REMOVAL OF COPPER USING SEAWEED

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REMOVAL OF COPPER USING SEAWEED

NUR SYAZWANI BINTI MOHD KHIR

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ABSTRAK

Penyelidikan rumpai laut sebagai penyerapan biologi logam berat baru-baru ini telah menjadi popular di kalangan penyelidik kerana keberkesanannya dalam penyingkiran logam berat dari air sisa. Lima makroalgae marin iaitu, Sargassum Polycystum sp. (Brown), Kappa Stratum sp. (Merah), Euchema Spinosum sp. (Merah), Kappa Alverezir sp (Merah), dan Caulerpa Lentifera sp. (Hijau) disaring untuk kapasiti pengambilan logam mereka untuk Cu pada pelbagai kepekatan awal 10, 20, 30, 40 dan 50 mg / L dan tempoh hubungan berubah 5 hingga 300 minit. Nilai penyerapan kuprum dalam spesies yang berlainan adalah dalam susunan Euchema Sphinosum sp.> Sargassum Polycystum sp. > Caulerpa Lentifera sp. > Kappa Alverezi sp. > Kappa Stratum sp. Kesan masa, pH dan dos telah dikaji. Nilai pemalar model Freundlich (1 / n berkisar dari 0.1253 dan 0.1962) dan isoterm Langmuir menunjukkan biosorpsi yang baik

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ABSTRACT

Investigation of seaweed as bioabsorbtion of heavy metal recently have been popular among researchers due to its effectiveness in removal heavy metal from wastewater. Five marine macroalgae namely, *Sargassum Polycystum sp.* (Brown),*Kappa Stratum sp.* (Red),*Euchema Spinosum sp.*(Red)*, Kappa Alverezir sp* (Red), and *Caulerpa Lentifera sp.*(green) were screened for their metal uptake capacities for Cu at various initial concentrations 10, 20, 30, 40 and 50 mg/L and variable contact period 5 to 300 minutes. The cu uptake value in the different species were in the order of *Euchema Sphinosum sp.*> *Sargassum Polycystum sp.* > *Caulerpa Lentifera sp.* > *Kappa Alverezi sp.* > *Kappa Stratum sp.* The effect of contact time, pH and adsorbent dosage were studied. The values of Freundlich model constants (1/n ranged from 0.1253 and 0.1962) and Langmuir isotherm indicated good biosorption.

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HMs	Heavy Metals
$Cu(OH)^2$	Copper Hydroxide
$CuSO_4$	Copper Sulphate
H_2O	Hydrogen Oxide (Water)
Cu^{2+}	Copper Ions
H^+	Hydrogen Ions
rpm	revolutions per minute
E.Spinosum	Euchema Spinosum
K.Alverezir	Kappa Alverezir
K.Stratum	Kappa Startum
S.Polycystum	Sargassum Polycystum
C.Lentifera	Caulerpa Lentifera

LIST OF ABBREVIATIONS

HMs	Heavy Metals
$Cu(OH)^2$	Copper Hydroxide
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S.Polycystum	Sargassum Polycystum
C.Lentifera	Caulerpa Lentifera

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Heavy metals occur as natural constituents of the earth crust and soil. Although there is no clear definition of a heavy metals, in most cases density is the defining factor; conventionally, heavy metals are defined as elements with metallic properties having an atomic number > 20 (Jing Yan, He Zhen, Yang Xiao, 2007). They refer to a group of metals and metalloids with atomic density greater than 4 g cm^3, or five times or more, greater than water; approximately 53 chemical elements falling to the category of Heavy Metal (Duruibe, J.O. Ogwuegbu, M.O.C, Egwurugwu, J.N, 2007). In general, the term Heavy Metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. However, in an ecological sense, any metal or metalloid that causes environmental pollution, or that cannot be biologically degraded, could be considered as a Heavy Metal (Herrera-Estrella, L.R., Guevara-Garcia, A.A, 2009). Microalgae are microscopic photosynthetic organisms found in both marine and fresh water environments, and possess a photosynthetic mechanism that is fairly similar to land plants. In terms of biomass, macro algae form the world largest group of primary producers, responsible for at least 32% of global photosynthesis Microalgae are aquatic organisms possess a molecular mechanisms that allow the macro algae to discriminate the non-essential Heavy Metals from essential ones, for growth. Researchers have globally emphasized on the advantages of using microalgae in metal bio sorption. The benefits include: rapid metal uptake capability, time and energy saving, eco-friendly, user-friendly, year round occurrence, ease of handling, recyclable or reusable, low- cost, faster growth rate (as compared to higher plants), high efficiency, large surface to volume ratio, ability to bind up to 10% of their biomass, with high selectivity (which enhances macro algae performance), no toxic waste generation, no synthesis required ,useful in both batch and continuous systems, and applicable to the waters that containing high metal concentrations or relatively low contaminant levels.

Copper (Cu) is one of most common heavy metals found in the environment and industrial wastewater because of the widespread use. Generally, Cu could be removed by chemical precipitation as a form of Cu $(OH)^2$, however, the process produces large volume of sludge to be disposed. The chemical precipitation is not effective to treat low concentration of metal. Recently, adsorption technology has been investigated to remove metals from water and wastewater because of the cost-effectiveness and easy operation. Many researchers reported that various materials including biomass and industrial by-products could be applied to remove toxic metals or metalloids as adsorbents. Additionally, biomass, such as wood, organic waste including sludge from wastewater/water treatment facilities and agricultural residue, has been used for oil production by fast pyrolysis [The textile dyeing and finishing industry has created a huge pollution problem as the industry is one of the most intensive industries on earth, and the number one polluter of clean water (after agriculture). More than 3600 individual textile dyes are being manufactured by the Industry today (Hasib, 2010) . The industry is using more than 8000 chemicals in various processes of textile manufacture including dyeing and printing. (Kant, 2012) Many of these chemicals are totally poisonous and causing damage to human health whether directly or indirectly. The large quantities of water are needed and required for textile processing, dyeing and printing. The daily water consumption of an average sized textile mill having a production of about 8000 kg of fabric per day is about 1.6 million litres. 16% of this is consumed in dyeing and 8% in printing (Kant, 2012). Specific water consumption for dyeing varies from 30 - 50 litres per kg of cloth depending on the type of dye used. The overall water consumption of yarn dyeing is about 60 litres per kg of yarn. Dyeing section contributes to 15% - 20% of the total waste water flow (Kant, 2012). Water is also required for washing the dyed and printed fabric and yarn to achieve washing fastness and bright backgrounds (Kant, 2012). Washing agents like caustic soda based soaps, enzymes and others are also used for the purpose to removes the surplus colour and paste from the substrate.

1.2 Problem Statement

Material industry and the wastewaters is one of the principle wellsprings of serious contamination issues around the world especially in Malaysia. In particular, the discharge of coloured effluent into the environment is undesirable, due to the colour and many dyes from wastewater are toxic or mutagenic to life. The aggregate colour utilization of the material business worldwide is in abundance of 107 kg/year, and an expected 90 % of this winds up on textures. Consequently, 1000 tonnes/year or more of dyes are discharged into waste streams by the textile industry worldwide. The textile industry also disposed heavy metals that cause pollution to water and risk to human health. Water is the important needs in human life. The polluted water need to treat for domestic usage. Moreover a current conventional biological treatment process is not very effective and high cost treatment.

Microalgae is the one of the potential biological method that could remove heavy metals from water. There are 5 types of microalgae use for screening which is brown colour, *Sargassum Polycystum sp*., Red colour microalgae which Is *Euchema Spihosum sp.*, *Kappa Alverezir sp*. And *Kappa Stratum sp*., and the red in colour is Green which is *Caulerpa Lentillifera sp*. All these microalgae is used to test and screen the heavy metal which is copper and decide the most potential microalgae that has high absorbtion of copper concentration.

1.3 Objectives of the Study

The objectives for screening the seaweed for removal of heavy metals are:

1. To screen the most potential macroalgae.
2. To determine the efficiency of seaweed as bio absorbent for heavy metal
3. To study the bio absorbent mechanism of isotherm (Langmuir and freundlich)

1.4 Scope of the Study

The main objective of this study is to screen the most potential microalgae for removal of heavy metals. A sample of water with copper concentration was tested and is screened to remove any impurities in the wastewater. The screened manure was transferred to a 100 L tank, diluted with water to achieve the desired solid concentration and then mixed completely. The experiment was carried out using the shaker incubator. Five types of macroalgae is tested which is *Sargassum Polycystum sp*.(brown), *Euchema Spihosum sp., Kappa Alverezir sp*. And *Kappa Stratum sp*.(red), *Caulerpa Lentillifera sp.* (green). The bioabsorption parameter used measure is the contact time within 5 to 300 minute and 0.2 to 1.4 g/L biosorbant dosage. The analysis is measured by using Langmuir and Freundlich isotherm approach.

1.5 Significance of Study

The treatment process by using seaweed can reduce the wastewater treatment cost. This is due to conventional approach on wastewater treatment is very costing. Seaweed is easily found and is widely used around the world. The use of seaweed on wastewater treatment become a new approach on resolving water pollution problems. Since the treatment of heavy metals using macro algae is low in cost, the macro algae can be commercial in the market and textile industry in other to reduce the environment pollution. Furthermore, the macro algae can be applied to treat wastewater efficienly.

CHAPTER 2

LITERATURE REVIEW

2.1 Macro algae

Macro algae, a biological marine plant that is widely used around the world due to its functionality. Macro algae are microscopic photosynthetic organism found in both marine and freshwater environments, and possess a photosynthetic mechanism that fairly similar to land plants (Al-Homaidan *et al.*, 2015). In term of biomass, they form the world's largest group of primary producers, responsible for at least 32% of global photosynthesis(Al-Homaidan *et al.*, 2015). Seaweed or macro algae refers to several species of macroscopic, multicellular, marine algae(Walford and Smith, 2006). The type of macro algae has been classified by three major groups through their colours characteristic which is red, brown and green macro algae. Macro algae are relatively simple aquatic plants that undergo photosynthesis process with unicellular reproductive structures. Macro algae range from unicellular organisms to non-vascular filamentous or thalloid plants (S Arun V, Pranabesh Sikdar, Deepthi A, 2016).

Table 2.1 Advantages and disvantages of using algal biomass for heavy metals removal from wastewater

Advantage	Disadvantage
No need to synthesise the product	If dead biomass used, energy needed for dying
Can be applied in wastewater with higher metal concentration than for membrane process	Microalgae need to be immobilized
High efficiency of metal removal	Microalgae have limited applicability in batch system
High uptake capacity	
Biomass can be generated	
Biomass can be re-used in many adsorption/ desorption cycles	
Selectivity for heavy metals ions	
Macroalgal biomass does not need to be immobilized	
No toxic chemical sludge generated	
Few chemicals needed for desorption and regeneration of biosorbent	
Can be used in continuous and discontinuous regimes	
If dead biomass used, no oxygen or nutrient supply required	
Suitable for aerobic and anaerobic effluent treatment units.	
Can be used all year round	
Low cost	

Source: (Brinza, Dring and Gavrilescu, 2018)

2.1.1 The Microorganism

The Macroalgae was obtained from Kudat, Sabah which are *Sargassum Polycystum sp.* (brown) *Euchema Spinosum sp.*, *Kappa Alverezir sp*., *Kappa Stratum sp*. (red) and *Caulerpa Lentillifera sp.* (green). All the macro algae has different characteristics to be determine as the most potential macro algae in removal of heavy metals. The macro algae will be used as bio absorbent for removal heavy metal which is copper (cu). The highest absorption of heavy metals will be consider as the most potential seaweed and have high efficiency.

2.1.2 Bio absorbent studies

Biosorption is the new method for the search of new technologies involving the removal of toxic metals from wastewaters that is lately has been given direct attention, based on metal binding capacities of various biological materials. Biosorption is defined as the biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake(Fourest and Roux, 1992) or according to (Davis, Volesky and Mucci, 2003),biosorption (biological adsorption) is the removal of heavy metals from an aqueous solution by the passive binding of dry biomass. It has been prove by many researcher that algae, bacteria and fungi and yeasts has a potential metal biosorbents.

The major advantages of biosorption compared to conventional treatment methods include (Kratochvil and Volesky, 1998) are low cost, high efficiency, minimisation of chemical and lor biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery.

The process of biosorption involves a solid phase (sorbent or biosorbent by biological material) and a liquid phase (solvent, usually water) containing a dissolved species to be sorbed (sorbate, metal ions)(Farooq *et al.*, 2010). The latter is attracted and bound there by a different mechanisms due to a higher affinity of the sorbent for the sorbate species (Das, Vimala and Karthika, 2008). The process is then continued until the equilibrium is performed between the amount of solid-bound sorbate species and its portion remaining in the solution. The distribution between the solid and liquid phases is determined by the degree of sorbent affinity for the sorbate.

Biosorbent material focused on strong biosorbent behaviour of certain micro-organisms towards metallic ions such as copper is a function of the chemical make-up of the microbial cells. It generally consists of dead and metabolically inactive cells. Several type of organisms like fungi, bacteria and algae have been used for biosorption processes. (Al-Homaidan *et al.*, 2015) (Aksu and Dönmez, 2006)

A few types of biosorbents would be an expansive range, binding, collecting, trapping the majority of heavy metals with no specific activity or explicit action, while others are specific for certain metals. A few research centers have utilized effortlessly accessible biomass whereas others have isolated specific strains of microorganisms and some have also processed the existing raw biomass to a certain degree to improve their biosorption properties and characteristics. Recent biosorption experiments have focused attention on heavy metals, which having toxic elements that should be removed from wastewater by using marine macroalgae.

There are a lot of species of macro algae and micro algae had been tested as heavy metal removal absorbent. Mostly the testing is the same so the comparison could be made. Table 2.1 and Table 2.2 is the summarized of a few macro and micro algae species in alphabetical order respectively. All the species had been found to be a good absorption and has high uptake capacity of heavy metals.

Table 2.2: Microalgal biosorbent

Algal Species	Metal Sorbed	References
Chlamydomonas reinhardtii	K, Mg, Ca, Fe, Sr, Co, Cu, Mn, Ni, V, Zn, As, C	(Mahan, Majidi and Holcombe, 1989)
Chlorella salina	Co, Zn, Mn	(Garnham, Codd and Gadd, 1992)
Chlorella sorokiniana	Ni	(Akhtar, Iqbal and Iqbal, 2004)
Chlorella vulgaris	Cd, Pb, Cu, Ag	(Gin, Tang and Aziz, 2002)
Chlorella miniata	Cr (VI)	(Han *et al.*, 2007)
Chlorococcum sp	Cd, Pb, Cu, Ag	(Gin, Tang and Aziz, 2002)
Cyclotella cryptica	Al, Zn, Pb, Cu, Cd	(Schmitt *et al.*, 2001)
Lyngbya taylorii	Pb, Cd, Ni, Zn	(Klimmek *et al.*, 2001)
Phaeodactylum tricornutum	Al, Zn, Pb, Cu, Cd	(Schmitt *et al.*, 2001), (Zhou, Huang and Lin, 1998)
Porphyridum purpureum	Al, Zn, Pb, Cu, Cd	(Schmitt *et al.*, 2001)
Scenedesmus quadricauda	Cd, Pb, Cu, Ag	(Gin, Tang and Aziz, 2002)
Scenedesmus subspicatus	Al, Zn, Pb, Cu, Cd	(Schmitt *et al.*, 2001)
Spirogyra sp.	Cr	(Gupta *et al.*, 2000)
Spirulina sp.	Cd	(Rangsayatorn *et al.*, 2002)
Spirulina platensis	Cr	(Li, Guo and Li, 2006)
Stichococcus bacillaris	K, Mg, Ca, Fe, Sr, Co, Cu, Mn, Ni, V, Zn, As, Cd, Mo, Pb, Se	(Mahan, Majidi and Holcombe, 1989)

Source:(Brinza, Dring and Gavrilescu, 2018)

Table 2.3 Macroalgal biosorbent

Algal Species	Metal Sorbed	References
Ascophyllum nodosum	Cd, Zn, Pb, Cu	(Sandau *et al.*, 1996)
Ascophyllum sp	Pb, Cd	(Volesky *et al.*, 1995)
Cladophora fascicularis	Pb	(Gin, Tang and Aziz, 2002)
Codium fragile	Cd	(Basso, Cerrella and Cukierman, 2002)
Colpomenia sinuosa	Cu, Ni	(Schiewer and Wong, 2000)
Corallina officinalis	Cd	(Basso, Cerrella and Cukierman, 2002)
Ecklonia sp	Cr	(Yun *et al.*, 2001)
Fucus vesiculosus	Cd, Zn, Pb, Cu	(Herrero *et al.*, 2006)(Murphy, Hughes and McLoughlin, 2007)
Fucus Ceranoides	Cd	(Herrero *et al.*, 2006)
Fucus serratus	Cd	(Herrero *et al.*, 2006)
Fucus spiralis	Cu	(Murphy, Hughes and McLoughlin, 2007)
Gracilaria fischeri	Cd, Cu	(Chaisuksant, 2003)
Gracilaria sp	Pb, Cu, Cd, Zn, Ni	(Sheng *et al.*, 2004)
Jania rubrens	Pb	(Hamdy, 2000)
Laminaria digitate	Cd, Zn, Pb, Cu	(Sandau *et al.*, 1996)
Laminaria japonica	Cd, Cu Pb	(Yin *et al.*, 2001),(Zhou, Huang and Lin, 1998)
	Pb	(Luo *et al.*, 2006)

Laurencia obtuse	Cr, Co, Ni, Cu, Cd	(Hamdy, 2000)
Padina pavonia	Cd, Ni	(Ofer, Yerachmiel and Shmuel, 2003)
	Pb	(Jalali *et al.*, 2002)
Padina sp	Cd	(Kaewsarn and Yu, 2001)
	Pb, Cu, Cd, Zn, Ni	(Sheng *et al.*, 2004)
	Cu	(Kaewsarn and Yu, 2001)
Palmaria palmate	Cu	(Murphy, Hughes and McLoughlin, 2007)
Petalonia fascia	Cu, Ni	(Schiewer and Wong, 2000)
Pilayella littoralis	Al, Cd, Co, Cr, Cu, Fe, Ni, Zn	(Carrilho and Gilbert, 2000)
Porphyra columbina	Cd	(Basso, Cerrella and Cukierman, 2002)
Sargassum asperifolium	Pb	(Hamdy, 2000)
Sargassum hemiphyllum	Cu, Ni	(Schiewer and Wong, 2000)
Sargassum hystrix	Pb	(Jalali *et al.*, 2002)
Sargassum natans	Pb	(Jalali *et al.*, 2002)
Sargassum sp	Cr	(Bishnoi *et al.*, 2007)
	Pb, Cd	(Cruz *et al.*, 2004)
	Pb, Cu, Cd, Zn, Ni	(Sheng *et al.*, 2004)

Source:(Brinza, Dring and Gavrilescu, 2018)

(Nirmal Kumar and Oommen, 2012) in their research on using freshwater alga which is *spirogyra hyalina sp.* as biosorbtion for removal heavy metals. Sorption and removal heavy metals by algal biosorbent largely depend on the initial concentration of metals in the solution (Nirmal Kumar and Oommen, 2012). Metal sorption initially increases with increase in metal concentration in the solution, and then becomes saturated after a certain concentration of metal (Mehta and Gaur, 2001).

Recently, an investigation on nutrients and heavy metal removal efficacy of seaweeds, *Caulerpa taxifolia* and *Kappaphycus alvarezii* for wastewater remediation were conducted by (Mithra *et al.*, 2012). Seaweeds are presented as very good sorbents, because the cell wall of green and brown algae contain alginate with the carboxyl and hydroxyl groups (Davis, Volesky and Mucci, 2003).

Removal characteristics of copper by marine macro-algae-derived chars also has been studied by(Cho *et al.*, 2013). Brown alga named Undaria pinnatifida were used to prove that it is useful for the removal or recovery of copper from aqueous solutions even though at a low dose of 0.1 g char/L, it can obtain a high adsorption capacity.

The mechanism of biosorption is quite complex, mainly in ion exchange, chelation, adsorption by a physical forces, entrapment in inter and intra fibrilliar capillaries and spaces of the network of the structural polysaccharide as a result of the gradient concentration and diffusion through cell walls and membranes.

The choice of metal for biosorption process by using the appropriate selection of metals approach for biosorption studies is dependent on the angle of interest and the impact of different metals, on the basis of which would be divided into four major categories: (i) toxic heavy metals (ii) strategic metals (iii) precious metals and (iv) radio nuclides. In terms of environmental pollution, it is mainly that categories (i) and (iv) are in the field of interest for removal from the environment and or from point source effluent discharges (Duruibe, J. O, Ogwuegbu, M. O. C. and Egwurugwu, 2007).

2.2 Heavy Metals

Heavy metals are conventionally defined as elements with metallic properties (ductility, conductivity, stability as cations, ligand specificity, etc.) and an atomic number >20 (Jing, He and Yang, 2007). Heavy metals are an element that can cause an environmental pollution especially when discharge into water that could harm aquatic lives and human health. The increasing of population, rapid urbanization and industrialization, have caused global concern worldwide. Increasing urbanization and industrialization have made HMs reach alarming toxic levels in the environment.(Suresh Kumar *et al.*, 2015).(Gaur and Adholeya, 2004) provide an ecological perspective stating that "a heavy metal" is a metal or metalloid element that causes environmental pollution, which does not have any vital function and is toxic at low concentration [such as lead (Pb) and mercury (Hg)], and it has a vital function but it is harmful to organisms at high concentration [such as copper (Cu) and molybdenum (Mo)].(Wang and Chen, 2009) categorized HMs of concern into three catagories: toxic metals [such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn and others] and radionuclides such as U, Th, Ra, and Am. Heavy metal removal may be accomplished by different mechanism. Figure 2.1 summarizes different possible mechanisms involved in heavy metal removal.

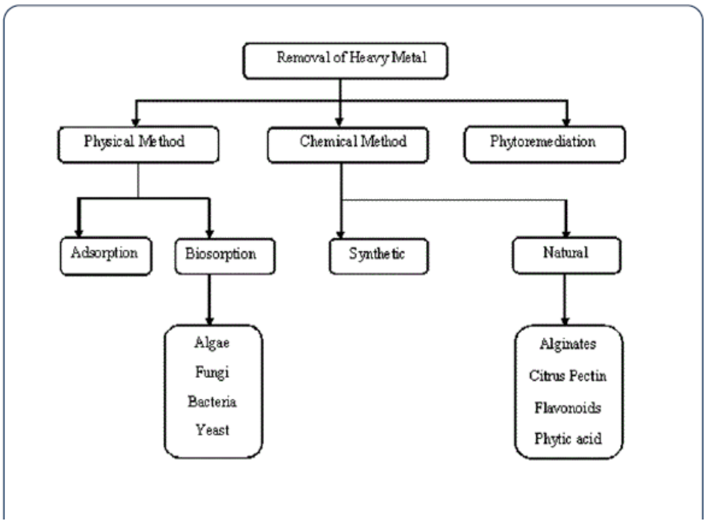

Figure 2.1: An overview of different mechanism involve in removal heavy metals. Source:(S and S, 2016)

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues inside the body(Islam *et al.*, 2006). The source of heavy metals includes food, water, air, absorption through skin and cause disease (Islam *et al.*, 2006). The most common route of exposure for children is ingestion (Islam *et al.*, 2006). The presence of metals in environment is a potential source of toxicity owing to their transport down the food chain and their subsequent bio-magnification (Garbisu and Alkorta, 2001). They cannot be destroyed biologically and get transformed into different oxidation states or different organic complex (Gisbert *et al.*, 2003)

2.2.1 Copper

The metal can be classified as a heavy metal, if it has a relatively high density which is bigger than the density of water by times and if it is toxic or poisonous at low concentrations. Heavy metal are non-biodegradable, toxic, and easy to accumulate at low concentrations in living organisms in general and in the human body in specific; they can cause serious illnesses, such as cancer nervous system damage, and kidney failures and can be deadly at high concentrations (Al-Saydeh, El-Naas and Zaidi, 2017).

Copper is well known as an essential trace element that is vital and easily found in life. Copper imbalance phenomenon causing the human to become copper-toxic or copper-deficient (which can include arthritis, insomnia, fatigue, migraine, headaches, depression, panic attacks, and attention deficit disorder). Copper has been used and quite popular among other heavy metals for centuries for disinfection, and has been an important element around the world especially in technology, medicine and culture. Generally, copper (Cu) is a toxic metal that is widely used and found in the environmental and industrial wastewater especially in the textile industry. Dye effluent that is produced from textile industry contains heavy metals especially copper.

2.3 Isotherm Model

The curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e , to the concentration of the solute in the liquid, Ce, with which it is in contact is called as an adsorption isotherm. Apart from that, at a given temperature, the adsorption isotherm is also refers an equation relating the amount of solute adsorbed onto the solid with the equilibrium concentration of the solute in solution.

q_e = amount of solute adsorbed per unit weight of solid at equilibrium. Unit is either g/g or mg/g

Ce = equilibrium concentration of solute remaining in solution when amount adsorbed equals q_e.

q_e/C_e relationship depends on the type of adsorption that occurs, multi-layer, chemical, physical adsorption, etc.

There are several models for predicting the equilibrium distribution. The most common model used is Langmuir and Freundlich.

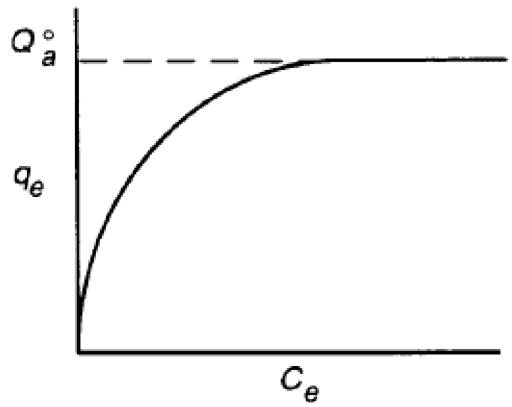

Figure 2.2(a) Langmuir

Source:(Walford and Smith, 2006)

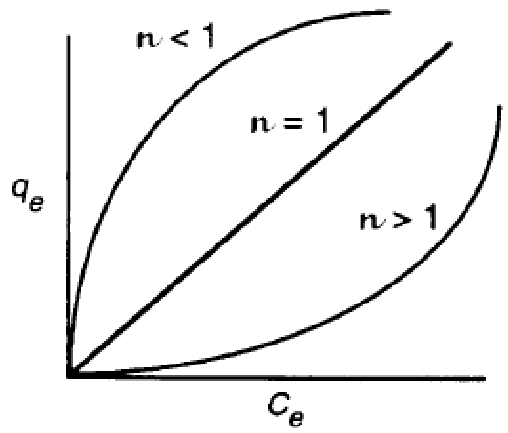

Figure 2.2 b) Freundlich

Source: (Walford and Smith, 2006)

The equation for Langmuir isotherm as follow:

$$q_e = \frac{qmax \times KL \times Ce}{1 + KL \times Ce} \tag{2.1}$$

The equation for Freundlich isotherm as follow:

$$q_e = K_f C_e^{1/n} \tag{2.2}$$

Adsorption is where free moving molecules of a gaseous or solutes process in a solution come close and bind themselves onto the surface of the solid. The binding or adsorption bonds depend on the nature of forces between the adsorbent (solid surface) and the adsorbate (gas or dissolved solutes) which can be whether strong or weak. When adsorption involves only chemical bonds between adsorbent and adsorbate, it is recognized as chemical adsorption or chemisorption. Chemical adsorption or chemisorptions acquires activation energy, can be very strong and not readily reversible. There are several factors that will influence the extent of adsorption from solution and is summarized in the table below.

Table 2.4 Factor and effect on adsorption.

Factor affecting adsorption	Effect on adsorption
Salute concentration	Increased solute concentration will increase the amount of adsorption occurring at equilibrium until a limiting value is reached.
Temperature	Process is usually exothermic, therefore, an increase in temperature will decrease adsorption
pH	pH influences the rate of ionization of the solute, hence, the effect is dependent on the species that is more strongly adsorbed
Surface area of absorbent	An increase in surface area will increase the extent of adsorption

Source: (Physical Pharmacy Practical, 2013)

Adsorption isotherms describe the equilibrium requirement for a molecule to adsorb on the adsorbent surface (Langmuir, 1918).In order to decide which isotherm will better describe the adsorption, all of the experimental data has to be analyzed with all of the isotherm equations. Table 2.5 shows the most frequently used isotherms for explaining the adsorption processes that are the Freundlich, Langmuir, Temkin, Elovich and Dubinin–Radushkevich isotherms in (Dubinin and Radushkevich, 1947), (Elovich and Larionov, 1962), (Freundlich, 1906) (Langmuir, 1918) and (Temkin, 1941). The best fit model was selected based on the determination coefficient (R^2). The Langmuir isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of dye molecules on the adsorbent surface. The energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface of montmorillonite (Fil, Özmetin and Korkmaz, 2012)(Kuleyin and Aydin, 2011)(Tehrani-Bagha *et al.*, 2011).

Table 2.5 Isotherm Model

Isotherm model	Linear form	Eq.	Plots	Ref.
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	(3)	(C_e/q_e) versus C_e	Langmuir (1918)
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	(4)	$\ln q_e$ versus $\ln C_e$	Freundlich (1906)
Temkin	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	(5)	q_e versus $\ln C_e$	Temkin (1941)
Elovich	$\ln \frac{q_e}{C_e} = \ln(K_E q_m) - \frac{1}{q_m} q_e$	(6)	$\ln (q_e/C_e)$ versus q_e	Elovich and Larionov (1962)
Dubinin – Radushkevich	$\ln q_e = \ln q_m - B\left(RT \ln(1+1/C_e)\right)^2$	(7)	$\ln q_e$ versus $(RT\ln(1+1/C_e))^2$	Dubinin and Radushkevich (1947)

Source:(Fil *et al.*, 2014)

CHAPTER 3

METHODOLOGY

3.1 Introduction

As indicated in the research title, this chapter includes the research methodology of the bioabsorbtion of seaweed. In more details, it is about the research strategy, the research method, the research approach, the methods of data collection, observing, processing and analysis activities conducted systematically and efficiently to get the result.

3.2 Research strategy

The research was held with respect to this dissertation was an applied one, but not new. Rather, numerous pieces of previous academic research exist regarding to the removal of heavy metal using seaweed by screening process. There are many kind of seaweed that had been done for research. As such, the proposed research took the form of a new research but on an existing research subject.

3.3 Research Method

In order to satisfy the objectives of the research, a study was conducted focusing more on the topic. To produce a higher quality finding of the research, there are some element that should be taken into the research. There are few steps on working for this dissertation includes:

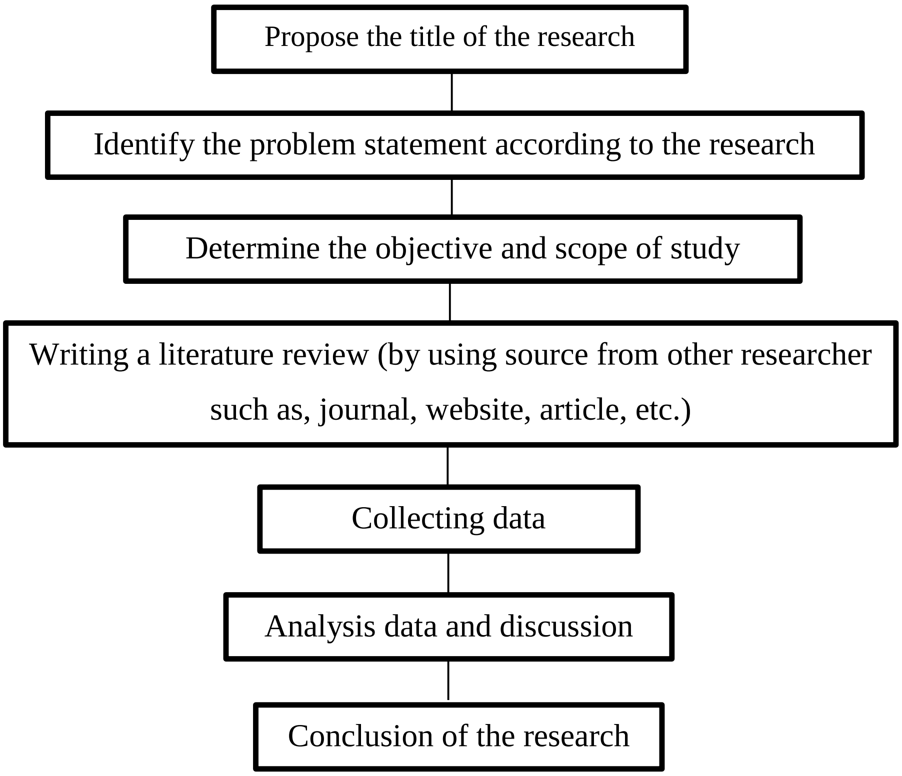

Figure 3.1 Element of the research

Refer to the steps mentioned, the objective and the statement problem is needed to broad the research and give clearly the purpose of the research. Objective is the things that is needed to achieve the results. Literature review is a research of other researcher that might had conducted nearly same research but using a different approach. This will help in understanding more on the research and produce a quality research and provides some information and details on our research topic. After doing some research, the experiment begin and the data is collected. It is important to collect the data since it is needed for analysis purpose. After analysed the data, a conclusion and summary regarding to the topic will be presented.

3.4 Preparation of seaweed

Macro algae act as biological absorption in this research. There are 5 types of microalgae use for screening which is brown colour, *Sargassum Polycystum sp*., Red colour microalgae which is *Euchema Spihosum sp.*, *Kappa Alverezir sp*. And *Kappa Stratum sp*., and the red in colour is Green which is *Caulerpa Lentillifera sp*. A common natural was collected and were brought for testing on laboratory. The alga then was washed 3 times using H_2O and then wash it with distilled water to remove the residual potassium. The chemically. Microalgae is then dried in an oven for a day before it is cut and pulverized by a grinding mill, and sieved through 0.7-mm and 1.5-mm meshes.

(a)

(b)

(c)

(d)

(e)

Figure 3.2: *Sargassum Polycystum sp, Kappa Stratum sp and Kappa Alverezir sp, Euchema Spinosum sp. and Caulerpa Lentifera sp.*

3.5 Preparation of copper solution

Copper solutions then were prepared by dissolving analytical grade Cu (SO4)/3H2O in deionized water. The initial cupric concentration ranged from 5 to 50 mg/L.

Figure 3.3 Copper Sulphate Solution

3.6 Screening of seaweed

Typically, 10 mg of seaweed was placed in a flask containing 100 mL of a copper solution with its pH adjusted to 5.0 ± 0.5, and the mixture was stirred at 130 rpm in a shaking incubator. After 5 h, the suspension was filtered, and the filtrate was analysed using AAS (Atomic Absorption Spectroscopy). The effects of the experimental parameters, such as the initial metal ion concentration 5–50 mg/L, pH 2-12 and sorbents dosage 0.2–1.4 g/L on the removal of Cu (II) ions were studied for a specific contact time of 5-300 minutes.

Figure 3.4: Analysis using AAS (Atomic Absorption Spetroscopy)

3.7 Isotherm Analysis

There are two types of isotherm used in this research which is Langmuir isotherm and Freundlich isotherm. The curve relating the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, Ce, with which it is in contact is called as an adsorption isotherm. Apart from that, at a given temperature, the adsorption isotherm is also refers an equation relating the amount of solute adsorbed onto the solid with the equilibrium concentration of the solute in solution. The best isotherm is choose based on the R^2 value from the graph trendline. The graph value were evaluated from the linear equation as follow:

$$y = mx + c \qquad 3.1$$

Original form — Linearized form

1. Langmuir model:

$$q = \frac{q_m . K_L . C}{1 + K_L . C} \qquad \frac{C}{q} = \frac{1}{K_L . q_m} + \frac{1}{q_m} . C$$

2. Freundlich model:

$$q = K_F . C^{\frac{1}{n}} \qquad \log q = \log K_F + \frac{1}{n} . \log C$$

Figure 3.5: The Linear equation for Langmuir and Freundlich isotherm
Source:(Malakootian, Almasi and Hossaini, 2008)

3.7.1 Langmuir Isotherm

The amounts of Cu adsorbed onto the seaweed is analysed against concentration of Cu in the solution and were fitted using the Langmuir isotherm model represented as follows:

The equation for Langmuir isotherm as follow:

$$q_e = \frac{qmax \times KL \times Ce}{1 + KL \times Ce} \qquad 3.2$$

Where q_{max} is the maximum amount of Cu adsorbed onto seaweed (mg/g), KL is a constant related to the adsorption energy (L/mg) varying with temperature, and Ceq is the equilibrium Cu concentration (mg/L). The model is based on certain assumptions. The Cu ions are chemically adsorbed at a fixed number of identical adsorption sites; each site can capture one Cu ion. The sites are energetically equivalent and there is no interaction between the adsorbed Cu ions. Based on these assumptions, the maximum adsorption of Cu ions means monolayer coverage adsorption sites with Cu. The maximum absorption capacity of microalgae for Cu is analysed based on Langmuir isotherm model fitting.

3.7.2 Freundlich Isotherm

The experimental data was fitted using another isotherm model, the Freundlich isotherm model:

The equation for Freundlich isotherm as follow:

$$q_e = K_f C_e^{1/n} \qquad 3.3$$

Where KF is a Freundlich constant and 1/n is the Freundlich isotherm parameter. The Freundlich isotherm parameter is the heterogeneity factor. A low 1/n value indicates that there is a strong interaction between the metal and the adsorbent. Considering the correlation coefficients, the adsorption of Cu onto Algae followed the Langmuir type, which suggests that which algae have limited adsorption sites for copper. The graph Log ce vs Log qe then is plotted for each macro algae for further results.

3.8 Bioabsorbtion parameter

The experiment was conducted in UMP Gambang Environmental Laboratory, Faculty of Civil Engineering and Earth Resources. The required parameter studied for the laboratory testing are contact time, dosage used and pH. The result of the experiment of removal of copper using seaweed are discussed as below. The percentage of removal were calculated as follow:

$$\%Removal: \frac{Co-Ce}{Co} \times 100 \quad 3.4$$

Percentage removal is calculated to know the efficiency of each macro algae in removal of copper ions. C_o is express as initial concentration of the solution and C_e is the concentration after removal process take place.

3.8.1 Contact Time

The effect of contact time was studied within 5 to 300 minutes at constant initial copper concentration of 100ml. Thus the solutions were shaken within 5 to 300 minutes with digital shaker. After required time intervals the suspension was filtered through filter paper (Whattman filter paper, mesh size: 0.45 microns). Each solution was filtered and the concentration of copper in the filtrate was measured. The instrument was calibrated with 0.25ppm, 0.50ppm and 0.75ppm, 1.00ppm and 2.00ppm copper solution and then samples were analyzed. A 0.5 g of biomass was added to glass flasks containing 100 ml of metal solution. The copper concentration was varied from 10 to 50 ppm, and contact time was kept at 300 minutes. Adsorption isotherms were obtained at pH 7.

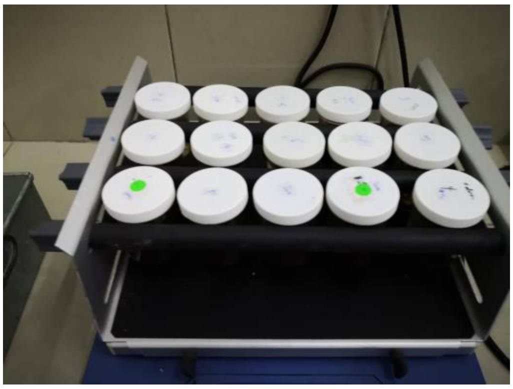

Figure 3.6: Macroalgae were shake in a shaking incubator.

3.8.2 Effect of Dosage in adsorbtion

The adsorbent dosage used for each seaweed to test adsorbtion of copper is 0.2g, 0.4g, 0.6g, 0.8g, 1.0g, 1.2g and 1.4g. Each dosage are mixed with 50ml of $CuSO_4$ solution. The mixture are then is shake in a shaking incubator for 130 rpm within 2 hours. From previous test, the optimum contact time was obtained at 2 hours. The mixture were then filtered and the data were recorded.

Figure 3.7: The biomass is filtered using manual filtration method.

3.8.3 Effect of pH in adsorbtion

The effect of pH of the macroalgae were studied at a room temperature between pH 2 until 12. The pH was adjusted using 0.1M NaOH solution. The initial concentration of 50mg/L of Copper were used with seaweed dosage of 0.2g due to its optimum dosage. After that, the mixture were shaken in shaking incubator for 130 rpm for 2 hour and the mixture were filtered. All the data were recorded.

3.9 Limitation of Study

As it is for every study, this dissertation had the following limitations:

1. The study only focus on removal of copper as heavy metals
2. The analysis of the seaweed a bioabsorbent may be influenced by factors which were not mentioned in this project
3. The study only focus for five types of seaweed only.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the outcomes on absorption properties of macro algae were examined. This chapter explain in details about the result that obtained by using macro algae in copper treatment. All the specimens in the experiment were subjected to effect of contact time, dosage and pH. The result of the experiment of removal of copper using seaweed are discussed as below. The percentage of removal were calculated as follow:

$$\%Removal: \frac{Co-Ce}{Co} \times 100 \qquad 4.2$$

Percentage removal is calculated to know the efficiency of each macro algae in removal of copper ions. C_o is express as initial concentration of the solution and C_e is the concentration after removal process take place.

4.2 Effect of contact time on Adsorption

The reading of initial concentrations of 50 mg/L of copper solution were recorded. The percentage of the removal for each macro were recorded in table 4.1 using 79 mg/L as initial concentration of copper solution.

Type`	**Kappa Alverezir**		**Kappa Stratum**		**Caulerpa Lentifera**		**Euchema Spinosum**		**Sargassum Polycystum**	
Time (min)	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**
5	21.4	73	14.9	81	19.95	75	16.1	75	21.6	723
10	19.35	76	14.3	82	19.4	75	15.8	80	21.1	73
15	18.5	77	13.35	83	19.05	75	15.25	81	20.8	74
20	17.6	78	12.5	84	18.35	77	11.6	85	20.5	74
25	17.15	78	11.85	85	18.05	77	9.4	88	19.4	75
30	15.25	81	12.7	84	17.7	78	8.5	89	18.8	76
60	16.1	80	13.25	83	18.95	76	7	91	18.5	77
120	17.35	78	13.45	83	19.55	75	6.4	92	19.45	75
180	17.8	77	13.75	83	19.85	75	7.8	90	20.1	75
240	18.3	77	14.75	81	20.45	74	8.6	89	20.75	74
300	18.7	76	15.5	80	20.75	74	10.65	87	21.85	72

Table 4.1 The percentage of removal of each macroalgae.

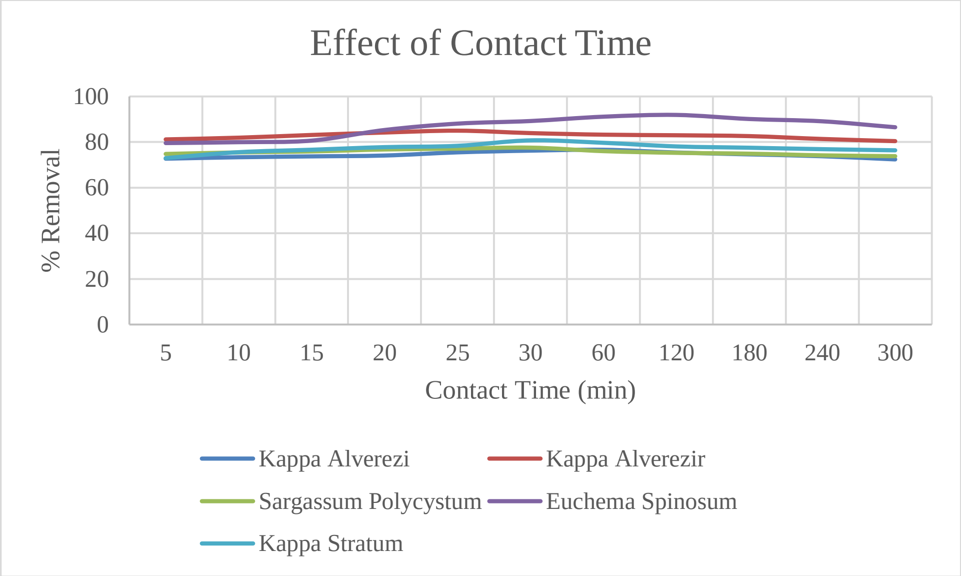

Figure 4.1: Effect of Contact Time on Removal of Copper.

From table 4.1, various contact time were studied to determine the optimal contact time according to the rate of adsorption. The optimum dosage of 0.6g, 0.8g, 0.6g, 0.8g and 0.6g were used for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum to study the effect of contact time. The results obtained as shown in figure 4.1 indicates that the maximal adsorption by contact time for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum are at 30 minutes, 25 minutes, 30 minutes, 120 minutes and 60 minutes respectively. From Figure 3, the highest absorbtion at optimal contact time is Euchema Sphinosum (92%) followed by Kappa Alverezir (85%), Kappa Stratum (81%), Caulerpa Lentifera (78%) and the lowest is Sargassum Polycystum (77%). It can be seen that the rate of adsorption is rapidly increase at early 30 minutes probably due to the fact that initially all sites on surface of the sorbent were vacant with more functional groups on the biomass surface and available for binding and copper adsorption (Saif et.al.,2012). At 180 to 300 min, there is slightly decrease in rate of adsorption due to possible release of copper in solution.

4.3 Effect of Adsorbent Dosage of Macroalgae to remove Copper

The reading of initial concentrations of 50 mg/L of copper solution were recorded. The percentage of the removal for each macro were recorded in table 4.2 using 108 mg/L as initial concentration of copper solution.

Table 4.2 The percentage of removal for dosage of each macroalgae.

Type	**Kappa Alverezir**		**Kappa Stratum**		**Caulerpa Lentifera**		**Euchema Spinosum**		**Sargassum Polycystum**	
Dosage (g)	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**
0.2	14.5	87	12.7	88	18.8	83	8.1	93	27.35	75
0.4	12.6	88	12.2	89	18.2	83	6.65	94	19.65	82
0.6	11.6	89	11.65	89	16.05	85	5.65	94	16.95	84
0.8	12.05	88	9.9	91	17.5	84	5.3	95	21.35	80
1	14.4	87	11	90	19.4	82	5.55	94	22.8	79
1.2	15.05	86	12.6	88	19.55	82	6.05	94	23.4	78
1.4	16.1	85	13.3	88	20.75	81	10.9	90	23.85	78

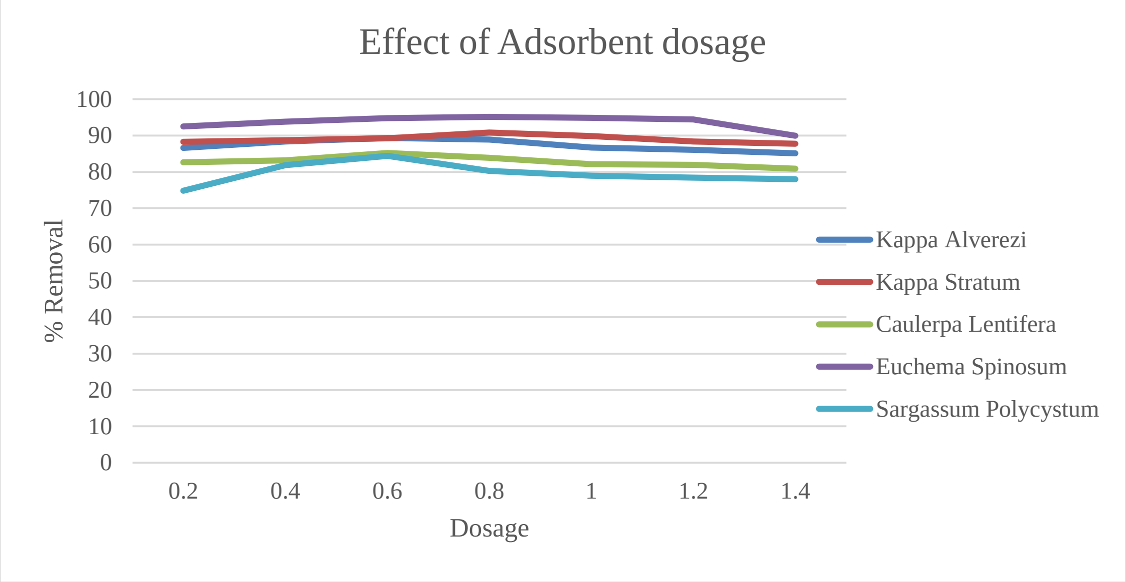

Figure 4.2: Effect of Dosage for removal Copper ions by macroalgae.

Based on table 4.2, the effect of dosage is tabulated in range of 0.2g to 1.4g. The effect of dosage in adsorption of Cu^{2+} is important in affecting the efficiency of removal Cu in aqueous solution. In order to get the optimum dosage for adsorption capacity of copper, the different dosage has been used with contact time, volume of sample, pH level, agitation speed and temperature which is 120 min, 50ml, 7, 130 rpm and at room temperature respectively. Results in figure 4.2 shows that increase in adsorption when the adsorbent dosage increase but it slightly drops when it achieve the optimum adsorbent dosage. Based on the figure 1, the optimum dosage for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum are 0.6g, 0.8g, 0.6g, 0.8g and 0.6g respectively. The maximum copper uptake for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum are 8.033mg/g, 6.131 mg/g, 7.663 mg/g, 6.419 mg/g and 7.588 mg/g, . From the comparison of percentage adsorbtion of each macroalgae, Euchema has the highest percentage adsorption which is 95% compared to Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, and Sargassum polycystum which are 89%,91%,85% and 84%. It shows that Euchema Spinosum has high surface area that enables it have the availability of binding more heavy metal compared to other macroalgae.

4.4 Effect of pH Level on Adsorption

The reading of initial concentrations of 50 mg/L of copper solution were recorded. The percentage of the removal for each macro were recorded in table 4.3 using 65.5 mg/L as initial concentration of copper solution.

Table 4.3 shows the percentage of removal of each macroalgae.

Type	**Kappa Alverezir**		**Kappa Stratum**		**Caulerpa Lentifera**		**Euchema Spinosum**		**Sargassum Polycystum**	
pH	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**	**Data (mg/L)**	**% Removal**
2	17.3	72	12.7	79	20.75	66	10.5	83	23.1	62
3	16.65	73	12.15	80	20.6	67	9.35	85	22.55	63
4	16.05	74	11.65	81	20.45	67	8.65	86	21.85	64
5	15.5	75	10.95	82	20.2	67	8.1	87	21.65	65
6	15.55	75	10.6	83	19.9	68	7.85	87	22.1	64
7	15.05	76	8.35	86	19.35	69	7.15	88	21.15	66
8	15.2	75	7.9	87	18.6	70	5.5	91	21.3	65
9	14.45	77	8.95	85	17.25	72	6.35	90	20.05	67
10	14.7	76	10.95	82	17.8	71	6.85	89	20.55	67
11	15.55	75	11.1	82	18.85	69	8.6	86	20.65	66
12	16.4	73	11.85	81	19	69	9.75	84	20.5	66

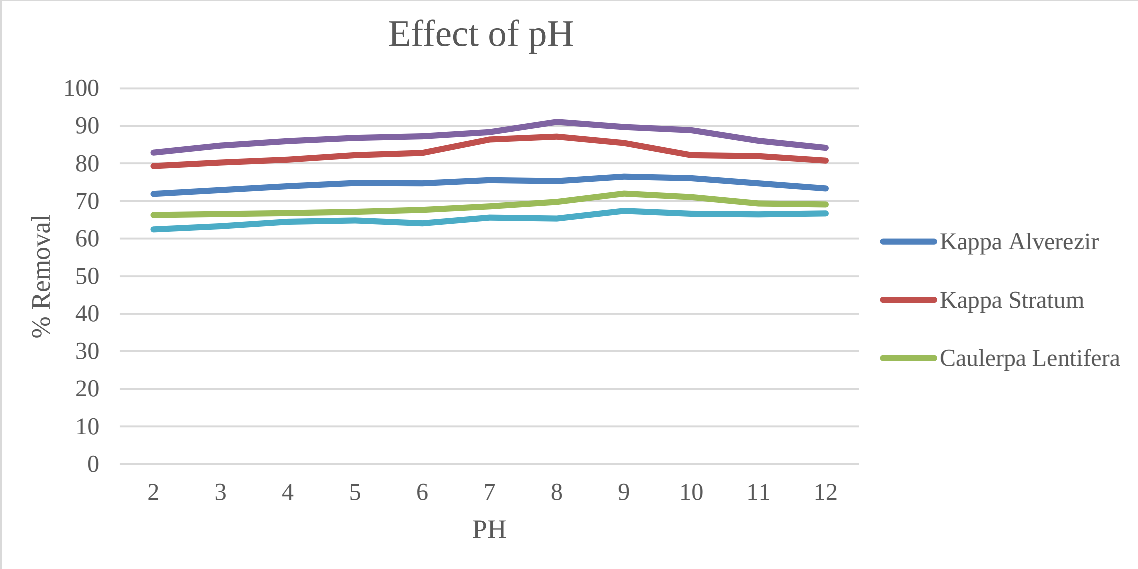

Figure 4.3: Effect of pH level for removal Copper ions by macroalgae.

The effect of pH were carried out by using pH from 2 to 12 based on table 4.3. Figure 4.3 shows that acidic condition did not really support Cu^{2+} adsorption due to the presence of hydrogen ions from aqueous solution. At low pH, there are many H^{+} in the solution and the higher concentration of H^{+} competes with Cu^{2+} for binding to the negatively charged active sites on a biomass surface.(Al-Homaidan *et al.*, 2015). The dosage that has been used for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum were 0.8g, 0.8g, 0.6g, 0.8g and 0.6g according to their optimum dosage from previous experiment. The maximum adsorption efficiency observed was Euchema Sphinosum (91%) at pH 8 .The maximum adsorption for the rest macroalgae are 77%, 87%, 72% and 67% for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, and Sargassum polycystum. Meanwhile, the maximum uptake of copper capacity for Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum are 3.921 mg/g, 3.350 mg/g, 3.688 mg/g, 3.454 mg/g and 3.500 mg/g. Based on Figure 2, the highest pH level of Kappa Alverezir, Kappa Stratum, Caulerpa Lentifera, Euchema Spinosum, and Sargassum polycystum are 9, 8, 9, 8 and 9. However, there was slightly decrease in uptake of Cu around pH 11 to 12 which could be attributed to the formation of Cu-OH which might have compete with functional binding sites for metal ions and reduced the availability of Cu adsorption. (Rao et.al.2005, Kumar et al,2006)

4.5 Adsorption Isotherm

4.5.1 Introduction

The adsorption isotherm is obtained at constant factors such as solution pH 7, Dosage 600 mg, contact time 120 minutes and it is tested at room temperature. The adsorbtion isotherm studied are Langmuir and Freundlich isotherm. Constant factor is important to ensure the data is same to make a comparison of both adsorption isotherm.

4.5.2 Langmuir Isotherm

Langmuir isotherm model represented as follow:

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo} \qquad 4.2$$

Where C_e is equilibrium concentration (mg/L), q_e is amount of adsorption equilibrium (mg/g), b is constant related to the energy (L/mg) and Q_o is the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g).

Table 4.4: The tabulation data of Langmuir Isotherm

Type	Kappa Alverezi			Kappa Stratum			Caulerpa Lentifera			Euchema Spinosum			Sargassum Polycystum		
Co (mg/L)	Ce (mg/L)	Ce/qe	q_e (mg/g)	Ce	Ce/qe (mg/L)	q_e (mg/g)	Ce (mg/L)	Ce/qe	q_e (mg/g)	Ce (mg/L)	Ce/qe	q_e (mg/g)	Ce (mg/L)	Ce/qe	q_e (mg/g)
24.25	2.35	1.2876	1.825	3.75	2.1951	1.708	4.85	3.0000	1.617	1.55	0.8194	1.892	5.80	3.7723	1.538
29.05	6.50	3.4589	1.879	6.60	3.5278	1.871	9.20	5.5617	1.654	3.65	1.7244	2.117	9.85	6.1563	1.600
29.35	9.40	5.6541	1.663	9.80	6.0153	1.629	10.25	6.4398	1.592	4.70	2.2880	2.054	11.00	7.1935	1.529
29.9	10.10	6.1212	1.650	10.75	6.7363	1.596	11.80	7.8232	1.508	5.05	2.4386	2.071	14.45	11.2233	1.288
30.25	11.60	7.4638	1.554	11.65	7.5161	1.550	16.05	13.5634	1.183	5.65	2.7561	2.050	16.95	15.2932	1.108

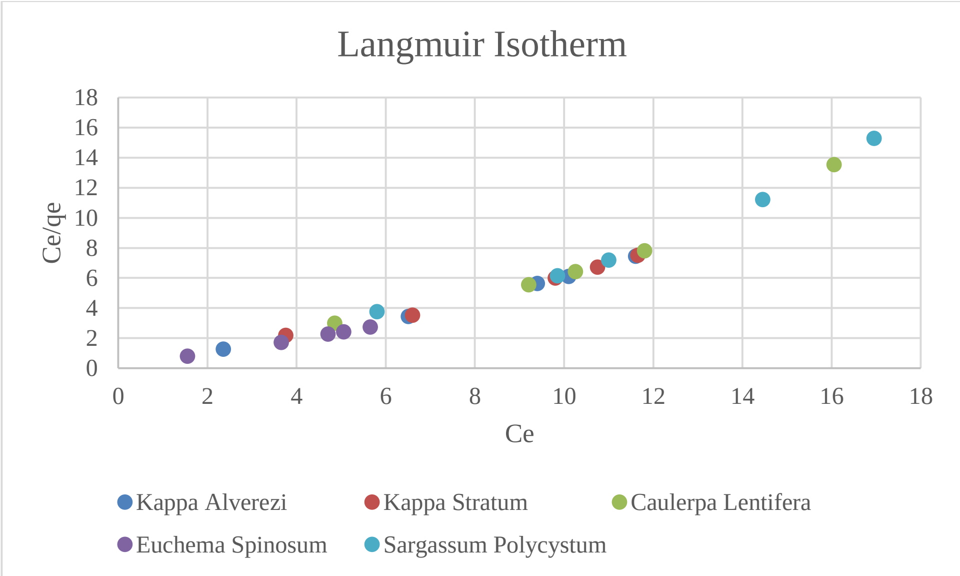

Figure 4.4: Langmuir Isotherm Illustration.

Table 4.4 shows that different concentration of copper solution will affect the removal capacity and affect the Langmuir adsorption isotherm. Figure 4.4 shows a linear graph which is may indicate a good biosorption of the copper by five different macro algae. Graph Ce vs Ce/qe is plotted to get the R^2 value from the trendline of the graph. The result were discussed in table 4.6.

4.5.3 **Freundlich Isotherm**

Freundlich isotherm model represented as follow:

$$Q_{eq} = K_F C_{eq}^{1/n} \quad 4.3$$

In this model, K_F (L/g) and 1/n are the constant to be determined from the data. For a good adsorbent, 0.2<1/n<0.8 and a smaller value 1/n indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent (J.I. Nirmal Kumar, Cini Oommen and Rita N Kumar, 2009).

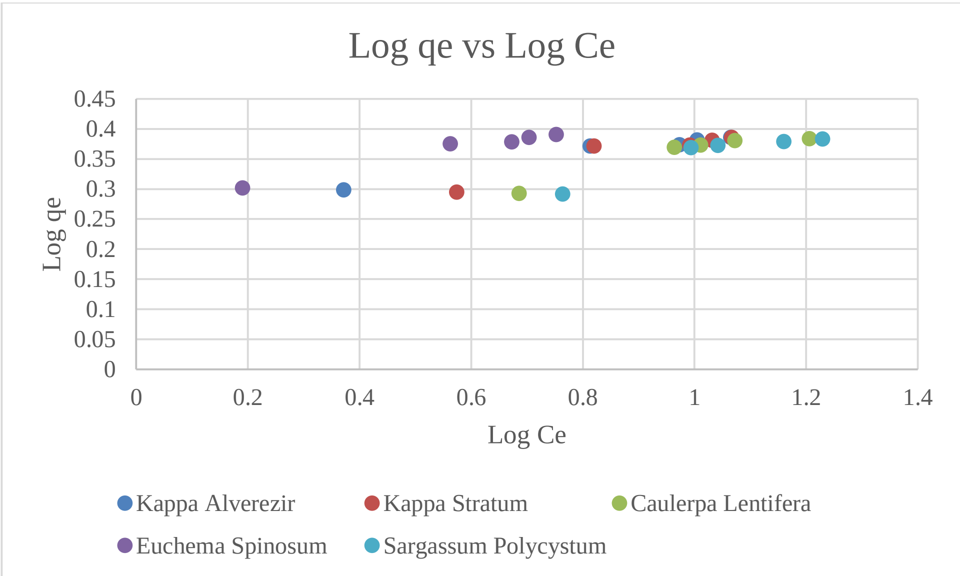

Figure 4.5: Graph of Log q_e vs Log C_e of Freundlich Isotherm.

Table 4.5 shows that different concentration of copper solution will affect the removal capacity and affect the freundlich adsorption isotherm. Figure 4.5 shows a scatter graph which is may indicate a good biosorption of the copper by five different macro algae. Graph Log Ce vs Log qe is plotted to get the R^2 value from the trendline of the graph. The result were discussed in table 4.6.

Table 4.5: The tabulation data of Freundlich Isotherm

Type	Kappa Alverezi		Kappa Stratum		Caulerpa Lentifera		Euchema Spinosum		Sargassum Polycystum	
Co (mg/L)	Ce (mg/L)	q_e (mg/g)	Ce (mg/L)	q_e (mg/g)	Ce (mg/L)	q_e (mg/g)	Ce (mg/L)	q_e (mg/g)	Ce (mg/L)	q_e (mg/g)
24.25	0.3711	0.2988	0.5740	0.2951	0.6857	0.2931	0.1903	0.3021	0.7634	0.2916
29.05	0.8129	0.3716	0.8195	0.3715	0.9638	0.3693	0.5623	0.3755	0.9932	0.3689
29.35	0.9731	0.3738	0.9912	0.3735	1.0107	0.3732	0.6721	0.3784	1.0414	0.3727
29.90	1.0043	0.3817	1.0314	0.3812	1.0719	0.3806	0.7033	0.3862	1.1598	0.3793
30.25	1.0644	0.3860	1.0663	0.3860	1.2055	0.3839	0.7520	0.3906	1.2291	0.3835

4.5.4 Discussion of Langmuir and Freundlich Isotherm.

Table 4.6: Isotherm constant for Cu bioabsorbtion

	Kappa Stratum	Kappa Alverezi	Caulerpa Lentifera	Euchema Spinosum	Sargassum Polycystum
Isotherm Constants					
Langmuir					
Qo (mg/g)	0.662	0.683	0.9404	0.4722	1.0351
b (L/mg)	0.4919	0.6138	2.5312	0.0599	3.2901
R2	0.989	0.9886	0.9473	0.9978	0.9545
Freundlich					
n	7.9808	5.8038	5.3908	6.3012	5.0968
R2	0.9554	0.8734	0.884	0.9698	0.8493

Freundlich and Langmuir isotherms were established for the biosorption process for heavy metal such as Copper. Langmuir shows the value of R^2 is in between 0.9473 and 0.9978. The value of *n*, of the Freundlich model, in the range of 1 to 10, indicates substantially better adsorption. The values of the model constants for the biosorption of metals by all the macroalgae are represented in Table 4.6. For the Freundlich equation, the values of 1/n ranged between 0.1253 and 0.1962 which indicates a good adsorption. R value varied from 0.8493 to 0.9698 for the metals studied. From the R value, it can be noted that the Langmuir isotherm model best fitted the equilibrium data.

4.6 Discussion

Based on the result that have been obtained from of the parameter observed, Euchema Spinosum is the best and the efficiency macroalgae in removal of Copper. This is due to Euchema Spinosum has larger surface area than other macroalgae that enables copper ions to bind at the surface. The percentage removal shows that Euchema Spinosum has higher reduction of Copper ions from the aqueous solution. Since the adsorption increase, thus, it is the most suitable macroalgae to treat Copper compared to Kappa Alverezir, Sargassum Polycystum, Kappa Stratum and Caulerpa Lentifera. In term of adsorption isotherm, which is Langmuir and Freundlich, Langmuir isotherm model is the best fitted isotherm compare to Freundlich isotherm. This is due to Langmuir has higher R^2 value compared to Freundlich. However, the values of 1/n ranged between 0.1253 and 0.1962 in Freundlich isotherm also indicates a good adsorption. From the result that have been obtained, macroalgae had a huge potential as biabsorbent and can be use efficienly on treating the wastewater.

CHAPTER 5

CONCLUSION

5.1 Introduction

In this chapter will explain about the main objectives of this research. The main objectives of this research are to screen the most potential macroalgae, to determine the efficiency of macro algae as bioabsorbent of copper and to study the bioabsorbent mechanism of isotherm. All the result that have been obtained will be conclude in this chapter.

5.2 Conclusion

This research use five different macroalgae in order to remove copper ions from aqueous solution. The five macroalgae were Sargassum Polycystum, Euchema Spinosum, Kappa Alverezir, Kappa Stratum and Caulerpa Lentifera. The synthetic water using copper sulphate were made and were mixed with five different seaweed using different parameters. Adsorption was found most commonly used to treat industrial wastewater such as by using macro algae and activated carbon. For this study, five macroalgae was obtained in Kudat, Sabah. The copper uptake of each macroalgae were analysed and the highest copper uptake is considered as the most potential macroalgae in adsorption of copper.

Bioabsorption process also were tested by other parameter such as contact time of the adsorbent, adsorbent dosage and effect of pH value. The test result for these parameter approved that Euchema has the highest and better adsorption of copper ions. Adsorption isotherm also shows that Langmuir isotherm model is the best fitted model due to R^2 value is higher compared to Freundlich.

Based on the objective, the higher copper uptake is *Euchema Spinosum* sp. followed by Ka*ppa Stratum sp., Kappa Alverezi sp., Caulerpa Lentifera sp.,* and *Sargassum Polycystum sp.* This make Euchema Spinosum is the most potential macro algae throughout this study on removal of copper. The efficiency of the biosorbent shows positive result through the effect of contact time, the effect of dosage and the effect of pH. All macro algae shows high percentage removal of copper ions. The adsorbtion isotherm shows that the macro algae has a good absorbtion and Langmuir isotherm is the best fitted isotherm model compared to Freundlich due to Langmuir Isotherm has higher R^2 value which is indicate a good bioabsorption.

5.3 Recommendation

Several recommendation were identified to develop the current research.

1) Analyzed the result using ICP (Inductively Couple Plasma) for easy handling.

2) Study the effect of Temperature and initial concentration to know the efficiency of macro algae as bioabsorbent in removing heavy metal.

3) Investigate the adsorption kinetics of heavy metals such as intra-particle diffusion model fitting, pseudo-first order kinetic model fitting and pseudo-second order kinetic model fitting for futher research.

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