

PERFORMANCE OF RED SEAWEED FOR
AZO DYE REMOVAL : ACID YELLOW 17

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REMOVAL : ACID YELLOW 17

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ABSTRAK

Efluen yang dirawat oleh industri kebiasaannya mempunyai kuantiti pewarna yang boleh dikesan. Efluen yang mengandungi pewarna akan memberi nilai estetik yang tidak menarik, merbahaya dan akan menimbulkan masalah alam sekitar. Efluen selalunya mengandungi sejumlah bahan cemar dan sisa pencemaran. Dalam usaha untuk menghapuskan pewarna ini, terdapat tiga kaedah yang dapat diguna pakai iaitu kaedah biologi, kaedah kimia dan kaedah fizikal. Salah satu kaedah fizikal, penjerapan adalah antara teknik yang paling berkesan untuk penyingkiran pewarna dari air sisa rawatan. Penjerapan adalah cara yang berkesan untuk membuang pewarna sintetik dari efluen perindustrian. Oleh itu, kajian ini dilakukan untuk menunjukkan mekanisme penyingkiran serapan daripada kationik pewarna asid kuning 17 (AY17) daripada larutan akueus dengan menggunakan biomas kering daripada rumput laut *Euchema Spinosum* sebagai biosorben. Kajian ini bertujuan untuk menentukan peratusan penyingkiran pewarna oleh rumput laut dan keadaan optimum penyingkiran pewarna di dalam empat parameter, masa sentuhan, pH, dos biosorben dan kepekatan awal. Berdasarkan hasil kajian, biomas menunjukkan kapasiti pembuangan perwarna dengan nilai tertinggi pada nilai pH awal 7, dos biosorben 0.04g, masa sentuhan 60 minit dan kepekatan awal pada 100 mg/L. Keputusan penjerapan dalam kajian ini menunjukkan bahawa semua penjerap memberi kesan untuk menyingkirkan pewarna daripada efluen industri.

ABSTRACT

In the treated effluents of industries, dyes are usually present in trace quantities. The untreated wastewaters containing dyes are aesthetically unpleasant and toxic which will greatly affect and pose environmental problems. The effluents commonly contain an amount of pollutants and contaminants. In order to remove these dyes, there are three methods available, which consists of biological method, chemical method and physical method. One of the physical method, adsorption is among the most effective techniques for dye removal from wastewater. Adsorption is an efficient way to remove synthetic dyes from industrial effluent. Therefore, this study was carried out to show mechanism of adsorptive removal of cationic dye acid yellow 17 (AY17) from its aqueous solution using dried biomass of seaweed *Euchema Spinosum* as a biosorbent. This study aims to determine the percentage of dye removal by seaweed and the optimum condition of dye removal in four parameters, which includes contact time, pH, biosorbent dosage and initial concentration. The results showed that the biomass exhibited the highest dye uptake capacity at initial pH value of 7, biosorbent dosage of 0.04g, contact time of 60 minutes and initial concentration of 100 mg/L. The adsorption results in this study indicated that the adsorbents were attractive candidates for removing acidic dyes from dye wastewater.

TABLE OF CONTENT

DECLARATION

TITLE PAGE

ACKNOWLEDGEMENTS	ii
ABSTRAK	iii
ABSTRACT	iv
TABLE OF CONTENT	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF SYMBOLS	x
LIST OF ABBREVIATIONS	xi
CHAPTER 1 INTRODUCTION	1
1.1 Background of Study	1
1.2 Problem Statement	5
1.3 Objectives	5
1.4 Scope of Study	6
CHAPTER 2 LITERATURE REVIEW	7
2.1 Introduction	7
2.2 Classification of Dyes	8
2.3 Problems Associated with Dyes	10
2.3.1 Method In Removal Of Dye Compounds	11
2.3.2 Biological Method	11

2.3.3	Chemical Method	12
2.3.4	Physical Method	12
2.4	Adsorption	13
2.5	Acid Yellow 17 Dye	15
2.6	Marine Seaweed As Biosorbent	16
2.6.1	Classification of Marine Seaweed	16
2.6.2	Uses of Seaweed	17
2.6.3	Euchema Spinosum (Red Seaweed)	18
CHAPTER 3 METHODOLOGY		21
3.1	Introduction	21
3.2	Preparation and Characterization of Biosorbent	22
3.3	Point of zero charge	24
3.4	Preparation of dye solution	24
3.5	Analytical measurements	26
3.5.1	Calibration Curve	26
3.5.2	Calculation of uptake capacity (q_e)	27
3.5.3	Calculation of percentage removal of dye	27
3.5.4	Effect of change in contact time on adsorption	28
3.5.5	Effect of change in absorbent dosage of seaweed on adsorption	29
3.5.6	Effect of change in pH of solution on adsorption	29
3.5.7	Effect of change in initial concentration of solution on adsorption	29
CHAPTER 4 RESULTS AND DISCUSSION		30
4.1	Introduction	30
4.2	Point of zero change	30

4.3	Effect of change in contact time on adsorption	31
4.4	Effect of change in absorbent dosage of seaweed on adsorption	35
4.5	Effect of change in pH of solution on adsorption	39
4.6	Effect of change in initial concentration of solution on adsorption	41
CHAPTER 5 CONCLUSION		44
5.1	Conclusion	44
REFERENCES		45

LIST OF TABLES

Table 4.1	Readings of initial pH, final pH, and difference in pH	30
Table 4.2	Different concentrations of dye solution	30
Table 4.3	The tabulation of data for contact time for removal of dye by Acid Yellow 17	30
Table 4.4	Different concentrations of dye solution	30
Table 4.5	The tabulation of data for dosage for removal of dye by Acid Yellow 17	30
Table 4.6	The tabulation of data for pH for removal of dye by Acid Yellow 17	30
Table 4.7	Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye	41
Table 4.8	Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye	41 - 42
Table 4.9	Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye	42

LIST OF FIGURES

Figure 1.1	The dyeing of fabric process	2
Figure 1.2	Advantages and disadvantages of physical and chemical methods of dye removal	3
Figure 1.3	<i>Euchema Spinosum</i>	4
Figure 2.1	The breakdown of dyes	9
Figure 2.2	Method of removal of dyes for textile effluents	11
Figure 2.3	Adsorption, where molecules will stick to the surface of the solid	14
Figure 2.4	The reaction between the ions of the molecules	14
Figure 2.5	The chain structure of Acid Yellow 17	15
Figure 2.6	Acid Yellow 17 in powder form	16
Figure 2.7	Brown algae, green algae, red algae	17
Figure 2.8	The location of red seaweed, Semporna, Sabah	18
Figure 2.9	<i>Euchema Spinosum</i> or also known as <i>Eucheuma denticulatum</i>	19
Figure 3.1	Process flow of removal of Acid Yellow 17 by <i>E. Spinosum</i> seaweed	21
Figure 3.2	Raw seaweed in its moist condition	22
Figure 3.3	Seaweed was first washed and rinsed with tap water, was thoroughly washed with doubly distilled water.	22
Figure 3.4	Seaweed was oven-dried at 60°C for 24 hours	23
Figure 3.5	Dried seaweed	23
Figure 3.6	Dried seaweed was blended to desired particle sizes, 0.7mm – 1.5mm	24
Figure 3.7	201987 SIGMA-ALDRICH Acid Yellow 17 dye	25
Figure 3.8	100mg/L Acid Yellow 17 dye	25
Figure 3.9	Vials containing mixed solution was placed in shaker	28
Figure 4.1	Graph of difference in pH against initial pH	31
Figure 4.2	Analysis of the dye concentrations	32
Figure 4.3	Effect of contact time on removal of Acid Yellow 17	34
Figure 4.4	Analysis of the dye concentrations	36
Figure 4.5	Effect of dosage on removal of Acid Yellow 17	38
Figure 4.6	Effect of pH on removal of Acid Yellow 17	40
Figure 4.7	Effect of concentrations on removal of Acid Yellow 17	43

LIST OF SYMBOLS

AY17	Acid Yellow 17
FAO	Food and Agriculture Organization of the United Nations
UV	Ultraviolet
ZPC	Zero Point of Charge
Fe	Iron
Ca	Calcium
OH	Hydroxide
DNA	Deoxyribonucleic acid
COD	Chemical oxygen demand
abs	absorption spectrum
rpm	revolutions per minute
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
C.I.	Colour Index
AC	Activated Carbon
E.Spinosum	Euchema Spinosum

LIST OF ABBREVIATIONS

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The massive uses of dyes industrially especially in the textile industry has caused concerns over time. In Malaysia, especially in the East Coast of Peninsular Malaysia, is well-known with their textile industry. The Tenun industry in Pahang has been recognized and established as Tenun Pahang Royal. In order to produce a quality made and attractive tenun fabric, the dyes' molecules used are designed to deliver a permanent colour to the fabrics. In the dyeing process, fabric are mixed with solution containing specific dyes and particular chemical material. After dyeing, both fibre molecules and dye molecules will have an uncut chemical bond. As a result, bright coloured and perennial fabric with high dye concentration are produced.

Unfortunately, brightly coloured, water-soluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems (Willmott et al., 1998). Thus, this act will eventually resulted in pollution to the surrounding environment. This pollution is considerably dangerous and toxic due to dye content which includes high concentration of colours, large amount of suspended solids, and high chemical oxygen demand (Kim et al., 2004).



Figure 1.1 : The dyeing of fabric process

Source : <http://www.thebatikboutique.com/>

Most of the Tenun industries do not prepare and provide of any pre-treatment before discharging the effluent into the stream and river. The untreated wastewaters are aesthetically unpleasant and toxic which will greatly affect and pose environmental problems. The effluents commonly contain an amount of pollutants and contaminants.

In several countries including Malaysia, environmental laws and regulations are enforced in order to control the pollution caused by industries. A certain criteria and standard of the effluent have to be met before releasing the effluents to the streams, rivers or surrounding. Hence, for protecting the environment and meet the stringent government law, many researchers try to find an effective and economical way of dye-containing wastewater treatment.

As a resolution to this problem, studies are done based on three categories, namely chemical, physical, and biological methods. At present, the main methods of textile dye-containing wastewater treatment are physical and chemical means as shown in Table 1.1.

Physical/chemical method	Advantages	Disadvantages
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-product
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amine
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface area for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Remove all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O ₂
Elektrokinetic coagulation	Economically feasible	High sludge production

Figure 1.2 : Advantages and disadvantages of physical and chemical methods of dye removal

Source : <https://www.researchgate.net/publication/271758811>

Conventional techniques for removing dyes in wastewater are difficult, costly and time consuming. With the current technologies, it is not capable to remove all classes of dyes. In order to do that, several technologies are combined to achieve satisfactory results, the decolourization efficiencies. Among the three methods, chemical, physical and biological methods, the most preferable and frequently used is the physical method which involves adsorption. Adsorption is a method which have higher possibility to remove the dye pollutants from aqueous system completely. Therefore, more researcher and scientists are focusing on this mechanism by searching and developing highly efficient and effective adsorbent.

Even though biological methods are generally cheap and simple to apply, this method are unable to be applied on more complex dye compounds such as in the activated sludge process. This is because of the most commercial dye compounds structure are generally complex and many dyes are non-biodegradable due to the chemical nature and molecular size (Kim et al., 2004).

Currently, few methods are being developed in order to treat the wastewater. However, it is almost impossible to be used individually due to the non-biodegradable organics content, high concentration of colours and high salinity. For such, oxidation process such as ozonation effectively decolorizes almost all dyes except disperse dyes but does not remove COD effectively (Almet al., 1999). Therefore, physical method involving adsorption is chosen for this case study. *Euchema Spinosum* or known as red seaweed is chosen as the adsorbent mechanism for adsorption to remove the dyes, specifically, Acid Yellow 17 from the wastewater.



Figure 1.3 : *Euchema Spinosum*

Source : <https://sc02.alicdn.com/kf/UT8kIKXXshaXXaFIFrXs/Dried-Eucheuma-spinosum-MC-38-below-Impurity.jpeg>

1.2 Problem Statement

Based on the observation in the small textile industries in Pahang, it was indicated that the effluent released into rivers and streams are not well-treated or partially treated. This is because of the traditional system implemented in the structure of the building. The structures of the process's materials and equipment are built traditionally and economically back in years ago. Improper and malfunction filtration system in the structure resulted in untreated effluents from the dyeing process.

The effluents from the process are aesthetically unpleasant and have exceed the concentration of the allowed value. The presence of very low concentrations of dyes in effluent is highly visible and undesirable (Nigam et al., 2000). The effluent contains high content of dyestuff, surfactants and other additives that are generally made up of organic compounds with a complex structure. This will resulted in the difficulty of the textile dyes separating from the wastewater. Therefore, it is difficult to treat textile wastewater with conventional methods as these organic compounds have poor bio-degradability.

Moreover, the high costs for the treatment of the wastewater are surely a main concern for the small textile industries. In order to treat the wastewater from the textile industries, a suitable and proper delivery material or method is needed to remove the various content of dyes in the effluent which is known as activated carbon. However, it is not economical and the best method for this case due to its expensive value. Thus, for this study, *Euchema Spinosum* was chosen because of the numerous availability of seaweed in Malaysia as well as due to its low cost.

1.3 Objectives

The objectives of this study are:

- i. To determine the optimum condition of parameters influencing the performance of the seaweed.
- ii. To determine the removal percentage of dye by red seaweed.

1.4 Scope of Study

The case study is focusing on determining the percentage of dye removal, specifically, Acid Yellow 17 by red seaweed or its scientific name, *Euchema Spinosum* and the optimum condition of dye removal for each parameter. The percentages were obtained from tests based on four parameters consists of contact time, pH, dosage and initial concentration. Thus, based on the results obtained from the parameter's tests, the percentages were determined and analysed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The textile industry is one of the largest sectors globally and thus using gallons of water mixed with synthetically made dyes. This industry is the key user of dyes and hence the prime source of water pollution, which risks aquatic as well as human life. Unfortunately, about a quarter of the percentage of the total produced dyes is released into the aquatic ecosystems without being removed from the effluents (Bukallah et al., 2007). Whether it is organic or non-organic, it is difficult to treat dyes because of their complex molecular structure. This properties makes them more stable and thus difficult to be biodegraded. Hundreds of thousands commercial dyes are being produced every year.

One of them is azo-dyes, which is the main classes of dyes. It is characterized by an azo group consisting of two nitrogen atoms. Azo compounds are compounds bearing the functional group $R-N=N-R'$, in which R and R' can be either aryl or alkyl. These dyes are applied in industries such as textile, cosmetic, food colorants, printing, and pharmaceutical industries. Usually, the effluents of these dyes will cause the coloration of water bodies once released and will likely to interfere with the transmission of light affecting aquatic life (Raghuvanshi et al., 2004).

In order to treat these wastewater, various treatment are proposed. These including precipitation, ion exchange, and adsorption. Adsorption by low cost biological materials is currently labelled as an effective technique for the treatment of dye-containing wastewater. The materials used is the dried organisms. Seaweed have been found to be potential and suitable bio sorbent because of their fast and easy growth as well as their wide availability.

These plants are being cultured and marketed massively in Sabah, Malaysia. Since the discovery of its cosmetic and sheer aesthetic attributes, these seaweed has become an important economic commodity of Sabah. Due to its wide availability and low cost, seaweed is chosen as the bio sorbent. The present work is to investigate the potential of this seaweed for the removal of Acid Yellow 17 from synthetic solution. Effects of four different parameters such as contact time, pH, bio sorbent dosage and initial dye concentration are considered.

2.2 Classification of Dyes

Dye can be defined as coloured substance whether natural or synthetic which is used to add or change a colour of something. It has an affinity to the substrate to which it is applied to and commonly applied in aqueous solution (Pereira and Alves 2012). The dyes and the pigments are coloured due to their absorbance of certain wavelengths of light more than others. It is estimated that over 10,000 different dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide (Zollinger 1999; Chequer et al. 2013).

There are several manner to classify dyes, as each of the dyes have their very own unique attributes. Dyes can be classified based on the source of materials, chemical classification, according to the nuclear structure and industrial classification of dyes. As shown in Figure 2.1, dyes can be classified into two type which consisted of natural and synthetic dye. Synthetic dyes are based on petroleum compound, whereas natural dyes are obtained from plant, animal, and mineral matters (Singh and Bharati 2014). Natural dyes are derived from plants, animals, fruits, insects, minerals and other natural resources. Natural dyes are usually perceived as harmless and safe for the environment.

However, natural dyes are scarce and expensive, because producing it requires a vast area of land. Sustainability is also an issue because their pigment may wash off overtime. This paves the way for the manufacturing of dyes in different pigments and in large quantities. Thus, synthetics dyes are created. Synthetic dyes became popular because of its lasting colour pay-off and wide range of colour choices. Synthetic dyes are made up of chemical compounds that can be harmful to humans, especially those who work in their production.

Synthetic dyes are extensively used in many fields of up-to-date technology, such as in various branches of the textile industry (Sokolowska-Gajda et al., 1996), some of the chemicals found in synthetic dyes are mercury, lead, chromium, copper, sodium chloride, toluene, and benzene. Exposure to large doses of these substances can be toxic and can have severe effects in the human body. Water pollution can also result from manufacturing synthetic dyes when untreated dye effluent is dumped directly on bodies of water. Nowadays, synthetic dyes have been employed for the control of the efficacy of sewage (Morgan-Sagastume et al., 1997) and wastewater treatment (Hsu and Chiang, 1997; Orhon et al., 1999),

For this case study, focuses will be given to the azo dye under the synthetics dye category. This is because the most used organic dyes for textiles contain an azo group in their structure (Bafana et al., 2011). The azo compound class accounts for 60 - 70% of all dyes. As you might expect, they all contain an azo group, $-N=N-$, which links two sp^2 hybridised carbon atoms (Iqbal 2008). Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (disazo), three (trisazo) or more.

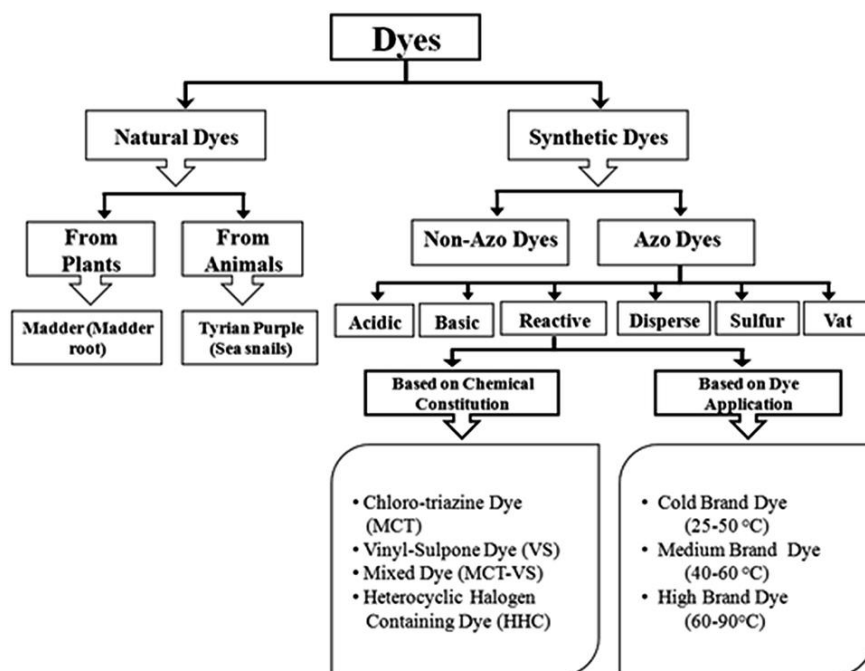


Figure 2.1 : The breakdown of dyes

Source :

<http://pubs.rsc.org/en/content/articlelanding/2014/ra/c4ra06658h/unauth#!divAbstract>

In theory, azo dyes can supply a complete rainbow of colours. However, commercially they tend to supply more yellows, oranges and reds than any other colours. These dyes are used in for cotton, viscose, cellulose acetate and polyester (O'Neill et al., 1999).

2.3 Problems Associated with Dyes

With respect to the number and production volumes, azo dyes are the largest group of colorants, constituting 60-70% of all organic dyes produced in the world. The success of azo dyes is due to the their ease and cost effectiveness for synthesis as compared to natural dyes, and also their great structural diversity, high molar extinction coefficient, and medium-to-high fastness properties in relation to light as well as to wetness. They have a wide range of applications in the textile, pharmaceutical and cosmetic industries, and are also used in food, paper, leather and paints. However, some azo dyes can show toxic effects, especially carcinogenic and mutagenic events. In recent studies, azo dyes were identified as predominant brominated compounds in house dust and also exhibit mutagenic responses at environmentally relevant concentrations (Peng et al., 2016).

Because of their commercial value, the impact (Guaratini and Zanoni, 2000) and toxicity (Walshall and Stark, 1999; Tsuda et al., 2001) of dyes that were released in the environment have been extensively studied. The toxic effects of the azo dyes may result from the direct action of the agent itself or of the aryl amine derivatives generated during reductive biotransformation of the azo bond. The azo dyes entering the body by ingestion can be metabolized to aromatic amines by the azoreductases of intestinal microorganisms. If the dyes are nitro, they can be metabolized by the nitroreductases produced by the same microorganism. Mammalian liver enzymes and other organizations may also catalyse the reductive cleavage of the azo bond and the nitroreduction of the nitro group. In both cases, if N-hydroxylamines are formed, these compounds are capable of causing DNA damage.

One of the most difficult tasks confronted by the wastewater treatment plants of textile industries is the removal of the colour of these compounds, mainly because dyes and pigments are designed to resist biodegradation, (Shaul et al., 1991) such that they remain in the environment for a long period of time.

2.3.1 Method in Removal of Dye Compounds

The technologies for dye removal have been divided into three principal categories: physical, chemical and biological methods as shown in Figure 2.2.

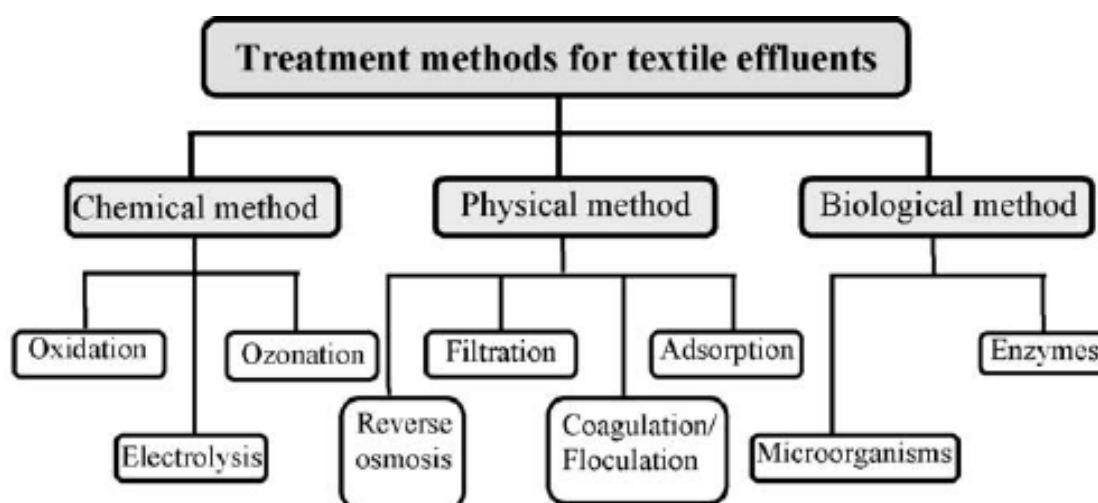


Figure 2.2 : Method of removal of dyes for textile effluents

Source : https://www.researchgate.net/figure/229404625_fig1_Fig-1-Treatment-methods-for-the-removal-of-dyes-from-wastewater-effluent

2.3.2 Biological Method

Biological treatment is the most economical alternatives when compared with other physical and chemical processes. Biodegradation methods such as fungal decolourization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan et al., 2001).

However, their application is often restricted because of technical constraint. Further, biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes (Robinson et al., 2001). Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Ravi Kumar et al., 1998). In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.3.3 Chemical Method

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use (Maria, 2014).

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.3.4 Physical Method

Different physical methods are also widely used, such as membrane – filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantages of the membrane processes is that they a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Adsorption is known as an equilibrium separation process and an effective method for water decontamination applications

(Dabrowski, 2001). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants.

Adsorption methods have attracted considerable interest due to their higher efficiency for the removal of a wide range of dyes. The selection of an adsorbent is based on characteristics such as high affinity, capacity for target compounds and the possibility of adsorbent regeneration (Subramaniam et al. , 2009). Although activated carbon (AC) is a very effective adsorbent for various types of dyes, it is not often used due to its high cost (Robinson et al. , 2001).

To make the process more economically feasible, some investigators use low-cost adsorbent materials like peat, bentonite clay, fly ash, polymeric resins, ion exchangers and many biological materials such as, corn/maize cobs, maize stalks, and wheat straw for the colour removal of dye wastewater (Ramakrishna and Viraraghavan, 1997). Thus, for this study, seaweed is used as the low-cost adsorbent.

2.4 Adsorption

As stated earlier, the mechanism chosen for this study is the physical methods by adsorption. Adsorption can be described as the process in which atoms, ions or molecules from a substance (it could be gas, liquid or dissolved solid) adhere to a surface of the adsorbent. Adsorption is a surface-based process where a film of adsorbate is created on the surface while absorption involves the entire volume of the absorbing substance. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent (Ramakrishna, 2013).

Absorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called “sorption”, and the reverse of “sorption” is called “desorption”. Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of formation of a layer of solid or gas on the substrate. Thus in the process of adsorption, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate (Abbas F. S., 2013).

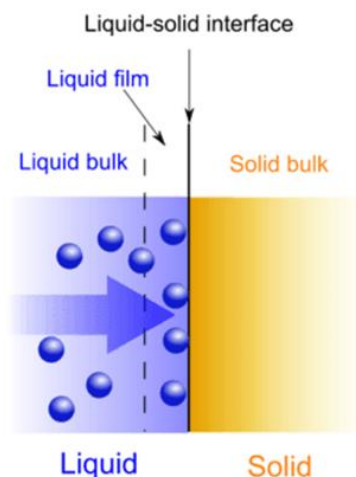


Figure 2.3 : Adsorption, where molecules will stick to the surface of the solid

Source : http://www.diffen.com/difference/Absorption_vs_Adsorption

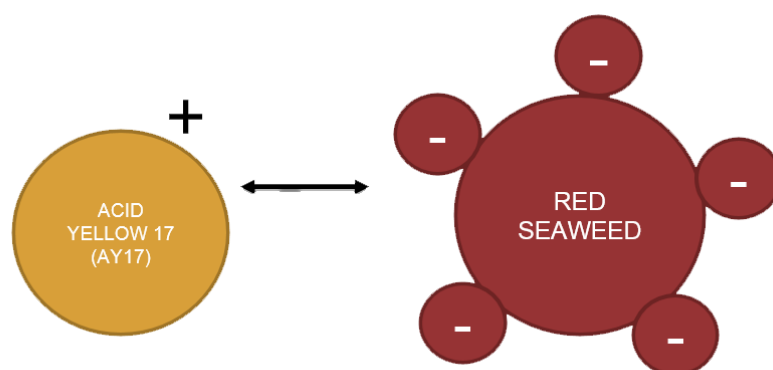


Figure 2.4 : The reaction between the ions of the molecules

In the adsorption process, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate (Abbas F. S., 2013). The process is influenced by many physicochemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Ramakrishna, 2013). Figure 2.3 shows the adsorption mechanism where the molecules or the particles of the liquid will stick to the surface of solid zone. The same concept applied between *Euchema Spinosum* and Acid Yellow 17. Once the process occurred, the molecules cannot be removed easily from each other.

2.5 Acid Yellow 17 Dye

Dyes are important particles in the textile and paper and pulp industries. But these dyes are harmful when it combines with the water bodies because these dyes contains organic and inorganic toxic chemicals. They are harmful at low concentrations also and disturb the aquatic life. For this study, Acid Yellow 17 is used as the dye. This is due to the existence of Acid Yellow 17 dye in the wastewater effluents of textile industries, paper industries originates most harmful environmental problems to living organisms and they are highly toxic to humans and as well as animals. Therefore, to adsorb anionic dyes such as Acid Yellow 17 and different pollutants from aqueous solution, it is best to consider seaweed as an effective alternative (Mahdi, 2014).

Acid Yellow 17 is a part of azo dye group. The dye content is 60 % and exhibit empirical formula of $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$. The chain structure of the dye can be seen in Figure 2.5. It consists of molecular formula of $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$, its molecular weight is 551.29.

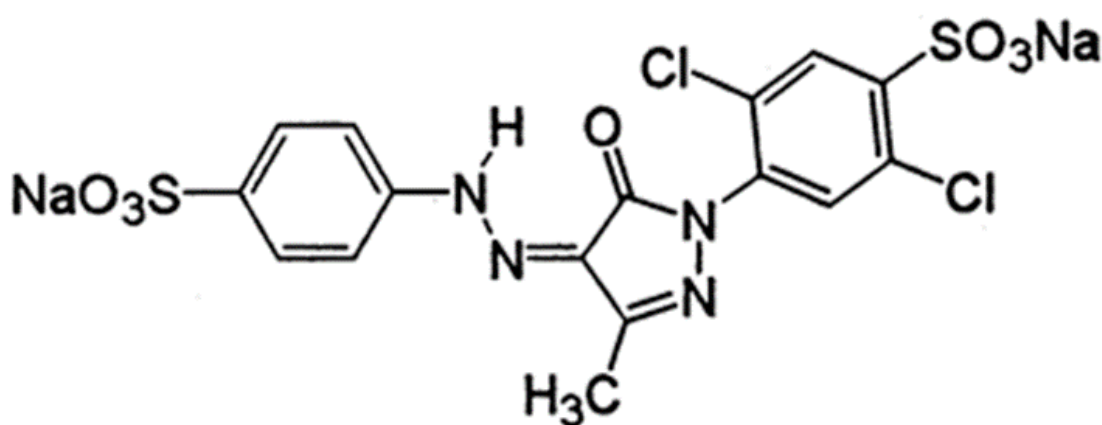


Figure 2.5 : The chain structure of Acid Yellow 17

Source :

<http://www.sigmaaldrich.com/catalog/product/sial/201987?lang=en®ion=MY>

The colour of this dye is brilliant yellow and comes in form of yellow powder as in Figure 2.6. It is soluble in water, slightly soluble in ethanol and acetone, insoluble in other organic solvents. It is mainly used for wool in strong acid dye in the bath dyeing, silk dyeing in acetic acid bath, polyamide fibre dyeing in formic acid dye bath.



Figure 2.6 : Acid Yellow 17 in powder form

Source : <https://5.imimg.com/data5/YL/WF/MY-4067899/acid-yellow-mgr-250x250.jpg>

2.6 Marine Seaweed as Biosorbent

2.6.1 Classification of Marine Seaweed

Seaweeds can be classified into three broad groups based on pigmentation: brown, red and green. Seaweeds are particularly useful organisms for studying diversity patterns and planning the conservation and sustainable use of inshore marine resources, and are also useful as indicators of climatic change (Van der Strate et al. 2002). Botanists refer to these broad groups as Phaeophyceae, Rhodophyceae and Chlorophyceae, respectively. Brown seaweeds are usually large, and range from the giant kelp that is often 20 m long, to thick, leather-like seaweeds from 2-4 m long, to smaller species 30-60 cm long (Blunden and Gordon 1986). Red seaweeds are usually smaller, generally ranging from a few centimetres to about a metre in length; however, red seaweeds are not always red: they are sometimes purple, even brownish red, but they are still classified by botanists as Rhodophyceae because of other characteristics. Green seaweeds are also small, with a similar size range to the red seaweeds.



Figure 2.7 : Brown algae, green algae, red algae

Source : <https://www.slideshare.net/nataliepopik/algae-book>

Seaweeds are also called macro-algae or algae. This distinguishes them from micro-algae (Cyanophyceae), which are microscopic in size, often unicellular, and are best known by the blue-green algae that sometimes bloom and contaminate rivers and streams (Mack et al. 2000). Naturally growing seaweeds are often referred to as wild seaweeds, in contrast to seaweeds that are cultivated or farmed.

2.6.2 Uses of Seaweed

Research into the life cycles of these seaweeds has led to the development of cultivation industries that now produce more than 90 percent of the market demand. Seaweed are used for restaurant and domestic use, food, agar, thickener, animal food stock, in cosmetic products, fertilizers and such.

Seaweed have been considered a valuable indicator for the assessment of heavy metals in coastal areas because of their accumulation capacity (e.g. Förberg et al., 1988). Moreover, there are potential uses for seaweed in wastewater treatment. Some seaweeds are able to absorb heavy metal ions such as zinc and cadmium from polluted water. Thus, for this study, seaweed is used as adsorbent for the removal of dye.

2.6.3 Eucheuma Spinosum (Red Seaweed)

Eucheuma is a group of red seaweeds/seaplants representing the subfamily Eucheumatoideae used in the production of carrageenan, an important product used in cosmetics, food processing, and industrial uses, as well as a food source for those living in Malaysia, Indonesia and the Philippines (Aquaculture Compendium, 2006). Some of the most significant species include *Betaphycus gelatinae*, *Eucheuma denticulatum*, and several species of the genus *Kappaphycus* including *K. alvarezii*. For this study, *Eucheuma Spinosum* are obtained from the triangle seawater of Semporna, Sabah, Malaysia as shown in Figure 2.8.

Though commercially significant, species of eucheuma are difficult to identify without the aid of close scientific examination, as different species may have very similar morphologies (Shao, 2014). It is assumed that eighteen to twenty species alone fall within the genus *Eucheuma*, represented by the groups *Cottoniformia*, *Eucheuma*, *Gelatiformia*, and *Anaxiferae*. *Eucheuma* are typically found below the low tide mark to the upper subtidal zone of a reef, growing on sand to rocky seafloor areas along a coral reef, where water movement is slow to moderate. Their growth is similar to terrestrial plant species, where eucheuma have a growing tip, or apical meristem, which is also capable of dividing to form new growing branches.



Figure 2.8 : The location of red seaweed, Semporna, Sabah (sources???)

Source : <http://philexaminer.com/?p=3615>

Commercial growth of *Eucheuma* is an important source of income for people living in developing nations, where the production of the low-valued seaweed can be a sustainable source of income with lower environmental costs compared to other sectors of aquaculture (Ma'ruf Kasim, 2016). As *eucheuma* are some of the most common and fastest growing species of seaweeds around, their commercial aspects are visible by large quantities being able to be grown and harvested over a short period of time, possessing the ability to reach ten times their body weight in around 45 to 60 days in warm tropical settings. Once harvested, the product can be dried, packaged, and then transported to areas ready for carrageenan extraction or used as a food supply.

The major producers of *eucheuma* algae include the Philippines and China, including Tanzania and Kiribati (Hayashi et al 2007). This may be underrepresented as countries including Indonesia and Malaysia, which are also significant producers of these species, do not accurately report their output to the FAO.

Over the last few years most of these seaweeds have been reclassified by marine biologists as they gain more knowledge of their structure. For red seaweed *Euchema Spinosum*, is now known as *Eucheuma denticulatum* and commercially was and is called "spinosum". This study used red seaweed, *Euchema Spinosum* also known as *Euchema Spinosum* as the adsorbent for the removal of dye. The seaweed will be referred as *Euchema Spinosum* or *Eucheuma Spinosum* in this thesis study.



Figure 2.9 : *Euchema Spinosum* or also known as *Eucheuma denticulatum* (Sources)

Source :

http://surialink.seaplant.net/HANDBOOK/Genera/image_reds/Eucheuma_pics/euchema_1.htm

Eucheuma Spinosum, a perennial red seaweed, is composed of rigid clumps of low-growing, cartilaginous thalli. These clumps can range in size depending on growing conditions, but are able to reach considerable size, up to 50 centimeters in length and weighing over 1 kilogram. The primary axis and regularly spaced branches are cylindrical, each bearing whorled spinose (spine-like) branchlets which sometimes develop into secondary lateral branches. This one species can be found in a variety of shades from brown to green to red, especially when cultivated.

Eucheuma Spinosum is most commonly found growing on coarse sand to rocky substrates in the intertidal to shallow subtidal zone where it is exposed to strong currents and wave action. This algae has the unique ability of its branches to form secondary holdfasts to other plants as well as the substrate, forming thick carpet-like beds of seaweed where individual plants are hard to distinguish. *Eucheuma Spinosum* is native to the Indian Ocean, but since being discovered as a source of iota carrageenan, it has been spread elsewhere through cultivation. It can be found in the following countries: Philippines, Indonesia, Vietnam, Cambodia, India, Madagascar, Tanzania, Fiji, Kiribati, Tonga, and Vanuatu (Luxton 1993; Lirasan & Twide 1993; Luxton et al 1987; Bindu 2011; Mollion & Braud 1993; Ohno et al 1996; Hayashi et al 2007; Ask & Azanza 2002).

Eucheuma Spinosum is an important crop that can be grown in rough, wave-tossed areas that are unsuitable for other, more delicate commercial seaweeds. Studies have also shown that this species can be useful as bioremediation for wastewater and nutrient saturated areas, especially around fish farms. It is the perfect biomass for the study as it is widely available and not costly.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter will provide the method and steps required for the experiment to be conducted. Figure 3.1 shows the process flow of removal of Acid Yellow 17 by E. Spinosum seaweed. First, seaweed *Euchema Spinosum* will be prepared, followed by preparation of Acid Yellow 17 dye. Next, tests on effect on contact time, adsorbent dosage, pH and initial concentration will be conducted. Finally, the collected data will be tabulated and analysed.

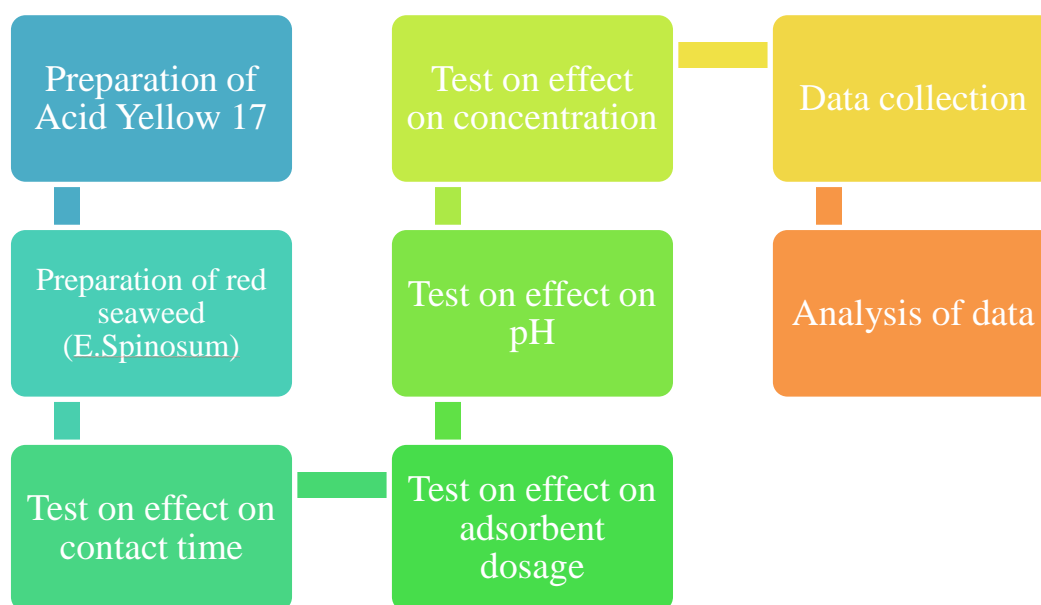


Figure 3.1 : Process flow of removal of Acid Yellow 17 by E. Spinosum seaweed

3.2 Preparation and Characterization of Biosorbent

As mentioned in the previous chapter, the biosorbent used was seaweed *Euchema Spinosum*. Raw biosorbent *Euchema Spinosum* was obtained from the triangle seawater of Semporna, Sabah, Malaysia. Biosorbent was washed in tap water for 3 times to remove the suspended materials and the sand. The seaweed are then washed again with distilled water for 2 times to ensure it is clean from any impurities which could interfere in light-absorbing phenomenon. Afterwards, it was oven-dried at 60°C to evaporate any kind of moisture from the bulk. Then it was blended and grounded into fine powder. The seaweed was then sieved at size of 0.7mm - 1.5mm.



Figure 3.2 : Raw seaweed in its moist condition



Figure 3.3 : Seaweed was first washed and rinsed with tap water, was thoroughly washed with doubly distilled water.



Figure 3.4 : Seaweed was oven-dried at 60°C for 24 hours



Figure 3.5 : Seaweed was oven-dried at 60°C for 24 hours



Figure 3.6 : Dried seaweed was blended to desired particle sizes, 0.7mm – 1.5mm.

3.3 Point of Zero Charge

Point of zero charge (PZC) is the pH at which the biomass surface has a neutral charge. It is an important characteristic for seaweed as it indicates the acidity/basicity of the adsorbent and the net surface charge of the molecule in solution. To measure the PZC, the pH of the solution is maintained by using 0.1 M Hydrochloric acid (HCl) and 0.1 M Sodium hydroxide (NaOH) solutions. Six samples of 50 mL of different pH solution with pH 2, 4, 6, 8, 10 and pH 12 were mixed with 50 mg of seaweed respectively. The initial and final reading will be recorded. All solution are then placed in the shaker at 150rpm for 24 hours. After reached equilibrium (24 hours), the final pH was measured making it possible to construct difference in pH vs. initial pH was plotted based on these data.

3.4 Preparation of Dye Solution

Acid yellow-17 (C.I. = 18,965, Chemical formula = $C_{16}H_{10}Cl_2N_4Na_2O_7S_2$ FW = 551.29, and nature = acid yellow-17) was obtained from S201987 SIGMA-ALDRICH. The dye comes in powder form with the colour of brilliant yellow.



Figure 3.7 : 201987 SIGMA-ALDRICH Acid Yellow 17 dye

The concentration of 1000 mg/L solution was prepared by adding 0.01g of acid yellow 17 dye in 1000 mL of volumetric flask and adding the distilled water up to the mark.



Figure 3.8 : 100mg/L Acid Yellow 17 dye

Acid yellow 17 solution as shown in Figure 3.8 recorded the pH value as 6 by pH meter. Then, stock solution was diluted up to different concentrations (e.g. 5 ppm, 10 ppm and 20 ppm) for subsequent experimental work. For this purpose, dilution formula was used.

$$C_1V_1 = C_2V_2 \quad 3.1$$

3.5 Analytical Measurements

The concentration of Acid Yellow 17 dye was estimated spectrophotometrically using UV-Visible Spectrophotometer. The maximum absorption wavelength (λ_{max}) for Acid Yellow 17 is 400. The measured wavelength of Acid Yellow 17 for three concentrations of 50 mg/L, 100mg/L and 200mg/L showed a result of 270. Thus, this value is settled onto the UV-Visible Spectrophotometer.

3.5.1 Calibration Curve

Calibration curve is the graph drawn for the absorbance of light by the acid yellow-17 dye as a function of concentration. This graph helps in determining the concentration of dye remaining in the solution or the amount of dye adsorbed on bio sorbent at any time, with the help of linear equation.

$$Y = mX + c \quad 3.2$$

where Y represents the absorbance, X represents the concentration of dye (mg/L), m is the slope of linear equation, and C is the intercept of the graph line. The linear equation is obtained by determining the regression line. Equation 3.2 is also known as the linear regression line where the line is a perfectly straight line. The regression equation is used in stats to find out what relationship, if any, exists between sets of data.

All the data obtained were in the form of absorption spectrum (abs) data. In order to convert the data, linear regression equation for each batch of solution made need to be determined. The equation can be determined by having different concentration of the dye

solution. Thus, the dye solution was diluted to create four different concentrations of 25mg/L, 50mg/L, 100mg/L and 200mg/L. The readings of the concentration are recorded. The Microsoft Excel software have been applied in order to analyse the data that was obtained by regression method.

3.5.2 Calculation of Uptake Capacity (q_e)

The uptake capacity, q_e or amount of Acid Yellow 17 adsorbed in mg/L at time t was computed by using the following equation.

$$q_e = \frac{C_0 - C_t}{w} \times V \quad 3.3$$

where, C_0 is the initial acid yellow 17 concentration in solution and C_t is the final acid yellow concentration in the solution within a given time t , respectively, V is the volume of the Acid Yellow 17 solutions in ml and w is the mass of adsorbent in grams.

3.5.3 Calculation of Percentage Removal of Dye

The readings of spectrophotometer were recorded and calculations were carried out to find removal efficiency of the adsorbent. Following formulae was used for calculation of removal capacity or efficiency:

$$\% \text{ removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad 3.4$$

where, C_0 is the initial acid yellow 17 concentration in solution and C_t is the final acid yellow concentration in the solution. The contact time of Acid Yellow 17, pH, absorbent dosage and initial concentration was investigated by varying any one parameter and keeping the other parameters constant.

3.5.4 Effect of Change in Contact Time on Adsorption

The contact time between adsorbent and adsorbate is one of the most important parameters that significantly affect the performance of dye removal. The effect of contact time on the percentage removal of Acid Yellow 17 dye was investigated at fixed initial dye concentration of 25mL and adsorbing seaweed dosage of 25mg. The pH was set to pH7 by adding 0.1M NaOH or 0.1M HCl solutions.

Three readings for each contact time were taken and average of the readings were calculated and recorded. All solution mixture were then placed into shaker for 130rpm for different duration. The contact time between the seaweed and the dye was setted to 5, 10, 15, 30, 40, 60, 80, 100, 120, 150, 180, 210, 240, 270, 300 and 360 minutes. The vial containing the mixture, were placed into centrifugal at 4000 (revolutions per minute) rpm for 3 seconds. All the data were recorded as in Chapter 4.

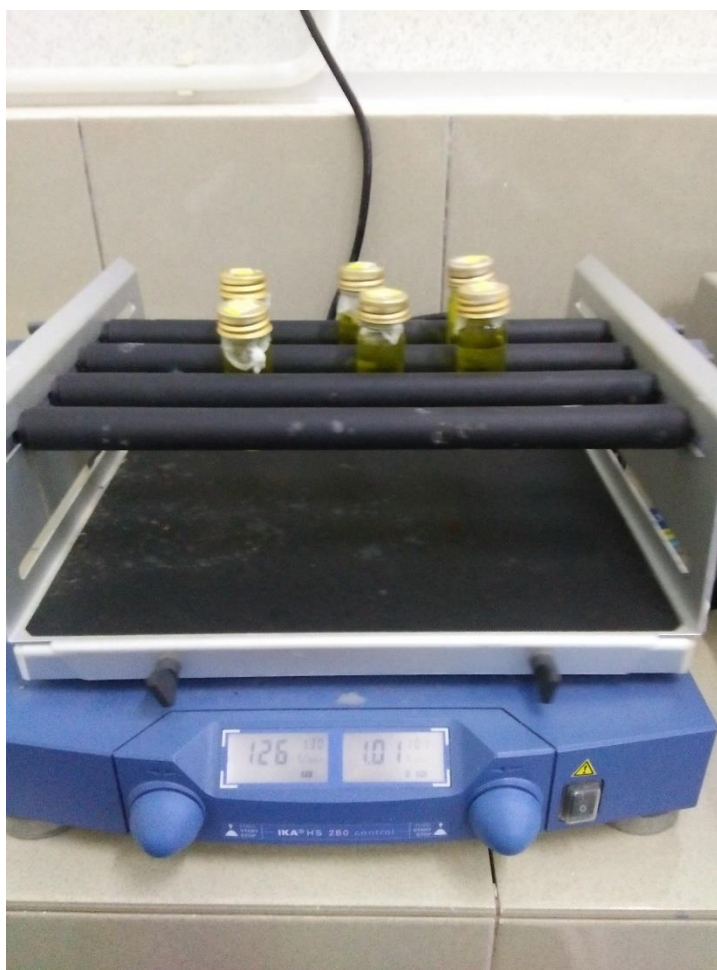


Figure 3.9 : Vials containing mixed solution was placed in shaker

3.5.5 Effect of Change in Absorbent Dosage of Seaweed on Adsorption

The dose of adsorbent on the percentage removal of Acid Yellow 17 dye varies among 0.01g, 0.015g, 0.02g, 0.025g, 0.03g, 0.035g, 0.04g, 0.045g and 0.05g. A solution of 100mg/L of Acid Yellow 17 dye are used. Each dosage are mixed with 25mL of the dye solution prepared before. The mixture of the dye solution with different dosage was then placed into a shaker for 130rpm with 60 minutes. From the previous tests done, the optimum contact time obtained was 60 minutes. Thus, this is the reason why the mixture was shaken for 60 minutes. The vial containing the mixture then, were placed into centrifugal at 4000rpm for 3 seconds. All the data were recorded.

3.5.6 Effect of Change in pH of Solution on Adsorption

The pH is one of the most important parameter controlling uptakes of dye from wastewater and aqueous solutions. The effect of pH on adsorption of dye on *Euchema Spinosum* was studied at room temperature by varying the pH of dye solution from 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. The pH was adjusted with the addition of 0.1M NaOH or 0.1M HCL solution. The initial concentration of 100mg/L of Acid Yellow 17 dye is used with seaweed dosage of 0.04 g. The dosage differ from the two previous test. This is as in the dosage test, 0.04g of seaweed dosage is the optimum dosage at highest percentage removal of dye. Then, the mixture are shaken at 130rpm for an hour and centrifugal at 4000rpm at 3 seconds. All the data were recorded.

3.5.7 Effect of Change in Initial Concentration of Solution on Adsorption

The effect of change in initial concentration on adsorption of dye on *Euchema Spinosum* was studied at room temperature by varying the initial concentration of dye solution from 50mg/L, 100mg/L and 200mg/L. Each dye solution was mixed seaweed dosage of 0.04 g. All solution mixture were then placed into a shaker for 130rpm at different duration and centrifuge at 4000rpm for 3 seconds. The contact time between the seaweed and the dye are 5, 10, 15, 30, 40, 60, 80, 100, 120, 150, 180, 210, 240, 270, 300 and 360 minutes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The results of the experiments carried out for the removal of Acid Yellow 17 dye from aqueous solution using *Euchema Spinosum* as adsorbent are discussed as below.

4.2 Point of zero change

The data obtained was tabulated as follows:

Table 4.1 Readings of initial pH, final pH, and difference in pH

pH initial	pH final	Difference in pH
2	1.98	0.02
4	6.93	-2.93
6	6.48	-0.48
8	7.13	0.87
10	8.33	1.67
12	11.33	0.67

The difference between the pH are calculated and recorded. The difference in pH are plotted against initial pH of the solution and shown in Figure 4.1. From the graph plotted, it was observed that the graph line intersect zero horizontal axis at pH 7. This result shows that the natural ion charge of the red seaweed, *Euchema Spinosum* is pH 7.

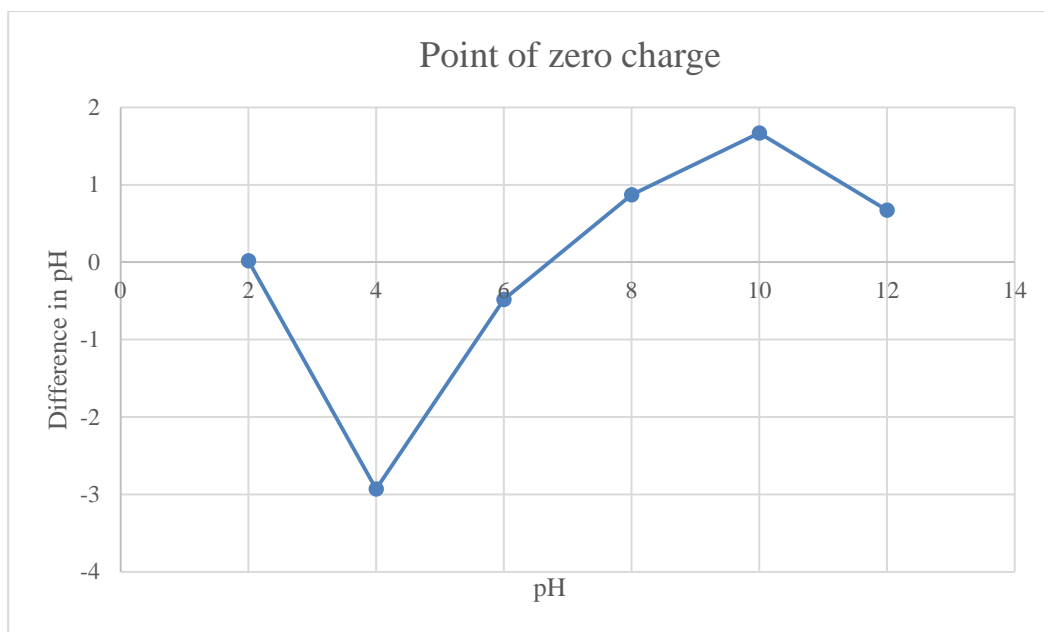


Figure 4.1 : Graph of difference in pH against initial pH

4.3 Effect of Change in Contact Time on Adsorption

The reading of four different concentrations of 25mg/L, 50mg/L, 100mg/L and 200mg/L were recorded. The readings of the concentration are recorded as in Table 4.2.

Table 4.2 Different concentrations of dye solution

Concentration (Y)	Abs data (X)
10	0.222
25	0.554
50	1.099
100	2.201

Based on the data obtained from Table 4.2, analysis of regression will be done using excel spreadsheet as shown in Figure 4.2. Based on the data in Figure 4.2, we can deduced an equation of:

$$Y = 45.5X + 0.116 \quad 4.1$$

where X is the average abs data we calculated. Thus, the percentage removal was obtained and tabulated in Table 4.3.

SUMMARY OUTPUT								
<hr/>								
<i>Regression Statistics</i>								
Multiple R	0.999997666							
R Square	0.999995333							
Adjusted R Square	0.999992999							
Standard Error	0.104381204							
Observations	4							
<hr/>								
ANOVA								
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>			
Regression	1	4668.728209	4668.728209	428503.1198	2.3337E-06			
Residual	2	0.021790871	0.010895436					
Total	3	4668.75						
<hr/>								
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.116493301	0.087982835	-1.324045772	0.316547884	-0.495052885	0.262066284	-0.495052885	0.262066284
abs	45.50195613	0.069510926	654.601497	2.3337E-06	45.20287476	45.80103751	45.20287476	45.80103751

Figure 4.2 : Analysis of the dye concentrations

Table 4.3 : The tabulation of data for contact time for removal of dye by Acid Yellow 17

Types	E.Spinosum						
Time (min)	1	2	3	average	Y (mg/L)	q_e (mg/g)	%removal
5	0.389	0.356	0.314	0.353	15.946	84	84
10	0.237	0.375	0.39	0.334	15.081	85	85
15	0.362	0.314	0.318	0.331	14.960	85	85
30	0.286	0.272	0.269	0.276	12.427	88	88
40	0.405	0.414	0.383	0.401	18.114	82	82
60	0.382	0.334	0.373	0.363	16.401	84	84
80	0.295	0.359	0.409	0.354	16.006	84	84
100	0.43	0.321	0.296	0.349	15.764	84	84
120	0.38	0.359	0.313	0.351	15.840	84	84
150	0.397	0.408	0.368	0.391	17.675	82	82
180	0.379	0.398	0.216	0.331	14.945	85	85
210	0.398	0.295	0.321	0.338	15.263	85	85
240	0.329	0.302	0.447	0.359	16.234	84	84
270	0.469	0.339	0.311	0.373	16.856	83	83
300	0.395	0.34	0.377	0.371	16.749	83	83
360	0.372	0.313	0.363	0.349	15.779	84	84

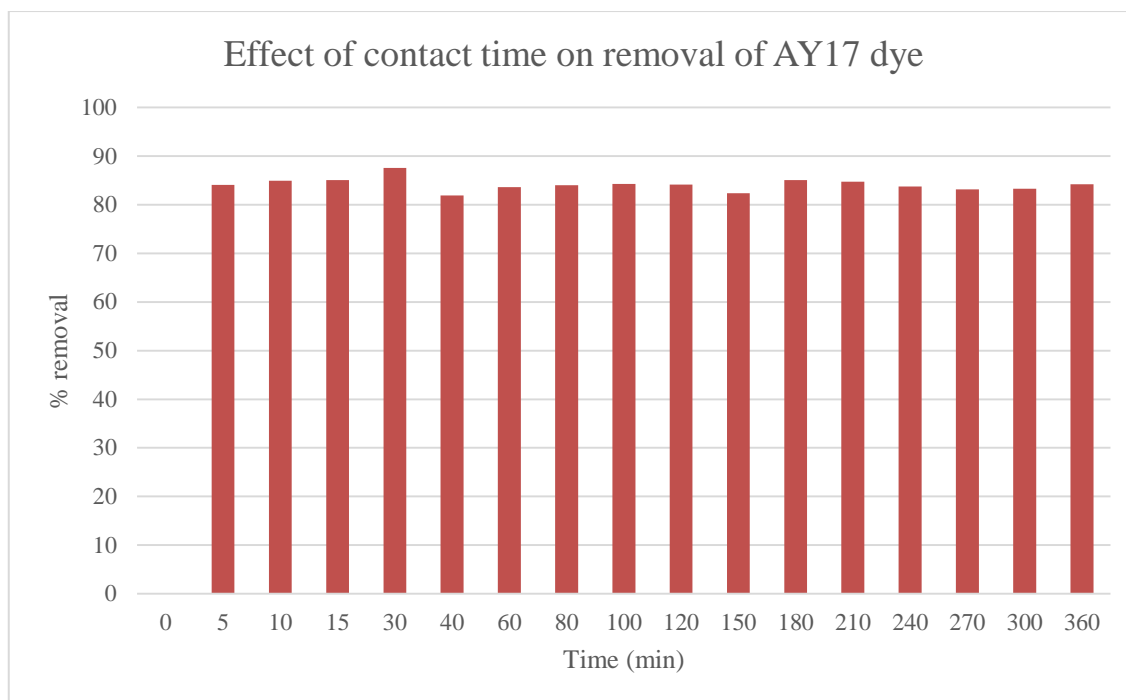


Figure 4.3 : Effect of contact time on removal of Acid Yellow 17

A graph of percentage removal against time as shown in Figure 4.3 have been plotted based on the data obtained from Table 4.3. The graph trend started to reach equilibrium at 60 minute. Even though the highest percentage recorded was 88% at 30 minutes, the data did not show a consistent trend after 30 minutes. Thus, the percentage may not be incorrect and thus ignored. It can be seen from the Figure 4.2, that the data trend is consistent. The percentage removal increases and decreases with the increase in dye concentration. The lowest percentage recorded is 82% while the highest percentage recorded is 88%.

The percentage of dye removal increased in the first 30 min of contact and shows a slight decrease until equilibrium was obtained. This can be explained by the strong attraction forces between the positive sites of cationic dyes and the anionic sites of the seaweed. Thus, the optimum time for the dye removal can be concluded at 60 minutes where the data started to reach its equilibrium state.

4.4 Effect of Change in Absorbent Dosage of Seaweed on Adsorption

The reading of four different concentrations of 25mg/L, 50mg/L, 100mg/L and 200mg/L were recorded. The readings of the concentration are recorded as in Table 4.4.

Table 4.4 Different concentrations of dye solution

Concentration (Y)	Abs data (X)
10	-0.953
25	0.125
50	0.582
100	2.968

Based on data obtained from Table 4.4, analysis of regression were done and the results were as in Figure 4.4. From Figure 4.4, the equation 4.2 will be deduced as below;

$$Y = 23.554X + 30.221 \quad 4.2$$

where X is the average abs data we calculated. Thus, the percentage removal was obtained and tabulated in Table 4.5.

SUMMARY OUTPUT

Regression Statistics								
Multiple R	0.988312449							
R Square	0.976761496							
Adjusted R Square	0.965142244							
Standard Error	7.365282229							
Observations	4							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	4560.255235	4560.255235	84.06406063	0.011687551			
Residual	2	108.4947646	54.24738231					
Total	3	4668.75						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	30.22100405	4.076541409	7.413393125	0.017713559	12.68106203	47.76094607	12.68106203	47.76094607
X Variable 1	23.55473321	2.569052665	9.168645518	0.011687551	12.50099174	34.60847467	12.50099174	34.60847467

Figure 4.4 : Analysis of the dye concentrations

Table 4.5 : The tabulation of data for dosage for removal of dye by Acid Yellow 17

m (gram)	Types	E. Spinosum						
	s/l	1	2	3	Average	Y (mg/L)	q_e (mg/g)	% removal
0.01	0.40	0.341	0.379	0.300	0.340	38.230	62	62
0.015	0.60	0.338	0.393	0.351	0.361	38.716	61	61
0.02	0.80	0.354	0.335	0.359	0.349	38.449	62	62
0.025	1.00	0.442	0.324	0.382	0.383	39.235	61	61
0.03	1.20	0.374	0.408	0.338	0.373	39.015	61	61
0.035	1.40	0.392	0.281	0.411	0.361	38.732	61	61
0.04	1.60	0.269	0.339	0.368	0.325	37.884	62	62
0.045	1.80	0.312	0.358	0.296	0.322	37.806	62	62
0.05	2.00	0.376	0.328	0.349	0.351	38.489	62	62

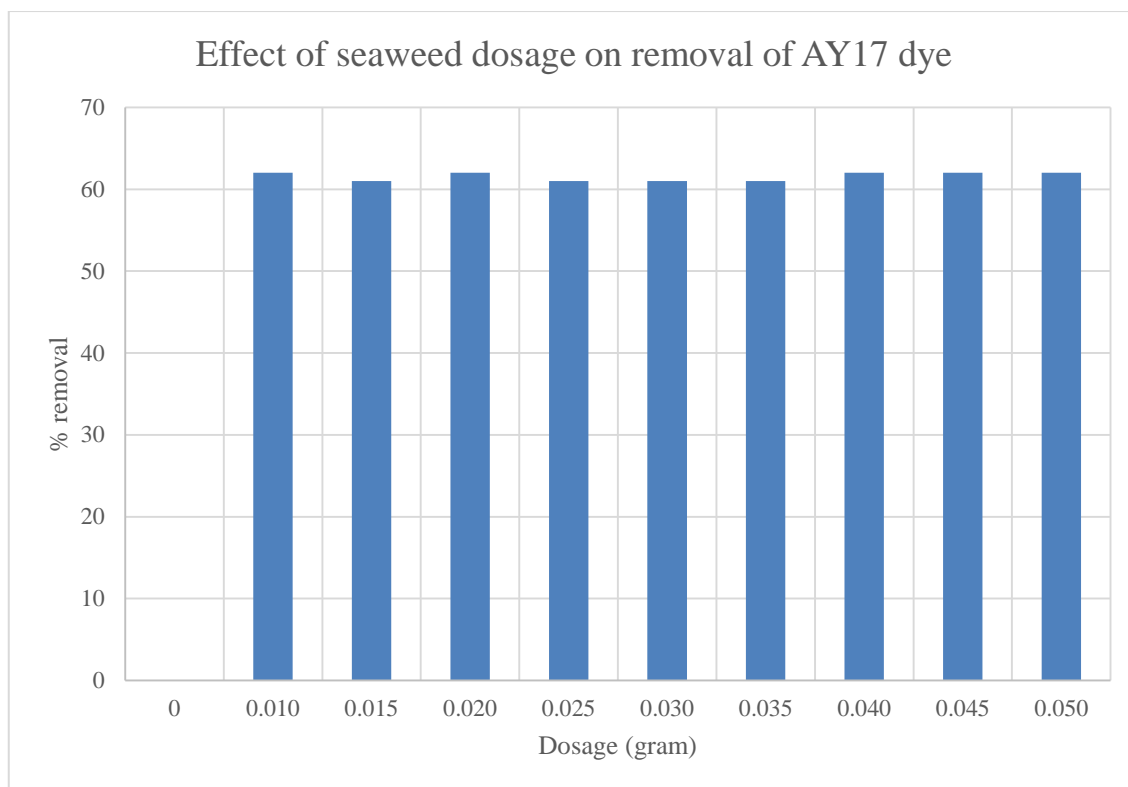


Figure 4.5 : Effect of dosage on removal of Acid Yellow 17

The results for effect of dosage on percentage removal of dye using *Euchema Spinosum* is presented in Table 4.5. It can be seen from the Figure 4.5 that the percentage removal is not consistent with slightly difference in the increase in dosage. The lowest percentage recorded is 62% while the highest percentage recorded is 61%. The graph trend started to reach equilibrium at dosage of 0.04g.

The percentage removal of the dye increased with the increase in dose of adsorbent, this may be due to the increase in availability of surface active sites resulting from the increased dosage of the adsorbent.

4.5 Effect of Change in pH of Solution on Adsorption

The dye solution used in this parameter is the same as solution batch used in absorbent dosage. Thus, the Equation 4.2 have been used to calculate q_e . The data calculated were as follows:

Table 4.6 : The tabulation of data for pH for removal of dye by Acid Yellow 17

E.spinosum							
pHo	1	2	3	Average	Y (mg/L)	q_e (mg/g)	% removal
3	0.391	0.394	0.446	0.410	39.886	60	60
4	0.384	0.481	0.503	0.456	40.962	59	59
5	0.395	0.4	0.411	0.402	39.690	60	60
6	0.413	0.462	0.371	0.415	40.004	60	60
7	0.391	0.298	0.336	0.342	38.269	62	62
8	0.378	0.42	0.321	0.373	39.007	61	61
9	0.386	0.367	0.421	0.391	39.439	61	61
10	0.42	0.378	0.405	0.401	39.666	60	60
11	0.345	0.492	0.417	0.418	40.067	60	60
12	0.48	0.305	0.354	0.380	39.164	61	61

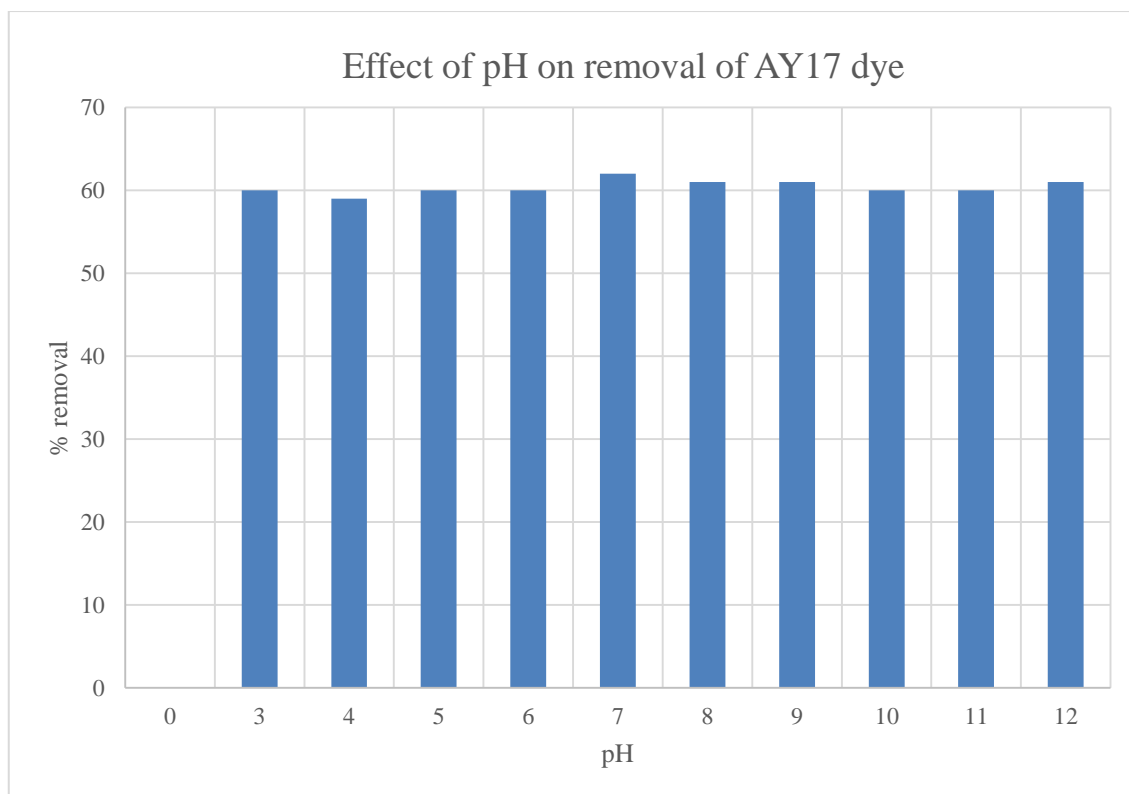


Figure 4.6 : Effect of pH on removal of Acid Yellow 17

It can be observed from the results shown in Table 4.6 and Figure 4.6 that the removal of dye by *Euchema Spinosum* was maximum at pH 7, other pH shows minimum adsorption. The lowest percentage recorded is 59% while the highest percentage recorded is 62%.

At pH 7, a significantly high electrostatic attraction exists between the negatively charged surface of the adsorbent and positively charged cationic dye. As the pH of the system decreases, the number of negatively charged sites decreases and the number of positively charged sites increases. A positively charged surface site on the adsorbent did not favour the adsorption of cationic dye due to electrostatic repulsion. A similar result has been reported in the literature (Ozcan et al., 2004).

4.6 Effect of Change in Initial Concentration of Solution on Adsorption

The dye solution used in this parameter is the same as solution batch used in absorbent dosage. The Equation 4.2 have been used in order to determine the q_e . The data calculated were as follows:

Table 4.7 : Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye

Type	Euchema Spinosum						
INITIAL : 50MG/L							
Time (min)	1	2	3	Average	C_e (mg/L)	q_e (mg/g)	removal %
5	0.261	0.318	0.377	0.319	37.73	62	62
10	0.287	0.376	0.410	0.358	38.65	61	61
15	0.318	0.398	0.388	0.368	38.89	61	61
20	0.387	0.376	0.322	0.362	38.74	61	61
30	0.308	0.360	0.401	0.356	38.61	61	61
40	0.344	0.328	0.354	0.342	38.28	62	62
50	0.308	0.344	0.361	0.338	38.17	62	62
60	0.323	0.311	0.289	0.308	37.47	63	63
70	0.267	0.401	0.309	0.326	37.89	62	62
80	0.324	0.396	0.311	0.344	38.32	62	62
100	0.412	0.365	0.320	0.366	38.83	61	61
120	0.320	0.312	0.351	0.328	37.94	62	62
150	0.371	0.298	0.385	0.351	38.50	62	62
180	0.384	0.365	0.333	0.361	38.72	61	61
200	0.356	0.381	0.377	0.371	38.97	61	61
250	0.382	0.304	0.361	0.349	38.44	62	62
300	0.371	0.310	0.343	0.341	38.26	62	62
350	0.303	0.382	0.312	0.332	38.05	62	62
400	0.366	0.298	0.344	0.336	38.14	62	62

Table 4.8 : Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye

Type	Euchema Spinosum						
INITIAL :100MG/L							
Time (min)	1	2	3	Average	C_e (mg/L)	q_e (mg/g)	removal %
5	0.361	0.369	0.290	0.340	38.23	62	62
10	0.341	0.342	0.342	0.342	38.27	62	62
15	0.311	0.365	0.369	0.348	38.43	62	62
20	0.442	0.324	0.372	0.379	39.16	61	61
30	0.374	0.411	0.322	0.369	38.91	61	61
40	0.388	0.297	0.356	0.347	38.39	62	62
50	0.279	0.311	0.332	0.307	37.46	63	63

Type	Euchema Spinosum						
INITIAL : 100MG/L							
Time (min)	1	2	3	Average	C_e (mg/L)	q_e (mg/g)	removal %
60	0.298	0.222	0.264	0.261	36.38	64	64
70	0.318	0.348	0.303	0.323	37.83	62	62
80	0.312	0.349	0.387	0.349	38.45	62	62
100	0.372	0.354	0.334	0.353	38.54	61	61
120	0.372	0.356	0.367	0.365	38.82	61	61
150	0.423	0.324	0.382	0.376	39.09	61	61
180	0.344	0.398	0.341	0.361	38.72	61	61
200	0.352	0.311	0.400	0.354	38.57	61	61
250	0.399	0.311	0.346	0.352	38.51	61	61
300	0.387	0.345	0.300	0.344	38.32	62	62
350	0.321	0.4	0.342	0.354	38.57	61	61
400	0.341	0.285	0.351	0.326	37.89	62	62

Table 4.9 : Data of initial concentration of 50mg/L for removal of Acid Yellow 17 dye

Type	Euchema Spinosum						
INITIAL : 200MG/L							
Time (min)	1	2	3	Average	C_e (mg/L)	q_e (mg/g)	removal %
5	0.323	0.312	0.341	0.325	37.88	62	62
10	0.333	0.311	0.342	0.329	37.96	62	62
15	0.354	0.356	0.355	0.355	38.58	61	61
20	0.401	0.243	0.368	0.337	38.17	62	62
30	0.367	0.421	0.343	0.377	39.10	61	61
40	0.367	0.341	0.355	0.354	38.57	61	61
50	0.299	0.333	0.366	0.333	38.06	62	62
60	0.321	0.308	0.311	0.313	37.60	62	62
70	0.356	0.333	0.323	0.337	38.17	62	62
80	0.341	0.329	0.334	0.335	38.10	62	62
100	0.321	0.333	0.325	0.326	37.91	62	62
120	0.376	0.365	0.356	0.366	38.83	61	61
150	0.397	0.323	0.388	0.369	38.92	61	61
180	0.367	0.377	0.322	0.355	38.59	61	61
200	0.377	0.354	0.397	0.376	39.08	61	61
250	0.364	0.377	0.396	0.379	39.15	61	61
300	0.389	0.355	0.377	0.374	39.02	61	61
350	0.311	0.411	0.322	0.348	38.42	62	62
400	0.362	0.31	0.371	0.348	38.41	62	62

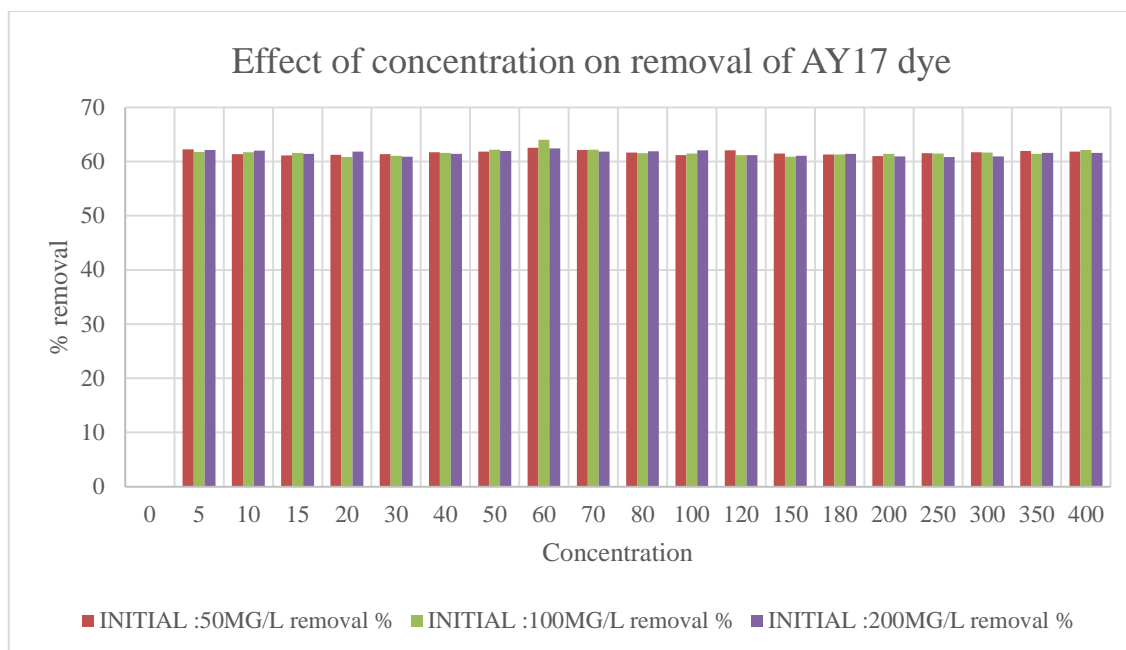


Figure 4.7 : Effect of concentrations on removal of Acid Yellow 17

Among the three concentrations used, the lowest percentage recorded is 62% while the highest percentage recorded is 64%. It can be seen from the Figure 4.5 that the percentage removal is consistent with slightly difference with the increase in dosage. The highest uptake of dye was recorded using 100m/L at 60 minutes with the percentage of 64%.

More than 63% of Acid yellow 17 are absorbed with initial dye concentrations of 100m/L. This is because a high initial concentration provided the necessary driving force to overcome the resistance to the mass transfer of dye between the aqueous and solid phase, and thus, increased the dye uptake. In addition, increasing initial dye concentration also increased the number of collisions between dye anions and sorbent, which enhances the sorption process (Aksu and Tezer 2005).

CHAPTER 5

CONCLUSION

5.1 Conclusion

In this study, the removal of colour from wastewater using a low cost adsorbent was performed using red seaweed or specifically, *Euchema Spinosum*. Synthetic water using Acid Yellow 17 was created and mixed with the seaweed using different variables. Adsorption method was chosen among lists of physical methods available as it follows surface phenomenon and more advantageous over the other available methods because of its low capital, operation costs and simple design.

Besides, adsorption is the most commonly used method for the removal of both organic and inorganic pollutants from industrial waste water. Adsorption material available from various sources such as natural sources, agricultural, and industrial wastes. For this study, the material referred to, is the red seaweed. Red seaweed, *Euchema Spinosum* was obtained from Semporna, Sabah was used as the low-cost biomass for the removal of Acid Yellow 17. Seaweed was chosen as the adsorbents due to its availability in Malaysia and its low costs.

From this study, the results indicated that the adsorption process was also enhanced by varying the parameters. The parameters used to investigate the adsorption process were adsorbent dose, contact time of adsorbent with dye solution, initial dye concentration on adsorbent, pH and temperature.

The test results for these parameters revealed that *Euchema Spinosum* did influenced the adsorption process. The biomass exhibited the highest dye uptake capacity at initial pH value of 7, dosage of 0.04g, contact time of 60min, and at concentration of 100mg/L. Thus, as a conclusion, the adsorption results in this study indicated that all the adsorbents were attractive candidates for removing acidic dyes from dye wastewater.

REFERENCES

- O'Neill C, Hawkes FR, Hawkes DL, Lourenyo ND, Pinheiro HM, Delee W. Colour in textile effluentssources, measurement, discharge consents and simulation: a review. *J Chem Technol Biotechnol*. 1999;74: 1009-1018.
- S. Cengiz and L. Cavas, "Removal of Methylene Blue by Invasive Marine Seaweed: *Caulerpa Racemosa* var. *Cylindracea*," *Bioresource Technology*, Vol. 99, 2008, pp. 2357-2363.
- Elumalai, S., & Saravanan, G. K. (2016). The role of microalgae in textile dye industrial waste Water recycle (phycoremediation). *International Journal of Pharma and Bio Sciences*, 7(4), B662–B673.
- Fakhry, E. M. (2013). *Padina pavonica* for the Removal of Dye from Polluted Water, 2013(October), 1983–1989.
- E. Forgacs, T. Cserhati and G. Oros, "Removal of Synthetic Dyes from Wastewaters: A Review," *Environment International*, Vol. 30, 2004, pp. 953-971.
- Gürses, A., Açıkyıldız, M., Güneş, K., & Gürses, M. S. (2016). Dyes and Pigments. <https://doi.org/10.1007/978-3-319-33892-7>
- Ali H. Biodegradation of synthetic dyes-a review. *Water Air Soil Pollut*. 2010; 213(1): 251-273.
- Gao J, Zhang Q, Su K, Chen R, Peng Y. Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge. *J Hazard Mater*. 2010;174(1-3):215-225. doi:10.1016/j.jhazmat.2009.09.039.
- P. Kaewsarn and O. Yu, "Cadmium (II) Removal from Aqueous Solutions by Pre-Treated Biomass of Marine Alga *Padina* sp.," *Environmental Pollution*, Vol. 112, 2001, pp. 209-213.
- H. S. Rai, M. S. Bhattacharyya, J. Singh, T. K. Bansal, P. Vats and U. C. Banerjee, "Removal of Dyes from the Effluent of Textile and Dyestuff Manufacturing Industry: A Review of Emerging Techniques with Reference to Biological Treatment," *Critical Reviews in Environmental Science and Technology*, Vol. 35, 2005, pp. 219-238.
- Freeman, H., 2013. Aromatic amines: use in azo dye chemistry. *Front. Biosci*. 18:145–164. <http://dx.doi.org/10.2741/4093>

Mondal, S. (2008). Methods of Dye Removal from Dye House Effluent—An Overview. *Environmental Engineering Science*, 25(3), 383–396. <https://doi.org/10.1089/ees.2007.0049>

Dawood, S., & Sen, T. K. (2014). Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. *J Chem Proc Engg J Chem Proc Eng*, 1(1), 1–11.

Gregory, P. (2009) ‘Dyes and Dye Intermediates’, in *Kirk-Othmer Encyclopedia of Chemical Technology*. doi: 10.1002/0471238961.0425051907180507.a01.pub2.

Elumalai, S. and Saravanan, G. K. (2016) ‘The role of microalgae in textile dye industrial waste Water recycle (phycoremediation)’, *International Journal of Pharma and Bio Sciences*, 7(4), pp. B662–B673.

Ong, S.-T. *et al.* (2011) ‘Dye Waste Treatment’, *Water*, 3(4), pp. 157–176. doi: 10.3390/w3010157.