REUSABILITY OF MACROALGAE (EUCHEMA SPINOSUM) AS BIOSORBENT FOR DYE REMOVAL

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ABSTRAK

Dalam projek ini, penyerapan dan penyingkiran pewarna biru Methylene (MB) ke atas makroalga, rumpai merah (E. Spinosum) dikaji. Eksperimen penyerapan-penyingikran dibuat untuk menentukan eluen yang paling berkesan untuk penyingkiran pewarna dan mengkaji kebolehgunaan semula makroalga sebagai biosorben. Antara enam eluen yang digunakan, eluen yang paling efektif ialah asid nitrik (HNO3). Bagi kebolehgunaan semula makroalga, empat kitaran penyerapan,-penyingkiran diperolehi yang menunjukkan peratusan penyerapan pewarna menurun daripada 94.51% hingga 48.45%, manakala peratusan penyingkiran berkurang daripada 51% kepada 23.4%. Bagi kesan kepekatan, keputusan menunjukkan bahawa 1.0M HNO_3 memperolehi peratusan penyingkiran yang lebih tinggi menggunakan paras pH yang berbeza (pH1-pH5) di mana ia berkurang daripada 31.98% kepada 25.71%, berbanding dengan peratusan penyingkiran 0.5M HNO_3 yang menurun daripada 27.42% kepada 25.43%. Walau bagaimanapun, kepekatan yang tinggi boleh menyebabkan kerosakan pada struktur biosorben, bagi menangani masalah ini, kajian lanjut perlu dilaksanakan dengan menggunakan eluen yang lain dengan kepekatan yang rendah untuk mengelakkan kerosakan pada struktur biosorben. Oleh itu, air suling digunakan dan kajian menunjukkan ianya berpotensi untuk digunakan sebagai eluen kos rendah kerana hasil yang diperoleh menunjukkan bahawa peratusan penyingkiran menurun daripada 26.26% kepda 21.94% dari pH 1 hingga pH 5. Kesimpulannya, hasil kajian ini menunjukkan bahawa makroalga boleh diguna pakai sebagai sorben mesra alam dan berkesan untuk penyingkiran pewarna.

ABSTRACT

In this research, biosorption and desorption of Methylene Blue (MB) dye from red macroalga, Euchema Spinosum (E. Spinosum) were observed. Biosorption-desorption experiment were conducted to determine the most effective eluent for dye desorption and investigate the reusability of macroalgae as biosorbent. Among of the six eluents used, the most effective eluent to be found was nitric acid (HNO_3). For reusability of the macroalgae, the four successive cycles of biosorption-desorption tests were obtained that show dye sorption efficiency decreased from 94.51% to 48.45% as well as desorption efficiency which is decreased from 51% to 23.4%. As for the effect of the concentration, the result indicated that 1.0M HNO_3 obtained higher desorption efficiency using different pH level (pH1-pH5) in which it decreased from 31.98% to 25.71%, rather than desorption efficiency of 0.5M HNO_3 which is decreased from 27.42% to 25.43%. However, high concentration may lead to the destruction of biosorbent structure, to tackle this problem further studies need to implement by using any other eluent with low concentration in order to avoid possible damage on biosorbent structure. Hence, distilled water is used and potential to be used as low cost eluent as the result obtained show that desorption efficiency was decreased from 26.26% to 21.94% from pH 1 to pH 5. In conclusion, the results of this study suggest that studied of macroalgae can favorably use as environmentally friendly and efficient sorbent for dye removal.

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LIST OF SYMBOLS

C_4H_6OH	1-Butanol
°C	Celcius
%	Percentage
$(CH_3)_2CO$	Acetone
H_3BO_3	Boric acid
$CHCl_3$	Chloroform
C_2H_5OH	Ethanol
Cf	Final MB dye concentration
D%	Desorption efficiency
g	gram
$C_3H_8O_3$	Glycerine
HCl	Hydrochloric Acid
HCL	Hydrogen chloride
Ci	Initial MB dye concentration
CgH_{18}	Isooctane
M	Mass
mg/g	Milligram per gram
mg/L	milligram per liter
$qe,_{biosorption}$	MB dye biosorption capacity
$qe,_{desorption}$	MB dye desorption capacity
CH_3OH	Methanol
MB	Methylene Blue
mL	Milliliter
min	minute
nm	nanometer
HNO_3	Nitric acid
NH3-N	Nitrogen ammonia
R%	Percentage removal
H_3PO_4	Phosphoric acid
KOH	Potassium Hydroxide
KI	Potassium iodide
rpm	Revolution per minute
s	seconds
NaCl	Sodium Chloride

NaOH	Sodium Hydroxide
Na_2SO_4	Sodium sulphate
$Na_2S_2O_3$	Sodium thiosulfate
V	Volume
C_8H_{10}	Xylene

LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand
DOE	Department of Environment
DW	Distilled Water
E.Spinosum	Euchema Spinosum
NTU	Nephelometric Turbidity Unit
SS	Suspended Solids
TS	Textile Sludge
WQI	Water Quality Index

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, environment pollutions are significantly increase through the year in Malaysia. There are three main types of environment pollutions which are air pollution, water pollution and land pollution. According to Department of Environment (DOE), Table 1.1 shows the result from the River Water Quality Monitoring Programme that had been conducted by them in order to analyse Water Quality Index (WQI). Based on the table, starting from 1998 it showed polluted river was 16 rivers and slightly reducing to 9 polluted rivers in 2005. However, from 2006 to 2012 it showed fluctuated results which from 15 polluted rivers become 12 polluted rivers. Unfortunately, the results showed the polluted rivers increase from 10 to 12 rivers from year 2013 to 2014. From the results, it can conclude that water pollution is one of the main contribution to the pollution in Malaysian, hence it need to be control and improve in order to prevent the quality of water become worst in the future.

Table 1.1: Number of River Basins Monitored by Category from 1998 to 2014 in Malaysia

Water Quality Category				
Years	Total River Basins Monitored	Polluted	Slightly polluted	Clean
1998	120	16	71	33
1999	120	13	72	35
2000	120	12	74	34
2001	120	13	47	60
2002	120	14	43	63
2003	120	9	52	59
2004	120	9	53	58
2005	146	15	51	80
2006	146	7	59	80
2007	143	7	45	91
2008	143	7	60	76
2009	143	9	64	70
2010	143	13	65	65
2011	140	11	53	76
2012	140	12	54	74
2013	140	10	56	74
2014	140	12	66	62

Source: (‘Alam sekitar’, 2015)

In addition, on Wednesday (25 May 2016), it was reported in Utusan Melayu that the total of 43 rivers, or 9% of rivers in the country, mostly in the urban areas are polluted, said Natural Resources and Environment Minister Wan Junaidi Tuanku Jaafar. Out of the 473 rivers monitored by the DOE which 186 rivers, or 39%, were slightly polluted while 244 rivers or 52% were clean. Even though the results showed clean rivers is more than polluted rivers, but all parties need to take part in the rivers cleanliness to ensure the continuity of Malaysia water resource.

Water pollution are growing concern due to present of toxic nature from wastewater resulting critical threat to environment and human health. Among of the sources of water pollution are come from domestic and industrial sewerage, effluents from manufacturing and agro-based industries and heavy metals from factories (Abdolali *et al.*, 2015). Nevertheless, one of the major sources of water pollution is dye content in wastewater from textile industry in many country which dangerous due to high content of chemical reagent (Wong *et al.*, 2017).

Therefore, the elimination of dye effluent from wastewater must be treated before discharge to the natural water bodies as protection to the environment and public health. Thus, various conventional methods are employed for dye removal in wastewater such as reverse osmosis, coagulation, flocculation, ion exchange, precipitation and membrane separation. The list of the methods shows a significant potential in order to remove dyes from wastewater. Despite of that, because of high chemical content of dyes, it becomes a challenge to deal as it involved complexity and high cost in operation including high energy requirements. To tackle the challenge, the used of low cost absorbents as effective alternative to the conventional methods resulting various successful application of these inexpensive cost, naturally occurring, readily available organic absorbents (biomass) in industrial effluents treatment using adsorption processes as reported in various studies. Therefore, biosorption has been declared as eco-friendly and cost effective alternative among currently used method for dyes removal and /or as wastewater treatment. Recently, there are many investigation by various group used macroalgae such as seaweeds as biosorption mechanism (Daneshvar *et al.*, 2017).

In this study, desorption mechanism may involve ion exchange whereby sorbed dyes are desorbed from the sorbent (macroalgae) to yield a small volume of concentrated dye solution. It will also be useful for reusability of the biosorbent and discarding them safely. The aim of this study is to determine the reusability of the macroalgae use for dye removal.

1.2 Problem Statement

Among of the various type of pollution water pollution is one of the pollution that need to be concerned for future generation in Malaysia. Water is the most important source that needed by living creature for living such as water for drinking, sanitation, food and agriculture, photosynthesis for plant and so on. Thus, water pollution must be prevent before it become worst. It is found that, dye contamination is one of the source that contribute to water pollution due to high in toxic content (Pang and Abdullah, 2013).

Contaminant of color dyes that found in wastewater effluent are resulting from direct production of the dye and also its effect from the textile and other industries. According to Niyaz Mohammad Mahmoodi in 2011, it is estimated that the annual dyes production discharged in effluent in manufacturing operations are 2%, while discharged from the textile including industries are 10%. As a solution, there are many kind of methods that had been employed such as reverse osmosis, coagulation, flocculation, ion exchange, precipitation and membrane separation for wastewater treatment. However, mostly the methods used require high energy, high in cost of operation and maintenance because of complexity of process and advanced technology requirement (Mahmoodi *et al.*, 2011).

Besides that, the present of toxic chemical from the dye can lead to a serious affects to the environment and human health. Due to this chemical pollution, the normal functioning cell is being disturbed and may cause living creature on the earth had to face impairment of important functions like respiration, osmoregulation, reproduction, and even mortality (Wong *et al.*, 2017). Thus, these problem need to overcome and to get a better and healthy life.

Indah Water stated that in Malaysia, there are two types of sewage treatment method which are preliminary and secondary sewage treatment. As for preliminary sewage treatment refers to physical unit operations and is the first stage of treatment applied to any sewage, while secondary sewage treatment refers to biological and chemical unit processes. However, for tertiary treatment systems which functioning on removal of nutrients, toxic substances including heavy metals and further removal of suspended solids and organic including reuse of water, is not applied in Malaysia. In turn, the alternative method need to be employ to improve the water treatment system in Malaysia.

In addition, there are various type of technologies used to overcome dye pollution such as such as coagulation and flocculation, biological oxidation, chemical precipitation, activated carbon adsorption, ion exchange, photo-catalys, photo-oxidation and membrane filtration. However, all of the technologies require expensive capital and operational price which made it become less effectiveness (Mokhtar *et al.*, 2017).

As a solution for all of the problems, the use of biosorption mechanism that can reduced the dye pollution, effective technology of wastewater treatment, environmentally friendly and economical price are require as well as the use of suitable regenerating agents are very important in order to improve the wastewater treatment system in Malaysia. Recently, there are many researchers had been used biomass such as fungi, vegetables and macroalgae as biosorbent for the research on biosorption mechanism and desorption eluents had been reported.

1.3 Objectives

The objectives of this project are:

1. To determine the most effective eluent for desorption

2. To investigate the reusability of macroalgae as biosorbent

1.4 Limitation of Research and Scope of Work

The limitation of research and scope of work of the project had been prepared to achieve the project objectives. Firstly, the mechanism used was Euchema Spinosum (E. Spinosum) macroalgae as biosorbent of dye which catogarized as red seaweeds. The macroalgae need to be blend to take a measure of standard size for biosorbent which range from 0.75 mm to 1.2 mm. However, due to the limitation of the apparatus, the size use for biosorbent in this research are from 0.6 mm to 1.18 mm. While the type of dye used is Methylene Blue (MB) dye. Secondly, there were six type of eluents were utilised for desorption test which are Hydrochloric Acid (HCL), Nitric acid (Phosphoric acid), Phosphoric acid (H_3PO_4), Potassium Hydroxide (KOH), Sodium Hydroxide (NaOH) and Sodium Chloride (NaCl) which had been provided in environmental lab. Thirdly, distilled water also have been used as low cost eluent to investigate the reusability depend on different level of pH. Next, the experiment that have been conducted are biosorption-desorption experiment and reusability experiments. From biosorption experiment, the MB dye solution sorption capacity (mg/g) and sorption efficiency (%) were obtained, while through desorption experiment, the MB dye desorption capacity (mg/g) and desorption efficiency (%) were determined to screening the most effective eluent. As for reusability the successive cycles of MB dye sorption and desorption process have been employ until the E. Spinosum are not capable to use for biosorption and desorption. Moreover, the reusability of the macroalgae also investigate by using different concentration of eluent (optimum eluent) to determine the effect of different concentration based on different pH level including determination the used of distilled water as low cost eluent.

1.5 Significant Research

The significance of this research is that we can use biosorbent which lead towards cheap agro-industrial waste, introducing a properly eco-friendly and cost effective technology both on operating and maintenance as a wastewater treatment to the society. Besides that, by using biosorbent, the secondary pollution volume can be reduced due to its higher sorption capacity for metals than commercial synthetic sorbents (Sohbatzadeh *et al.*, 2017).

In year 2017, based on Sohbatzadeh, the use of biosorbent is cost effectiveness because it is made up from abundant or waste material. In spite of that, the sorbent that derived from it in a simple process lead to most low priced for economical metal removal application.

In addition, the use of biosorbent also can improved the health of living things on earth due to its chemical stability and non-toxicity. According to the finding, the use of macroalgae as biosorbent facilitates the applications like reducing organic dyes in the waste water treatment and as antibacterial agent for medical and environmental application (Pandimurugan and Thambidurai, 2016b).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Pollution

Pollution that occur on the Earth's are very dangerous for both environmental and living things such that humans, animals and vegetation. It can effect to the health of living organism that can cause fatal as it can bring potential health hazard. Based on the fact above, the definition of the pollution is suitable as it is an unpleasant change in both physical and chemical or biological characteristics of water, air and soil that may give negative impact to the life or forming a probable health hazard of any living things on the Earth (Alina Bradford, 2018).

Susan Berg, 2017 also stated that pollutant can be categorize as any materials which causes pollution is known as a pollutant. Pollutant is any chemical or geochemical such as dust, sediment and grit or materials, biotic elements or its product, or physical factor which is heat that liberated purposely through human activity to the environment such as a concentration that may cause unfortunate damage or unpleasant affect. Moreover, a pollutant also can be defined as any substances such as solid, liquid or gaseous that found in concentration as it may lead to the damaging of environment. Pollutants also can be refer as residues of waste by human.

The sources of pollutant can be obtained from many cases of contamination such as lakes or rivers that are contaminated by water from chemical from the factories, the air that polluted by automobile exhausts, industries or thermal power plants and also the land that polluted with garbage littered by human. From the pollution cases above made all over the world take this cases as serious concern on the rivers become dull, the decomposed of fish on sea shores, drying of tree, the food matters that being cycled from toxic chemical and ailment plague that arise often (Susan Berg, 2017).

2.2 Types of Pollution

Figure 2.1: Water Pollution
Source: (Bernama, 2016)

Based on read and digest website, there are numerous type of pollutions that categorized according to the part of the environment which resulting on specific causes of that pollution. Every of these types own it individually causes and consequences. Among of the main types of pollution is water pollution that associates with contamination of several water bodies as shown in **Error! Reference source not found.** above. Many of living organisms rely on these water bodies and their nutritious for living and support their life. The causes of water pollution had been identified such as the dump of industrial waste into water bodies that affect the imbalance chemical in the water that lead to the death of aquatic creatures, utilization of insecticides, pesticides and ripening chemicals on plant meet the ground water system or close by stream, utilization of detergents for the purposed to wash the clothes that affect eutrophication condition which prevent sunlight from getting into and decrease the oxygen values that causing an inhabitable environment, and also a certain natural catastrophe like hurricane and flash floods that causing the combination between water and harmful substances on the land.

Figure 2.2: Air Pollution

Souce: (*Malaysia air quality ‘unhealthy’ as haze obscures skies*, 2014)

Secondly, air pollution also known as contaminated air that present in the atmosphere as shown in **Error! Reference source not found.** above. This pollution may compromise on respiration system of every living organisms as air is needed for respiration process. The causes of air pollution are due to the released of gases from internal combustion engines combine with poisonous gases, released of gases that contain sulphur dioxide and carbon monoxide which blend with the air and clouds tend to causing acid rains and the burning of disposed plastic, wood and rubber including the released of carcinogenic gases to the atmosphere (Bakar, 2016).

Figure 2.3: Soil Pollution

Soure: (Rebecca Lake, 2017)

Thirdly, **Error! Reference source not found.** above shows the condition of soil pollution which the utilization of artificial chemicals such as pesticides, insecticides and ripening agents affecting on soil stripping. The used of these artificial chemical causing vegetation absorb the nitrogen from the soil which unsuitable for vegetation to growth. Besides that, the vegetation play a role to hold soil together which prevent the soil from erosion and split (Rebecca Lake, 2017).

Figure 2.4: Thermal Pollution
Source: (Published, 2015)

Next, read and digest also stated that thermal pollution as shown in **Error! Reference source not found.** above which causing from the increasing of temperature in the ecosystem due the excessive heat energy released into the environment from natural disaster or unnatural method. This pollution causing polar ice caps melt and may lead to rise in water levels. While for radioactive pollution which take place when metals of radioactive break apart releasing hazardous beta rays that can effect on health. Normally, this pollution occur due to radioactive waste from nuclear power plants getting in water bodies.

Other than that, the pollution such as noise pollution and light pollution that rarely occur because it occur depend on condition of the place. Noise pollution occur when there are excessive of noise in the outdoors. For example, hon sound from vehicle on the road, operation of heavy machinery in the open space and many more. This pollution also dangerous as it can damage our ear drum and lead to deafness. While for light pollution occur due to the very bright lighting that used for function or from building causing the excessive light go direct into the retina of the eyes causing tension in the eyes (Alina Bradford, 2018)

2.3 Pollution in Malaysia

In 25 May 2016, it was reported that 43 rivers in Malaysia had been polluted. According to Natural Resources and Environment Minister, Wan Junaidi Tuanku Jaafar, nine per cent of rivers in the country, especially in the urban areas are contaminated. In addition, 39% or 186 out of 473 rivers are slightly polluted that monitored by Department of Environment. He also stated that among of the sources that contributed to water pollution in Malaysia are wastewater plants, industries and commercial premises at the Seminar on Water Resources Security in the Context of Sustainable Development Goals. In addition, he also received a report that the turbidity level has reached 6,000 Nephelometric Turbidity Unit (NTU) at one major river in Malaysia. It could be dangerous as 1,000 NTU reading may cause a water treatment plant to be closing down. Furthermore, water pollution is the highest percentage of pollution among the other types of pollution in Malaysia which is 63.41% (Bakar, 2016).

Department of Environmental (DOE) stated that, major sources of pollutants are Biochemical Oxygen Demand (BOD), Nitrogen ammonia (NH3-N) and also Suspended Solids (SS). It was reported that improvement that had been done on water quality in Malaysia in 2007 reduce BOD contaminated rivers from 22 rivers in 2006 to 12 rivers in 2007 as well as rivers that polluted by NH3-N reduced from 42 rivers to 36 rivers, while for SS contaminated rivers remain unchanged. BOD pollutants made up from untreated sewage wastes from both agricultural and industrial areas. For NH3-N pollutants its major sources are come from domestic sewage and livestock, while sources for most SS pollutants are from opening of land (Jabatan Alam Sekitar, 2015).

Although the water quality are improve, this matter still need to be monitored as stated by Syieluing Wong in 2017, in which one of the source that contributed to water pollution is from industry activity. He also said the most recognizable source of wastewater pollution is textile industry which related to the emission of dyes that contain highly in recalcitrant and toxic. In 2013, Yean L. Pang also said that textile industry is one of the rapid growing industries and remarkably contributes to the Malaysia economic growth especially man-made textile fiber such as batik.

Hand-made batik in Malaysia is very popular in Malaysia especially at the East Coast of Peninsular Malaysia. For Malay community in Malaysia, the hand-made batik is a traditional inherited industry. So that, it become importance to the economic growth primarily in the sates of Terengganu and Kelantan which had been produced man–made fiber with nylon, polester filament and staple content near to 400 000 tons in 2008. About 1.03% of man-mad fibers of Malaysia contributed to the world’s production. In 2008, it was announced that fifteenth largest producer of textile fiber was Malaysia and ninth largest in Asian region. Nevertheless, the textile industry in Malaysia produced big amount of textile fibers and affix notable effects to the quality of environment including to the liquid effluent (Pang and Abdullah, 2013).

As conclusion from the matter above, with the highest amount of production of textile fiber, it produced high rate of wastewater discharge with great load of contaminants. The dye release to the environment for dyeing textile fiber and finishing processes is a predominant source of water pollution (Pang and Abdullah, 2013). When dye release into water bodies, the dye molecule oppose degradation by natural means such as microorganism and light action due to its molecule continue for long time as their big and complex structures of molecules. These dyes prevent sunlight from entering into the water, therefore photosynthesis of aquatic plants are less. This especially true for Methylene blue (MB) which have high in concentration and dark in color, hence lead to catastrophic to the ecosystem of aquatic. Moreover, the bio-magnification and bioaccumulation effect from dye molecules in the marine ecosystem may compromised the safety of seafood. In view of risk to human health, the uptake of seafood may lead unpleasant effects to nervous system of human (Wong *et al.*, 2017).

In addition, textile sludge (TS) is also one of the source of pollution that generated by textile industry. The sludge consist high in metal ions resulting from aluminium and iron that emerge from coagulant and flocculants including phosphorus, nitrogen and potassium that produced via chemicals used textile dying and processing. TS is considered as schedule waste in Malaysia, hence its treatment incur price to the textile manufacturers. So that, a better alternative need to apply for disposal of TS (Wong *et al.*, 2017).

2.4 Dye

Dye is substance that functional as conveyance of colour to paper, leather, textiles and variety materials in which the colour will not change when that material being wash, heat, light or any factors that likely to be exposed. In addition, dyes are made up from fine ground solid that disseminate in liquid such as paint, ink or mix with other materials which distinct from pigments. Pigments normally provide brighter colours. Manly, dyes are organic compounds due to carbon contain while pigments are inorganic compounds due to no carbon contain (Edward Noah Abrahart, 2011).

Since 1850, dyes were made up from natural resources such as from plants, trees and lichens and sometimes some of it were from insects. Figure 2.5 and Figure 2.6 shows the common plants that used to make dye. However, after several years, in 1856, the demand of the natural dyes is reduced due to high in price and involved complex process in it production, so that synthetic dyes were produced and being used in many country (Edward Noah Abrahart, 2011).

Figure 2.5: Genus Indigofera
Source: (Edward Noah Abrahart, 2011)

Figure 2.6: Isatic Tinctoria
Souce: (Edward Noah Abrahart, 2011)

There are several operation in producing dyes. The general operations that involve are association of specific material in order to get a colour level based on measurement of moisture, heat and the fabric, then the dye molecules must located within fibre microstructure as well as the formation of covalent bonds that chemically react from substituents on dye molecules and the fibre.

For dyeing operations, the dye must become closely and evenly associated with a specific material to give level (even) colouring with some measure of resistance to moisture, heat, and light. These factors involve both chemical and physical interactions between the dye and the fabric. The dyeing process must place dye molecules within the microstructure of the fibre. The dye molecules can be anchored securely through the formation of covalent bonds that result from chemical reactions between substituents on the molecules of the dye and the fibre (Edward Noah Abrahart, 2011).

Synthetic dyes are divide into several classifications which are triphenylmethane dyes, anthraquinone dyes and azo dyes. In 1878, Emil Fischer established triphenylmethane structures that showed the methyl carbon of ptoluidine becomes the primary carbon bonded to the three of aryl groups in which each nitrogen in aniline blue bears (phenyl group) and crystal violet are dimethylated. While for anthraquinone dyes, it also known as the tructure for benzene and proposed by the German chemist Friedrich August Kekule. This type of dye become dominance of elucidation of structural (aromatic compound) and led towards the development of the dye industry. Next, azo dye in which it reaction become the most vital process in synthetic dye industry. The reaction produced between interaction pf nitrous acid and arylamine yields (Edward Noah Abrahart, 2011).

2.5 Methylene Blue Dye

Methylene blue (MB) dye is an ordinary dye used in textile industries and grouped as azo dye group in cationic (thiazine) which brings positive charge molecules. MB also had been reported that a few acute exposures to living form although it is categorized as not strongly hazardous dye. In addition these also can cause symptom. The reported cases such as vomiting, respiratory problem, eye irritation, diarhea and nausea which causing a symptom of gastrointestinal tract irritation, cyanosis, profuse sweating, dyspnea and many more (Mokhtar *et al.*, 2017). Figure 2.7 shows the MB dye that used in this research.

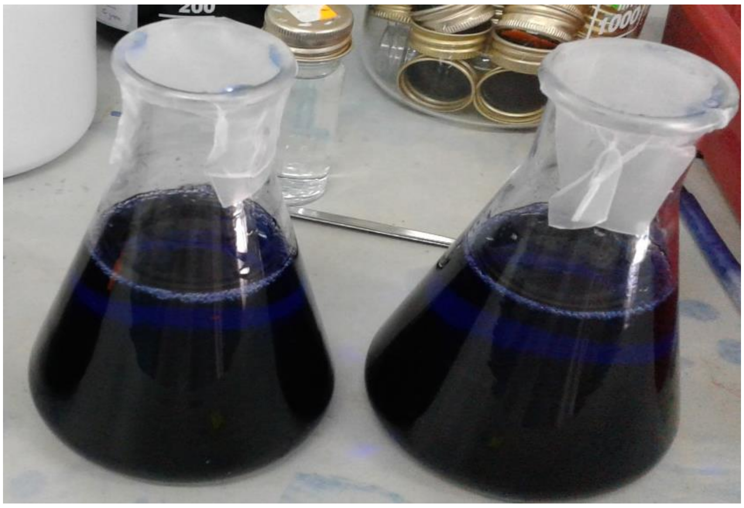

Figure 2.7: Methylene Blue (MB) Dye

According to the previous research, textile dyeing process had been used azo-dye because of its simplicity in production, low in cost, simplicity in application, durability and accessible in several colors. However, the revealing of azo-dye can cause allergic, carcinogenic, mutagenesis and detrimental health to living organisms. Apart from that, the toxic content in azo-dye also not just produced by the parent molecule but also via their products of degradation because of bio recalcitrant and xenobiotic (Mokhtar *et al.*, 2017).

2.6 Biomass

According to Freya in 2009, biomass is a matter constituted of living or recently living organisms which can be cremated or broken down via anaerobic digestion to produce energy. On top of that, the used of biomass in energy production control the price of energy production and impact to the environment in North America. Biomass can be obtained from plant, residues from forest industries, by-products from wood remanufacturing (Figure 2.8), residues from agriculture and waste product (Figure 2.9), municipal and industrial wastes(Figure 2.10), residues from rendering plants, ethanol or biodiesel production plants (Figure 2.11), waste from construction sites (Figure 2.12), land clearings, husks or shells from grains, peanuts, walnuts (Figure 2.13), cotton seeds as well as peel from citrus fruits (Cai *et al.*, 2017).

Figure 2.8: By-products from Wood Remanufacturing

Source: (*Construction & Demolition — Marketplace*, 2016)

Figure 2.9: Residues from Agriculture and Waste Product

Source: (*Stubble Digest*, 2018)

Figure 2.10: Municipal and Industrial Wastes

Source: (Kike Calvo, 2011)

Figure 2.11: Ethanol Production Plants

Source: (Jean-Francois Denault, 2018)

Figure 2.12: Waste from Construction Sites

Source: (*Five Techniques for Sustainable Building Construction*, 2015)

Figure 2.13: Walnuts
Source: (David Wolfe, 2015)

Biomass is divided into three types which are natural biomass, residual biomass and energy corps. Natural biomass is formed without any human intervention. While for residual biomass whether in dry or wet condition also known as wet spills called biodegradable which can be obtained from urban and industrial wastewater treatment as well as livestock waste. For energy crops, it generated for the purpose of biomass fuel transformable production which divided into existing corps like cereals, oilseeds, sugar beet and many more, lignocelluloses forest such as poplar and willow, and lignocelluloses crops (*Types of Biomass*, 2012).

According to R. Pandimurugan in 2016, the used of biomass as absorbent material for dye removal from wastewater had been proposed in many research. For example, they utilize chelating and complexing sorbents such as biological material of chitin, peat, yeast, chitosan, fungi or bacterial biomass to remove dye from solutions. Nowadays, there are several researchers purpose to use macroalgae such as seaweed as one of the alternatives for dye removal for wastewater treatment.

2.7 Introduction of Macroalgae

Macroalga (singular) or macroalgae (plural) are also known as seaweeds and other benthic which they attached to the bottom seawater algae that cannot see via naked eye. Seaweeds are also one of the plant group that live and find either in seawater or brackish water environment (Cai *et al.*, 2017). Seaweed surface consist of photosynthesis pigments function as tool to trap the present sunlight and nutrient in the saltwater to help them undergo photosynthesis process and produce food. They also can be seek in coastal region amidst high tide to low tide and in the sub tidal area until reach to a depth where 0.01% photosynthesis light is accessible (Wang and Chen, 2009).

Figure 2.14: Brown Seaweed, Sargassum on the Inshore Great Barrier Reef
Source: (*Introduction to seaweeds*, 2010)

Macroalgae are formed via ranging of crusts, foliose (leafy), and filamentous (thread like) forms with noncomplex structure of branching, to more complex forms accompanied by greatly specialized structures for light capture, flotation, breeding, and appendix to the seafloor. For the size of coral reef macroalgae reach until 3m to 4m in high which the range from a few millimeters to plants such as Sargassum as shown in Figure 2.14 above. The growth of macroalgae is by attached to the hard surfaces either rock or dead coral. Besides that, macroalgae have a complex cycle of life, broad of various reproduction modes which most of them rebreeding by release of sexually and asexually that produced gametes and or spores (propagules) and by spread of vegetative and or fragmentation which the plant pieces will breaking off to breed new individuals (Abdellaoui, Pavlovic, Bouhent, Benhamou, Barriga, *et al.*, 2017).

Figure 2.15: Sargassum (Brown Algae)

Source: (*Brown algae are used for fibromyalgia, cancer, osteoarthritis*, 2010)

Figure 2.16: Ulta Lactuta (Green Algae)

Source: (M.D Guiry, 2014)

Figure 2.17: Euchema Spinosum (Red Algae)

In 2008, M.A. Hashim reported that seaweeds are coming in three main groups based on their color types such as brown (Phaeophyta), green (Chlorophyta) and red (Rhodophyta) algae. In addition, the major element is polysaccharide which consist of alginate, carrageenan and polycolloid that competent to bind surface pollutant. Figure 2.15 above shows one of the type of brown algae (phaeophyta) which the green color influenced over the xanthophyll pigment fucoxanthin which makes masks the other pigments (Hashim and Chu, 2008). Besides that, in brown algae, the predominant active group are alginate and sulfate (Mokhtar *et al.*, 2017).While the green algae (Chlorophyta) obtained the green color from chlorophyll a and chlorophyll b as shown in Figure 2.16 above. It also have polysaccharides that manly bonded with cellulose and protein in the cell wall. As for red algae (Rhodophyta) shown in Figure 2.17 above, the result of the color are from phycoerythrin pigment presence which reflects the red light and absorbs blue light. On top of that, they also are characterized by the form of sulfated polysaccharides such as carrageenan. From the previous research that conducted by Nadiah Mokhtar in 2017, it stated that all species of red, brown and green macroalgae have high potential in MB dye removal MB from aqueous solution. However the best type of algae that suitable to use as biosorbent is red algae due to it shows an excellent performance in maximum biosorption capacity (qmax).

2.8 Structure of Macroalgae

There were over 100 species of macroalgae can be found in all coastal waters around the world. Although the most of the seaweeds live on a hard surface by anchor on the soil like rocks and shells, but still there were a few species of the seaweeds live over mud or sandy bottoms in the creeks and back bays (*Seaweed*, 2017).

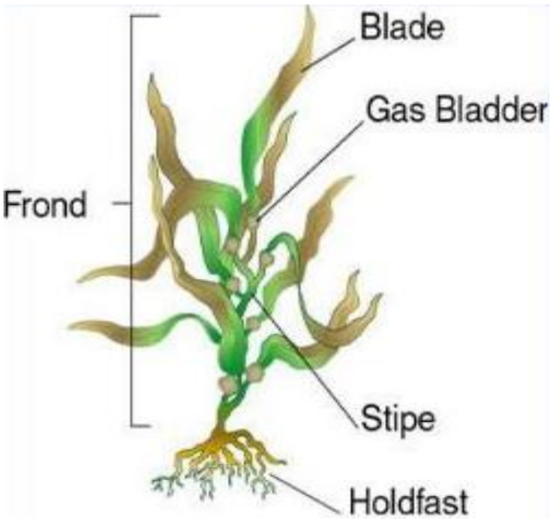

Figure 2.18: Structures of Macroalgae
Source: (Feryal Jamal Kherissat, 2014)

The structure of the typical macroalgae contain thallus, holdfast, stipe, blade and air bladder as shown in Figure 2.18. Seaweed absorb water and nutrient throughout the thallus also known as algal body. Holdfast is an exceptional basal structure which hold or help to attach the algae on the surface of rock or other algae. Besides that, stipes help seaweeds to reach the sunlight and absorb shock when it bending due to wave. While, lamina or blade is evened structure somewhat leaf like. The function of the blade is for reproduction due to it contain reproductive structures and chlorophyll on its surfaces or for photoynthesis. Lastly, air bladder or gas bladder also known as pneumatocyst which filled with carbon dioxide which assist to grips the blades closed to the light at the surface (Feryal Jamal Kherissat, 2014).

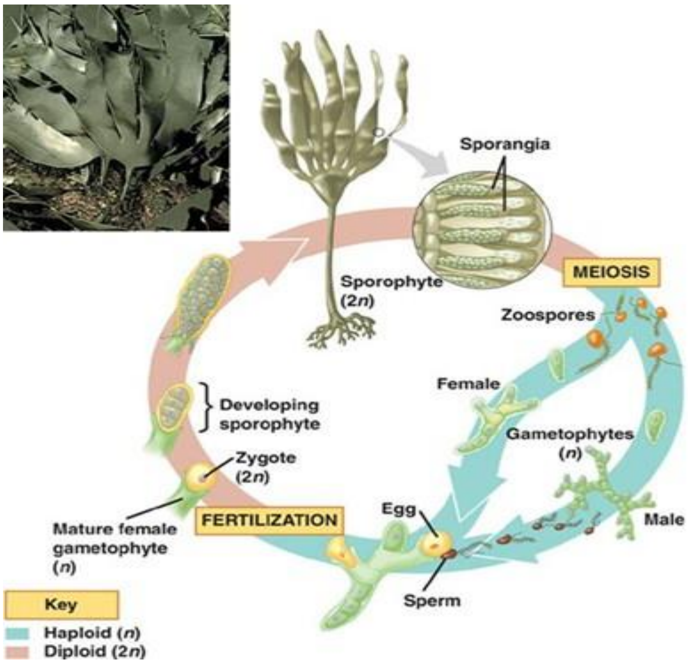

Figure 2.19: Life Cycle of Macroalgae

Source: (Tyrone Clarke, 2016)

According to Figure 2.19, it showed the life cycle of macroalgae. The life cycle of macrolagae starting from the production of pores via sporophyte by meiosis. Then, spores growing into gemotophytes. After that, gametes is produce via gemotophytes by mitosis. The process continue with the growth of sporophyte in which gametes unite into zygote and grows into sporophyte (Tyrone Clarke, 2016).

2.9 The Used of Macroalgae

Figure 2.20: Porphyra
(M.D Guiry, 2014)

Seaweeds are used in many ways such as food, herbalism, filtration and other. As for food, people in East Asia such as Japan, China and Korean used seaweeds to make variety of food like seaweed soup, sushi, rolling rice and rice ball. The type of seaweed that used for sushi wrap is pophyra categorized as red seaweed as shown in Figure 2.20. Moreover, in Wales they made a bread from seaweed to make lever and then used it to make lever bread together with oats (Tyrone Clarke, 2016).

Figure 2.21: Alginate
Source: (Prashant Lokare, 2013)

For herbalism or as medicine, the typical seaweed that used is alginates (Figure 2.21) which use for wound dressing and dental mould. In addition, carrageenans, alginates and agaroses are used in application of biomedicine which prepared from agar via purification. Furthermore, seaweed extract also had been used in diet supplementary which it can expand in the stomach and made the body become full which reduced eating desired (Tyrone Clarke, 2016).

Figure 2.22: Phytoplankton
Source: (*Phytoplankton*, 2018)

Seaweed required strong process of photosynthesis due to its massive affinity for nutrients that easily evacuate undesired nutrients from water. The general type of seaweed that used for filtration is phytoplankton as shown in Figure 2.22. The various types of nutrients such as carbon dioxide, ammonia, ammonium nitrate, nitrite, phosphate, iron and copper are absorb rapidly by the seaweed in filtration process (Tyrone Clarke, 2016).

2.10 Coagulation and flocculation methods

Methods of coagulation and flocculation are important part for treatment of water including a wastewater treatment. In coagulant process, metal coagulants that normally used were divided into two main categories which are based on aluminium and based on iron. Coagulants based on aluminium are aluminium sulfate, aluminium chloride and sodium aluminate. While coagulants based on iron are ferric sulfate, ferrous sulfate, ferric chloride and ferric chloride sulfate. In addition, chemical substance that used as coagulants are hydrated lime and magnesium carbonate. The potentiality of absorption characteristics in order to form multi-charged polynuclear complexes determine the effectiveness of aluminium and iron coagulants. The pH of the system command the nature of complexes. The coagulants process is occur when metal coagulants are added to water, then metal ions start hydrolized expeditiously to producing series of metal hydrolysis species. The efficiency of rapid combination between pH and coagulant dosage discover which hydrolysis species is effective for treatment (Frechen., 2014).

Flocculation occur when the liquid generate velocity gradients which allow the particles attract to each other and bound together and make them become large, called as flocs. When flocs are produced it cannot remain suspended due to large size, therefore the flocs being transfer to next process for further treated using filter press. Figure 2.23 shows the process of coagulation and flocculation (*Coagulation and flocculation in wastewater treatment*, 2013).

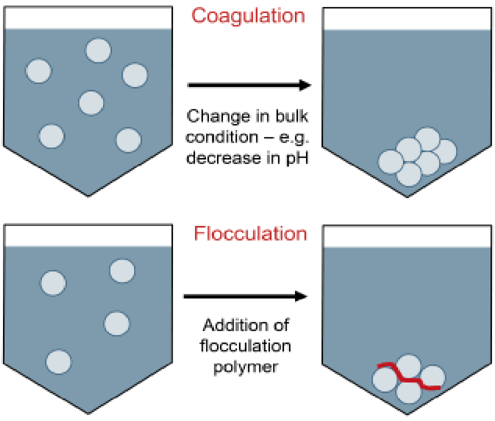

Figure 2.23: Process of Coagulation and Flocculation

Source: (*Coagulation and flocculation in wastewater treatment*, 2013)

2.11 Activated Carbon Adsorption Method

Recently, the carbons was implement in many of wastewater treatment in order to purify water and air leaving a facility in waste. Method of activated carbon adsorption have a remarkable potential to arrest contamination of water-dissolved that affect taste, odor, color, and toxic-promoting species. Adsorption phenomena takes place via surface interactions between contaminants and carbon graphitic platelet surfaces for removal. There are several sizes of activated carbon used for wastewater treatment such as powdered activated carbon and granular activated carbon.

Figure 2.24: Powdered Activated Carbon
Source: (*Activated Carbon For Drinking Water*, 2018)

Figure 2.24 shows powdered activated carbon which grind from milimeter granular activated carbon which display kinetics and a larger for contaminant removal compared to granular activated carbon. The occurrence of sporadic contaminant such as algae blooms and industrial spills that polluted municipal influent waters can used powdered activated carbon. During clarification process, activated carbon will be added to settling unit in order to evacuate contaminants. Moreover, it also help to defend against sudden influent combination on fixed activated granular carbon beds (Henry Nowicki, 2016).

Besides that, if the used of granular activated carbon were not enough and they lack of infrastructure, powdered activated carbon can be used for removal in sporadic contaminant occurrence. The individual use powdered carbon is employ as batch process to evacuate contaminants to tolerate regulated maximum contamination levels (MCLs) but not obligatory to zero or non-detected contamination (Henry Nowicki, 2016).

Figure 2.25: Granular Activated Carbon
Source: (*Granular activated carbon*, 2015)

Figure 2.25 showed granular activated carbon that used form contaminants removal to concentration under analytical detection limits and only needed about one to fourth amount of carbon between influent and effluent than powdered. Nonetheless, installation of infrastructure of fresh carbon and removal the spent granular activated carbon for furnace reactivation are require. The process of wastewater treatment using granular activated carbon is continuous and thermal reactivation is needed as it multiple-use product. The used of thermal reactivation can be classified the carbon as "green chemistry" (Henry Nowicki, 2016).

Granular activated carbon assist to control vapour phase municipal wastewater hydrogen sulphide and any odour. The large size of activated carbon allow gas streams to flow through carbon beds not inhibited and reduce the use of fans and necessary energy on order to blare gas stream via tight beds (Henry Nowicki, 2016).

2.12 Membrane Filtration Method

In 1960, membrane filtration method was introduced for water purification with the enhancement of high performances synthetic membranes. Nowadays, the employment of membranes in water treatment become popular, so that it being upgraded using new materials and implemented in various configuration. Membranes are made up from thin and porous sheets material that allow to split up contaminants from water via application of driving force such as remove the bacteria, and other microorganisms, micropollutants and natural organic which can cause colour, tastes and odours to the water (*Membrane Filtration*, 2009).

Water treatment process implement various types of memmbranes such as microfiltration (M-F), ultrafiltration (U-F), reverse osmosis (R-O) and nanofiltration (N-F) membranes. Microfiltration membranes have the biggest size of pores and usually decline big particles and various microorganism as shown in Figure 2.26. While ultrafiltration membranes have tinniest size of pores than microfiltration membranes and it can eliminate bacteria as well as soluble macromolecules such as proteins as shown in Figure 2.27. For reverse osmosis membranes, it consider as non-porous, hence it can reject particles and low molar mass species such as salt ion and organics ion Figure 2.28. The latest which is new membranes is nanofiltration also known as membrane separation due to cut-off lies between reverse osmosis and ultrafiltration as shown in Figure 2.29 (*Membrane Filtration*, 2009).

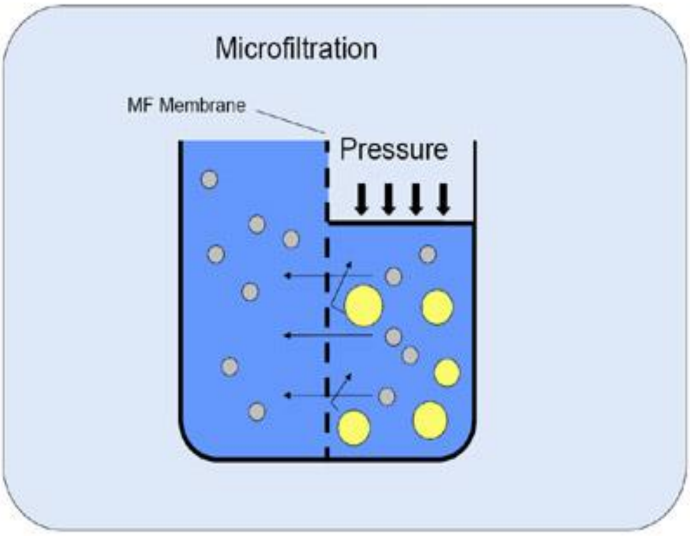

Figure 2.26: Microfiltration Membrane
Source: (*Membrane processes*, 2009)

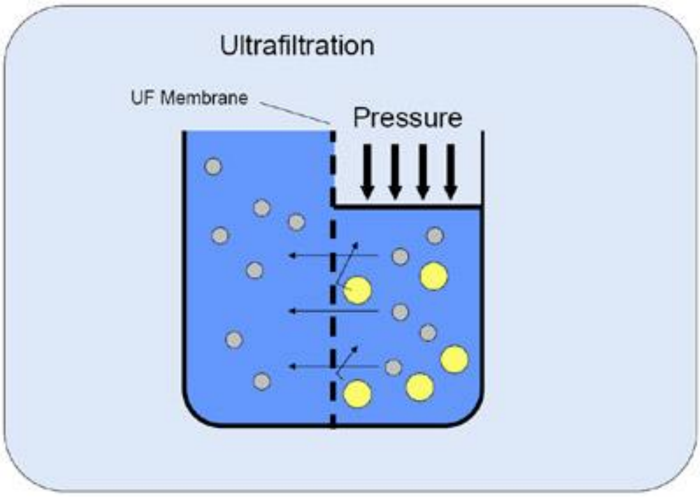

Figure 2.27: Ultrafiltration Membrane

Source: (*Membrane processes*, 2009)

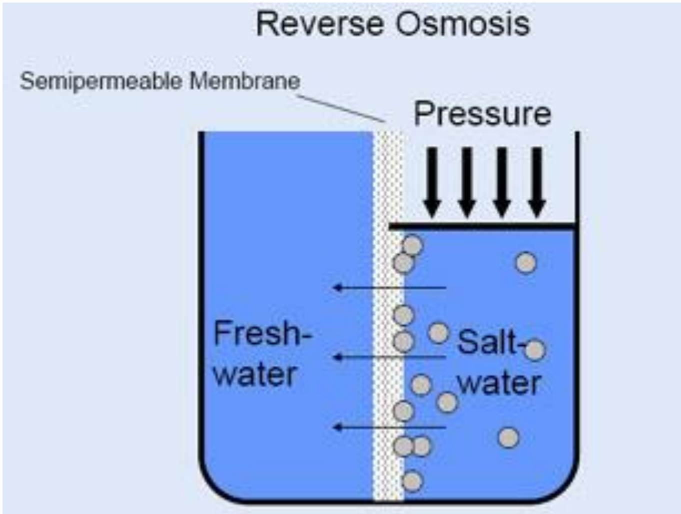

Figure 2.28: Reverse Osmosis Membrane

Source: (*Membrane processes*, 2009)

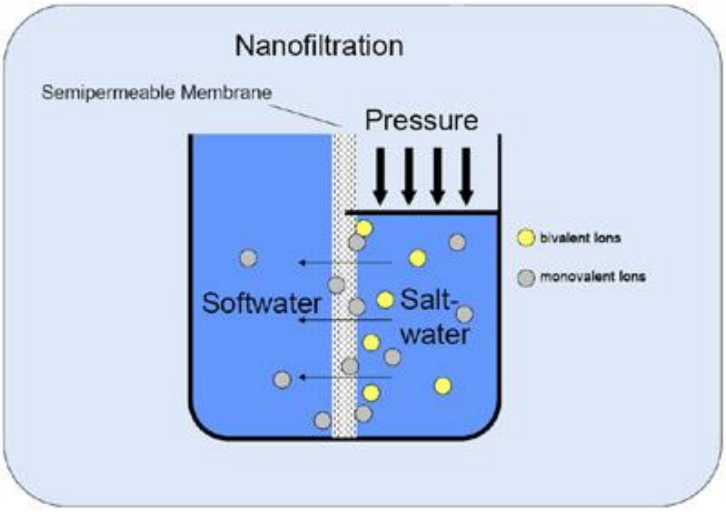

Figure 2.29: Nanofiltration Membrane
Source: (*Membrane processes*, 2009)

2.13 Biosorption- Desorption Method

As had been discuss before, effluent of dyes discharge to wastewater is one of the main source of water pollution and serious threat for both environment and human health (Pandimurugan and Thambidurai, 2016a). Hence, there are various techniques were employed for dye removal such as coagulation, flocculation, biological oxidation, chemical precipitation, activated carbon adsorption, photo-catalyst, ion exchange, membrane filtration and photo-oxidation. Among of all the techniques, the best process that shown great potential in removing dye effluent is adsorption. However, dealing with the dyes effluents is still challenging as it require high capital and operational costs. Thus, it provoked many researcher to propose an attractive alternative towards low cost biosorbent such as macroalgae for biosorption (Mokhtar *et al.*, 2017).

Biosorption can be described as the process of metal or metalloid species, compounds and particulates elimination from solution via biological material (Wang and Chen, 2009). On the other hand, biosorption method in dye remediation are consider as practicable process technology, cheap operating cost, perceptible efficiency and availability of biomass and reduction of secondary pollution volume (Hubbe et al., 2012). Based on Robalds et al, biosorption mechanisms were divided into several groups which are physical adsorption, ion-exchange, complexation and microprecipitation. For physical adsorption is refer as mechanism by which molecules bonding to solid surface. It occur due to the relatively weak electrostatic and van der Waals forces from umbrella term. As for ion-exchange mechanism is refer as identical replacement of light metal ions in solid phase via the metal ion in solution. While for metal complexation is refer as the species formation by the bonding of one or more metal ions which conquer over central position and amount of anions or ligands. Next, has been use to signalize the location of precipitation occur which locally at the biosorbent surface or within biosorbent pores due to local conditions (Mokhtar *et al.,* 2017).

However, according to Atefeh Abdolali in 2015, the crucial biosorption disadvantage is release immense amount of solid biomass or aqueous solution accompanied by high concentration of heavy metals of dye to environment. To prevent this case attributing to solid biomass, proper desorbing and regenerating agent (eluent) are apply in order to keep this method effective (Abdolali *et al.*, 2015). Moreover, Ehsan Daneshvar stated that the regeneration of sorbent is critical to maintain the treatment low in cost, reducing the disposal problem, and it also open an opportunity in valuable materials recovery. Apart from that, mechanism of desorption may include ion exchange or complexation processes in which the dyes that were sorbed were desorbed from the sorbent to produce a small amount of solution of concentrated dye. Furthermore, desorption allow the reuse of the biosorbent and disposed them safely which known a reusability of biosorbent used. Reusability of the microalaga can be investigate through many methods such as batch experiment (biosorption-desorption experiment, thermal desorption, deionized water, different concentration).

2.14 Reusability

Reusability is the process to treat the discharged of dye in order to reduce toxicity in dye effluent. Therefore, desorption process is the pillar in order to determine the reusability of macroalgae. There are many methods that have been used in previous study for reusability of biosorbent. Among of the method is the cycle of biosorption-desorption process. In this method, reusability is investigate via several cycle of biosorption-desorption cycle until biosorbent is not capable to be used as biosorbent as biosorption and desorption efficiency are low (Daneshvar *et al.,* 2017).

Secondly, reusability via different concentration of eluent. Based on previous study, they stated that high desorption efficiency was obtained when the high concentration is used due to strong electrostatic forces rather than low concentration eluent. Nevertheless, high concentration of eluent can cause damage on biosorbent structures which classified as ineffective method. Consequently, addition of other chemical substances are needed to modified the electrostatic forces and long term used of biosorbent (Daneshvar *et al.*, 2017).

Lastly, the application of electric field in desorption process. According to previous study, utilize of electric field improves the rate of regeneration of biosorbent significantly. The reusability is achieved due to supplant of forced of desorption from desorption equilibrium to weak concentration. Figure 2.30 shows the application of electric field in desorption process.

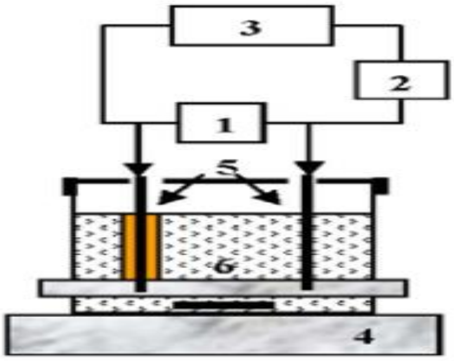

Figure 2.30: Application of Electric Field in Desorption Process

Source: (Tassist *et al.*, 2009)

CHAPTER 3

METHODOLOGY

3.1 Introduction

In Chapter 3, the methodology was explained in term of the experiments, procedures, materials, equipment and equations that involved in the research. Experiments that involved in the research were biosorption and desorption. Then, the procedures of the biosoprtion and desorption experiments were briefed including the procedure of the reusability process. While the main materials that used were Euchema Spinusom (red seaweed), methylene blue dye, six type of eluents (HCl, NaOH, H_3PO_4, KOH, NaCl and HNO_3) and distilled water. Next, the equipment used for the research were spectrophotometer, pH meter, centrifuge, and so on. Lastly, for equation there were four equations that involved to calculate biosorption and desorption efficiencies such as biosorption capacity equation, percentage removal equation, MB dye desorption capacity equation, and desorption efficiency equation. Figure 3.1 shows the flow chart of the methodology for the study.

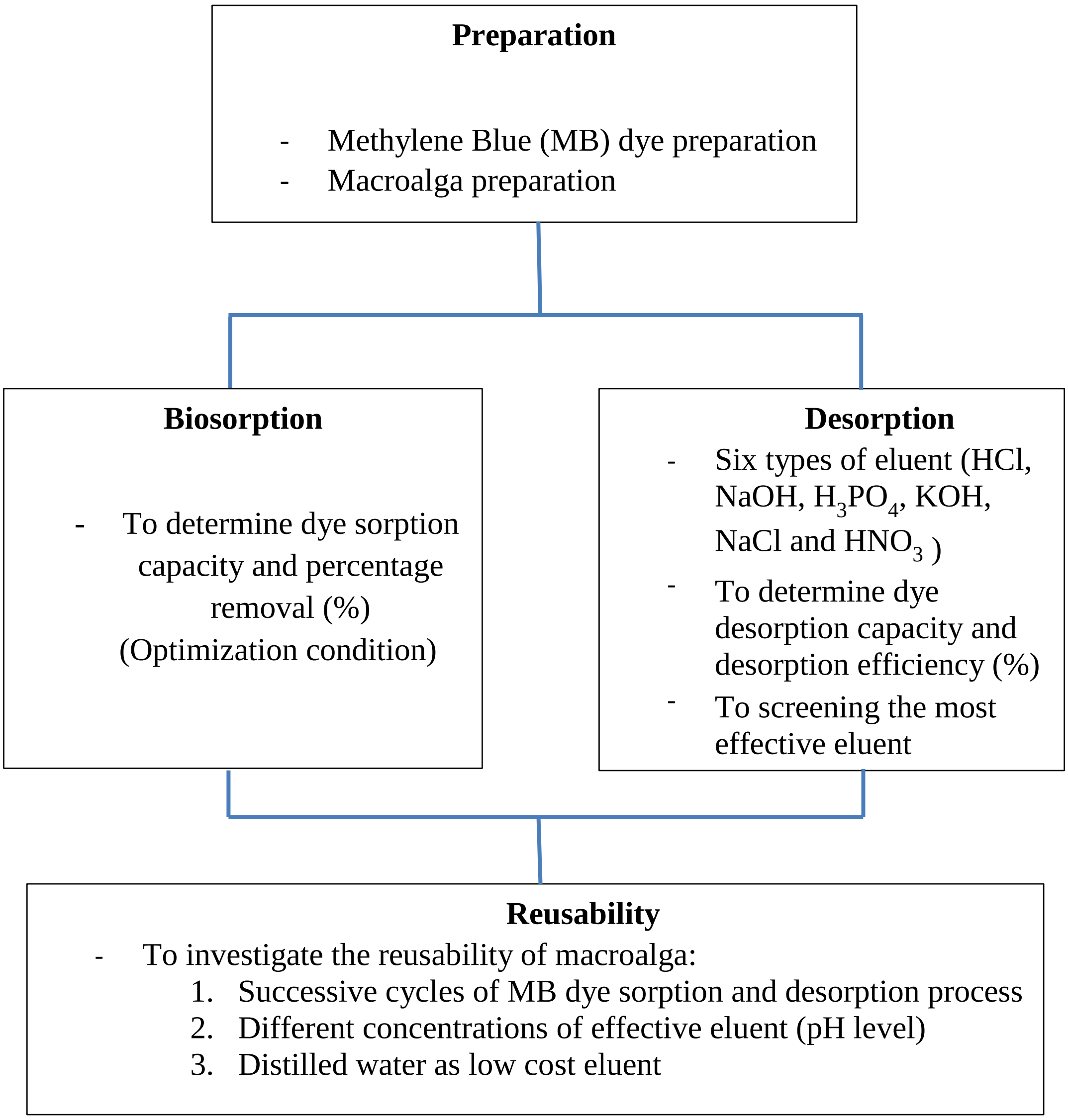

Figure 3.1: Flow Chart of the Methodology

Figure 3.1 shows the list of the experiments that have been conducted for the research. All of the experiments have been conducted in order to observe and collect the data as well as analyse the data to ensure that the proposed objectives of the research are achieve. The flow chart commenced with preparation of MB dye and macroalgae before performing any of the experiment. Next, the experiment continued with biosorption experiment to determine the dye sorption capacity of the macroalgae using optimization condition. After that, desorption experiment were conducted by using six type of eluents such as HCl, NaOH, H_3PO_4, KOH, NaCl and HNO_3 to screening the optimum desorption efficiency in order to determine the most effective eluent. Then, reusability experiment were performed. Reusability have been investigated via repetition of both biosorption and desorption experiments by using the most effective eluent to get successive cycles of MB dye sorption and desorption process. In addition, desorption experiment were conducted by using different concentration of eluent and being observed based on pH level to check on the effect of the concentration for reusability of macroalgae. Besides that, distilled water was used as other alternative that used non-acidic eluent and to determine it potentiality as low cost eluent for reusability of biosorbent.

3.2 MB Dye Preparation

1g of Methylene Blue was dissolved in 1L of distilled water to prepare 10000 mg/L an aqueous MB solution. The addition of either 0.1M of sodium hydroxide (NaOH) or 0.1M of hydrochloric acid (HCL) was needed to control initial pH reading which is 7. All chemicals were obtained from HmbG with analytical grade. Figure 3.2 shows on how the stock solution of MB dye was prepared.

Figure 3.2: Preparation of Stock Solution of MB Dye

3.3 Macroalgae (biosorbent) Preparation

Raw Macroalgae (E. Spinosum)

Crush Macroalgae

Figure 3.2: Preparation of Macroalgae

Figure 3.3: Sieve

Euchema Spinosum (E. Spinosum) of macroalgae were collected from factory of algae in Kunak, Sabah. The collected maroalgae were washed with tap water three times followed by rinsing of distilled water in order to removed irrelevant debris and salts on the macroalgae. The wet macroalgae were then dry in an oven (UFB500, Memmert) at 60 °C for 24 hours. Finally, dried macroalgae were choped and blend using blender and then sieved (Figure 3.3). The crush macroalgae were group in particle size of 0.6 to 1.18 mm and stored in tight plastic as shown in Figure 3.2.

3.4 Biosorption Performance

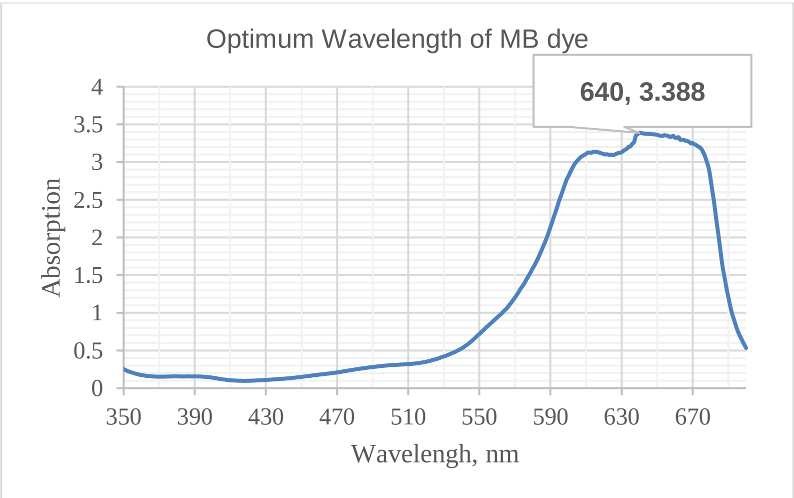

Figure 3.4: The Optimum Wavelength of Methylene Blue (MB) dye

The MB solution concentration pre and post biosorption were measured by using a UV–vis spectrophotometer (UV–vis spectrophotometer, DR5000, Arachem) at 640 nm wavelength as shown in Figure 3.4. All of the equipment were accurately calibrated followed the instructions by manufacturer. The measurement of pH value was measured with a pH meter (Mettler Toledo). The agitation of speed of orbital shaker (Excella E1, Edison, New Jersey, USA) was set at 130 rpm. The solutions were centrifuged at 4000rpm for 60s by using centrifuge (Centrifuge 2420, Japan). The result of all data were obtained from the mean of triplicates with average.

3.5 Biosorption Experiment

The test was conducted by adding 0.025g of biosorbent into 250mL MB solution with 100mg/L of initial dye concentration at pH 7 in room temperature. Mixture were mixed by using shaker at 130 rpm at 27 °C for within equilibrium time. Then, separated the biosorbent particles and MB solution via centrifuging at 4000rpm for 3s. The residual dye concentration was estimated using the UV–vis spectrophotometric technique at optimum wavelength of 640 nm wavelength. Figure 3.5 shows the addition of macroalgae into MB dye for biosorption.

The MB dye biosorption capacities (qe, mg/g) and the percentage removal (R, %) of MB dye were calculated based on:

$$\mathrm{qe} = \frac{(\mathrm{Ci}-\mathrm{Cf})\mathrm{V}}{\mathrm{M}} \qquad 3.1$$

$$R(\%) = \frac{(Ci-Cf)}{Ci} \times 100 \qquad 3.2$$

Where Ci and Cf (mg/L) are the initial and final MB dye concentration in the solution respectively, M(g) is the macroalgae mass and ∀ (L) is the MB solution volume.

Thereafter, the collected samples were clean with distilled water and put it into the oven at 60 °C for 24 hours to use for desorption test later.

Figure 3.5: Addition of Macroalgae into MB Dye for Biosorption

3.6 Desorption Experiment

Six different chemical reagents such as hydrochloric acid (HCL), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), potassium hydroxide (KOH), sodium chloride (NaCl) and nitric acid (HNO_3) were attempted as eluents (rinsing agent) for desorption experiment. Each of the concentration of eluent was 0.5M for the experiment. Desorption experiments were performed by using conical flask filled with 250 mL of eluents solution. After that, 5 mg of MB dye loaded macroalga powder was added in 25 mL of eluents solution (300 mg/L). Next, the mixture was mixed by using shaker 130 rpm at 27 °C for 120 min. Then, macroalgae mass separated from the blend by centrifuging at 4000 rpm for 4 min. Finally, the concentration of desorption was measured using the UV–vis spectrophotometric technique at optimum wavelength of 640 nm wavelength.

The MB dye desorption capacity ($q_{e,\ desorption}$, mg/g) and desorption efficiency (%) of MB dye were calculated using:

$$q_{e,desorption} = \frac{V(C_f)}{M} \qquad 3.3$$

$$D\ \% = \frac{q_{e,desorption}}{q_{e,biosorption}} \times 100 \qquad 3.4$$

Where $q_{e, desorption}$ is represent as the amount of desorption of dye from per gram of dye saturated sorbent at equilibrium (mg/g), C_f is represent as concentration of MB in the desorbing solution (mg/L), V is the volume of eluent solution (L) and M as weight of dye saturated macroalga. While for D% represent as efficiency of MB dye desorption (%) and $q_{e, desorption}$ and $q_{e, biosorption}$ are MB dye desorption and biosorption capacity (mg/g), respectively. Figure 3.6 shows the condition of the eluent after two hours of desorption experiment and Figure 3.7 shows macroalgae after desorption experiment.

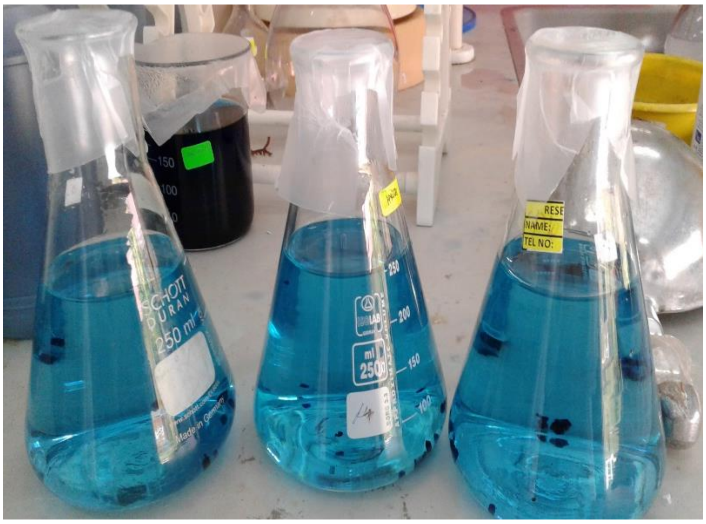

Figure 3.6: Condition of Eluent After Desorption

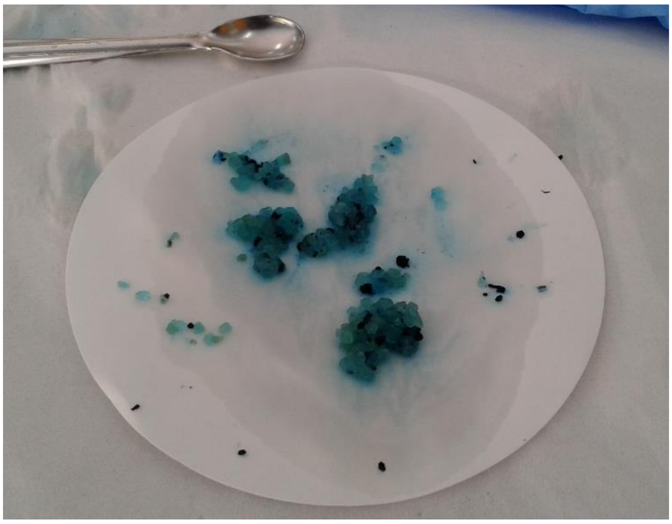

Figure 3.7: Biosorbent After Desorption Process

3.7 Reusability

Reusability experiment was employed by using the most effective eluent (HNO3) to obtain biosorption-desorption successive cycle until biosorbent was not capable to use for dye removal. Next, desorption experiment were conducted using different concentration of eluent which are 1.0M HNO3 and 0.5M HNO3 to observe on the effect of the concentration for dye removal based on pH level (pH 1 to pH 5). Then, distilled water is used as other alternative and to determine it potentiality as low cost eluent for reusability of macroalgae.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The results for this research were gained from laboratory works according to the scope of work in sub chapter 1.4. Based on the results, topic that need to be discuss are preparation of adsorbate and biosorption process, biosorption studies, desorption studies and reusability. The aim of the preparation of adsorbate and biosorption process are to get calibration curve of absorbtion by plotting the graph simultaneously linear equation is gained. While for biosorption studies are discuss about data obtained from the biosoprtion experiment by using optimization condition to conduct the experiment to get maximum biosorption efficiency. Next, the aim for the desorption studies are to get the result to achieve objective one which is to determine the most effective eluent from the six eluents used for the experiment. Meanwhile, the purpose of the result of reusability is to determine on how many successive cycle for the macroalgae to be regenerate after biosorption-desorption process of MB dye, effect of concentration for reusability of macroalgae and potential used of deionized water as low cost eluent.

4.2 Preparation of adsorbate and biosorption process

A stock solution of 1 g/dm3 was prepared by dissolving 1g of the dye in distilled water fill in a 0.5-dm3 volumetric flask to the mark. From this stock solution, working solutions were prepared by serial dilution depend on the desired concentrations, these solution were utilized to generate a calibration curve. The desired solutions follow according to the optimization condition as stated in sub chapter 3.5. The working solutions were prepared six times according to the six differences type of eluents in order to get their own calibration curve as shown in Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6. From the calibration curve, the linear equation, y = mx +

c for each calibration curve as shown in Table 4.1m, Table 4.2, Table 4.3, Table 4.4 and Table 4.5 were obtained in order to get the reading of absorption from UV-vis spectrophotometer. Besides that, linear equation of the calibration curves were essential and also preliminary step for the calculation of biosorption and desorption efficiencies.

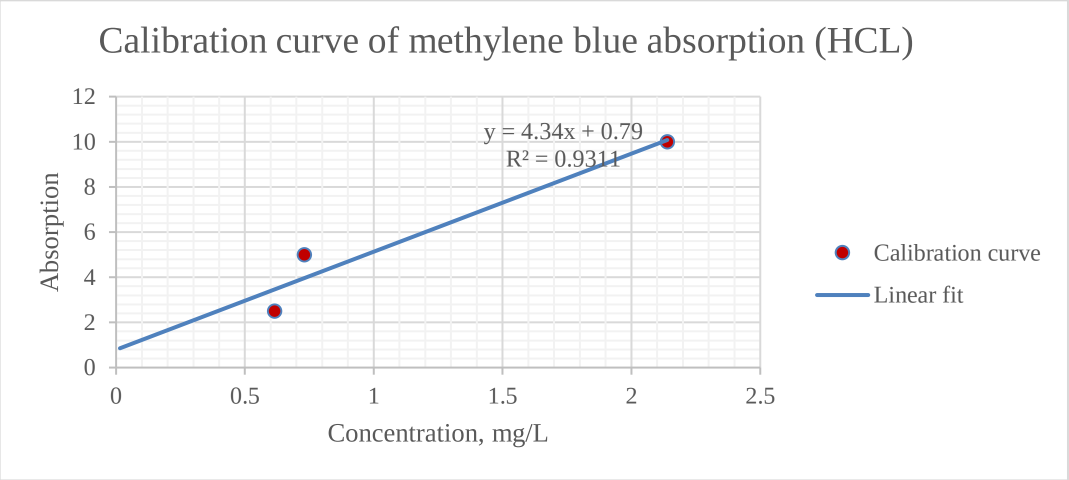

Figure 4.1: Calibration Curve of MB Dye Absorption (HCl)

Table 4.1: Data of Linear Equation of Calibration Curve of MB Dye Absorption (HCl)

Equation	y = a+bx	
Adj. R-square	0.93107	
	Value	Standard error
Intercept	0.79073	1.59774
Slope	4.34208	1.18147

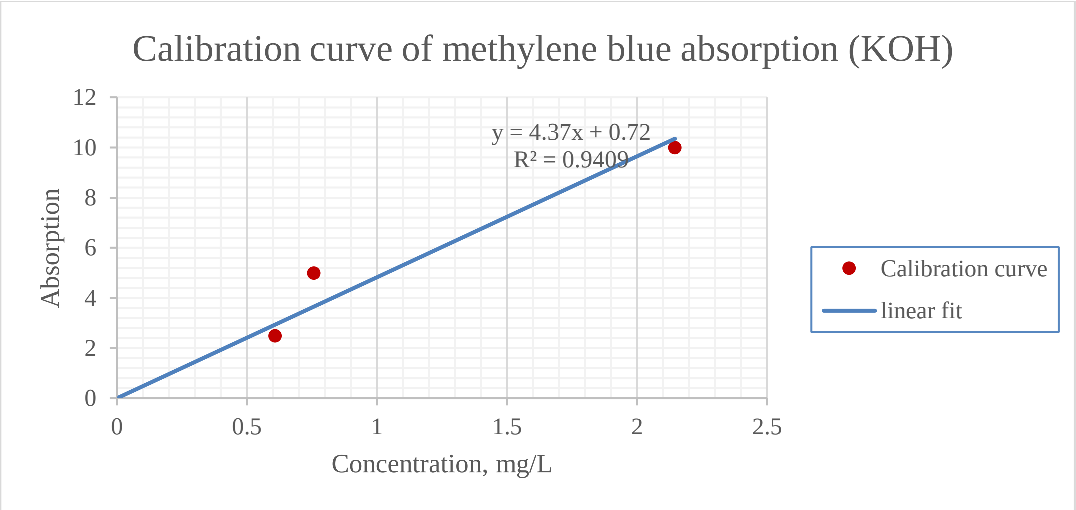

Figure 4.2: Calibration Curve of MB Dye Absorption (KOH)

Table 4.2: Data of Linear Equation of Calibration Curve of MB Dye Absorption

Equation	y = a+bx	
Adj. R-square	0.94094	
	Value	Standard error
Intercept	0.71595	1.48920
Slope	4.37010	1.09481

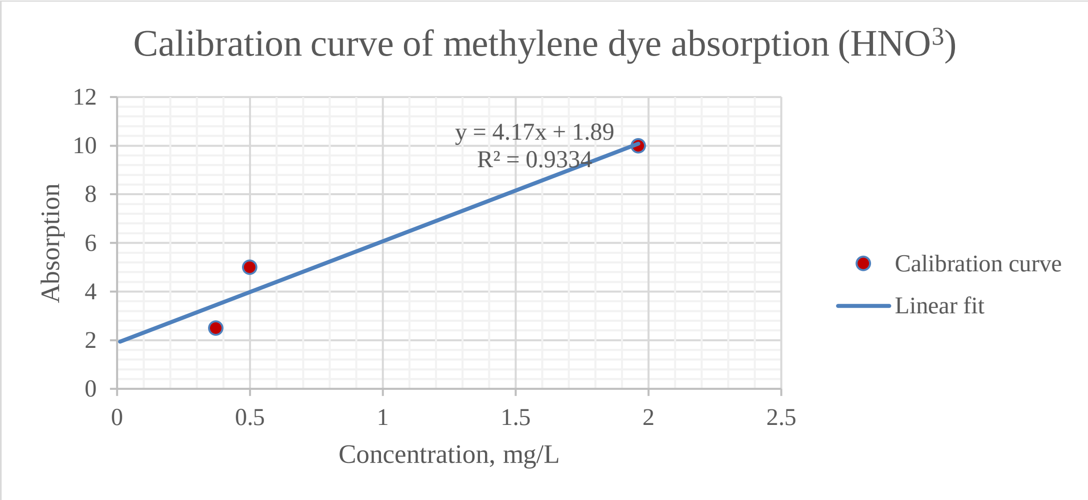

Figure 4.3: Calibration Curve of MB Dye Absorption (HNO^3)

Table 4.3 Data of Linear Eqution of Calibration Curve of MB Dye Absorption (HNO^3)

Equation	y = a+bx	
Adj. R-square	0.93341	
	Value	Standard error
Intercept	1.89315	1.32477
Slope	4.17392	1.11485

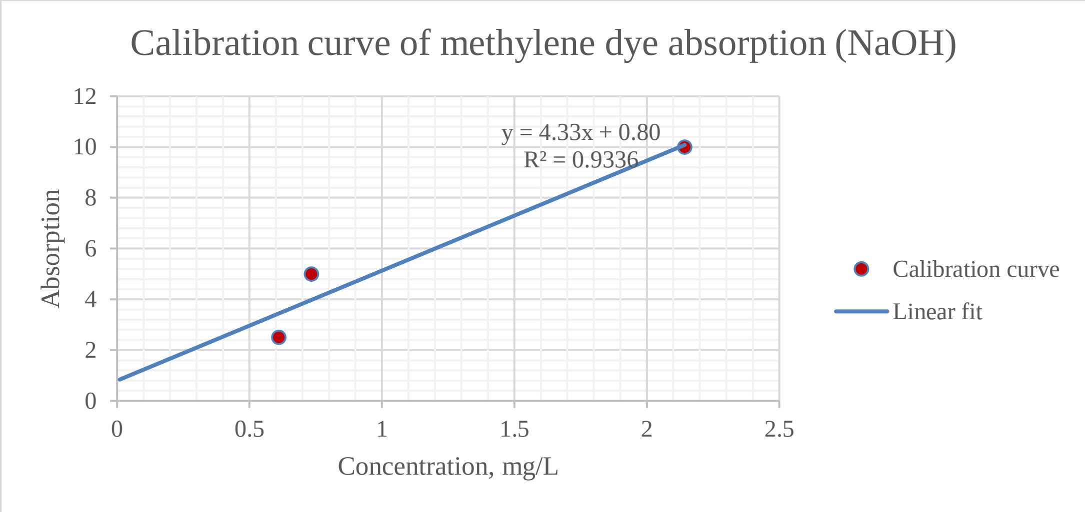

Figure 4.4: Caibration Curve of MB Dye Absorption (NaOH)

Table 4.4: Data of Linear Equation of Calibration Curve MB Dye Absorption (NaOH)

Equation	y = a+bx	
Adj. R-square	0.93361	
	Value	Standard error
Intercept	0.79675	1.56502
Slope	4.33316	1.15550

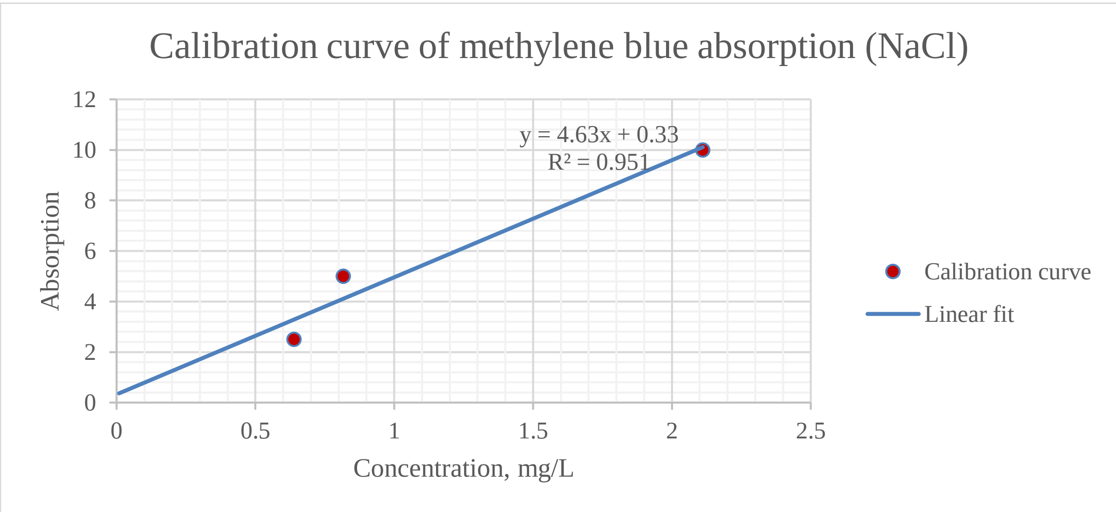

Figure 4.5: Calibration Curve of MB Dye Absorption (NaCl)

Table 4.5: Data of Linear Equation of Calibration Curve MB Absorption (NaCl)

Equation	y = a+bx	
Adj. R-square	0.95104	
	Value	Standard error
Intercept	0.32502	1.42766
Slope	4.63403	1.05149

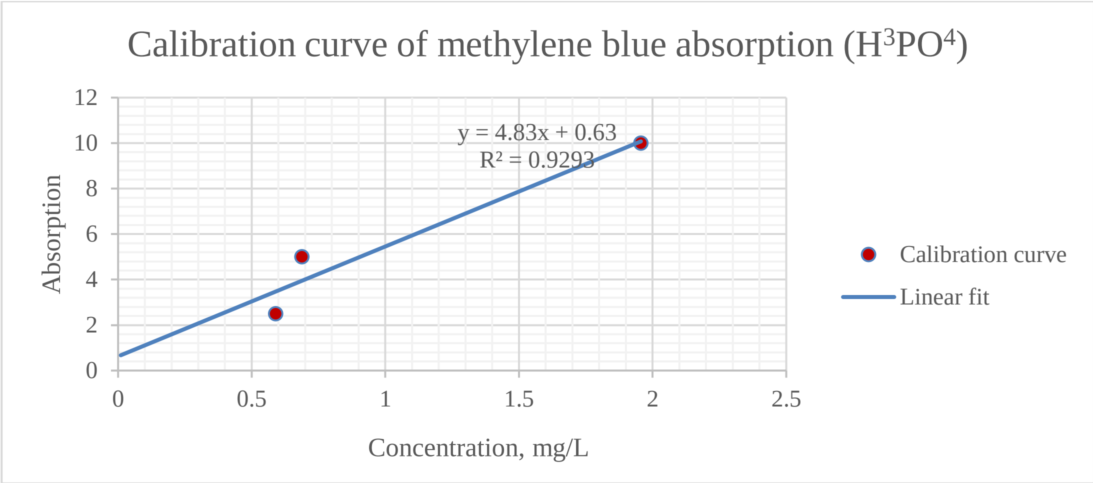

Figure 4.6: Calibration Curve of MB Dye Biosorption (H^3PO^4)

Table 4.6: Data of Linear Equation of Calibration Curve of MB Dye Absorption (H^3PO^4)

Equation	y = a+bx	
Adj. R-square	0.93107	
	Value	Standard error
Intercept	0.62497	1.65858
Slope	4.83151	1.33258

Reusability method involved two experiments which are bisorption and desorption. When any method involving biosorption experiment, it require calibration curve in order to get linear equation. As for this report, reusability obtained four successive cycles of MB dye biosoprtion and desorption process. Hence, calibration curve of the cycle 1 until 4 were obtained as shown in Figure 4.7, Figure 4.8 and Figure 4.9 as well as their linear equations as shown in Table 4.7, Table 4.8 and Table, 4.9. However, the calibration curve and linear equation of cycle 1 similar to the calibration curve and linear equation for nitric acid (HNO_3) eluent (Figure 4.3 and Table 4.3). I t is because this method is continuity from biosorption experiment for HNO_3 eluent.

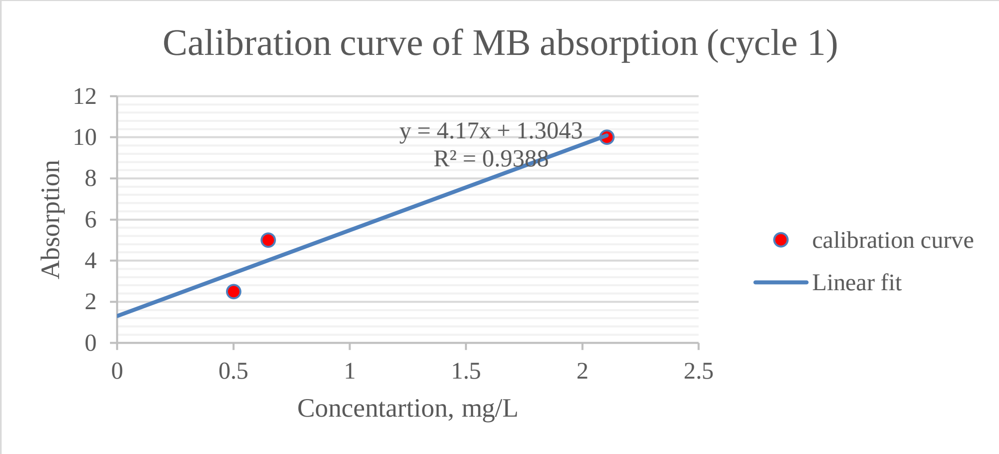

Figure 4.7: Calibration Curve of Cycle 2

Table 4.7: Data of Linear Equation of Cycle 2

Equation	y = a+bx	
Adj. R-square	0.93884	
	Value	Standard error
Intercept	1.30431	1.38954
Slope	4.17422	1.06539

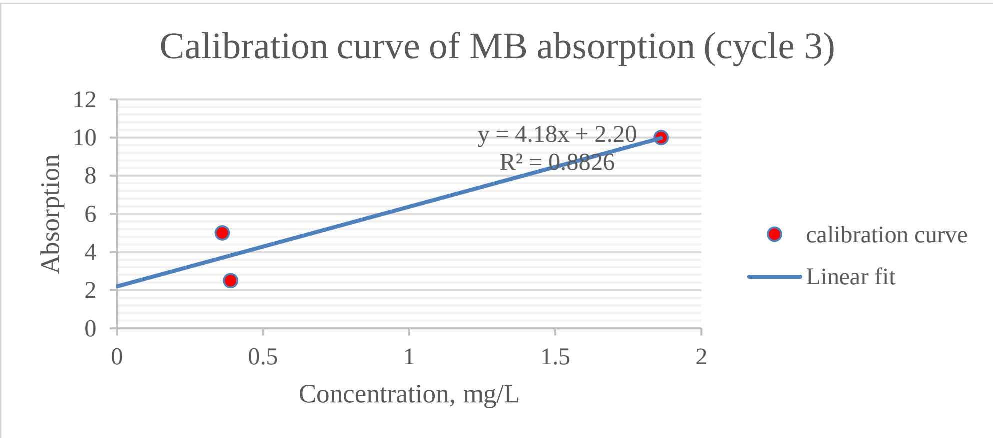

Figure 4.8: Calibration Curve of Cycle 3

Table 4.8: Data of Linear Equation of Cycle 3

Equation	y = a+bx		
Adj. R-square	0.88256		
		Value	Standard error
	Intercept	2.19548	1.70373
	Slope	4.17824	1.52413

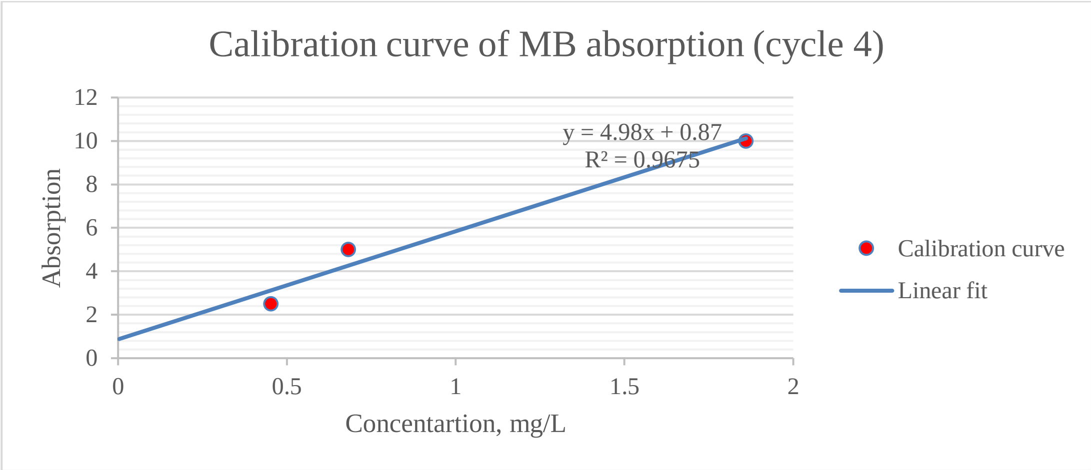

Figure 4.9: Calibration Curve of Cycle 4

Table 4.9: Data of Linear Equation of Cycle 4

Equation	y = a+bx	
Adj. R-square	0.96752	
	Value	Standard error
Intercept	0.86615	1.06966
Slope	4.97547	0.91167

As for reusability experiment that using different concentration of HNO_3, it also involve biosorption of MB dye. Figure 4.9 and Table 4.9 shows the calibration curve and linear equation for that biosorption.

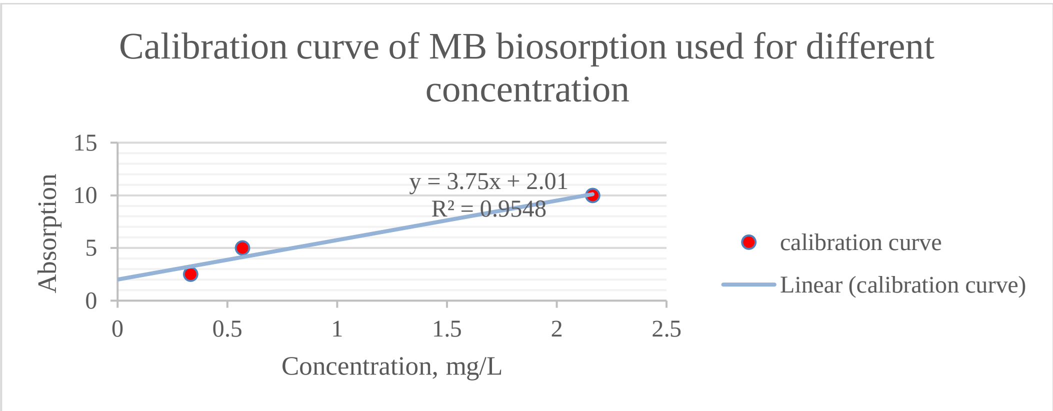

Figure 4.10: Calibration Curve of MB Absorption for Concentration Effect

Table 4.10: Data of Linear Equation of Concentration Effect

Equation	y=a+bx	
Adj. R-square	0.95482	
	Value	Standard error
Intercept	2.00606	1.06412
Slope	3.74733	0.81514

Determination of distilled water (DW) as low cost eluent for reusability of macroalgae, require biosorption process. As biosorption was involved, calibration curve was needed to get the linear equation in order to calculate desorption efficiency using DW. Figure 4.11 showed the calibration curved of MB dye absorption for distilled water (DW) as eluent as well as its linear equation data in Table 4.11.

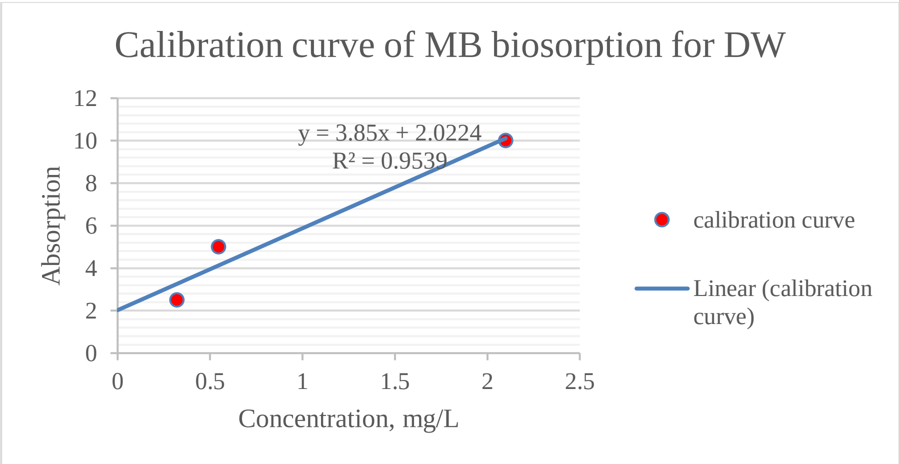

Figure 4.11: Calibration Curve of MB Absorption for DW

Table 4.11: Data of Linear Equation of MB Absorption for DW

Equation	y=a+b^2x	
Adj. R-square	0.95387	
	Value	Standard error
Intercept	2.02236	1.07275
Slope	3.85337	0.84737

4.3 Biosorption Studies

Table 4.12: Removal Efficiency and Sorption Capacity of MB Dye Solutions

Type of eluents	Range of pH	Initial concentration, C_i (mg/L)	Final concentration, C_f (mg/L)	Biosorption Capacity (mg/g), $q_e = \frac{(Ci-Cf)V}{M}$	Percentage Removal (%), $R = \frac{Ci-Cf}{Ci} \times 100$
HCL	7	300	17.788	391.961	94.07
KOH	7	300	16.772	393.372	94.41
HNO_3	7	300	16.457	393.809	94.51
NaOH	7	300	17.543	392.302	94.15
NaCl	7	300	17.600	392.222	94.13
H_3PO_4	7	300	17.911	391.790	94.03

As for the biosorption experiment, the conical flask fill with 250 mL of MB dye (300mg/L) solution was added with 0.81 g of red alga at pH 7 also determine as optimization condition at which maximum sorption capacity can be obtained at parameter used. The range of the pH, dosage of the red alga, volume of MB dye solution and initial concentration were kept constant. The collected dye sorption efficiency were different according to the six type of eluents as shown in Table 4.12. The figure shows the range of maximum percentage removal were in the range from 94.03% to 94.51% which proved the high sorption capacity was in optimization condition. Next, the dye loaded macroalga were utilized for desorption and reusability experiments.

4.4 Desorption Studies

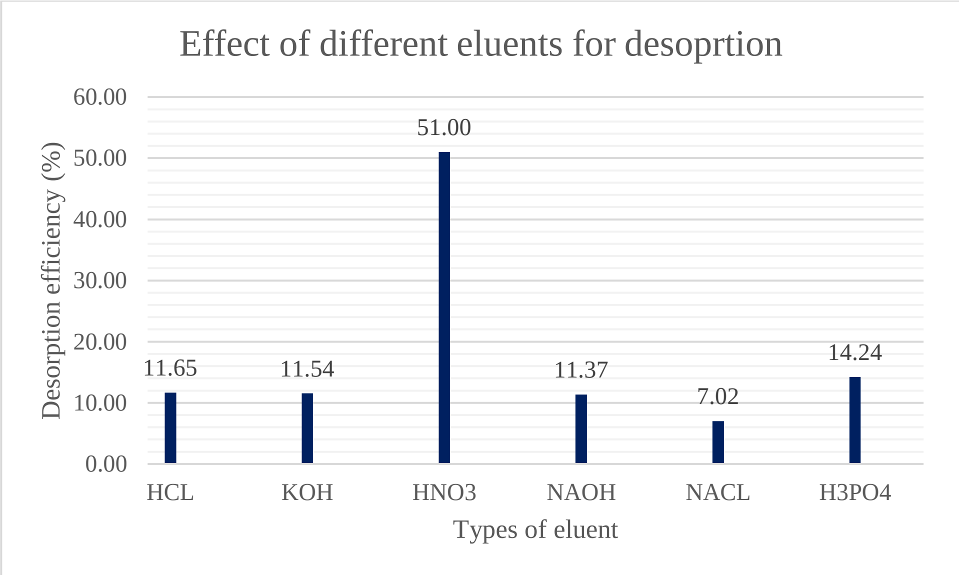

Figure 4.12: Desorption Efficiency vs Types of Eluent

Table 4.13: Percentage of Biosorption-desorption Efficiency of Six Different Eluents

Types of eluent	Biosorption efficiency (%)	Desorption efficiency (%)
Hydrochloric acid (HCl)	94.07	11.65
Potassium Hydroxide (KOH)	94.41	11.54
Nitric Acid (HNO_3)	94.51	51.00
Sodium Hydroxide (NaOH)	94.15	11.37
Sodium Chloride (NaCl)	94.13	7.02
Phosphoric acid (H_3PO_4)	94.03	14.24

Desorption study was sensible to desorb and treated the adsorbed dye including reusability of biosorbent for another cycle of application. The agent of desorbing must be non-polluting, cost effectiveness and not damaging the structure of biosorbent. In this study, desorption experiment was conducted by using six different types of eluent such as HCl, KOH, HNO_3, NaOH, NaCl and H_3PO_4 as chemical rinsing agent after biosorption process to investigate desorption of MB from red macroalga. From Figure 4.12 and table 4.13, it can be seen that the maximum and minimum desorption efficiency of MB were obtained from HNO_3 and NaCl which are 51% and 7.02%, respectively. The low of desorption efficiency of MB by NaCl solution might be due to aviolet-colored complex configuration between eluent and desorbed MB dye in the test solution along with arduousness of measuring dye concentration at optimum wavelength 640nm as stated by Ehsan Daneshvar, 2017.

According to Ehsan Daneshvar, the amount of positively charged located on the biomass rises under condition of acidity. Therefore, desorption efficiency of MB can be increase because of repulsion of electrostatic that occur between cationic dye molecule and positively charged located on the biomass (Hubbe et al., 2012). Furthermore, the maximum desorption efficiency might be due to large amount of H^+ in the acidic solution as well as conversion of the H^+ with the MB ions on macroalgae (Daneshvar *et al.*, 2017). Hence, the desorbing agents primarily contain hydrogen ions (H^+) which are able to produce more cations in the solution are consider as more effective eluents for desorption of cationic dye. Moreover, the factors such as diversion of biomass structures, specific modification and conditions of experiment lead to the dissimilar result in desorption efficiency based on different previous studies (Daneshvar *et al.*, 2017). As a result, nitric acid was selected as the most effective eluent and used for further experiment to investigate the reusability of the macroalgae.

4.5 Reusability

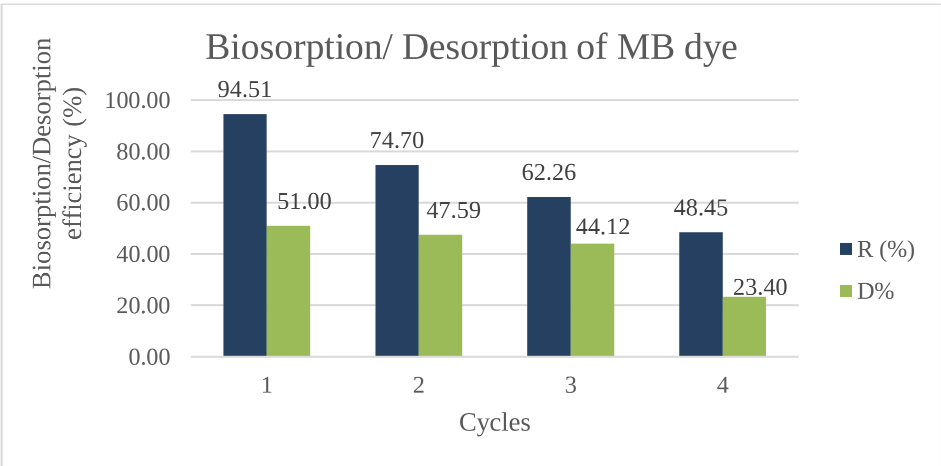

Figure 4.13: Biosorption-desorption Cycles of MB Dye onto E.Spinosum

Table 4.14: Biosorption Efficiency and Desorption Efficiency of the Cycles

	Cycle 1		Cycle 2		Cycle 3		Cycle 4	
Biosorbent	R (%)	D (%)	R (%)	D (%)	R (%)	D (%)	R (%)	D (%)
(E. Spinosum)	94.5	51	74.7	47.59	62.26	44.12	48.45	23.4

The desorbing agent that used for the reusability of the macroalgae was HNO_3 which consider as the best eluent for the regeneration of red seaweed among all of the eluents use for desorption study. The reusability of biosorbents in various biosorption-desorption cycles is exceptional advantage for sludge management and economical applications.

Figure 4.13 shows the four successive cycles of biosorption-desorption tests were gained. The percentage of biosoprtion efficiency (R %) and desorption efficiency (D %) were presented in Figure 4.13 and Table 4.14. The graph showed that the percentage of biosorption efficiency was decreased significantly from cycle 1 to cycle 2 which is from 94.5% to 74.50% .Then, it steadily decreased from 74.7% to 62.26 % in cycle 2 to cycle 3. However it continued decreased crucially from cycle 3 to cycle 4 which is 62.6% to 48.45%. While for desorption efficiency, the data showed it decreased gradually from cycle 1 to cycle 4 which is 51% to 44.12%. Despite that, from cycle 3 to the last cycle the percentage of desorption efficiency was greatly decreased which is from 44.12% to 23.4%.

The factors of the result of biosorption efficiency percentage might be due to protonation of certain biosorption location or the presence of functional group on the surface of macroalga by acidic eluent, the saturation of the accessible binding spot on the biosorbent by molecules of MB dye and disintegration of macroalga particles upon consecutive biosorption-desorption cycles (Daneshvar *et al.*, 2017). For desorption efficiency, the high desorption efficiency at cycle 1 (51%) might be due to biosorption occur at the external surface of macroalgae. While from Table 4.13 showed the lowest desorption efficiency is 23% which probably due to strong chemical interaction of biosorbent that prevent desorption of MB dye (Abdellaoui, Pavlovic, Bouhent, Benhamou and Barriga, 2017). From the result both biosorption and desorption efficiency percentage, it indicated that desorption efficiency was low than biosoprtion efficiency due to some heterogeneity present on the surface of macroalga and some binding spot with greater energy (Daneshvar *et al.*, 2017).

4.5.1 Effect of Concentration

Apart from that, the effect of the concentration is being observed to check whether it effect on desorption efficiency for reusability of E.Spinosum. However, desorption efficiency is investigate using different pH level from pH 1 to pH 5. The result are as follow in which Cf is final concentration (mg/L), while qf represent amount of dye desorption from per gram of dye saturated macroalga(mg/g):

Table 4.15: Desorption Efficiency of MB Dye in 0.5M and 1.0M of HNO_3 Concentration

	0.5 M			**1 M**		
pH	Cf	qf	D%	Cf	qf	D%
1	2.173	108.656	27.42	2.535	126.750	31.98
2	2.123	106.125	26.78	2.280	114.000	28.76
3	2.093	104.625	26.40	2.145	107.250	27.06
4	2.053	102.656	25.90	2.089	104.438	26.35
5	2.016	100.781	25.43	2.038	101.906	25.71

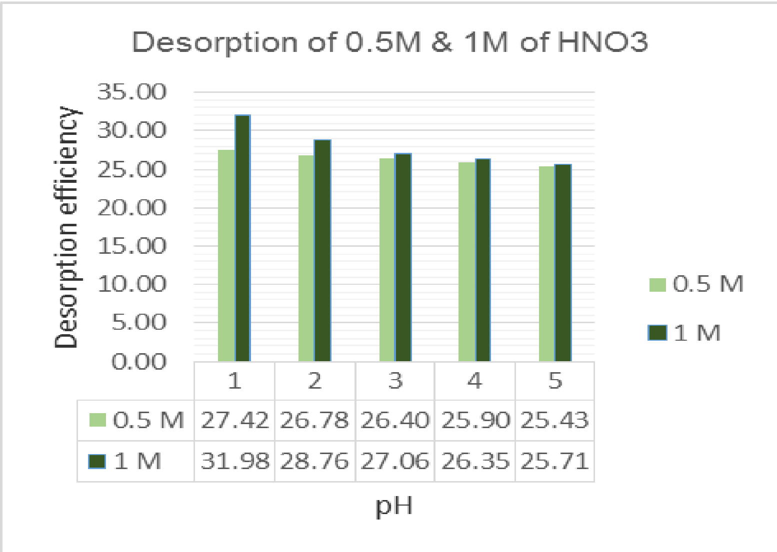

Figure 4.14: Desorption Efficiency of 0.5M and 1.0M of Nitric Acid

According to Figure 4.14, it showed that desorption capacity was slowly decreased from 27.42% to 25.43% at pH 1 until pH 5 respectively for desorption of MB dye in 0.5M of HNO_3. While desorption efficiency of MB dye in 1.0M of HNO_3 was moderately decreased from 31.98% at pH 1 to 28.76% at pH 2. Then, it starting to decreased gradually from 28.76% to 25.71% at pH 2 until pH 5. From the result obtained, it is foremost to mention that the desorption efficiency are drop due to dilution of eluent (Bernardo, Rene and Alfaro-De la, 2009). As compare with 1.0M HNO_3 concentration, desorption efficiencies were greater than desorption efficiency in 0.5M HNO_3 from pH 1 to pH 5. However, high concentration may lead to the destruction of biosorbent structure (Abdolali *et al.*, 2015), to tackle this problem further studies need to be carried out with other eluent with low concentration to minimize possible damage on biosorbent structure.

4.5.2 Potential Used of Deionized Water as Low Cost Eluent

Table 4.16: Result of Percentage of Desorption Efficiency Using Distilled Water (DW)

Ph	Cf (mg/L)	qe (mg/g)	D%
1	2.082	104.080	26.26
2	2.043	102.155	25.77
3	1.839	91.953	23.20
4	1.751	87.525	22.08
5	1.739	86.948	21.94

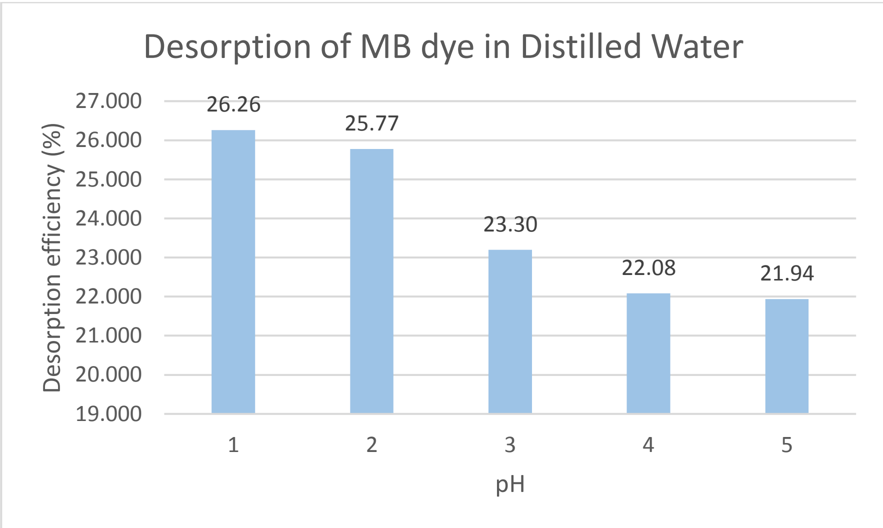

Figure 4.15: Desorption of MB Dye in Distilled Water (DW)

As for other alternative, distilled water was used and to determine as potential used as low cost eluent. High concentration of HNO_3 contain high acid content, so it required high cost for treatment process and damaging biosorbent structure (Abdolali *et al.*, 2015), to improve the problem, distilled water is employ. Based on the Figure 6, desorption efficiency was gradually drop from 26.26% to 21.94% from pH 1 to pH 2. Then, it decreased significantly from 25.77% to 23.30% from pH 2 to pH 3. However, desorption efficiency slightly fall starting from 23.30% (pH3) to 21.94 (pH5). In addition, the result also indicated that the maximum desorption efficiency was 26.26% at pH 1 which more acidity than minimum desorption efficiency at pH 5, 21.94% which low acidity. This situation occurs due to high content of acid that have strong electrostatic energy to attract MB dye molecule from the surface of macroalga (Tassist *et al.*, 2009). Therefore, it can be conclude that deionized water is potential to be used as low cost eluent for dye treatment.

CHAPTER 5

CONCLUSION

5.1 Introduction

In chapter 5, all of the results obtained will be conclude according to the objectives of the project. The objectives of the project are to determine the most effective eluent among the six types of eluent and to investigate the reusability of the macroalgae for dye removal. Recommendation also will be made to improve the results obtained to be more accurate and effective.

5.2 Conclusion

As conclusion, from the desorption studies, the result showed that the most effective eluent for MB dye removal was hydrochloric acid (HNO_3) among the other six types of eluent. The best eluent was determined based on maximum desorption efficiency that found to be 51% by HNO_3. The result denotes that the conversion of hydrogen H+ takes place in the acidic reagent with absorbed the molecules of MB dye on the surface of macroalga (Daneshvar et al., 2017). Then, HNO_3 was used to investigate the reusability of the macroalga in which four successive cycles were achieved. Moreover, the effect of the concentration found that high concentration, 1.0M HNO_3 have high desorption efficiency than low concentration 0.5M HNO_3. However, high concentration may lead to the destruction of biosorbent structure (Abdolali et al., 2015), to tackle this problem further studies need to be carried out with other eluent with low concentration to minimize possible damage on biosorbent structure. In addition, high acidic concentration is costly more in dye treatment process. Therefore, distilled water was used and determine as low cost eluent. According to the result, desorption efficiency of DW was success to be obtained at different level of pH, this indicated that DW can be used for reusability of macroalga and has potential used as low cost eluent for dye removal. Overall, the results of this study suggest that studied macroalga is acceptable to be use as environmentally friendly and efficient sorbent for dye removal.

5.3 Recommendations

Based on the result, the four successive cycle of biosorption-desorption experiments showed that reusability was investigated however not satisfied as expected outcome which five successive cycle was obtained referring to previous studies due to low desorption efficiency. As for improvement, the acid eluent should mix with alcohol that can improve desorption efficiency as stated by Ehsan Daneshvar, 2017. For example, from the previous study they used the mixture of 1-butanol and HCl that remarkably enhanced desorption efficiency due to electrostatic attraction and also hydrophobic interaction including H-bonding that attach MB dye to the alga mass (Daneshvar *et al.*, 2017).

Besides that, desorption also can carry out by applying electric field through eluent which called as forced desorption. According to the previous study, the advantageous of forced desorption are enhances the desorption flow by escalating the concentration gradient and convince a better stabilization of the desorbent acid pH by generating H^+ ions at the anode via water oxidation (Tassist *et al.*, 2009).

In a nutshell, the recommendations the used of the mixture of alcohol and acid based including application of electric field for desorption experiment can be alternatives to improve desorption efficiency, so that data analysed is satisfactory for the research of reusability of macroalgae.

REFERENCES

Abdellaoui, K., Pavlovic, I., Bouhent, M., Benhamou, A. and Barriga, C. (2017) ‘A comparative study of the amaranth azo dye adsorption/desorption from aqueous solutions by layered double hydroxides’, *Applied Clay Science*. Elsevier B.V., 143, pp. 142–150. doi: 10.1016/j.clay.2017.03.019.

Abdellaoui, K., Pavlovic, I., Bouhent, M., Benhamou, A., Barriga, C., *et al.* (2017) ‘Studies on sorption, desorption, regeneration and reuse of sugar-beet pectin gels for heavy metal removal’, *Journal of Environmental Chemical Engineering*. Elsevier Ltd, 140(1–3), pp. 480–490. doi: 10.1016/j.clay.2017.03.019.

Abdolali, A. *et al.* (2015) ‘Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies’, *Bioresource Technology*. Elsevier Ltd, 193, pp. 477–487. doi: 10.1016/j.biortech.2015.06.123.

Activated Carbon For Drinking Water (2018) *Decarbons.com*. Available at: http://www.deqcarbons.com/drinking-water/ (Accessed: 13 June 2018).

‘Alam sekitar’ (2015).

Alina Bradford (2018) *Pollution Facts & Types of Pollution*, *Live Science*. Available at: https://www.livescience.com/22728-pollution-facts.html (Accessed: 22 May 2018).

Bakar, J. M. A. (2016) ‘Kualiti air sungai Malaysia membimbangkan’. Available at: http://www.utusan.com.my/sains-teknologi/alam-sekitar/kualiti-air-sungai-malaysia-membimbangkan-1.334427 (Accessed: 13 May 2018).

Bernama (2016) *43 Rivers In Malaysia Polluted, Says Minister*, *malaysiandigest.com*. Available at: http://malaysiandigest.com/news/613026-43-rivers-in-malaysia-polluted-says-minister.html (Accessed: 13 May 2018).

Bernardo, G. R. R., Rene, R. M. J. and Alfaro-De la, A. D. la T. (2009) ‘Chromium (III) uptake by agro-waste biosorbents: Chemical characterization, sorption-desorption studies, and mechanism’, *Journal of Hazardous Materials*, 170(2–3), pp. 845–854. doi: 10.1016/j.jhazmat.2009.05.046.

Brown algae are used for fibromyalgia, cancer, osteoarthritis (2010) *Pinterest.com*. Available at: https://www.pinterest.com/pin/319474167287527415/?lp=true (Accessed: 13 May 2018).

Cai, J. *et al.* (2017) ‘Review of physicochemical properties and analytical characterization of lignocellulosic biomass’, 76(October 2016), pp. 309–322. doi: 10.1016/j.rser.2017.03.072.

Coagulation and flocculation in wastewater treatment (2013) *Aquarden Technologies*.

Available at: http://aquarden.com/technology/coagulation-and-flocculation/ (Accessed: 13 June 2018).

Construction & Demolition — Marketplace (2016) *Tennessee Materials Marketplace*. Available at: http://tennessee.materialsmarketplace.org/construction-demolition/ (Accessed: 13 June 2018).

Daneshvar, E. *et al.* (2017) 'Desorption of Methylene blue dye from brown macroalga: Effects of operating parameters, isotherm study and kinetic modeling', *Journal of Cleaner Production*. Elsevier Ltd, 152, pp. 443–453. doi: 10.1016/j.jclepro.2017.03.119.

David Wolfe (2015) *Eat 5 Walnuts & Wait 4 Hours: This is What Will Happen To You! - DavidWolfe.com*. Available at: https://www.davidwolfe.com/eat-5-walnuts-wait-4-hours-this-is-what-will-happen-to-you/ (Accessed: 13 June 2018).

Edward Noah Abrahart, J. B. S. (2011) *dye | Definition & Types | Britannica.com*. Available at: https://www.britannica.com/technology/dye (Accessed: 11 June 2018).

Feryal Jamal Kherissat (2014) *Kelp Forest*. Available at: https://www.slideserve.com/ehren/by-feryal-jamal-kherissat (Accessed: 22 June 2018).

Five Techniques for Sustainable Building Construction (2015) *For Construction Pros*. Available at: https://www.forconstructionpros.com/business/article/12068798/five-techniques-for-sustainable-building-construction (Accessed: 13 June 2018).

Frechen. (2014) *Handbook of environmental odour management.* IWA Publishing.

Granular activated carbon (2015). Available at: https://www.dreamstime.com/stock-photo-granular-activated-carbon-water-filter-texture-background-image50378304 (Accessed: 13 June 2018).

Hashim, M. A. and Chu, K. H. (2008) 'Biosorption of cadmium by brown, green, and red seaweeds', *Chemical Engineering Journal*, 97(2–3), pp. 249–255. doi: 10.1016/S1385-8947(03)00216-X.

Henry Nowicki, G. N. (2016) *The basics of activated carbon adsorption*. Available at: https://www.watertechonline.com/the-basics-of-activated-carbon-adsorption/ (Accessed: 13 June 2018).

Hubbe et al. (2012) 'Cellulosic Substrates for Removal of Pollutants From Aqueous Systems: A Review. 2. Dyes', 7, pp. 2592–2687.

Introduction to seaweeds (2010). Available at: http://www.niobioinformatics.in/seaweed/introduction.htm (Accessed: 13 May 2018).

Jabatan Alam Sekitar (2015) *Pengenalan kepada Status Kualiti Air Sungai | Jabatan Alam Sekitar*. Available at: https://www.doe.gov.my/portalv1/info-umum/kualiti-air-sungai/275 (Accessed: 13 May 2018).

Jean-Francois Denault (2018) *Cellulosic ethanol*. Available at: https://www.britannica.com/technology/cellulosic-ethanol (Accessed: 13 June 2018).

Kike Calvo (2011) *city dump*. Available at: https://www.alamy.com/stock-photo-la-chureca-spanish-slang-word-for-city-dump-is-the-municipal-domestic-43196632.html (Accessed: 13 June 2018).

M.D Guiry (2014) *The Seaweed Site: information on marine algae*. Available at: http://www.seaweed.ie/algae/ulva.php (Accessed: 13 May 2018).

Mahmoodi, N. M. *et al.* (2011) 'Preparation, characterization and dye adsorption properties of biocompatible composite (alginate/titania nanoparticle)', *Desalination*. Elsevier B.V., 275(1–3), pp. 93–101. doi: 10.1016/j.desal.2011.02.034.

Malaysia air quality 'unhealthy' as haze obscures skies (2014) *malaymail.com*. Available at: https://www.malaymail.com/s/716465/malaysia-air-quality-unhealthy-as-haze-obscures-skies#jBMIXyjSxpC7i2oz.97 (Accessed: 13 May 2018).

Membrane Filtration (2009). Available at: https://www.sswm.info/sswm-university-course/module-6-disaster-situations-planning-and-preparedness/further-resources-0/membrane-filtration (Accessed: 13 June 2018).

Membrane processes (2009) *Fuma Tech*. Available at: https://www.fumatech.com/EN/Membrane-processes/index.html (Accessed: 13 June 2018).

Mokhtar, N. *et al.* (2017) 'Journal of Environmental Chemical Engineering Biosorption of azo-dye using marine macro-alga of Euchema Spinosum', *Journal of Environmental Chemical Engineering*. Elsevier, 5(6), pp. 5721–5731. doi: 10.1016/j.jece.2017.10.043.

Pandimurugan, R. and Thambidurai, S. (2016a) 'Novel seaweed capped ZnO nanoparticles for effective dye photodegradation and antibacterial activity', *Advanced Powder Technology*. doi: 10.1016/j.apt.2016.03.014.

Pandimurugan, R. and Thambidurai, S. (2016b) 'Synthesis of seaweed-ZnO-PANI hybrid composite for adsorption of methylene blue dye', *Journal of Environmental Chemical Engineering*. Elsevier B.V., 4(1), pp. 1332–1347. doi: 10.1016/j.jece.2016.01.030.

Pang, Y. L. and Abdullah, A. Z. (2013) 'Current Status of Textile Industry Wastewater Management and Research Progress in Malaysia: A Review', *CLEAN - Soil, Air, Water*. Wiley-Blackwell, 41(8), pp. 751–764. doi: 10.1002/clen.201000318.

Phytoplankton (2018). Available at: https://reefphyto.co.uk/collections/phytoplankton (Accessed: 22 June 2018).

Prashant Lokare (2013) *Sodium Alginate*. Available at: http://www.viiprachemicals.com/sodium-alginate--1597962.html (Accessed: 22 June 2018).

Published (2015) *Different Types of Pollution: Causes of Water, Air, Soil, Thermal, Light and Noise Pollution, readanddigest.com*. Available at: https://readanddigest.com/what-are-different-types-of-pollution/ (Accessed: 13 May 2018).

Rebecca Lake (2017) *Types of Environmental Pollutants*, *Livestrong.com*. Available at: https://www.livestrong.com/article/177248-how-do-factories-pollute-the-air/ (Accessed: 22 May 2018).

Seaweed (2017) *Seagrass LI*. Available at: http://www.seagrassli.org/ecology/fauna_flora/seaweed.html (Accessed: 22 June 2018).

Sohbatzadeh, H. *et al.* (2017) 'Insights into the biosorption mechanisms of U(VI) by chitosan bead containing bacterial cells: A supplementary approach using desorption eluents, chemical pretreatment and PIXE–RBS analyses', *Chemical Engineering Journal*. Elsevier B.V., 323, pp. 492–501. doi: 10.1016/j.cej.2017.04.088.

Stubble Digest (2018) *Soil Technologies Corp*. Available at: https://www.soiltechcorp.com/product/stubble-digest (Accessed: 13 June 2018).

Susan Berg (2017) *Types of Pollutants, Sciencing.com*. Available at: https://sciencing.com/types-pollutants-5270696.html (Accessed: 22 May 2018).

Tassist, A. *et al.* (2009) 'Removal and recovery of copper from aqueous solutions by Streptomyces rimosus biomass: Enhancement of regeneration by desorption-electrolysis coupling', *Desalination and Water Treatment,* 3(1–3). doi: 10.5004/dwt.2009.462.

Types of Biomass (2012) *amtsolar.com*. Available at: http://www.amt-solar.com/index.php/en/biomasse/types-of-biomass (Accessed: 13 May 2018).

Tyrone Clarke (2016) *Coastal Communities*. Available at: http://slideplayer.com/slide/6618482/# (Accessed: 22 June 2018).

Wang, J. and Chen, C. (2009) 'Biosorbents for heavy metals removal and their future', *Biotechnology Advances*. Elsevier Inc., 27(2), pp. 195–226. doi: 10.1016/j.biotechadv.2008.11.002.

Wong, S. *et al.* (2017) 'From pollutant to solution of wastewater pollution: Synthesis of activated carbon from textile sludge for dye adsorption', *Chinese Journal of Chemical*

Engineering. Elsevier B.V. doi: 10.1016/j.cjche.2017.07.015.

APPENDIX A
SAMPLE APPENDIX 1

Figure 5.1: Macroalgae Dried in an Oven

Figure 5.2: Sieve (size:0.7-1.5mm)

Figure 5.3: Preparation of MB Dye

Figure 5.4: Eluent Fill in Median Bottles

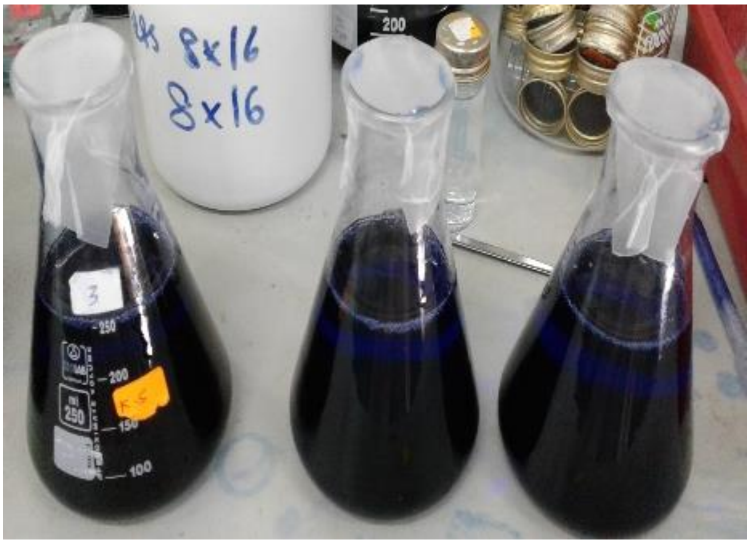

Figure 5.5: MB Dye for Biosorption

Figure 5.6: Desorption of MB Dye

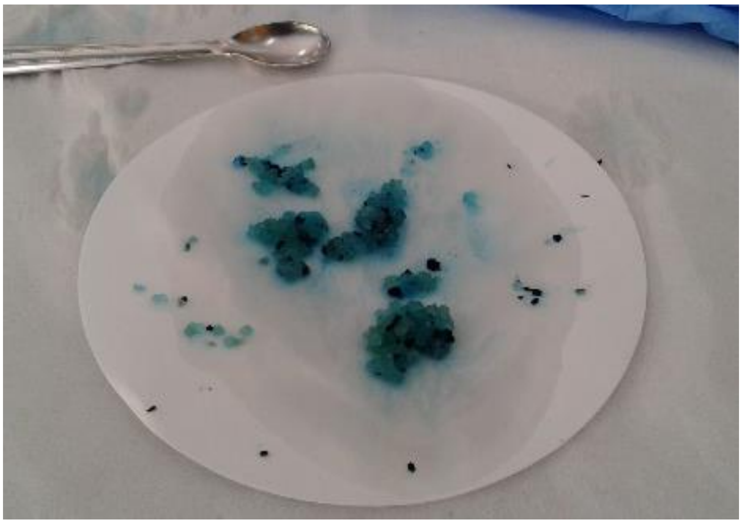

Figure 5.7: MB Dye Loaded Macroalgae

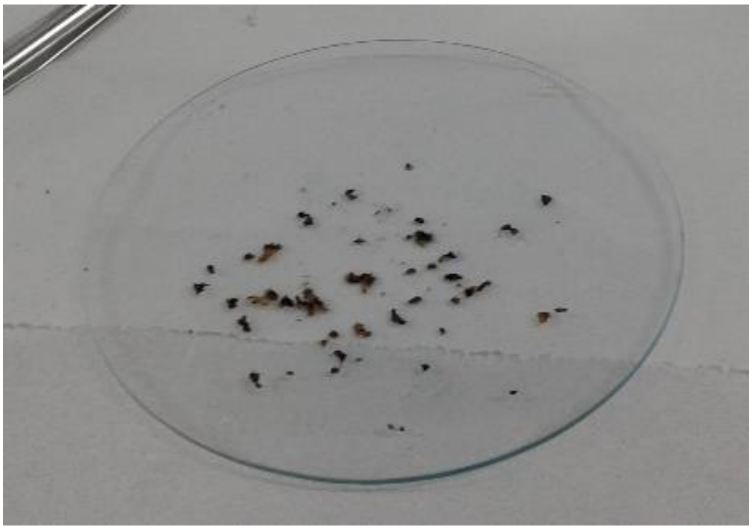

Figure 5.8: Dried Macroalgae After Desorption