BIOSORPTION OF Pb USING FRESHWATER ALGAE

(*SCENEDESMUS QUADRICAUDA*)

by

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14228

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical)

September 2014

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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(CHEMICAL)

Approved by,

____

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2014

CERTIFICATION OF ORIGINALITY

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

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(NURLIANA FARHANA SALEHUDDIN)

ABSTRACT

The presence of heavy metals due to anthropogenic activities have caused chronic effects on human health. Heavy metals are also toxic to plants, animals and micro-organisms in the environment. Due to that, various methods have been developed to remove these heavy metals including chemical precipitation, electrochemical treatment, ion exchange, membrane technology and coagulation-flocculation. Somehow, these methods have many disadvantages such as produce high quantity of sludge and high cost for it to be conducted. Hence, an alternative process known as biosorption using algae is considered due to its low cost and ease of availability. However, biosorption process using algae has several major concerns especially on how to maximize the biosorption of heavy metal concentration. This research work focuses on the biosorption of Pb using freshwater algae by varying the biosorbent dosage, pH value and concentration of Pb solution in order to maximize the biosorptivity. Pb content was quantified using Atomic Absorption Spectroscopy (AAS). The maximum Pb uptake by the biosorbent was calculated using Langmuir and Freundlich isotherms. It was observed that the maximum biosorption in 60 ppm Pb can be achieved when using 0.05g biosorbent and at pH value of 4. The freshwater algae has the ability to adsorb Pb until 150 ppm of concentration metal solution and the maximum biosorption is 158.73 (mg/g) at optimum operating condition.

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Table of Contents

CERTIFICATION OF APPROVAL i
CERTIFICATION OF ORIGINALITY ii
ABSTRACT iii
ACKNOWLEDGEMENT iv
List of tables vii
List of figures viii
CHAPTER 1: INTRODUCTION 1
1.1 Background 1
1.2 Problem Statement 4
1.3 Objectives 4
1.4 Scope of Study 5
1.5 Relevancy and Feasibility of Project 5
CHAPTER 2: LITERATURE REVIEW 6
2.1 Methods of Removal Heavy Metals 6
2.2 Types of Biosorbent in Biosorption Process 8
2.2.1 Algae 8
2.2.2 Fungi 9
2.2.3 Bacteria 9
2.2.4 Waste materials 9
2.3 Factors That Affect Biosorption of Pb Using Freshwater Algae Biomass 10
2.3.1 pH value of heavy metals solution 10
2.3.2 Contact time 10
2.3.3 Temperature 10
2.3.4 Biosorbent dosage 10
CHAPTER 3: METHODOLOGY 13
3.1 Project Flow Chart 13
3.1.1 Apparatus Used In the Experiment 14
3.1.2 Chemicals 14

3.1.3 Availability of Apparatus/Equipment 15
3.2 Experimental Methodology 16
3.2.1 Material preparation 16
3.2.2 Preparation of biosorbent 16
3.2.3 Experimental procedure for pH analysis 17
3.2.4 Experimental procedure for biosorbent dosage 17
3.2.5 Experimental procedure for initial concentration of Pb 17
3.2.6 Instrumentation 18
3.2.7 Time Management 18
3.3 Gantt Chart and Key Milestone 19
CHAPTER 4: RESULT AND DISCUSSION 20
4.1 Effect of pH Value on The Biosorption 20
4.2 Effect of Biosorbent Dosage (freshwater algae) on the Biosorption 22
4.3 Effect of Initial Metal Ion Concentration on the Biosorption 24
4.4 Equilibrium Isotherms 26
CHAPTER 5: CONCLUSION & RECOMMENDATION 30
REFERENCES 28
APPENDIX 31

List of tables

Table 1: Comparison of concentration heavy metals with background value in Klang Strait 2
Table 2: Comparison concentration of heavy metals in Malaysia with other countries 3
Table 3: Advantages and disadvantages of biosorption [15, 22] 8
Table 4: The effects of heavy metals to health of human [18] 11
Table 5: Chemical used in the project 14
Table 6: Apparatus used in the preparation of biosorbent 15
Table 7: Total time needed for the experiment 18
Table 8: Gantt chart for final year project 19
Table 9: The results for the effect of pH on biosorption 20
Table 10: The results for the effect of biosorbent dosage on biosorption 22
Table 11: The results for the effect of initial Pb concentration on biosorption 24
Table 12: Data for Freundlich and Langmuir isotherms 27
Table 13: Summary of isotherm model parameter for S.quadricauda biomass 28
Table 14: Comparison of maximum biosorption uptake with other freshwater algae 29

List of figures

Figure 1: Project flow Chart 13
Figure 2 : Effect of pH on biosorption of Pb ions by freshwater algae (S.Quadricauda) 21
Figure 3: Effect of biosorbent dosage on biosorption of Pb ions by freshwater algae (S.Quadricauda) 23
Figure 4: Effect of initial concentration Pb solution on biosorption of Pb ions by freshwater algae (S.Quadricauda) 25
Figure 5: Plotting of Freundlich isotherm 27
Figure 6: Plotting of Langmuir isotherm 28

CHAPTER 1: INTRODUCTION

1.1 Background

Heavy metal pollution has become one of the most vital problem to the environment. The major contributors of these heavy metals are form rapid development of many industries such as mining, surface finishing, pesticide, manufacturing and others. Table 1 shows sediment samples that was collected from Port Klang and the results showed concentration of some heavy metals, such as As, Cd and Pb were comparatively higher than the background values. The average concentration of Ar is about three times higher, Cd four times higher and Pb two times higher than heavy metals background value [1].

Port Klang which is located in Malaysia is one of the industrial area that involve in a lot of chemicals and contribute to the pollution in environment. These heavy metals being polluted into the environment through the releasing of wastewater that not treated properly by the industries. These heavy metals then will accumulate in the plants as they cannot be degraded. The persistent of these heavy metals in environment pose harm to human.

Table 1: Comparison of concentration heavy metals with background value in Klang Strait

Concentration of heavy metal (mg/kg)	Al	Fe	Mn	As	Cu	Cr	Cd	Pb	Ni	V	Zn
The average concentration of heavy metal in Klang Strait [2]	14,724	6,547	231.43	60.36	17.43	46.4	0.82	59.45	11.44	52.00	51.05
Heavy metals Background value in Klang	85,100	41,922	349.18	18.79	23.21	53.71	0.18	39.8	32.77	71.59	141.22

A comparison of total concentrations heavy metals at mangrove sediments was also conducted to show the differences. Table 2 shows that compared to the other countries, the concentration Pb is higher than the other heavy metals. The sources of these heavy metals are basically from the anthropogenic activities and because Pb is considered as the most toxic and hazardous to environment hence the urgency of removal is needed [3]. There are number of methods have been introduced to remove these heavy metals such as chemical precipitation, electrochemical treatment, ion exchange, membrane technology and coagulation-flocculation.

For example, chemical precipitation method precipitating the metal into insoluble form. Then, separation being done to remove the solid that contained heavy metals. Meanwhile, for electrochemical method it uses cathode and anode to attract the ions of heavy metals. These conventional methods have several disadvantages where they require high chemical consumption, produce large volume sludge, expensive to be conducted and ineffective [4-6]. Hence, the needed of other method that is low cost arise such as biosorption.

Biosorbtion process can be defined as the accumulation and concentration of pollutants from aqueous solutions by the used of biological materials, thus allowing the recovery and environmentally acceptable disposal of the pollutants [3-5].

Table 2: Comparison concentration of heavy metals in Malaysia with other countries

Country	Cd	Cr	Cu	Pb	Zn	Reference
Peninsular Malaysia	0.80	6.00	31.90	83.10	4.30	[7]
Singapore (Buloh River)	0.18	16.61	7.06	12.28	51.24	[8]
Singapore (Khatib Bongsu River)	0.27	32.07	32.00	30.98	120.23	[8]
Australia (Brisbane River)	< 0.10	13.30	3.10	20.10	40.80	[9]

Hong Kong (Mai Po)	0.50	7.80	41.90	161.60	277.20	[10]

Biosorption can be conducted using algae, bacteria, fungi and waste materials as biosorbent. This study will focus on algae in the form of biomass as biosorbent due to it has low nutrient requirements, large production in term of biomass and it does not produce toxic substances compared to the other biosorbents [11, 12]. Besides, algae showed higher removal percentage of heavy metals compared to the others.

1.2 Problem Statement

The current method of removal heavy metals such as chemical precipitation, ion exchange and others have a lot disadvantages such as they need high initial capital, maintenance and operation cost. They also produce large volume of sludge that required additional cost in order to manage it. Thus, an alternative process known as biosorption using algae is being considered due to it is low cost and ease of availability.

1.3 Objectives

The objectives of this study are:

1. To study the biosorption of Pb using freshwater algae, *S.Quadricauda*.
2. To investigate the biosorption of Pb by varying biosorbent dosage, pH value and concentration of heavy metals solutions.

1.4 Scope of Study

Dried freshwater algae will be used to adsorb Pb. Then, concentration of the heavy metals uptake will be calculated through Freundlich and Langmuir isotherms. These isotherms were found to be the best guide to determine whether the biosorption process is favourable or not.

1.5 Relevancy and Feasibility of Project

The source of biosorbent is algae which can be easily obtained and the biosorption is a relevant process to be done. By proper planning and execution, this project can be completed as per scope before the date of completion as the biosorption method used do not consume much time.

CHAPTER 2: LITERATURE REVIEW

2.1 Methods of Removal Heavy Metals

Metals can be divided as light, heavy and metalloids (semi-metals) based on the chemical and physical properties. Heavy metal is a term that used for metals and metalloids that have atomic density greater than 5 g cm^{-3} while "toxic heavy metal" used to stress the effect of these elements on the environment specifically their influenced on the flora and fauna. Based on other research, metals that can be classified as heavy metal are: Cu (Copper), Co (Cobalt), Cr (Chromium), Cd (Cadmium), Fe (Iron), Zn (Zinc), Pb (Lead), Sn (Tin), Hg (Mercury), Mn (Manganese) , Ni (Nickel),V (Vanadium) and etc [13].

There are many methods can be used to remove heavy metals from the environment. Based on Fu and Wang (2011), chemical precipitation is a simple process that applicable to different metals and it is low cost to be conducted. However, it produces large volume of sludge and requires high cost for disposal. Second method is by using electrochemical treatment. It also applicable for all types of heavy metals and suitable for the treatment of very toxic waste. It runs by electricity and easy to be operated. The disadvantages of this treatment, it needs high initial capital, maintenance and operation cost. Besides, it requires continuous supply of electricity where it will add more cost to it [14].

Next, ion exchange also can be used to remove heavy metals. It has high regeneration capacity but at the same time involves high initial capital and maintenance cost [15]. For membrane technology, it has been found that it generated low solid waste and consume less quantity of chemicals. Somehow, this kind of technology only valid at room temperature. This is due to at high temperature membrane deterioration can be rapid. As it uses membrane to remove heavy metals thus it also has high maintenance and operation cost [16].

Another method that can be used is coagulation-flocculation where it has good sludge settling and dewatering characteristics but it consumes too much chemicals to coagulate the heavy metals [17]. Lastly, the recent method that has been discovered is biosorption process. This method has many advantages such as low cost to be conducted, high efficiency due to its short operation time, minimize used of chemical and biological sludge. The most unique feature of this method is the bisorbent can be reused ant regenerated after several times of usage [18].

2.2 **Types of Biosorbent in Biosorption Process**

2.2.1 Algae

In this study, the method that will be used is biosorption through algae. It is a process where biomaterial or biopolymer is engaged as sorbent. This is due to higher attraction of the sorbent for the sorbate species, the latter is attracted and removed by different mechanisms. The process continuous till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution [6].Recently, the use of aquatic plants especially micro and macro algae has gained much attention due to their capability to adsorb metals and taking up toxic elements from the environment or rendering them less harmful [6, 19, 20]. Biosorption process has their own advantages and disadvantages which being listed in Table 3.

Table 3: Advantages and disadvantages of biosorption [15, 22]

Advantage	**Disadvantage**
Low cost	Metal desorption is necessary when metal interactive sites are full
High efficiency	Potential for biological process improvement is limited because cells are not metabolizing
Chemical minimization	No potential for biologically altering the metal valency state
Regeneration of biosorbent and possibility of metal recovery	-

2.2.2 Fungi

Fungus where belongs to group of organisms that has been demonstrated from the past studies where some of them are typically related with heavy metal rich subrata and can be even considered as hyper accumulators of heavy metals [21]. On the other hand, it can be exposed to heavy metals from the atmosphere and are very well known from biomonitoring studies focused on heavy metal pollution [22]. Somehow, in order to used fungi as biosorbent they are largely depends on parameters such as pH, metal ion and biomass concentration, physical or chemical pre-treatment of biomass and presence of various legends in solution [23]. Hence, to use fungus in this project is quite troublesome and some of the fungus produces toxic substance.

2.2.3 Bacteria

The walls of bacteria are efficient metal chelators through a wide spectrum of uptake capacities may be inhibited. Metal binding may be at least a two stage process first involving interaction between metal ions and reactive groups followed by inorganic deposition of increased amounts of metal. Somehow, there are only several types of bacteria that capable in biosorption of heavy metals [24].

2.2.4 Waste materials

In this case, a variety of by-products where it is cheap and inexhaustible to be used such as wool, olive cake, sawdust, almond, coal and others. There are less abundance of past research involved waste material as biosorbent.

2.3 Factors That Affect Biosorption of Pb Using Freshwater Algae Biomass

The major factors affect the biosorption processes are:

2.3.1 pH value of heavy metals solution

At lower pH, the concentration of positive charge increased on the sites of biomass surface which restricted the approach of metal cations to the surface of biomass. As pH increased the proton concentration decrease and surface biomass is more negatively charged. The biosorption of the positively charged metals ions increased until reach maximum biosorption.

2.3.2 Contact time

The rate of metal ion biosorption was highest in the beginning due to high affinity of free metal ion binding sites on bio sorbent but after equilibrium, the removal efficiency did not significantly changed due to complete coverage of active [25].

2.3.3 Temperature

Temperature does not influence the biosorption processes in the range of 20 to 35 degree Celcius. At high temperature the interaction rate between biomass and heavy metal ion decrease. The boundary layer is reduced with rising temperature and resulted in a decreasing removal rate of heavy metal ions [26].

2.3.4 Biosorbent dosage

The biosorption increased with subsequent increasing the biosorbent dose and almost became constant at higher dosage than 0.1 g/100 ml and 0.2 g/100 ml for Pb, respectively. It can be explained by the formation of aggregates of the biomass at higher doses, which decreases the effective surface area of biosorption [27].

2.4 Reasons Choosing the Dead Cells over Live Cells

The use of dead cells offers the following advantages over live cells:

- There is no toxicity limitations when remove the metal.
- No necessity for growth media and nutrients where it is troublesome and consume time. The biomass can be reused due to the ability to desorb the metals.
- Biomass-based treatment systems can be applied to traditional adsorption models in use[28].

2.5 Effects of Heavy Metals towards Health and Environment

Due to properties of heavy metal where it is stable and persistent environmental contaminants since it cannot be degraded or destroyed, therefore it causes major environmental and health problems [29]. Despite the source of the heavy metals in the soil, the excessive amount of it can cause soil quality degradation, crop yield decreasing, and poor quality of agricultural products, posing significant hazards to human, animal, and ecosystem health [30]. The uptake of heavy metals from soil and translocation from roots to fruits are varies depending on the species of plant. The metals do not accumulate in the fruits therefore leafy vegetables, herbs and root crops have more risk than fruiting crops [31].In terms of health, the effects of heavy metals can be seen in the Table 4.

Table 4: The effects of heavy metals to health of human [18]

Heavy metal	Effects
Arsenic (As)	Well-known as a poison and a carcinogen.
Cadmium (Cd)	Toxicity is linked with reproduction problem because it affects sperm and reduces birth weight.
Chromium (Cr)	Excessive amount can cause toxicity.

Lead (Pb)	Lead poisoning is one of the most prevalent public health problems in many parts of the world. It also affects the brain and causing hyperactivity.
Mercury (Hg)	Toxic even at low concentrations. May also cause development of autoimmunity, in which a person's immune system attacks its own cells.
Nickel (Ni)	High amounts can occur in food crops growing in polluted soils. Uptake of high quantities of nickel can cause cancer, respiratory failure, birth defects, allergies, and heart failure

Technologies that can be included to clean up the heavy metals are excavation which is physical removal of contaminated material or stabilization of the metals on site or lastly by using growing plants to stop the spread of contamination heavy metals(phytoremediation) [32].

CHAPTER 3: METHODOLOGY

3.1 Project Flow Chart

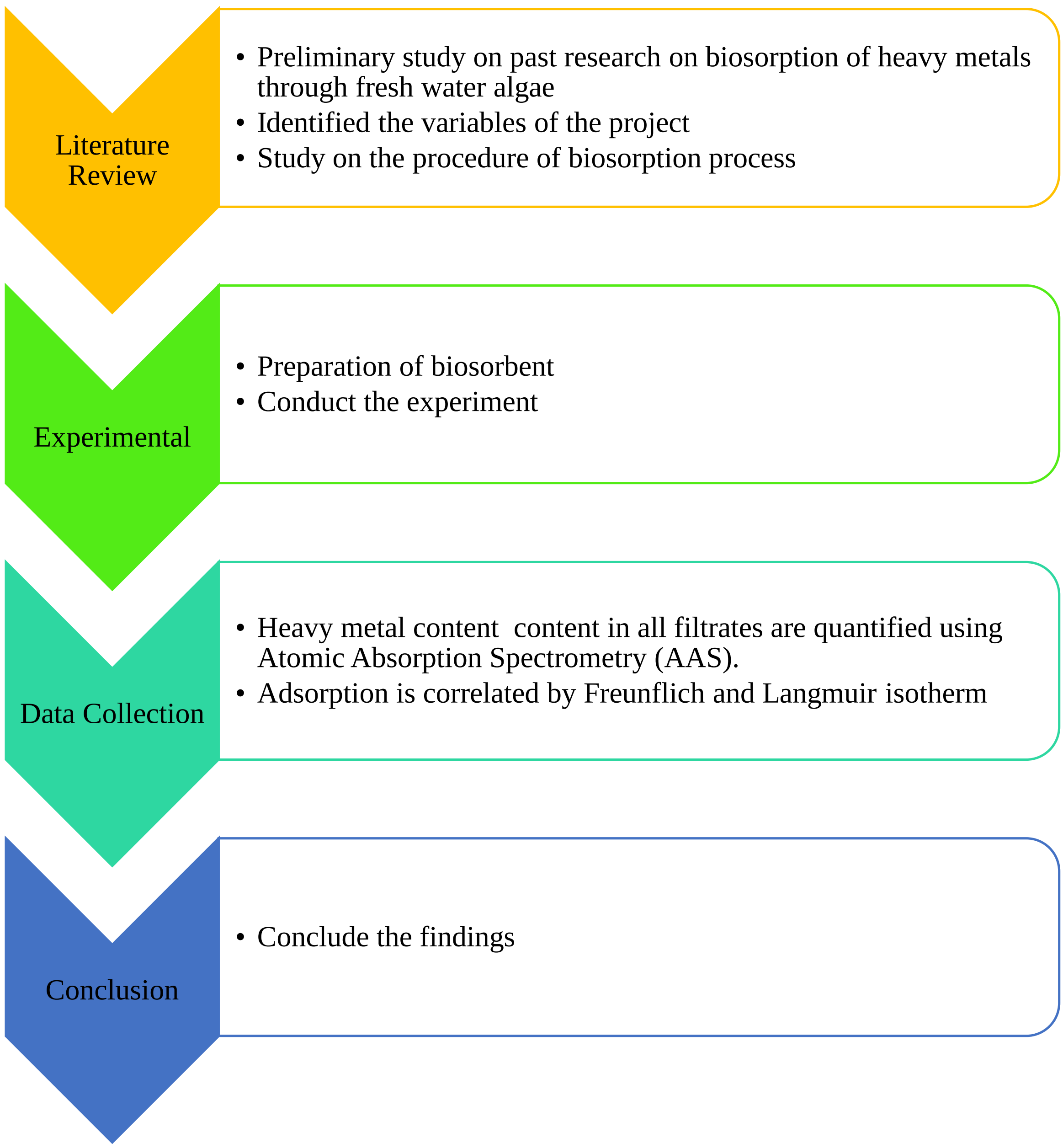

Figure 1: Project flow Chart

3.1.1 Apparatus Used In the Experiment

The apparatus used in this project included a centrifuge in which it is used to separate the algae from the heavy metal solution, a lamp of -2500 lux as the source of light energy in order to cultivate the algae as well as an oven to assist in drying the algae for experimental works. In addition, the Erlenmayer flasks are used throughout the process of conducting the experiment to contain the solutions while a rotary shaker is used to shake the solutions so that they mix well. This is vital in ensuring a reliable results for the experiment. Furthermore, a weighing scale is utilised to obtain the actual weight of the algae required in this experiment. Last but not least is the filter papers to filtrate the algae from heavy metal solution.

3.1.2 Chemicals

The chemicals used in this study are lead nitrate, hydrocholoric acid, sodium hydroxide and freshwater algae biomass. Lead nitrate is used as source of heavy metal while hydrochloric acid and sodium hydroxide function to vary the pH level of lead nitrate solution for experimental work. The properties of each chemical are tabulated in Table 5.

Table 5: Chemical used in the project

Chemical Name	Chemical Formula	Mw (g/mol)	Total Mass / Volume for whole experiment
Lead Nitrate	$Pb(NO_3)_2$	331.20	10.8 L
Hydrochloric Acid	HCl	36.46	20 ml

Sodium Hydroxide	NaOH	40.00	20 ml
Freshwater algae biomass	-	-	20 g

3.1.3 Availability of Apparatus/Equipment

The availability of the equipment utilized in this study are recorded in Table 6.

Table 6: Apparatus used in the preparation of biosorbent

Apparatus	Operating Parameter	Remarks
Polyethylene bottle	-	Available in laboratory
Oven	Temperature: 80°C Duration: 24 hours	Available in block 4
Centrifuge	Speed : 4500 rpm Duration : 5 minutes	Available in block 4
Erlenmeyer Flask	-	Available in laboratory
Rotary Shaker	Speed : 180 rpm Duration : 120 minutes	Available in block 4

3.2 Experimental Methodology

The main guidance of this research is Kumar,J.I.,Oommen,C.,J Environ Biol. 33 (2012) 27 and K.Ali et al., Biosorption of cadmium and lead from aqueous solution by fresh water algae Anabaena sphaerica biomass. 4, 2013: p. 367-374.

3.2.1 Material preparation

1. Freshwater algae (*S.Quadricauda*) were cultivated in BG 11 medium with macro elements.
2. Algal should be in logarithmic phase of growth as it being introduced to the standard algal culture media.
3. Algal cultures were incubated at 24 ± 2 ℃ under continuous illumination (-2500 lux).
4. The containers of algal were swirled once daily to prevent clumping and adherence of the algal cells to the containers.
5. After 10 to 14 days, the cultures were centrifuged at 4500 rpm for 5 min. Then, biomass at maximum growth were collected.

3.2.2 Preparation of biosorbent

1. Collected algae were washed twice with tap water and double distilled water to eliminate adhering foreign particles.
2. Then, dried in the oven at 80 degree Celsius.
3. Lastly, the biomass were grounded and sieved through 2 mm mesh size sieve and stored in polyethylene bottles.

3.2.3 Experimental procedure for pH analysis

1. Batch equilibrium experiment is performed at room temperature in 250 ml Erlenmayer flask containing aqueous solution of Pb at known concentrations at 60 ppm (Lead nitrate) by adjusting the pH at 2, 3, 4, 5 and 6 using HCl and NaOh. Each at 100 ml.

2. 100 mg algae were weighed and added to each flask. The mixtures were agitated on a rotary shaker at 180 rpm for 120 min. Each concentration was controlled without addition of heavy metals.

3. Mixtures then being filtered and amount of heavy metal adsorbed were analysed. Experiment was repeated thrice to get accurate results.

3.2.4 Experimental procedure for biosorbent dosage

1. Batch experiment at room temperature of Pb at 60 ppm (Lead nitrate).
2. The biosorbent dosage varied from 0.025 g to 0.20 g being added at metal solutions at optimum pH chooses from the first experiment. The mixtures were agitated on rotary shaker at 180 rpm for 120 min.
3. Mixtures then being filtered and amount of heavy metal adsorbed were analysed. Experiment was repeated thrice to get accurate results.

3.2.5 Experimental procedure for initial concentration of Pb

1. Batch equilibrium experiment was performed at room temperature in 250 ml Erlenmayer flask containing aqueous solution of Pb
2. 30, 60, 90, 120 and 150 mg/liter were prepared using analytical grade Lead Nitrate at the fixed pH.
3. Maximum dose of algae was weighed from previous experiment to each flask.
4. Mixtures then being filtered and amount of heavy metal adsorbed were analysed. Experiment was repeated thrice to get accurate results.

3.2.6 Instrumentation

Heavy metal content in filtrates were quantified using Atomic Absorption Spectrometry (AAS). Atomic absorption spectrometry (AAS) is an analytical that measures the concentrations of elements. It makes use of the wavelengths of light specifically absorbed by an element. Atoms of different elements absorb characteristic wavelengths of light. A calibration curve is used to determine the unknown concentration of an element. A calibration curve is plotted which is continually rescaled as more concentrated solutions are used, the more concentrated solutions absorb more radiation up to a certain absorbance [33]. The amount of metal adsorbed at equilibrium, q (mg g^{-1}), which represents the heavy metal uptake from the difference in metal concentration in the aqueous phase before and after adsorption was calculated.

3.2.7 Time Management

Time management is important in conducting an experiment as this is to make sure that the experimental can be proceed smoothly without overlapping with other's schedule. Below shows the estimation of time needed for each task in this project in Table 7.

Table 7: Total time needed for the experiment

Task	Total time needed
Preparation of biosorbent	One month
Experiment 1	24 hours (1 day)
Experiment 2: pH value	72 hours (3 days)
Experiment 3: Biosorbent dosage	120 hours (5 days)

3.3 Gantt Chart and Key Milestone

Table 8: Gantt chart for final year project

No	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project work continuous														
2	Submission of Progress Report														
3	Project work continuous														
4	Pre-SEDEX														
5	Submission of Draft Final Report														
6	Submission of Dissertation (Soft bound)														
7	Submission of Technical Paper														
8	Viva														
9	Submission of Project Dissertation Hard bound)														

CHAPTER 4: RESULT AND DISCUSSION

4.1 Effect of pH Value on The Biosorption

The variables that are kept constant throughout this experiment include concentration of Pb solution, mass of biosorbent and speed of mechanical shaker. The concentration of Pb solution is kept constant at 60 ppm for 100 ml. Then, the mass of biosorbent used in this experiment is fixed at 0.1 g. The experiment is conducted in mechanical shaker for 120 minutes at 180 rpm.

Table 9: The results for the effect of pH on biosorption

pH	**2**	**3**	**4**	**5**	**6**
Average C_f (ppm)	54.78	33.19	15.09	28.21	28.37
Percentage Biosorption (%)	8.70	44.70	74.90	53.00	52.70
Metal uptake, q (mg/g)	5.22	26.81	44.91	31.79	31.63

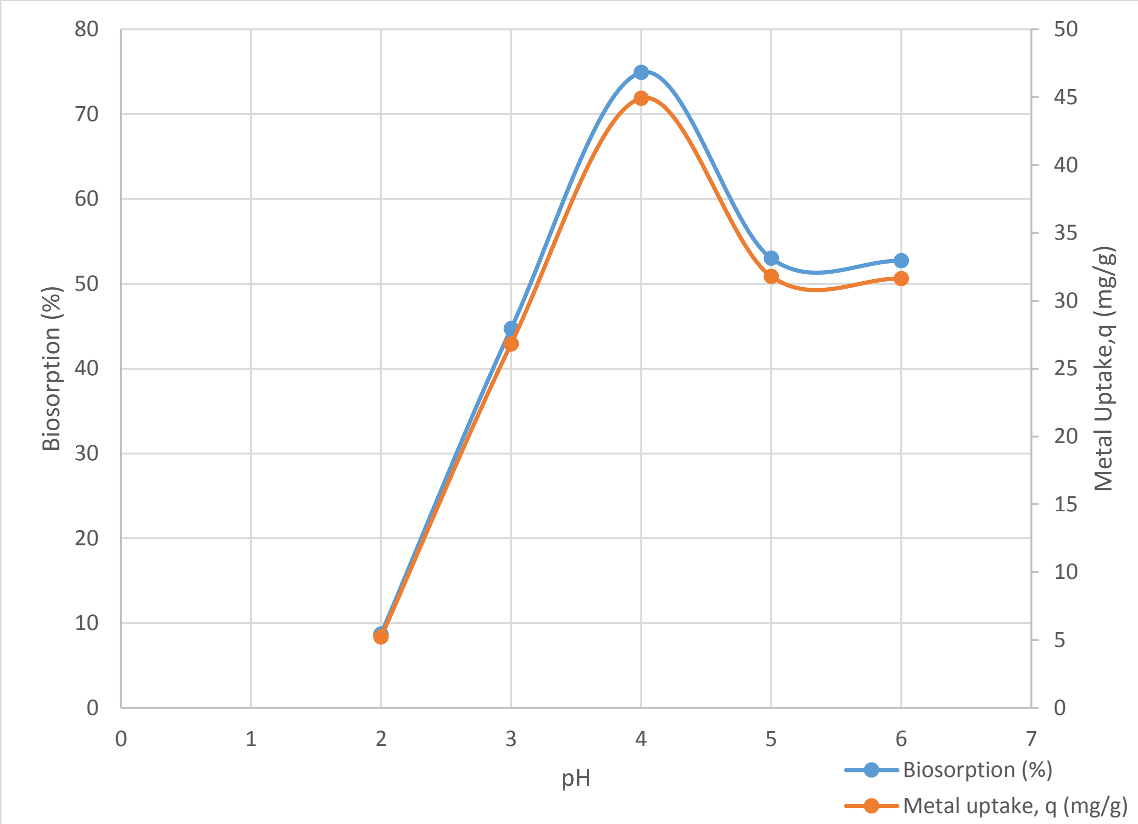

Figure 2 : Effect of pH on biosorption of Pb ions by freshwater algae (*S.Quadricauda*)

As explained earlier in the chapter 2, the pH value plays a significant part in the adsorption of metals with biosorbents. The effects of pH on the biosorption of Pb ions onto *S.Quadricauda* can be seen in Figure 2. The optimum removal of Pb ions occurred at pH 4 where the percentage biosorption reached 74.9 % with optimum uptake for 44.91 mg/g. Therefore, an optimum pH 4 was selected for next experiments.

There was an increasing in biosorption capacity with increasing of pH from 2 to 4. This is due to at lower pH there are restrictions for metal cations to approach surface of biosorbents as competition occurred with large quantities of protons. As the pH increased, the proton concentrations decreased and overall surface of *S.Quadricauda* became negative, then attract Pb ions until reaching maximum biosorption. This was also observed by Xue-Jiang et al. (2006).

While at pH value higher than 4 biosorption studies could not be performed because precipitation of Pb ions in the form of $Pb(OH)_2$ started to occur. Hence, it caused the biorsorption percentage and uptake to decrease due to lack of surface are of biosorbent to bind the Pb ions.

4.2 Effect of Biosorbent Dosage (freshwater algae) on the Biosorption

The variables that are kept constant throughout this experiment include concentration of Pb solution, mass of biosorbent and speed of mechanical shaker. The concentration of Pb solution is kept constant at 60 ppm for 100 ml and at pH 4. The experiment is conducted in mechanical shaker for 120 minutes at 180 rpm.

Table 10: The results for the effect of biosorbent dosage on biosorption

Biosorbent Dosage (g)	**0.025**	**0.05**	**0.1**	**0.15**	**0.2**
Average C_f (ppm)	15.61	7.75	15.50	32.12	42.65
Percentage Biosorption (%)	74.00	87.10	74.20	46.50	30.00
Metal uptake, q (mg/g)	177.56	104.50	44.50	18.60	8.70

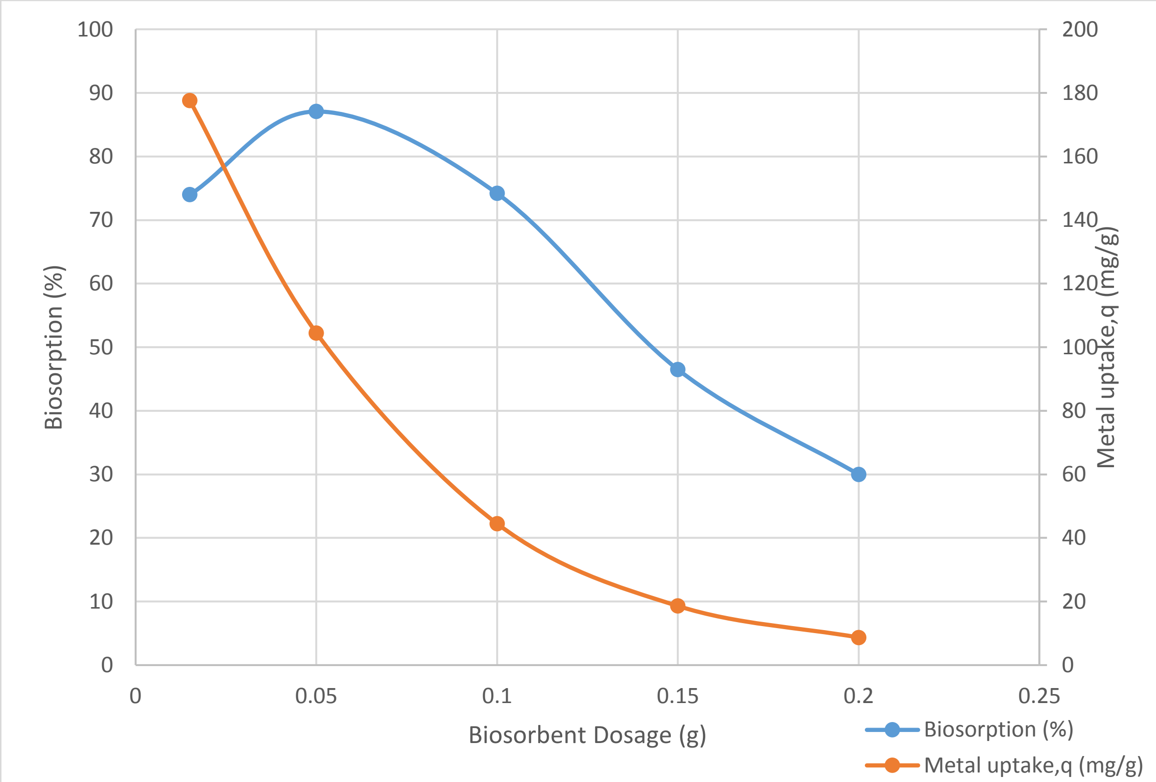

Figure 3: Effect of biosorbent dosage on biosorption of Pb ions by freshwater algae (*S.Quadricauda*)

Besides pH value, biosorbent dosage is also an important factor to be considered. The sorbent-sorbate equilibrium of the system are determined from the values. The effect of *S.Quadricauda* dosage on the removal of Pb ions was studied using different dosage in the range of 0.025 g to 0.2 g suspended in 100 ml Pb solution where the concentration is 60 ppm. Figure 3 shows the percentage of removal versus biosorbent dosage. The results show that the maximum biosorption was observed with 0.05 g dose. But the Pb uptake started to decrease when the dosage was more than 0.05g.

The reason for this may be at 0.05 g, all of the binding sites were fully utilized. This is probably due to all sites being totally exposed and saturated faster. As the dosage increased, partial aggregation and screening effect on the biomass surface started to occur, thus giving a rise to the decrease of active sites and lowering the biosorption [34].

4.3 Effect of Initial Metal Ion Concentration on the Biosorption

The variables that are kept constant throughout this experiment include concentration of Pb solution, mass of biosorbent and speed of mechanical shaker. Then, the mass of biosorbent used in this experiment is fixed at 0.05 g in 100 ml Pb solution at pH 4. The experiment is conducted in mechanical shaker for 120 minutes at 180 rpm.

Table 11: The results for the effect of initial Pb concentration on biosorption

Initial Concentration of Pb (ppm)	**30**	**60**	**90**	**120**	**150**
Average C_f (ppm)	2.11	12.18	23.95	56.39	71.04
Percentage Biosorption (%)	93.00	79.70	73.40	53.00	52.60
Metal uptake, q (mg/g)	55.78	95.64	132.10	127.22	157.92

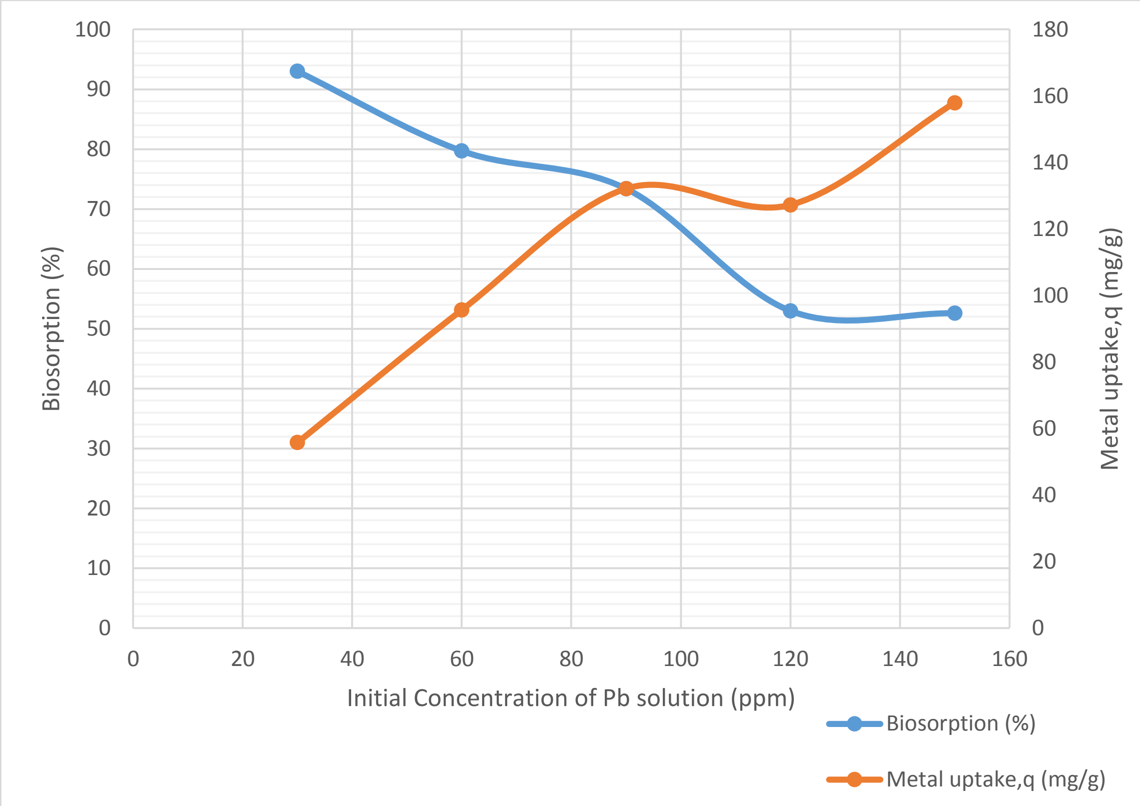

Figure 4: Effect of initial concentration Pb solution on biosorption of Pb ions by freshwater algae (*S.Quadricauda*)

Figure 4 showed the effect of initial concentration of Pb solution on the percentage biosorption. The rate of biosorption is a function of initial concentration of metal ions, which makes it an important factor to be considered for effective biosorption. The results in Figure 4 showed that the biosorption of Pb ions at the beginning was 93 % with uptake about 55.78 mg/g. As the initial concentration increased the percentage of biosorption decreased. This can be related to the fact that, at the beginning all binding sites were vacant hence resulting high Pb biosorption. With the increasing of metal concentration, less active sites were available on the surface of *S.Quadricauda* [35]. It can be concluded that, the algae biomass *S,Quadricauda* capable to biosorp Pb until 150 ppm. The optimum uptake occurred when initial concentration of Pb solution at 150 ppm for 157.92 mg/g.

4.4 Equilibrium Isotherms

Due to their simplicity, the Freundlich and Langmuir equations are the most widely used models to describe the relationship between equilibrium metal biosorption q (mg/g) and final concentrations C_f (mg/L).

Freundlich Isotherm presented by the following equations:

$$q = K_f \, C_f^{\frac{1}{n}} \ldots\ldots\ldots (1)$$

In the linearized form,

$$log\ q = log\ K_f + \frac{1}{n} log\ C_f \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In order to calculate the metal uptake by the algae, following formula being used:

$$q = v \frac{C_i - C_f}{m} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where

q = Metal uptake (mg metal / g of biosorbent)

v = Volume of liquid sample (L) = 0.1L

C_i = Initial concentration of Pb in the solution (mg/L)

C_f = Equilibrium (residual) concentration of metal in the solution (mg/L)

m = Mass of the algae biomass (g)= 0.05 g

Langmuir isotherm presented by the following equation:

$$\frac{C_f}{q} = \frac{1}{Qb} + \frac{C_e}{Q} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

C_f = Equilibrium (residual) concentration of metal in the solution (mg/L)

q = Metal uptake (mg metal / g of biosorbent)

$Q\left(\frac{mg}{g}\right)$ $and\ b$ are Langmuir constants related to mono layer capacity sorption and sorption energy, respectively.

Table 12: Data for Freundlich and Langmuir isotherms

Initial concentration of Pb, C_i (ppm)	**30**	**60**	**90**	**120**	**150**
Final concentration of Pb, C_f (ppm)	2.11	12.18	23.95	56.39	71.04
Log C_f (ppm)	0.32	1.09	1.38	1.75	1.85
Metal uptake, q (mg/g)	55.78	95.64	132.10	127.22	157.92
Log q (ppm)	1.75	1.98	2.12	2.10	2.20
C_f/q (g/L)	0.038	0.127	0.181	0.443	0.450

Freundlich Plotting

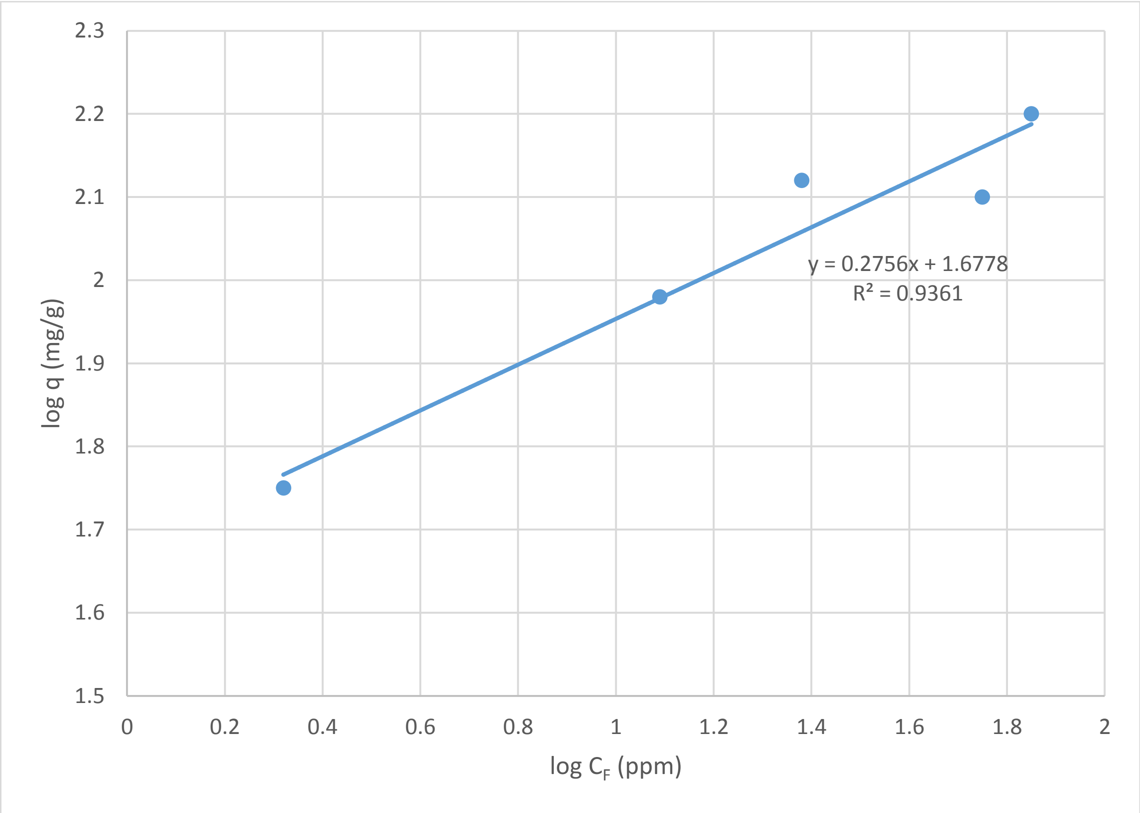

Figure 5: Plotting of Freundlich isotherm

Langmuir Plotting

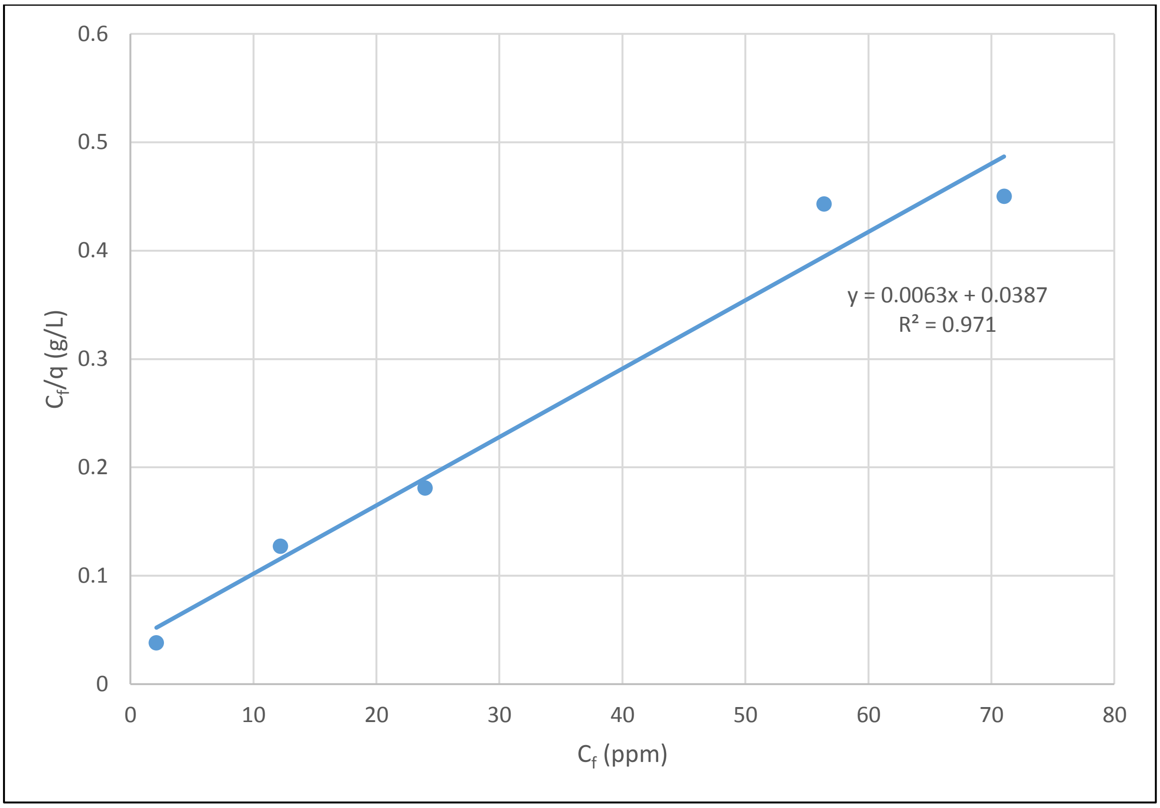

Figure 6: Plotting of Langmuir isotherm

<u>Summary of isotherm model parameters for *S.Quadricauda* biomass</u>

Table 13: Summary of isotherm model parameter for *S.quadricauda* biomass

Freundlich model			Langmuir model		
K_f	1/n	R^2	Q_{max} (mg/g)	1/b	R^2
47.620	0.276	0.936	158.730	0.163	0.971

From the Freundlich isotherm plot, the value of K_f and 1/n can be determined and summarized in Table 13. The value of K_f indicate the adsorption capacity and represent adsorption intensity. The value of 1/n less than 1, indicated that the biosorption process for Pb onto *S.Quadricauda* was favourable at the studied experimental conditions and it is good biosorbent.

Compared to Freundlich (R= 0.936), Langmuir isotherm (R=0.971) can describe the adsorption of Pb onto algal biomass better. Next the optimum uptake for *S.Quadricauda* is 158.73 mg/g.

4.5 Comparison of Uptake of Pb with Other Adsorbents (freshwater algae)

Table 14: Comparison of maximum biosorption uptake with other freshwater algae

Adsorbent	Q_{max} (mg/g)	Reference
Spirogrya sp.	140.84	[36]
Oedogonium sp.	145.00	[37]
Nostoc sp.	93.50	[37]
Ulva lactuca sp.	34.70	[38]
S.Quadricauda sp.	158.73	Current study

From Table 14, it proved that *S.Quadricauda* could be used as potential biosorbent to remove Pb from the environment and industry. This can be shown by the current study in which it demonstrated the highest uptake of heavy metal, $Q_{max.}$ The *S.Quadricauda* is able to adsorp 158.73 mg of lead per one gram of it species. In comparison to other species of biosorbent, *S.Quadricauda* possess the largest uptake of Pb and it has achieved all the objectives required for this study.

CHAPTER 5: CONCLUSION & RECOMMENDATION

This project was designed to investigate the capability of freshwater algae (*S.Quadricauda*) in adsorps Pb and maximize the biosorption by varying the parameters. Parameters involved were pH value of Pb solution, dosage biosorbent and initial concentration of Pb solution. The maximum biosorption capacities were 158.73 mg/g at optimum operating conditions. The data showed that Pb biosorption were fitted to both Freundlich and Langmuir isotherms. Based on the results, *S.Quadricauda* can be used as low cost biomass to remove heavy metals from the environment.

For further improvement, more parameters and heavy metals could be investigated for removal by algae biosorbent.

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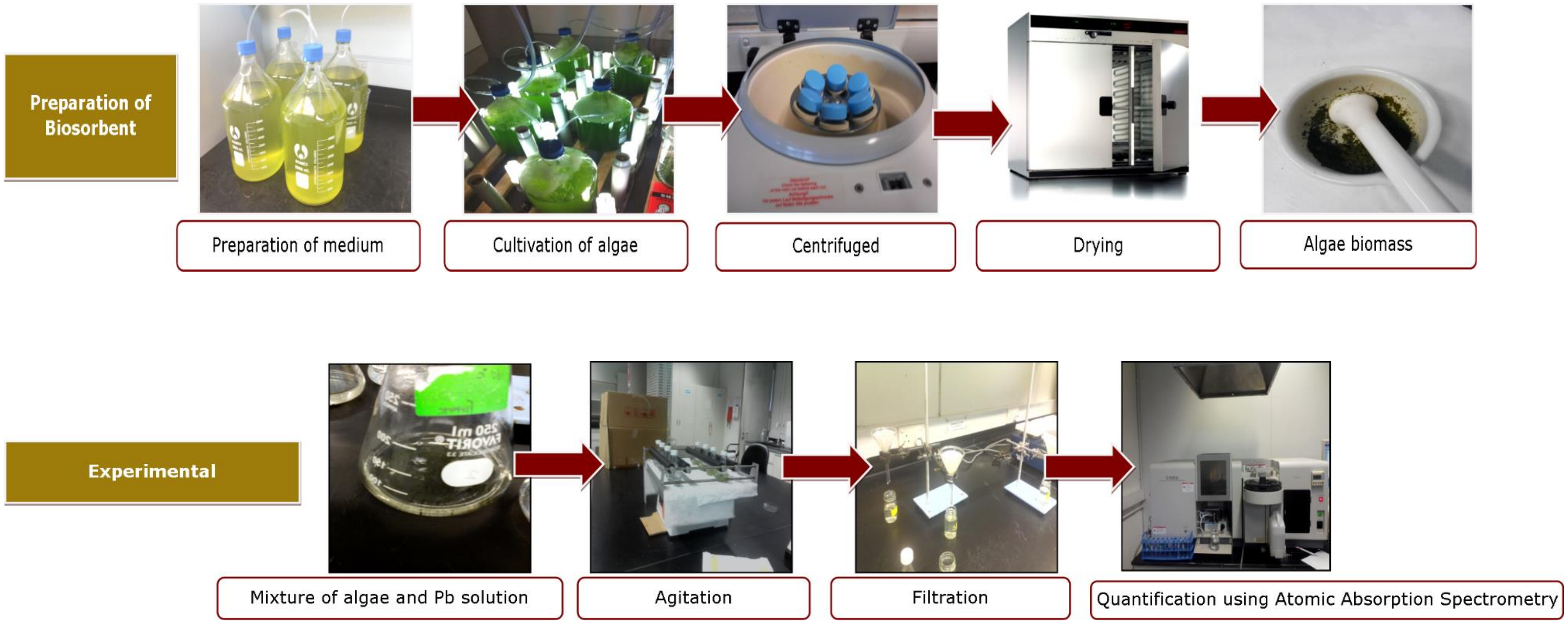
APPENDIX


Preparation of Biosorbent
Preparation of medium
Cultivation of algae
Centrifuged
Drying
Algae biomass
Experimental
Mixture of algae and Pb solution
Agitation
Filtration
Quantification using Atomic Absorption Spectrometry