{C_0 - C_1}{C_0} x100\% \tag{4.2}$$

Where C_0 is the initial concentration of metal ions in oily wastewater and C_1 is concentration of metal ions after being treated using chitosan.

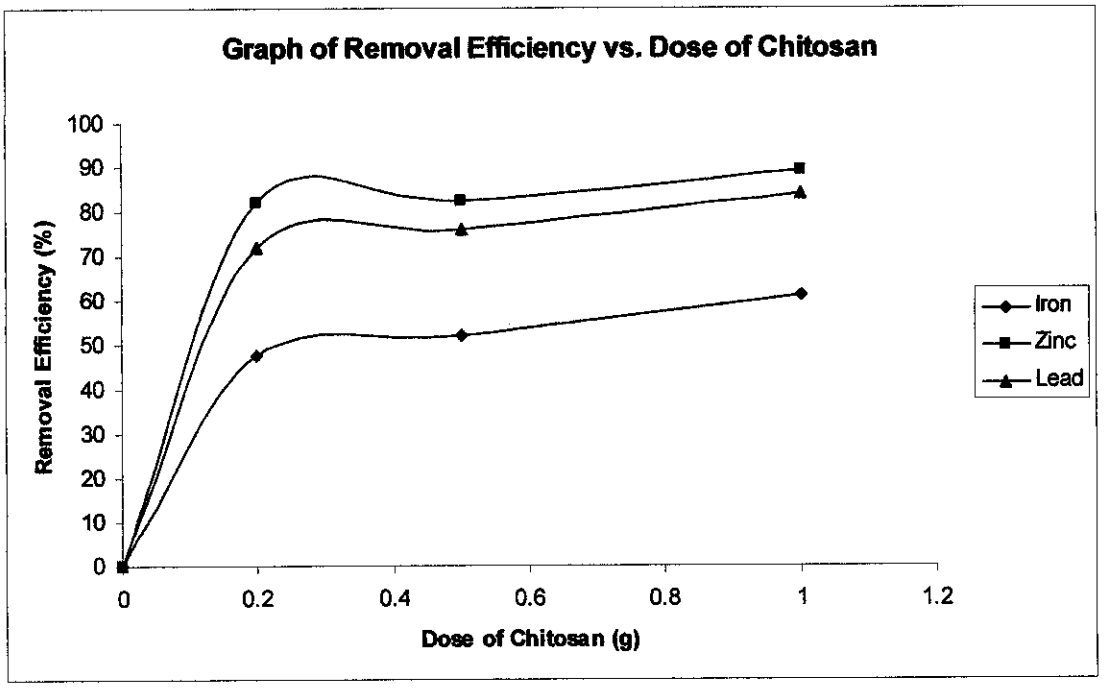

Figure 4.1 The influence of dose of chitosan added on removal efficiency of iron, zinc, and lead in oily wastewater.

From the Figure 4.1, it can be observed that removal efficiency of the metal ions using chitosan in generally improved with increasing dose. This is expected due to the fact that the higher dose of chitosan in the sample solution, the greater the availability of exchangeable sites for the ions. As shown in the graph, the selectivity of chitosan to the metal ions decreases in order $Zn^{2+} > Pb^{2+} > Fe^{2+}$.

4.4 Effect of Contact Time

Effect of contact time is studied by varying the contact time of chitosan while dose of chitosan added is kept optimum. The result is expressed as the removal efficiency *(E)* of the chitosan on iron, zinc, and lead. The removal efficiency *(E)* is defined as in Equation 4.2.

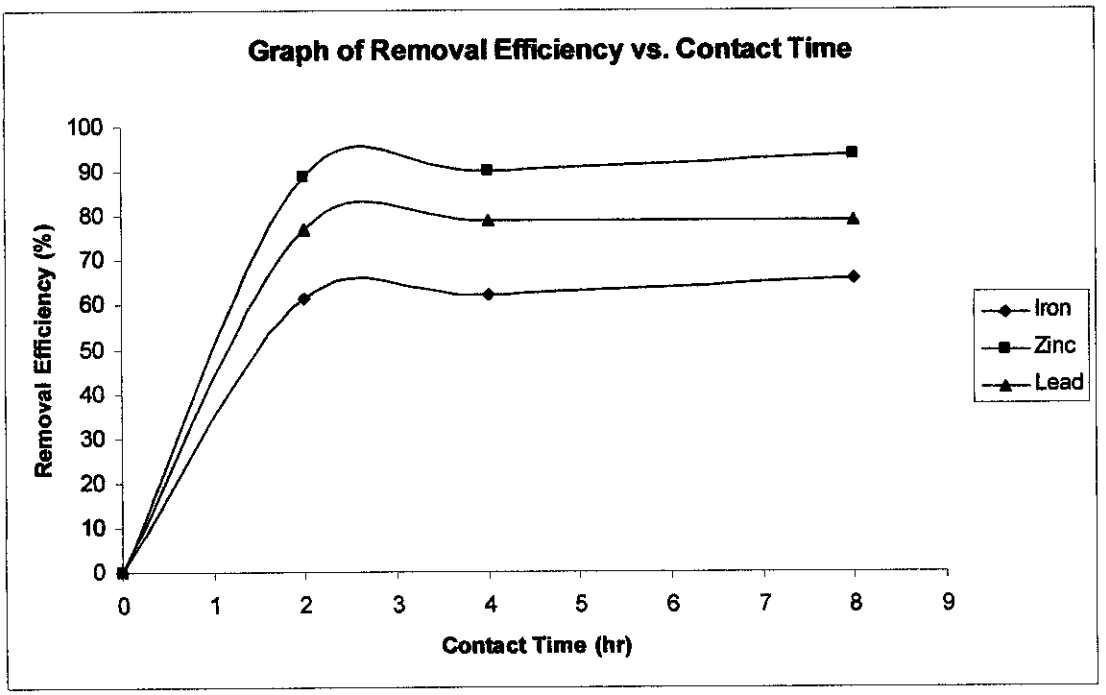

Figure 4.2 The effect of contact time on removal efficiency of iron, zinc, and lead in oily wastewater.

From the Figure 4.2, it can be seen that the removal efficiency increased with an increase in contact time. The iron removal efficiency increased from 61.48% to 62.10% when the contact time increased from 2 hour to 4 hour. Increase the contact time from 4 hour to 8 hour results in increase zinc removal from 89.92% to 93.70%. The trend for lead removal is nearly constant as the contact time is increased from 4 hour to 8 hour. This is because the amount of lead is approximately removed into completion within this contact time. As indicated in the graph, the selectivity of chitosan to the metal ions decreases in order $Zn^{2+} > Pb^{2+} > Fe^{2+}$.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Chitin is extracted from crab shell powder through demineralization and deproteination process. The weight percentage of chitin extracted from crab shells powder is 45.51 wt %. Chitosan is obtained by deacetylation of chitin using concentrated sodium hydroxide. The weight percentage of chitosan yield from the deacetylation process is 69.94 wt %.

From the study conducted, the efficiency of the metal ion removal in the oily wastewater is proportionally increases with the dose of chitosan added. The percentage removal of zinc, lead and iron at optimum dose of chitosan added is 89.08%, 84.00%, and 61.36% accordingly. Increasing the contact time also results in increases of percentage removal of metal ions. The percentage removal of zinc, lead, and iron at optimum contact time is 93.70%, 78.85%, and 65.58% accordingly. From the results obtained, the selectivity of chitosan decreased in order $Zn^{2+} > Pb^{2+} > Fe^{2+}$.

5.2 Recommendations

As described in the methodology section, the crab shells took four days to dry under the sun due to the bad weather. For this reason, it is recommended to dry the crab shells in oven with controlled temperature instead of sun drying. In this way, the time taken to complete the experiments can be reduced and saved.

In addition, further study can be carried out on removal efficiency of metal ions based on pH and agitation speed. In the future, the study on adsorption isotherm also can be done to examine the adsorption capacity and thus deepen the knowledge about adsorption itself.

APPENDICES

APPENDIX A

APPLICATIONS OF CHITOSAN

Table A.1 Applications of chitosan (Goosen, 1997).

Applications	Examples
Water Treatment	Removal of Metal Ions Flocculants/Coagulant: Proteins Dyes Amino Acids Filtration
Pulp and Paper	Surface Treatment Photographic Paper Carbonless Copy Paper
Medical	Bandages, Sponges Artificial Blood Vessel Blood Cholesterol Control Tumor Inhibition Membranes Dental/Plaque Inhibition Skin Burns/Artificial Skin Eye Humor Fluid Contact Lens Controlled Release of Drugs Bone Disease Treatment

Cosmetics	Make-up Powder Nail Polish Moisturizers Fixtures Bath Lotion Face, Hand and Body Creams Toothpaste Foam Enhancing
Biotechnology	Enzyme immobilization Protein separation Chromatography Cell Recovery Cell Immobilization Glucose Electrode
Agriculture	Seed Coating Leaf Coating Hydroponics/Fertilizer Animal Feed Additive
Membranes	Reverse osmosis Permeability Control Solvent Separation

APPENDIX B

FLAME ATOMIC ABSORPTION SPECTROMETRY

Flame atomic absorption is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use. Figure B.1 shows which elements are commonly detected through atomic absorption. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve.

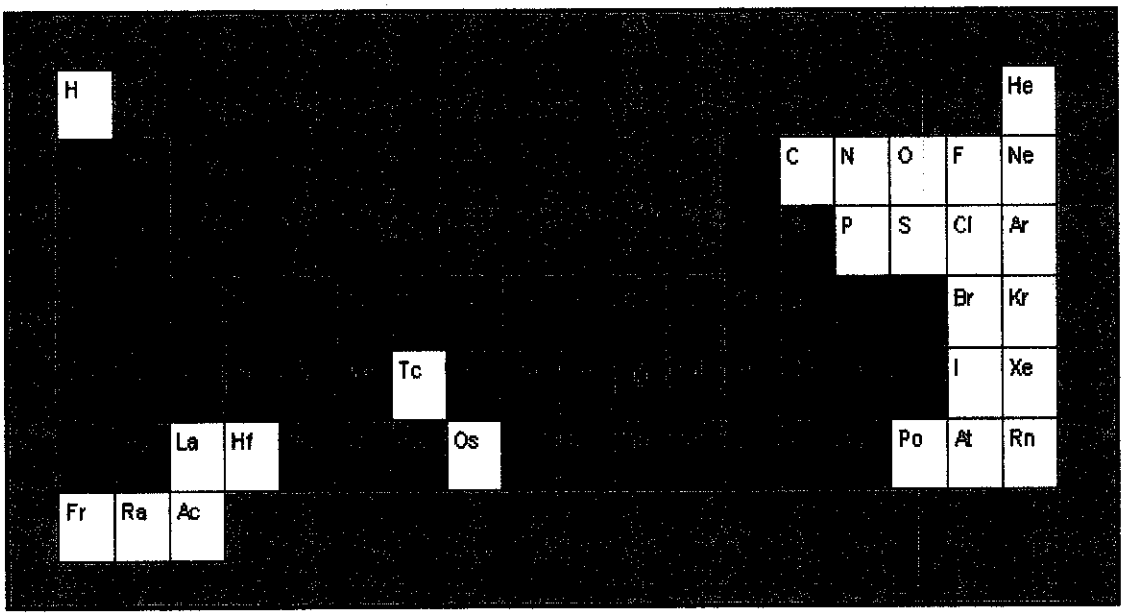

Figure B.1 Elements detectable by FAAS are highlighted in pink.

The technique of Flame Atomic Absorption Spectroscopy (FAAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C.

During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths, as shown in Figure B.2.

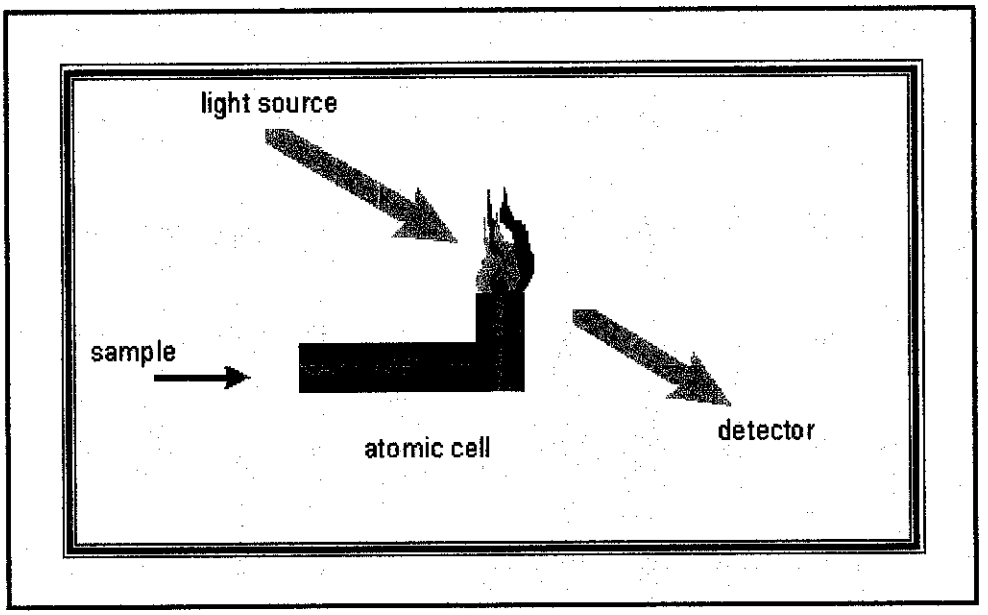

Figure B.2 Operation principles of FAAS.

The characteristic wavelengths are element specific and accurate to 0.01-0.1nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photon multiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample.

Flame atomic absorption hardware is divided into six fundamental groups that have two major functions: generating atomic signals and signal processing. Signal processing is a growing additional feature to be integrated or externally fitted to the instrument. The instrument parts are shown in Figure B.3.

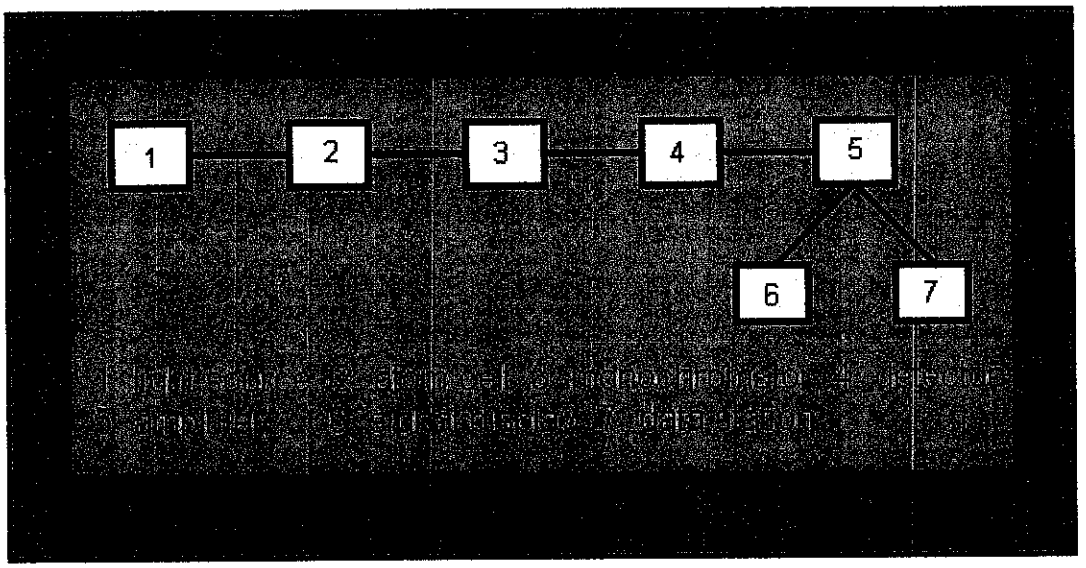

Figure B.3 Schematic diagrams of basic instrumental parts of FAAS.

A cathode lamp (1) is a stable light source, which is necessary to emit the sharp characteristic spectrum of the element to be determined. A different cathode lamp is needed for each element, although there are some lamps that can be used to determine three or four different elements if the cathode contains all of them. Each time a lamp is changed, proper alignment is needed in order to get as much light as possible through the flame, where the analyte is being atomized, and into the monochromator.

The atom cell (2) is the part with two major functions: nebulization of sample solution into a fine aerosol solution, and dissociation of the analyte elements into free gaseous ground state form. Not all the analyte goes through the flame; part of it is disposed.

As the sample passes through the flame, the beam of light passes through it into the monochromator (3). The monochromator isolates the specific spectrum line emitted by the light source through spectral dispersion, and focuses it upon a photomultiplier detector (4), whose function is to convert the light signal into an electrical signal.

The processing of electrical signal is fulfilled by a signal amplifier (5). The signal could be displayed for readout (6), or further fed into a data station (7) for printout by the requested format.

As with other analytical techniques, atomic absorption spectrometry requires careful calibration. The idealized calibration or standard curve is stated by Beer's law that the absorbance of an absorbing analyte is proportional to its concentration as shown in Figure B.4.

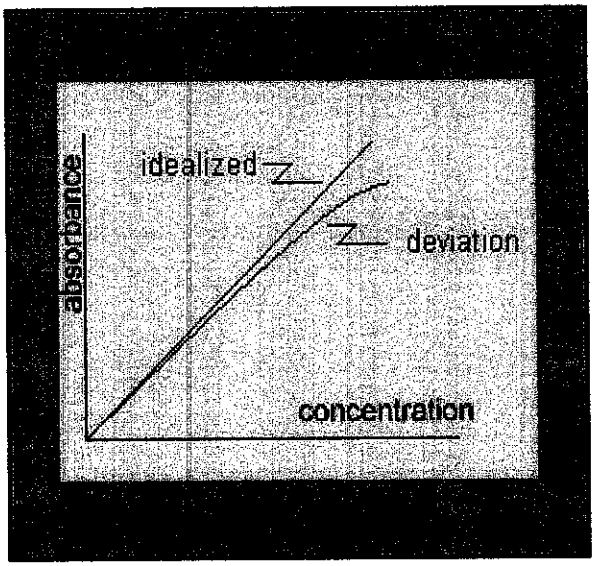

Figure B.4 Idealized and deviation response curve.

APPENDIX C

EXPERIMENTAL DATA

Table C.1 Tabulated data for the study of influence of dose, and effect of contact time for iron, zinc, and lead.

Metal ions	Initial Conc. (ppm)	*E*(%) for Influence of Dose			*E*(%) for Effect of Contact Time		
		0.2 g	0.5 g	1.0 g	2 hr	4 hr	8 hr
Fe^{2+}	8.10	47.78	51.85	61.36	61.48	62.10	65.58
Zn^{2+}	2.38	81.93	82.35	89.08	88.66	89.92	93.70
Pb^{2+}	0.52	72.00	76.00	84.00	76.92	78.85	78.85