BIOSORPTION OF COPPER USING IMMOBILISED *EUCHEUMA COTTONII SP*. BIOMASS USING ONE-FACTOR-AT-TIME (OFAT)

HADI AFIFI BIN SULAIMAN

B. ENG TECH. (HONS) ENERGY AND ENVIRONMENT

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT			
Author's Full Name :	HADI AFIFI BIN SULAIMAN		
Date of Birth :			
Title :	BIOSORPTION OF COPPER USING IMMOBILISED		
	UECHEUMA COTTONII SP. BIOMASS USING ONE-		
	FACTOR-AT-TIME		
Academic Session :	n : SEMESTER I 22/23		
I declare that this thesis is cl	assified as		
□ CONFIDENTIAL	(Contains confidential information under the Official Secret Act 1997)*		
□ RESTRICTED	(Contains restricted information as specified by the		
	organization where research was done)*		
\boxtimes OPEN ACCESS	I agree that my thesis to be published as online open access		
	(Full Text)		
I acknowledge that Universiti Malaysia Pahang reserves the following rights:			
1. The Thesis is the Pro	operty of Universiti Malaysia Pahang		
2. The Library of Univ	ersiti Malaysia Pahang has the right to make copies of the		
thesis for the purpose of research only.			
3. The Library has the right to make copies of the thesis for academic exchange.			
Certified by:			
HADIAEIELBIN SULAIMAN RADIAH BINTI MOKHTAR			



SUPERVISOR'S DECLARATION

I hereby declare that I have checked this proposal and in my opinion, this proposal is adequate in terms of scope and quality for the award of the degree of Engineering Technology (Energy & Environmental)

(Supervisor's Signature)			
FULL NAME	: DR NADIAH BTE MOKTHAR		
POSITION	: SENIOR LECTURER		
DATE	: 14/2/2023		

(Co-supervisor's Signature) FULL NAME : POSITION : DATE :



STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

(Student's Signature) FULL NAME : HADI AFIFI BIN SULAIMAN

ID NUMBER : TC19023

DATE : 13 February 2023

BIOSORPTION OF COPPER USING IMMOBILISED *EUCHEUMA COTTONII SP.* BIOMASS USING ONE-FACTOR-AT-TIME (OFAT)

HADI AFIFI BIN SULAIMAN

Thesis submitted in fulfillment of the requirements For the award of the degree of B. Eng. Tech (Hons) Energy & Environmental

Faculty of Civil Engineering Technology

UNIVERSITI MALAYSIA PAHANG

FEBUARY 2023

ACKNOWLEDGEMENT

Alhamdulillah, first and foremost, I would want to express my heartfelt thanks to Allah SWT for the direction and assistance in providing me with the health and strength to successfully complete my thesis.

I'd also want to express my gratitude and admiration to my committed and capable supervisor, Madam Nadiah Bt Mokhtar, for her ongoing support of my study, providing ideas, crucial advise, and inspiration. Her advice was invaluable during the research and writing of this thesis. Thank you for providing me this opportunity and allowing me to gain from the experience of conducting this study under your supervision.

Special thanks go to the whole Environmental Laboratory personnel, as well as Puan Azimah, Encik Suhaimi, and Encik Qauri. They were always patient in teaching me and guiding me through the experiment for this study. The experiment could not be carried out without their permission to enter the laboratory and direction. Not to mention, many thanks to Sabah suppliers that provided the Eucheuma Cottonii for research purposes.

I'd want to thank my revered parents, Sulaiman Bin Suran and Zabidah Bt Hashim, for their unending encouragement, support, and care. Without them, this thesis would not have been conceivable.

I'd want to use this occasion to express my heartfelt gratitude to my Senior Design Project II partners, especially Nur Mashitah Binti Mohd Nawi and Dr Nadiah Bt Mokhtar. They are an excellent partner with whom to work on this project and provide the most assistance. They also provide me with suggestions and feedback on my research to help me better it in a variety of ways.

Thank you.

ABSTRAK

Satu jenis efluen industri yang sering dihasilkan oleh sisa kimia, pembuatan, kumbahan, penyaduran elektrik, dan perlombongan ialah logam berat, juga dirujuk sebagai logam toksik. Penyingkiran logam berat daripada air sisa boleh dilakukan pada kos yang berpatutan melalui biosorpsi. Untuk mengeluarkan logam berat daripada efluen industri, Eucheuma Spinosum sp. yang tidak bergerak, kadangkala dikenali sebagai rumpai laut merah, telah digunakan sebagai biosorben. Biosorben yang diperbuat daripada rumpai laut tidak bergerak telah digunakan untuk mengeluarkan logam berat daripada efluen industri. Penyingkiran logam berat daripada air sisa boleh dilakukan pada kos yang berpatutan melalui biosorben. Kajian ini bertujuan untuk menilai masa sentuhan pertama, dos, pH permulaan, dan kepekatan awal penyingkiran zine. Air sisa sintetik dicipta dengan melarutkan 150ml Kuprum 1000mg/l dalam 1L air suling untuk menghasilkan larutan 1000 mg/L Cu2+. Ia ditentukan berapa banyak Cu pada asalnya wujud dalam sisa sintetik. Selepas tidak bergerak, rumpai laut dibersihkan dengan air suling. Semasa adunan masih digaul, 0.25g serbuk rumpai laut ditambah. Campuran itu kemudiannya disuntik ke dalam larutan kalsium klorida 3 g menggunakan picagari. Selepas itu, air suling digunakan untuk mencuci manik alginat yang telah dirawat sebelum ditukar kepada Kalsium Klorida CaCI2. Selepas itu, campurkan dan biarkan ia sejuk pada suhu bilik. Seterusnya, masa sentuhan awal, dos, dan kepekatan awal diperiksa berhubung dengan keberkesanan rumpai laut tidak bergerak sebagai biosorben. Berat biosorben ditentukan sebelum dan selepas pengeringan, penyingkiran maksimum Cu berlaku dengan dalam 30 minit untuk rumpai laut yang tidak bergerak. Manakala bagi rumpai laut mentah pula ialah 10 minit, masing-masing. Dos selanjutnya mempunyai penyerapan yang besar, dengan kadar penyerapan permulaan 92.08% pada 0.1g. Apabila pengaruh masa sentuhan dimasukkan, kadar penyingkiran ialah 88% dan 89% antara 5 dan 40 minit. Kesimpulannya, biosorpsi menggunakan Euchuema Cottonii mungkin merupakan keputusan terbaik untuk mengeluarkan kuprum dalam air buangan berbanding Euchuema Cottonii mentah.

ABSTRACT

A type of industrial effluent that is frequently created by chemical waste, manufacturing, sewage, electroplating, and mining is heavy metal, also referred to as toxic metal. Heavy metal removal from wastewater may be done at a reasonable cost via biosorption. In order to remove heavy metals from industrial effluent, immobilised Eucheuma Spinosum sp., sometimes known as red seaweed, has been used as a biosorbent. Biosorbent made from immobilised seaweed has been used to remove heavy metals from industrial effluent. Heavy metal removal from wastewater may be done at a reasonable cost via biosorbent. This study aims to evaluate the first contact time, dose, starting pH, and initial concentration of the zine removal. The synthetic wastewater was created by dissolving 150ml Copper 1000mg/l in 1L of distilled water to create a 1000 mg/L Cu2+ solution. It is determined how much Cu originally existed in synthetic waste. After being immobilised, the seaweed was cleaned with distilled water. While the mixture is still being mixed, 0.25g of seaweed powder is added. The mixture was then injected into a 3 g calcium chloride solution using a syringe. After that, distilled water was used to wash the treated alginate beads before they were changed into Calcium Chloride CaCI2. Following that, blend and let it cool to room temperature. Next, initial contact time, dosage, and initial concentration are examined in relation to the effectiveness of immobilised seaweed as a biosorbent. The biosorbent's weight is determined both before and after drying. Maximum removal of Cu took place with in 30 minutes for the immobilised seaweed. Meanwhile for the raw seaweed is 10 minutes, respectively. Further dosages had substantial absorption, with a starting absorption rate of 92.08% at 0.1g. When the influence of contact time is included, the elimination rate is 88% and 89% between 5 and 40 minutes. In concluded, biosorption using Euchuema Cottonii might be the best decision making for removal copper in wastewater compared to raw Euchuema Cottonii.

TABLE OF CONTENTS

Table of Contents	
ACKNOWLEDGEMENT	6
ABSTRAK	7
ABSTRACT	
TABLE OF CONTENTS	9
LIST OF TABLE	
LIST OF FIGURE	
LIST OF SYMBOL	
CHAPTER 1	
INTRODUCTION	
1.1 Background of study	
1.2 Problem statement	14
1.3 Objective of study	15
1.4 Scope of study	15
1.5 Significant of study	16
CHAPTER 2	17
LITERATURE REVIEW	17
2.1 Wastewater	17
2.2 Biosorbent	
2.2.1 Mechanism	19
2.2.1.1 Temperature	19
2.2.1.2 pH	
2.2.1.3 Metal	
2.3 Heavy Metal	
2.4 Biosorption	21

2.5 Mechanism	
2.6 Mechanism of biosorption process	
2.7 Factor effecting biosorption	
2.7.1 Contact time	
2.7.2 pH	
2.7.3 Dosage	
2.7.4 Pacticle size	25
2.8 Eucheuma Cottonii	
2.9 Wastewater Standard	
3.0 Copper Concentration in Wastewater	
CHAPTER 3	
METHODOLOGY	
3.1 Introduction	
3.1.2 Flowchart research procedure	
3.2 Material and Apparatus	
3.3 Chemical	
3.4 Apparatus	
3.5 Preparation of Aqueous Solution	
3.6 Preparation of Immobilization Seaweed Eucheuma Cottonii SP	
3.7 Biosorption Experiment Procedure	
3.8 Data analysis	
4.0 Summary	
CHAPTER 4	
RESULT AND DISCUSSION	
CHAPTER 5	
CONCLUSION AND RECOMMENDATION	
REFERENCE	44

APPENDICES	8
------------	---

LIST OF TABLE

Table 1.1	Advantage/Disadvantage of biosorption	24
Table 1.2	The removal rate uses powder from fruit waste to remove heavy metals	27
Table 1.3	Parameter limits of effluent of standards A and B	29,30
Table 1.4	Standard concentration of heavy metal in drinking water	26
Table 1.5	Table 1.5: Apparatus	33
Table 4.1	Percentage removal effect by contact time with immonilised seaweed	38
Table 4.2	Percentage removal effects by contact time with raw seaweed	38
Table 4.3	Effect dosage by using optimum raw seaweed at 10 minutes	39
Table 4.4	Effects dosage by using optimum contact time immobilized seaweed at 30 minutes.	40
Table 4.5	Effects of initial concentration	41
	LIST OF FIGURE	
Figure 1	Eucheuma spinosum (Red Seaweed)	28
Figure 2	Industrial waste water	31
Figure 3	Flow diagram for the research procedure	32
Figure 4	Preparation of Aqueous Solution	34
Figure 5	Flow of process of immobilization Eucheuma Cottonii SP	35
Figure 6	The immobilized of Eucheuma Cottonii before and after	35
Figure 7	Percentage removal effects by contact time with immobilised seaweed and raw seaweed.	39
Figure 8	Comparison of dosage between immobilised and raw seaweed	40
Figure 9	Effect initial concentration	42

LIST OF SYMBOL

%	percentage
mg/L	milligram per liter
°C	degree celcius
ml	millimeter
g	grams
L	Liter

CHAPTER 1

INTRODUCTION

1.1 Background of study

Due to the huge heavy metal toxicity, non-biodegradability, and pervasive presence in natural and human-altered environments, which eventually enter the food chain (algae, fish, etc.) (Houari et al., 2019). Due to global industrial expansion and rapid industrial growth, an increasing amount of hazardous waste products are being released into the aquatic environment on a daily basis (Li et al. 2020). Heavy metals, radioactive substances, zinc, pesticides, medicines, chemicals, and oil contaminants are examples of pollutants (Akpomie & Concradie, 2019). Their frequency has rapidly increased in recent years, particularly in underdeveloped countries.

Toxic heavy metals are a type of pollutant that has an immediate effect on people and animals. Metals and copper found in wastewater have the potential to impair human health if they come into touch with it on a regular basis, resulting in major health issues or illnesses. Copper may be utilised in a broad range of manufacturing applications, including fabrics, sheets, drinks, and plastics. For example, industrial wastewater containing zinc, lead, copper, cadmium, and chromium can contaminate groundwater resources, posing a severe groundwater contamination concern. The current situation over industrialisation has resulted in ecological imbalance and the destruction of natural resources during the last few decades (Afindy Kadir et al., 2014).

Because heavy metals are non-biodegradable, they pose a major environmental risk. It is critical to remove high amounts of dangerous heavy metals from wastewater (Ahmed et al., 2021). To remove these toxic metals from wastewater, physical treatment methods such as solvent extraction, reverse osmosis, adsorption, and ion exchange, as well as chemical processing methods such as adsorption and complexation, have all been developed and thoroughly investigated (Houari et al., 2019).

Biosorption, according to Nyamunda (2019), is an innovative, dependable, competitive, and low-cost approach for heavy metal ion removal due to its high efficiency and ease of use. As part of the adsorption mechanism, heavy metals attach to the surface

of biomaterials via functional groups such as ester, amino, hydroxyl, sulfhydryl, carboxyl, phenolic, and phosphate. Regardless of what has transpired in the past, these approaches will continue to be used have drawbacks such as insufficient pollutant removal, high reagent or energy needs, and being too costly to treat low levels of heavy metal in wastewater. Biosorbents are derived from three main sources: (1) nonliving biomass such as wood, seaweed, lignin, shrimp, krill, squid, and crab shell; (2) algal biomass; and (3) microbiological biomass such as bacteria, fungus, and yeast (Nyamunda et al., 2019).

1.2 Problem statement

Precipitation, coagulation, biodegradation, photodegradation, membrane separation, and adsorption were among the most dependable and promising wastewater treatment strategies researched in most nations a decade ago for heavy-metal removal from wastewater. Adsorption has been selected as the most effective recovery method. When comparing these techniques, adsorption offers various significant advantages, including economical, technical, and environmental advantages that make it preferable to other water treatment technology or approaches (Ahmad et al., 2021). The cheap cost of the materials used in the planning, convenience of service, great performance, and environmental friendliness are only a few of the advantages.

Using commercial biomass as seaweed as adsorption appears to be the most successful way for removing various types of zinc from wastewater. Despite its effectiveness, commercially available activated carbon is costly and difficult to renew. 2021). Furthermore, the disadvantages of these conventional methods include chemical consumption, high toxic sludge generation, initial operating cost, low biodegradability of certain zinc, adsorbent regeneration cost and time, adsorbent elimination, sludge treatment cost, membrane clogging, low throughput, and elimination of concentration in membrane processes (Uddin, 2017).

Wastewater thrown into river systems, particularly heavy-metal container wastewater, pollutes the air and endangers the life of microorganisms in the water. Water toxicity increases over time, rendering it unsafe for human consumption and killing marine species (Bhattacharjee et al., 2020). According to the Environmental Quality Report 2010, an estimated 50% of Malaysia's river water is contaminated. The pollution level in the drainage basin of many industrial sites has typically increased. The pollution

level in the neighbouring site's watershed has increased as a result of industrialization, and most of the wastewater generated from industries contains toxins and is dumped into the surface water.

To minimise the detrimental impacts of heavy metal toxicity, several ways have been developed to limit the amount of heavy metals in wastewater. Precipitation, electrochemical reduction, ion exchange, reverse osmosis, and reduction are all water treatment processes. However, the vast majority of these therapies are too costly. As a result, a less expensive therapy, biosorption, has been found to minimise the high cost of treatment. The most widely used adsorbents for heavy metal removal in wastewater are prohibitively expensive. As a result, the goal of this study is to identify the least expensive adsorbent derived from agricultural waste that can effectively remove heavy metals from wastewater.

1.3 Objective of study

There are several objective for this study based on the problem statement.

- To prepare immobilised seaweed to be as biosorbent for wastewater removal.
- To determine the performance of immobilised seaweed in terms of contact time, initial concentrations and dosage.

1.4 Scope of study

This study suggests treating copper ions in synthetic wastewater with a red macroalga called Eucheuma Cottonii sp. The Eucheuma Cottonii was collected in Sabah obtained from supplier assisted by supervisor that be used as biomass adsorbent for this project.

This study looked at the levels of heavy metals like copper ions in real wastewater. For its biosorption capabilities, one species of red seaweed (E. Cottonii) was widely researched. Two techniques of biosorption process were employed for the study on the influence of the first initial contact time, dose, and starting concentration, which would compose the study's parameters. This experiment necessitates a number of steps, including the manufacture of seaweed and heavy metals. The gathered seaweed was washed and cleaned in preparation for the oven drying technique (Memmert, UNB100). Following drying, the seaweed was ground using a dry mill blender (Butterfly) and sieved at size (600µm).

Reduces the particle size to help in immobilisation. Sodium alginate (Duchefa Biochemistry) is the chemical used in immobilised algae studies. Calcium chloride is also used to harden the immobilised beads (Bendosen). After the immobilisation method, do the biosorption experiment and collect data with a spectrophotometer D5000 (HACH UV-VIS). Copper standard solution traceable to SRM from NIST Cu(NO3)2 in HNO3, 0.5 mol/l 1000mg/l Cu was used to create the synthetic wastewater. Certipur® is the material used to create the aqueous solution (R&M Chemicals). Hydrochloric acid, HCL, and sodium hydroxide, NaOH (HmbG Chemicals) are used to modify the pH of an aqueous solution.

The efficiency of immobilised seaweed will be tested in terms of contact time, effect of dose, and initial concentration utilising batch biosorption in One-Factor-At-Time (OFAT) (5 samples) and the percentages of removal will be computed using the equation.

1.5 Significant of study

The objective of this research is to eliminate copper that pollute the environment especially in water. Copper is heavy metal that can cause harm to human body, these heavy metal are not biodegradable, if there is no action been taken might can cause serious pollute to environment. This study being conducted to demonstrate the efficiency of microalga (Eucheuma Cottonii) know as red algae as biosorpbent in water treatment. The potential to optimise the utilisation of algae and the advantages of algae for the wastewater treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is water that has been polluted by domestic, industrial, or commercial usage. Water constitutes 99.9% of the composition of wastewater. Organic debris, microorganisms, and inorganic compounds account for 0.1 percent (%) of wastewater composition. Wastewater effluents are released into a variety of bodies of water, including lakes, ponds, streams, rivers, estuaries, and oceans. As a result, the composition of all wastewater is constantly changing and extremely variable, making it difficult to define the word in a single way (Tuser 2020).

Industrial wastewater is wastewater emitted from industrial and commercial sources that may include hazardous contaminants, endangering the quality of receiving waterways or interfering with publicly owned treatment plants that will receive such effluent discharges. In general, industrial effluent contains suspended particles, colloidal solids, and dissolved solids. Furthermore, industrial waste may have abnormally high acidity or alkalinity, as well as high or low amounts of coloured debris. In addition, industrial effluent may contain inerts, organic or inorganic compounds, toxic substances, and dangerous microbes.

Heavy metal pollution may be present in industries such as mosaic, food processing, electrical appliance production, and chemical compound processing (Phadtare & Patil, 2015). Heavy metals must be removed from industrial effluent because they damage water bodies and are hazardous to numerous life forms (Phadtare & Patil, 2015). Heavy metal water pollution creates severe environmental problems due to the potentially dangerous impacts of heavy metals on both humans and the environment (Husoon et al., 2013).

2.2 Biosorbent

Biosorption is characterised as a quick, energy-free process in which biological materials or biopolymers serving as sorbents may remove contaminants such as heavy metals from wastewater via metabolically mediated or physicochemical adsorption mechanisms. Biosorption, which was first detected in the 1970s by the concentration of heavy metals and radioactive elements from different algae, has gained increasing interest in recent decades as a developing and low-cost promising technique. The biosorption phenomenon occurs primarily as a result of the attraction between biosorbent and adsorbates.

Biosorption has several benefits over traditional removal techniques, including use of cheap and renewable abundant biomaterials. Treatment of a huge volume of wastewater due to fast kinetics. High selectivity and recovery of specific heavy metals, multiple heavy metals treatment and mixed wastes. Relatively low operational cost and low capital investment. Temperature, pH and coexisting ions as a wide range of physicochemical conditions. Highly reduced volume of hazardous waste formed.

Heavy metal biosorption from aqueous solutions is a relatively recent method that has been demonstrated to be a highly promising process for heavy metal contamination remediation. The primary benefits of biosorption include the utilisation of low-cost biosorbents and its great efficacy in decreasing heavy metal ions. Biosorption techniques are ideal for treating dilute heavy metal effluent. Typical biosorbents can be obtained from three sources (R. Apiratikul and P. Pavasant, 2008) non-living biomass includes bark, lignin, shrimp, krill, squid, and crab shell; algal biomass; and microbiological biomass, which includes bacteria, fungus, and yeast.

Biosorbents, on the other hand, have been found to be employed in cycles. Adsorbent regeneration allows for its reuse in subsequent cycles and allows for the recovery of adsorbed components. Adsorbents can be regenerated by utilising particular processes that entail the use of chemical reagents. With 0.1 M HCl, the metal-loaded papaya wood was fully desorbed. There was no reduction in the effectiveness of heavy metal removal from their respective solutions and the metal-loaded biomass over five cycles of repeated biosorption-desorption. The study suggests the possibility of a unique application of papaya wood, which is a source of environmental deterioration and is normally useless for the treatment of heavy metal-contaminated wastewater (A. Saeed, 2005). Using a 10 mM HCl solution, the Zn+2 ions were gradually desorbed from Botrytis cinerea (B. cinerea) biomass. The biosorbent can be regenerated with up to 98 percent recovery and reused five times in biosorption-desorption cycles, according to desorption and reusability experiments.

2.2.1 Mechanism

Because of the affinity between biosorbent and adsorbate, mechanisms such as adsorption, adsorption, ion exchange, surface complexion, and precipitation are involved in the biosorption process. In general, dead (inactive) biomass from diverse biological sources is superior to active (alive) biomass for heavy metal removal during the biosorption process. In fact, while temperature and pH can influence bacterial growth features, heavy metal recovery is difficult, and their metabolic process is influenced by their toxicity. Inactive biomass, on the other hand, is freely accessible as a by-product and waste and does not require biological growth substrate or food, which might raise the biological and chemical oxygen demand in wastewater.

2.2.1.1 Temperature

Heavy metal bioremediation is heavily impacted by either the physicochemical condition of pollutants or the metabolic activity of microorganisms. Low temperatures in the 20–35°C range are generally ideal for heavy metal removal effectiveness. However, high temperatures are detrimental to microbial living cells and reduce metal adsorption.

2.2.1.2 pH

The pH of the solution is substantially pH-dependent and is likely one of the most crucial factors in heavy metal biosorption. In reality, the pH of the solution has a significant impact on the type of biomass binding sites, chemical species in solution and their solubility, and functional groups on the surface of microorganisms. Due to competition, the biosorption of metals such as Co, Cu, Cd, Ni, and Zn is decreased at low pH levels.

2.2.1.3 Metal

Metal solution and biomass concentration: The driving force provided by the initial concentration contributes to the reduction of the resistance between the solution and the biosorbent. Generally, metal uptake increases concomitant with initial concentration with an optimum removal percentage at low initial concentration. Heavy metals have been discharged into the environment in large quantities as a result of increasing industrialisation and overpopulation.

Their existence in nature and in waste is then seen as a serious worldwide issue that may damage all kinds of life. Biosorption is the most cost-effective and technically possible method of dealing with heavy metals in water. Biosorption is a new technology and passive adsorption method that involves adsorption of biological components on cell surfaces and is usually reversible and metabolism-independent. During this procedure, pollutants such as copper (Cu), etc. are affected. Bacteria, fungus, and algae are often used as biological biosorbents for heavy metal remediation.

2.3 Heavy Metal

Copper metal is produced by the copper mining and smelting industries, the brass and bronze manufacturing sectors, the electroplating industries, and the excessive use of copper-based agrichemicals (Madhava Rao et al., 2006). Cu(II) ions provide major toxicological problems; it is often recognised to accumulate in the brain, skin, liver, and kidneys. Davis et al. (2000) found that it is both essential and harmful to the pancreas and myocardium. Heavy metal contamination in ecosystems has been exacerbated by rapid industrialisation and a rise in global population.

Because of their accumulation in living organisms, heavy metal ions (Zn(II), Cu(II), Pb(II), Cd(II), and others) have become an ecotoxicological concern of great interest and growing significance. These hazardous metals are discharged into the environment in a variety of ways. Examples include coal combustion, sewage waste waters, automobile emissions, mining operations, and the use of fossil fuels. Filtration, chemical precipitation, reverse osmosis, solvent extraction, and membrane techniques are the traditional methods for heavy metal removal (Karabulut et al., 2000).

Copper's ubiquitous presence raises major toxicological concerns; it has been shown to accumulate in the brain, skin, liver, pancreas, and myocardium. Since copper is such a common substance, there are several real or prospective causes of copper contamination. Copper may be found in food, particularly shellfish, liver, mushrooms, almonds, and chocolate. In a nutshell, any copper-based processing or container may contaminate a product such as food, water, or drink. Copper is necessary for human life and health, yet it is also potentially harmful, as are all heavy metals. Continued inhalation of copper-containing sprays, for example, has been associated to an increase in lung cancer among exposed employees.

Furthermore, even at low concentrations, copper is a highly hazardous metal, and coppercontaminated wastewater must be cleaned before being discharged into the environment. Copper levels in the blood can harm red blood cells and impair their capacity to transport oxygen. Copper levels in the body may have an effect on male fertility. Copper sensitivity is increased in people with Wilson's disease and in certain newborns (babies under one year old). Their bodies are unable to efficiently eliminate excess copper.

Because of its low cost and good quality of treated water, the biosorption method has proven to be superior to other techniques. It generates wastewater. Because of its great biosorption ability, activated carbon is commonly employed as a biosorbent (Uzun and Guzel, 2000; Vasu, 2008). The purpose of this study was to determine the efficacy of Chaetomorpha Antennina sp. powder in removing copper ions from aqueous solutions. Solution, as well as predicting the best removal conditions and biosorption isotherms with their associated constants.

2.4 Biosorption

The research for new innovation for removing harmful metals from wastewaters has focused on biosorption, which is based on the metal binding capabilities of diverse biological materials. Biosorption is the capacity of biological materials to adsorb heavy metals from wastewater via metabolically mediated or physicochemical adsorption routes (Fourest andRoux, 1992). Metal biosorbents have been discovered in algae, bacteria, fungus, and yeasts (Volesky, 1986). The primary benefits of biosorption over traditional treatment procedures are as follows: (Kratochvil and Volesky, 1998 a).

- Low cost
- High efficiency
- Minimisation of chemical and lor biological sludge
- No additional of biosorbent
- Possibility of metal recovery.

A solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, generally water) containing a dissolved species to be sorbed are involved in the biosorption process (sorbate, metalions). Because of the sorbent's increased affinity for the sorbate species, the latter is drawn and bonded there by several methods. The procedure is repeated until an equilibrium is reached between the amount of solid-bound sorbate species and their proportion in the solution. The sorbate's distribution between the solid and liquid phases is determined by the sorbent's affinity for it (N. Ahalya). Some biosorbents are broad-spectrum, binding and collecting the bulk of heavy metals with no particular action, whilst others are metal-specific.

Some laboratories employed readily accessible biomass, while others isolated specific strains of microbes, and yet others treated the existing raw biomass to some extent in order to increase its biosorption capabilities. Recent biosorption investigations have focused on waste materials that are by-products or trash from large-scale industrial processes. For example, waste mycelia from fermentation operations, olive mill solid wastes (Pagnanelli et al 2002), activated sludge from sewage treatment facilities (Hammaini et al 2003), biosolids (Norton et al 2003), aquatic macrophytes (Norton et al 2003). (Keskinkan et al. 2003).

Because the biosorption process is based on biomass or microorganisms, no subsequent chemical sludge is produced. The use of microorganisms in biosorption does not necessitate the supply of nutrients. As a consequence, biosorption is a reasonably simple procedure that does not require the services of a specialist (Vishal Mishra, 2013). Biosorption has its own set of advantages and disadvantages. The advantages and drawbacks of biosorption are shown in Table 1.1.

Advantages	Disadvantages	
Low cost.	Early saturation.	
High efficiency	The potential for biological process	
mgn entelency.	improvement.	
Minimization of chemical and biological	No potential for biologically altering	
sludge.	the metal valency state.	
Regeneration of biosorbent and possibility		
of metal recovery.		

Table 1.1The advantages and disadvantages of biosorption treatment.

2.5 Mechanism

Biosorption Mechanisms: Because microorganisms have a complicated structure, there are several methods for the metal to be taken up by the microbial cell. Biosorption processes vary and are not completely understood. They can be categorised using a variety of characteristics. According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into:

- I. Metabolism depends
- II. Non-metabolism dependent

According to the location where the metal removed from solution is found, biosorption can be classified as:

- I. Extra cellular accumulation/precipitation
- II. Cell surface sorption
- III. Intracellular accumulation

2.6 Mechanism of biosorption process

Biosorption employs adsorption mechanisms such as ionic, chemical, and physical adsorption. By generating compounds with negatively charged reaction sites, metal ions might be adsorbed on the cell surface. Several ligands discovered on fungal cell walls are hypothesised to facilitate metal chelation. Among them are hydroxyl, carboxyl, phosphate, sulphydryl, and amine groups (Ramachandra et al., 2005). Biosorption is mediated by the interaction of cell wall functional groups with metal ions. Microbial cell walls are composed of polysaccharides, lipids, and proteins. These components have a range of roles in metal ion binding, including the creation of metal ion binding sites. Metal ion biosorption is a fast and unaffected by cell metabolic process (Vishal Mishra, 2013).

The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, often water) containing a dispersed species to be sorbed (adsorbate, metal/zinc). The degree of adsorbent affinity for the adsorbate determines the distribution of the adsorbate between the solid and liquid phases. Because of the adsorbent's strong attraction for the adsorbate species, it is attracted and bound in a variety of ways. The process is continued until the amount of solid-bound adsorbate species and the amount of solution remaining are determined (Ramachandra et al., 2005).

2.7 Factor effecting biosorption

2.7.1 Contact time

Contact time is the amount of time provided for the biosorption process. Although the period of contact between the biosorbent and the sorbate has no direct influence on biosorption capacity, it can be a limiting factor. Under testing circumstances, increased contact time would allow the biosorbent material to exhibit its maximal biosorption capability. When the biosorbent's maximum biosorption capacity is attained under given conditions, the binding sites are fully saturated, and increasing contact time has no further impact (Redha, 2020).

2.7.2 pH

It's an important element to consider. It influences metal ion solubility and biomass binding sites. At lower pH values, metal biosorption is inhibited. Typically, the pH range for metal adsorption is 2.5–6. Above this threshold, the biosorbent's ability to adsorb metals is impaired (Shamim, 2018). PH influences both the chemistry of biosorbent functional groups and the chemistry of metal ions. As previously indicated, the pH at which biosorption takes place is crucial and has a direct influence on biosorption capacity and, in some cases, the mechanism by which biosorption takes place. The biosorption capacity frequently rises with pH until it reaches its maximum capacity, at which point it decreases (Redha, 2020).

Higher pH levels can occasionally reduce overall sorption effectiveness by generating metal precipitates due to the reduction in solubility. To reduce metal hydroxide precipitation, it is crucial to know the limiting pH for metal solubility in complex biosorption systems. Bhattacharjee and colleagues (2020). Biosorption of metal ions such as copper, cadmium, nickel, cobalt, and zinc is often decreased at low acidic pH. Metal cations and hydronium ions fight for the biosorbent's binding sites (Redha, 2020).

At low pH, the functional groups of the biosorbent prefer hydronium ions because the functional groups are protonated, and repulsive interactions between the functional groups and metal cations would prevent the two from attracting. However, as the pH rises, deprotonation causes negative charges to form on functional groups such as carboxyl, hydroxyl, and phosphate groups. Although increasing the pH ensures that all acidic groups are deprotonated, free metal cations begin to precipitate as metal hydroxides, lowering the efficiency of the metal removal process. This would increase metal cation binding, hence improving biosorption capacity and speed (Redha, 2020).

2.7.3 Dosage

At low biomass doses, the specific adsorption of metal ions increased. On the other hand, using a low biomass dose in complicated polluted water may increase competition for the biosorbent's binding site, decreasing the biosorbent's biosorption potential. Increased biomass doses minimise competition among metal ions that bind to functional groups when more than one metal ion is present (Redha, 2020).

2.7.4 Pacticle size

Particle size is crucial for efficiently extracting heavy metals from the medium. The surface area property is critical in the case of biofilms. Metal ion binding to microbial cell walls has previously been demonstrated. Even though internal metal adsorption requires a lot of energy, bacteria prefer it to wall adsorption (Shamim, 2018). Furthermore, the faster and greater adsorption capacity of smaller adsorbent particles might be attributable to the fact that smaller particles have a bigger and more easily accessible surface area (Barka et al., 2013). Table 2.3 shows the removal rate of certain heavy metals using several types of fruit food waste in powder form.

et
i et
t

Table 1.2The removal rate uses powder from fruit waste to remove heavy metals.Source: Liu et al. (2012), Othman et al. (2014), Shartooh et al.

2.8 Eucheuma Cottonii

Eucheuma cottonii seaweed is common in Asia, Africa, and Oceania and has showed promise as a biochar base material. Seaweed grows quickly in contrast to terrestrial crops and has a high carbon dioxide fixing rate. Seaweed is abundant and readily available, and it thrives well in an aquatic setting. Malaysian seaweed output was around 14,900 metric tonnes in 2010 and is expected to increase to over 22 metric tonnes in 2022. The lignocellulose component is appealing as a basis material for biochar adsorbent, which is the focus of this research. To the best of our knowledge, the creation of seaweed-based bio-sorbents for methylene blue (MB) removal has seldom been documented, emphasising the uniqueness of our study. Eucheuma cottonii seaweed was obtained from Sabah, Malaysia.



Figure 1 Euchuema Cottonii SP.

Seaweed is a vast untapped maritime bioresource comprised of hundreds of species, the development of which does not compete with land plants for arable land, fertiliser, or fresh water supplies. Seaweed biomass is made up of various sugar polymers with little or no lignin. As a result, no severe pretreatment is required, which often hampers the usage of lignocellulosic biomasses (Hou et al., 2017). Seaweeds, unlike terrestrial biomass, do not require fresh water or fertilisers to grow and do not induce indirect land use change.

The benefits listed above demonstrate the great potential of using seaweed biomass as a feedstock for the development of third generation liquid biofuels. The unusually high glucose content (56.7%) in a wild-growing brown seaweed species (Laminaria digitata, taken in Denmark in summer 2012) emphasised the feasibility of utilising this seaweed biomass for biofuel generation (Hou et al, 2015).

Seaweeds can contain a lot of protein, and there are a lot of distinct carbohydrate molecules in seaweed. Because there are hundreds of unexplored species, new structural and storage carbohydrates may be identified (Wei et al, 2013). Seaweed protein can supplement the protein supply required by the rising human population, for example, as fish feed. The high levels of ash in seaweeds (up to 40%) can help with closed-loop mineral fertiliser usage, including primary, secondary, and trace elements. Minerals from fertiliser runoff can therefore be recycled by separating them from seaweeds that have adsorbed them. Furthermore, utilising the 'integrated multi-trophic aquaculture' (IMTA) strategy, seaweeds are envisioned as an environmental re-mediation technique in large-scale fish and shellfish production. This proposal makes use of seaweeds' capacity to swiftly adsorb minerals required for growth (1 year's worth in 1 day). In this method,

seaweeds adsorb nutrients from farmed fish waste. The adsorbing property of seaweed can greatly minimise trash run-off from fish farms.

As a result, they are a considerably more sustainable biomass source than firstand even second-generation biomass sources. Seaweeds have greater volumetric production rates (biomass per volume per time) and biomass densities than microalgae. Because of their chemical makeup, macroalgae are a complementary biomass source to microalgae (a lipid-based biorefinery platform) and lignocellulosic biomass (a lignin- and cellulose-based biorefinery platform). Seaweeds, like lignocellulosic biomass, require relatively mild processing conditions. In general, lower temperatures, less severe acid conditions, and shorter reaction periods are required. The quantity of carbohydrates in seaweeds varies greatly seasonally. Variations in rhamnose in Ulva sp. between June and September, for example, and mannitol in Laminaria digitata between 5 and 32% over a year have been documented. Because seaweed decomposes fast, seasonal harvesting and the development of storage systems are required (Adams et al., 2011).

Because seaweed contains only around 20% dry matter, drying processes prior to processing do not appear to be energy efficient (van Hal et al, 2014). Aqueous biorefinery methods must consequently be developed, although product concentrations are naturally limited. Even without the addition of water, the beginning concentration of, say, sugars is restricted to roughly 14%, based on a total carbohydrate level of 70%. Furthermore, large-scale mechanised open sea farming techniques will need to be developed. This should bring seaweed raw material prices down to competitive levels.

2.9 Wastewater Standard

According to Malaysia's Environmental Law, ENVIRONMENTAL QUALITY ACT, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000:

Parameter	Unit	Standard A	Standard B
Temperature	°C	40	40
pH Value	-	6.0-9.0	5.59
BOD5 at 20°C	mg/1	20	50
COD	Mg/1	50	100
Suspended Solids	Mg/1	50	100
Mercury	Mg/1	0.005	0.05

Table 1.3Parameter limits of effluent standard A and B

Cadmium	Mg/1	0.01	0.02	
Chromium, Hexavalent	Mg/1	0.05	0.05	
Arsenic	Mg/1	0.05	0.10	
Cyanide	Mg/1	0.05	0.10	
Lead	Mg/1	0.10	0.5	
Chromium, Trivalent	Mg/1	0.20	1.0	
Copper	Mg/1	0.20	1.0	
Manganese	Mg/1	0.20	1.0	
Nickel	Mg/1	0.20	1.0	
Tin	Mg/1	0.20	1.0	

3.0 Copper Concentration in Wastewater

Copper metal is produced by the copper mining and smelting industries, the brass and bronze manufacturing sectors, the electroplating industries, and the excessive use of copper-based agrichemicals (Madhava Rao et al., 2006). Cu(II) ions provide major toxicological problems; it is often recognised to accumulate in the brain, skin, liver, and kidneys. Davis et al. (2000) found that it is both essential and harmful to the pancreas and myocardium. Heavy metal contamination in ecosystems has been exacerbated by rapid industrialisation and a rise in global population.

Because of their accumulation in living organisms, heavy metal ions (Zn(II), Cu(II), Pb(II), Cd(II), and others) have become an ecotoxicological concern of great interest and growing significance. These hazardous metals are discharged into the environment in a variety of ways. Examples include coal combustion, sewage waste waters, automobile emissions, mining operations, and the use of fossil fuels. Filtration, chemical precipitation, reverse osmosis, solvent extraction, and membrane techniques are the traditional methods for heavy metal removal (Karabulut et al., 2000).

Copper's ubiquitous presence raises major toxicological concerns; it has been shown to accumulate in the brain, skin, liver, pancreas, and myocardium. Since copper is such a common substance, there are several real or prospective causes of copper contamination. Copper may be found in food, particularly shellfish, liver, mushrooms, almonds, and chocolate. In a nutshell, any copper-based processing or container may contaminate a product such as food, water, or drink. Copper is necessary for human life and health, yet it is also potentially harmful, as are all heavy metals. Continued inhalation of copper-containing sprays, for example, has been associated to an increase in lung cancer among exposed employees. Furthermore, even at low concentrations, copper is a highly hazardous metal, and copper-contaminated wastewater must be cleaned before being discharged into the environment. Copper levels in the blood can harm red blood cells and impair their capacity to transport oxygen. Copper levels in the body may have an effect on male fertility. Copper sensitivity is increased in people with Wilson's disease and in certain newborns (babies under one year old). Their bodies are unable to efficiently eliminate excess copper.

Because of its low cost and good quality of treated water, the biosorption method has proven to be superior to other techniques. It generates wastewater. Because of its great biosorption ability, activated carbon is commonly employed as a biosorbent (Uzun and Guzel, 2000; Vasu, 2008). The purpose of this study was to determine the efficacy of Chaetomorpha Antennina sp. powder in removing copper ions from aqueous solutions. Solution, as well as predicting the best removal conditions and biosorption isotherms with their associated constants.



Figure 2 Industrial mines wastewater contain with copper

CHAPTER 3

METHODOLOGY

3.1 Introduction

The method of analysis and research carried out to attain the objectives indicated in the first chapter will be discussed in this section of the chapter. This chapter focuses mostly on the test processes that have been developed.

3.1.2 Flowchart research procedure

Figure 3.1 depicts the overall technique for using immobilised Eucheuma Cottonii sp. to biosorb copper ions from aqueous solutions. The content of synthetic copper aqueous solution was determined using a HACH Spectrophotometer DR5000. Using biosorption research, determine the effectiveness of immobilised seaweed in terms of contact time, dose, and starting concentration.



Figure 3 Flow diagram for the research procedure

3.2 Material and Apparatus

Sodium alginate is the substance utilised in immobilised algae studies (Duchefa Biochemistry). Copper standard solution was utilised to make the aqueous solution (R&M Chemicals). In addition, the immobilised beads are hardened using calcium chloride (Bendosen). To modify the pH of an aqueous solution, sodium hydroxide (HmbG Chemicals) and hydrochloric acid are utilised.

3.3 Chemical

Chemical used in this study are Calcium Chloride CaCl2, Sodium Alginate, Copper Standard Solution, Cu(NO3)2, Distilled Water,, Copper Buffer Pillow Reagent, Asid Hidrocloric HCL, and Natrium Hydroxide NaOH.

3.4 Apparatus

Several equipment and apparatus has been used in this research process. Most of the apparatus provided by laboratory. Below are the list of apparatus.

No	Apparatus	Specification
1.	Sieve	Size: 600µm
2.	Breaker	100ml, 250ml, 500ml
3.	Dry mill blender	Brand: butterfly
4.	Volumetric flask	1000 ml
5.	Measuring cylinder	25 ml, 50ml, 100 ml, 500 ml, 1000 ml
6.	pH meter	Brand: MITTLER TOLEDO
		SevenCompact
7.	Analytical balance	Manufacture: Sartorius
8.	Spectrophotometer	HACH UV-VIS Spectrophotometer
		DR5000
9.	Spatula	-
10.	Filter paper	540 Harden Ashless, CAT No.145
11.	Centrifuge	1000rpm-4000rpm
12.	Centrifuge Tube	NEST 15/50ml
13.	HACH Sample cell	10ml
14.	Oven	Memmert UNB100
15.	Rotating Lab Shaker	Rs16000

Table 1.5List of apparatus

3.5 Preparation of Aqueous Solution

150ml of copper standard solution pentahydrate was dissolved in 1 L of distilled water to make a copper solution with a concentration of 1000 ppm. A volumetric flask was used to make the solution. The working solution was made up of 100 ppm by diluting the copper solution with distilled water.



Figure 4 Preparation of Aqueous Solution

3.6 Preparation of Immobilization Seaweed Eucheuma Cottonii SP

A 0.25 g of dried algae was combined with 3 percent (w/v) sodium alginate. Using a syringe, the alginate alga combination was then added to a 3% (w/v) calcium chloride (CaCl2) solution. The alginate beads were created and swirled together for 1 hour using a magnetic stirrer at 3500 rpm. The alginate bead was then taken from the calcium chloride solution and washed with distilled water to remove any leftover calcium chloride. The beads were dried on filtered paper for 30 minutes after being exposed to the air.



Figure 5 Flow of process of immobilization Eucheuma Cottonii SP.



Figure 6 The immobilized of Eucheuma Cottonii before and after

3.7 Biosorption Experiment Procedure

The purpose of this research is to assess the efficacy of algae as a copper adsorbent in wastewater. 10ml of wastewater samples were placed in each test tube. There are 10 test tubes, 5 of which are blank samples and 5 of which contain a mixture of wastewater and copper buffer pillow reagent. The sample tube is place on the shaker for the specified period of 5, 10, 20, 30, 40 minutes. The sample was immediately transferred to a centrifuge balance which is speed of 4000 rpm. The present time taken in the centrifuge balance is the same as it was previously. Finally, the percentage of copper removal following these treatments is calculated using data from spectrophotometer in the equation.

3.8 Data analysis

The biosorption capacity (qe) was calculated by using Equation 3.1 (Ibrahim et al., 2016).

Metal Removal R (%) =
$$\frac{Ci - Cf}{Ci} x \ 100\%$$

Where Co was the initial Cu2+ ions concentration (ppm) and Ce was the final Cu2+ ions concentration (ppm). The removal efficiencies obtained were compared to the red seaweed used as biosorbent.

4.0 Summary

Biosorption technique is choosing in removing heavy metal is due to it can effectively remove heavy metal at low cost, since the biomass is normally a biological substance that can be cultivated easily. The biosorption process need to determine the proper procedure and apparatus. The chemical used in this study are sodium hydroxide (NaOH), sulphuric acid (H2SO4) and zinc sulphate (ZnSO4). Meanwhile there is 16 apparatus to use to running the whole process. The immobilised process that show in figure above there is 7 step for each setup. The final analysis to obtain are the biosorption capacity by the equation given. The capacity of adsorption can be improved by physical treatment such as reduce the size of biomass and immobilized with calcium alginate.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This study used seaweed biomass (Euchuema Cottonii SP) as biosorbent to remove Cu from synthetic wastewater. A spectrophotometer was used to monitor the Cu concentration before and after the treatment with a biosorbent. The treatment was done by to type of product, immobilised seaweed and raw seaweed. The purpose is to compared which is the best way to remove Cu from synthetic wastewater. This chapter focuses on the effect of different parameters conducted for Cu removal synthetic wastewater by seaweed biomass and rate removal (ROR%)

4.2 Contact time effect (Raw seaweed and immobilised)

It has been observed that maximum removal of Cu took place with in 30 minutes for the immobilised seaweed. Meanwhile for the raw seaweed is 10 minutes, respectively. But, removal percentage that adsorb from immobilised is greater than raw seaweed. Table 4.1 and Table 4.2 shows that adsorption of raw seaweed takes less time than immobilised seaweed. This is due to the pores of raw seaweed being more open to adsorb Cu. Meanwhile, sodium alginate forms a rigid coating on immobilised seaweed. The biosorbent's optimal metals biosorption performance under defined conditions was demonstrated by the equilibrium duration and amount of metals adsorbed at this time. According to Nasir and Darul (2008), the adsorption capacity for synthetic wastewater was 114 mg/L as a consequence of an equilibrium being reached in which the rate of adsorption of molecules from the surface equals the rate of desorption of molecules from the surface.

Time (Mins)	Initial (Blank)	Initial (Copper)		Final (Blank)	Final (Copper)	Initial - Final	/Initial	ROR %
5	0.00	4.77*5	23.85	0.00	4.79	19.06	0.799	79.92
10	0.00	2.32*10	23.20	0.00	2.43	20.77	0.895	89.53
20	0.00	2.44*10	24.40	0.00	2.51	21.89	0.897	89.71
30	0.00	2.29*10	22.90	0.00	2.29	20.61	0.900	90.00
40	0.00	3.66*5	18.30	0.00	3.55	14.75	0.806	80.60

Table 4.1 Percentage removal effect by contact time with immonilised seaweed

Table 4.2 Percentage removal effects by contact time with raw seaweed

Time (Mins)	Initial (Blank)	Initial (Copper)		Final (Blank)	Final (Copper)	Initial - Final	/Initial	ROR %
5	0.00	1.33*10	13.30	0.00	1.49	11.81	0.888	88.80
10	0.00	1.50*10	15.00	0.00	1.64	13.36	0.891	89.07
20	0.00	1.65*10	16.50	0.00	1.87	14.63	0.887	88.67
30	0.00	1.96*10	19.60	0.00	2.25	17.35	0.885	88.67
40	0.00	1.82*10	18.20	0.00	2.12	16.08	0.884	88.35

According to the table, the removal time is consistent between 10 and 30 minutes. The removal has been adsorbed at a rate of more than 70% since it began. This is due to the kinetic adsorption of Cu by molecule algae as soon as it is introduced in synthetic wastewater. The algae's quick reaction continues to adsorb into the algae's pores. The longer it stays in synthetic wastewater, the less kinetic adsorption it has. This indicates that the ideal period is between 10 and 30 minutes. Because the algal molecules have been loaded with Cu, adsorption is inhibited. This is because a larger starting concentration offers more driving force, which increases the mass transfer of adsorbate to adsorbent. As a result, the starting concentration has a significant impact on adsorption capacity in any adsorbate-adsorbent combination (Fouzia Mashkoor et al., 2018).

According to the graph below, raw seaweed concentration is rapidly. Because of its inherent characteristics, the algae's molecule adsorbs Cu rapidly. Cu may be adsorbed more than 80% within as few as 5 minutes. The best period is 10 minutes, during which all of the Cu that adsorbs the scum loaded with algal pores is released. The adsorption process, however, is not as significant as immobilised, which is 89%. Unfortunately, after

10 minutes, the progress ceased and reduced dramatically. Because algae does not solidify like immobilised seaweed, raw seaweed cannot be reused in the adsorption process. Therefore, at the later stage of adsorption, the molecules have to traverse farther and deeper into the micropores of the adsorbent which encounters much larger resistance (Fouzia Mashkoor et al., 2018).



Figure 7 Percentage removal effects by contact time with immobilised seaweed and raw seaweed.

4.3 Effect of dosage (Raw Seaweed and Immobilised Seaweed)

The effect of dosage on biosorbent alteration is illustrated in tables 4.3 and 4.4 below. There are two types of adsorbents: raw seaweed and immobilised seaweed. The effects and responses of both to Cu are detailed in this section.

Dosage (gm)	Time (mins)	Initial (Blank)	Initial (Copper)		Final (Blank)	Final (Copper)	Initial - Final	/ Initial	ROR %
0.1	10	0.00	1.57*10	15.70	0.00	1.73	13.97	0.890	88.98
0.2	10	0.00	1.16*10	11.60	0.00	1.70	9.90	0.853	85.34
0.3	10	0.00	1.85*10	18.50	0.00	3.56	14.94	0.808	80.76
0.4	10	0.00	1.74*10	17.40	0.00	1.31	16.09	0.925	92.47
0.5	10	0.00	1.53*10	15.30	0.00	1.47	13.82	0.904	90.39

Table 4.3Effect dosage by using optimum raw seaweed at 10 minutes

According to the data in table 4.3, the best period is 10 minutes, which is derived from raw seaweed contact time data. In the process of treating Cu in synthetic wastewater, the total dose of 5 samples was measured. The dose of 0.4g produces the highest removal (92.47%). This demonstrates that raw seaweed is more effective in adsorbing in a short period of time. When it takes a long time, however, the proportion of copper metal ions released increases as the amount of biosorbent is raised until the saturation point is achieved. Furthermore, increasing the amount of biosorbent reduces the biosorbent's adsorption capability.

Dosage	Time	Initial	Initial		Final	Final	Initial	/	ROR
(gm)	(mins)	(Blank)	(Copper)		(Blank)	(Copper)	- Final	Initial	%
0.1	30	0.00	4.85*10	48.50	0.00	3.84	44.66	0.921	92.08
0.2	30	0.00	1.64*10	16.40	0.00	1.67	14.73	0.898	89.82
0.3	30	0.00	1.63*10	16.30	0.00	1.75	14.55	0.893	89.26
0.4	30	0.00	4.11*10	41.10	0.00	3.09	38.01	0.925	92.48
0.5	30	0.00	3.98*10	39.80	0.00	2.75	37.05	0.931	93.09

 Table 4.4
 Effects dosage by using optimum contact time immobilized seaweed at



Dosage(mg) Vs ROR%

Figure 8 Comparison of dosage between immobilised and raw seaweed.

According to Table 4.4, the dose of 0.5g is the most efficient for adsorbing copper metal ions as immobilised. The best time to utilise is 30 minutes. Cu removal was achieved at a rate of 93.03%. In reality, additional doses exhibit high adsorption, with a start of 92.08% at 0.1g. As seen in the chart above, roughly 88%-93% always seems to be successful. When compared to the effect of contact time, the removal rate is 88% and 89% between 5 and 40 minutes (Table 4.1). When it comes to raw seaweed, the removal decreased after the first 10 minutes. The analysis revealed that immobilised seaweed performs better in the biosorption of copper in wastewater treatment.

4.4 Effect of Concentration

The effect of initial copper concentration on biomass adsorption was investigated in 10ml of test solution produced using copper stock solution at varied starting copper concentrations (1.0, 2.0, 3.0, 4.0, and 5.0 mg/L). The equilibrium time, dose, and initial concentration were all held constant throughout the trial, unless otherwise noted. Upon biosorption, it was discovered that a homogenous outcome was produced with a final concentration of 0.37 and a removal of 72.38%. A spectrophotometer was used to obtain this result. The total time required to get this outcome is 40 minutes. The initial concentration percentage of biosorption reduced as the initial concentration increased, whereas metal ion adsorption capacity increased. We found that as the amount of biomass increased, the percentage of biosorption grew but metal ion adsorption capacity decreased (Rezaei, 2016). After making biosorption, It was found that a homogeneous result was obtained from the final concentration is 0.37 with a removal of 72.38%. This result was taken using a spectrophotometer device. The effective time taken to get this result is 40 minutes.

Time (mins)	Initial	Initial	Final Initial	Final Initial		
	Concentration	Concentration	Concentration	Concentration	ROR %	
	(Blank)	(Copper)	(Black)	(Copper)	/ •	
5	0.00	1.70	0.00	1.09	35.88	
10	0.00	1.56	0.00	0.66	57.69	
20	0.16	1.54	0.16	0.85	44.80	
30	0.17	1.75	0.17	0.76	56.57	
40	0.17	1.34	0.17	0.37	72.38	

Table 4.5Effects of initial concentration



Figure 9 Effect initial concentration

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

According to the study's purpose, a conclusion has been achieved in this chapter. The project's objectives have been met with success. This chapter wraps up the preceding chapter's findings and discussion. In addition, based on the findings, a few recommendations are made to enhance the efficiency of biosorption in removing Cu from synthetic wastewater.

5.2 Conclusion

To begin with, the procedure of immobilisation of Euchuema Cottonii SP has effectively generated beads. A meticulous approach has been established in order to produce a faultless immobilisation process. Seaweed beads were utilised in the biosorption experiment to collect the data stated in the second objective, namely the impact of contact duration, dose effect, and beginning concentration.

In conclusion, the study's goal was met with success. Copper may be removed from synthetic wastewater by Eucheuma Cottonii. The ideal contact duration, dose effect, and starting concentration of the biosorbent to work successfully are 30 minutes and 0.5g dosage. Furthermore, the influence of dose had an effect on the biosorbent's performance. With 0.4g of dose, the processed immobilised removed 93% of copper in synthetic wastewater compared to raw seaweed, which removed 92%. Raw seaweed cannot be reused in the adsorption process because algae does not harden like immobilised seaweed. As a result, at a later stage of adsorption, the molecules must go farther and deeper into the adsorbent's micropores, where they meet significantly greater resistance (Fouzia Mashkoor et., 2018).

There are other methods for treating wastewater and removing heavy metals from water, such as ion exchange, but they all require a lot of money and energy, making treatment of wastewater difficult. Nonetheless, the Euchuema Cottonii of red alage can be deployed to remediated wastewater for heavy metal adsorption. According to the data and description above, the red algae biosorbent adsorption method may be used to treat wastewater, giving additional benefits such as being the most cost-effective way. If the concentration and dose are significant, biosorbent treatment may be superior to standard wastewater treatment.

5.3 Recommendation

As demonstrated by the results and discussion above, Eucheuma Cottonii can cure industrial effluent. On the other hand, the red alage biosorbent's potential to remove heavy metals from wastewater can be enhanced. Based on the findings, a few recommendations may be made. The following are the recommendations:

- I. Research on other parameter such as effect of temperature
- II. Research on other heavy metal such as nickel, lead, zinc and cadmium.
- III. The wasted of heavy metal after watched the immobilized beads may can be detach using desorption process and can be reused for other purpose.
- IV. Research on use of other algae species such as brown algae or green algae.

REFERENCE

- Arumugam, N., Chelliapan, S., Kamyab, H., Thirugnana, S., Othman, N., & Nasri, N. (2018). Treatment of Wastewater Using Seaweed: A Review. *International Journal of Environmental Research and Public Health*, 15(12), 2851. https://doi.org/10.3390/ijerph15122851
- Altowayti, W. A. H., Othman, N., Al-Gheethi, A., Dzahir, N. H. binti M., Asharuddin, S. M., Alshalif, A. F., Nasser, I. M., Tajarudin, H. A., & AL-Towayti, F. A. H. (2021). Adsorption of Zn2+ from Synthetic Wastewater Using Dried Watermelon Rind (D-WMR): An Overview of Nonlinear and Linear Regression and Error Analysis. *Molecules*, 26(20), 6176. <u>https://doi.org/10.3390/molecules26206176</u>
- Akar, T., Kaynak, Z., Ulusoy, S., Yuvaci, D., Ozsari, G., & Akar, S. T. (2009). Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode. *Journal of Hazardous Materials*, 163(2-3), 1134–1141. <u>https://doi.org/10.1016/j.jhazmat.2008.07.084</u>
- Adams, J. M. M., Toop, T. A., Donnison, I. S., & Gallagher, J. A. (2011). Seasonal variation in Laminaria digitata and its impact on biochemical conversion routes to biofuels. *Bioresource Technology*, 102(21), 9976–9984. https://doi.org/10.1016/j.biortech.2011.08.032
- Al-Saydeh, S. A., El-Naas, M. H., & Zaidi, S. J. (2017). Copper removal from industrial wastewater: A comprehensive review. *Journal of Industrial and Engineering Chemistry*, 56, 35–44. <u>https://doi.org/10.1016/j.jiec.2017.07.026</u>
- Aydın, H., Bulut, Y., & Yerlikaya, Ç. (2008). Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management*, 87(1), 37–45. <u>https://doi.org/10.1016/j.jenvman.2007.01.005</u>
- Blanco, A., Sanz, B., LlamaM. J., & Serra, J. L. (1999). Biosorption of heavy metals to immobilised Phormidium laminosum biomass. *Journal of Biotechnology*, 69(2-3), 227–240. <u>https://doi.org/10.1016/s0168-1656(99)00046-2</u>_BIOSORPTION_OF
 COPPER_FROM_AQUEOUS_SOLUTION_BY_CHAETOMORPHA
 ANTENNINA_ALGAE_BIOMASS. *J. Environ. Health. Sci. Eng*, 8(4).
 <u>https://applications.emro.who.int/imemrf/Iran_J_Environ_Health_Sci_Eng/Iran_J_Environ_Health_Sci_Eng_2011_8_4_383_392.pdf</u>

- Charif Gakwisiri, Raut, N., Amal Al Saadi, & Abrar Al-Ajmi. (2012, July 4). A Critical Review of Removal of Zinc from Wastewater. ResearchGate; unknown. <u>https://www.researchgate.net/publication/263094272_A_Critical_Review_of_Re</u> <u>moval of Zinc from Wastewater</u>
- Chu, K. H., & Hashim, M. A. (2007). Copper biosorption on immobilized seaweed biomass: Column breakthrough characteristics. *Journal of Environmental Sciences*, 19(8), 928–932. <u>https://doi.org/10.1016/s1001-0742(07)60153-3</u>

Education. (2019). Greetings, How adsorption capacity of an adsorbent is related to its Removal Effeciency? ResearchGate; ResearchGate. https://www.researchgate.net/post/Greetings_How_adsorption_capacity_of_an_ad sorbent_is_related_to_its_Removal_Effeciency#:~:text=using%20the%20equatio n%2C-,adsorption%20capacity%20(%20mg%2Fgm)%20%3D%20%5B(%20Co%20%2 D%20Ce,for%20the%20calculation%20is%20correct

- Eka Putri, Lily Surayya. "THE ADSORPTION of HEAVY METALS from INDUSTRIAL WASTEWATER USING SARGASSUM CRASSIFOLIUM." International Journal of GEOMATE, vol. 17, no. 59, 1 July 2019, 10.21660/2019.59.4603. Accessed 22 June 2022. Hou, X., From, N., Angelidaki, I., Huijgen, W. J. J., & Bjerre, A.-B. (2017). Butanol fermentation of the brown seaweed Laminaria digitata by Clostridium beijerinckii DSM-6422. *Bioresource Technology*, 238, 16–21. https://doi.org/10.1016/j.biortech.2017.04.035
- Hou, X., From, N., Angelidaki, I., Huijgen, W. J. J., & Bjerre, A.-B. (2017). Butanol fermentation of the brown seaweed Laminaria digitata by Clostridium beijerinckii DSM-6422. *Bioresource Technology*, 238, 16–21. https://doi.org/10.1016/j.biortech.2017.04.035
- Karabulut, S., Karabakan, A., Denizli, A., & Yürüm, Y. (2000). Batch removal of copper(II) and zinc(II) from aqueous solutions with low-rank Turkish coals. *Separation and Purification Technology*, 18(3), 177–184. https://doi.org/10.1016/s1383-5866(99)00067-2
- Kadir, A., Daud, Z., Khaled, N., & Latiff, A. (2014, April 3). HEAVY METAL REMOVAL IN A COMBINED UASB-DFAF AND HUASB-DFAF SYSTEM REACTORS TREATING MUNICIPAL WASTEWATER. ResearchGate; unknown. <u>https://www.researchgate.net/publication/262300785_HEAVY_METAL_REMO</u>

VAL IN A COMBINED UASB-DFAF AND HUASB-

DFAF_SYSTEM_REACTORS_TREATING_MUNICIPAL_WASTEWATER Kratochvil, D. (1998). Advances in the biosorption of heavy metals. *Trends in Biotechnology*, *16*(7), 291–300. <u>https://doi.org/10.1016/s0167-7799(98)01218-9</u> Kratochvil, D. (1998). Advances in the biosorption of heavy metals. *Trends in Biotechnology*, *16*(7), 291–300. <u>https://doi.org/10.1016/s0167-7799(98)01218-9</u>

- Lakshmi, B. (2021, February 25). *Ionic liquids to remove toxic metal pollution*. ResearchGate; unknown. <u>https://www.researchgate.net/publication/349590601_Ionic_liquids_to_remove_t</u> <u>oxic_metal_pollution</u>
- Ortiz, C., Héctor Cid Silva, & Barros, D. (2017, February 22). *Metal Removal by Seaweed Biomass*. ResearchGate; unknown. <u>https://www.researchgate.net/publication/313963927_Metal_Removal_by_Seawe</u> <u>ed_Biomass</u>
- Rezaei, H. (2016). Biosorption of chromium by using Spirulina sp. Arabian Journal of Chemistry, 9(6), 846–853. <u>https://doi.org/10.1016/j.arabjc.2013.11.008</u>
- Sani, A. (2021, December 2). National Standard For Drinking Water Quality Malaysia. SaniChem New; SaniChem New. <u>https://www.sanichem.my/post/national-standard-for-drinking-water-quality-document#:~:text=Drinking%20Water%20Quality%20Standard,the%20health%20of%20the%20consumer.</u>
- Saeed, A. A. H., Harun, N. Y., Sufian, S., Siyal, A. A., Zulfiqar, M., Bilad, M. R., Vagananthan, A., Al-Fakih, A., Ghaleb, A. A. S., & Almahbashi, N. (2020). Eucheuma cottonii Seaweed-Based Biochar for Adsorption of Methylene Blue Dye. *Sustainability*, *12*(24), 10318. <u>https://doi.org/10.3390/su122410318</u>
- Tuwo, A., Yasir, I., Zainuddin, Syafiuddin, Tresnati, J., & Aprianto, R. (2021). Seaweed
 Eucheuma spinosum J. Agardh 1847, is it a bioaccumulator? *IOP Conference Series: Earth and Environmental Science*, 763(1), 012052.
 https://doi.org/10.1088/1755-1315/763/1/012052
- unknown. (2021, February 25). *Standard concentration of heavy metals in drinking water*. ResearchGate; ResearchGate.

https://www.researchgate.net/figure/Standard-concentration-of-heavy-metals-indrinking-water tbl1 349590601

- unknown. (2009, May 6). *Table 3 Trace elements of some drinking water standards*. ResearchGate; ResearchGate. <u>https://www.researchgate.net/figure/Trace-elements-of-some-drinking-water-standards_tbl2_240808063</u>
- Wei, N., Quarterman, J., & Jin, Y.-S. (2013). Marine macroalgae: an untapped resource for producing fuels and chemicals. *Trends in Biotechnology*, 31(2), 70–77. <u>https://doi.org/10.1016/j.tibtech.2012.10.009</u>

APPENDICES

APPENDIX A

<image>

















Preparation of synthetic wastewater



APPENDIX B

Process immobilization of seaweed (Euhuema Cottonii sp)





