BIOSORPTION OF COPPER, CHROMIUM AND ZINC FROM TEXTILE WASTEWATER USING EUCHEMA SPINOSUM (RED ALGA)

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ABSTRAK

Oleh sebab pertumbuhan pesat ekonomi di era ini, banyak industri telah dibina dalam menyediakan masyarakat dengan bekalan dan keperluan. Air menjadi perkara yang paling penting kerana setiap pembangunan menggunakan air sebagai sumber utama walaupun untuk industri tekstil. Walau bagaimanapun, banyak air sisa yang dihasilkan semasa pembuatan menyebabkan risiko kepada manusia dan benda hidup yang lain. Oleh kerana rawatan air memerlukan pengeluaran bahan kimia dalam menyelesaikan masalah air sisa, kajian ini telah menggunakan alga macro yang berkesan dan boleh didapati secara meluas dalam sistem akuatik sebagai biosorben dalam mengeluarkan logam berat dari air sisa sebenar. Kajian ini bertujuan untuk meminimumkan penggunaan kimia dalam rawatan air yang menggunakan alga makro semulajadi sebagai biosorben melalui kaedah mudah iaitu kaedah penjerapan. Makro alga adalah bahan biologi yang mempunyai potensi untuk mengumpul logam berat ke permukaan alga makro. Proses biosorpsi ini dapat mengurangkan jumlah logam berat di dalam air buangan tanpa sebarang bahaya kepada manusia dan alam sekitar. Macro alga adalah biomas yang tidak toksik yang menyediakan nutrien dan benefisiari lain kepada industri makanan. Dalam kajian ini, sampel alga merah dan sampel efluen tekstil memilih untuk mengkaji keberkesanan alga merah sebagai biosorben dalam mengeluarkan logam berat dari air sisa. Sampel alga makro merah yang dikenali sebagai Euchema Spinosum dikumpulkan dari Kunak, Sabah manakala sampel air sisa tekstil dikumpulkan dari Tenun Diraja Pahang yang terletak di Kuantan, Pahang. Satu dos optimum dan masa hubungan telah dikenal pasti semasa penyelidikan untuk menyiasat penjerapan maksimum tembaga, kromium dan zink. Dos yang dipilih yang digunakan dalam eksperimen ialah 0.25 g, 0.5 g, 0.75 g, 1.0 g, 1.25 g dan 1.5 g. Selepas itu, masa hubungan terpilih untuk ujian percubaan adalah 1 jam, 8 jam, 16 jam, 24 jam, 32 jam, 40 jam, 48 jam, 52 jam dan 58 jam. Peralatan makmal yang digunakan untuk mengukur kandungan logam berat adalah Spektrofotometer UV-VIS. Faktor pencairan 50 ml air suling digunakan untuk mencairkan sampel air buangan tekstil kerana ketebalan warna berasal dari pewarna yang digunakan dalam pembuatan tekstil. Spektrofotometer UV-VIS tidak dapat mengukur nilai julat berat logam berat jika kandungan logam berat terlalu tinggi. Pengenceran sampel diperlukan dalam eksperimen ini untuk menampung peralatan makmal. Seterusnya, penghapusan peratusan setiap logam berat telah dikira. Keputusan dan perbincangan telah diperiksa dan direkodkan. Dos yang optimum untuk ketiga-tiga logam berat ini adalah 20 g / L. Masa hubungan optimum yang dijumpai untuk penyingkiran Tembaga ialah 24 jam manakala masa hubungan optimum untuk Chromium dan Zinc adalah 40 jam. Kapasiti penjerapan tertinggi Chromium, Zink dan Tembaga adalah 92.67%, 90% dan 76% masing-masing. Selain itu, kandungan awal Copper menunjukkan nilai tertinggi diikuti oleh Chromium dan Zinc. Selepas itu, Tembaga adalah kapasiti pengambilan logam yang paling berat untuk biosorpsi berbanding dengan Chromium dan Zink. Kesimpulannya, Euchema Spinosum didapati sangat berkesan dalam menghilangkan Chromium dan Zink tetapi kurang berkesan dalam mengeluarkan Tembaga dari air sisa tekstil.

ABSTRACT

Due to the rapid growth of economy in this era many industries were build up in providing the community with supply and need. Water became the most crucial thing since every development is using water as the main source even for the textile industry. However, the abundant of waste water produce during the manufacturing has cause the risk toward human and other living things. As water treatment need the production of chemical in solving waste water issue, this research has come out to use the cost effective and widely available macro alga in aquatic system as biosorbent in removing heavy metals from the real waste water. This research was intended to minimize the use of chemical in water treatment which using the natural macro alga as biosorbent through simple method that is adsorption method. Macro alga is a biological material that has a potential to accumulate the heavy metals onto the surface of the macro alga. This biosorption process can reduce the amount of heavy metals inside the waste water without any harm to human and environment. Macro alga is a non-toxic biomass that provide nutrients and other beneficiaries to the food industry. In this research, a sample of red alga and a sample of textile effluents was chose to study the effectiveness of red alga as biosorbent in removing heavy metals from waste water. The sample of red macro alga known as Euchema Spinosum was collected from Kunak, Sabah while the sample of textile waste water was collected from Tenun Diraja Pahang located at Kuantan, Pahang. An optimum dosage and contact time were identified during the research to investigate the maximum adsorption of copper, chromium and zinc. The selected dosages used in the experiment are 0.25 g, 0.5 g, 0.75 g, 1.0 g, 1.25 g and 1.5 g. After that, the selected contact times for the experiment chose are 1 h, 8 h, 16 h, 24 h, 32 h, 40 h, 48 h, 52 h and 58 h. The laboratory equipment used to measure the heavy metals content is UV-VIS Spectrophotometer. A dilution factor of 50 ml of distilled water is used to dilute the sample of textile waste water due to the thickness of color came from dye used in manufacturing of the textiles. The UV-VIS Spectrophotometer cannot measure over range value of heavy metals if the content of heavy metals is too high. Dilution of sample is necessary in this experiment to accommodate the laboratory equipment. Next, the percentage removal of every heavy metals were calculated. The results and discussions was examined and recorded. The optimum dosage for these three heavy metals is 20 g/L. The optimum contact time found for Copper removal is 24 hours while the optimum contact time for Chromium and Zinc is 40 hours. The highest adsorption capacity of Chromium, Zinc and Copper is 92.67%, 90% and 76% each. Besides, the initial content of Copper shows the highest value followed by Chromium and Zinc. After that, Copper was the least heavy metal uptake capacity for the biosorption compare to Chromium and Zinc. In conclusion, Euchema Spinosum is found very effective in removing Chromium and Zinc but less effective in removing Copper from the textile waste water.

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LIST OF SYMBOLS

Cu	Copper
Cr	Chromium
Zn	Zinc
Pb	Lead
$Cu(NO_3).3H_2O$	Copper Nitrate
Cd	Cadmium
COD	Chemical Oxygen Demand
MCL	Maximum Contaminant Levels
Euchema Sp.	Euchema Spinosum
NaOH	Sodium Hydroxide
UV-VIS	Ultraviolet Visible Spectrophotometry
rpm	Revolution per minute
mg	Milligram
g	Gram
L	Litre
FTIR	Fourier Transform Infrared Spectroscopy
mm	Millimetres
HNO3	Nitric Acid
ml	Millilitres
h	Hour

LIST OF ABBREVIATIONS

Cu	Copper
Cr	Chromium
Zn	Zinc
Pb	Lead
$Cu(NO_3).3H_2O$	Copper Nitrate
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rpm	Revolution per minute
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h	Hour

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water treatment is significant in daily life. Water is the main source to human but untreated water is not able to keep human are protected from health diseases. Water treatment is the process to treat water or improve the quality of water to make it acceptable for specific end use. Water treatment involved technologies, science, engineering, business and art. Nowadays, there are variety of industries that used water treatment to avoid the existence of non-useable waste water. There are several ways to treat or disinfect the water. In our water treatment system, chlorination is the most widely used method to disinfect the water. It is a most reactive elements and can be found dissolved in sea water or salty lake. The chlorine is produce through chemical oxidation. Since it is very reactive and corrosive gas, chlorine need a proper precaution in the production.

This research is using macro algae as bio sorbent in the real waste water. The main purpose of the use of macro algae is to produce a clean and healthy water same as the chlorine function. Macro algae by definition are unicellular algal species that can survive individually or in chains or clusters. Macro alga exist in both suspended forms (that free-float in a water body) and attached forms (that adhere to a submerged surface) and are one of the most important groups of organisms on the planet. Macro algae cultures offer a modern solution of wastewater tertiary treatment together with the production of potentially valuable biomass, which can be used for several purposes (biogas and biofuel production, composting, as animal feed or in aquaculture and production of fine chemicals).

The macro algae use the nutrients (inorganic nitrogen and phosphorus) in order to grow and have the capacity to remove heavy metals and some toxic organic compounds (dyes and antibiotics) and to reduce, also, the chemical and biochemical oxygen demand. In conclusion, water treatment has been studied over decades and there are many ways in water treatment. This research is done to produce a clean and healthy water that are acceptable for specific uses such as drinking and cook. This bio sorbent method is capable to prove an effective alternative to the waste water treatment system. Bio sorbent by chance is the method of absorbing any contaminant such as heavy metals in the real waste water.

1.2 Problem Statement

Nowadays, there are many development of industry from various types. This development gives a rapid growth of economy, technologies, food and beverages, and textiles. However, there must be risks to everything that give profit and beneficiaries to the human kind. Water are the most common sources that having pollutant issue especially industries that used water as main sources. It is not a crime to produce wastewater during manufacturing but how the waste water treated is the main issue. There are several industries that do not treat the wastewater well which cause the water pollution. The issue that arise when the water is not treated properly is what will happen to human health and other living things.

The untreated water may contain any numbers of contaminants such as bacteria, viruses, parasites, heavy metals, pesticides, fertilizers, and human and animal waste. This contaminated water can attack the human health and cause to death. To prevent any negative issues water is significant to treatment. Due to some circumstances, such as the cost of water treatment that quite crucial become the main purpose to abandon the wastewater treatment. This study was undergoing to used other option to treat water such as using macro algae as bio sorbent. Since algae are easy to acquire, this biological material can help to reduce the cost of wastewater treatment. In addition, the natural source of macro alga is a better choice for the treatment instead of producing more chemical reagent to solve the water issues.

1.3 Objectives

i. To determine the characteristic of the real waste water.

ii. To study the effectiveness of bio sorbent for the removal of heavy metals.

1.4 Scope of Research

This research is proposing to do a water treatment of real waste water using Euchema Spinosum which is a red macro alga. The real waste water is collect from a textile industry located at Tenun Diraja Pahang, Kuantan Pahang. This study used to investigate the level of heavy metals content such as Copper, Zinc and Chromium in the real waste water. The samples are collected and tested in laboratory before use to the next step of treatment. The parameter to be cover in this study are the optimum dosage, optimum contact time and Copper, Zinc and Chromium content in the samples of real waste water.

In addition, this research is to study the effectiveness of macro alga as bio sorbent in treating the real waste water. The most effective macro alga from screening process is choose to be produce as bio sorbent. Macro alga are reacted as bio sorbent to the real wastewater. Instead of using macro alga to produce activated carbon for water treatment, this study is conduct to use macro algae as natural bio sorbent to the real wastewater. The macro alga is tested to absorb heavy metal such as Copper, Zinc and Chromium in the real wastewater. The macro algae will be process into small particles and mix to the samples. The content of heavy metals in the samples will be observed and analyses to prove the effectiveness of bio sorbent in reducing the heavy metals content in the samples.

1.5 Significance of Research

This research is done to prove the effectiveness of macro alga as bio sorbent in water treatment. Algae can easily be found in the aquatic system and there is variety type of algae. This research can maximize the use of algae and gain the benefits of algae toward the waste water treatment system. Macro alga also can be other alternative of water treatment of real waste water.

This research also can replace the chlorine production for water treatment. As chlorine is hard to produce and acquire because chlorine dissolved in sea water or salty lake, this research can produce a natural bio sorbent to absorb heavy metals and treat the real waste water. This research can save the cost and time for water treatment instead of producing chemical such as activated carbon that commonly used in water treatment. Besides that, this research is using simple method of adsorption.

The process of turning macro algae into bio sorbent is very cost effective and beneficial. Furthermore, macro alga is easy to find and less dangerous compare to other chemical used in water treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Textile industry is one of the oldest and largest industrial sectors in light industry, produces fabrics, textiles, knitted garments, and other items of various types of plants, animals, and chemical fibers. The textile industry occupies an important place in the production of social products and personal needs satisfaction. The industry includes the following parts: early processing of raw materials for textile, full and felting, and production of cotton fabrics, linen, fur fabrics, silk fabrics, non-woven fabrics, jute and jute, nets, clothing accessories and textile impressions, and clothing knitting. Textile products are used in the manufacture of clothing and footwear and in other industrial sectors, such as furniture and machine building industries.

In East Coast peninsular Malaysia such as Kelantan and Terengganu there are many small based family businesses for Batik production. The process of Batik product consumes a lot of water from the beginning till the last process of rinsing the textile in the production. R Ananthashankar (2013) stated that 200 L of water used to produce 1 kg of textiles. After that, the textile waste water produce contains high amount of dyes, and chemicals containing trace metals such as Chromium (Cr), Copper (Cu), and Zinc (Zn). Since the production of textiles using water as the main source the water produced by the production is quite high. Moreover, the water discharged without a proper treatment to the river or drainage can cause water pollution and harm both human and aquatic organisms as well (R Ananthashankar, 2013).

A research state that textile waste water contains chemicals, total suspended solids, high pH and COD value and heavy metals. This is the main objective of the research project which is using textile effluents as the indicator of heavy metals removal using macro alga. Textile wastewater can harm human health and aquatic organisms which can lead to chronical diseases. In addition, there also states that most of Batik industries does not have any treatment units because of the high cost of installation. This is the reason of abandoning the water treatment system and produce a water pollution (Birgani et al., 2016).

One of the heavy metals inside the textile waste water is Cadmium (Cd) which has been classified as a human carcinogen and teratogen impacting lungs, liver and kidney because among heavy metals Cadmium (Cd) is extremely toxic and tend to accumulate inside the waste water (Pyrzynska, 2019). The use of conventional methods in removing heavy metals inside the waste water can be very expensive because of the large volumes of waste water dispensed.

This research is to remove the heavy metals from textile wastewater to ensure human health and other living things and environment are protected since heavy metals can cause diseases and death. Based on previous research, textile effluents have been proven contain many contaminants, dye, heavy metals and other unspecified materials which can disturb the ecosystems especially in the stream and river since mostly discharge of textile effluent is end at the natural water flowing like river. The heavy metals characteristic choose for this research is Copper, Chromium and Zinc.

Table 2.1: The MCL Standards for Copper, Chromium and Zinc (Gunatilake, 2015).

Heavy metal	Toxicities	MCL(mg/L)
Copper	Liver damage, Wilson disease, insomnia	0.25
Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05

Based on Table 2.1, these three heavy metals can cause several health problems to human kind. Table 2.1 stated that Copper can cause to liver damage, Wilson disease and insomnia. After that, Zinc element can cause to depression, lethargy, neurological signs and nervous system. Lastly, the Chromium element can cause the headache, diarrhea, nausea, vomiting and carcinogen (Gunatilake, 2015).

2.2 Method in Removing Heavy Metals from Textile Wastewater

There are various methods in removing heavy metals from real wastewater such as Physico-chemical methods, Chemical Precipitation, Coagulation and Flocculation, Electrochemical Treatments, Ion Exchange, Membrane Filtration, Electrodialysis and Biological Methods. However, conventional technologies cannot be applied effectively toward textile effluents because of high amount of silica, wax and heavy metals (Birgani et al., 2016).

Therefore, several methods in water treatment has been evaluated to study the advantages and disadvantages of each method.

2.2.1 Adsorption

Adsorption is an in all respects altogether save cost, helpful and simple operation method. This method demonstrates high metal evacuation proficiency and is connected as a speedy method for a wide range of wastewater medications. Adsorption is turning into a mainstream method, in light of the fact that in this procedure the adsorbent can be reused and metal recuperation is conceivable (M.A., 2011).

2.2.1.1 Biosorption

The biosorption process has received special attention in the last ten years as a low cost environmental-friendly technology that uses raw biomass for the sequestration of heavy metals present in water. This method provides an effective means of purifying metal-containing wastewaters, besides simplicity of design and operation, fast adsorption and desorption kinetics, availability of biosorbents worldwide and the possibility of biomaterial reuse (Hackbarth et al., 2015). Besides that, adsorption is a simple method that easy to handling compare to other physical methods. Biosorption is the process of dissolved solids such as atoms, ions or molecules from liquid that attach to the adsorbent (Bobade & Eshtiagi, 2015). This process can remove the heavy metals content from liquid such as industrial waste water effectively based on the efficiency of adsorbent. For this study, a red macro alga known as Euchema Spinosum is used for the adsorption process to remove certain heavy metals characteristics.

Adsorption method is the most recognized and popular method because of the cost effectiveness, easy recovery, simplicity of operation and high efficiency. This method also stated that the effectiveness of adsorption has significant impacts from the process parameters such as solution pH, temperature, contact time and dosage of adsorbent. After that, the used of adsorption method is due to the widely used of activated carbon and ion-exchange resins remain relatively expensive materials (Pyrzynska, 2019).

Moreover, the uptake capacity is depending on the effectiveness of the adsorbent and the real wastewater. The higher number of binding sites, better ion-exchange ability and formation of new functional groups are affected by the chemically modified biosorbent which can show better adsorption capacities than unmodified forms. However, this research has intended to minimize the use of chemical in water treatment. Therefore, a natural unmodified macro alga is used for the biosorption of heavy metals.

From a research that conducted on the same study about the potential of seaweed in removing heavy metals, the research has found that biosorption is the promising method and very cost effective compare to other conventional methods proposed (Html, 2015).

According to the literature review, the bio adsorbents represent a promising green technology and potentially they can be applied at full-scale wastewater treatment. Bio adsorbents are relatively cheap in terms of cost, available in large amounts and easily accessible as most of the bio adsorbents are wastes from agricultural production or by-products from industry (Pyrzynska, 2019).

Lastly, a research also found agreed with the capabilities and the advantages of using biosorption method. Adsorption technology in removing heavy metals from waste water is investigate due to the cost effective and simple handling method (Cho et al., 2013). Besides, the factor influencing the adsorption capacity of heavy metals toward macro alga are algal dosage, pH, contact time, initial metals ion concentration and temperature.

Furthermore, different factors lead to the varies in adsorption results because of the biological process that are differs from each factors (Rangabhashiyam & Balasubramanian, 2018).

2.2.1.2 Activated carbon (AC)

At present, activated carbon (AC) is the for the most part utilized adsorbent around the world. AC is not just productive in evacuation of overwhelming metals, yet in addition for different contaminants present in water or wastewater. These can be utilized in both cluster and segment mode activity because of the high surface territory, microporous structure and porosity properties. In the planning of initiated carbon, numerous agrarian waste biomasses are utilized, for example, bagasse (Onal Y., Akmil-Bas C., Sarıcı-Ozdemir C., Erdogan S., 2007), coconut shell, tea squander, nut body (Oliveira F.D., Paula J., Freitas O.M., Figueiredo S.A., 2009), apple squander (Maranon E., Sastre H., 1991), sawdust (Ajmal M., Khan A.H., Ahmad S., Ahmad A., 1998), rice husk (Naiya T.K., Bhattacharya A.K., Mandal S., Das S.K., 2009), banana essence (Low K.S., Lee C.K., Leo A.C., 1995), tree rind (Gundogdu A., Ozdes D., Duran C., Bulut V.N., Soylak M., 2009) and actuated cotton strands (Kang K.C., Kim S.S., Choi J.W., Kwon S.H., 2008).

The adsorption limit of the lignocellulosic material can be expanded by physical and concoction change of adsorbents. This biological material is exorbitant in nature at the mechanical dimension. In this way, specialists are concentrating on the utilization of ease adsorbents for the treatment task.

2.2.1.3 Low-Cost Adsorbents

With the accessibility and affordability of different waste materials, modern side-effects, agrarian squanders and other common waste materials, the low-cost procedure has turned out to be well known these days. The emphasis on choosing minimal effort adsorbent is a direct result of the mind-boggling expense of financially enacted carbon.

Researchers are getting ready mechanical results as low cost adsorbents, for example, pulp and paper waste (Stniannopkao S., Sreesai S., 2009), fertilizer waste (Gupta VK., Srivastava SK., Mohan D., Sharma S., 1997), steel converter slag (Mendez A., Barriya S., Fidalgo J.M., Gasco G., 2009), steel making slag (Kim D.H., Shin M.C., Choi H.D., C.l. Seo, Baek K., 2008), sugarcane bagasse (Soliman E.M., Ahmad S.A., Fadl A.A., 2011), bagasse fly fiery remains (Gupta V.K., Rastogi A., Nayak A., 2010)that are normal.

2.2.2 Chemical Precipitation

Chemical precipitation is a straightforward and exceptionally regular procedure to evacuate substantial metals because of the straightforwardness in task and economical nature (Ku Y., Jung I.L., 2001). Chemical precipitation method is utilized for the treatment of metal-containing wastewater by framing an insoluble hasten through the expansion of synthetic compounds (Karthikeyan K.G., Elliott H.A., Cannon F.S., 1996). Some other substance precipitation methods are additionally utilized, for example, hydroxide precipitation, sulfide precipitation and substantial metal chelating precipitation.

As precipitant operators, lime and limestone are most usually utilized in concoction precipitation due to being a straightforward procedure, accommodation and adequacy in treating inorganic effluents at higher concentrations (Mirbagherp S.A., Hosseini S.N. , 2004).

Regardless of the preferences, there must be some disadvantages, for example, requiring an abundance measure of synthetics in the treatment. Chemical precipitation has some different disadvantages, for example, generation of exorbitant slop and the issue of ooze transfer into nature.

2.2.3 Ion Exchange

The particle trade strategy is fundamentally founded on the capability to trade cations with metals in the wastewater (Pagano M., Petruzzelli D., Tiravanti D., Passino R., 2000). There are various sorts of materials utilized, which might be regular (alumina, carbon, silicates) or engineered (zeolites and saps). Among them, zeolites are most liberally utilized in the particle trade process (Fernandez Y., Maranon E., Costrillon L., Vazquez I., 2005). The particle trade process happens by the two cations and anions trade in watery medium by particle trade. The downside of this strategy is that this method is very touchy to the pH of the arrangement, and the particle trade is non-particular in task.

2.2.4 Membrane process

The membrane filtration method utilized various sorts of films and expulsion of different overwhelming metals in fluid arrangement. This procedure expels oils, suspended solids, overwhelming metals, and natural and inorganic materials (Fu F., Wang Q., 2011). Various types of this procedure are utilized dependent on the span of the particles, for example, Ultrafiltration (UF), Nanofiltration (NF), Reverse Osmosis (OS) and Electrodialysis (ED), contingent upon the kind of wastewater.

2.2.4.1 Ultrafiltration

In this strategy, disintegrated particles, heavy metal particles and different contaminants are sifted utilizing a membrane, according to the atomic size. Various sorts of membranes permit just the section of low atomic solutes, and the staying ones, for example, bigger particles and overwhelming metals, do not go through and are isolated out. Ultrafiltration has additionally been isolated into subcategories, for example, micellar improved ultrafiltration said by Landaburu-Aguirre et al. (2012), complexation–ultrafiltration and chelating improved ultrafiltration.

2.2.4.2 Nanofiltration

Nanofiltration is layer partition system that is utilized in overwhelming metal division from fluid arrangements (Al-Rashdi B., Samerfield C., Hilal N., 2011). This method is connected to the expulsion of various overwhelming metals, for example, copper, arsenic, nickel and chromium. Nanofiltration is dependable, similarly simple to work and has low vitality utilization than others (Erikson, 1988).

2.2.4.3 Reverse Osmosis

Reverse osmosis (RO) system is utilized essentially for the partition and fractionation of natural and inorganic sub positions and overwhelming metals in fluid and non-aqueous arrangements. The RO strategy can be utilized to treat various sorts of modern effluents, viz., synthetic, material, petro-substance, electrochemical, sustenance, paper and tannery indus attempts (Mohsen-Nia M., Montazeri P., Modaress H., 2007). In mix with the pilot film reactor, this method is proficient in metal evacuation at abnormal state. Reverse osmosis has a few impediments additionally and expends high power for the siphoning weight and also the reclamation of the film.

2.2.4.4 Electro Dialysis

Electro dialysis (ED) is a division procedure where dis-unraveled particles are expelled starting with one arrangement then onto the next arrangement over a charged film under an electric field (Sadrzadeh M., Mohammadi T., Ivakpour J., Kasiri N., 2008). This method is utilized in the treatment of wastewater just as in the creation of drinking water from seawater, partition and recuperation of substantial metals particles and in salt generation (Sadrzadeha M., Mohammadi T., Ivakpour J., Kasiri N. , 2009). This method is connected for overwhelming metal expulsion, for example, chromium, copper and ferrous, by different analysts.

2.2.5 Flotation

Flotation has been broadly connected for the expulsion of toxic metal particles from wastewater (Polat H., Erdogan D., 2007). Different methods of flotation are particle flotation, dissolved air flotation (DAF) and precipitation flotation. DAF is a more regularly utilized procedure than some other flotation methods in the expulsion of heavy metals from watery solutions (Zabel T., 1984).

2.2.6 Chemical coagulation

Coagulation method is utilized to plan colloids. Some coagulates are utilized, for example, aluminum, ferrous sulfate and ferric chloride that kill debasements present in wastewater or water. Coagulation is a significant technique appeared by different researchers (El Samrani A.G., Lartiges B.S., Villie´ras F., 2008). Ferric chloride arrangement and polyaluminium chloride (PAC) coagulants are utilized in heavy metal expulsion.

2.2.7 Electrochemical method

Electrochemical method includes the redox responses for metal expulsion affected by outer direct current in the electrolyte arrangement. The coagulation procedure destabilizes colloidal particles by including a coagulant and results in the sedimentation procedure (N.K., 2004). For increment in the rate of coagulation, the flocculation procedure happens which upgrades the difference in insecure particles into massive floccules (Semerjian L., Ayoub G.M. , 2003).

2.3 Macro alga as Biosorbent

In this research, macro alga is used for the biosorption process as the biological material that present in unmodified form in order to minimize the chemical consumption in wastewater treatment. Based on the Figure 2.1, the macro alga chose for the removal of Copper, Chromium and Zinc is Euchema Spinosum which is a red alga group that widely available in saltwater especially at Sabah and Sarawak. Macro alga can react as biosorbent to remove heavy metals from wastewater through biosorption process that adsorbing the heavy metals ion to the surface.

Figure 2.1: Euchema Spinosum (red alga)

Macro alga is widely available in marine environment. Macro alga that known as seaweed has been used as a main food in Korea for a long time ago such as brown algae, tangles, laver, and sea lettuce. This type of alga also reported as an application in producing bio-oil. For brown seaweed, the alkali earth metals were quite high meanwhile the content of toxic metals such as Pb and Cu were zero. The major source of the heavy metals adsorption toward the seaweed was the exchangeable cation capacity of seaweed char (Cho et al., 2013).

Macro alga gives many positives feedbacks such as higher efficiency, free from nutrient requirements, economical, easy biomass collection, wide availability of biomass both in fresh and saltwater, comparatively higher surface area and higher binding affinity towards the heavy metals (Rangabhashiyam & Balasubramanian, 2018). There are also stated that a dead biomass alga can improves the macro alga performances because this type of alga did not affect by the heavy metals toxicity.

Many styles of biomass in non-living kind have been studied for a serious metal uptake capacities and suitability to be used as bases for biosorbent development. These embody bacteria biomass, fungi, bark, water algae, marine alga. Among these, marine macro-algae (seaweeds) square measure the foremost promising sort of biosorbents studied (Lee & Park, 2012).

Alga has more than hundreds species in the world. Alga can be categorized into three different groups based on the color that is red, green and brown alga. Figure 2.2, 2.3 and 2.4 shows the three colour of green, red and brown alga respectively. The biosorption of heavy metals such as Copper, Cadmium, Lead and Zinc are caused by the different mechanism such as ion exchange, complex formation, and electrostatic interaction, being ion exchange the most important (Ortiz-Calderon, Silva, & Vásquez, 2017). The mechanism that occur between alga and the metals ion has a maximum adsorption process which the removal of heavy metals by this alga become very effective. Algae have proved to be natural economic cation exchanger, abundantly available with high surface area to volume ratio among the biosorbent materials (Pyrzynska, 2019).

Figure 2.2: Example of green alga

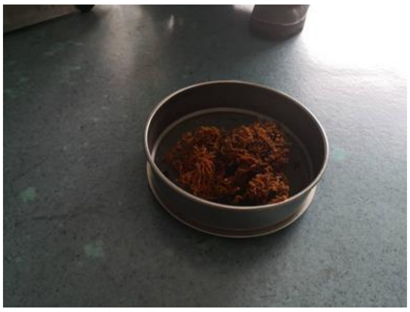

Figure 2.3: Example of red alga

Figure 2.4: Example of brown alga

In this research, a red macro alga known as Euchema Spinosum is used as biosorbent for adsorption method to remove Copper, Chromium and Zinc. However, this research only focus on the effectiveness of Euchema Spinosum even though there are more types of macro alga has been used for this adsorption process. After that, the chemical and physical properties of Euchema Spinosum play the important role in exchangeable cation between alga and the sample of textile wastewater. Euchema Spinosum has a cell wall component which consist of 40 to 70 percent of seaweed salt free dry weight this component contain a small amount of cellulose and minor amount of unspecified materials (EVANS, 2013).

A red alga is a least focused group among other species which constitute different binding sites like hydroxyl, carboxyl, amino, and sulfhydryl that responsible for adsorption of the heavy metals (Html, 2015).

2.4 Modified and Unmodified Macro Alga

In wastewater treatment, biosorption method offer a cost effective and simple handling manner by using biological material such as macro alga whether in modified or unmodified form. Macro alga is a species that exist in the water system either in fresh water or saltwater. This biological material can be modified or pre-treated for the wastewater treatment. There are various ways in modifying macro alga for better adsorption process of heavy metals especially. When modification of macro alga involved, chemical consumption become the solution.

Macro alga also used in different type of condition. As an activated carbon or char macro alga can remove heavy metals from aqueous stream and air. The char obtained from pyrolysis of macro alga to remove copper from a water system was examined (Cho et al., 2013). Herein, the modified algal biomass is prepared by treatment algae with solution of 0.1 N NaOH to increase the functional groups that play an important role in biosorption process (Ali, Abd El-Aty, Badawy, & Ali, 2018). Ali et. al also conducted an experiment using the chemically modified alga toward adsorption of adsorbent.

Other than that, a green type of macro also used as biosorbent. This type of alga was used as phenol removal adsorbent as an effective biosorbent. The air-dried macro algae were pre-treated with 0.1 N sulfuric acid before contacting the dried macro alga with the synthetic phenol containing solution. The pretreatment aids in stabilizing the algae and retain the reactive sites intact. The present study showed that the chemically modified green macro alga C. scalpelliformis can be used effectively as an adsorbent for the removal of phenol from aqueous solutions (Aravindhan, Rao, & Nair, 2009). Somehow a macro alga also useful in modification into activated carbon which is a very effective conventional method that widely used for water treatment system. Production of commercial activated carbons is still an expensive process.

Eventhough, modified macro alga can effectively remove the heavy metals the cost of pretreatment of macro alga is quite expensive and need proper treatment. The chemical consumption become necessary for water treatment involving modified macro alga. This research intended to minimize the use of chemical in wastewater treatment system and to provide a very cost effective wastewater treatment for the society. Most of Batik industries do not have water treatment unit because of the high cost of installation. Moreover, that is the major problem of Batik industries that caused the Batik industries to discharge the non-treated wastewater (Birgani et al., 2016).

In this research, unmodified macro alga is used as biosorbent to remove Copper, Chromium and Zinc. This unmodified macro alga is collected as raw material from Kunak, Sabah in dead biomass form. The process of preparing macro alga as biosorbent do not use any chemical consumption or pretreatment. The macro alga is natural and organic which is very safe to human health and environment. Macro alga also does not contain any toxic metals and very eco-friendly.

2.5 Experimental

A research conducted by other researchers had done an experimental using red alga as biosorbent to remove phosphate from water. The procedure of preparing the red alga was done naturally using dead biomass of red alga into powdery form. The alga was washed twice with running water and five times with deionized water. The washed biomass was oven-dried at 60 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.10–0.25 mm) and stored in polypropylene bottles until use (Rathod, Mody, & Basha, 2014).

When the biosorbent is prepared, the adsorption process is ready to take place. The three structural characteristics is used for the biosorption process that is centrifuge, orbital shaker and UV-VIS Spectrophotometry. The biosorbent and the sample of wastewater are mix together. Then, the solution is shake using the orbital shaker at 130rpm/hour. After that, the solution is centrifuge at 4000rpm/60second. Lastly, the solution is analyzed using UV-VIS Spectrophotometer to identify the percentage removal of heavy metals.

2.6 Parameters for Biosorption of Heavy metals

In this research, the study was intended to removes heavy metals from textile waste water using macro alga as biosorbent. The biosorption process will be analyze in terms of biosorbent dosage and contact time. From previous research papers, there were many experiments were done in removing heavy metals using either same or different macro algae. The biosorption method were analyze in terms of varying parameters.

According to (Sabur, Khan, & Safiullah, 2012), after Ph of 6.0 above the absorption of phenol using green macro alga was decreasing and that phenomena might because of the higher electrostatic repulsion between the biosorbent and the phenol solution. In range of 1 to 10 Ph of the solution the result of uptake capacity of copper, cadmium and chromium might be differing according to Ph level of the textile waste water because of the positive and negative charge produce by the mechanism between the biosorbent and the heavy metals content.

Besides that, (Sabur et al., 2012), also analyze the biosorption process in term of initial concentration. Sabur et al. (2012) said that the equilibrium uptake capacity of phenol increased from 1.72 to 20.10 mg per gram of biosorbent when the initial concentration of the solution was 10 to 150 mg/L at 30 ^{o}C.

The dosage also influenced the biosorption process because the effectiveness of the process in removing heavy metals quite differs according to the dosage used of the biosorbent. The equilibrium uptake capacity of phenol decreased from 32.62 to 9.40 kg/g when the dosage of biosorbent was increased from 2 to 10 g/L. This statement was explained that the available phenol was insufficient to cover all the exchangeable sites when higher dosage was put into the phenol solution that resulting in low phenol uptake (Sabur et al., 2012).

According to the research varying parameters has an effect on the adsorption of heavy metals such as Copper, Lead, Ferum and Zinc. The parameters studied in this research are effect of temperature, effect of contact time, effect of initial concentration, kinetic modelling and biosorption isotherms. Besides that, the maximum uptake capacity of these heavy metals was reach up to 83.88, 85.89, 21.27, and 54.13%, respectively, within 90 min. Based on FTIR study revealed that the biomass has a cell wall matrix presence of carboxylic, sulfonic acid, and sulfonate groups which attribute to the adsorption of metals ion (Html, 2015).

2.7 Euchema Spinosum (Red Alga)

For this research, Euchema Spinosum is choose for the biosorption of Copper, Chromium and Zinc. This type of alga is used as biological material through biosorption process to adsorb the heavy metals onto the surface. Based on Figure 2.5, this macro alga is collected from Kunak, Sabah which is widely available in marine ecosystem and easy to acquire. This macro alga also very cost efficient and do not have any toxic metals that could harm human and environment.

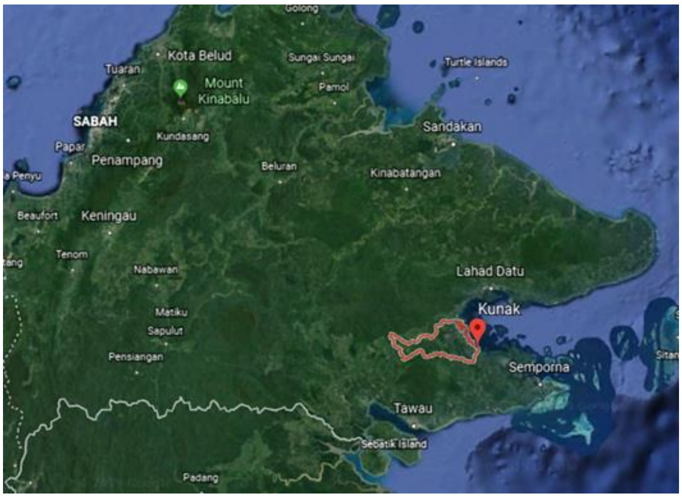

Figure 2.5: The location of red seaweed at Kunak, Sabah

Source: https://earth.google.com

Euchema Sp. formerly known as Eucheuma denticulatum and Eucheuma cottonii respectively. This macro alga not only available in Malaysia but widely available in the world especially in the Philippines, tropical Asia, East Africa, and the Western Pacific region. After that, Indonesia and the Philippines are the second and third largest seaweed producers in the world and these seaweed has a largest proportions cultivated there. Eucheuma Sp. are mainly cultivated as a biomass supply for the carrageenan that macro alga possess (Materials, 2019).

Euchema Spinosum is most usually discovered developing on coarse sand to rough substrates in the intertidal to shallow subtidal zone where this type of alga is presented to solid flows and wave activity. This green growth has the novel capacity of branches to shape optional holdfasts to different plants just as the substrate, framing thick floor covering like beds of ocean growth where singular plants are difficult to recognize. Euchema Sp. is local to the Indian sea, yet since being found as a wellspring of particle carrageenan, Euchema Spinosum has been spread somewhere else through cultivation. This type of alga tends to be found in the accompanying nations that is Philippines, Indonesia, Vietnam, Cambodia, India, Madagascar, Tanzania, Fiji, Kiribati, Tonga, and Vanuatu.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter is explaining on how the experiment being conducted for Euchema Spinosum a red macro alga as bio sorbent to the textile waste water. This chapter also explained the methodology of the process and each structural characteristic used to analyse the compound solution.

3.2 Material

In this experiment, there are a few material was used to investigate the effectiveness of Euchema Spinosum to remove heavy metals content from textile wastewater. The material used are Euchema Spinosum (Red Alga), textile effluents, copper reagent, Chromium reagent, Zinc reagent and distilled water (H_2O).

3.3 Preparation of sample

For preparation of sample, there are 2 materials that were used in this experiment are Euchema Spinosum (red alga) and textile effluence.

3.3.1 Macro alga

Figure 3.1 shows a dead biomass macro alga which is Euchema Spinosum a red alga is choosing from the screening process to identify the most effective macro alga toward heavy metals adsorption. The macro alga is collected from Kunak District in the Tawau Division of Sabah, Malaysia. The macro alga is wash using tap water and dry in an oven for a day to produce a complete dry macro alga. After that, the dried macro alga is cut and pulverize by a grinding mill to produce small particle or powder shape of macro alga. Then, the powder is sieve using 0.6 mm to 1.18 mm sieve size. The passing percentage of macro alga is ready to use as bio sorbent for textile waste water treatment.

Figure 3.1: Euchema Spinosum (Red Macro Alga)

3.3.2 Textile waste water

Figure 3.2 shows textile effluents that collected from Tenun Diraja Pahang factory located in Kuantan, Pahang. Moreover, the sample is preserve before experimental to avoid any changes in sample content during experimental test. The sample is preserve using 40^{o}C of Nitric acid (HNO3) and the pH value of the sample is below than 2.0 pH. The sample is preserve to prevent the growth of microbial bacteria and sealed to prevent air oxidation which can change the properties of textile wastewater (Sabur et al., 2012). In addition, before the preservation of sample the initial pH value of the textile waste water is taken to determine the characteristic of the sample.

Figure 3.2: Textile Wastewater from Tenun Diraja Pahang

3.3.3 Adsorption

The characteristic of heavy metals that are proposed to be investigate are Copper, Zinc and Chromium. These heavy metals are used to study the effectiveness of macro alga toward adsorption. Firstly, the copper solutions are preparing by dissolving analytical grade Cu(NO3).3H2O in the textile waste water. This procedure is done in order to identify the capacity of copper content adsorb by macro alga. Besides that, other heavy metals content is identifying directly to the textile waste water with adding selected chemical reagent that is used for each type of heavy metals.

Next, the textile waste water is tested using UV spectrophotometer to analyse the initial content of each parameter inside the solution. Then, 50 ml of textile effluents is placed in the 100 ml flask at 20 oC. After that, the solution is mixed with 1000 mg of powdered macro alga and the mixture is stirred at 130 rpm in a shaking incubator. Then, after several hours the solution is placed inside the centrifuge machine at 4000 rpm/60 second to allow the mixture in uniformity and well stirred. Lastly, the solution is analyse using UV spectrophotometer to determine the capacity of Copper (Cu), Zinc (Zn) and Chromium (Cr) content adsorb by the macro alga.

3.3.4 Dosage

A red macro alga known as Euchema Spinosum can be influenced by various parameter to maximize the adsorption capacity of Copper, Chromium and Zinc. One of the parameter cover in this research is the amount of dosage for the biosorbent in adsorption process. Euchema Spinosum can reach the optimize dosage in adsorbing these heavy metals. Moreover, when the dosage is higher than the optimum limit for dosage the percentage of adsorption can decrease because the heavy metals molecules are insufficient to cover all the exchangeable sites on the biosorbent. Then, this process will resulting a low heavy metals uptake capacity (Aravindhan et al., 2009).

In removing Copper, Chromium and Zinc from the textile wastewater several selected dosages were used to investigated the effectiveness in adsorption process. The dosage that cover this experimental laboratory is 5 g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L and 30 g/L. After that, among these six readings the optimum dosage will be identified to investigate the maximum adsorption of Copper, Chromium and Zinc.

3.3.5 Contact Time

Contact time is the process where the exchangeable sites on biosorbent and macro alga involved. The contact time is one of the parameter that can enhanced the capability of Euchema Spinosum in removing Copper, Chromium and Zinc. Besides, the optimum contact time to identify the maximum adsorption take place will be investigated. In this research, 9 selected contact times are chosen to acquire the optimum contact time for the macro alga to react with the textile wastewater.

The contact time used to study the effectiveness of the biosorbent is 1h, 8h, 16h, 24h, 32h, 40h, 48h, 52h and 56h. Then, the contact time used for the textile sample is different from synthetic solution that is used for adsorption method because the textile wastewater require higher contact time compare to synthetic solution.

3.4 Flow chart

Flow chart is a diagram of the sequence of movement or actions of things involve in a complex system or activity. In this research, overall research flow and the preparation of biological material as bio adsorbent which is Euchema Spinosum (red alga) is presented in the flow chart. This flow chart gives a clear information or sequence of work that had to be done in this research.

3.4.1 Overall research flow

Based on the Figure 3.3, the overall research flow represents the work process of this research from the beginning until the last step of work progress. The material used in this research is a red macro alga known as Euchema Spinosum and a sample of textile effluents. After that, this dead biomass is collected from Kunak, Sabah while the textile effluents are collected from Tenun Diraja Pahang factory located at Kuantan, Pahang. This Euchema Spinosum is prepared as bio adsorbent through several processes from solid shape of macro alga into small particles of alga. Next, the initial content of copper, chromium and zinc are identified using UV-VIS spectrophotometer. Then, both of the materials preparation are used for biosorption process. An optimum dosage and contact time is investigated through several selected dosage and contact times. Finally, after the biosorption of these 3 heavy metals using Euchema Spinosum, the content of heavy metal is taken and the percentage removal of copper, chromium and zinc is calculated to identify the maximum adsorption capacity of heavy metals.

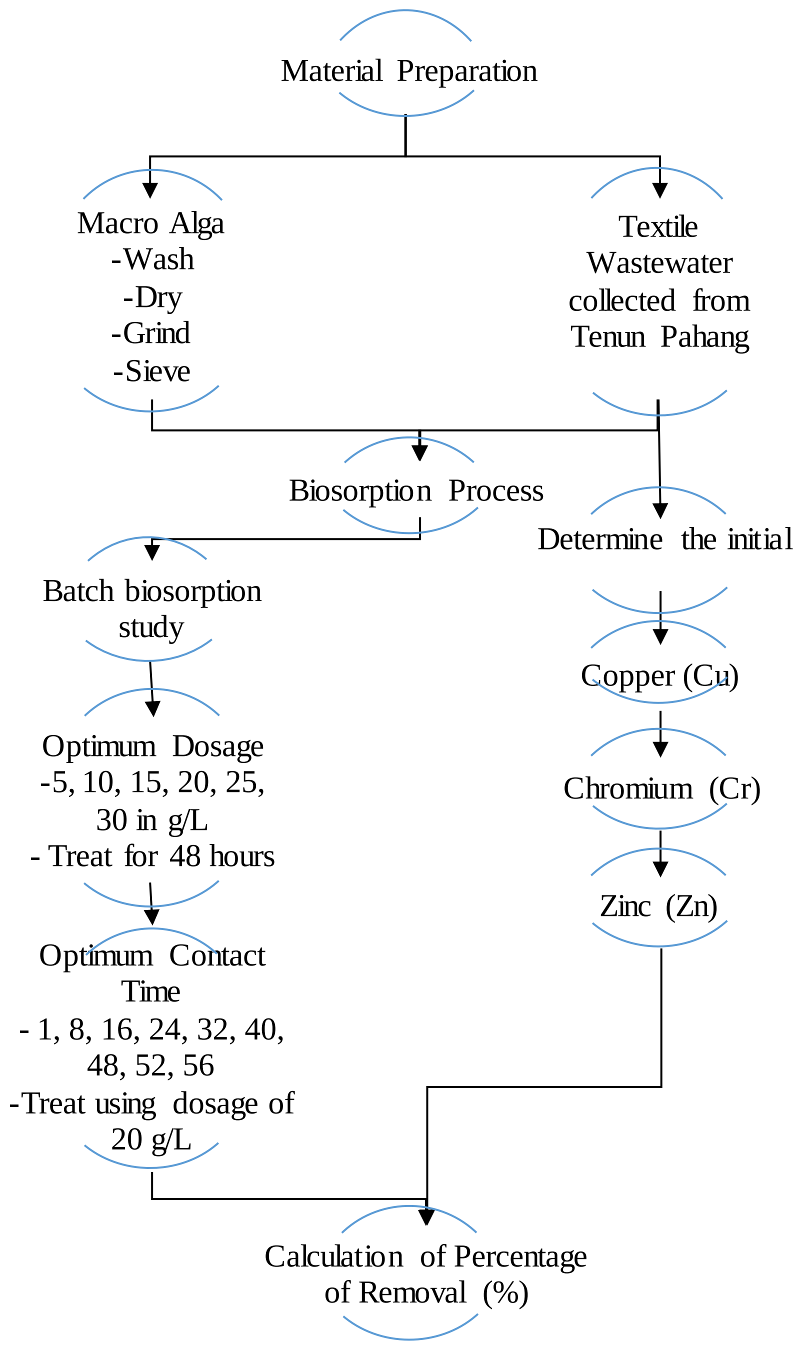

Figure 3.3: Overall research flow

3.4.2 Preparation of Biosorbent

The macro alga is wash using tap water 3 times and rinse with the distilled water for 2 times to remove other unwanted materials.

Then, the macro alga is dried in an oven for 24 hours to completely dry the macro alga.

After that, it is grind to small piece of macro alga using grinding mill.

The crushed macro alga is sieve into small particle size between 0.6 to 1.18 mm.

Lastly, the macro alga is ready for adsorption process as biosorbent.

Figure 3.4: Steps of the preparation of Biosorbent

3.4.3 Adsorption of Copper, Chromium and Zinc

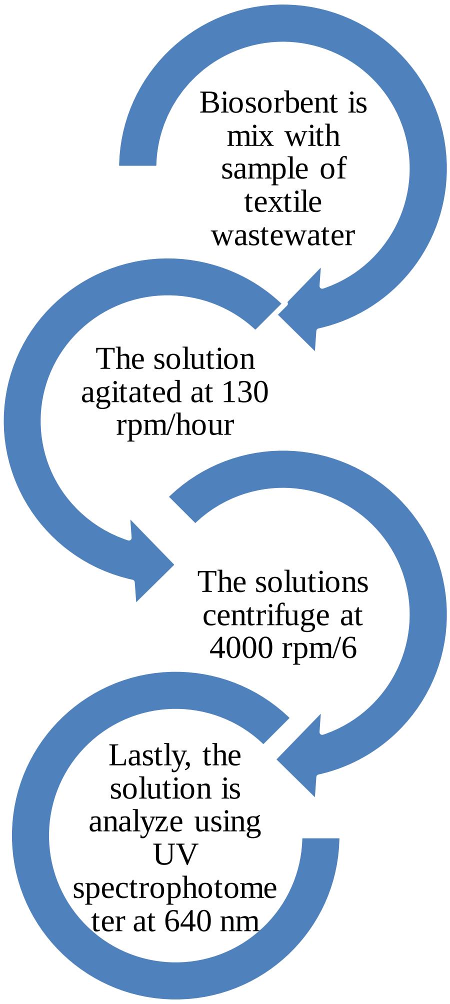

Figure 3.5: Adsorption of Copper, Chromium and Zinc

Based on the Figure 3.5, the figure shows the step for mixing the biosorbent with the sample of textile water collected form Tenun Diraja Pahang Batik factory located at Kuantan, Pahang. Then, the solution is agitated at 130 rpm/hour to improve the contact and produce a reduction in the agglomeration of the liquid and change its normal properties.

Next step is the solutions will be undergoing centrifugation process. Centrifugation is a technique used for the separation of particles from a solution according to their size, shape density, viscosity of the medium and rotor speed. The particle suspended in the solution medium and placed in a centrifuge tube. The tube is then placed in a rotor and spun at a define speed. There are three sorts of centrifuge intended for various applications. Modern scale centrifuge is regularly utilized in assembling and waste preparing to residue suspended solids, or to isolate immiscible fluids. A model is the cream separator found in dairies. High speed axes and ultracentrifuges ready to give high increasing velocities can isolate fine particles down to the Nano-scale, and atoms of various masses.

Huge axes are utilized to reproduce high gravity or speeding up conditions (for instance, High-G preparing for aircraft testers). Medium-sized centrifuge is utilized in clothes washers and at some swimming pools to wring water out of textures. Gas axes are utilized for isotope detachment, for example, to improve atomic fuel for fissile isotopes. For this research, the solution will be centrifuge at the speed of 4000 rpm/6.

Lastly, the solution is analyse using UV spectrophotometer at 640 nm. UV/Vis spectrophotometer is routinely utilized in chemical or environment laboratory for the quantitative assurance of various analysis, for example, transitions metal particles, profoundly conjugated organic compound, and organic macromolecules. Spectroscopic analysis is usually completed in solutions yet solids and gases may likewise be considered.

UV spectrophotometer uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions.

Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

3.5 Structural characteristics

Briefly, structural characteristic shows the equipment used in order to complete this research. There are 6 equipment that are used such as oven, grinding mill, sieve, centrifuge machine, incubator shaker and UV spectrophotometer. All of the equipment are provided to the students at the Environmental Laboratory at FKASA building.

3.5.1 Oven

Figure 3.6 shows the drying oven model Memmert-VO200COOL used to dry the sample of macro alga at 80 ^oC to 100 ^oC to produce a complete dry macro alga from water used during wash the macro alga. Based on the Figure 3.7, this is an electric machine used for heat purposes. An oven is a thermally, insulated chamber used for the heating, baking, or drying of substances.

Figure 3.6: Memmert-VO200COOL Drying Oven

3.5.2 Blender

A blender is used to crush the dead biomass of macro alga after oven-dried processed. Blender uses mechanical forces to break the structure of macro alga into small pieces. After that, the solid structure of macro alga will change into powdery form after grinded. Based on the Figure 3.7, a blender used for this experiment is a dry type blender that use electricity as the main source for the power. Besides that, the purpose of using blender are to increase the surface area of a solid, manufacturing of a solid with a desired grain size and pulping of resources.

Figure 3.7: Panasonic Blender PSN-MXSM1031

3.5.3 Sieve

Next, ASTM Sieve is a device that used to separate the crushed macro alga into sizing particle required for bio sorbent. The required size for the macro alga is 0.6 to 1.18 mm according to sieve size. Sieving is a basic method for isolating particles of various sizes. A sieve, for example, utilized for filtering powder has little openings. Coarse particles are isolated or separated by crushing against each other and screen openings. Depending on the kinds of particles to be isolated, sieve with various sorts of openings are utilized. Sieve is additionally used to isolate stones from sand. Sieving assumes a critical job in nourishment ventures where strainers (frequently vibrating) are utilized to keep the pollution of the item by remote bodies. Based on the Figure 3.8, the structure of the modern sieve is here of essential importance.

Figure 3.8: ASTM Sieve

3.5.4 Centrifuge machine

A centrifuge is a bit of hardware that puts an item in revolution around a settled pivot (turns around), applying a power opposite to the hub of turn (outward) that can be exceptionally solid. The centrifuge works utilizing the sedimentation guideline, where the centrifugal acceleration makes denser substances and particles move outward in the spiral course. In the meantime, protests that are less dense are displaced and move to the middle. In a laboratory facility centrifuge that utilizes test tubes, the spiral speeding up makes denser particles settle to the base of the cylinder, while low-density substances ascend to the top. Refer to the Figure 3.9 showing the centrifuge machine that are used in this experiment.

There are three sorts of centrifuge intended for various applications. Modern scale centrifuge is regularly utilized in assembling and waste preparing to residue suspended solids, or to isolate immiscible fluids. A model is the cream separator found in dairies. High speed axes and ultracentrifuges ready to give high increasing velocities can isolate fine particles down to the Nano-scale, and atoms of various masses.

Huge axes are utilized to reproduce high gravity or speeding up conditions (for instance, High-G preparing for aircraft testers). Medium-sized centrifuge is utilized in clothes washers and at some swimming pools to wring water out of textures. Gas axes are utilized for isotope detachment, for example, to improve atomic fuel for fissile isotopes.

Figure 3.9: Centrifuge-EBA 270

3.5.5 Orbital Shaker

An orbital shaker is a laboratory equipment used to blend, mix, or disturb substances in a cylinder or carafe by shaking them. This equipment is primarily utilized in the fields of chemical and biology. A shaker contains a wavering board that is utilized to put the cups, measuring glasses, or test tubes. In spite of the fact that the attractive stirrer has recently come to supplant the shaker, this equipment is yet the favoured decision of equipment when managing huge volume substances or when simultaneous agitation is required. Figure 3.10 shows the example model of incubator shaker that are used in this experiment.

Figure 3.10: Orbital shaker

3.5.6 UV spectrophotometer

UV-Vis spectrophotometer of model DR-5000 is routinely utilized in chemical or environment laboratory for the quantitative assurance of various analysis, for example, transitions metal particles, profoundly conjugated organic compound, and organic macromolecules. Spectroscopic analysis is usually completed in solutions yet solids and gases may likewise be considered. UV spectrophotometer uses light in the visible and adjacent ranges.

The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Figure 3.11: UV-Vis spectrophotometer of model DR-5000

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The results of the experiments carried out for the removal of Copper (Cu), Chromium (Cr) and Zinc (Zn) from textile waste water using Euchema Spinosum a red macro alga as biosorbent are discuss as below.

4.2 Effect of Change in Amount of Dosage on Adsorption

An experiment was carried out to determine the optimum dosage of biosorbent in maximum adsorption of Copper, Chromium and Zinc elements from textile waste water. The reading of six different amount of dosage were selected which is 5 g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L and 30 g/L.

Table 4.1 shows the initial content of Copper, Chromium and Zinc in the textile wastewater that have been collected from Tenun Diraja Pahang. The content is shown in term of mass concentration, C_o, in milligram per litre. For Copper, the initial content of mass concentration is 12.5 mg/L. Next, the Chromium initial content of mass concentration is 7.5 mg/L. lastly is for the initial content of Zinc in the textile wastewater is 5.0 mg/L of mass concentration.

Table 4.1: The initial content of Copper, Chromium and Zinc in Textile Wastewater

Heavy metals	Mass Concentration, C_o (mg/L)
Copper	12.5
Chromium	7.5
Zinc	5.0

After the initial content of Copper, Chromium and Zinc were identified the adsorption of those heavy metals were conducted using Euchema Spinosum for seven days. The results from the experiment were examined and discussed. Based on the data analysis this research can deduced an equation of:

$$\% \text{ removal} = (Co - Ce) / Co \times 100\% \qquad \text{(Eq. 4.1)}$$

Thus, the percentage removal of Copper, Chromium and Zinc can be calculated and the effectiveness of Euchema Spinosum as biosorbent can be investigated.

Table 4.2: The tabulation of data for dosage for removal of Copper, Chromium and Zinc

Dosage (g/L)	Mass Concentration After Adsorption, C_e (mg/L)			Percentage of Removal (%)		
	Copper	Chromium	Zinc	Copper	Chromium	Zinc
5	5.0	1.50	1.5	60	80	70
10	5.0	1.10	2.5	60	85.33	50
15	6.5	0.9	1.5	48	88	70
20	3.0	0.55	0.5	76	92.67	90
25	6.5	1.35	1.0	48	82	80
30	4.5	0.90	2.5	64	88	50

Table 4.2 shows the tabulation of data for the removal of Copper, Chromium and Zinc from textile waste water using 6 different dosages. The lowest amount of Copper reduce after the biosorption process is 3.0 mg/L. Besides, the lowest amount of Chromium reduce after the biosorption process is 0.55 mg/L while the lowest amount of Zinc reduce is 0.5 mg/L. These three heavy metals show an effective results of adsorption because the initial content of each heavy metals in the textile effluents is higher than the amount of heavy metals after biosorption. Among these three heavy metals, Chromium shows the most potential heavy metals uptake capacity compare to Copper and Zinc.

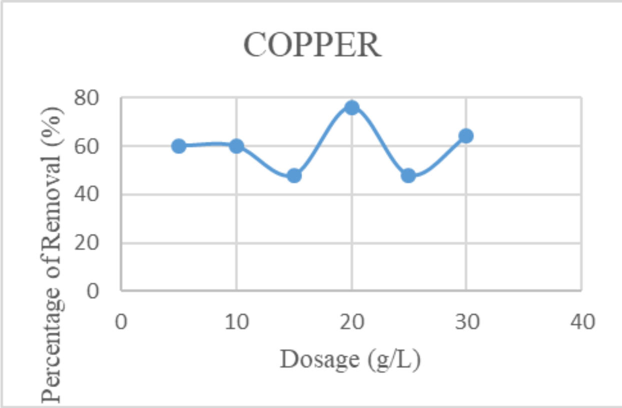

Figure 4.1: Effect of amount of dosage on percentage removal of Copper

According to figure 4.1, the optimum dosage for Copper removal is 20 g/L which having a value of 76% percentage of removal. Based on the figure, the percentage of removal for Copper at the lower amount of dosage were consistent between 5 g/L and 10 g/L with percentage removal of 60%. The percentage removal of Copper was rapidly decrease when the optimum dosage of 20 g/L was achieved. The lowest percentage of removal for the six different amount of dosage for Copper is 48% while the highest percentage of removal is 76% as recorded in Table 4.2.

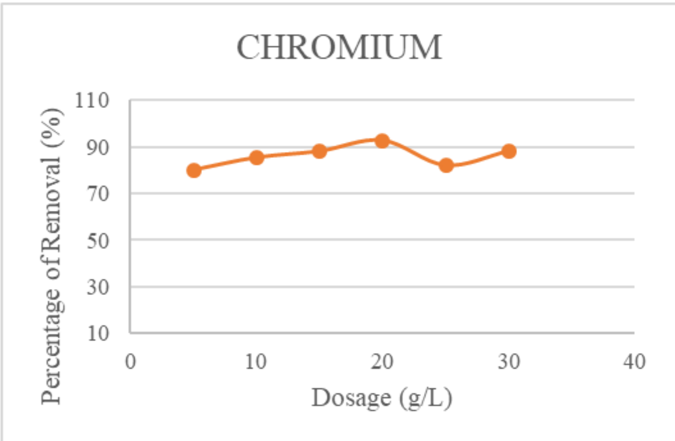

Figure 4.2: Effect of amount of dosage on percentage removal of Chromium

According to figure 4.2, the optimum dosage for Chromium is 20 g/L with percentage removal of 92.67%. Based on the figure shows, the percentage removal of Chromium is slightly increase at 5 g/L to 20 g/L amount of dosage. However, the percentage of removal for Chromium decrease when the optimum dosage of 20 g/L was achieved. Moreover, the lowest percentage removal of six different amount of dosage for Chromium is 80% while the highest percentage of removal for Chromium is 92.67%.

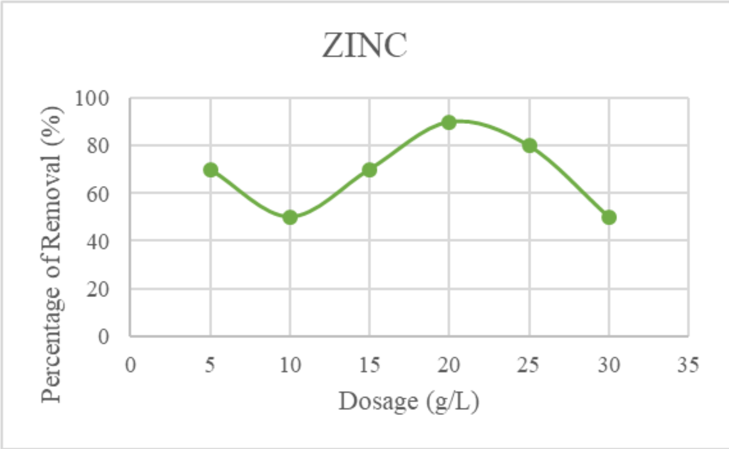

Figure 4.3: Effect of amount of dosage on percentage removal of Zinc

According to figure 4.3, the optimum dosage for Zinc is 20 g/L with the percentage removal of 90%. Based on the figure shows, the percentage of removal for Zinc are increase at amount of dosage 10 g/L to 20 g/L. However, the percentage of removal for Zinc is decrease after the optimum dosage for Zinc is acquired. The lowest percentage removal of Zinc for the six different amount of dosage is 50% while the highest percentage removal of Zinc is 90%.

4.3 Effect of Change in Contact Time on Adsorption

Other than amount of dosage, effect of change in contact time on adsorption was also studied. This parameter was investigated to identify the required time for the adsorption of Copper, Chromium and Zinc needed to acquire the maximum adsorption capacity of these heavy metals. The reading of nine different of contact time were selected for this parameter. The contact time is 1h, 8h, 16h, 24h, 32h, 40h, 48h, 52h and 56h.

Table 4.3 shows the initial content of Copper, Chromium and Zinc in the textile wastewater that have been collected from Tenun Diraja Pahang. The content is shown in term of mass concentration, Co, in milligram per litre. For Copper, the initial content of mass concentration is 8.0 mg/L. Next, the Chromium initial content of mass concentration is 1.65 mg/L. lastly is for the initial content of Zinc in the textile wastewater is 2.5 mg/L of mass concentration.

Table 4.3: The initial content of Copper, Chromium and Zinc in Textile Wastewater

Heavy metals	Mass Concentration, C_o (mg/L)
Copper	8.0
Chromium	1.65
Zinc	2.5

Thus, the percentage removal of Copper, Chromium and Zinc can be calculated using the same equation deduced at amount of dosage parameter. The results from the experiment were calculated to obtained the percentage removal of Copper, Chromium and Zinc.

Table 4.4 shows the tabulation of data for the removal of Copper, Chromium and Zinc from textile waste water using 9 different contact times. The lowest amount of Copper reduce after the biosorption process is 5.5 mg/L. Besides, the lowest amount of Chromium reduce after the biosorption process is 0.35 mg/L while the lowest amount of Zinc reduce is 0.5 mg/L. These three heavy metals show an effective results of adsorption because the initial content of each heavy metals in the textile effluents is higher than the amount of heavy metals after biosorption. Among these three heavy metals, Chromium shows the most potential heavy metals uptake capacity compare to Copper and Zinc.

Table 4.4: The tabulation of data for contact time for the removal of Copper, Chromium and Zinc

Contact Time (hour)	Mass Concentration After Adsorption, C_e (mg/L)			Percentage of Removal (%)		
	Copper	Chromium	Zinc	Copper	Chromium	Zinc
1	6	0.65	2.0	25	60.6	20
8	7.5	0.60	1.0	6.25	63.64	60
16	7.0	0.90	1.0	12.5	45.45	60
24	5.5	0.70	1.5	31.25	57.58	40
32	7.0	0.85	1.5	12.5	48.48	40
40	7.0	0.35	0.5	12.5	78.79	80
48	7.0	0.55	0.5	12.5	66.67	80
52	7.0	1.00	1.0	12.5	39.39	60
56	6.5	0.75	1.0	18.75	54.55	60

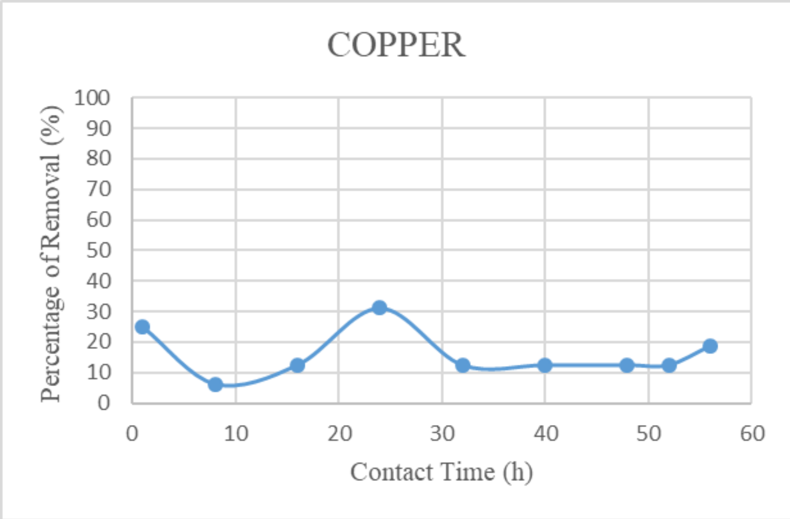

Figure 4.4: Effect of contact time on percentage removal of Copper

Based on the figure 4.4, the optimum contact time for Copper is 24 hours with the percentage removal of 31.25%. Then, the percentage removal at contact time 1-hour initiate to decrease and moderately increase at 8 hours contact time until 24 hours of contact time. After that, the percentage of removal for Copper started to decrease after optimum contact time of 24 hours with the consistent percentage removal of 12.5% from 32 hours until 52 hours of contact time. According to the nine reading of contact time, the highest percentage of removal is 31.25% while the lowest value of Copper uptake is 6.25%.

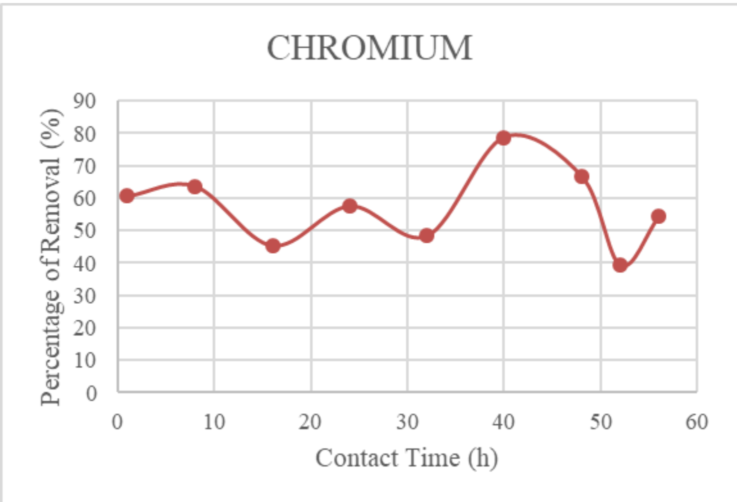

Figure 4.5: Effect of contact time on percentage removal of Chromium

According to figure 4.5, the optimum contact time for the Chromium's removal is 40 hours with the percentage removal of 78.79%. In addition, the percentage of removal at 1 hour to 40 hours fluctuated until the maximum adsorption for these nine readings of contact time was acquired at 40 hours. After that, the percentage removal of Chromium is started to dropped to the value of 39.39%. For Chromium, the lowest percentage of removal for these nine selected contact time is 39.39% and the highest value of adsorption is 78.79% which shows that Euchema Spinosum is very effective in removing Chromium heavy metal.

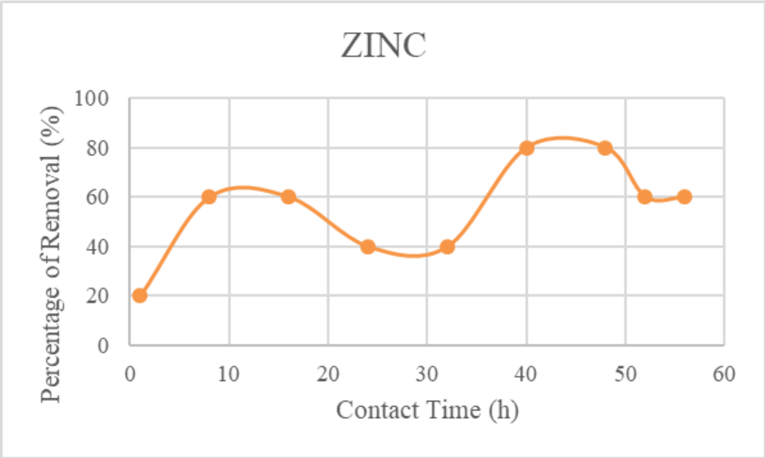

Figure 4.6: Effect of contact time on percentage removal of Zinc

Based on figure 4.6, the optimum contact time for the removal of Zinc is 40 hours with the percentage removal of 80%. The graph shows that the percentage removal of Zinc fluctuated with the equilibrium value between two contact time. For the 8 hours and 16 hours contact time the percentage of removal for Zinc share the same value of 60% removal. After that, the pattern remains the same until the last contact time of 56 hours. Moreover, the lowest percentage for Zinc removal is 20% while the highest value achieved is 80%. For conclusion, Euchema Spinosum has the capability in removing Zinc heavy metal same to the Copper and Chromium heavy metal.

4.4 Comparison between Copper, Chromium and Zinc uptake capacity

4.4.1 Effect on Dosage

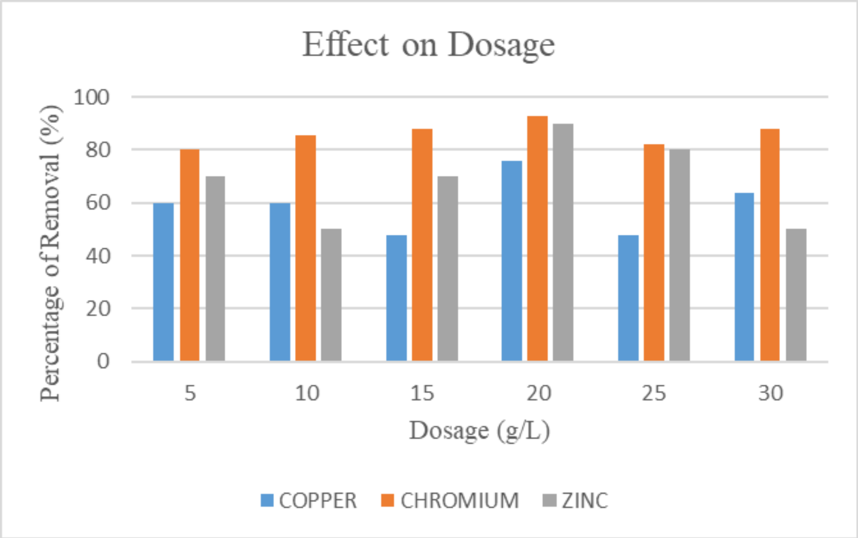

Figure 4.7: Effect of dosage on Copper, Chromium and Zinc

The graph of percentage of removal for the three heavy metals which is Copper, Chromium and Zinc are shown at figure 4.7. These three heavy metals undergo the same experiment on six different amount of dosage to identify the maximum adsorption of each heavy metals based on the dosage control. From the illustrated graph, Copper shows the lowest percentage of adsorption compare to Chromium and Zinc. Besides that, Chromium shows the highest percentage of adsorption compare to Copper and zinc.

From the experiment, this research has found that Copper content inside the textile waste water is higher compare to Chromium and Zinc. Moreover, the initial content of each heavy metals were tested using UV-VIS Spectrophotometer to calculate the percentage of removal or adsorption. For the parameter of dosage, this research has found that the optimum dosage for these three heavy metals have an equal amount of dosage which is 20 g/L.

Then, the percentage of adsorption tend to decrease after dosage of 20 g/L because at the higher amount of dosage the percentage adsorption become lower due to the available heavy metals molecules are insufficient to cover all the exchangeable sites on the biosorbent, which is commonly will resulting in low heavy metals uptake (Aravindhan et al., 2009).

4.4.2 Effect on Contact Time

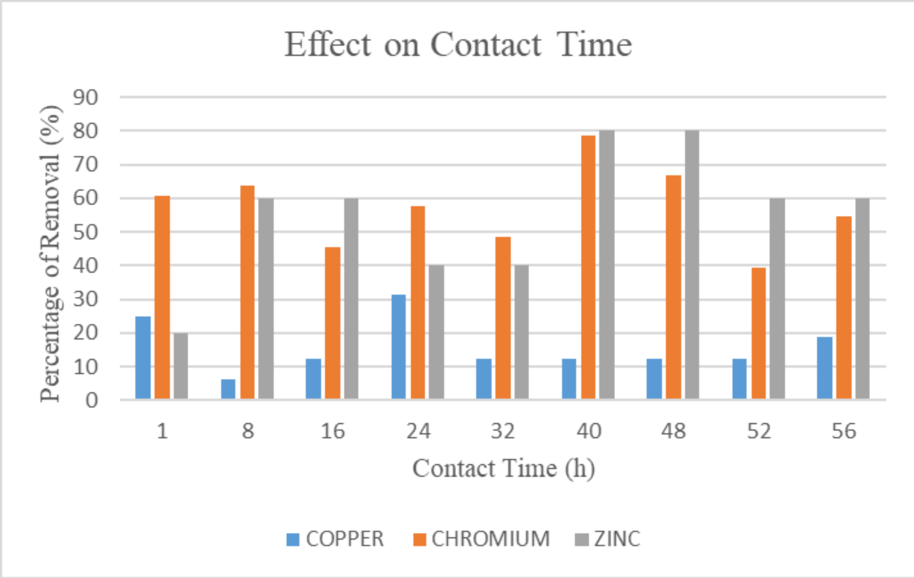

Figure 4.8: Effect of Contact Time on Copper, Chromium and Zinc

Based on figure 4.8, the optimum contact time for the reaction between Chromium and Zinc is 40 hours while the optimum contact time for Copper is 24 hours. Difference from synthetic waste water, the textile waste water need higher contact time to achieve the maximum absorption of heavy metals using macro alga.

From the result obtained, the maximum absorption of copper is 31.25 % with 2.5 mg/L reduced. After that, the maximum absorption of chromium is 78.79 % with 1.3 mg/L reduced while the maximum absorption of zinc is 80% with 2.0 mg/L reduced. Once the biosorption process reached the state of equilibrium, there will not be any further binding of the biosorbate on the biomass (Rangabhashiyam & Balasubramanian, 2018).

Besides that, chromium and zinc elements has lower amount of content inside the waste water compare to copper element. Proven that the thickness of colour inside waste water solution show that the solution contains higher amount of copper. The wide spread use of copper is the reason to copper as heavy metals that commonly found in environment and industrial waste water (Cho et al., 2013).

The highest value of absorption from three elements which is copper, chromium and zinc is 92.67%. From the result obtained shows that Euchema Spinosum a red macro alga has an ability to remove heavy metals from real waste water. The negative functional group of the macro alga reacted with the positive charge of elements inside the waste water can create the reduction of the heavy metals content inside the waste water.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In this research, the heavy metals removal was conducted for Copper, Chromium and Zinc from textile wastewater using a cost effective red macro alga known as Euchema Spinosum. This red alga has a wide availability in our aquatic ecosystem which offer a low price and easy to acquires. A sample of textile wastewater was collected from textile industry in Kuantan, Pahang known as Tenun Diraja Pahang. After that an adsorption method was chosen among other lists of physical methods available because of the low capital, operation costs and simple method.

Besides that, adsorption method is the most commonly used method for the removal of organic and inorganic pollutants from different sources of wastewater. Moreover, there are variety of natural sources used as biosorbent either from the industrial or agricultural sources. Then, there are many research conducted for the effectiveness of various sources of biosorbent in treating the waste water. For this research, a red macro alga or common name as seaweed was chosen to investigate the effectiveness in removing certain heavy metals such as Copper, Chromium and Zinc.

The red macro alga was prepared as biosorbent for the adsorption method in removing Copper, Chromium and Zinc. After that, the initial content of each heavy metal was identified to calculate the percentage of adsorption after the treatment process. The equipment's used in this research are drying oven, grinding mill, sieve, orbital shaker, centrifuge equipment and UV-VIS spectrophotometer. After that, in order to test the removal of these heavy metals three chemical reagent were used as the standard to identify the content of heavy metals.

From this study, the results indicated that adsorption process was also influenced by varying parameters such as amount of dosage and the contact time. Selected readings for each parameter were used to test the adsorption capacity to investigated the maximum adsorption of the Copper, Chromium and Zinc.

After that, the results revealed that Euchema Spinosum has an influenced on the adsorption method. The biomass exhibited the highest Copper uptake capacity at dosage of 20 g/L and contact time of 24 hours. Then, the highest Chromium and Zinc uptake capacities are at dosage of 20 g/L and contact time of 40 hours. From this research, Chromium has the highest percentage of adsorption with the value of 92.67% which shows that Euchema Spinosum is very effective as biosorbent to remove certain heavy metals.

Thus, as conclusion this research has achieved final objective that is to study the effectiveness of biosorbent for the removal of Copper, Chromium and Zinc. This indicate that adsorbent are attractive candidates for removing these heavy metals.

5.2 Recommendation

Based on the study that have been done, there are a few recommendations that can be applied in a way to improvise the result.

I. Use a proper veil for the UV-VIS Spectrophotometer test for better results obtain.

II. Investigate the pH, initial concentration and kinetic modelling for the efficiency of macro alga in removing heavy metals.

III. Use Atomic Absorption Spectrometry (AAS) for easy handling and cost effective purposes.

IV. Dilution factor need to be done for textile waste water since the heavy metals content is quite high and the colour is very thick.

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