REMOVAL OF BASIC BLUE 3 AND BASIC YELLOW 11 USING *SARGASSUM BINDERI* (PHAEOPHYCEAE)

By

TAN PEI LING

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ABSTRACT

Removal of Basic Blue 3 and Basic Yellow 11 using *Sargassum binderi* (Phaeophyceae)

Tan Pei Ling

In the present study, comparative batch and continuous adsorption of two basic dyes – Basic Blue 3 (BB3) and Basic Yellow 11 (BY11) by using indigenous brown seaweed, *Sargassum binderi* (Sargassaceae, Phaeophyceae) was conducted in search of the optimum sorption conditions. From the present study, incubation temperature and pH of solution did not exert any significant effect in sorption of both dyes by *S. binderi*. Approximately 90% of 100 mg/L BB3 and BY11 removal in single dye solution was achieved by agitate 1 g and 0.5 g of *Sargassum binderi*, respectively, at 200 rpm. In the single dye system, sorption of both basic dyes by *S. binderi* was found to obey Langmuir and Freundlich isotherm models with high correlation coefficient value. Removal of both BB3 and BY11 was an exothermic process with negative values of ΔH^o and ΔG^o. Kinetic modelling analysis revealed that both systems fitted well to pseudo-second-order kinetic model with $R^2 > 0.99$ which indicates the involvement of chemisorptions process. Removal of BB3 and BY11 in binary dyes system was optimised by using Central Composite Design (CCD) of Response Surface Methodology (RSM). Significant effects of two critical variables, ie sorbent dosage and contact time were identified with $p < 0.05$ through Plackett Burman analysis. Following that, the RSM experiments based on CCD was applied in deriving a statistical model for improvement of dyes sorption processes by using *S. binderi*. The model predicted that by using 2.23 g of *S. binderi* in contact with 100 mg/L binary solution and agitated at 200 rpm for 122 min and incubated at temperature of 30^{o}C, would resulted in 97.33% and 93.74% of BB3 and BY11, respectively. The proposed model fitted significantly well to the experimental data with more than 95% confidence level. The overall errors (0.01%) were small indicating the proficiency of RSM methods for optimizing removal of dye in binary solutions. In addition, sorption processes of BB3 and BY11 in both single and binary dye systems were also determined by using a continuous down-flow mode fixed-bed column. Three operating parameters, bed heights, effect of liquid flow rates and effect of initial dye concentrations were investigated on the basis of breakthrough curves. The best condition in continuous mode of removal for both single dye and binary dye systems was 10 cm of bed height with 10 mL/min of liquid flow rate by applying 100 mg/L of initial dye concentration requires longer time for exhaustion of column. Bed-Depth-Service-Time model, Mass Transfer Zone model, Thomas model and Yoon-Nelson model were applied into the system for removal of dye compounds from single dye solution and binary dye solution. Removal of basic dyes by column studies was found to comply well with these models with high R^2 values ($R^2 > 0.95$). From present study, it was found that *S. binderi* was an effective biosorbent in removal of two basic dyes (BB3 and BY11).

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DECLARATION

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

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TAN PEI LING

Date : _________________

APPROVAL SHEET

This thesis entitled "**REMOVAL OF BASIC BLUE 3 AND BASIC YELLOW 11 USING *SARGASSUM BINDERI* (PHAEOPHYCEAE)**" was prepared by **TAN PEI LING** and submitted as partial fulfillment of the requirements for the degree of Master of Science at Universiti Tunku Abdul Rahman.

Approved by :

(Dr. Wong Ching Lee) Date :……………………
Supervisor/ Assistant Prof.
Department of Science
Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

(Dr. Hii Siew Ling) Date :……………………
Co-Supervisor/ Associate Prof.
Department of Chemical Engineering
Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

FACULTY OF ENGINEERING AND SCIENCE
UNIVERSITI TUNKU ABDUL RAHMAN

Date : ___________

SUBMISSION THESIS

It is hereby certified that **TAN PEI LING (ID NO: 08UEM08113)** has completed this thesis entitled "**REMOVAL OF BASIC BLUE 3 AND BASIC YELLOW 11 BY USING SARGASSUM BINDERI (PHAEOPHYCEAE)**" under the supervision of **DR. WONG CHING LEE** (Supervisor) from the Department of Science, Faculty of Engineering and Science, and **DR. HII SIEW LING** (Co-Supervisor) from the Department of Chemical Engineering, Faculty of Engineering and Science.

I understand that University will upload softcopy of my thesis in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

Yours truly,

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TAN PEI LING

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LIST OF ABBREVIATIONS

$\triangle G^o$	Gibbs free energy
$\triangle H^o$	enthalpy change
$\triangle S^o$	entropy change
%	Percentage
b	Langmuir constant (L/mg)
BB3	Basic Blue 3
BDST	Bed-depth-service-time
BOD	Biological oxygen demand
BY11	Basic Yellow 11
$\mathrm{C_B}$	Concentration of effluent at breakthrough (mg/L)
CCD	Central composite design
$\mathrm{C_e}$	Equilibrium concentration (mg/L)
$C_{e,ad}$	Equilibrium concentration on the adsorbent (mg/L)
cm	Centimeter
C_o	Highest concentration of solution
$\mathrm{C_o}$	Initial dye concentrations (mg/L)
COD	Chemical oxygen demand
f	Fractional capacity
$\mathrm{F_m}$	Liquid flow rate (mL/min)
FTIR	Fourier transform infra-red spectroscopy
g	Gram
h	Hour
HTMZ	Height of mass transfer zone
K	Adsorption rate constant (L/mg.h)
k_2	Pseudo-second-order kinetic constant (g/mg.min)
K_d	Distribution coefficient for the adsorption for Thermodynamic analysis
K_F	Freundlich constants (mg/g(L/mg)$^{1/n}$)
$\mathrm{k_{YN}}$	Yoon-Nelson rate constant (1/min)
mg/g	Milligram per gram

mg/L	Milligram per litre
mins	Minutes
mL	Mililitre
mmol/L	Milimolar per Litre
MTZ	Mass transfer zone
n	Freundlich constant
N_o	Adsorption capacity (mg/cm^3)
q_e	Amount of dye adsorbed at equilibrium over unit mass of sorbent (mg/g)
Q_e	Maximum sorption capacity (mg/g)
R	Universal gas constant (8.314 J/mol.K)
R_L	Crucial characteristic of Langmuir adsorption model
RSM	Response surface methodology
SEM	Scanning electron microscopy
t	Service time (h)
T	Absolute temperature at Kelvin (K)
UV	Ultra-violet
UV/VIS	Ultraviolet / Visible
V	Linear flow velocity of feed to bed (cm/h)
v	Volume (mL)
V_e	Total volume (mL)
W	Weight (g)
Z	Bed depth of column (cm)
τ	Time to achieve 50% breakthrough (min)

CHAPTER 1

INTRODUCTION

Malaysia, one of the richest countries in terms of natural resources and now come to a declining state in conjunction of growth with agriculture, industrialisation as well as tourism. World wildlife Fund (WWF)-Malaysia (Norporat, 2009) stated that Malaysia is now facing tons of environmental problems such as pollution of inland and marine waters, soil and coastal erosion, overfishing and coral reef destruction, deforestation, water pollution, air pollution as well as disposal of waste.

Water pollution is one of the environment problems which will cause severe impact to living organisms. Developing countries around the world emphasises on the urbanisation followed by industrialisation were the contributor to environmental pollutions especially water pollution, in other word, these countries were improving but at the same time, destroying the earth. Industrialisation of many sectors such as food, pharmaceuticals, leather, textile, cosmetics, paper, printing, etc. used natural or synthetic dye compounds to colour their end products (Garg *et al*., 2004). Wastewater from these industries contains dye pollutants which is the culprit of the environmental contamination (Hameed and Daud, 2008). Presence of these colours in water sources even in a minute amount is aesthetically unpleasant where it prevents penetration of light into the water system and affects the photosynthesis process. Eventually, it will disrupt the life cycle of living organism and might lead to the devastation of water ecosystem (Turabik, 2008). Some of these dyes are toxic and carcinogenic, therefore the necessity of dye wastewater undergo pretreatment prior of disposal is important (Uddin *et al*., 2009). Among these industries, textile industry was the main contributor of wastewater effluent due to high consumption of water during dyeing, washing and finishing processes (Selene *et al*., 2008). These wastewater consist high content of other products besides dye compounds such as dispersants, acids, bases, salts, detergents, oxidants, etc (Selene *et al*., 2008). Therefore, discharge from textile industries were usually high in colour content, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and suspended solid (Garg *et al*., 2004).Thus, direct discharge of textile wastewater into municipal water stream is definitely impermissible.

Textile industry was growing fast which contributes to the mass usage of synthetic dye compounds in dyeing process. Synthetic dyes were preferable in textile industries due to their stability, ease of use, low cost and the availability of colours (Aksu and Karabayir, 2008). Standard wastewater treatment methods (the conventional treatment methods) were found to be ineffective due to the stability and non-biodegradable of synthetic dye compounds (Aksu and Karabayir, 2008). The available conventional treatment method or was known as physico-chemical technique consisting of flocculation, ozonation, chemical coagulation, precipitation, adsorption, etc where each of them have limitations such as high cost and production of hazardous by-products (Reife *et al*., 1998). Adsorption of dye wastewater by activated carbon was the most effective treatment method from the list of conventional treatment methods but it is pricey and difficult to be regenerated (Rubin *et al*., 2005).Thus, researchers switch their interest in search of a better alternative and in recent years, readily available agricultural wastes have become the main focus of researches as substitute of activated carbon (Pehlivan *et al*., 2008).

Adsorption is a mass transfer process by which substrate or sorbate is transferred from liquid phase and bound to the surface of a solid by physical or chemical interactions (Pehlivan *et al*., 2008). Biosorption, a group of adsorption process with the usage of dead biomass ranges from fungi, bacteria, algae, chitin to agricultural waste is a metabolism- independent process (Aksu *et al*., 2009). Sorption of dye compounds might be attributed by the presence of various functional groups on the surface of biosorbent (Pehlivan *et al*., 2008). High selectivity, efficient, cost effective, excellent removal performances, potential of regeneration and availability were the beauty of adsorption process that caused it to be outstanding among the available conventional treatment methods (Aksu *et al*., 2009).

Marine seaweeds, or macroalgae were found to be abundant around the ocean in the world (Vijayaraghavan and Yun, 2008). It has been proven from various studies that selected species of seaweeds showed high sorption capacities for a wide range of heavy metals (Hashim and Chu, 2004; Bekci, *et* *al*., 2009; Hii *et al*., 2009). Seaweeds were grouped into three basic division based on their colour, namely, brown (Phaeophyceae), red (Rhodophyceae) and green (Chlorophyceae). The great sorption capacities towards heavy metals were due to the presence of cell wall properties where both electrostatic attraction and complexation play an important role in biosorption process (Davis *et al*., 2003). Brown seaweeds (Phaeophyceae) were found to effectively remove heavy metals (Davis *et al*., 2003). *Sargassum* is one of the dominant species in the division of Phaeophyceae in terms of species number (Phang, 2006). It was found that *Sargassum* species was preferred in biosorption of heavy metals as compared to other seaweeds due to their polysaccharide content (Vieira and Volesky, 2000). However, the role of seaweeds in removal of dye compounds was not extensively studied despite of their excellent binding capabilities towards heavy metals. Therefore, the aim of this study is to investigate the capability of locally available *Sargassum* species, *Sargassum binderi* to remove basic dyes, Basic Blue 3 (BB3) and Basic Yellow 11 (BY11).

The main objectives of present study are:

1. to determine the efficiency of *S. binderi* in removal of basic dyes (BB3 and BY11) in single dye system via batch mode of adsorption process.
2. to search for the optimum operating conditions for removal of binary dye by using Response Surface Methodology (RSM).
3. to investigate the optimum conditions in removal of single and binary dyes by using fixed-bed down-flow continuous mode column.

4. to study the kinetics sorption of BB3 and BY11 removal under batch and continuous mode of adsorption process.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Dyes

Zollinger (2003) described colour based on their characteristics to emit and absorb light in the visible range (400-700 nm). Natural colourants have been widely used ever since prehistoric time especially in cave drawings (Zollinger, 2003). The first synthetic dye, mauve, was discovered by Perkin in 1856 which marked the drastic change in the usage of natural colourants leads to the beginning of the modern synthetic dyes era and water pollution (Zollinger, 2003).

Two major classification of colourant includes pigments and dyes. The major difference between these two was based on the solubility. Pigments were practically insoluble in the media which was used to be coloured whereas dyes were completely or at least partially soluble in aqueous solution (Zollinger, 2003). Pigments required attachment to a substrate or additional compounds (eg. polymer in paint, plastic, etc) while dyes were used to apply directly to the substrate (leather, paper, textile, etc) from liquid and have specific affinity to a given substrate (Zollinger, 2003).

Dyes give colour to a material through binding with that particular material (Allen and Koumanova, 2005). Dyes were ionic, aromatic organic compounds with acryl ring structure and delocalises electron systems (Allen and Koumanova, 2005). Colour of the dyes were contributed by the presence of chromophore group which is a radical configuration consisting of conjugated double bonds with delocalised electrons such as azo (-N=N-); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or –CH=N-); nitroso (-NO or N-OH); nitro (-NO_2 or =NO-OH); and sulphur (C=S) (Allen and Koumanova, 2005). Aromatic structure of chromophore normally contains benzene, naphthalene or anthracene rings where they were part of chromogen-chromophore structure with an auxochrome or the ionising groups (Allen and Koumanova, 2005).

Varieties of dye groups were found to be available in the market based on the chromophore groups. Among these dyes, anthroquinone, phthalocyanine, triarylmethane and azo dyes were the most important dye groups (Aksu *et al.*, 2007). Most commonly type of dyes used in industries was Azo dyes which were highly discharged in the wastewater effluent (Babu *et al.*, 2007). Dyes can also be classified into three major groups based on their dissociation in an aqueous solution, namely, anionic, cationic and non-ionic. Anionic groups of dyes includes direct, acid and reactive dyes; while cationic dyes were the basic dyes; and non-ionic dyes were dispense dyes (Mishra and Tripathy, 1993).

Dyes can also be classified according to the chemical structure or by usage. Classification by usage of dyes has advantages in describing the type of dyes based on the usage or method of application before considering of the chemical structures due to dye nomenclature and jargon of dyes (Hunger, 2003). Table 2.1 lists the usage classification of dyes based on the method of applications or type of usage applied (Hunger, 2003).

Table 2.1: Usage classification of dyes (Hunger, 2003).

Class	Principle substrates	Method of application	Chemical types
Acid	nylon, wool, silk, paper, inks, and leather	usually from neutral to acidic dye baths	Azo (including premetallised), anthraquinone, triphenylmethane azine, xanthene, nitro and nitroso
Azoic	components and compositions cotton, rayon, cellulose acetate and polyester fiber	impregnated with coupling component and treated with a solution of stabilized diazonium salt	azo
Basic	paper, polyacrylonitrile, modified nylon, polyester and inks	applied from acidic dyebaths	cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	cotton, rayon, paper, leather and nylon	applied from neutral or slightly alkaline baths containing additional electrolyte	azo, phthalocyanine, stilbene, and oxazine
Disperse	polyester, polyamide, acetate, acrylic and plastics	fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	azo, anthraquinone, styryl, nitro, and benzodifuranone

Table 2.1: Continued

Class	Principle substrates	Method of application	Chemical types
Fluorescent brighteners	soaps and detergents, all fibers, oils, paints, and plastics	from solution, dispersion or suspension in a mass	stilbene, pyrazoles, coumarin, and naphthalimides
Food, drug, and cosmetic	foods, drugs, and cosmetics		azo, anthraquinone, carotenoid and triarylmethane
Mordant	wool, leather, and anodized aluminium	applied in conjunction with Cr salts	azo and anthraquinone
Oxidation bases	hair, fur, and cotton	aromatic amines and phenols oxidized on the substrate	aniline black and indeterminate structures
Reactive	cotton, wool, silk, and nylon	reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic
Solvent	plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes	dissolution in the substrate	azo, triphenylmethane, anthraquinone, and phthalocyanine
Sulfur	cotton and rayon	aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur- containing products on fiber	Indeterminate structures
Vat	cotton, rayon, and wool	water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	anthraquinone (including polycyclic quinones) and indigoids

2.2 Azo Dyes: Azo Chromophore

Azo dyes were the most important commercially available dyes which cover almost 50% of the dye available in the market (Hunger, 2003). Azo dyes, consist of azo group with nitrogen nitrogen double bonds (-N=N-) at least and can contain two (diazo), three (trisazo), rarely four (tetrakisazo) or more (olyazo) azo groups associated with chromophores contributes to the bright colour of the dyes and were classified as the largest class of dyes used in textile industry (Hunger, 2003; Aksu *et al*., 2007). These azo groups were attached to two groups by which at least one or usually both were aromatic groups (Hunger, 2003). Fragile azo bonds were prone to the production of reductive cleavage and degradation products such as aromatic amines (Leechart *et al*., 2009). The most labile portion of azo dyes was the azo linkages and it can be easily breakdown by enzyme in mammals including man. Azoreductase, an enzyme responsible in cleavage and reduction of azo linkage into two parts were widely found in various parts of organs in living organism such as spleen, kidney, lung, heart, brain, liver and muscle tissues (Leechart *et al*., 2009). Aromatic amines comprises of chemical causing acute and chronic effect produced from reduction of azo linkage were absorbed in intestine and excreted in urine might cause severe impact towards living organism (Leechart *et al*., 2009). Azo dyes cover a wide variety of dyes namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes (Aksu *et al*., 2007). Therefore, azo dyes was characterised as the culprit of water pollution by textile wastewater as more than 15% of these textile dyes end up in the wastewater stream (Park and Choi, 2003).

2.3 Basic Dyes

Basic dyes are in the category of cationic dyes and carries localised or delocalised positive charge in their molecules (Hunger, 2003). These dyes can be converted into water-insoluble dye bases by the addition of basic which give rise to the name “Basic Dyes” (Hunger, 2003). Among various types of dye available, basic dyes were found to be the brightest class of soluble dyes widely used by textile industry (Hamdaoui and Chiha, 2007). Basic dyes are one of the commercially available synthetic dyes. These dyes are stable due to the presence of aromatic and various functional groups which in turn render recalcitrant effect of the dyes (Marungrueng and Pavasant, 2007). The wide range of basic dyes was the common dye colourant for acrylic, nylon and wool dyeing process (Marungrueng and Pavasant, 2007). Basic dyes were used in textile such as silk, leather, paper, cotton, mordent with tannin dyeing process as well as ink and copying paper in office supplies industry (Hunger, 2003). Initially, basic dyes were employed for printing of cellulose acetate but gradually become important in textile dyeing process in par of the development of synthetic fibers such as polyacrylonitrile, acid-modified polyester and polyamide fibers (Hunger, 2003). Basic dyes have great tinctorial strength where obvious colouration can be observed at concentration as low as 1 ppm (Mao *et al*., 2008).

Positive charge of cationic dyes can either be localised or delocalised. Cationic dyes with delocalised positive charge are classified with methine dyes (Hunger, 2003). Basic Yellow 11 (BY11) was one of the methine dyes where it gives rise to high colour strength and was practically used in dyeing of polyacrylonitrile fibers (Hunger, 2003). Another type of basic dye used in this study is Basic Blue 3 (BB3). BB3 is an oxazine cationic dyes which form positively charged ions due to dissociation with positively electric charge delocalised over the entire molecule (Hunger, 2003). The properties and structure of BY11 and BB3 were listed in Table 2.2 and Figure 2.1, respectively.

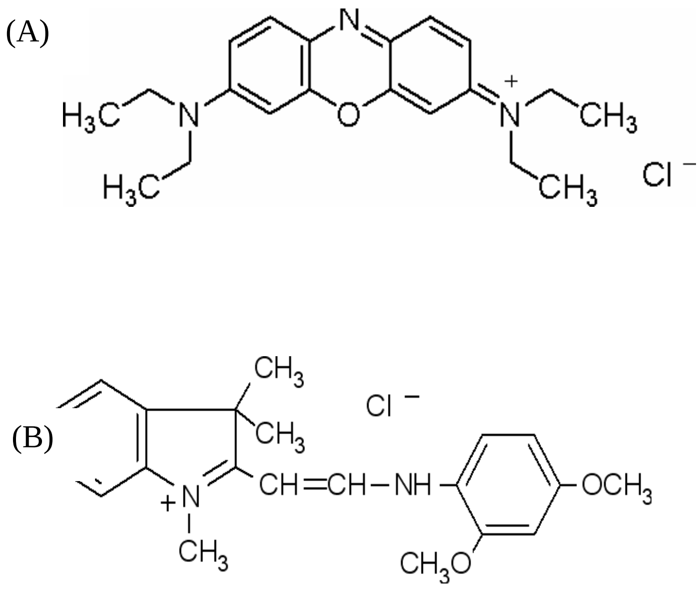


Figure 2.1: Chemical structure of:
(A) Basic Blue 3 (BB3)
(B) Basic Yellow 11 (BY11)

(Source: Sigma Aldrich, United States of America)

Table 2.2: Properties of Basic Blue 3 (BB3) and Basic Yellow 11 (BY11)

Properties	**Basic Blue 3**	**Basic Yellow 11**
Cas Number	33203-82-6	4208-80-4
Empirical Formula	$C_{20}H_{26}ClN_3O$	$C_{21}H_{25}ClN_2O_2$
Molecular Weight	359.89	372.89
Colour Index Number	51004	48055
Composition	Dye content, 25 %	Dye content, ~20%
UV absorption, λ_{max}	654 nm	413 nm

(Source: Sigma Aldrich, United States of America)

2.4 Problems Associated with Dyes

Synthetic dyes were used extensively nowadays in many industries like textiles, pharmaceutical products to food due to their stability, ease of use as well as low in cost (Aksu *et al*., 2007). Currently, there are more than 100,000 types of dyes available commercially (Demirbas *et al*., 2008). These dyes consist of synthetic origin and complex structure which contributes to their stability and infavourable towards decolourisation (Demirbas *et al*., 2008; Tan *et al*., 2010). Water is crucial for humans and living organisms where seventy percent of the earth surfaces are covered by water resources, therefore, dyes containing wastewater is totally unaesthetic towards the environment. Colour in water supply should be less than 15 true colour units (Cobalt platinum units), and colour can be identified at concentration as low as 5 units through naked eyes (Nemerow *et al*., 2009). Even a minute concentration of dye compounds in solution were highly visible and might limits aquatic productivity by preventing light penetration into water system, affecting photosynthesis processes and eventually devastating the ecosystem (Turabik, 2008). Dye compounds also contain varieties of harmful organic substances which will affect the life cycle of aquatic organisms (Demirbas *et al*., 2008). Dyes will cause acute or chronic effects on living organism depending on the time of exposure as well as concentrations (Wang *et al*., 2008).

One of the main contributors of water pollution due to dye pollutants was textile industry. Production of fabric from textile industry consumed large volumes of water and chemicals during the wet processing process. Chemical reagents used in this process were highly varied in their chemical composition and ranged from inorganic compounds to polymers and organic products (Mishra and Tripathy, 1993).

2.5 Textile Effluents: Environmental Concerns

Traditionally, dyeing and finishing of fabric in textile industry generated large amount of waste and was also consume large amount of energy. One kilogram of finished fabric required approximately 200 litres of water for the production, dyeing and finishing process and this caused high demand in water supply which seriously creates pollution issues due to the production of effluent (EPA, 1998). Textile effluent, mainly wastewater from dye bath and finishing process typically consist of dye content in the range of 10 mg/L to

200 mg/L and was considered as highly coloured (Ali *et al.*, 2009). Besides high content of colourants, textile effluents consist wide range of chemicals, saline and non-biodegradable compounds contribute to the high value of BOD and COD (Ali *et al.*, 2009). Figure 2.2 illustrate the general operations in textile production.

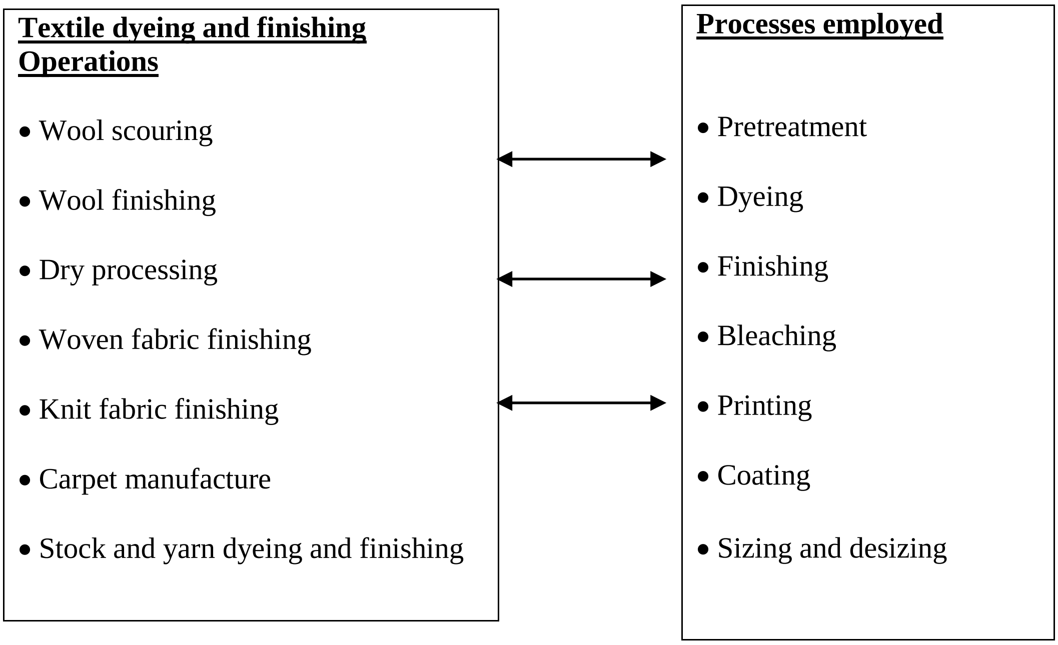


Figure 2.2: General operations and process employed in textile production (EPA, 1998).

The overall characteristics of effluent from textile mills vary from the type of textiles produced. Table 2.3 listed the general effluent characteristics of textile mills based on the process in production of fabrics. Risk factors of water pollution by textile industry were mainly associated with wet processes comprises of scouring, desizing, and bleaching due to the high production of wastewater (Yusuff and Sonibare, 2004).

Table 2.3: General effluent characteristics of textile mills

Process	Effluent composition	Nature
Sizing	Starch, waxes, carboxymethyl cellulose (CMC), polyvinly alcohol (PVA), wetting agents	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High in BOD, COD, Suspended solid (SS), Dissolved Solids (DS)
Bleaching	Sodium hypochlorite, chlorine, sodium hydroxide, hydrogen peroxide, acids, surfactants, sodium silicate, sodium phosphate, short cotton fibre	High alkalinity, high SS
Mercerising	Sodium hydroxide, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuffs urea, reducing agents, oxidising agents, acetic acid, detergents, wetting agents	Strongly coloured, high BOD, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly coloured, high BOD, oily appearance, SS
Finishing	Inorganic salts, formaldehyde	Slightly alkaline, low BOD

(Source: Pollution Research group [PRG], 1998)

Table 2.4: Estimation of degree of dyes fixation and loss in effluent for different dye-fiber combination

Dye application class	Fibre	Degree of fixation (%)	Loss of effluent (%)
Acid	Polymide	89 – 95	5 - 20
Basic	Acrylic	95 – 100	0 - 5
Direct	Cellulose	70 –95	5 - 30
Disperse	Polyester	90 – 100	0 - 10
Metal - complex	Wool	90 – 98	2 - 10
Reactive	Cellulose	50 – 90	10 -50
Sulphur	Cellulose	60 – 90	10 - 40
Vat	Cellulose	80 – 95	5 - 20

(Source : Ramachandra, Ahalya and Kanamadi, 2008)

Production of wastewater from textile industry was highly in colour, BOD as well as COD. These contaminants were crucial and will severely contaminate the river body. The Department of Environment Malaysia (DOE) set a list of limitations for discharge of effluent into the river body to avoid severe pollution and devastation of the water ecosystem. These limitations are listed in the National Water Quality Standards for Malaysia (Table 2.5).

Table 2.5: National water quality standards for Malaysia

Parameters	Unit	Classes					
		I	IIA	IIB	III	IV	V
Ammoniacal Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	›2.7
BOD	mg/l	1	3	3	6	12	›12
COD	mg/l	10	25	25	50	100	›100
DO	mg/l	7	5-7	5-7	3-5	‹3	‹1
pH		6.5-8.5	6-9	6-9	5-9	5-9	-
Colour	TCU	15	150	150	-	-	-
Elec. Conductivity*	umhos/cm	1000	1000	-	-	6000	-
Floatables		N	N	N	-	-	-
Odour		N	N	N	-	-	-
Salinity (%)	%	0.5	1	-	-	2	-
Taste		N	N	N	-	-	-
Total Dissolved Solid	mg/l	500	1000	-	-	4000	-
Total Suspended Solid	mg/l	25	50	50	150	300	300
Temperature (C)	°C	-	Normal +2°C	-	Normal +2°C	-	-
Turbidity (NTU)	NTU	5	50	50	-	-	-
Faecal Coliform **	counts/100mL	10	100	400	5000 (20000)^{a}	5000 (20000)^{a}	-
Total Coliform	counts/100mL	100	5000	5000	50000	50000	›50000

Notes		
N	:	No visible floatable materials or debris or No objectionable odour, or No objectionable taste
*	:	Related parameters, only one recommended for use
**	:	Geometric mean
A	:	maximum not to be exceeded

Table 2.5: Continued

Class	Uses
CLASS I	Conservation of natural environment water supply 1- practically no treatment necessary Fishery 1 – very sensitive aquatic species
CLASS IIA	Water Supply II – conventional treatment required Fishery 11- sensitive aquatic species
CLASS IIB	Recreational use with body contact
CLASS III	Water Supply 111 – extensive treatment required Fishery 111 – common, of economic value, and tolerant species livestock drinking
CLASS IV	Irrigation

(Source: DOE, 2008)

DOE Malaysia plays an important role in monitoring of water quality in each of the river basins in Malaysia. It has been reported that from 1,064 monitoring stations in 143 river basins throughout Malaysia, 638 (60%) of the stations were found to be clean, 376 (approximate 35%) was slightly polluted and 50 (5%) were polluted in year 2006. However, this condition improved in year 2007 with increasing numbers of clean monitoring stations of river basins (DOE, 2008).

According to the Interim Report by DOE, colour concentration as low as 150 True Colour Unit (TCU) is totally impermissible to the environment and extensive treatment process is required prior of disposal. In order to maintain and improve the cleanliness of river basins, it is important to emphasize on the treatment methods of wastewater from industries. There are various ways in conventional treatment method to effectively remove pollutants from these effluents but each of these treatment methods have drawbacks which further provokes researchers to search for better alternatives (Reife *et al*., 1998).

2.6 Methods in Removal of Dye Compounds

Discharge of dyes from effluent to sewage has serious impact towards environment. Removal of these compounds from aqueous solutions was crucial and important in the sense of prevention from pollution. Pretreatment methods can be classified into three major groups: (i) Biological method, (ii) Chemical method, and (iii) Physical method. Various pretreatment methods despite of biological, chemical or physical methods have been developed and applied in industrial scale such as flocculation, chemical coagulation, sedimentation, ozonation, adsorption, bioremediation, etc., but these treatment methods possess drawbacks which limits their application towards the industrial scale (Reife *et al*., 1998).

These were the common pretreatment method used in industries and each of these conventional treatment methods has its disadvantages. The major drawbacks of these methods were listed in Table 2.6.

Table 2.6: Conventional wastewater treatment methods

Method	**Main features / characteristics**	**Advantages**	**Disadvantages**
Adsorption	• Non-hazardous end products	• Low cost • No regeneration needed • Dye-adsorbed materials • can be used as substrates in solid state fermentation	• Some adsorbents have low surface area • Possible side reactions loss of adsorbents • Performance dependents on wastewater characteristics
Advanced chemical oxidation	• Chemical treatment process involving ultrasound and UV activation to remove contaminants from wastewater	• Non-hazardous end products	• Highly cost
Biological processes	• Living or non-living organism as biosorbent in removal of contaminants from aqueous solution	• Environmental friendly • Public acceptance • Economically attractive	• Slow process • Needs adequate nutrients • Narrow operating temperature range
Coagulation and Precipitation	• Convert nonsettleable solid to heavier settleable solid through physical-chemical changes by coagulant chemicals	• Effective for all dyes	• Highly cost • High sludge production
Electro coagulation	• Passing of electrical current through water to remove contaminant particles	• Removes small colloidal particles • Without usage of coagulants • Low sludge production • Low cost	• Not effective for all available dyes
Electrochemical oxidation	• Production of ozone and hydroxyl • radicals on the surface of anode • materials and oxidise harmful compounds	• No production of sludge • Breakdown compounds are non-hazardous • No chemicals required	• Highly cost

Table 2.6: (Continued)

Method	**Main features / characteristics**	**Advantages**	**Disadvantages**
Liquid-liquid extraction	• A mass transfer process involving contact of feed materials with special solvent to remove contaminants	• Low cost • Low energy consumption • Variety of solvents available	• Occurrence of emulsification • Effluents need to undergo
Nanofiltration	• Separate soluble ions from water through a semi permeable membrane	• Removes nearly all dye types • High effluent quality • Easy to scale-up	• High investment costs • membrane fouling • Effluent must be treated before disposal
Ozonation	• Uses Ozone to remove pathogen A toxic gas with strong odour, as a powerful oxidising agent in disinfection of wastewater treatment process	• No production of sludge • No alternation in volume	• Highly cost • Short half life
Supported liquid membrane	• Bound soluble chemical substrates in by complexing chemical functional groups	• Minimal loss of extractants • Simple to operate • Low energy consumption • Easy to scale-up • Low cost	• Occurrence of emulsification
Sedimentation	• Used after flocculation process to remove and separate solid from water in a sedimentation basin or tank	• Reduce the amount of suspended solid	• Sludge formation
Ion Exchange	• Employs same principle as adsorption and requires resin	• Simplicity High performance	• Resin deterioration • Unstable water • Turbidity • Iron organic colour • Bacterial-slime fouling

(Source : AWWA, 2003)

2.7 Adsorption

Adsorption was described as the most effective treatment method as compared to the standard conventional wastewater treatment method. Adsorption involves accumulation of substances at two phases, the solid phase and a liquid phase (Nicholas, 2005). Organic pollutants or even dye molecules from aqueous solution were transferred to a solid phase and subsequently into the porous structure of sorbent and these saturated solid adsorbent with organic pollutants can be regenerated or kept away from direct contact with the environment (Geankoplis, 2003; Lima *et al*., 2008). Adsorption took place where solid particles attracts component in aqueous phase to its surface and attached together through chemical or physical bonding (Demirbas *et al*., 2008). In order for the adsorption process to occur effectively, adsorbent used in adsorption process must provide an extremely large surface area for the adhesion of organic pollutants (AWWA, 2003). There are two types of adhesion; either physically or by Van der Waals interactions and both interactions were reversible (Geankoplis, 2003). There are few types of commercial adsorbent readily available for industries such as activated carbon, silica gel, activated alumina, molecular sieve zeolites, synthetic polymers or resins and so on (Geankoplis, 2003). Granular activated carbon (GAC) is the most effective solid-phase adsorbent used in public water treatment due to its surface chemistry and surface area (AWWA, 2003).Difference sizes of the porous structure on the surface of activated carbon provide spaces to adsorb both large and small contaminant molecules (AWWA, 2003). Once all the surface pores were saturated by adsorbed materials, the carbon eventually exhausted and losses it’s ability to absorb any substances from aqueous solution (AWWA, 2003).

2.7.1 Adsorption by Activated Carbon

Activated carbon was made up from raw materials such as bituminous coal, lignite, peat, wood, bone, petroleum-based residues, nutshells and so on (Nemerow *et al*., 2009). Early usage of carbon was reported in sugar solution purification and water filtration process (Carbtrol, 1992). The ability to remove numerous pollutants efficiently led to the increase in the usage for industries (Carbtrol, 1992). Both granular and powder activated carbon are reported to be an efficient common sorbent in removal of contaminants from wastewater with high surface area to volume ratio. Carbtrol (1992) reported that 1 gram of commercial activated carbon have surface area approximately to 1,000 square meters. Activated carbon will gradually lose the ability to absorb substances from wastewater when the porous structures were saturated with substances over a period of time depending on the type and concentration of organic substances (AWWA, 2003). Saturated activated carbon needs to be replaced with new carbon and regeneration of carbon can be done by using the same activation method or reuse purposes (AWWA, 2003).

There are several types of carbon adsorption process in conventional treatment method such as fixed-bed, expanded-bed, and moving-bed contactors. Each carbon adsorption method differs in the design of the column and direction of the water flow as shown in Table 2.7.

Table 2.7: Characteristics of column adsorption process

Column Adsorption Process	**Characteristics**
Fixed bed column	Water flow direction was from the top of the activated carbon column towards downwards and the effluent was withdrawn at the bottom of the column.
Expanded-bed column	Water flow direction was totally opposite with the fixed-bed column where it flows from the bottom towards upwards and the carbon bed was allowed to expand.
Moving-bed column	Spent carbon will be continuously replaced by fresh carbon.

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

Activated carbon used in carbon adsorption process was not cost effective despite of the high ability in removal of dye residues from aqueous solution, therefore, researches have been conducted in search of cheaper alternative to replace the highly cost activated carbon (Lima *et al*., 2008). Table 2.8 tabulated the list of researches conducted in search of cheap and effective sorbent especially from agriculture or industries' waste as replacement for activated carbon in removal of textile dyes compounds.

Table 2.8: Previous research on the removal of different dyes by agricultural biosorbent

Dyes	Sorbent	Sorption Capacity (mg/g)	References
2,4-dinitrophenylhydrazine	Bamboo waste activated carbon	884.96	Nwabanne and Mordi, 2009
Acid Red 114	Sesame seed shell	102.04	Thinakaran *et al*., 2008
	Cotton seed shell	153.85	
	Pongam seed shell	204.08	
Astrazon yellow	Apricot stone activated carbon	221.23	Demirbas *et al*., 2008
Basic Blue 3	*Hevea brasiliensis* seed coat	227.27	Hameed and Daud, 2008
Basic Red 13	Tree fern	408.00	Ho *et al*., 2005
Basic Red 46,	Bentonite	256.40	Turabik, 2008
Basic Yellow 26		333.30	
Basic Yellow 28	Boron waste	75.00	Olgun and Atar, 2009
Basic Red 46		74.73	
Crystal violet	Kaolin	31.94	Nandi *et al*., 2009
Brilliant green		30.59	
Direct blue 86	Orange peel	33.78	Nemr *et al*., 2009
Indigo carmine dye	Rice husk ash	65.90	Lakhmi *et al*., 2009
Malachite green	Oil palm trunk fibre	149.35	Hameed and El-Khaiary, 2008a
Methyl violet	Sunflower (*Helianthus annuus* L.) seed hull	92.59	Hameed, 2008
Methylene Blue	Mansonia wood sawdust	23.80	Ofomaja and Ho, 2008
	Indian Rosewood sawdust	56.40	Garg *et al*., 2004
	Pineapple stem	119.05	Hameed *et al*., 2009
	Beer brewery waste	4.92	Tsai *et al*., 2008
	Banana stalk waste	243.90	Hameed *et al*., 2008b
	Pomelo (*Citrus gandis*)	344.83	Hameed *et al*., 2008a
	Broad been peels	192.70	Hameed and El-Khaiary, 2008b
	Coconut husk activated carbon	434.78	Tan *et al*., 2008b

Table 2.8(Continued)

Dyes Involved	**Sorbent**	**Sorption Capacity (mg/g)**	**References**
Methylene Blue	Tea waste	85.16	Uddin *et al*., 2009
	Papaya seed	555.56	Hameed, 2009a
	Spent tea leaves	300.05	Hameed, 2008b
	Coconut (*cocos mucifera*) bunch waste	70.92	Hameed *et al*., 2008c
	Rattan sawdust	294.14	Hameed, *et al*., 2007
	Wood apple shell	36.90	Malarvizhi and Sulochana, 2008
	Guava (*Psidium guajava*) leaf powder	295.00	Ponnusami *et al*., 2008
	Gypsum	36.00	Rauf *et al*., 2009
	Jute fiber carbon	225.64	Senthilkumar *et al*., 2005
	Dehydrated peanut hull	161.30	Ozer *et al*., 2007
Methylene Blue, Acid Blue 25	Hazelnut shells	76.00 57.00	Ferroro, 2007
Procion Yellow MX Remozol Brilliant Violet Reactive Blue H5G	Poly (methylmethacrylate) grafted chitosan	250.00 357.00 178.00	Singh *et al*., 2009
Reactive Blue 19, Reactive Black 5, Reactive Red 120	Modified basic oxygen furnace slag	76.00 60.00 55.00	Xue *et al*., 2009
Reactive Brilliant Blue	*Aspergillus fumigatus*	190.50	Wang and Hu, 2008
Reactive Yellow 145, Reactive Red 194, Reactive Brilliant Blue	Sorel’s cement	107.67 120.89 103.14	Hassan *et al*., 2009
Remazol Black B	Cotton plant wastes	50.90	Tunc *et al*., 2009
Rhodamine B	*Rhizopus oryzae*	11.25	Das *et al*., 2008
	Parthenium biomass	59.17	Lata *et al*., 2008
Sandocryl golden yellow C-2G	*Caulerpa scalpelliformis*	27.00	Aravindhan *et al*., 2007

2.7.2 Adsorption by Fixed-bed Column and Breakthrough Curves

Batch adsorption process was widely used in laboratory scale for treatment of small volume textile effluent but it is non-practical towards the industrial scale (Emmanuel *et al.*, 2010). Whereas, packed bed column was found to be more effective as compared to batch adsorption process in cyclic sorption and desorption process as it make use of the concentration gradient which create driving force for better adsorption efficiency and allows efficient utilisation of sorbent capacity (Aksu and Gonen, 2004). Wastewater was purified through the physicochemical process by flowing through the fixed-bed column (Emmanuel *et al.*, 2010). Large volume of wastewater can be treated in a continuous mode by using a fixed-bed column and this serve as an advantage over the batch adsorption process (Aksu and Gonen, 2004). Continuous mode of fixed-bed column possess some advantages including high yield operations and easily scale-up from bench scale analysis (Aksu and Gonen, 2004). Mass transfer resistance is the important criteria for fixed-bed column processes and the process is in unsteady state (Geankoplis, 2003). The effectiveness of the fixed-bed column design focuses on the shape of breakthrough curves and the velocity of liquid through the bed (Emmanuel *et al.*, 2010).These breakthrough curves were used in fixed-bed adsorption process to predict the saturation time and performance of the said column. Breakthrough point was defined by AWWA (2003) as the point in a filtering cycle where turbidity-caused materials start to pass through the filter. Figure 2.3 illustrate the typical breakthrough pattern of a granular activated carbon bed.

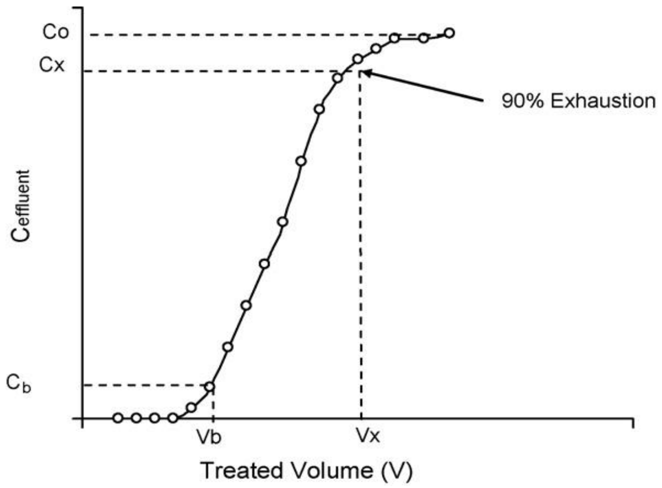


Figure 2.3: Typical breakthrough curve for a fixed-bed column (Al-Degs *et al.*, 2009)

A typical breakthrough curve was affected by several factors such as (Russell, 2006):

(i) Particle size (diameter of particle)
(ii) Adsorbate concentrations
(iii) Temperature
(iv) Molecular weight (an inverse variation depends on the compound weight and configuration of pore diffusion controls)
(v) pH
(vi) Individual properties of solute and carbon
(vii) Iodine number

Column has advantage over filter bed where it can be manufactured according to necessary sizes and provide desired empty bed contact time (EBCT) (AWWA, 2003). EBCT generally described as the time water in contact with activated carbon passes through the bed (AWWA, 2003). EBCT is also the important parameter used to predict the performance of a column where lower EBCT was obtained for a fixed bed-depth column at higher liquid flow rate (Nicholas, 2005).

The area where adsorbent removes sorbate from aqueous solution was named as Mass Transfer Zone (MTZ) and this zone must possess certain bed depth to provide sufficient time for the sorbate in contact with the sorbent (Geankoplis, 2003; Nicholas, 2005). Breakthrough occurs in two conditions where either due to insufficient zone depth or exhaustion of the bed, the latter showed that fixed-bed column was saturated with pollutants and need to be replaced with fresh adsorbent (Nicholas, 2005).

2.8 Marine Seaweeds as Biosorbent

2.8.1 Classification of Marine Seaweeds

Malaysia is a tropical country surrounded with extensive coastline providing excellent habitat for varieties of marine seaweeds (Phang, 2006). Marine seaweeds were known as macroalgae and were included in the kingdom of plantae but were distinguished from other chlorophyll containing plants based on the sexual reproduction system (Davis *et al.*, 2003). Marine algae was categorised into three main groups comprises of (i) Chlorophyceae (green seaweeds), (ii) Rhodophyceae (red seaweeds), and lastly (iii)

Phaeophyceae (brown seaweeds) (Davis *et al*., 2003). Traditionally, seaweeds have been fully utilised as animal feed, food, fertilisers and traditional medicine (Phang, 2006), hence, contribute great impact in economical sector in Malaysia. Besides that, seaweeds also serve as one of the potential adsorbent in removal of some metal ions. These seaweeds in regardless of their division posses advantages in adsorption process due to the large surface area, high renewal nature, low cost and promising sorption capacity towards certain metal ions (Davis *et al*., 2003; Alluri *et al*., 2007; Chen and Yang, 2005). Marine algae contain polyfunctional groups from polysaccharides in cell wall in removal of cationic and anionic metal ions which involves chemical interactions such as ion exchange, surface complex formation, microprecipitation, chelation as well as coordination (Chen and Yang, 2005; Alluri *et al*., 2007). Among the three major divisions of marine algae, brown algae act as an outstanding adsorbent in removal of heavy metals (Wang and Chen, 2009). This might be contributed by high content of alginic acid and fucoidan in the cell wall of brown seaweeds (Davis *et al*., 2003; Alluri *et al*., 2007).

2.8.2 Phaeophyceae (Brown seaweeds)

Phaeophyceae, brown seaweeds consist of large thallus, normally grow on the coral reefs, rocky shores, mangroves and sandy area (Phang, 2006). Under the division of Phaeophyceae, *Sargassum* and *Dictyota* dominates in species number while *Padina* were commonly found along the coastal area in

Malaysia (Phang, 2006). *Turbinaria* and *Lobophora variegata* was often found near to *Padina* on the intertidal coral reefs (Phang, 2006).

Brown colour of these seaweeds was contributed by carotenoid fucoxanthin which is brown in colour and also various pheophycean tannins in the chloroplast of the plant (Davis *et al*., 2003). Typical cell wall of brown seaweeds mainly consists of alginic acid and fucoidan which was found to plays important role in removal of certain metal ions from aqueous solution (Davis *et al*., 2003; Alluri *et al*., 2007). Alginate acid or alginate is the common name of a linear polysaccharides containing 1,4-linked β-D-mannuronic (M) and α-L-guluronic (G) acid arranged in a non-regular, blockwise order along the chain (Davis *et al*., 2003) On the other hand, Fucoidan which was normally found in family of Laminariaceae is a branched polysaccharide sulfate ester with L-fucose 4-sulfate building blocks as the major component.

The key functional groups typically plays important role in adsorption process were carboxylic groups which is found abundantly in acidic functional groups of brown seaweeds (Davis *et al*., 2003). Adsorption of metal ions was found to tightly correlate with the presence of the carboxylic groups in alginate polymers (Davis *et al*., 2003). Sulfonic acid of fucoidan was the second most abundant acidic functional groups presents in the cell wall of brown seaweeds which typically plays secondary role in adsorption process except during metal ions uptake at low pH (Davis *et al*., 2003). These key functional groups therefore contribute to the high capability of brown seaweeds as a potential adsorbent in removal of cationic and anionic metal ions. The same theory applied in removal of metal ions can be implemented in removal of dye compounds by substituting metal ions solution with synthetic dye solution compounds. Figure 2.4 shows the herbarium and fresh specimen of *S. binderi* (brown seaweeds) found in the coastal area of Malaysia which is also the key component in this research to remove basic dyes from aqueous solution.

Figure 2.4: herbarium (left) and fresh (right) specimen of *S. binderi*

S. binderi, an indigenous phaeophycea found in Cape Rachado, Port Dickson, Seremban. *S. binderi* consist of discoid holdfast and compressed smooth branches (Borowitzka *et al*., 2007). Leaves of this seaweed are lanceolate to linear with cuneate basses and acute apices. Primary branches of *S. binderi* was flattened, and with large leaves (Noiraksar and Ajisaka, 2008). Vesicles of *S. binderi* are in sphere shape to elliptical shape with leafy pedicel which aid in the floating of the plant in marine water. *S. binderi* is a monoecious plant with androgynous and flattened receptables (Nairaksar and Ajisaka, 2008).

Functional groups available on the cell wall of *Sargassum* such as alginate acid, fucoidon and sulfonic acid, contribute to the capability of seaweeds in removal of contaminants from aqueous solution. Research have been conducted to investigate the ability of various seaweeds such as *Caulerpa racemosa* var *cylindracea* (Cengiz and Lavas, 2008), *Enteromorpha* (Jayaraj *et al*., 2011), *Turbinaria conoides* (Hii *et al*., 2009), but none of the studies have been done on *S. Binderi.* Therefore, the capability of *S. binderi* to remove dye compounds remains unrevealed. Presence study concentrated in investigation of *S. binderi* to remove basic dye compounds (BB3 and BY11). The capability of *S. binderi* in removal of these dyes will be discussed in detailed in this thesis.

2.9 Isotherm Analysis

The efficiency of adsorption process was determined by isotherm analysis. The uptake behaviour of sorbate was described by isotherm models such as Langmuir and or Freundlich isotherm analysis in batch adsorption process. As for continuous mode fixed-bed column, the mechanism was determined by Mass Transfer Zone (MTZ) Model, Bed Depth Service Time (BDST) Model, Yoon Nelson Model and Thomas Model in determination of the uptake behaviour by sorbent as well as optimisation process.

2.9.1 Langmuir Isotherm Analysis

Langmuir isotherm model was the first isotherm model derived. Langmuir isotherm model assumes that only homogenous adsorbent surface exist or in other words, monolayer type of adsorption occurs which is probably reasonable for the assumption in gas adsorption process (Droste, 1997; Seader and Henley, 2003). At equilibrium, saturation point was been achieved with no further adsorption process to be taken place, therefore, it is assumed that only one molecule will occupied one single site. Linearised form of Langmuir equation was as follow (Equation 2.1) :

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad \text{(Eq. 2.1)}$$

Where q_e is the amount of dye adsorbed at equilibrium over unit mass of sorbent (mg/g), C_e is the equilibrium concentration (mg/L), Q_o the maximum sorption capacity (mg/g) and b is the Langmuir constant (L/mg). Linear plot of $1/q_e$ vs $1/C_e$ was plotted in order to determine the best fit isotherm data for the adsorption system. Crucial characteristic of Langmuir adsorption model was expressed as dimensionless separation factor, R_L which can be derived from Equation 2.2 :

$$R_L = \frac{1}{(1 + bC_o)} \qquad \text{(Eq. 2.2)}$$

b is the Langmuir adsorption constant (L/mg) and C_o is the highest concentration of solution. R_L value indicates the favourable condition of adsorption process with the status of adsorption to be favourable at $0 < R_L < 1$, unfavourable if $R_L > 1$ and lastly linear or irreversible if $R_L = 1$ (Hameed, 2008).

2.9.2 Freundlich Isotherm Analysis

Another popular isotherm model applied to the adsorption process was Freundlich adsorption isotherm. Freundlich model suggested that sorption process involved heterogenous sorption with different classes of adsorption sites (Aravindhan *et al*., 2007). Freundlich assumes that heterogenous type of adsorption occurs with non-uniform distribution of heat over the surface of the sorbent (Brunauer, 1943). Freundlich isotherm was express as in Equation 2.3, and linearised equation was shown in Equation 2.4.

$$q_e = K_F C_e^{1/n} \qquad \text{(Eq. 2.3)}$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \qquad \text{(Eq. 2.4)}$$

K_F (mg/g(L/mg)$^{1/n}$) and n were Freundlich constants derived from the linear slope of ln q_e versus ln C_e. Freundlich magnitude of exponent, 1/n indicates favourable condition of adsorption with value of $n > 1$. Freundlich constant, n, gives indication on how favourable the adsorption process occurs. Value of n in the range of 1 to 10 represents favourable adsorption condition. Linear plot of ln q_e versus ln C_e were employed in the system in order to determine the favourable isotherm model.

2.9.3 Mass Transfer Zone (MTZ)

The efficiency of a fixed-bed column depends on the shape of a breakthrough curve. The breakthrough curve was greatly affected by parameters such as effect of flow rate, concentrations of solute nature in adsorption equilibrium and rate of adsorption (Doran, 1995). Al-Degs *et al.*, (2009) reported that sorbate concentrations, bed depth and liquid flow rate was the most affecting variables among these parameters. The major five steps in contributing significant resistance to adsorption process were as follow:

(i) Transfer of sorbate from bulk liquid to the boundary layer of liquid surrounding the particles.

(ii) Diffusion of sorbate through the stagnant liquid film surrounding the particles.

(iii) Transfer of sorbate into the internal pores of sorbent.

(iv) Occurrences of the actual adsorption process.

(v) Surface diffusion along the internal pore surfaces.

Breakthrough curves are normally expressed in normalised concentration (ratio of outlet concentration to inlet concentration) over time (Aksu and Gonen, 2004). The shape of a breakthrough curves indicates occurrence of adsorption process through a fixed-bed column. Concentration of solutes in liquid phase and solid phase (adsorbent) varies with time and the position in the fixed-bed as adsorption proceeds (Geankoplis, 2003). Mass transfer and adsorption take place when the liquid or sorbate first come into contact with the bed and the concentrations of sorbate outlet eventually increased as time passed by (Geankoplis, 2003). The place where majority adsorption takes place was known as the Mass Transfer Zone (MTZ) (Geankoplis, 2003). The zone moves down the column when sorbate is continuously feed into the fixed-bed column until equilibrium was reached (Geankoplis, 2003).

MTZ is constant in the height or depth as it moves downward the fixed-bed column (Geankoplis, 2003; Unuobonah *et al*., 2010). Equation 2.5 shows the total time taken (t_x) for the establishment of MTZ, where MTZ moves down the length of the fixed-bed and comes out of the column (Unuabonah *et al*., 2010).

$$t_x = \frac{V_e}{F_m} \qquad \text{(Eq. 2.5)}$$

V_e indicates the total volume (mL) and F_m was the liquid flow rate (mL/min). Area under the breakthrough curve from breakthrough point to saturation point represents the total sorbate sorbed by sorbent, q_{total} (Aksu and Gonen, 2004; Calero *et al*., 2009). Effect of bed depth caused in delay or longer t_x value where longer time is required for the establishment of MTZ, from inlet of the bed to outlet of the column (Unuabonah *et al*., 2010). Equation 2.6 shows the calculation for time (t_g) required in downward movement of MTZ in the column

$$t_g = \frac{V_e - V_b}{F_m} \qquad \text{(Eq. 2.6)}$$

V_b indicates total volume at breakthrough point (mL). Calculation for the height of MTZ (HMTZ), cm; and Rate Movement of MTZ (RMTZ), cm min^{-1}, can be carried out by using Equation 2.7 and 2.8:

$$\frac{HMTZ}{H} = \frac{t_g}{t_x - t_f} \qquad \text{(Eq. 2.7)}$$

$$RMTZ = \frac{HMTZ \ x \ F_m}{V_{0.9} - V_{0.02}} \qquad \text{(Eq. 2.8)}$$

H indicates the bed depth of column (cm), $V_{0.9}$ was outlet volume at 90% breakthrough whereas $V_{0.02}$ was at 2% breakthrough point (Unuabonah *et al.*, 2010).

Fractional Capacity, *f* (Equation 2.9) in MTZ was defined as elimination efficiency of sorbate by sorbent at breakthrough point. The sorbent will continue to remove sorbate from aqueous solution under limiting condition (Unuabonah *et al.*, 2010; Namane and Hellal, 2006).

$$f = \frac{1 - t_f}{t_g} \qquad \text{(Eq. 2.9)}$$

2.9.4 Bed Depth Service Time (BDST) Model

BDST model is a simple approach used to predict the relationship between bed depth, Z (cm) and service time, t (min) (Vijayaraghavan *et al.*, 2005; Kumar and Bandyopadhyay, 2006; Padmesh *et al.*, 2006a; Mohan and Sreelakshmi, 2008). This model was originally derived from Bohart and Adams based on the surface reaction rate theory as illustrated in Equation 2.10 (Mohan and Sreelakshmi, 2008)

$$t = \frac{N_0}{C_o V} Z - \frac{1}{C_o K} \ln\left(\frac{C_o}{C_B} - 1 \right) \qquad \text{(Eq. 2.10)}$$

Where C_o indicates the initial dye concentrations (mg/L), C_B is the concentration of effluent at breakthrough (mg/L). K is the adsorption rate constant (L/mgh), N_o the adsorption capacity (mg/cm^3), Z indicates the bed depth of column (cm), V the linear flow velocity of feed to bed (cm/h), lastly, t is the service time (h).

Model proposed by Adam and Bohart requires data from at least nine individual column experiments, hence, it is laborious and time consuming (Kumar and Bandyopadhyay, 2006). Hutchins (1973) then further simplified Adam and Bohart's model through some modification of the equations and reduce the number of individual column experiments to be conducted from nine to three fixed-bed column and was named as BDST model (Kumar and Bandyopadhyay, 2006; Mohan and Sreelakshmi, 2008). Modified equation of BDST model was shown in Equation 2.11.

$$Z_o = \frac{V}{KN_o} \ln\left(\frac{C_o}{C_B} - 1\right) \qquad \text{(Eq. 2.11)}$$

Where Z_o indicates the critical bed depth required for the column. Linear plot of service time, t (h) againt bed depth (cm) were used to determine critical bed depth of column (Padmesh *et al.*, 2006a).

2.9.5 Thomas Model

Thomas model was widely used to characterise the performance of column in a packed-bed column (Padmesh *et al.*, 2005b; Aksu *et al.*, 2007). It is used to calculate the adsorption rate constant as well as solid phase concentration of sorbate on the sorbent in continuous mode of studies (Sivakumar and Palanisamy, 2009b). Thomas Model is expressed as in Equation 2.12 and linearised as in Equation 2.13.

$$\frac{C}{C_o} = \frac{1}{1 + \exp\left(\frac{k_{Th}}{Fm}\left(q_o M - C_o Veff\right)V\right)} \tag{Eq. 2.12}$$

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{TH} q_o M}{Fm} - K_{TH} C_o t \tag{Eq. 2.13}$$

M is the mass of sorbent (g), kinetic coefficient, K_{TH} and adsorption capacity, q_o of Thomas Model can be determined from linear plot of ln [(C_o/C_t)-1] versus service time, t (min). Thomas model, unlike other model assumes Langmuir kinetics of adsorption-desorption process and no axial distribution of sorbate on sorbent is derived through the adsorption process. The main weakness of thomas model is the rate driving force obeys second-order reversible kinetic reactions where adsorption is not usually controlled by chemical processes but by interphase mass transfer (Aksu aand Gonen, 2004). This model also assumes that separation factor is constant but it is applicable to both favourable and unfavourable isotherms (Aksu and Gonen, 2004; Padmesh *et al*., 2005).

2.9.6 Yoon and Nelson Model

Yoon and Nelson Model addressed adsorption process based on the assumption that the rate of decrease in probability of adsorption of each sorbate is proportional to the probability of sorbate adsorption and probability of sorbate breakthrough on sorbent (Aksu and Gonen, 2004; Ozturk and Kavak, 2005; Han *et al*., 2009; Sivakumar and Palanisamy, 2009a). This model is a simple model as compared to other mathematical models for adsorption process and does not requires detailed data on the characteristics of sorbent, type of sorbent as well as physical characteristics of adsorption bed (Aksu and Gonen, 2004).

Equation 2.14 represents linearised Yoon and Nelson equation in single component system:

$$\ln \frac{C}{C_o - C} = k_{YN} t - \tau k_{YN} \qquad \text{(Eq. 2.14)}$$

K_{YN} indicates the rate constant (min^{-1}), τ is the time to achieve 50% breakthrough (min) and lastly, t is the time for breakthrough (min). Plot of linear graph ln $C/(C_o$-$C)$ against time, t were used to determine values of k_{YN} and τ as according to Equation 2.14 (Aksu and Gonen, 2004; Calero *et al.*, 2009).

2.10 Kinetic Analysis

The uptake mechanism of sorbate by sorbent can be described by two kinetic analysis models: (i) Lagergran's Pseudo-first-order Kinetic Model (Liu and Liu 2008), and (ii) Ho's Pseudo-second-order Kinetic Model (Ho, 2003). These two models differ in the type of uptake mechanism by sorbent. The correlation coefficient, R^2 values was used to determine the appropriateness of kinetic models that best fitted to the adsorption system.

2.10.1 Kinetic Analysis: Pseudo-first-order Kinetic Model

Pseudo-first-order was theorised by Lagergran as shown in Equation 2.15 which was further integrated as linearised form shown in Equation 2.16.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{(Eq. 2.15)}$$

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\,t \qquad \text{(Eq. 2.16)}$$

q_t indicates the sorption capacity at time t (mg/g), q_e is the sorption capacity at equilibrium (mg/g), and k_1 is the constant. Linear plot of log ($q_e - q_t$) versus t was used in determination of k_1 constant (min^{-1}) and R^2 values which indicates the best fitted kinetic model.

2.10.2 Kinetic Analysis: Pseudo-second-order Kinetic Analysis

Pseudo-second-order kinetics which was found to be the famous kinetic model as compared to the others was expressed in Equation 2.17.

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{qe}\,t \qquad \text{(Eq. 2.17)}$$

k_2 (g/mg.min) indicates pseudo-second-order kinetic constant which was derived from linear plot of t/q_t versus t.

2.11 Thermodynamic Analysis

Thermodynamic indicates the spontaneous mode of biosorption occurrences in nature. Parameters involved in thermodynamic studies were Gibbs free energy (△G^o), enthalpy change (△H^o) and entropy change (△S^o) determined from Equation 2.18, 2.19 and 2.20.

$$K_d = \frac{C_{e,ad}}{C_e} \qquad \text{(Eq. 2.18)}$$

$$\Delta G^o = -RT \ln K_d \qquad \text{(Eq. 2.19)}$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \text{(Eq. 2.20)}$$

Where K_d correspond to the distribution coefficient for the adsorption, $C_{e,ad}$ indicates equilibrium concentration on the adsorbent (mg/L). R is the universal gas constant (8.314 Jmol^{-1}K^{-1}) and T is the absolute temperature at Kelvin (K). △G^o showed the degree of feasibility and spontaneity of sorption process (Aksu *et al.*, 2008). △H^o and △S^o was obtained from linear plot of ln K_d versus 1/T.

2.12 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is defined as a collection of statistical and mathematical techniques which is useful for developing, improving and optimising processes (Myers and Montgomery, 2002; Gonen and Aksu, 2008). RSM is powerful in optimising multi variables with minimal amount of experiments required (Gonen and Aksu, 2008; Ay *et al.*, 2009). RSM applications normally come in sequential (Myers and Montgomery, 2002). The first part is the screening experiment where critical variables were evaluated and selected. Plackett-Burman (1946) statistical analysis plays an important role in this phase where selection of critical variables was conducted through a twelve experimental runs (Reddy *et al*., 2008; Bari *et al*., 2009). The significance of Plackett-Burman analysis were expressed by the coefficient of determination, R^2 and statistically significance is determined by F-test, whereas, significance of regression coefficients was by t-test (Chen *et al*., 2009). Once these critical variables have been identified, determination of variables range nearer to the optimal condition will be conducted by using the first-order model and optimisation technique, namely Method of Steepest Ascent Path (Myers and Montgomery, 2002).The direction of steepest ascent path were mainly depends on the signs and magnitudes of the regression coefficients from the first-order model (Myers and Montgomery, 2002; He and Tan, 2006; Chen *et al*, 2009). Experiments will be conducted along the steepest ascent path until no increment in the response was obtained and this particular point will be used as the center point for further optimisation process (Chen *et al*., 2009). Second phase of RSM analysis is the continuance of optimisation process where a second-order model will be used and analysed to obtain optimum condition for the processes finalised by determination of small region of interest (Myers and Montgomery, 2002). Central Composite Design (CCD) is a second-order model widely used in the second phase of RSM where it consist of 2^n factorial runs with 2n axial runs and six replicates of n_c, center runs (Myers and Montgomery, 2002; Hameed *et al*., 2008b). CCD is a method suitable for fitting of a quadratic surface and in the same time optimises significant parameters with minimal number of experiments and analyse the interactions between the critical variables through Response Surface Contours (Myer and Montgomery, 2002; Hameed *et al*., 2008b).

Apart from the explanation above, RSM generally constitute of three major steps (Gonen and Aksu, 2008):

(i) Design of the experiment

(ii) Response Surface Modelling through regression

(iii) Optimisation process.

RSM is a useful and powerful tool in contributions towards designing of experiments with multiple variables from developing, improving and optimisation of the processes with the aim of finding suitable estimation and relationship between sets of independent variables (factors) and dependent variables (response) (Gonen and Aksu, 2008).

CHAPTER 3

GENERAL MATERIALS AND METHODS

3.1 Preparation of Sorbent

Fresh *S. binderi* was collected from Cape Rachado, Port Dickson, Seremban, Malaysia. Seaweeds were washed under running tap water to remove sand, salt particles and foreign particles on the surface of seaweeds. The cleaned seaweeds were then rinsed several times with distilled water and dried in oven at 60^{o}C for 24 h.

3.2 Pretreatment of Seaweeds

In aim to avoid organic leaching, chemical modification of *S. binderi* was conducted by contacting 1.5 g of seaweeds (intact or powderised) with 0.2 % v/v of formaldehyde solution and agitated at 150 rpm for 24 h. Treated seaweeds were then rinse thoroughly with distilled water to remove formaldehyde residual on the seaweeds and dried in oven at 60^{o}C for 24 h. Dried treated seaweeds were kept in a tightly closed container with silica gel until further usage.

3.3 Preparation of Dye Stock Solution

Synthetic dye stock solution for both Basic Blue 3 (BB3) with C.I. No. 51004 and Basic Yellow 11 (BY11) with C.I. No. 48055 was prepared by dissolving 1 g of dye powder with 1000 mL of distilled water. Working solutions were then prepared by diluting dye stock solution with distilled water to subsequent required concentrations.

3.4 Calibration of Dye Solutions Standard Curve

Series of dye concentrations were prepared by diluting 1000 mg/L of dye stock solution and analysed by using double beam UV/VIS spectrophotometer (Perkin Elmer, United States of America). Calibration graphs of both dyes were plotted and used to determine the concentrations of dye solutions during adsorption process (Appendix C to F).

Figure 3.1 illustrates the overall flow of experimental workds conducted in the current study.

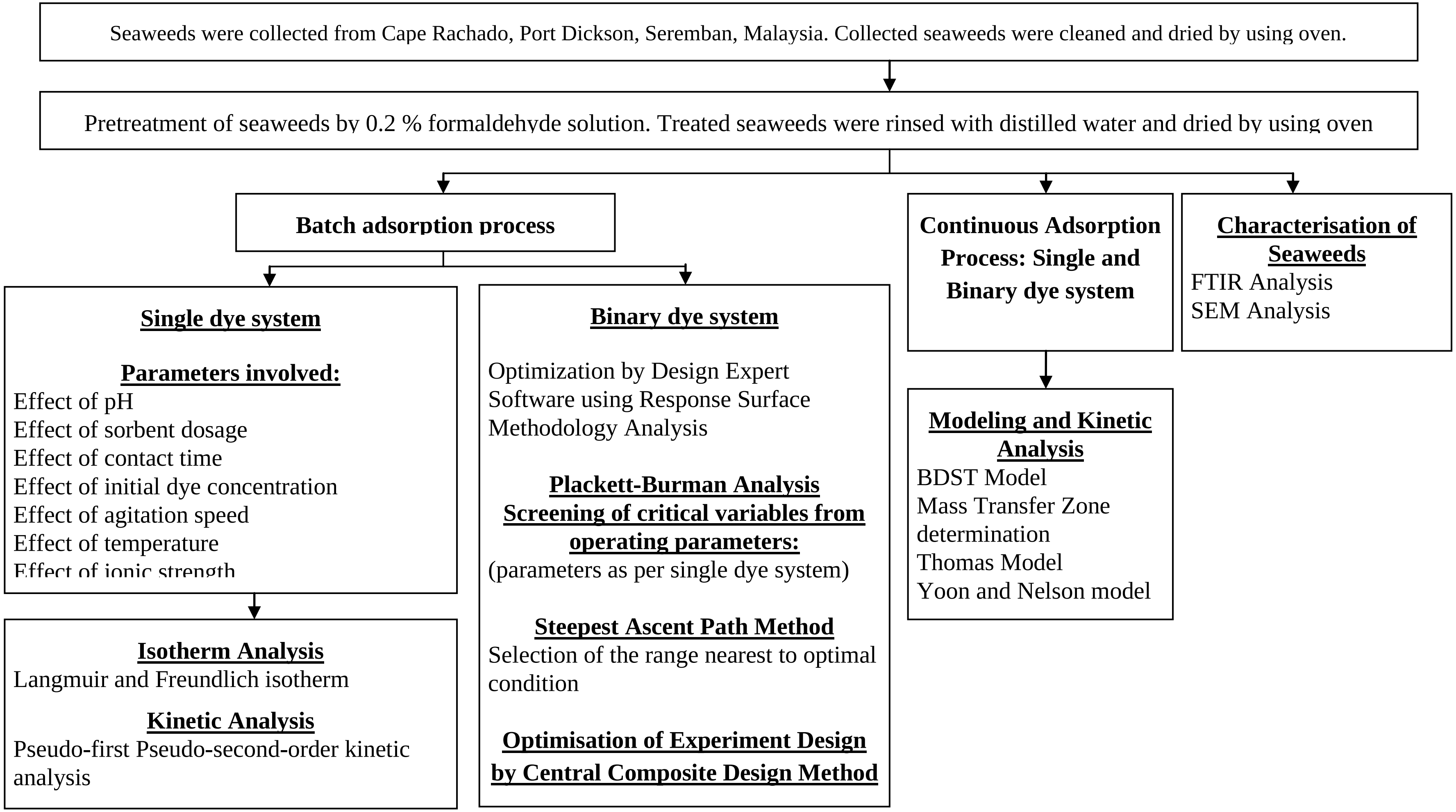


Figure 3.1: Summary of the whole experimental design

CHAPTER 4

BATCH ADSORPTION PROCESS VIA CONVENTIONAL OPTIMISATION METHOD

4.1 Introduction

Conventional type of wastewater treatment used until today possesses disadvantages despite on the capability in removal of pollutant from water system (Chen and Yang, 2005). Therefore, researchers were keen in search of alternative with low cost and high capability to replace the existing standard wastewater treatment method.

From economical and simplicity point of view, adsorption is one of the conventional and most effective treatment methods (Lakhsmi *et al*., 2009). However, usage of activated carbon which is the preferable sorbent used in adsorption method is too expensive and laborious (Hameed *et al*., 2008a). This phenomenon provokes researches to look for low cost sorbent preferably from the waste of agricultural or industries.

Marine seaweeds was categorised as one of the potential adsorption due to the high renewable nature and feasibility (Aravindhan *et al*., 2007). Various marine seaweeds have been widely used in removal of heavy metals and the same theory may be applied in adsorption of dye waste from wastewater.

In this study, capability of *S. binderi* in removal of basic dyes (BB3 and BY11) from single dye system was investigated. Sorption behaviour of seaweeds towards these basic dyes was determined by various isotherm and kinetic analysis. In addition, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were applied to investigate and characterise the structure and functional groups available on the surface of seaweeds.

4.2 Materials and Methods

4.2.1 Batch Adsorption Process

Batch adsorption studies were carried out by contacting fixed amount of pretreated seaweeds with 150 mL of the synthetic dye solutions and agitated in shaking incubator (Figure 4.1) at 130 rpm, 30^{o}C for 4 hours, unless otherwise stated. Sample (5 mL) were drawn from each flask at pre-determined time interval and the remaining concentration of dyes were analysed with double beam UV/VIS spectrophotometer

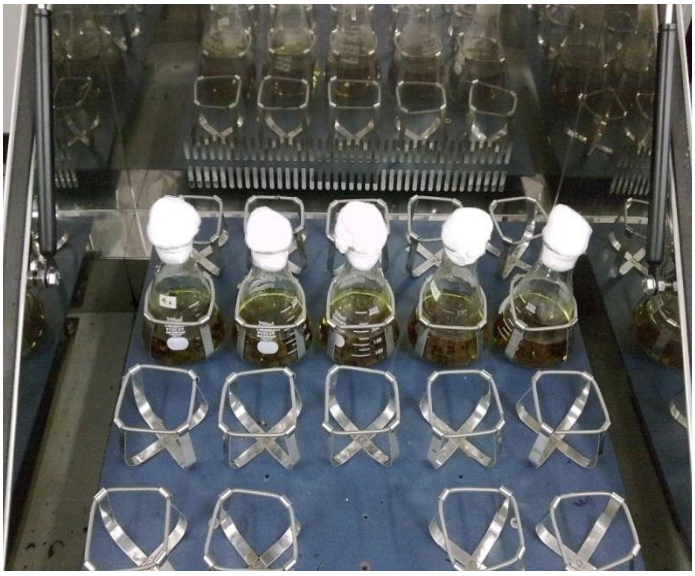


Figure 4.1: Flask containing seaweeds with synthetic dye solution in shaking incubator

Sorption capacity, q_e (mg/g) of seaweeds was calculated by using Equation (4.1) and % of dye removal is calculated by using Equation (4.2).

$$q_e = \frac{(C_o - C_e)V}{W} \qquad \text{(Eq. 4.1)}$$

$$\%\ \text{uptake} = \frac{C_o - C_e}{C_o}\ x\, 100\,\% \qquad \text{(Eq. 4.2)}$$

whereby C_o (mg/L) is the initial concentration of dye solution and C_e (mg/L) is concentration of dye solution at equilibrium; V (L) is the volume of solution, W (g) is the dry weight of biosorbent used.

4.2.2 Effect of Sorbent Dosage

Effect of sorbent dosage on the removal of dyes was determined by agitating various amount of sorbent (0.1 g, 0.5 g, 1.0 g, 1.5 g and 2.0 g) with 150 mL of dye solution (100 mg/L) at 130 rpm, 30°C

4.2.3 Effect of pH

A series of working solutions with different pH values were prepared from stock solution. pH of these working solutions (range of pH 2 to pH 9) were adjusted by using 1 M NaOH or 1 M HCl. Following that, batch adsorption process was conducted by contacting 1 g of seaweeds with 150 mL of dye solutions and agitated at 130 rpm, 30°C for 4 h. Sampling was done at predetermined time interval followed by analysis of sample with double beam UV/VIS spectrophotometer. The most efficient pH condition in removal of dyes was then selected as the pH of dye solution for subsequent parameters.

The range of pH more than pH 9 was not studied as BB3 and BY11 tends to form precipitation when the pH goes up to pH 10 onwards.

4.2.4 Effect of Initial Dye Concentrations and Contact Time

Series of different dye concentrations range from 100 to 1000 mg/L were prepared from stock solution and batch adsorption process was conducted by contacting 1 g of seaweed with 150 mL of dye solutions, agitated at 130 rpm, 30^oC for 4 h. Sampling was performed at pre-determined time interval and sample was analysed by using double beam UV/VIS spectrophotometer.

4.2.5 Effect of Agitation Speed

Dye solution (150 mL, 100 mg/L) were agitated with 1 g of seaweeds at various agitation speeds (50, 100, 150, 200 and 250 rpm) at 30^oC for 4 h. Sampling process was done at pre-determined time interval and analysed by using double beam UV/VIS spectrophotometer. Optimum agitation speed with highest sorption efficiency obtained from this study was selected for the effect of ionic strength.

4.2.6 Effect of Ionic Strength

Effect of ionic strength on dye removal was conducted by incorporating various concentrations of ionic salt compound, NaCl (10 mmol/L, 50 mmol/L, 100 mmol/L and 500 mmol/L) into dye solutions. Batch biosorption process was conducted and samples were withdrawn at specific time interval.

4.2.7 Isotherm Analysis

Linearised Langmuir isotherm model (Eq. 2.1)

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad \text{(Eq. 2.1)}$$

Linear plot of $1/q_e$ (g/mg) versus $1/C_e$ (L/mg) were used to determine the best fit isotherm data for Langmuir isotherm modeling. As for Freundlich isotherm modelling, linear plot of ln q_e versus ln C_e were used to determine the isotherm of adsorption by seaweed from Equation 2.4.

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \qquad \text{(Eq. 2.4)}$$

4.2.8 Kinetic Analysis

Pseudo-first-order and pseudo-second-order were applied to both single dye systems. R^2 values and comparison of calculated sorption capacity, q_e values and experimental q_e values would be used to verify the application kinetics in uptake of dye compound by *S. binderi.*

4.2.9 Thermodynamic Analysis

Thermodynamic analysis was applied in this study for determination of in-depth information on energetic changes related with adsorption process through Gibbs free energy ($\triangle G^o$), enthalpy change ($\triangle H^o$) and entropy change ($\triangle S^o$). In the present study, Thermodynamic analysis was conducted by using different temperature of dye system (25, 30, 35, 40, 45, 50, 55, 60°C) by using water bath shaking incubator while keeping other operating parameter constant.

Thermodynamic analysis was determined by Equation 2.20 via linear plot of ln K_d versus $1/T$.

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad \text{(Eq. 2.20)}$$

4.2.10 Statistical Analysis

Mean values obtained from each respective operating parameter were analysed with statistical analysis software, SAS. Significance level of each parameter was tabulated in respective tables with different letters. Mean values in the same column not followed by the same letter are significantly different ($p < 0.05$).

4.2.11 Characterisation of seaweeds

Characterisation of seaweed was conducted by using SEM and FTIR analysis. SEM analysis determines the changes of surface morphology while FTIR analyse the functional groups available in seaweeds.

4.2.12 Scanning Electron Microscopy Analysis (SEM)

Surface structure of seaweeds, before and after chemical modification process as well as after adsorption with dye compounds were analysed by Scanning Electron Microscopy (SEM) (Philips, XL30 ESEM) at 20.0 kv and 500 magnification (Figure 4.2). Dried seaweeds were cut into pieces and coated with gold coating (Figure 4.3) before viewing process. Coated seaweeds were kept in drying incubator for further usage.

Figure 4.2: Image of SEM equipment

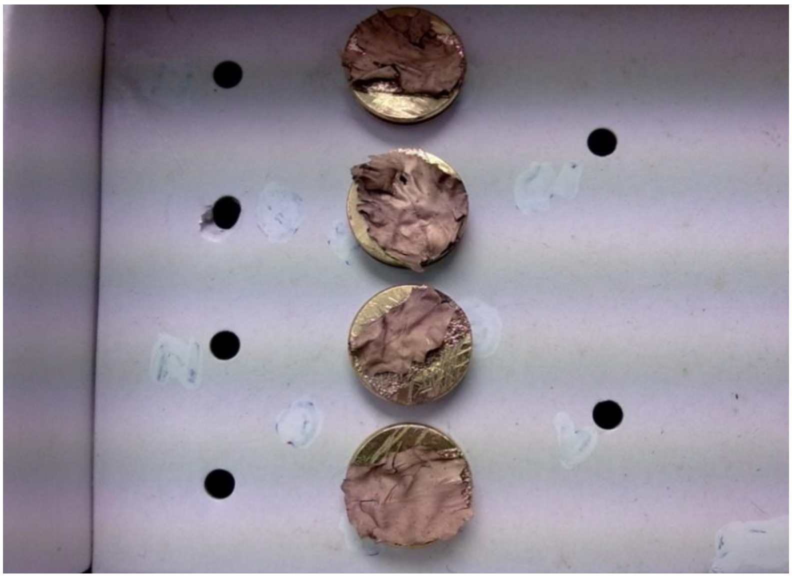


Figure 4.3: Gold coated dried seaweed for SEM viewing

4.2.13 Fourier Transform Infrared Spectroscopy (FTIR)

Identification of functional groups available on the surface of seaweed (before and after sorption process) was determined by using Fourier Transform Infrared Spectroscopy (Perkin Elmer) and spectra were collected from wavelength range of 400 to 4000 cm^{-1} and was analysed by using the software, Spectra (Perkin Elmer). Powderised seaweeds were mixed with KBr powder and ground with pestle and mortar. Pellet of KBr and seaweeds mixture were prepared by pressing at 10 tons for approximately 5 min before proceed with reading of the functional groups by FTIR. Spectra obtained from various mixtures of seaweeds and KBr powder were obtained and analysed.

4.3 Results

4.3.1 Effect of Sorbent Dosage

Figure 4.4 illustrates the sorption capacity and % uptake of BB3 and BY 11 by using different dosage of *S. binderi*. Uptake of both BB3 and BY11 by *S. binderi* increased tremendously with increment sorbent dosage from 0.1 g to 2.0 g and level-off thereafter. Uptake of BB3 by *S. binderi* increased from 91.8% to 99.4% while uptake of BY11 by *S. binderi* increased from 95.6% to 99.9%.

In contrast to % uptake, sorption capacity of *S. binderi* in removal of BB3 and BY11 declined from 137.7 mg/g to 7.5 mg/g, and 143.4 mg/g to 7.5 mg/g, respectively.

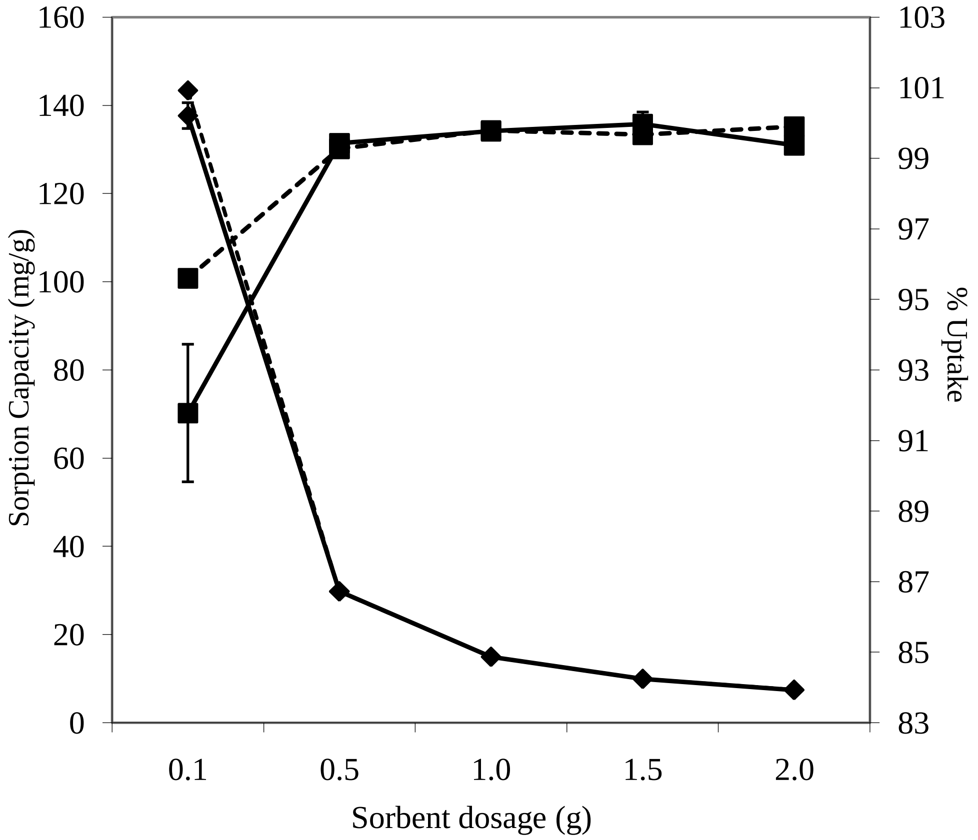


Figure 4.4: Percentage uptake and sorption capacity by *S. binderi* for removal of 100 mg/L (——) BB3 and (·····) BY11 in effect of sorbent dosage, agitated at 130 rpm 30°C.
Symbols: (◆), Sorption capacity; (■), % Uptake
Error bar indicates the mean ± standard deviation of triplicates. For data points without error bars, the errors were smaller than the size of the symbols.

4.3.2 Effect of Initial Dye Concentrations and Contact Time

As shown in Figure 4.5, % uptake of both BB3 and BY11 by *S. binderi* declined with increasing of initial dye concentration from 100 mg/L to 5000 mg/L. Percentage of BB3 dye uptake by *S. binderi* decreased drastically from 99.1% to 49.6%. While on the other hand, % of BY11 uptake is not as drastic as BB3 with less than 20% of dye uptake (99.3 % to 81.3%) with increasing of initial dye concentration.

Figure 4.5 shows that sorption capacity of BB3 and BY11 increased from 14.9 mg/g to 372.0 mg/g, and 29.8 mg/g to 1219.2 mg/g, respectively.

Figure 4.6 illustrates that the uptake of both dyes (BB3 and BY11) were rapid at the beginning of sorption process (first 10 min of the experiment), followed by slower adsorption process before reaching stationary after 30 min of experiment.

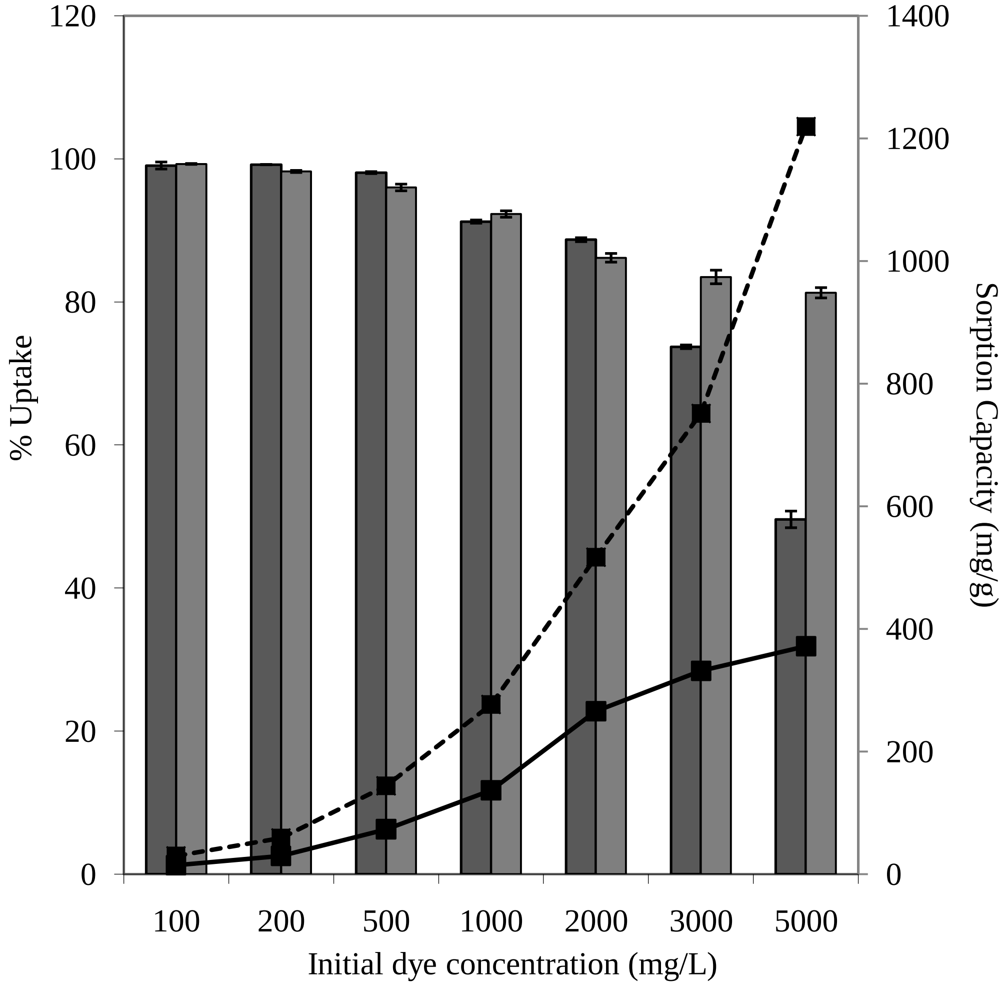


Figure 4.5: Effect of initial dye concentration in removal of (—— , ■) BB3 and (····· , ■) BY11, agitated at 130 rpm, 30°C.
Symbols: (■), Sorption capacity.
Error bar indicates the mean ± standard deviation of triplicates. for data points without error bars, the errors were smaller than the size of the symbols.

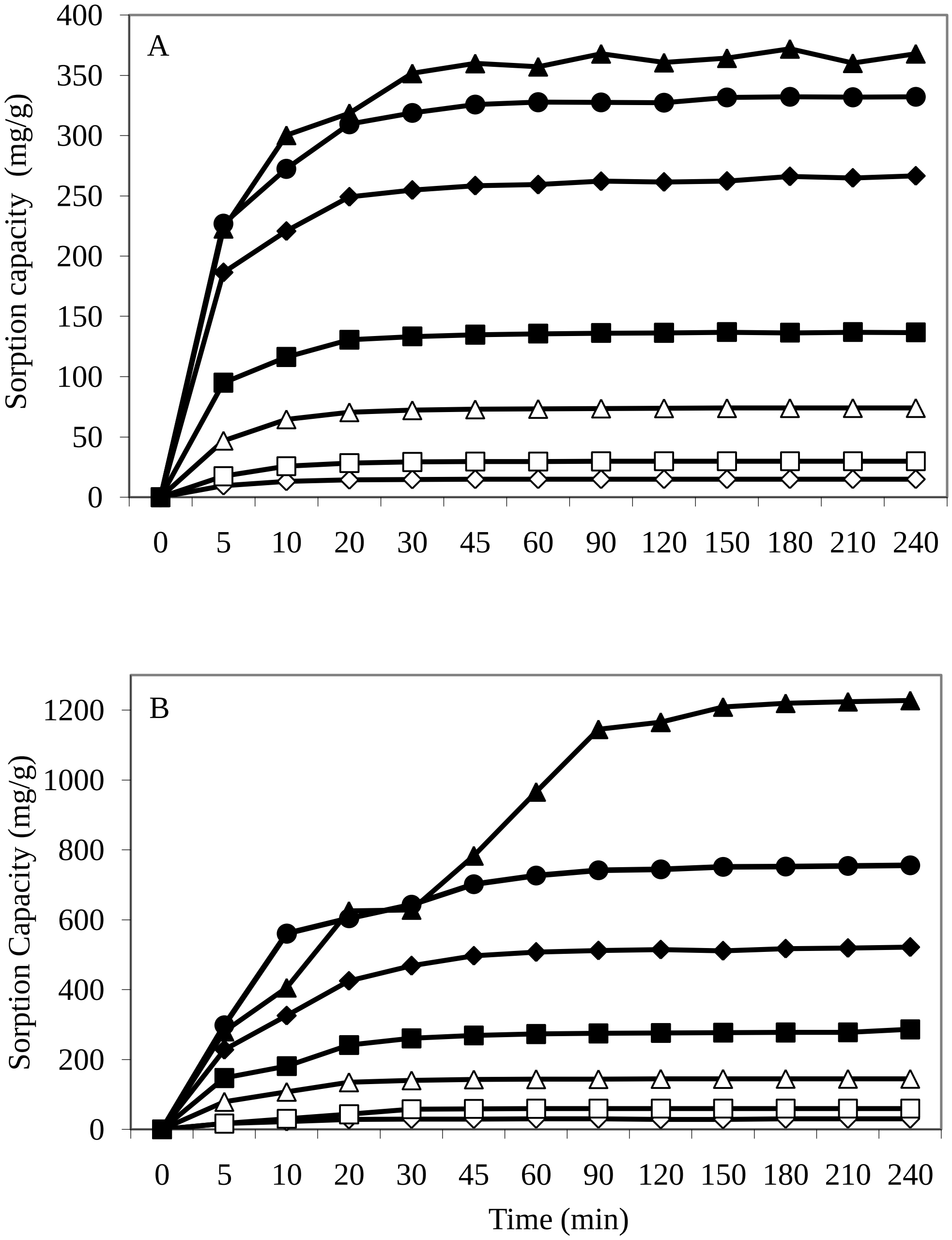


Figure 4.6: Effect of contact time. (A) BB3 (B) BY11
Symbols: (▲), 5000 mg/L; (●), 3000 mg/L; (◆), 2000 mg/L;
(■), 1000 mg/L; (△), 500 mg/L; (□), 200 mg/L;
(◇), 100 mg/L.
Error bar indicates the mean ± standard deviation of triplicates. for data points without error bars, the errors were smaller than the size of the symbols.

4.3.3 Effect of pH

Effect of pH in removal of BB3 and BY11 was done by adjusting pH of dye solution from pH 2 to pH 9. In present study, sorption capacities of *S. binderi* were found to be almost stationary throughout the pH range (pH 2 to pH 9), at 14 mg/g and 29 mg/g for BB3 and BY11 removal, respectively (Figure 4.7). As for the % of uptake, seaweeds exhibited excellent removal efficiency for both BB3 and BY11 (approximately 99%) throughout the pH range. However, uptake of BY11 at pH 2 by *S. binderi* was found to be slightly lower (97% uptake) from the rest of the pH range. One way ANOVA analysis denoted no significant difference among the sorption capacity and % uptake of both BB3 ($p > 0.05$) and BY11 ($p > 0.05$) by seaweed.

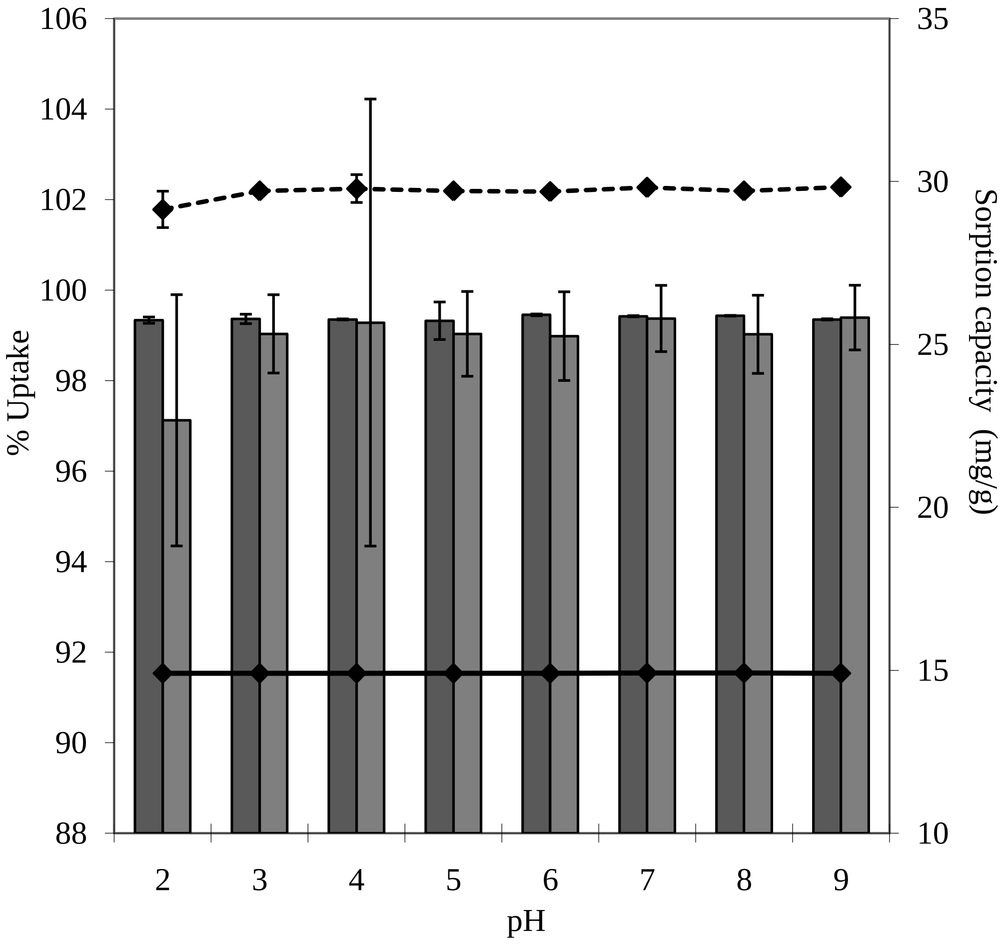


Figure 4.7: Effect of pH in removal of 100 mg/L (—, ■) BB3 and (·····, ■) BY11, agitated at 130 rpm, 30^oC.
Symbols: (◆), Sorption capacity.
Error bar indicates the mean ± standard deviation of triplicates. for data points without error bars, the errors were smaller than the size of the symbols.

4.3.4 Effect of Agitation Speed

Table 4.1 illustrates the effect of agitation rate in removal of BB3 and BY11 by *S. binderi*. Uptake of dyes was constant (approximately 99% BB3 uptake and 98% BY11 uptake) even with increasing of agitation speed from 50 rpm to 250 rpm. However, time for the system to reach equilibrium slightly decreased from 90 minutes to 30 minutes for both systems when the agitation speed increases from 50 rpm to 250 rpm. One way ANOVA analysis denoted no significant difference in % of dye uptake and equilibrium time for removal of both BB3 ($p > 0.05$) and BY11 ($p > 0.05$) in effect of agitation speed.

Table 4.1 Effect of agitation speed in removal of 100 mg/L BB3 and BY11 by *S. Binderi* at 30^{o}C.

Agitation speed (rpm)	**% Uptake**		**Equilibrium time (min)**	
	BB3	BY11	BB3	BY11
50	99.2^{a}	98.1^{a}	90	90
100	99.1^{a}	98.5^{a}	45	60
150	99.1^{a}	98.9^{ab}	45	45
200	99.1^{a}	98.5^{ab}	30	45
250	99.1^{a}	98.8^{b}	30	30

$^{a-b}$ mean values in the same graph not followed by the same letter in the same column are significantly different ($p < 0.05$).

4.3.5 Effect of Ionic Strength

Effect of ionic strength on the sorption of dyes by *S. binderi* was investigated by adding NaCl in various concentrations (10 mmol/L to 500 mmol/L) into the dye systems of BB3 and BY11. From the study, % uptakes of BB3 and BY11 by *S. binderi* were affected with the presence of ionic compounds in the system (Figure 4.8). Both system, BB3 and BY11 recorded approximately 10% and 12% of reduction in % dye uptake, respectively, with increment of NaCl concentration from 10 to 500 mmol/L.

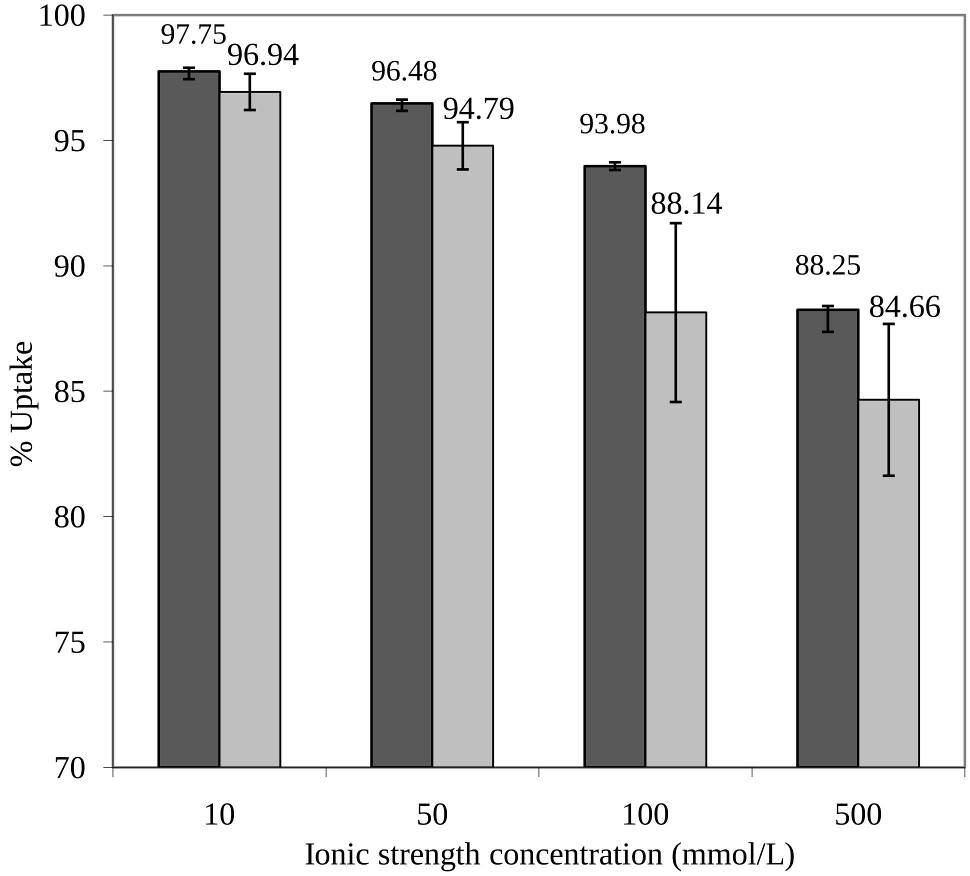


Figure 4.8: Effect of ionic strength in removal of 100 mg/L (■), BB3; (□), BY11, agitated at 200 rpm, 30°C.
Error bar indicates the mean ± standard deviation of triplicates. for data points without error bars, the errors were smaller than the size of the symbols.

4.3.6 Isotherm Analysis

Figure 4.9 and 4.10 shows the linear plot of linearised Langmuir and Freundlich isotherm analysis for batch adsorption of BB3 and BY11 using *S. binderi*, respectively. Both isotherm models exhibited high correlation coefficient, R^2 values (> 0.9). From table 4.3, maximum sorption capacity (Q_o) of *S. binderi* towards BB3 and BY11 were 238.1 and 192.3 (mg/g), respectively. Freundlich constant, K_F ((mg/g(L/mg)$^{1/n}$) for both systems were 22.4 and 32.5, respectively, with n values of 2.5 and 2.0.

In addition, the essential characteristics of Langmuir isotherm analysis which was described in dimensionless separation factor (R_L) of both systems were in the range of 0 to 1 (Table 4.2).

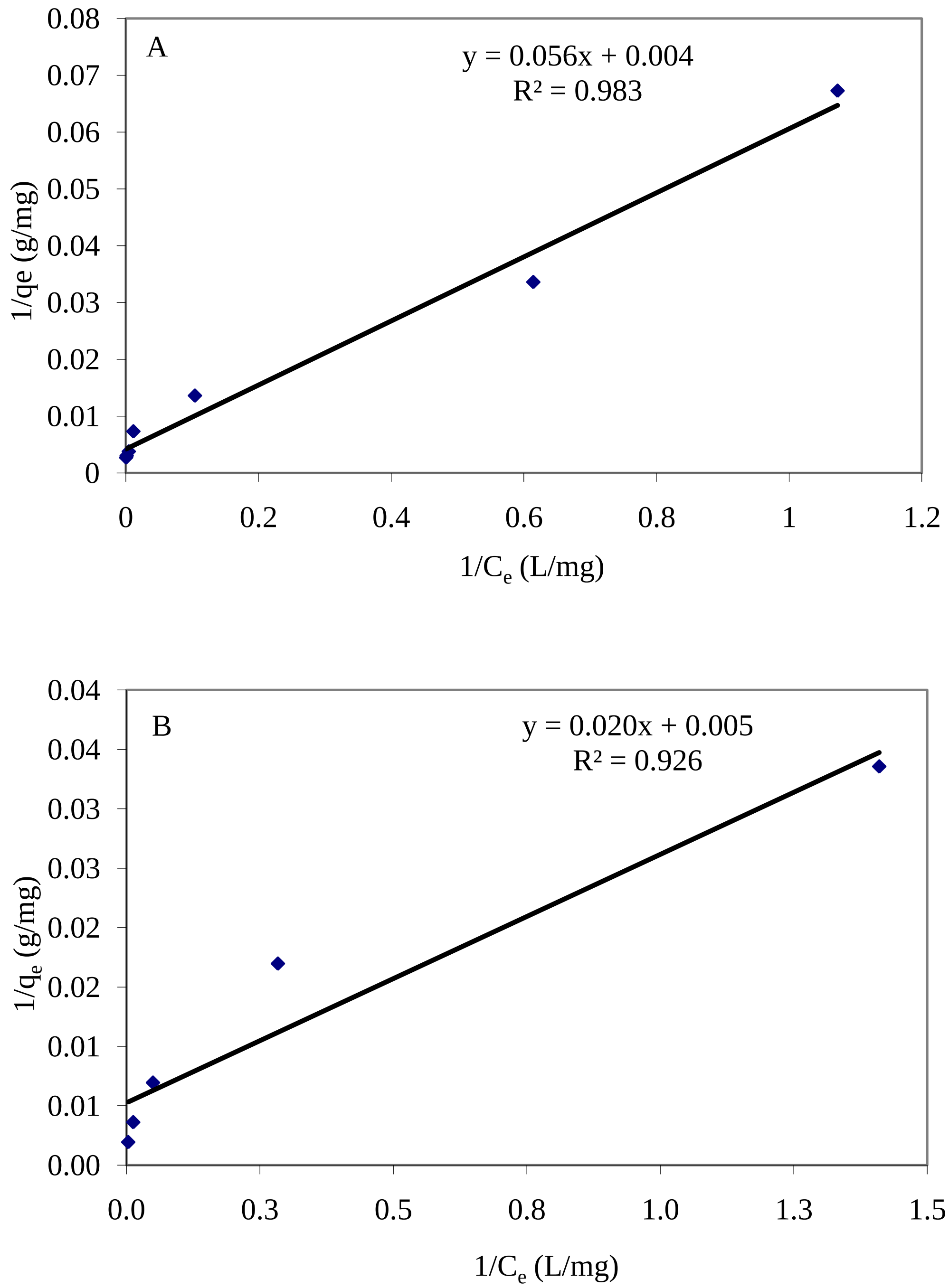


Figure 4.9: Linearised Langmuir isotherm curve for (A)BB3 and (B) BY11.

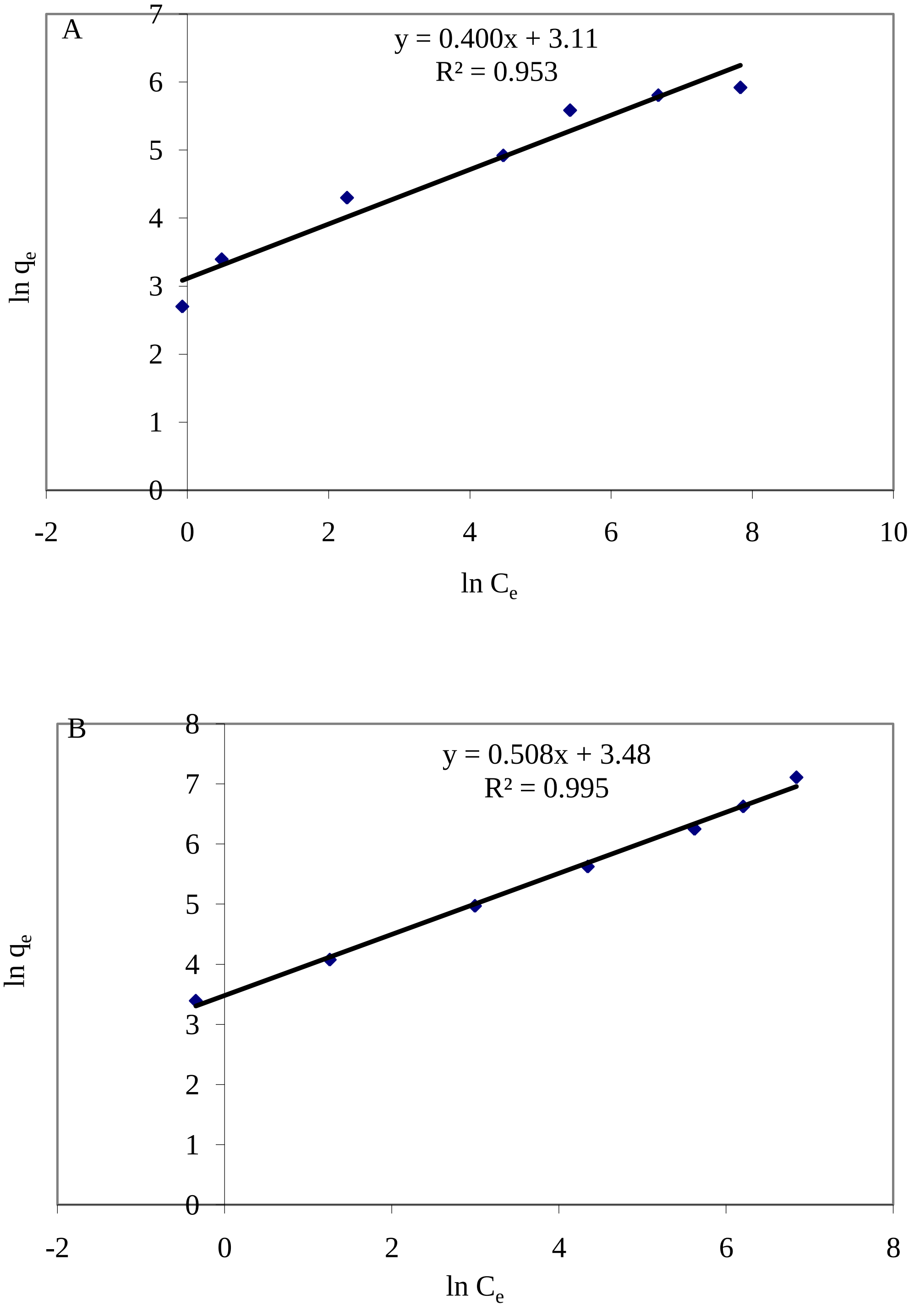


Figure 4.10: Linearised Freundlich isotherm curve of (A)BB3 and (B) BY11

Table 4.2: R_L values from Langmuir isotherm model from various initial dye concentrations in removal of BB3 and BY11 by seaweed.

Initial Dye Concentrations (mg/L)	**R_L (10^{-2})**	
	BB3	**BY11**
100	11.84	3.86
200	6.29	1.97
500	2.62	0.80
1000	1.33	0.40
2000	0.67	0.20
3000	0.45	0.13
5000	0.27	0.08

Table 4.3: Comparison of Langmuir and Freundlich isotherm constants for removal of BB3 and BY11 by *S. binderi*.

	Parameter values	
Langmuir isotherm	BB3	BY11
Q_o (mg/g)	238.1	192.3
b (L/mg)	0.1	0.2
R^2	0.9835	0.9266
Freundlich isotherm		
K_F (mg/g(L/mg)$^{1/n}$	22.4	32.5
n	2.5	2.0
R^2	0.9538	0.9959

4.3.7 Kinetic Analysis

The bahaviour of adsorption process was further described by pseudo-first-order and pseudo-second-order kinetic analysis. As displayed in Table 4.4 and 4.5, removal of BB3 and BY11 by *S. binderi* fitted well to pseudo-second-order model where the correlation coefficient model (R^2) values were closer to unity (> 0.99).

Calculated q_e values of pseudo-second-order model in removal of BB3 and BY11 were found to compliance well with q_e values determined experimentally, respectively, which further confirms that both systems obeys pseudo-second-order model.

Table 4.4: Pseudo-first-order and pseudo-second-order kinetic model for removal of BB3 by *S. binderi*.

C_o	$q_{e,\ exp}$	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
(mg/L)	(mg/g)	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
100	14.9	0.032	1.3	0.7970	0.061	15.0	0.9999
200	29.8	0.034	4.2	0.8960	0.022	30.1	0.9999
500	73.6	0.033	12.7	0.9102	0.009	74.6	1.0000
1000	136.8	0.034	23.3	0.8539	0.006	134.0	1.0000
2000	266.1	0.032	80.4	0.7176	0.002	270.3	0.9999
3000	331.8	0.037	86.8	0.8773	0.002	333.3	1.0000
5000	382.0	0.019	45.0	0.2607	0.001	370.4	0.9996

Table 4.5: Pseudo-first-order and pseudo-second-order kinetic model for removal of BY11 by *S. binderi*.

C_o	$q_{e,\ exp}$	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
(mg/L)	(mg/g)	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	R^2
100	29.8	0.027	5.8	0.6522	1.33×10^{2}	30.0	0.9992
200	58.9	0.031	14.2	0.7741	2.53×10^{3}	61.7	0.9981
500	144.0	0.031	28.4	0.8493	3.04×10^{3}	147.1	0.9999
1000	276.9	0.011	73.4	0.6336	8.33×10^{4}	285.7	0.9996
2000	517.0	0.021	155.4	0.7536	3.97×10^{4}	526.3	0.9990
3000	751.4	0.037	458.8	0.8367	2.49×10^{4}	769.2	0.9998
5000	1219.2	0.039	2138.5	0.8178	2.65×10^{5}	1428.6	0.9956

4.3.8 Thermodynamic Analysis

Figure 4.11 and Table 4.6 illustrates the thermodynamic analysis of adsorption of both systems (BB3 and BY11) by *S. binderi*. From the analysis, negative values of ΔH^o (kj/mol) (BB3 = -18.4, BY11 = -32.4) and ΔS^o (kj/mol/k) (BB3 = -0.0021, BY11 = -0.065) were obtained for both single dye system. The crucial thermodynamic analysis element, ΔG^o for both BB3 and BY11 were found to be negative as well which indicates the spontaneity of adsorption process in nature.

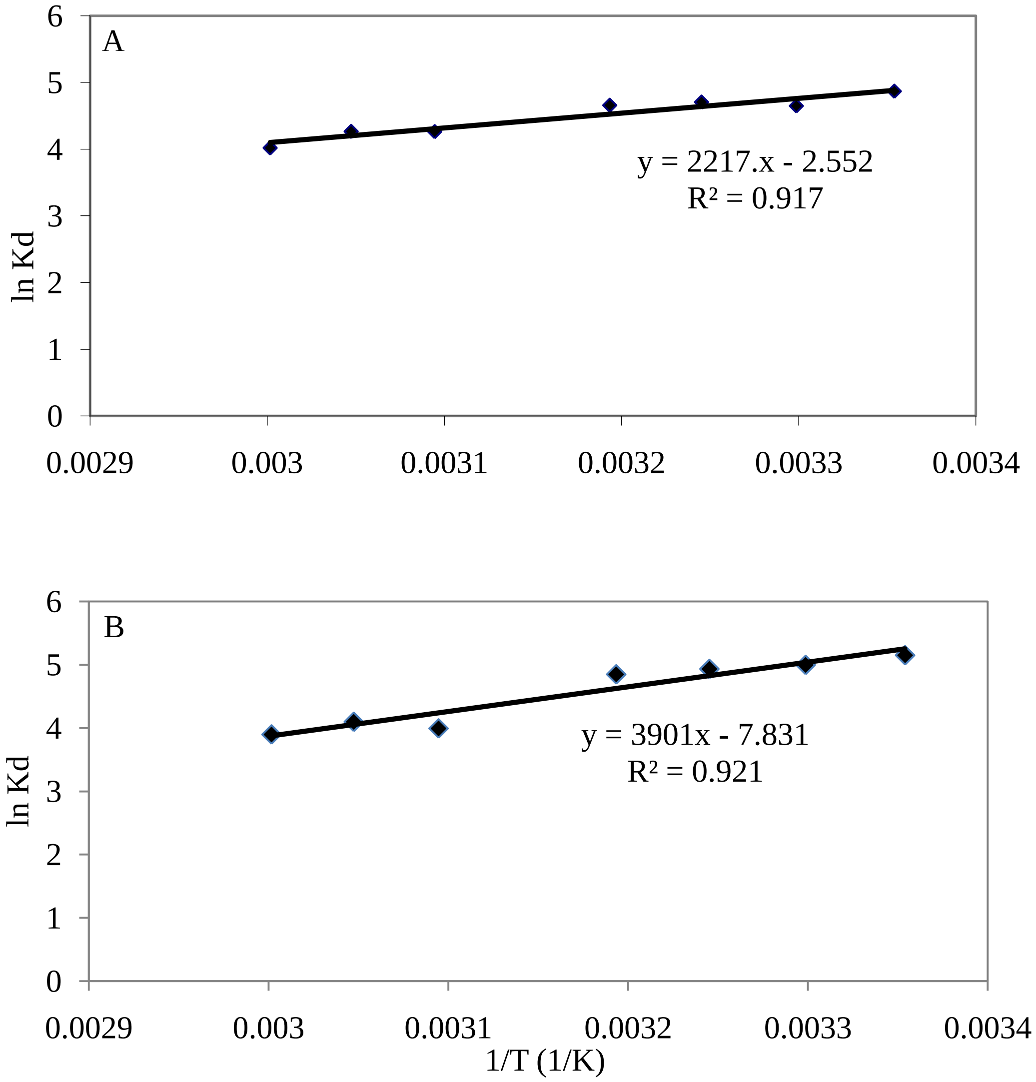


Figure 4.11: Linearised thermodynamic analysis curve for (A)BB3 and (B) BY11.

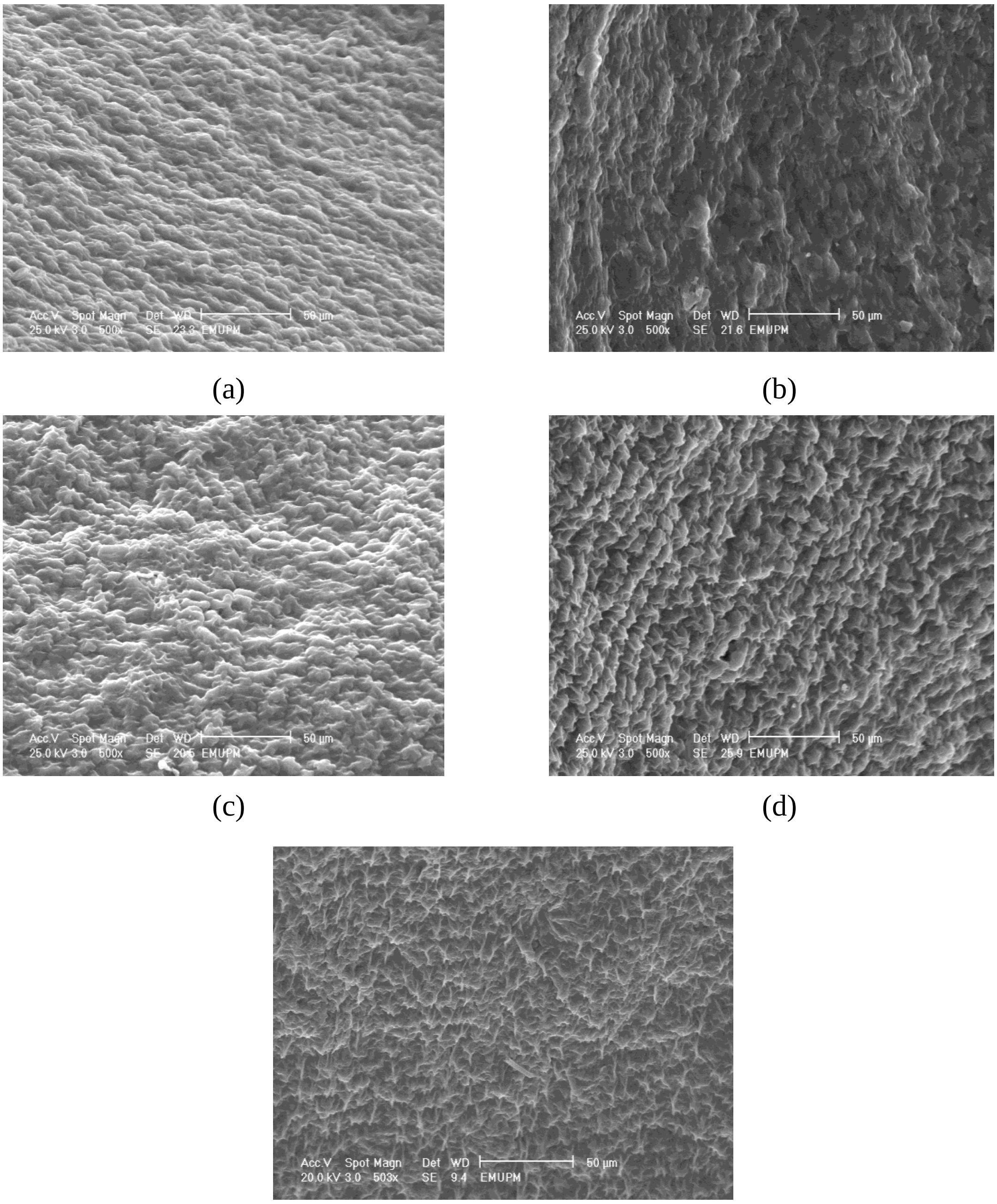
Table 4.6: Tabulated data for thermodynamic analysis for removal of 100 mg/L BB3 and BY11 by *S. Binderi* at 200 rpm, 30^{o}C.

Temperature (^{o}C)	Kelvin (K)	BB3			BY11		
		ΔG^{o}	ΔH^{o} (kj/mol)	ΔS^{o} (kj/mol/k)	ΔG^{o}	ΔH^{o} (kj/mol)	ΔS^{o} (kj/mol/k)
25	298.2	-12070.2	-18.4	-0.002	-12768.	-32.4	-0.065
30	303.2	-11720.0			-12595.5		
35	308.2	-12059.6			-12639.2		
40	313.2	-12131.7			-12622.9		
45	318.2	-12645.6			-10703.8		
50	323.2	-11458.0			-10726.5		
55	328.2	-11645.4			-11175.9		
60	333.2	-11137.3			-10793.8		

4.3.9 Characterisation of Seaweed

Figure 4.12 illustrates the SEM micrograph of seaweeds before and after adsorption process. It was found that obvious protuberance occurred on the surface of seaweed after adsorption process. Protuberances were seen to be more obvious after adsorption of binary dye compounds (combination of BB3 and BY11).

The surface functional groups were scanned through the spectra from 4000 cm^{-1} to 400 cm^{-1}. Few functional groups were identified from the spectra as illustrated in Figure 4.13. Functional groups occurred along the spectra were N-H group (3440 – 3450 cm^{-1}), C=O group (1635 – 1640 cm^{-1}), S=O group (1035-1355 cm^{-1}), and O-H group (605 – 675 cm^{-1}).



(a) (b)

(c) (d)

(e)

Figure 4.12 : SEM images of *S. binderi.*

(a) Raw seaweed (before pretreatment)
(b) Treated seaweed (with 0.2% formaldehyde)
(c) After adsorption with BB3
(d) After adsorption with BY11
(e) After adsorption with binary dye solution (BB3 and BY11)

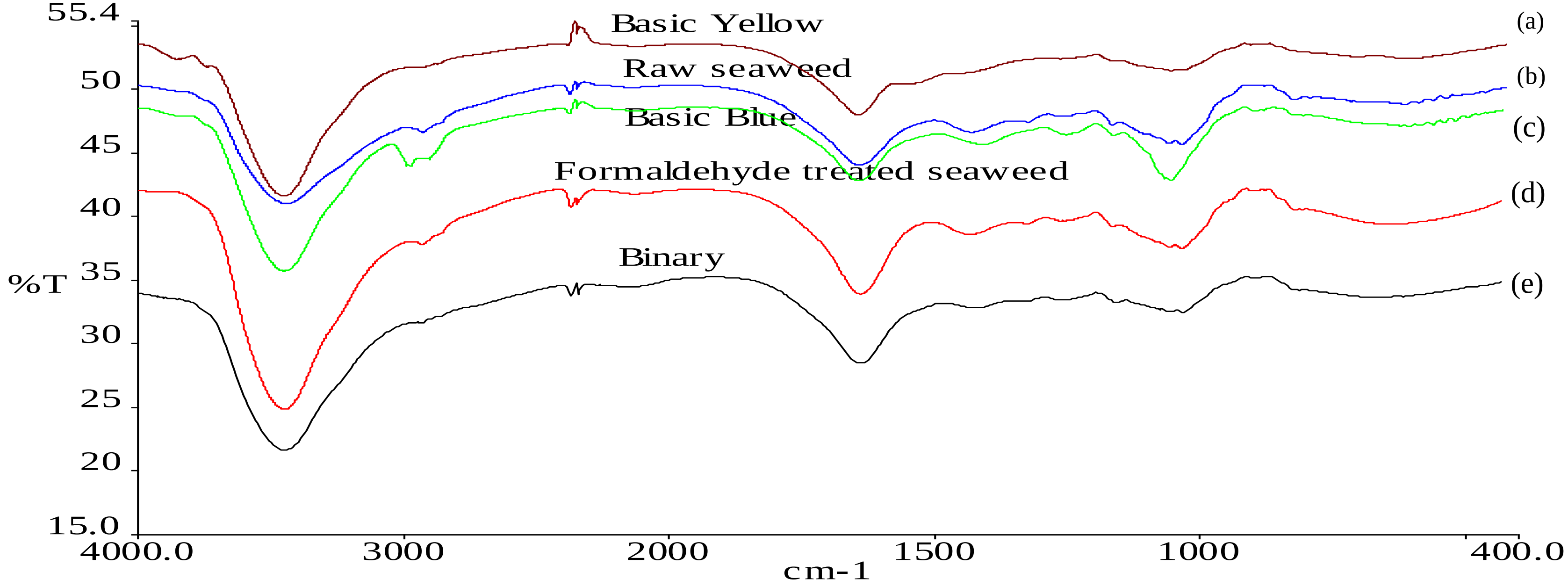


Figure 4.13: FTIR spectrum of *S. binderi*

(a) After adsorption with BY11
(b) Raw seaweed (before pretreatment)
(c) After adsorption with BB3
(d) Pretreated seaweed (Pretreated with 0.2% formaldehyde)
(e) After adsorption with binary dye solution (BB3 and BY11)

4.4 Discussions

4.4.1 Effect of Sorbent Dosage

Usage of seaweeds in adsorption process have been extensively studied and well established especially in metal ions but only few reports the removal of organic pollutants such as dye compounds (Davis *et al*., 2003; Aravindhan *et al*., 2007). These studies reported removal of dye compounds by marine seaweeds such as *Turbinaria conoides* (Hii *et al*., 2009), *Caulerpa racemosa var cylindracea* (Bekci *et al*., 2009) and proves that marine seaweeds have the potential in removal of dye compounds, therefore, the capability of brown seaweed, *S. binderi*, in removal of these organic pollutants (basic dyes) in batch adsorption process has been conducted to determine the potential of the seaweeds as the starter for industrial wastewater sector. The effect of sorbent dosage was investigated in this study where removal of dyes increased with increasing of seaweed dosage from 0.1 g to 2.0 g (Figure 4.4). The was due to the increase of available binding sites on the surface of seaweeds which led to rapid and enhancement of dye compounds uptake by adsorbent (Garg *et al*., 2004; Aravindhan *et al*., 2007; Singh *et al*., 2009; Theivarasu and Mylsamy, 2010). With more available binding sites on the surface of sorbent (seaweed) due to higher seaweed loading, more dye compounds can be sorbed by sorbent, hence, contributing the decrease in equilibrium concentration and increase in percentage of total dye compounds uptake by seaweed (Lata *et al*., 2008).

Sorption capacity (mg/g) is the total dye sorbed per unit gram of sorbent. In present study, sorption capacity was found decreased with increasing of sorbent dosage. This phenomenon might be attributed by overlapping of sorbent dosage or aggregation in total of adsorption sites on the surface of seaweeds and caused in diminishing of total amount of dye sorbed by one gram of seaweeds at higher sorbent dosage (Grag *et al*., 2004). This lead to decrease in surface area and available binding sites, thus, decreases in total amount of dye sorbent by seaweeds (Singh *et al*., 2009).

Similar phenomena was reported in removal of various type of dye compounds by using sorbent such as sawdust (Garg *et al*., 2004), rice hull (Ong *et al*., 2007), peanut hull (Ozer *et al*., 2007), parthenum biomass (Lata *et al*., 2008), seed shells (Thinakaran *et al*., 2008), chitosan (Singh *et al*., 2009), and so on.

4.4.2 Effect of Initial Dye Concentrations and Contact Time

From present study, percentage uptake of dyes decreased gradually while sorption capacity increased when initial dye concentrations increased from 100 mg/L to 5000 mg/L (Figure 4.5).

Higher initial dye concentration provides higher driving force to overcome mass transfer resistance between sorbent and dye compounds, thus, enhances the uptake of dye compounds by unit of sorbent (Aravindhan *et al*., 2007; Hameed, 2009a). In addition, higher chances of collision between sorbent and sorbate at higher initial dye concentrations augmented uptake of dye compounds by seaweeds and therefore, lead to improvement of sorption capacity (Aravindhan *et al*., 2007). On the other hand, percentage uptake of BB3 and BY11 tends to decrease at higher initial dye concentration (Figure 4.5). This might be attributed by overwhelming in numbers of dye compounds at higher initial dye concentrations against the available binding sites (Tunc *et al*., 2009). Unoccupied binding sites become lesser at higher initial dye concentration and contribute to reduction in percentage of dye uptake. Tunc *et al*., (2009) reported similar uptake phenomena of Remazol Black B reactive dye by cotton plant wastes.

From present study, uptake of dye per unit of sorbent was recorded to increase with time until equilibrium where no more dye compounds were sorbed by seaweed (Figure 4.6). Uptake of dyes were rapid in the beginning of adsorption process due to the abundance of available binding sites on the surface of seaweed and gradually slowed down when these sites were occupied (Hameed, 2008c). Dye compounds initially reacts with the boundary layer of sorbent which give rise to rapid uptake and eventually slowed down when it diffuses into the porous structure of sorbent (Hameed *et al*., 2007; Nemr *et al*., 2009). In addition, slower rate of dye uptake during adsorption process might be contributed by the electrostatic encumbrance or repulsion of positively charged sorbed seaweeds with the remaining dye compounds in the solutions, which contributes to longer contact time required for the system to reach equilibrium (Figure 4.6) (Nemr *et al*., 2009).

4.4.3 Effect of pH

pH plays an important role in adsorption process especially in adsorption capacity where it exert influence to both available binding sites and chemistry of solution (Demirbas *et al*., 2008; Nemr *et al*., 2009; Xue *et al*., 2009).

As shown in Figure 4.7, pH possess insignificant effect in removal of both dye compounds (BB3 and BY11) as % uptake of dyes (approximately 99% of removal) and sorption capacity (14 mg/g for BB3, and 29 mg/g for BY11) were almost stationary throughout the pH range from pH 2 to pH 9. Theoretically, alteration in the surface charges of sorbent and aqueous chemistry occurred in corresponding to changes of pH (Rajeshkannan *et al*., 2010). Lower pH consist higher number of H^+ ions which might lead to competition with positively-charged cation dye compounds for negatively-charged functional groups on the surface of seaweeds (Hameed, 2008a; Senthilkumar *et al*., 2005). In contrast, increasing in pH of the solution might lead to an increased in negative charges on the surface of sorbent which enhances the uptake of positively-charged dye compounds due to the electrostatic attraction forces (Hameed, 2008a). Cell wall of *S. binderi* is mainly made of negatively-charged alginate or alginic acid which is the key functional group for adsorption process, followed by sulfonic acid from fucoidan (Davis *et al.*, 2003). Sulfonic acid typically plays secondary role in adsorption process except during adsorption at low pH and this explained the insignificant effect of pH for removal of both systems by seaweed (Davis *et al.*, 2003).

4.4.4 Effect of Agitation Speed

As illustrated in Table 4.1, although the removal of both dyes by *S. binderi* was found to be almost constant (approximately 99% of dye uptake) the each system required different time frame to reach equilibrium adsorption phase. Theoretically, higher agitation rate will boost up the uptake of dyes by adsorbent through decrease of film resistance to mass transfer adjacent to the sorbent particles, therefore, enhance the adsorption process (Ong *et al.*, 2007). However, from present study, uptake of both dyes by seaweeds was found to be independent with agitation speed.

High agitation speed records shorter time required for equilibrium. However, ANOVA analysis in sorption capacity and % uptake denoted no significant effect in removal of both dye compounds with increasing of agitation speed. Therefore, 200 rpm was chosen as the optimum agitation speed for subsequent parameters.

4.4.5 Effect of Ionic Strength

Surfactants, especially the ionic surfactants were typically presence in real textile wastewater (Janos *et al*., 2009). Apart from pH, these surfactants (ionic strength) give great impact in the uptake of dye compounds by adsorbent. Salt, a surfactant normally plays important role in dyeing of textile and in the same time, give rise to high ionic strength which affect greatly in uptake of dyes (Xue *et al*., 2009).

According to Xue *et al*., (2009) ionic strength is the factor that controls on the electrostatic and non-electrostatic interactions between sorbent and sorbate. Results from present study proved this theory by achieving the reduction of percentage dye uptake in both dye system with the increasing of ionic strength concentrations from 10 to 500 mmol/L (Figure 4.8). The phenomena might be due to suppression of electrical double layer surrounding the sorbent surface at high ionic strength concentrations and lead to a decrease in the electrostatic potential which leads to reduction in coulombic free energy, thus, causes decreasing trend in basic dyes adsorption (Wang *et al*., 2008). In the same time, these positively charged sodium ions might compete with the negatively charged available binding sites and decreases the uptake of dye compounds by seaweed (Schiewer and Wong, 2000). Wang *et al*., (2008) reported the similar way of adsorption process in removal of malachite green and methylene blue by rice bran and wheat bran.

4.4.6. Langmuir and Freundlich Isotherm Analysis

As the first-derived isotherm model, Langmuir isotherm model assume that only homogenous adsorbent surface exist which is probably reasonable for the assumption in gas adsorption process (Droste, 1997). At equilibrium, saturation point has been achieved with no further adsorption process to be taken place, therefore, it is assumed that only one molecule will occupied one single site (Cheng *et al*., 2008). On the other hand, Freundlich model suggested that sorption process involved heterogenous sorption with different classes of adsorption sites, or multilayer adsorption (Aravindhan *et al*., 2007; Singh *et al*., 2009). Freundlich isotherm models predict that the dye concentrations on the sorbent increases if the concentration of the solutions increases (Cheung *et al*., 2009). The fitness of isotherm models describing the type of adsorption was determined by correlation coefficient value, R^2. Higher R^2 values, preferable nearer to unity were used to determine the fitness of the isotherm models.

In current study, removal of both BB3 and BY11 was found to obey both Langmuir and Freundlich isotherm models with high correlation coefficient values ($R^2 > 0.9$, Table 4.3). Therefore, the results suggested that homogeneous and heterogenoues adsorption occurred simultaneously in uptake of both dye compounds by *S. binderi*.

The essential characteristics of Langmuir isotherm model, R_L values indicate the favourability of sorbent towards adsorption process. From Table 4.2, it was observed that R_L values of both systems were between the range of 0 to 1, indicating favourable adsorption process (Cheng *et al*., 2008; Sivakumar and Palanisamy, 2009a).

Freundlich constant (K_F) and *n* values derived from Freundlich isotherm models serves as an indication of adsorption capacity of seaweed (Ozer *et al*., 2007; Pehlivan *et al*., 2008). K_F values (mg/g(L/mg)$^{1/n}$) of both dye systems were 22.4 and 32.6 for BB3 and BY11, respectively (Table 4.2). The value of K_F defined as the adsorption or distribution coefficient signifies the amount of dye compounds sorbed by seaweeds for a unit equilibrium concentration (Tan *et al*., 2008). Freundlich magnitude of exponent (1/*n*) indicates favourable condition of adsorption with value of $n > 1$ (Tan *et al*., 2008). As shown in table 4.3, *n* values of BB3 and BY11 were 2.5 and 2.0, respectively, which indicates favourable towards adsorption process.

4.4.7 Pseudo-first-order and Pseudo-second-order Kinetic Analysis

Malarvizhi and Sulochana (2008) stated that adsorption of sorbate by porous structure type of sorbent consist of three consecutive steps:

(i) Film diffusion process through the transport of sorbate to the external surface of the sorbent.

(ii) Particle diffusion process where sorbate is transported within the pores of the sorbent.

(iii) Lastly, pore diffusion of the sorbate into the interior surface of the sorbent.

Isotherm modeling does not describe the uptake behavior or the above stated mechanism in removal of these basic dye compounds by adsorbent. Therefore, two kinetic models, namely pseudo-first-order and pseudo-second-order kinetic models were applied in this study to further describe the adsorption process.

As indicated by Table 4.4 and 4.5, both dye systems fitted well with pseudo-second-order kinetic model, with high R^2 values (nearer to unity) in comparison to R^2 values from pseudo-first-order model. Low values of R^2 from pseudo-first-order kinetic model indicates that uptake of both dyes does not concentrate on one site per dye molecule (Oliveira *et al.*, 2008). Furthermore, calculated q_e values of pseudo-second-order kinetic models were found compliance with the experimental q_e values, which further confirms that uptake mechanism of both dye system follows pseudo-second-order model. Therefore, based on pseudo-second-order, uptake of BB3 and BY11 by seaweed was assumed to be controlled by chemical process or in other words, chemisorptions which involve valency forces through sharing or exchange of electrons (Hameed, 2008; Thinakaran *et al.*, 2008). The occurrence of chemisorptions is controlled by strong intraparticle bonding, such as ionic and covalent bonding, contributes to the irreversible adsorption process (Allen and Koumanova, 2005). In contrast, another type of weak adsorption process-physisorption, is a reversible adsorption process due to weak intraparticle bonding such as Van de Waals, hydrogen and dipole-dipole bonding between sorbent and sorbate (Allen and Koumanova, 2005; Xue *et al.*, 2009).

4.4.8 Thermodynamic Analysis

Thermodynamic denoted the spontaneous mode of adsorption occurrences in nature. Important thermodynamic properties such as Gibbs free energy ($\triangle G^o$), enthalpy change ($\triangle H^o$) and entropy change ($\triangle S^o$) were determined from the Van’t Hoff equation (Eq.20).

As illustrated in Figure 4.11, linear plot from thermodynamic analysis with high R^2 values (> 0.9) indicates the fitness of the model into uptake of BB3 and BY11 by seaweed. The negative enthalpy change value ($\triangle H^o$ BB3 =

-18.4 kj/mol and $\triangle H^o$ BY11 = -32.4 kj/mol) indicates direct measure of the strength in bonding between sorbent and sorbate (Lakshmi *et al*., 2009). The negative values of enthalpy change suggested that uptake of BB3 and BY11 by seaweed is an exothermic process in nature. Another vital property from thermodynamic analysis is the Gibbs free energy ($\triangle G^o$) which indicates the spontaneity and feasibility of adsorption process in nature (Cheng *et al*., 2008; Thinakaran *et al*., 2008; Lakshmi *et al*., 2009). From table 4.6, negative values of $\triangle G^o$ shows that removal of BB3 and BY11 occurs spontaneously in nature with high affinity degree of dye compounds in each of the sorbent surface (Aksu and Karabayir, 2008). Besides, values of $\triangle G^o$ of both system was found to inversely proportional towards temperature, which indicates lesser occurrences of driving forces, thus, resulted in lesser adsorption capacity (Tan *et al*., 2008). The same phenomena was observed in removal of anionic azo dyes by chitosan (Singh *et al*., 2009) and removal of malachite green by granular sludge (Cheng *et al*., 2008). As calculated by using Van't Hoff equation, the standard entropy change ($\triangle S^o$) in removal of BB3 and BY11 was -0.0021 and -0.0651 (kj/mol/K), respectively which reveals the decrease in randomness at solid/solution interface without alternation in the surface of the sorbent (Ozer *et al*., 2007; Aksu and Karabayir, 2008; Tan *et al*., 2008).

4.4.9 Characterisation of Seaweeds

Surface structure of the seaweeds before and after adsorption process was conducted by using SEM analysis. From Figure 4.12, it is clearly shown that surface protuberance and microstructure occurred after adsorption process (image c, d, e). These protuberances were found to become more obvious after adsorption of binary dye compounds. From Figure 4.12, it was observed that formation of protuberances were due to adsorption process instead of the pre-treatment by 0.2% of formaldehyde where SEM image of raw *S. binderi* and after pre-treatment shows almost similar morphology. Adsorption was said to occur through observation of these protuberance on the surface of seaweeds. The same phenomenon was observed in removal of copper by *Sargassum* sp. (Chen and Yang, 2005).

Functional groups were identified through the spectra obtained from FTIR analysis (Figure 4.13). Functional groups obtained from the spectra were N-H group (3440 – 3450 cm^{-1}), C=O group (1635 – 1640 cm^{-1}), S=O group (1035-1355 cm^{-1}), lastly, O-H group (605 – 675 cm^{-1}). N-H groups from the spectra belongs to the amine groups, while C=O groups were from the carboxylic group, S=O group from sulfonic acid, lastly, O-H groups from H-bonded groups. These functional groups were found to coincide with the alginate acids and sulfonate from fucoidon on the surface of seaweed which aids in the removal of basic dyes from aqueous solution.

4.5 Concluding Remarks

Removal of two basic dyes has been investigated. Agitation rate and pH was observed to have insignificant effect in removal of both basic dyes by seaweed. Dye uptake by seaweed decreased with increasing of initial dye concentrations and ionic strength concentration. Uptake of dyes increased with increasing of sorbent dosage for both removal of BB3 and BY11. From the present study, heterogeneous and homogeneous type of uptake was observed to occur simultaneously in removal of both BB3 and BY11 by seaweed. The system was found to follow pseudo-second-order model where uptake of dye compounds was controlled by chemisorption. Thermodynamic analysis shows that adsorption process of BB3 and BY11 by seaweed is an exothermic process.

CHAPTER 5

OPTIMISATION OF BINARY DYE ADSORPTION BY USING RESPONSE SURFACE METHODOLOGY

5.1 Introduction

Conventional optimisation method is an optimisation method where only one factor was investigated at a time and keeping other factors constant (Song *et al*., 2007). The conventional optimisation process was very tedious and laborious, where only interaction of one factor can be investigated at one time and neglects the interactions between several parameters (Song *et al*., 2007). In view of that, statistical optimisation method becomes a useful tool to obtain better optimisation process in a short period of time as compared to the conventional optimisation method. Response surface methodology (RSM) is a factorial design which offers optimisation of multi factors affecting the experiment simultaneously (Song *et al*., 2007; Reddy *et al*., 2008). RSM is a collection of statistical and mathematical techniques which give rise to an effective modelling and investigation in the interactions between multi variables simultaneously (Tan *et al*., 2008; Ay *et al*., 2009). Plackett-Burman (PB) analysis is the first step in design of experiment where critical variables were screened and evaluated from a twelve experiment runs in order to reduce the numbers of factors in optimisation process (Reddy *et al*., 2008; Sukhwinder and Kannan. 2010). Critical variables selected from PB analysis will be applied into RSM for further optimisation process. Central Composite Design (CCD) is the standard experimental design analysis from RSM suitable for fitting of quadratic surfaces in optimisation process with minimum numbers of experiment required (Hameed *et al*., 2008d).

The objective of present study is to screen the critical variables, followed by optimisation process through statistical analysis, the Response Surface Methodology (RSM) and validation of the proposed experimental condition.

5.2 Materials and Methods

Optimisation of binary dye solution (combination of BB3 and BY11) in batch adsorption process was conducted by using Expert® Version 7.1.3 software with serial number 3013-2789 from Stat-Ease, Inc. 5.2.1(Minneapolis, United States of America).

5.2.1 Optimisation of Binary Dyes Removal by Using Response Surface Methodology (RSM) Method

Optimisation of batch adsorption process in removal of binary synthetic dye solution (mixture of BB3 and BY11) was conducted by using Design-Expert® Version 7.1.3 software by Stat-Ease, Inc. Serial experiments were conducted as designed by the software and the significance of the proposed optimised experimental conditions was tested by one way ANOVA analysis.

5.2.2 Plackett-Burman Analysis

The initial step in statistical optimisation method is to screen and select the critical variables which possess significant effect in removal of BB3 and BY11 by *S. binderi*. Plackett-Burman (PB) analysis was used to screen the critical variables by a twelve run experiments. Plackett-Burman (PB) design is a two level fractional design and is an useful tool to screen large numbers of factors which might give rise to significant effect by minimal numbers of experiment to be conducted (Reddy, Wee, Yun, and Ryu, 2008). In present study, 7 variables were screened through a twelve experimental run. Range of each respective variable (Table 5.1) was selected and applied into the Design-Expert Software for the screening process in order to select the critical variables and eliminate the insignificant one. Each factors were tested and evaluated at low (-1) and high (+1) levels. Determination of significant critical variables was conducted via student t-test.

Table 5.1: Plackett-Burman design component for screening of significant factors in adsorption of BB3 and BY11 by *S. binderi*.

Factors / Variables	Levels	
	-	+
pH (A)	2	9
Initial Dye Concentration (B, mg/L)	100	1000
Sorbent Dosage (C, g)	0.1	2.0
Agitation speed (D, rpm)	50	200
Temperature (E, ^{o}C)	20	60
Contact Time (F, min)	5	240
Ionic Strength (G, mmol/L)	10	100

5.2.3 Path of the Steepest Ascent

Significant variables screened by PB analysis were further optimised by an optimisation process, the path of the steepest ascent. Coordinates of the steepest ascent path were determined by the signs of coefficient estimations from PB analysis where '+' sign indicates increasing of parameter values and vice versa (Li *et al*., 2009). Path of the steepest ascent was initiated by the centre range of each respective critical variable derived from PB analysis and series of experiments were conducted until maximum dye uptake, ie., the response was achieved. Trial and error experiments were designed based on the coefficient estimation from PB analysis (Table 5.2) until the uptake of BB3 and BY11 remained maximum and constant. Positive (+) sign of coefficient estimation for both critical variables (sorbent dosage and contact time) were recorded from PB analysis. Centre range of both variables were used as the origin in design of experiment and gradually increased in the parameter values until the uptake of both BB3 and BY11 remained constant.

Table 5.2: Design of path of the steepest ascent

Run	Sorbent Dosage (g)	Contact Time (min)
Origin	1.05	122.5
1	1.20	152
2	1.40	182
3	1.60	212
4	1.80	242
5	2.00	272
6	2.20	302

5.2.4 Central Composite Design (CCD) and Response Surface Analysis (RSM)

Central Composite Design (CCD) is a RSM analysis widely used for fitting of a second-order response surface. CCD consists of 2^n factorial runs with 2n axial runs and n_c center runs (six replicates). Independent factors obtained from PB analysis were applied into CCD of RSM for optimisation process. In present study, two independent significant factors (sorbent dosage and contact time) screened from PB analysis were investigated at five levels (-α, -1, 0, +1, +α) with a total of 14 experimental runs where α value was fixed to 1.141 (rotatable). Each experimental runs were conducted in duplicates. Uptake of BB3 and BY11 dye compounds was fitted by using a second-order polynomial equation and multiple regressions, with general form of second-order polynomial equation as shown in Equation (5.1):

$$Y = \beta_o + \Sigma\beta_i X_i + \Sigma\beta_{ii} X_i^{\ 2} + \Sigma\beta_{ij} X_i I_j \qquad \text{(Eq. 5.1)}$$

where Y indicates the predicted response, X_i and X_j exhibited the independent factors, β_o is the intercept, β_i the linear coefficient, β_{ii} is the quadratic coefficient, lastly, β_{ij} is the interaction coefficient.

Significance of the regression model proposed by RSM was evaluated from analysis of variance (ANOVA), regression coefficient, *p* and *F* values calculated by Design Expert Software.

5.2.5 Validation of Proposed Optimised Condition by RSM

Validation experiment was conducted as according to the proposed condition for the maximum removal of dyes. Following that, experimental values were compared with the predicted values in determination of the validity of proposed experimental condition by software. Experiments were conducted in triplicates.

5.3 Results

5.3.1 Plackett-Burman Analysis

A twelve run experiments have been conducted in screening of the critical variables by Plackett-Burman Analysis.

Table 5.3 and 5.4 displays the ANOVA analysis derived from Plackett-Burman (PB) Analysis in % uptake of BB3 and BY11 dye compounds in binary dye system. From the results in present study, both models were found to be significant with p-value < 0.05. Two common critical variables screened from PB Analysis were sorbent dosage and contact time with $p < 0.05$ (Table 6.1 and 6.2). Model equations for removal of BB3 and BY11 were calculated from PB analysis in terms of coded factors were as follow (Eq. 5.2 and 5.3):

$$\%\ \text{Uptake of BB3} = +45.59 + 0.36A - 7.96B + 32.40C + 7.10D + 3.35E + 11.27F - 6.58G \qquad \text{(Eq. 5.2)}$$

$$\%\ \text{Uptake of BY11} = +50.82 + 9.13A - 5.16B + 24.64C + 1.98D + 6.54E + 15.22F - 5.68G \qquad \text{(Eq. 5.3)}$$

Where:

A = pH
B = initial concentration (mg/L)
C = sorbent dosage (g)
D = agitation speed (rpm)
E = temperature (^oC)
F = contact time (min)
G = ionic strength (mmol/L)

These models showed high correlation coefficient values ($R^2 > 0.95$) (R^2 for BB3 = 0.9683 and R^2 for BY11 = 0.9804).

Table 5.3 : ANOVA analysis for removal of BB3 by using PB analysis

Source	Sum of Squares	df	Mean Square	F value	p-value Prob > F
Model	16145.54	7	2306.51	17.44	0.0075*
pH	1.58	1	1.58	0.012	0.1983
Initial concentration	759.54	1	759.54	5.74	0.0746
Sorbent dosage	12600.36	1	12600.36	95.29	0.0006*
Agitation speed	605.06	1	605.06	4.58	0.0992
Temperature	135.01	1	135.01	1.02	0.3694
Contact time	1524.83	1	1524.83	11.53	0.0274*
Ionic Strength	519.16	1	519.16	3.93	0.1186
Residual	528.92	4	132.32		
Cor Total	16674.46	11			

* Statistically significant at 95% of confidence level

Table 5.4 : ANOVA analysis for removal of BY11 by using PB analysis

Source	Sum of Squares	df	Mean Square	F value	p-value Prob > F
Model	12330.53	7	1761.50	28.51	0.0029*
pH	1001.20	1	1001.20	16.21	0.0158*
Initial concentration	320.02	1	320.02	5.18	0.0852
Sorbent dosage	7238.09	1	7238.09	117.89	0.0004*
Agitation speed	47.08	1	47.08	0.76	0.4319
Temperature	513.39	1	513.39	8.31	0.0449*
Contact time	2778.26	1	2778.26	44.97	0.0026*
Ionic Strength	387.49	1	387.49	6.27	0.0664
Residual	247.11	4	61.78		
Cor Total	12577.64	11			

* Statistically significant at 95% of confidence level

5.3.2 Path of the Steepest Ascent

The two common critical variables determined from PB analysis (sorbent dosage and contact time) were applied into the path of steepest ascent to determine the region nearest to the optimum condition before optimisation by RSM.

From PB analysis, coefficient estimate of sorbent dosage and contact time of BB3 removal by *S. binderi* was found to be +32.40 and +11.27, respectively (Table 5.5). As for BY11 removal by seaweed, coefficient estimation of sorbent dosage and contact time was shown to be +24.64 and +15.22, respectively (Table 5.6). An experimental design in determination of the path of steepest ascent was designed initiated by the centre range of the critical variables (as illustrated in Table 5.2) and increased due to the '+' sign of coefficient estimation. Experiments were conducted according to the designed condition until a constant response (% uptake of BB3 and BY11) observed (Table 5.7). Run 4 of the designed experiment from path of the steepest ascent exhibited the starting of equilibrium in % of BB3 and BY11 dye uptake (maximum dyes uptake) by contacting 1.80 g of seaweed and agitated at 200 rpm, 30^{o}C for 242 mins which give rise to 97.86% and 94.22% dye uptake, respectively.

Table 5.5 Coefficient estimate of BB3 removal in PB design experiments

Factor	Coefficient Estimate
Intercept	45.49
pH	0.36
Initial concentration	-7.96
Sorbent dosage	32.40
Agitation speed	7.10
Temperature	3.35
Contact time	11.27
Ionic strength	-6.58

Table 5.6 Coefficient estimate of BY11 removal in PB design experiments

Factor	Coefficient Estimate
Intercept	50.82
pH	9.13
Initial concentration	-5.16
Sorbent dosage	24.64
Agitation speed	1.98
Temperature	6.54
Contact time	15.22
Ionic strength	-5.68

Table 5.7 Experiment design and results of the steepest ascent path

Run	Sorbent dosage (g)	Contact time (min)	% Uptake	
			BB3	BY11
Origin	1.05	122.5	87.36	85.11
1	1.20	152.0	91.73	89.46
2	1.40	182.0	94.53	91.96
3	1.60	212.0	94.42	91.96
4*	1.80	242.0	97.86	94.22
5	2.00	272.0	97.92	94.24
6	2.20	302.0	98.31	94.20

5.3.3 Central Composite Design (CCD) and Response Surface Analysis (RSM)

As shown in Table 5.8, the observed % of BB3 and BY11 uptake by *S. binderi* were found almost close to the predicted values.

The ANOVA analysis as shown in Table 5.9 and 5.10 suggested by RSM through CCD analysis in removal of BB3 was found to be significant with $p < 0.05$ and insignificant lack of fit ($P > 0.05$) (Table 6.8). In addition, significant model was observed in removal of BY11 by *S. binderi*, with $p < 0.05$ and insignificant lack of fit ($P > 0.05$) which signifies the validity of the model (Table 6.8).

Equations between the interactions of critical variables (sorbent dosage and contact time) were given in Equation 5.4 and 5.5 by CCD in RSM:

$$\%\ \text{BB3 Uptake} = +96.99 + 5.08*A + 0.81*B - 0.095*A*B - 2.70*A^2 - 0.19*B^2 - 1.30*A*B^2 \quad \text{(Eq. 5.4)}$$

$$\%\ \text{BY11 Uptake} = +93.37 + 3.40*A + 0.022*B - 0.85*A*B - 3.39*A^2 - 0.25*B^2 - 1.20*A*B^2 \quad \text{(Eq. 5.5)}$$

where, A indicates sorbent dosage (g) and B is the contact time (min). The fit of model was found to be $R^2 = 0.9937$ and $R^2 = 0.9875$ for removal of BB3 and BY11, respectively.

Interactions between critical variables were shown in the 3D contour plot given by Design-Expert Software through CCD analysis (Figure 5.1). Both 3D contour plots were found to be in elliptical shape with proportional relationship in between sorbent dosage and contact time for % of dyes uptake.

Table 5.8 Central composite design of RSM in optimisation of BB3 and BY11 uptake by seaweed.

Run	Sorbent dosage (g)	Contact time (min)	% of BB3 Uptake		% of BY11 Uptake	
			Observed	Predicted	Observed	Predicted
1	1.1	362.0	91.3	89.6	88.4	86.8
2	1.8	242.0	96.6	97.3	92.9	92.9
3	1.1	122.0	89.7	91.3	87.2	88.6
4	2.6	122.0	97.6	98.7	93.3	91.3
5	2.6	362.0	98.7	97.1	91.1	93.5
6	1.8	242.0	97.2	97.1	93.9	93.5
7	1.8	242.0	97.0	97.1	93.5	93.5
8	1.8	242.0	97.0	84.3	93.6	81.6
9	0.7	242.0	84.1	98.6	81.5	91.2
10	1.8	72.3	95.0	95.4	92.2	92.7
11	1.8	242.0	96.5	97.6	92.6	92.7
12	1.8	242.0	97.6	96.7	93.7	93.2
13	2.7	242.0	98.0	96.7	91.1	93.2
14	1.8	411.7	97.7	96.7	93.0	93.2

*Predicted value included block of corrections

Table 5.9 ANOVA analysis of parameters in CCD for removal of BB3 by seaweed.

	Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**P-value Prob > F**	
Block	0.25	1	0.25				
	Model	**219.81**	**6**	**36.64**	**157.09**	**<0.0001**	**Significant**
	A	103.40	1	103.40	443.39	<0.0001	
	B	5.19	1	5.19	22.24	0.0033	
	AB	0.036	1	0.036	0.15	0.7080	
	A^2	54.00	1	54.00	231.54	<0.0001	
	B^2	0.26	1	0.26	1.10	0.3347	
	AB^2	3.40	1	3.40	14.57	0.0088	
	Residual	1.40	6	0.23			
	Lack of Fit	**0.61**	**2**	**0.30**	**1.52**	**0.3220**	**Not significant**
	Pure Error	0.79	4	0.20			
	Cor Total	221.47	13				

* A = Sorbent dosage (g), * B = Contact time (min)

Table 5.10 ANOVA analysis of parameters in CCD for removal of BY11 by seaweed.

	Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	**P-value Prob > F**	
Block	0.41	1	0.41				
	Model	**153.57**	**6**	**25.60**	**78.88**	**<0.0001**	**Significant**
	A	46.27	1	46.27	142.59	<0.0001	
	B	3.928 x 10^{-3}	1	3.928 x 10^{-3}	0.012	0.9160	
	AB	2.91	1	2.91	8.97	0.0241	
	A^2	85.01	185.01	261.98	<0.0001	<0.0001	
	B^2	0.46	1	0.46	1.41	0.2800	
	AB^2	2.88	1	2.88	8.87	0.0247	
	Residual	1.95	6	0.32			
	Lack of Fit	**0.73**	**2**	**0.36**	**1.19**	**0.3924**	**Not significant**
	Pure Error	1.22	4	0.30			
	Cor Total	155.93	13				

* A = Sorbent dosage (g), * B = Contact time (min)

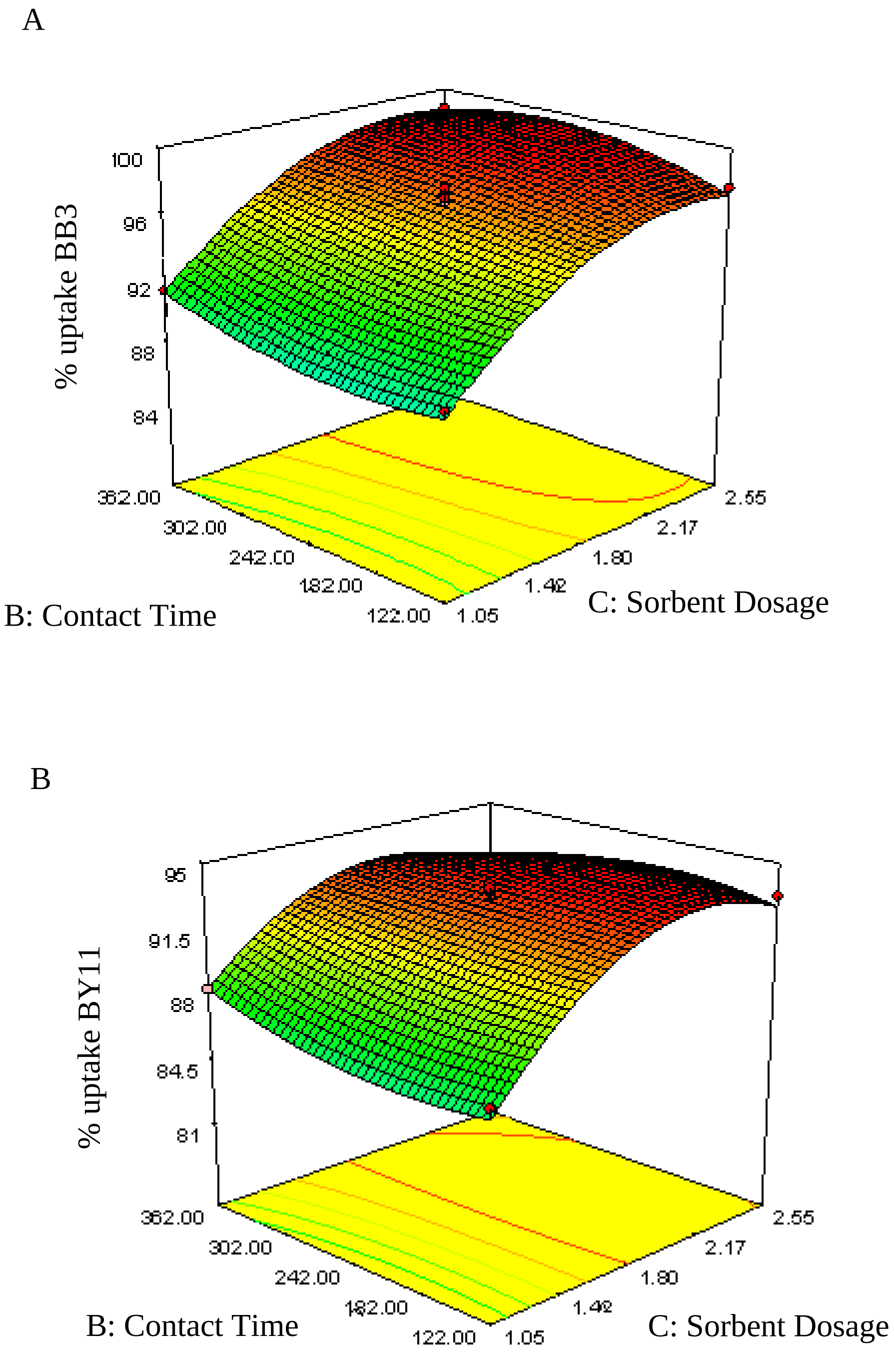


Figure 5.1: Three D (3D) Contour Plot showing the relationship between critical variables in removal of

(A) BB3 (B) BY11

5.3.4 Validation Experiment

From RSM analysis, the proposed condition for maximum uptake of BB3 and BY11 would be by contacting 2.22 g of seaweed, agitate at 200 rpm, 30^{o}C for 122 mins which give rise to approximate 97% and 93% dyes uptake, respectively.

Validation experiment in present study for removal of BB3 and BY11 recorded almost similar results as proposed by the RSM. In addition, removal of BB3 and BY11 optimised through conventional optimisation method were compared with the validation experiment (Figure 5.2). From Figure 5.2, removal of both BB3 and BY11 by *S. binderi* exhibited lower % of dyes uptake (both BB3 and BY11) as compared to the optimised condition proposed by RSM.

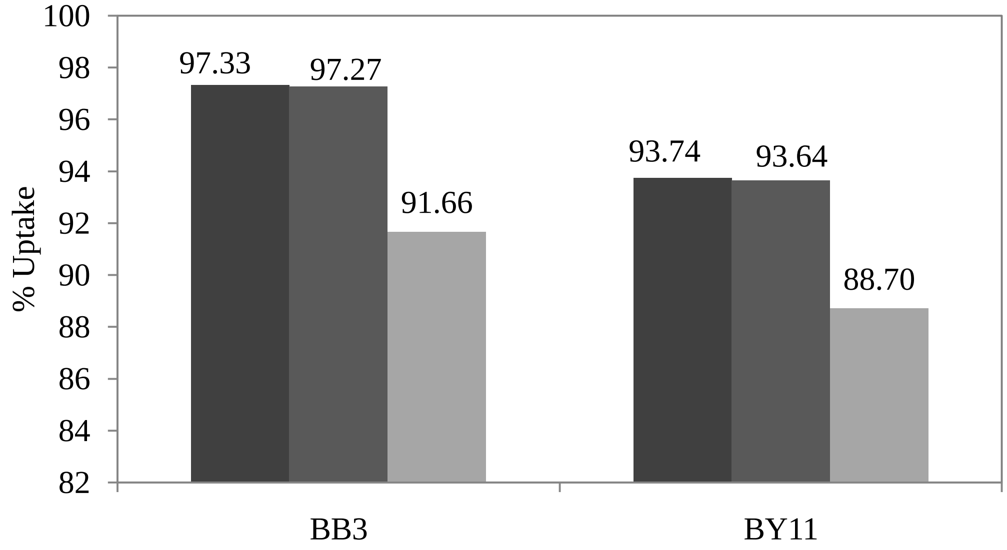


Figure 5.2 Comparison in removal of BB3 and BY11 (binary dye system) by S. binderi under
(■), Proposed % uptake by RSM;
(■), Validation experimental data;
(■), % uptake achieved through conventional optimisation technique
Error bar indicates the mean ± standard deviation of triplicates. For data points without error bars, the errors were smaller than the size of the symbols.

5.4 Discussion

5.4.1 Plackett-Burman Design

Plackett-Burman design is the first step of statistical optimisation method to screen and select critical variables which give rise to significant effect to the outcome of the studies (Plackett and Burman, 1946). Plackett-Burman analysis is a two level fractional design for determination up to k = N-1 variables in N runs, and N is the multiple of 4 (Myers and Montgomery, 2002). These two level fractional designs allows screening and evaluation of critical variables which might give rise to significant effect in the end response, in the same time eliminate the insignificant variables or factors (Seraman *et al.*, 2010). Fractional factorial designs of PB analysis allow unbiased estimation of main effects with smallest possible variance or components (Seraman *et al.*, 2010).

In present study, seven variables were implemented in PB analysis and screened for the significance variable. Adequacy of each respective variables or factors were analysed by student’s t-test for ANOVA analysis. From PB analysis (Table 5.3 and 5.4) in removal of BB3 and BY11 from binary dye solution via batch mode of adsorption process, sorbent dosage and contact time were found to be the critical variables where p-values obtained were less than 0.05, indicating the significance of the variables (Reddy *et al.*, 2008). Only variables with significant effects (p-value < 0.05) were further implemented in RSM analysis. First-order model is the suggested equation in removal of both BB3 and BY11 by *S. binderi*. Correlation coefficient (R^2) values of models derived from PB analysis were 0.9683 for BB3 and 0.9804 for BY11, indicating the validity of the model. Besides that, these two models were found nearly 96% of variability in the response which is the % of dye uptake by seaweed can be explained by the model (Li *et al*., 2009).

5.4.2 Path of the Steepest Ascent

Two selected and significant critical variables from PB analysis were furthered analysed by path of the steepest ascent method where appropriate direction of potential improvement process were applied in determination of nearest region towards optimum condition (Myers and Montgomery, 2002; Chen and Chen, 2009; Li *et al*., 2009). The direction of the steepest ascent path method was determined by the coefficient estimated values from PB analysis (Table 5.5 and 5.6) where + sign indicates ascending direction and vice versa (Myers and Montgomery, 2002). Series of experimental design was conducted as according to the direction from coefficient estimate as shown in Table 5.7. Run 4 (1.8 g *S. binderi*, agitate at 200 rpm for 242 min) from the experimental design of path of the steepest ascent recorded the beginning of the highest % BB3 and BY11 dyes uptake (BB3 = 97% and BY11 = 93%) (Table 5.7). This condition was suggested as the nearest point to the optimum condition and was chosen as the centre point for subsequent optimisation process by RSM analysis.

5.4.3 Central Composite Design (CCD) and Response Surface Analysis (RSM)

Response surface methodology (RSM) is defined as an empirical statistical technique for determination of multiple regression analysis by optimisation of multi variables at the same time (Preetha and Viruthagiri, 2007). RSM is a collection of statistical and mathematical techniques which is useful in development, improvement and optimisation process (Seraman *et al.*, 2010). The application of RSM analysis was used to evaluate the empirical relationship between response function and other independent variables by a quadratic polynomial equation (Ay *et al.*, 2009).

In present study, optimisation process was continued from steepest ascent path method at which the point nearest to the optimum condition (sorbent dosage and contact time) was determined. Central Composite Design (CCD) is a second-order response surface widely used in the process of optimisation (Myers and Montgomery, 2002). In present design, a 2^2 factorial CCD design with 4 axial runs ($\alpha = 1.414$) and 6 replicates in the centre give rise to 14 sets of experiments for response surface modelling.

Significance of the regression coefficients from RSM model were determined by ANOVA analysis from student's t-test (Table 5.9 and 5.10) (Secula *et al*., 2008). P-values obtained from student's t-test and Fischer's F-test exhibited the validity and significance of the regression model by RSM (Secula *et al*., 2008). Regression coefficient of each respective factors were evaluated and determined by student's t-test while P values were used to check the interactions between variables in removal of both dyes by *S. binderi* (Ravikumar *et al*., 2006). P-values obtained from both dyes uptake (Table 5.9 and 5.10) were significantly low (< 0.0001) indicating the extremely significant interactions between the independent variables and regression coefficient (Yao *et al*., 2009).

In addition, quadratic regression models exhibited high correlation coefficient (R^2) values at 0.9937 for BB3 removal and 0.9875 for BY11 with very low probability value (p-value prob > F = < 0.0001), which indicates that the terms in uptake of BB3 and BY11 by seaweed is very significant (Song *et al*., 2007; Yao *et al*., 2009). Besides that, values of the adjusted R^2 for removal of both dyes by *S. binderi* exhibited total variation of 98% for BB3 and 97% for BY11 uptake was due to the independent variables (sorbent dosage and contact time) and only approximately 2% (BB3) and 3% (BY11) of the total variations cannot be explained by the model (Song *et al*., 2007).

High F-values from the results (BB3 = 157.09 and BY11 = 78.88) indicates that the model was significant (Li *et al*., 2009). Both models suggested that there is only 0.01 % of chances that a “Model F-Value” could occur due to noise. Another important term in RSM ANOVA analysis is the lack of fit value. The “Lack of Fit F-Value” obtained from both BB3 and BY11 as illustrated in table 5.9 and 5.10 was 1.52 and 1.19, respectively indicates the lack of fit is not significant relative to the pure error. The model suggested that there is a 32.20% and 39.24% for BB3 and BY11 removal, respectively that “Lack of Fit F-Value” could occur due to noise.

Three D (3D) response surface contour plot further explained the interactions between the independent variables and determination of the optimum conditions for each respective variables (Li *et al*., 2009; Rajeshkannan *et al*., 2010). Elliptical shape of contour plot indicates excellent interactions between variables and from the contour plot (Figure 5.1), there is mutual interactions between sorbent dosage and contact time. The same phenomenon was also observed in removal of Acid Blue 9 by brown seaweed, *Turbinaria conoides* (Rajeshkannan *et al*., 2010). From the contour plot. It was also observed that the % uptake of both dyes were found to increase when higher sorbent dosage was in contact with the dye solution at a longer time period.

5.4.4 Validation of Proposed Optimised Condition by RSM

Validation of experiments conducted by contacting 2.22 g of seaweed and agitated at 200 rpm, 30^{o}C for 122 minutes. Results achieved experimentally was found to comply well with predicted values (Figure 5.2). Uptake of both BB3 and BY11 was found to be higher as compared to the removal of BB3 and BY11 in single dye system through conventional optimisation method (Figure 5.2), hence, the condition proposed by RSM can be concluded to be effective and valid.

5.5 Concluding Remarks

RSM is an useful tools for optimisation of basic dyes (BB3 and BY11) by marine seaweed, *Sargassum binderi*. From the present study, optimisation of *S. binderi* in removal of basic dyes was sucessfully achieved in a shorter period of time as compared to the conventional optimisation method. The validity and significance of the optimisation results were confirmed by analysis of variance (ANOVA). Interactions between variables were take into consideration by RSM optimisation method which serves as an additional advantage for a better optimisation process. Higher % dyes uptake by *S. binderi* were observed in optimisation by RSM as compared to the conventional optimisation method, therefore, optimisation of basic dyes removal of SB by RSM was found to be succesful and valid.

CHAPTER 6

CONTINUOUS MODE OF ADSORPTION – COLUMN STUDIES

6.1 Introduction

Adsorption is the most promising conventional treatment method found to be available showing advantages such as simplicity, low cost, and efficiency (Lakshmi *et al.*, 2009). Batch adsorption process as discussed in previous chapter was the common laboratory bench scale studies conducted in search of the potential low cost sorbent as an alternative to the expensive activated carbon. Batch adsorption process is a simple adsorption process by treating a small constant volume of effluents but was found to be less efficient and practical in industrial scale (Unuabonah *et al.*, 2010). Although batch adsorption process was impractical towards industrial scale due to large volume of wastewater generated, it provides useful information such as the optimum pH, initial dye concentrations, sorbent dosage, the efficiency of sorbent in removal of dyes, and etc for fixed-bed column studies.

A fixed-bed column was used to investigate the efficiency of *S. binderi* in removal of basic dyes (BB3 and BY11) in continuous mode where *S. binderi* was continuously in contact with dye solutions (Unuabonah *et al.*, 2010) Fixed-bed column provides advantages such as simplicity, easily to scale up and practical in industrial scale (Lodeiro *et al*., 2006; Unuabonah *et al*., 2010).

Performance of the column was evaluated by breakthrough curves i.e., graph of normalised concentrations (C/C_o) versus service time (t). Breakthrough was said to occur when the given concentration was observed at the outlet effluent of the column (Lodeiro *et al*., 2006). Few models were applied into the column studies in determination of the efficiency of column design as well as the optimisation process of column such as Thomas model, Yoon Nelson model, Mass Transfer Zone model and Bed-Depth-Service-Time (BDST) model.

6.2 Materials and Methods

Continuous mode of adsorption studies was conducted by a downward liquid flow column through a fixed-bed depth ground *S. binderi* in a custom made glass column (2 cm id x 24 cm height) (Figure 6.1). *S. binderi* were packed into the custom made column and allows contacting with continuous flow of synthetic dye solutions through a fixed liquid flow rate at room temperature (30^oC), unless otherwise stated. Effluent at the outlet of column was collected at predetermined time interval and analysed by using double beam UV/VIS spectrophotometer in determination of the concentration of effluent solution. Operation of the column study was terminated when the effluent at outlet of column exhausted ($C/C_o = 0.9$) in which no dyes uptake occurs by *S. binderi* when solution flows through the column. Few operating parameters (effect of bed depth, effect of flow rate and effect of initial dye concentrations) were applied into column studies for determination of column design and dye uptake efficiencies of *S. binderi*.

Figure 6.1: Column setup for continuous studies

Breakthrough time and saturation of column was determined through a breakthrough curve. The total volume of dye effluent (V_{eff}) was calculated by the Equation (6.1):

$$V_{eff} = F_m \cdot t_{total} \qquad \text{(Eq. 6.1)}$$

Where, F_m indicates the liquid flow rate (mL/min) and t_{total} is the time total flow time (min).

Total amount of dye compounds (M_{total}) flow into the column was determined by using Equation (6.2):

$$M_{total} = \frac{C_o F_m t_{total}}{1000} \qquad \text{(Eq. 6.2)}$$

C_o is the initial dye concentrations (mg/L). Equilibrium uptake of dye compound (q_{eq}) or was known as column capacity was calculated by Equation (6.3) by dividing amount of dye sorbed by sorbent (M_{ad}) with W, weight of sorbent used (g)

$$q_{eq} = \frac{M_{ad}}{W} \qquad \text{(Eq. 6.3)}$$

Lastly, the total amount of dyes compound removed by seaweed in respect of flow volume was calculated as according to the Equation (6.4) below:

$$Total\ dye\ removed\ (\%) = \frac{M_{ad}}{M_{total}}\ x\,100 \qquad \text{(Eq. 6.4)}$$

M_{ad} indicates the amount of dye sorbed (mg/g) determined from the area under the breakthrough curve.

In the present study, the efficiency of seaweed in continuous removal of basic dye compounds were determined by using three different dye systems: BB3 single dye system, BY11 single dye system and binary dye system (combination of BB3 and BY11).

6.2.1 Effect of Bed Depth

The effect of bed depth was conducted by contacting various amount of ground seaweeds into the column made up to a fixed bed depth (2.5, 5, 7.5 and 10 cm). Working solution of 100 mg/L was allowed to percolate through the fixed-bed column at a liquid flow rate of 10 mL/min with the aid of a peristaltic pump (Masterflex Economic Pump, United States of America). Effluent from each respective column was then collected at a predetermined time interval and analysed by using double beam UV/VIS spectrophotometer.

6.2.2 Effect of Liquid Flow Rate

Effect of liquid flow rate was investigated by contacting a fixed bed depth ground seaweeds (10 cm) in the column with various liquid flow rate (10, 15, 20 and 25 mL/min) at room temperature. Working solution of dye compounds with 100 mg/L dye concentrations were flow through the fixed-bed column at various liquid flow rate. Effluent at the outlet of column was collected at predetermined time interval and analysed by double beam UV/VIS spectrophotometer in determination of the effluent concentration until the system reaches equilibrium where no more dyes were removed by *S. binderi*.

6.2.3 Effect of Initial Dye Concentrations

The effect of initial dye concentrations were studied by contacting a fixed bed depth (10 cm) column with various initial dye concentrations (100, 200, 300 and 500 mg/L) for BB3, BY11 and binary dye system and setting other operating parameters constant (liquid flow rate of 10 mL/min, fixed bed depth of 10 cm and room temperature, $30^{o}C$), unless otherwise stated. Effluent from column outlet was collected at predetermined time interval until saturation point ($C/C_o = 0.9$) was achieved.

6.2.4 Modelling of Column Data

The efficiency of the column design and optimisation of column studies in removal of BB3, BY11 and binary dye system was analysed by few models such as BDST Model, Thomas Model, Yoon-Nelson Model and Mass Transfer Zone (MTZ). These models were used to determine adsorption kinetics in column studies.

Linear plot of service time, t (h) versus bed depth (cm) were used in BDST model from the modified BDST equation as follow (Eq. 2.11)

$$Z_o = \frac{V}{KN_o} \ln\left(\frac{C_o}{C_B} - 1\right) \qquad \text{(Eq. 2.11)}$$

Linearised Thomas model (Eq. 2.13)

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{K_{TH}q_oM}{Fm}-K_{TH}C_ot \qquad \text{(Eq. 2.13)}$$

were used in determination of the performance of a packed-bed column. Linearised Yoon-Nelson model used in present study was as follow (Eq. 2.14)

$$\ln\frac{C}{C_o-C}=k_{YN}t-\tau k_{YN} \qquad \text{(Eq. 2.14)}$$

Lastly, the efficiency of the column in removal of BB3 and BY11 compounds were determined by MTZ with involvement of various equations:

(i) total time taken for establishment of MTZ,

$$t_x=\frac{V_e}{F_m} \qquad \text{(Eq. 2.5)}$$

(ii) time required for movement of MTZ through the column,

$$t_g=\frac{V_e-V_b}{F_m} \qquad \text{(Eq. 2.6)}$$

(iii) height of MTZ (HMTZ),

$$\frac{HMTZ}{H}=\frac{t_g}{t_x-t_f} \qquad \text{(Eq. 2.7)}$$

(iv) rate movement of MTZ (RMTZ),

$$RMTZ = \frac{HMTZ \ x \ F_m}{V_{0.9} - V_{0.02}} \quad \text{(Eq. 2.8)}$$

(v) fractional capacity, *f*

$$f = \frac{1 - t_f}{t_g} \quad \text{(Eq. 2. 9)}$$

These equations were applied in each column to investigate the efficiency of column in uptake of both BB3 and BY11.

6.3 Results

6.3.1 Effect of Bed Depth

Figure 6.2 shows the breakthrough curves of each dye systems with various bed depths (A: BB3 single dye system, B: BY11 single dye system, C: BB3 in binary dye system, and D: BY11 in binary dye system). Similar trend of breakthrough curves were observed for different dye systems. Time for all systems to reach 10% of breakthrough was found increased with increase of bed depth. In addition, duration for the systems to reach 10% of breakthrough become longer as the bed depth increased.

From Figure 6.2, duration for 10% of breakthrough in removal of BB3 from single dye system by seaweeds increases from 25 to 270 min with increase of bed depth from 2.5 to 10 cm. Similar breakthrough curve was also achieved in removal of BY11 single dye system where duration for 10% of breakthrough increased as well (5 to 555 min). As for removal of BB3 and BY11 in binary dye system, time for 10% breakthrough increases from 5 to 195 min with the increasing of bed depth. These breakthrough curves were found to become broaden as the bed depth increased. The data were then applied into BDST model where the critical bed depth was determined.

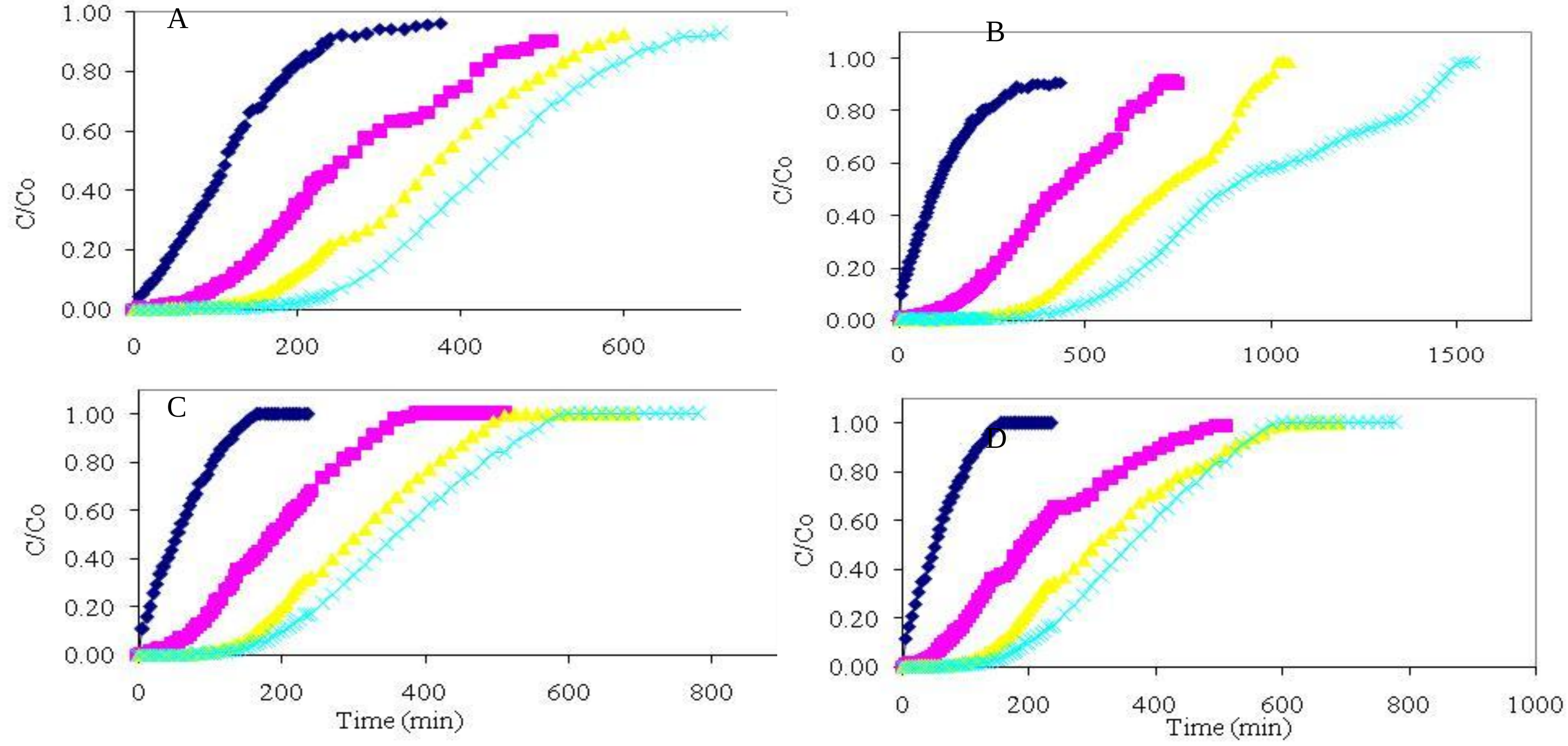


Figure 6.2 Breakthrough curve in dye removal by *S. binderi* at different bed depth of packed *S. Binderi*.
(A) BB3 single dye system (B) BY11 single dye system (C) BB3 binary dye system (D) BY11 binary dye system
Symbols: (◆), 2.5 cm; (■), 5.0 cm; (▲), 7.5 cm; (X), 10cm.

6.3.2 Bed-Depth-Service-Time (BDST) Model

Data from 10% of breakthrough curve were applied into the equation of BDST models and verification of the fitness of column design was by the correlation coefficient, R^2 values. The higher the R^2 values, the better the model fits to the column condition.

As shown in Figure 6.3, R^2 values in removal of dye compounds, in regardless of either single dye system, and binary dye system, were found to be high ($R^2 > 0.95$) indicating the suitability of the BDST model into the system.

The sorption capacity of the bed per unit bed volume, N_o (mg/cm) is calculated from the slope of BDST model, as listed in Table 6.1. The values of N_o are 10.3 mg/cm for BB3 single dye system, 24.4 mg/cm for BY11 single dye system, 8.6 mg/cm for BB3 in binary dye system and 8.3 mg/cm for BY11 in binary dye system. The rate constant of BDST model, K (L/mgh) calculated from the intercept of BDST linear plot, are 0.003 L/mgh for BB3 in single dye system, 0.01 L/mgh for BY11 in single dye system, 0.02 L/mgh for removal of BB3 in binary dye system, 0.02 L/mgh in BY11 removal in binary dye system.

Critical bed depth was the crucial parameter values derived from BDST model where it stated the minimum depth of bed required for column design.

Critical bed depth derived from BDST model for each respective dye systems were found to be 1.6 cm (BB3 single dye system), 2.5 cm (BY11 single dye system), 2.1 cm (BB3 binary dye system) and 2.1 cm (BY11 binary dye system).

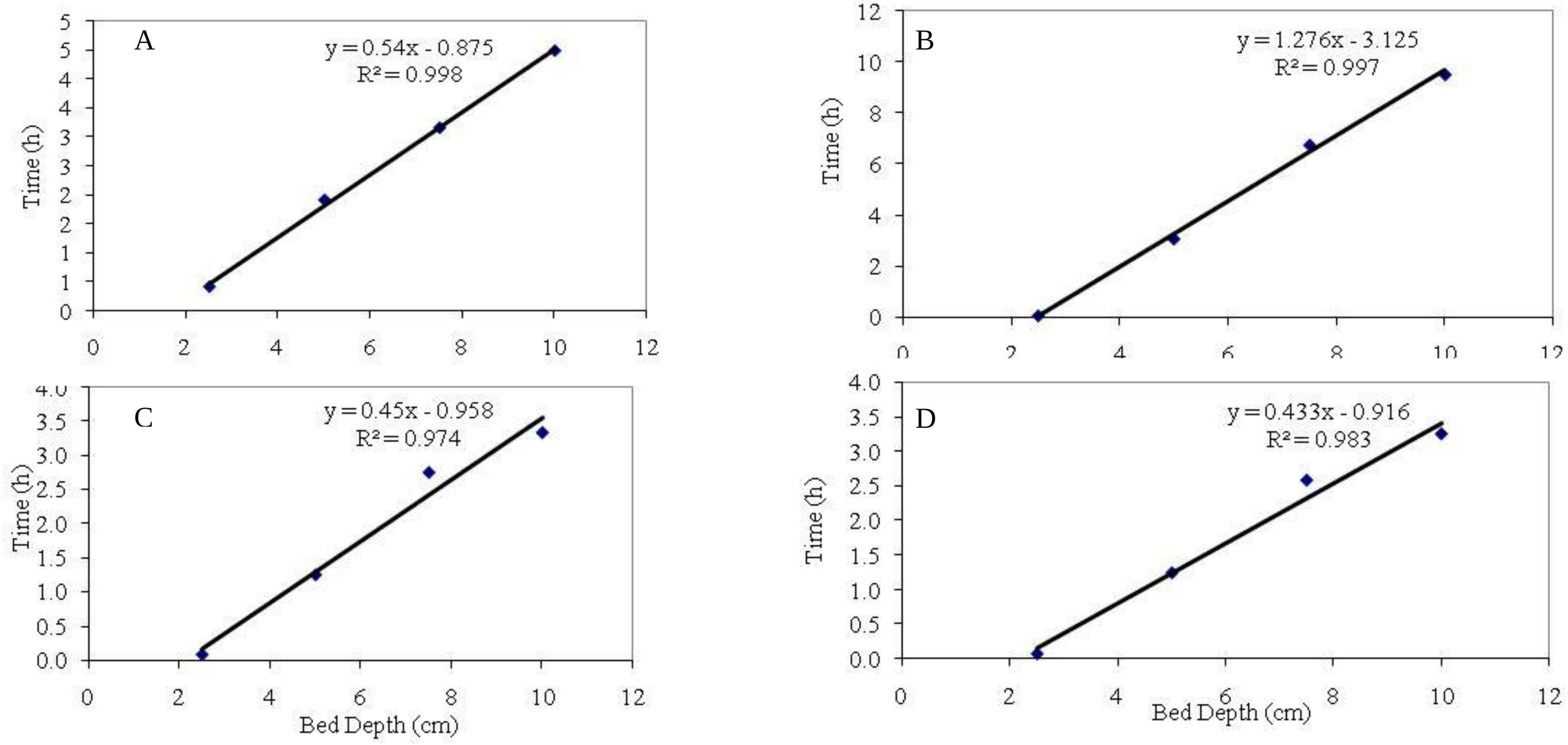


Figure 6.3 BDST model plot for
(A) BB3 single dye system (B) BY11 single dye system (C) BY11 binary dye system (D) BB3 binary dye system

Table 6.1 Parameter values from BDST model in removal of dyes from single and binary dye system by *S. binderi*.

Dye System	**Critical bed depth, Z_o (cm)**	**Sorption capacity of the bed per unit bed volume, N_o (mg/cm)**	**Rate Constant, K (L/mgh)**	**R^2**
Basic Blue 3	1.62	10.31	0.0025	0.9986
Basic Yellow 11	2.46	24.38	0.007	0.9972
Basic Blue 3 (Binary)	2.13	8.60	0.023	0.9837
Basic Yellow 11 (Binary)	2.11	8.28	0.024	0.9748

6.3.3 Effect of Liquid Flow Rate

The effect of liquid flow rate was studied by varying the liquid flow rate at 10, 15, 20 and 25 mL/min, and setting other operating parameters such as temperature (30^{o}C), initial dye concentration (100 mg/L), and bed depth (10 cm) constant for each respective dye systems. A 5 times higher fixed bed depth (10 cm) than the critical bed depth calculated based on BDST model was chosen for subsequent parameters.

Breakthrough curves were used to evaluate the column efficiency in effect of liquid flow rate. Similar pattern of breakthrough curves were observed for all systems. These breakthrough curves recorded a decrease trend in duration for 10% of breakthrough with the increasing of liquid flow rate. Each respective dye system was found to saturate faster as the liquid flow rate increases from 10 to 25 mL/min (Figure 6.4).

From the results, the duration for 10% breakthrough decreased from 270 to 65 min for BB3 removal in single dye system, 555 to 120 min for BY11 removal in single dye system, and from 195 to 55 min for removal of BB3 and BY11 removal in binary dye system. It was observed that the duration required for the system to achieve 10% breakthrough and column saturation declined as the liquid flow rate increased (Figure 6.4).

Overall, the S curves of breakthrough were found to be steeper when the liquid flow rate increases from 10 to 25mL/min for each of the dye system.

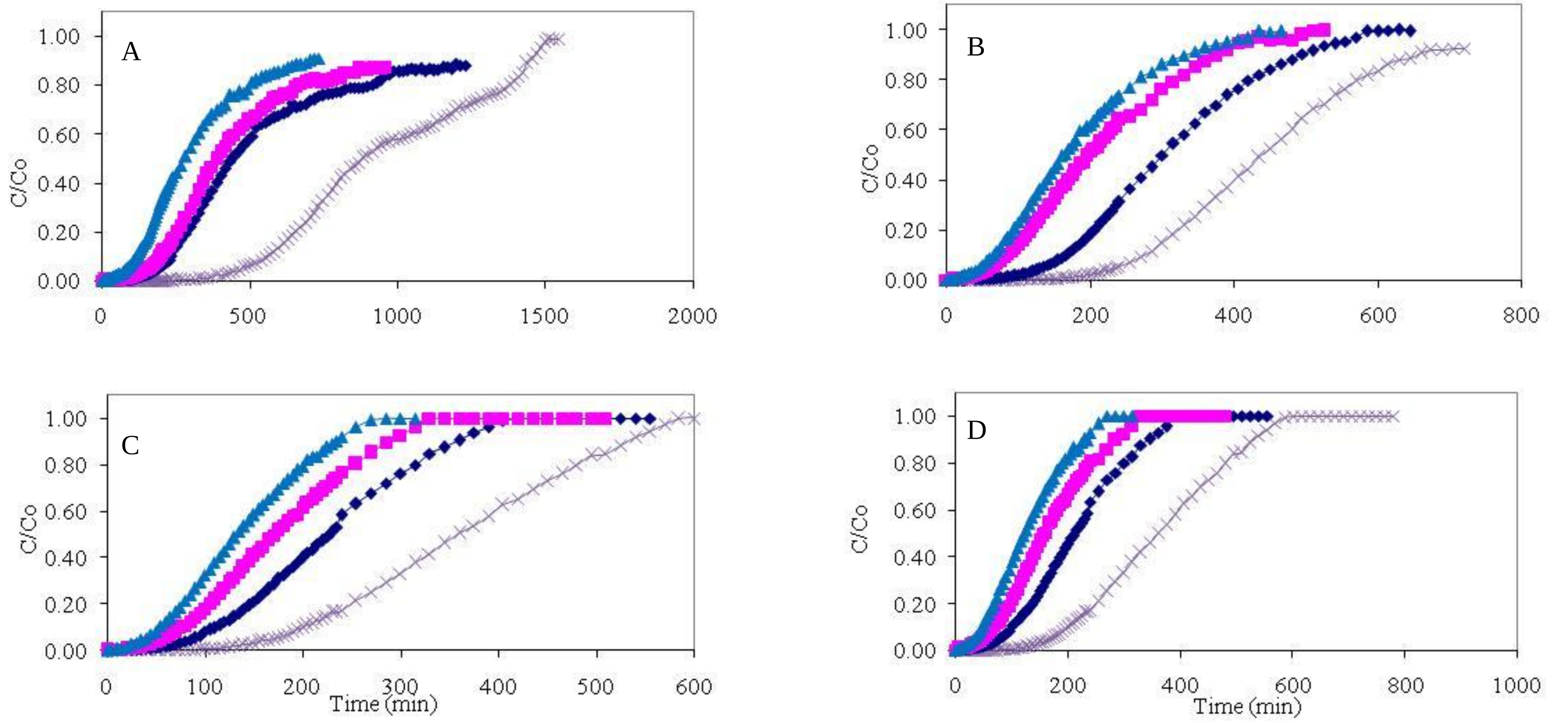


Figure 6.4: Breakthrough curve in removal of basic dyes by S. Binderi using different liquid flow rate.
(A) BB3 single dye (B) BY11 single dye system (C) BB3 binary dye system (D) BY11 binary dye system
Symbols: (▲), 10 mL/min: (■), 15 mL/min; (◆), 20 mL/min; (X), 25 mL/min.

6.3.4 Effect of Initial Dye Concentrations

By varying the inlet dye concentrations from 100, 200, 300 to 500 mg/L, the duration for the systems to achieve 10% of breakthrough was found to decrease with increasing of dye concentrations (Figure 6.5). Similar pattern of breakthrough curves was observed for both single dye systems and binary dye system in removal of dyes by using *S. binderi*.

As shown in Figure 6.5, duration required for the system to reach 10% of breakthrough become shorter, from 270 to 90 min for removal of BB3 and from 555 to 175 min for removal of BY11 in single dye system, respectively, and from 195 to 80 min for removal of BB3 and BY11 in binary dye system. In correspondence of the breakthrough, time for the system to reach saturation point decreases as well with increasing of initial dye concentrations from 100 to 500 mg/L. The S curve shape of the breakthrough curves become steeper and nearer to zero as the initial dye concentration increases.

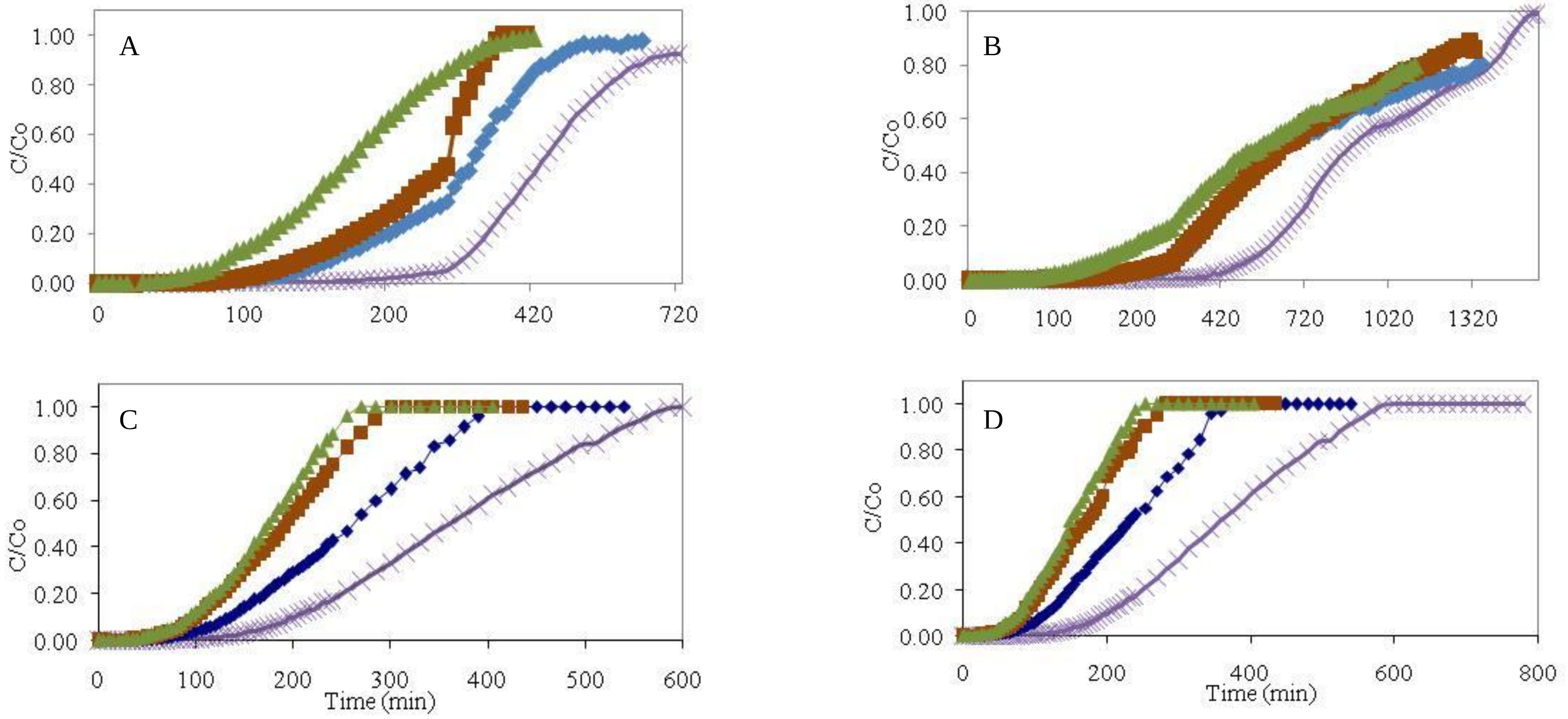


Figure 6.5: Breakthrough curve for removal of basic dyes by *S. binderi* using different initial inlet dye concentrations.
(A) BB3 single dye system (B) BY11 single dye system (C) BB3 binary dye system (D) BY11 binary dye system
(B) Symbols: (▲), 100 mg/L: (■), 200 mg/L; (◆), 300 mg/L; (X), 500 mg/L.

6.3.5 Mass Transfer Zone (MTZ) Model

In the present study, MTZ model was applied to each operating parameters investigated in column studies and results are as listed in Table 6.2 to 6.4.

For the effect of bed depth, total duration taken for formation of MTZ during uptake of dye compounds in the column (t_x) was recorded to increase with increasing of bed depth from 2.5 to 10 cm. Similar increasing trend was also observed in the total duration for the MTZ to move down the column (t_g) as the bed depth increased (Table 6.2). In the same time, the height of MTZ (HMTZ) was found to act parallel with the bed depth where HMTZ values obtained from each respective dye systems were almost similar with the bed depth. Overall, the rate movement of MTZ (RMTZ) was found to be proportional with the bed depth of column where the values derived from MTZ model increase with increasing of bed depth. Fractional capacity (*f*) was found to rise as bed depth increases (Table 6.2).

In the effect of liquid flow rate, t_x, t_g and fractional capacity was found to decrease as the liquid flow rate increases from 10 to 25 mL/min (Table 6.3). In addition, HMTZ was found to be similar with the column bed depth throughout the increasing of liquid flow rate. On the other hand, RMTZ marked declining trend as the liquid flow rate increases.

As for the effect of initial dye concentrations, the values of t_x, t_g and fractional capacity decreases with increasing of initial dye concentration from 100 to 500 mg/L. Also, RMTZ marked an increased, regardless of the type of dye system (single or binary dye system) as the initial dye concentration passes through the column increased (Table 6.4).

Table 6.2 MTZ model parameters at different bed depth.

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	t_x (min)	t_g (min)	t_f (min)	HMTZ (cm)	RMTZ (cm min^{-1}) (10^{-3})	Fractional Capacity, *f* (10^{-3})
BB3	100	10	2.5	285	280	5	2.5	11.10	14.30
	100	10	5.0	510	485	25	5.0	10.60	49.48
	100	10	7.5	600	515	85	7.5	15.50	163.10
	100	10	10.0	720	570	150	10.0	19.60	261.40
BY11	100	10	2.5	435	430	5	2.5	6.95	9.30
	100	10	5.0	750	745	5	5.0	7.14	5.37
	100	10	7.5	1050	865	185	7.5	9.49	212.70
	100	10	10.0	1545	1260	285	10.0	8.55	225.40
Binary: BY11	100	10	2.5	155	150	5	2.5	21.00	26.70
	100	10	5.0	495	490	5	5.0	10.20	8.16
	100	10	7.5	615	560	55	7.5	16.00	96.40
	100	10	10.0	675	610	65	10.0	19.80	104.90
Binary: BB3	100	10	2.5	165	160	5	2.5	19.40	25.00
	100	10	5.0	390	385	5	5.0	15.40	10.40
	100	10	7.5	510	425	85	7.5	19.70	197.60
	100	10	10.0	585	490	95	10.0	22.50	191.80

Table 6.3 MTZ model parameters at different liquid flow rate.

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	t_x (min)	t_g (min)	t_f (min)	HMTZ (cm)	RMTZ (cm min^{-1})	Fractional Capacity, *f*
BB3	100	15	10	630	570	60	10	0.0230	0.1035
	100	20	10	510	490	20	10	0.0281	0.0388
	100	25	10	435	420	15	10	0.0317	0.0333
BY11	100	15	10	1230	1155	75	10	0.0103	0.0641
	100	20	10	960	920	40	10	0.0121	0.0424
	100	25	10	735	715	20	10	0.0326	0.0266
Binary: BY11	100	15	10	390	385	5	10	0.0294	0.0104
	100	20	10	330	325	5	10	0.0357	0.0123
	100	25	10	270	265	5	10	0.0444	0.0151
Binary: BB3	100	15	10	420	385	35	10	0.0308	0.0883
	100	20	10	330	310	20	10	0.0377	0.0613
	100	25	10	285	275	10	10	0.0444	0.0327

Table 6.4 MTZ model parameters at different initial dye concentrations.

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	t_x (min)	t_g (min)	t_f (min)	HMTZ (cm)	RMTZ (cm min^{-1})	Fractional Capacity, *f*
BB3	200	10	10	645	570	75	10	0.0256	0.1298
	300	10	10	360	290	70	10	0.0325	0.2379
	500	10	10	405	375	30	10	0.0417	0.0773
BY11	200	10	10	1350	1215	135	10	0.0090	0.1103
	300	10	10	1155	1045	110	10	0.0105	0.1043
	500	10	10	1110	1045	65	10	0.0103	0.0612
Binary: BY11	200	10	10	375	370	5	10	0.0308	0.0108
	300	10	10	285	265	20	10	0.0426	0.0717
	500	10	10	255	235	20	10	0.0476	0.0809
Binary: BB3	200	10	10	405	355	50	10	0.0308	0.1380
	300	10	10	300	260	40	10	0.0435	0.1500
	500	10	10	270	235	35	10	0.0488	0.1447

6.3.6 Thomas Model and Yoon-Nelson Model

As shown in Table 6.5 to 6.7, Thomas constant, K_{TH} (L/mg.min) was observed to be slightly decreased with increasing of bed depth and initial dye concentration but increased with higher flow rate. The sorption capacity of *S. binderi*, q_o (mg/g) increases with higher flow rate and bed depth but declined at higher initial dye concentrations. In contrast of the Thomas constant, the Yoon-Nelson rate constant, K_{YN} (1/min) marked a decreased in the value when the bed depth of column increased but increased with higher flow rate and initial dye concentrations. τ (min) from Yoon-Nelson model which is the time required from 50% breakthrough was found to increase with increasing of bed depth. τ recorded to be declined at higher flow rate and initial dye concentrations.

Table 6.5 Column data and parameters obtained from Thomas Model and Yoon-Nelson Model at different Bed Depth

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	Thomas Model			Yoon-Nelson Model		
				K_{TH} (Lmg^{-1} min^{-1})	q_o (mg/g)	R^2	K_{YN} (min^{-1})	τ (min)	R^2
Basic Blue	100	10	2.5	2×10^{-4}	122.8	0.9840	0.020	122.8	0.9840
	100	10	5.0	1.5×10^{-4}	123.9	0.8670	0.015	297.5	0.8670
	100	10	7.5	1.5×10^{-4}	108.9	0.9230	0.015	392.1	0.9230
	100	10	10.0	1.7×10^{-4}	125.4	0.9280	0.017	495.5	0.9280
Basic Yellow	100	10	2.5	9×10^{-5}	126.7	0.9030	0.009	126.7	0.9030
	100	10	5.0	9×10^{-5}	200.7	0.9560	0.009	481.8	0.9560
	100	10	7.5	1×10^{-4}	207.8	0.9600	0.010	727.4	0.9600
	100	10	10.0	7×10^{-5}	254.3	0.9500	0.007	10004.4	0.9500
Binary: Basic Blue	100	10	2.5	3.5×10^{-4}	56.8	0.9630	0.037	54.0	0.9640
	100	10	5.0	2.1×10^{-4}	80.9	0.9540	0.015	223.5	0.9370
	100	10	7.5	2.3×10^{-4}	87.4	0.8980	0.015	347.1	0.9380
	100	10	10.0	1.8×10^{-4}	96.3	0.9430	0.014	392.2	0.9690
Binary: Basic Yellow	100	10	2.5	3.7×10^{-4}	54.0	0.9640	0.035	56.8	0.9630
	100	10	5.0	1.5×10^{-4}	93.1	0.9370	0.021	194.1	0.9540
	100	10	7.5	1.5×10^{-4}	97.0	0.9410	0.023	314.6	0.8980
	100	10	10.0	1.4×10^{-4}	99.3	0.9690	0.018	380.3	0.9430

Table 6.6 Column data and parameters obtained from Thomas Model and Yoon-Nelson Model at different liquid flow rate.

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	Thomas Model			Yoon-Nelson Model		
				K_{TH} ($Lmg^{-1} min^{-1}$)	q_o (mg/g)	R^2	K_{YN} (min^{-1})	τ (min)	R^2
Basic Blue	100	15	10	1.8×10^{-4}	124.5	0.9350	0.018	327.7	0.9350
	100	20	10	1.7×10^{-4}	120.3	0.9150	0.017	237.6	0.9150
	100	25	10	1.8×10^{-4}	126.5	0.9230	0.018	199.8	0.8230
Basic Yellow	100	15	10	6×10^{-5}	283.2	0.8580	0.006	745.8	0.8580
	100	20	10	8×10^{-5}	280.4	0.8850	0.008	553.8	0.8850
	100	25	10	9×10^{-5}	251.5	0.8640	0.009	397.3	0.8640
Binary: Basic Blue	100	15	10	2.4×10^{-4}	87.4	0.9390	0.022	218.0	0.9700
	100	20	10	2.6×10^{-4}	91.9	0.930	0.023	173.8	0.9660
	100	25	10	2.9×10^{-4}	90.4	0.9460	0.029	142.8	0.9460
Binary: Basic Yellow	100	15	10	2.2×10^{-4}	82.8	0.9700	0.024	230.2	0.9390
	100	20	10	2.3×10^{-4}	88.0	0.9660	0.026	181.4	0.9330
	100	25	10	2.7×10^{-4}	86.2	0.9570	0.029	142.8	0.9460

Table 6.7 Column data and parameters obtained from Thomas Model and Yoon-Nelson Model at different initial dye concentrations

Dye Systems	Concentration C_o (mg/L)	Flow rate (mL/min)	Bed depth (cm)	Thomas Model			Yoon-Nelson Model		
				K_{TH} (Lmg^{-1} min^{-1})	q_o (mg/g)	R^2	K_{YN} (min^{-1})	τ (min)	R^2
Basic Blue	200	10	10	9.0×10^{-5}	177.0	0.8980	0.018	349.7	0.8980
	300	10	10	1.1×10^{-4}	178.3	0.9640	0.033	234.8	0.9640
	500	10	10	5.4×10^{-5}	244.8	0.9210	0.027	193.4	0.9210
Basic Yellow	200	10	10	2.5×10^{-5}	513.0	0.8470	0.005	1009.6	0.8470
	300	10	10	2.0×10^{-5}	639.9	0.8720	0.006	842.5	0.8720
	500	10	10	1.2×10^{-5}	884.2	0.7650	0.006	698.5	0.7650
Binary: Basic Blue	200	10	10	1.2×10^{-4}	131.2	0.9380	0.023	232.2	0.9700
	300	10	10	1.1×10^{-4}	144.5	0.9120	0.030	175.1	0.9760
	500	10	10	7.0×10^{-5}	222.1	0.9500	0.034	154.7	0.9730
Binary: Basic Yellow	200	10	10	1.1×10^{-4}	117.6	0.9700	0.024	259.0	0.9380
	300	10	10	1.0×10^{-4}	133.0	0.9760	0.034	190.2	0.9120
	500	10	10	6.8×10^{-5}	195.8	0.9730	0.035	175.5	0.9500

6.4 Discussion

6.4.1 Effect of Bed Depth

In this study, the bed depth was varied 2.5, 5, 7.5 and 10 cm while setting other operating parameters constant. Dye solution (100 mg/L) was allowed to contact with fixed-bed depth column at flow rate of 10 mL/min until the outlet effluent of column reaches saturation point at C/C_o value 0.9 or approximately 90% of the total inlet concentration.

As illustrated in Figure 6.2, time for adsorption column to achieve 10% of breakthrough increased when bed depth increased from 2.5 to 10 cm, meaning that, time for the column to saturate with dye compounds become longer as well. With increasing of the bed depth, the depth of bed in which dye compounds passes through increases and therefore, longer time required for both breakthrough and column saturation (Goel *et al*., 2005). This might be contributed by the increased of surface area with increasing of bed depth, hence, causes the number of available binding sites on the surface of seaweed increased (Lodeiro *et al*., 2006; Tan *et al*., 2008; Baral *et al*., 2009; Uddin *et al*., 2009). Removal of Methylene Blue by Oil Palm shell activated carbon recorded the similar type of uptake process (Tan *et al*., 2008).

Besides that, increasing of bed depth in column resulted in longer time for breakthrough and saturation point which in turn causes broadening of mass transfer zone in breakthrough curve (Padmesh *et al*., 2006b; Ahmad and Hameed, 2010). Although higher bed depth was preferable in removal of dye compounds, some literature surveys stated that too high bed depth might not be useful for a single column due to higher flow resistance (Netpradit *et al*., 2004). To overcome the flow resistance, multiple beds will be more desired to achieve better column performance (Netpradit *et al*., 2004).

6.4.2 Bed-Depth-Service-Time (BDST) Model

BDST Model, a simplified model derived by Adam and Bohart Model, and modified by Hutchins which is based in the relationship between bed depth (Z) and service time (t) in a fixed-bed column (Unuabonah *et al*., 2010). BDST model physically measured the column bed capacity and determine the critical bed depth (Padmesh *et al*., 2005). From literature survey, at least nine approach or experiments were required for collection of data in Adam and Bohart Model, which in turn lead to high cost and laborious (Adak *et al*., 2006). The model was then simplified by Hutchins to become BDST model which only requires three out of nine experiments to be conducted for the collection of data purposes (Adak *et al*., 2006). Theoretically, BDST model assumed that intraparticle diffusion and external mass transfer resistance is neglectable as the adsorption kinetics is controlled by the surface chemical reaction between the sorbate and the unoccupied sorbent, thus, the sorbate will be adsorbed directly to the surface of the sorbent (Han *et al*., 2008). Basically, BDST focused on the estimation of some important parameter such as sorption capacity of the bed per unit bed volume (N_o), adsorption rate constant (K) and critical bed depth (Z) (Ayoob *et al*., 2007).

Linear plots of BDST model at flow rate of 10 mL/min for each respective dye systems with high R^2 values ($R^2 > 0.9$) indicates the suitability and validity of the model (Figure 6.3). Sorption capacity of the bed per unit bed volume, N_o (mg/cm) calculated from the BDST plot was 10.31, 24.38, 8.60 and 8.28 for BB3 single dye system, BY11 single dye system, BB3 in binary dye system and BY11 in binary dye system, respectively. BDST model rate constant, K_a (L/mgh) characterises the transfer rate of the sorbate from aqueous solution to the solid phase as the sorbent passes through the fixed-bed sorbent (Uddin *et al*., 2009; Vijayaraghavan *et al*., 2005). Large K_a value shows high sorbent efficiency where even short bed will avoid breakthrough (Uddin *et al*., 2009; Vijayaraghavan *et al*., 2005). However, in present study, K_a values were relatively small (Table 6.1), hence, higher bed depth will be required for the column system to avoid breakthrough from occur.

The crucial parameter from BDST model is the determination of critical bed depth (Z) which can be calculated from the linear plot of the model. From Table 6.1, critical bed depth required for each respective system (BB3 single dye system, BY11 single dye system, BB3 in binary dye system and BY11 in binary dye system) was found to be approximately 2.5 cm which indicates the minimum bed depth required to avoid breakthrough (Upendra and Manas, 2006). Therefore, the optimum bed depth of the fixed-bed column in present study was set to 10 cm which is five times of the critical bed depth and also the highest bed depth studied in effect of bed depth.

6.4.3 Effect of Liquid Flow Rate

As illustrated in Figure 6.4, typical breakthrough curves (S curves) with zero sorbate in the beginning of adsorption process indicates that the uptake was rapid and was fully adsorbed by sorbent, leaving the outlet effluent free from dye compounds (Aksu *et al.*, 2007). From the results, it is clearly described that uptake of these dyes were strongly affected by liquid flow rate where breakthrough curves was found to become steeper as the liquid flow rate increased from 10 to 25 mL/min. With increasing of liquid flow rate, concentration of dye compounds from effluent of column increased rapidly which resulted in steeper breakthrough curves (Qaiser *et al.*, 2009). The same phenomenon was observed in removal of Reactive Black 5 dyes by chitosan (Barron-Zambrano *et al.*, 2010). Time for the column to achieve 10% of breakthrough and saturation point were found to decrease as the liquid flow rate increases from 10 to 25 mL/min, where column gets saturated faster with increasing of liquid flow rate. As the liquid flow rate increases, time for the sorbent to resist in the column (residence time) become shorter, hence, dye compounds exited faster from the column before these dyes bind to the available binding sites on *S. binderi* (Aksu and Gonen, 2004; Barron-Zambranor *et al*., 2010; Qaiser *et al*., 2009).

Column was found to perform better at lower flow rate as dye compounds get more chances to bind with the available binding sites on the surface of sorbent due to longer residence time. In addition, these dye compounds have more time to diffuse into the porous structure of sorbent through intra-particular adsorption process which lead to better column performance (Qaiser *et al*., 2009). Therefore, minimum flow rate 10 mL/min was chosen as the optimum liquid flow rate and applied for the subsequent parameter in determination of the optimum initial dye concentration for better performance of a column.

6.4.4 Effect of Initial Dye Concentrations

Typical S shape curves (Figure 6.5) were obtained for each respective breakthrough curves. Each of these breakthrough curves exhibited the same trend where breakthrough and saturation time become shorter as the initial dye concentration increased from 100 to 500 mg/L, in which column gets saturated faster. Breakthrough curves of dye systems were observed to be steeper with increasing of initial dye concentration. Lower liquid concentration will give rise to longer breakthrough time with broader breakthrough curves. Diffusion of dye compounds into the porous structure of sorbent can be described as concentration dependent and this phenomenon might be attributed by lower concentration gradient at lower initial dye concentration which caused slower transport of dye compounds (Goel *et al*., 2005; Aksu *et al*., 2007). Available binding sites will be occupied by dye compounds in a faster pace at higher initial dye concentrations which give rise to a shorter breakthrough and saturation time (Aksu *et al*., 2007). Time for dye compounds detected in the outlet effluent of column become shorter as excessive dye compounds were flushed out from the column due to saturation of available binding sites with dye compounds. The same phenomenon was recorded in removal of Methylene Blue by oil palm shell (Tan *et al*., 2008a).

6.4.5 Mass Transfer Zone (MTZ) Model

Mass Transfer Zone (MTZ) is the portion of fixed-bed depth involved in adsorption process where dye compounds is actively removed from liquid phase to solid phase (sorbent) (Namane and Hellal, 2006). The length of MTZ was controlled by numerous factors such as nature of the sorbent, liquid flow rate, bed depth, particle size of sorbent, initial dye concentrations and pH (Al-Degs *et al*., 2009). In addition, effect of bed depth, liquid flow rate and initial dye concentrations was found to be the crucial parameters in affecting the uptake of dyes by seaweeds and also the performance of the column (Al-Degs *et al*., 2009).

For the formation of MTZ in the effect of bed depth, it was found that t_x and t_g decreases as the bed depth increased (Table 6.2). Longer time was required for the system to achieve breakthrough and saturation with higher bed depth, therefore, lead to an increase in MTZ (Unuabonah *et al.*, 2010). RMTZ which is the rate movement of MTZ increased as the bed depth increased. Longer time was required for removal of dye compounds by adsorbent at higher bed depth due to increase in available binding sites (Al-Degs *et al.*, 2009). Fractional capacity, *f,* determines the elimination efficiency of the sorbent (Namane and Hellal, 2006). From Table 6.2, removal of dye compounds exhibited higher *f* values as the bed depth increased, indicated that *S. binderi* used in the present study was found to have ability to remove dye compounds from solution under limiting condition (Unuabonah *et al*., 2010).

In present study, Fractional capacity, t_x and t_g were found to decreased at higher liquid flow rate and initial dye concentrations (Table 6.3 and 6.4). The decreased in the MTZ parameter values might be due to limitation of binding process during adsorption when the liquid flow rate and initial dye concentrations increases (Unuobonah *et al*., 2010). On the other hand, RMTZ in effect of initial dye concentration increased with increasing of initial dye concentrations (Table 7.4), which might be due to the decreasing of available binding sites at higher initial dye concentrations, eventually leads to a shorter time for establishment of the saturation column (Unuabonah *et al*., 2010).

6.4.6 Thomas Model and Yoon-Nelson Model

Thomas model is a famous model used to describe adsorption data of a column where it assumes Langmuir kinetics of sorption-desorption process without axial dispersion and in the same time, proposed that the rate of driving force obeys second-order reversible reaction kinetics (Vijayaraghavan and Prabu, 2006). While on the other hand, Yoon-Nelson Model theorise that the rate of decrease in the probability of adsorption for each respectively sorbate is proportional to the probability of sorbate adsorption and probability of sorbate breakthrough on the surface of sorbent (Aksu *et al*., 2007).

From Table 6.5 to 6.7, Thomas constant (K_{TH}) was found to increase with increasing of liquid flow rate, while the values decreased at higher bed depth and initial dye concentration (Table 6.6). The increasing trend of K_{TH} with increasing of liquid flow rate was due to domination of external mass transfer (Aksu *et al*., 2007). The crucial parameter of Thomas model, q_o increased as bed depth, liquid flow rate and initial dye concentrations increased (Table 6.5 to 6.7). Therefore, removal of dye compounds by seaweed was found to be efficient at higher bed depth and lower initial dye concentrations. Thomas model is considered as a suitable adsorption models in column studies provided that the external and internal diffusions is not the limiting steps (Aksu and Gonen, 2004).

As the bed depth increased, K_{YN} decreased while τ increased (Table 6.5 to 6.7), indicated that higher number of available binding sites which lead to better removal of dye compounds from both single and binary dye system. The same phenomena were observed for removal of reactive dyes by *Rhizopus arrhizus* (Aksu *et al*., 2007) and removal of Chromium by olive stone (Calero *et al*., 2009).

K_{YN} increased while τ decreased as the flow rate and initial dye concentrations increased (Table 6.6 and 6.7). The phenomenon might be due to occurrences of shorter breakthrough time and the column gets saturated faster with increasing of either flow rate or initial dye concentration (Calero *et al*., 2009). Higher initial dye concentration might increase the forces that control the mass transfer in the liquid phase (Calero *et al*., 2009).

6.5 Concluding Remarks

Removal of dye compounds from both single and binary dye systems were studied via continuous adsorption process, the column studies. From the present studies, effect of three crucial operating parameters (effect of bed depth, effect of flow rate and effect of initial dye concentration) were investigated. From the results, column tends to achieve breakthrough or column saturation at a longer period of time with higher bed depth, lower flow rate and lower initial dye concentration. From present study, the optimum column condition to achieve maximum dye uptake was found to be 10 cm bed depth (seaweed) in contact with 100 mg/L dyes concentration (both single and binary dye system) at 10 mL/min liquid flow rate.

CHAPTER 7

CONCLUSIONS AND FUTURE PROSPECTIVES

7.1 Conclusions

In batch adsorption process, operating parameters such as sorbent dosage, initial dye concentration, and ionic strength were found to exhibit significant effect in the removal of BB3 and BY11 from single dye solution. Uptake of these dyes was found increased with increasing of sorbent dosage and decreased as the initial dye concentrations increased. Ionic strength interrupts the removal of dye compounds where uptakes of dyes were affected (decreased) by the increasing of ionic strength concentrations. On the other hand, pH and agitation speed did not show any significant effect in removal of basic dyes by seaweed. Both BB3 and BY11 systems were found to obey Freundlich isotherm model indicating that heterogeneous type of adsorption occurs during uptake of dye compounds by *S. binderi*. Both systems were also found to obey pseudo-second-order kinetic modeling in which chemisorptions process occurs in removal of basic dyes by seaweed. Uptake of BB3 and BY11 was found to be an exothermic process from the thermodynamic analysis.

Based on the Plackett-Burman design, sorbent dosage and contact time was found to be the critical variables which possess significant effects in the removal of BB3 and BY11 from binary dye system by using batch adsorption process. Following that, these critical variables derived from Plackett-Burman analysis were applied into CCD of RSM for further improvement of dye removal process. From the study, it was found that the optimisation process by RSM was significant with p-values < 0.05. Sorbent dosage and contact time were found to have interaction as exhibited from the elliptical contour plot through RSM analysis. Optimised adsorption condition for the removal of binary dye compounds from aqueous solution was found to be valid and practical through contacting 2.22 g of *S.binderi* with 100 mg/L dye solution and agitated at 200 rpm, 30^{o}C for 122 mins.

Continuous removal of dye compounds from single dye solution and binary dye solution were also investigated by using a custom-made column. From the results, bed depth, initial dye concentrations and liquid flow rate were found to be crucial parameters with significant effects in the removal of dyes from aqueous solution. Time for breakthrough and saturation of column were found to be longer as the bed depth increased. The column saturated faster when initial dye concentrations and liquid flow rate increased. Critical bed depth of the column for removal of dye compounds from single and binary dye solution was found to be approximately 2.5 cm as calculated from BDST model. From the present study, column performed well at higher bed depth, lower liquid flow rate and lower initial dye concentrations.

Sargassum binderi was found to have excellent adsorption capability in the removal of basic dyes (BB3 and BY11) in both single dye system and binary dye system. Hence, it can be categorised as one of the potential adsorbent in the removal of these basic dyes via industrial scale.

7.2 Future Prospectives

Sargassum binderi is an excellent natural sorbent in removal of two basic dyes (BB3 and BY11) through present study. For future prospective, the capability of *Sargassum binderi* in the removal of other types of dye compounds such as reactive dyes, acid dyes, anthroquinone dyes, etc can be investigated as preliminary test in the optimisations of the uptake condition for better adsorption performance. Besides, the capability in various dye removal by other species of indigenous seaweeds other than brown seaweeds can be investigated and optimised.

Removal of various types of dyes in batch as well as column adsorption process can be conducted via statistical optimisation method (RSM) for better optimisation process incorporating interactions between different variables at the same time.

Up scaling processes can also be conducted in the uptake of basic dye compounds as preliminary test for industrial scale. The optimum conditions in the removal of various dye compounds via bench scale column study can be furthered continued through this up scaling process as preparation for commercialisation.

Desorption of dyes from the seaweeds after adsorption can be conducted by chemical treatment process. Chemicals with acidic or alkaline characteristics can be used to treat seaweeds after adsorption process to remove dye compound from the surface of seaweeds and collect for purification purposes. Dye compounds after desorption can be furthered purified for reuse purposes. Seaweeds after desorption process can be reused for adsorption of dye compounds from aqueous solution. This cycle can be repeated few times until the adsorbent (seaweeds) were fully degraded or unable to adsorb dye compounds. Further studies are required for desorption process as well as purification of used dye compounds in the economic point of view.

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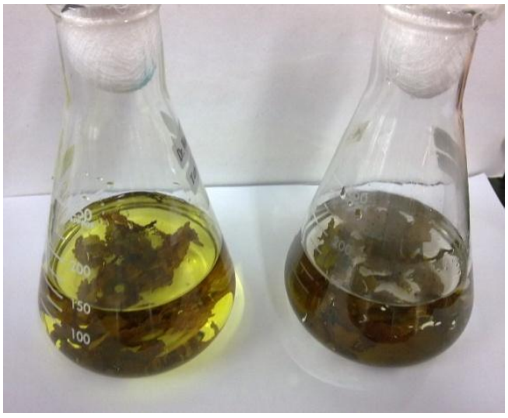
APPENDIX A

General Apparatus and Chemicals

Main equipments used in this study were : Double Beam lambda 35 Spectrophotometer (Perkin Elmer), shaking incubator (Labtech, Korea), custom made column (i.d 2cm x 24 cm height), pH meter (Sartorious Pb-100), drying oven (Memmert). General analytical grade chemicals used were Basic Yellow 11 (Sigma Aldrich), Basic Blue 3 (Sigma Aldrich), formaldehyde solution minimum 37% (Fisher Scientific), Potassium Bromide (KBr) Spectroscopy Grade (Merck), hydrochloric acid (Merck) and Sodium Hydroxide pellet (Merck).

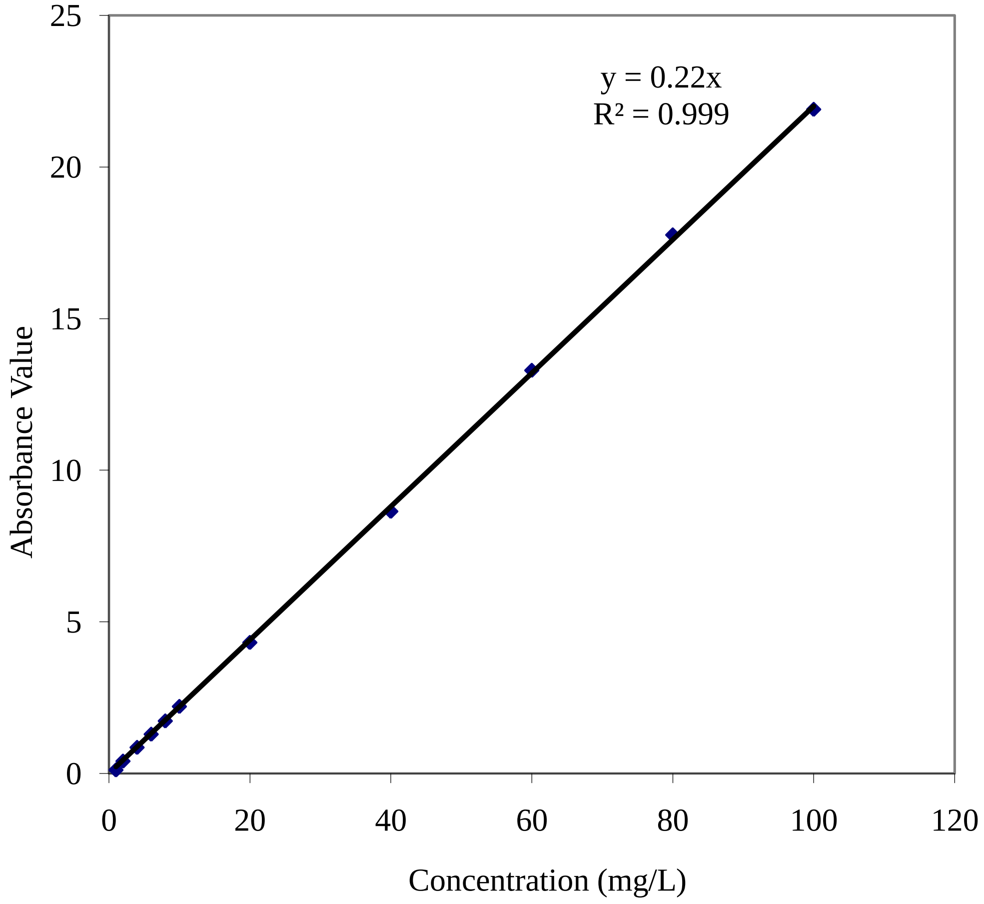
APPENDIX B

Image of BY11 dye solution before and after batch adsorption process



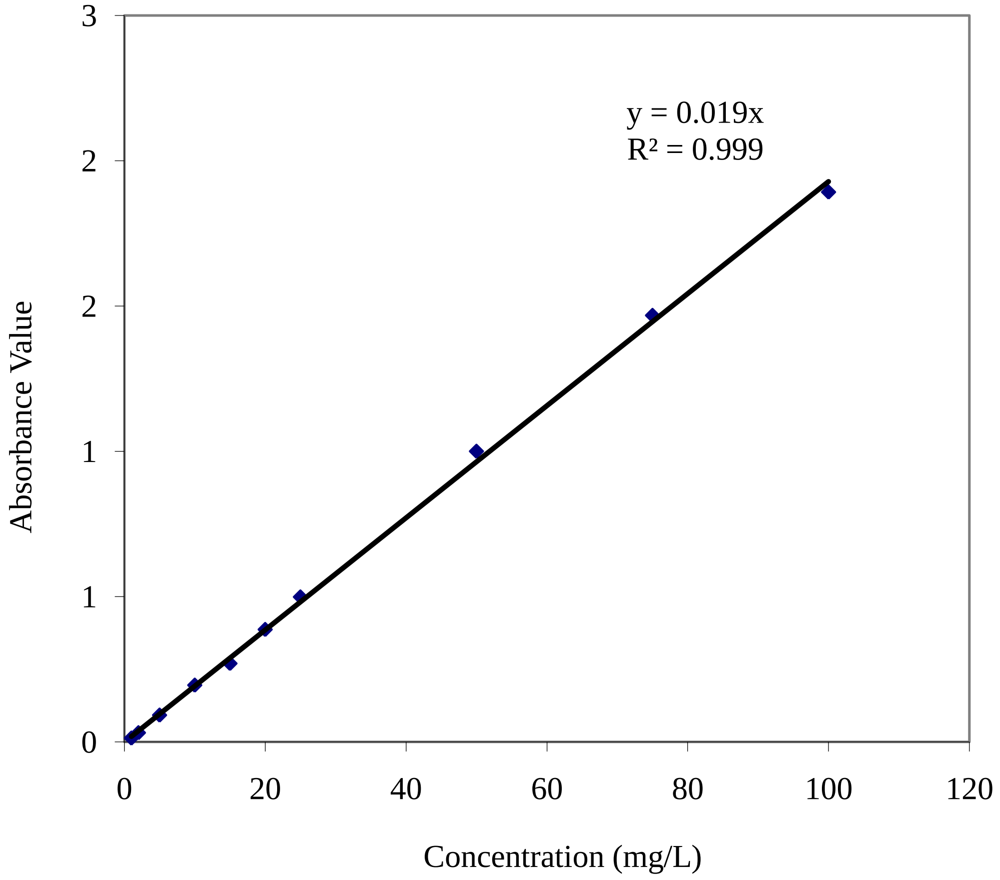
APPENDIX C

Standard curve of Basic Blue 3 (BB3) in single dye system



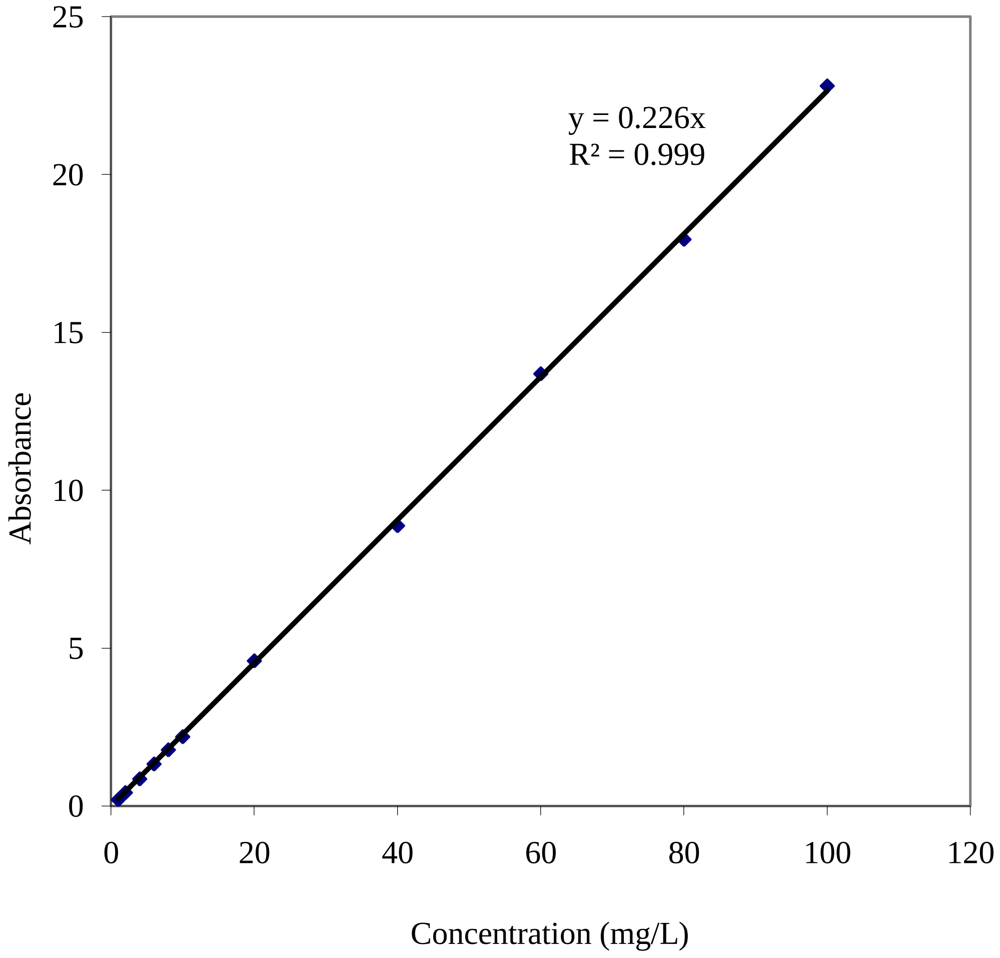
APPENDIX D

Standard curve of Basic Yellow 11 (BY11) in single dye system



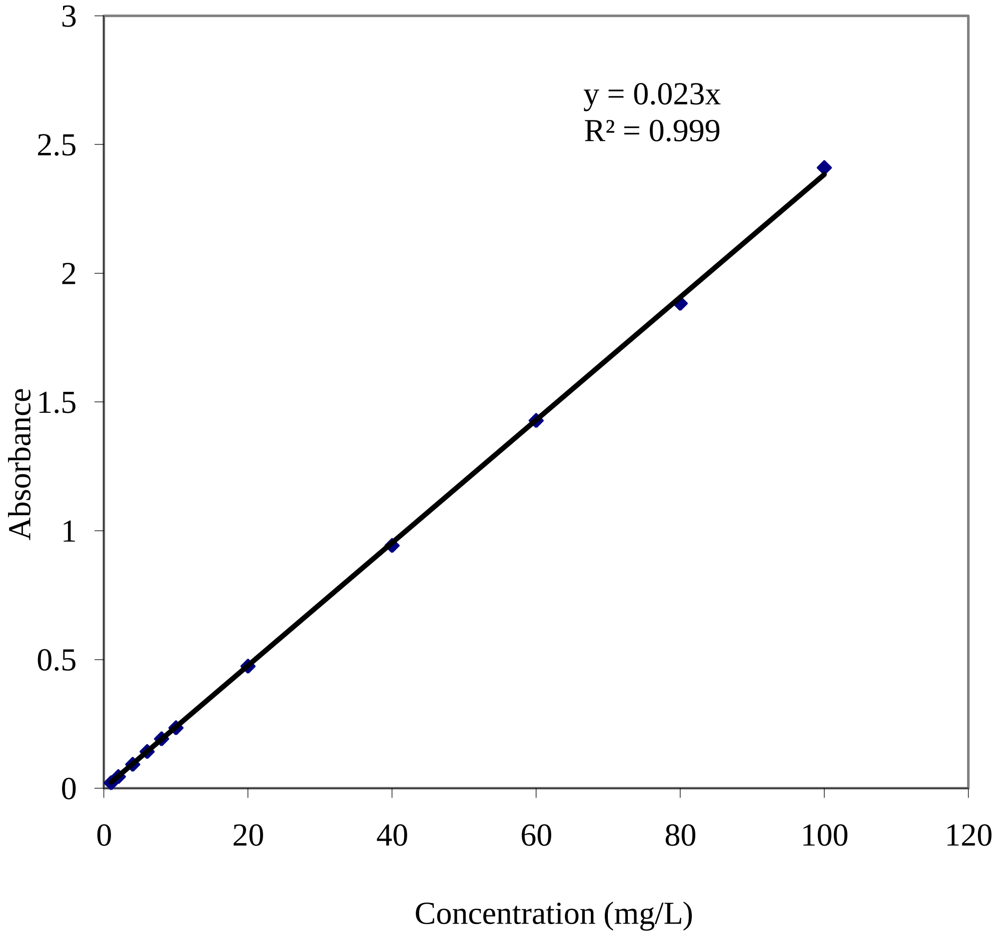
APPENDIX E

Standard curve of Basic Blue 3 (BB3) in binary dye system



APPENDIX F

Standard curve of Basic Yellow 11 (BY11) in binary dye system



APPENDIX G

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Equilibrium and Kinetic Studies for Basic Yellow 11 Removal by *Sargassum binderi*

Pei-Ling Tan, Ching-Lee Wong, Siew-Teng Ong and Siew-Ling Hii
Department of Science, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur, Malaysia

Abstract: Dyes have been widely used in many industries such as textile, paint and also ink industry. Discharge of dyes from these industries need to undergo treatment prior of disposal to avoid ecosystem to be devastated. Upon this, *Sargassum binderi*, a species of brown seaweed was used as a low cost biosorbent to remove a basic dye, Basic Yellow 11 (BY11). Various parameters such as pH, initial concentration and sorbent dosage were conducted using batch sorption process. In this study, *S. binderi* exhibited good performance (almost 100% of BY11 removal) with 1 g of sorbent dosage in 100 mg L^{-1} of dye solution. pH of the solution, however, does not seem to have high influence on removal of BY11. Langmuir, Freundlich and Temkin isotherm models were used to study sorption behaviors of *S. binderi* at equilibrium stage. From the analysis, the sorption of BY11 onto the *S. binderi* was found obeyed Freundlich model with coefficient correlation (R^2) value of 0.9959 which indicates heterogeneous layers of sorption. The Freundlich constant, K_F and n values obtained were 32.46 mg g^{-1} (L mg^{-1})$^{1/n}$ and 1.968, respectively. Value of Freundlich component, n, was more than 1 indicates favourable adsorption process of this system. The kinetic sorption of BY11 using *S. binderi* were analyzed by using pseudo-first-order, pseudo-second-order and intraparticular diffusion model. The sorption process followed pseudo-second-order kinetic which involved chemisorption. Calculated q_e values from pseudo-second-order kinetic model were found fitted well with the experimental q_e values. Each R^2 values from linear regression line of pseudo-second-order kinetic model were more than 0.99. In this study, *S. binderi* was proven to have high sorption efficiency towards BY11 and thus, it can be categorized as one of the promising biosorbent to be applied in treating the effluent discharge from industries.

Key words: *Sargassum binderi*, basic yellow 11, sorption capacity, equilibrium isotherm, kinetic studies

INTRODUCTION

Dyes have been widely used in many industries. These industries will therefore release coloured effluent which requires treatment process to remove intense colour prior of disposal. Upon this, colour was the first pollutant to be identified by using naked eyes. Among all dyes, basic dyes or also known as aniline dyes were widely used in textile industries due to its strong tinctorial strength and brightness (http://www.jagson.com/basic_dyes.htm.). Basic dyes were not light sensitive and will not fade under direct exposure of light (http://www.jagson.com/basic_dyes.htm.). Thus, this characteristic will reduce the visibility of light into the water even it is in low concentration. Reduction of light penetration will then lead to low photosynthesis rate and thus, caused the whole ecosystem in the water to be severely impaired (Turabik, 2008).

Various researches have been carried out in search of effective method to remove colour compound from effluent. Several conventional methods were applied in removing dye component from dye solutions such as flocculation, chemical precipitation, filtration, oxidation, coagulation, adsorption and membrane separation (Aksu *et al*., 2008). Adsorption by conventional activated carbon was found to be the most effective method. In this adsorption process, dye compound was conveyed from solutions to solid form, reducing the volume of effluent to the minimum and subsequently saturated adsorbent can be either regenerated or avoided from direct contact with the environment (Lima *et al*., 2008). However, usage of activated carbon was expensive which limits its application to large scale of wastewater treatment (Lima *et al*., 2008). Hence, alternative adsorbent which is low in cost and with high removal capability is in great interest of researchers around the world. The ability of dye removal by low cost agricultural waste such as beer brewery waste (Tsai *et al*., 2008), *Hevea brasiliensis* seed coat (Hameed *et al*., 2008a), banana stalk waste (Hameed *et al*., 2008b), coconut bunch waste

Corresponding Author: Siew-Ling Hii, Department of Science, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur, Malaysia
Tel: +603-41079802 Fax: +603-41079803

(Hameed *et al*., 2008c), coconut-husk (Jain and Shrivastava, 2008) and rice hull (Ong *et al*., 2007) were conducted by various researchers and it was proven that these agricultural wastes consist of promising potential in the removal of various dyes.

Sargassum binderi, a species of brown seaweed which was found to be abundant, especially from coastal area around Malaysia and with high regeneration rate was used as low cost biosorbent in this study. Brown seaweeds consist of high alginic acid content which contributes to the binding capability towards dye compound in solution (Davis *et al*., 2003).

MATERIALS AND METHOD

Biosorbent preparation: *Sargassum binderi* was collected from coastal area in Port Dickson, Seremban, Malaysia. Harvested seaweed was then washed under running tap water to remove solid particles on the surface of the seaweed. Cleaned seaweed was then washed with deionized water several times before drying at 80°C for 24 h. Chemical modification of seaweed was then carried out by contacting 10 g L^{-1} of dried seaweed with 0.2% formaldehyde for 24 h at 30°C and the mixture were agitated at 150 rpm. The objective of this treatment process was to avoid organic leaching which is a common phenomenon observed in marine algae. Organic leaching will then lead to secondary pollution which might devastate the biosorption process in water and wastewater treatment (Chen and Yang, 2005). Treated seaweed was then washed with deionized water several times to remove the residues of formaldehyde. The cleaned seaweed was dried in oven at 60°C for 24 h.

Sorbate: Synthetic dye solution of Basic Yellow 11 (BY11) (Sigma Aldrich, United States of America) was used in this study. Stock solution with concentration of 1000 mg L^{-1} was prepared without further purification. Any of the solutions used in this adsorption experiment were prepared from this stock solution to the desired concentrations by successive dilution. The properties and structures of BY11 is listed and shown in Fig. 1. A calibration curve was constructed with concentration ranging from 1 to 1000 mg L^{-1}. The concentration of BY11 in the solution were measured by using double beam UV/VIS spectrophotometer (Perkin Elmer, United States of America) at the maximum wavelength of 413 nm.

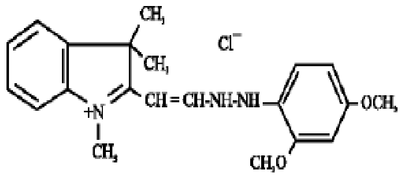

Fig. 1: Structure of BY11 (Sigma Aldrich, United States of America)

Batch biosorption process: Batch biosorption process was conducted by contacting 1 g of treated sorbent (unless otherwise stated) with a fixed volume of sorbate (150 mL) and agitated at 130 rpm, 30°C for 4 h. The pH of solution and the concentration of dyes were varied according to experiments. A fix amount of sorbate was collected at predetermined time interval for determination of dye residual. Calculation of sorption capacity, q_e (mg g^{-1}) was conducted based on the Eq. 1:

$$qe = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where, C_0 and C_e indicates initial concentration (mg L^{-1}) and concentration of sorbate at equilibrium (mg L^{-1}), respectively. V is the volume of sorbate (L) and W is the weight of sorbent (g).

Percentage of BY11 uptake (% uptake) by seaweed was calculated using Eq. 2:

$$\text{Uptake (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Effect of pH: A series of working solutions with different pH values were prepared from stock solution. pH of these working solutions were altered by using 1 M NaOH and 1 M HCl from the range of pH 2 to pH 9.

Effect of Initial dye concentration and contact time: Series of different dye concentrations range from 100 to 1000 mg L^{-1} were prepared and batch biosorption was conducted by contacting 1 g of seaweed with 150 mL of dye solution.

Effect of sorbent dosage: Effect of sorbent dosage was determined by agitate various amount of sorbent dosage (0.1, 0.5, 1.0, 1.5 and 2.0 g) with 150 mL of sorbate (100 mg L^{-1}) at 130 rpm, 30°C.

Equilibrium and kinetic studies: Equilibrium isotherms were determined by using initial concentration parameter. Langmuir, Freundlich and Temkin isotherm were applied for removal of BY11 by *S. binderi*. Determination of isotherm applied by *S. binderi* in this BY11 was conducted by comparing the correlation coefficient, R^2 value for each respective isotherm.

Pseudo-first-order, pseudo-second-order and intraparticular diffusion model were applied to the system by pH studies. R^2 values and comparison of calculated sorption capacity, q_e and experimental q_e verify the application kinetics in uptake of dye compound by *S. binderi*. Equations applied in determination of isotherm and kinetics studies were shown in discussion.

RESULTS AND DISCUSSION

Effect of pH: pH was found to be an important parameter which affect significantly on adsorption process especially for cationic dye adsorption (Wang *et al*., 2008). Figure 2 shows the removal of BY11 by *S. binderi* in pH range from 2 to 9. Sorption capacity, q_e of *S. binderi* increased from 29.14 mg g^{-1} in pH 2 to 29.71 mg g^{-1} in pH 3 and level off thereafter. Cationic dyes (basic dyes) possessed positively charge groups which play important role in binding of with surface charge of sorbent (Wang *et al*., 2008). These surface charges were greatly influenced by pH of the solution (Wang *et al*., 2008). This phenomenon can be explained by the presence of excessive H$^+$ ions which competes with positively charged dye compounds, hence, inhibits binding of dyes on the surface of biosorbent (Aravindhan *et al*., 2007). Similar outcome were reported by adsorption of methylene blue by pineapple stem (Hameed *et al*., 2009). The % uptake of dye and sorption capacity of seaweed remained almost constant with the increasing of pH from 3 to 9 (Fig. 2). Therefore, pH does not have significant influence towards removal of BY11 by *S. binderi*.

Brown seaweed consist high content of alginic acid, followed by sulfonic acid or fucoidon (Aravindhan *et al*., 2007). Carboxyl groups in alginic acid contribute to the binding of dye compounds, while sulfonic acid which usually plays secondary role bound effectively in adsorption at low pH (Davis *et al*., 2003). Although, removal of BY11 was the lowest at pH 2, the q_e value obtained from pH 2 was not significantly low as compared to q_e values of pH 3 to pH 9. Hence, the original pH of BY11 (approximate pH 5.41) was used for subsequent experiments.

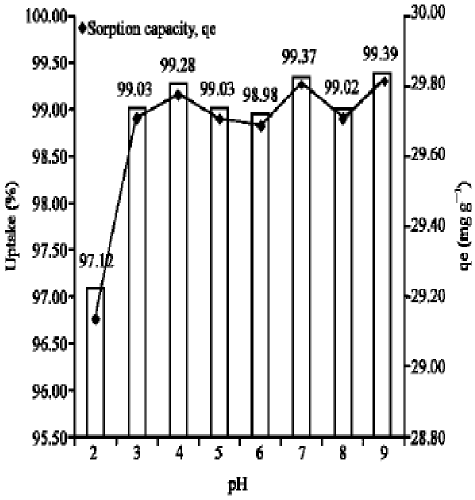

Fig. 2: Effect of pH in uptake of BY11 by *S. binderi*

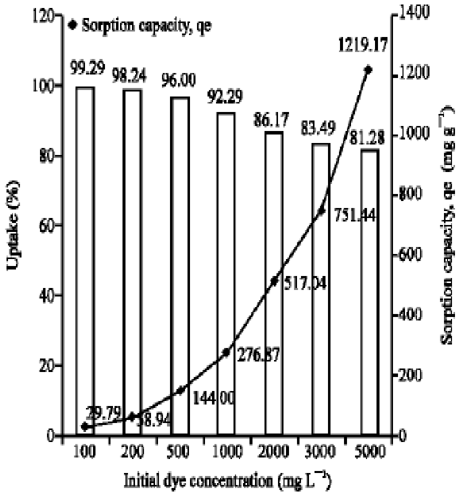

Fig. 3: Effect of initial concentration in removal of BY11 by *S. binderi*

Effect of initial concentration and contact time: As shown in Fig. 3, percentage of BY11 uptake decreased from 99.29 to 81.28, while the q_e value increased from 29.79 to 1219.17 mg g^{-1}. Higher chances of collision between dye compound and seaweed occurred with increasing of initial concentrations, thus enhance the dye absorbed by *S. binderi*. Similar phenomena was observed in removal of basic dye by apricot stone activate carbon (Demirbas *et al*., 2008), pumpkin seed hull (Hameed and El-Khaiary, 2008) and jute fiber carbon (Senthilkumaar *et al*., 2005). Figure 4 showed the time profile of sorption capacity of *S. binderi* in solution containing different dye concentration. Duration of time required for the system to achieve equilibrium increased with the increasing of initial concentrations from 60 to 180 min for initial concentration of 100 to 1000 mg L^{-1}, respectively. Uptake of BY11 by *S. binderi* was rapid in the beginning of adsorption process. The process were then gradually decreased and become constant when the system reaches equilibrium. The occurrence of this trend might be due to the rapid uptake of dye compound on the surface of the adsorbent until it reaches saturation level and lastly dye compounds will gradually diffuse into the porous structure of the adsorbent, thus contributes to

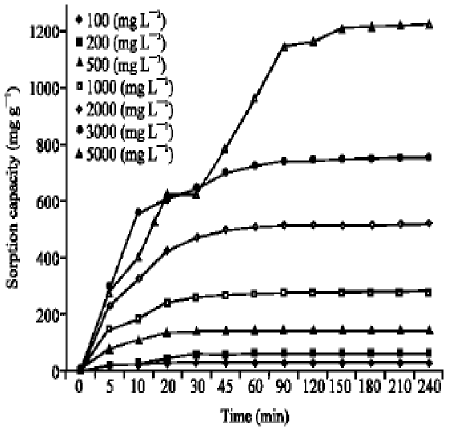

Fig. 4: Sorption capacity for removal of BY11 by *S. binderi* in various initial concentrations

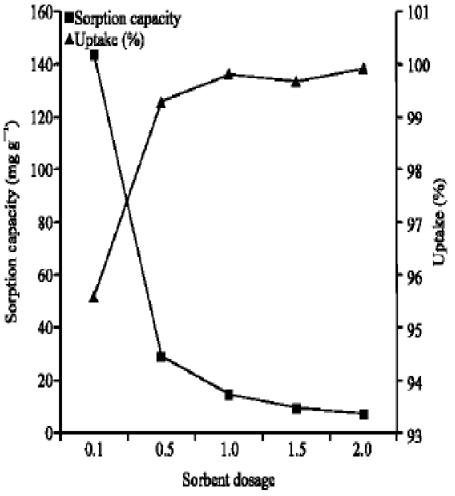

Fig. 5: Effect of sorbent dosage in removal of BY11 by *S. binderi*

longer contact time in order for the system to reach equilibrium (Senthilkumaar *et al*., 2005).

Effect of sorbent dosage: Effect of sorbent dosage on removal of BY11 by *S. binderi* was investigated by varying amount of sorbent dosage while other condition such as initial concentration (100 mg L^{-1}), temperature (30°C) and agitation speed (130 rpm) were kept constant. The uptake of BY11 removal by *S. binderi* increased from 91.78 to 99.37% with increasing of sorbent dosage. On the other hand, sorption capacity declined from 137.67 to 7.45 mg g^{-1}, as shown in Fig. 5. The increasing trend as observed in uptake of BY11 with the sorbent dosage might be attributed to the increased of surface area and presence of additional available binding sites (Ozer *et al*., 2007). However, this was inversely proportional to the sorption capacity of *S. binderi*. Increasing of sorbent dosage might lead to the overlapping of surface area due to the restricted area made available and thus, lead to reduction of effective surface area which plays important role in uptake of dyes (Garg *et al*., 2004).

Isotherm analysis: Langmuir isotherm model was the first isotherm model derived. Langmuir isotherm model assume that only homogenous adsorbent surface exist which is probably reasonable for the assumption in gas adsorption process (Droste, 1997). At equilibrium, saturation point has been achieved with no further adsorption process to be taken place, therefore, it is assumed that only one molecule will occupied one single site. Linearised form of Langmuir equation was as follow (Eq. 3):

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad (3)$$

where, Q_o and b indicates Langmuir constant which can determined from the linear plot of $1/q_e$ versus $1/C_e$. The q_e is the sorption capacity of *S. binderi* (mg g^{-1}) while C_e is the equilibrium concentration (mg L^{-1}).

Crucial characteristic of Langmuir adsorption model was expressed as dimensionless separation factor, R_L which can be derived from Eq. 4:

$$R_L = \frac{1}{(1 + bC_o)} \qquad (4)$$

where, b is the Langmuir adsorption constant (L mg^{-1}) and C_o is the highest concentration of solution. R_L value indicates the favourable condition of adsorption process with the status of adsorption to be favourable at $0 < R_L < 1$, unfavourable if $R_L > 1$ and lastly linear or in other words irreversible if $R_L = 1$.

Another popular isotherm model applied to the adsorption process was Freundlich adsorption isotherm. Freundlich model suggested that sorption process involved heterogenous sorption with different classes of adsorption sites (Aravindhan *et al*., 2007). Linearized Freundlich equation was shown in Eq. 5:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \qquad (5)$$

where, K_F (mg g^{-1} (L $mg^{-1})^{1/n}$) and n were Freundlich constants derived from the linear slope of ln q_e versus ln C_e. Freundlich magnitude of exponent, 1/n indicates favourable condition of adsorption with value of n > 1.

Temkin isotherm equation was based on the assumption where sorption energy decreased linearly as

Table 1: Comparison of Langmuir, Freundlich and Temkin isotherm constants for removal of BY11 by *S. binderi*

Models	Parameter values
Langmuir isotherm	
Q_o (mg g^{-1})	192.3077
b (L mg^{-1})	0.2488
R^2	0.9266
Freundlich isotherm	
K_F (mg g^{-1} (L $mg^{-1})^{1/n}$	32.46
n	1.968
R^2	0.9959
Temkin isotherm equation	
A (L g^{-1})	0.4385
B	141.70
R^2	0.7579

Table 2: R_L values from Langmuir isotherm model in different initial dye concentrations

Initial dye concentrations (mg L^{-1})	R_L (10^{-3})
100	38.60
200	19.70
500	7.97
1000	4.00
2000	2.01
3000	1.34
5000	0.80

the coverage of adsorbent decreased (Hameed and Duad, 2008). Temkin model assumed that adsorption take place through the characterization of uniform distribution in binding energies up to a certain level. Equation of Temkin isotherm was as Eq. 6:

$$q_e = B \ln A + B \ln C_e \qquad (6)$$

Intercept and slope of linear plot from q_e versus C_e was used to calculate the value of A and b constant whereby B = RT/b. b, indicates Temkin constant which is related to the heat of sorption (J mol^{-1}), while A is the Temkin isotherm constant (L g^{-1}), R was the gas constant with the value of 8.314 (J mol^{-1} K) and lastly T was the absolute temperature with the unit of Kelvin.

Isotherm constants obtained from each equation were presented in Table 1. From the correlation coefficient obtained (R^2), the sorption process was found fitted well to Freundlich isotherm with R^2 values of 0.9959. Freundlich constant, K_F and n was 32.46 (mg g^{-1} (L $mg^{-1})^{1/n}$) and 1.968, respectively. The R^2 value of Langmuir isotherm was 0.9266 and it might indicate that homogeneous surface adsorption occurred but in a minor way. R_L values obtained from each respective initial dye concentrations were tabulated in Table 2. Each respective concentrations show favourable occurrence of monolayer adsorption with R_L values in between 0 and 1 (Hameed, 2008). On the other hand, this system does not obey Temkin isotherm equation at all time with the least value of R^2 (0.7579). Therefore, adsorption of BY11 by *S. binderi* occurred heterogeneously in majority, while homogenous process happened to be in minor.

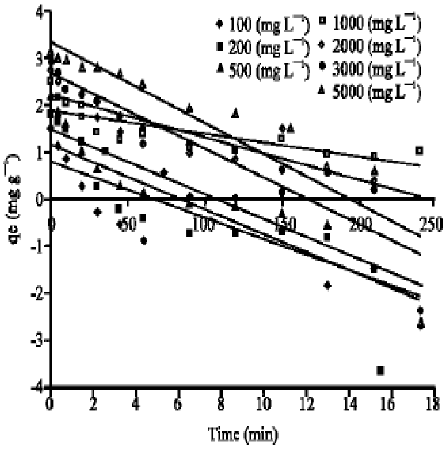

Fig. 6: Pseudo-first-order kinetics for removal of BY11 by *S. binderi*

Kinetic studies: The behavior of adsorption process were studied by using three kinetic models which comprises of pseudo-first-order, pseudo-second-order and intraparticular model. The correlation coefficient, R^2 values was used to determine the appropriateness of kinetic models that best fitted to the adsorption system.

Pseudo-first-order was theorized by Lagergran (Liu and Liu, 2008) with Eq. 7:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (7)$$

which was further integrated to:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (8)$$

where, q_t indicates the sorption capacity at time t (mg g^{-1}), q_e is the sorption capacity at equilibrium (mg g^{-1}) and k_1 is the constant. Linear plot of log (q_e-q_t) versus t (Fig. 6) was used in determination of k_1 constant (min^{-1}) and R^2 values which indicates the best fitted kinetic model.

Pseudo-second-order kinetics which was found to be the famous kinetic model as compared to the others was expressed in Eq. 9:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where, k_2 (g mg.min) indicates pseudo-second-order kinetic constant which was derived from linear plot of t/q_t versus t (Fig. 7).

R^2 and calculated q_e values obtained from both kinetic models were tabulated in Table 3. From the results, calculated q_e values derived from pseudo-second-order kinetic models was found to be compliance well to

Table 3: Comparison of R^2 values and constant of Pseudo-first and Pseudo-second-order in removal of BY11 by *S. binderi*

		Pseudo-first order kinetic model			Pseudo-second order kinetic model		
C_0 (mg L^{-1})	q_e, exp (mg g^{-1})	k_1 (min^{-1})	q_e, cal (mg g^{-1})	R^2	k_2 (10^{-5}) (g mg^{-1} min)	q_e,cal (mg g^{-1})	R^2
100	29.79	0.0269	5.80	0.6522	1331.00	30.03	0.9992
200	58.94	0.0313	14.23	0.7741	252.80	61.73	0.9981
500	144.00	0.0313	28.37	0.8493	304.20	147.06	0.9999
1000	276.87	0.0113	73.43	0.6336	83.33	285.71	0.9996
2000	517.04	0.0207	155.38	0.7536	39.67	526.32	0.9990
3000	751.44	0.0368	458.78	0.8367	24.85	769.23	0.9998
5000	1219.17	0.0394	2138.45	0.8178	26.49	1428.57	0.9956

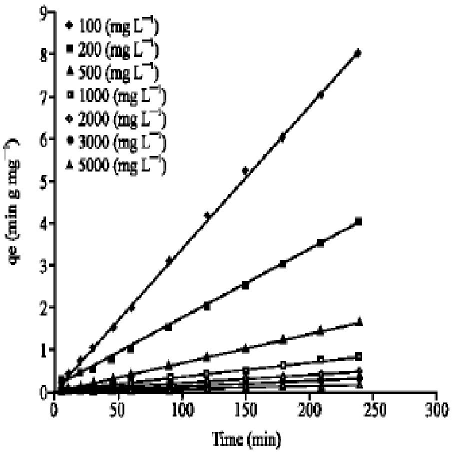

Fig. 7: Pseudo-second-order kinetics for removal of BY11 by *S. binderi*

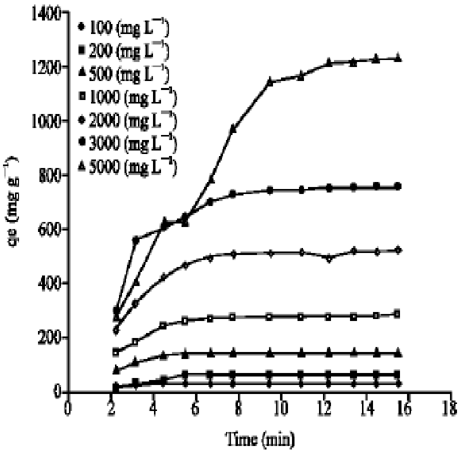

Fig. 8: Intraparticular diffusion model in adsorption of BY11 by *S. binderi*

experimental q_e values as compared to pseudo-first-order kinetic model. R^2 values obtained from pseudo-second-order kinetic model were more than 0.99 for all concentrations. Kinetic constants decreased with the increasing of initial concentrations. Pseudo-second-order kinetic model predicts the overall adsorption mechanism that occurs during the adsorption process (Fan *et al*., 2008). Since, pseudo-second-order kinetics model was best fitted with this system, it can be suggested that the adsorption process was controlled by chemical process or in other words, chemisorption (Hameed, 2008).

Diffusion mechanism might occur in adsorption process, therefore, intraparticular diffusion model was applied to the kinetic data and the equation applied is Eq. 10:

$$q_t = k_{id}^{1/2} + C \tag{10}$$

where, k_{id} was the intraparticular diffusion rate constant (mg/(gmin$^{1/2}$) and *C* is the intercept which was derived from the linear plot of q_t versus $t^{1/2}$ as shown in Fig. 8. Theoretically, diffusion was said to occur in adsorption process if linear plot was obtained and intraparticular diffusion was the rate-controlling step if these lines passed through origin (Fan *et al*., 2008). In removal of BY11 by *S. binderi*, diffusion occurred in adsorption process but these lines deviates from the origin which indicates that diffusion is not the only rate-controlling step.

From intraparticular plot obtained, the first sharp region indicates surface adsorption followed by intraparticular diffusion in the second region (Hameed, 2009). The first region illustrates boundary layer diffusion through mesopore diffusion while the second region indicates intraparticular diffusion by micropore diffusion (Lakshmi, 2009). From Fig. 8, it was proven that uptake of dye occurs initially through boundary layer diffusion as shown in the first sharp region and gradually transform to intraparticular diffusion in the second region.

CONCLUSION

The ability of *S. binderi* in removal for basic dye (BY11) was determined in this study. Various affecting parameters have been conducted in this study to determine the capability of BY11 uptake in batch sorption process. Effect of pH does not possess significant influence towards binding of BY11 compound by *S. binderi*. Uptake of BY11 increased with the increasing of sorbent dosage. On the other hand, it was found that the removal of BY11 decline with the increasing of initial dye concentration. Removal of BY11 by *S. binderi* was found to obey Fruendlich model in which was heterogenous sorption with sorption capacity of 32.46 (mg g^{-1} (L $mg^{-1})^{1/n}$) and n value of 1.968 which indicates favourable adsorption process. It was also found that the adsorption process followed pseudo-second-order kinetic with the occurrence of chemisorption process as. *S. binderi* was found to be abundance along the coastal area in Malaysia and with high regeneration rate and thus, it might be a potential low cost biosorbent with high adsorption capability.

ACKNOWLEDGMENTS

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APPENDIX H

SHELL Inter-Varsity Student Paper Presentation Contest (SSPEC) 2010 Abstract

Award Won: 2nd Prize in paper (ORAL) presentation in Postgraduate Division

Comparative studies of *Sargassum binderi* and *Caulerpa lentilifera* in removal of Basic Yellow 11

Pei-Ling Tan

Abstract

Presence of dye compounds in aqueous solution not only hazardous to human health, but in the same time destroys the whole ecosystem. Wastewater from industries such as textile, paint, and ink contributes to pollution of water due to release of dye containing discharge to the water stream. These wastewater required to undergo pretreatment prior of discharge to minimize chances of pollution towards water ecosystem. Upon this, two species of seaweeds, *Sargassum binderi* (SB) and *Caulerpa lentilifera* (CL) were investigated in determination of their ability to remove a basic dye, Basic Yellow 11 (BY11). Various parameters were applied in batch biosorption process such as pH, initial dye concentrations and sorbent dosage. Both seaweeds showed high performance (almost 100 %) in removal of BY11 with 1 g of sorbent dosage in 100 mg/L dye concentration. Isotherm models (Langmuir and Freundlich model) were applied in this study to determine the sorption behavior of both seaweeds. The results obtained indicated that both isotherm models can be accepted ($R^2 > 0.9$) where homogenous and heterogenous adsorption occurred simultaneously. The kinetic analysis of SB and CL were determined by pseudo-first-order and pseudo-second-order. R^2 values from pseudo-second-order for both SB and CL were found to be more than 0.99. Calculated q_e values of SB and CL were compliance with experimental q_e values, thus, both systems were said to obey pseudo-second-order which involved chemisorption. The ability of SB and CL in removal of BY11 were promising, therefore, both seaweeds can be categorized as an effective adsorbent in application towards industrial scale.

APPENDIX I

Abstract for 1st Natural Conference on Natural Resources, organized by Universiti Malayia Kelantan, 2010

Comparative sorption studies in decolourisation of basic dye by Sargassum binderi (Phaeophyceae) and Caulerpa lentilifera (Chlorophyceae)

Pei-Ling Tan[1], Hoay-Ven Fau[1], Ching-Lee Wong[1] & Siew-Ling Hii[2]*

1Department of Science, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur
Tel: +603-41079802, Fax: -603-41079803

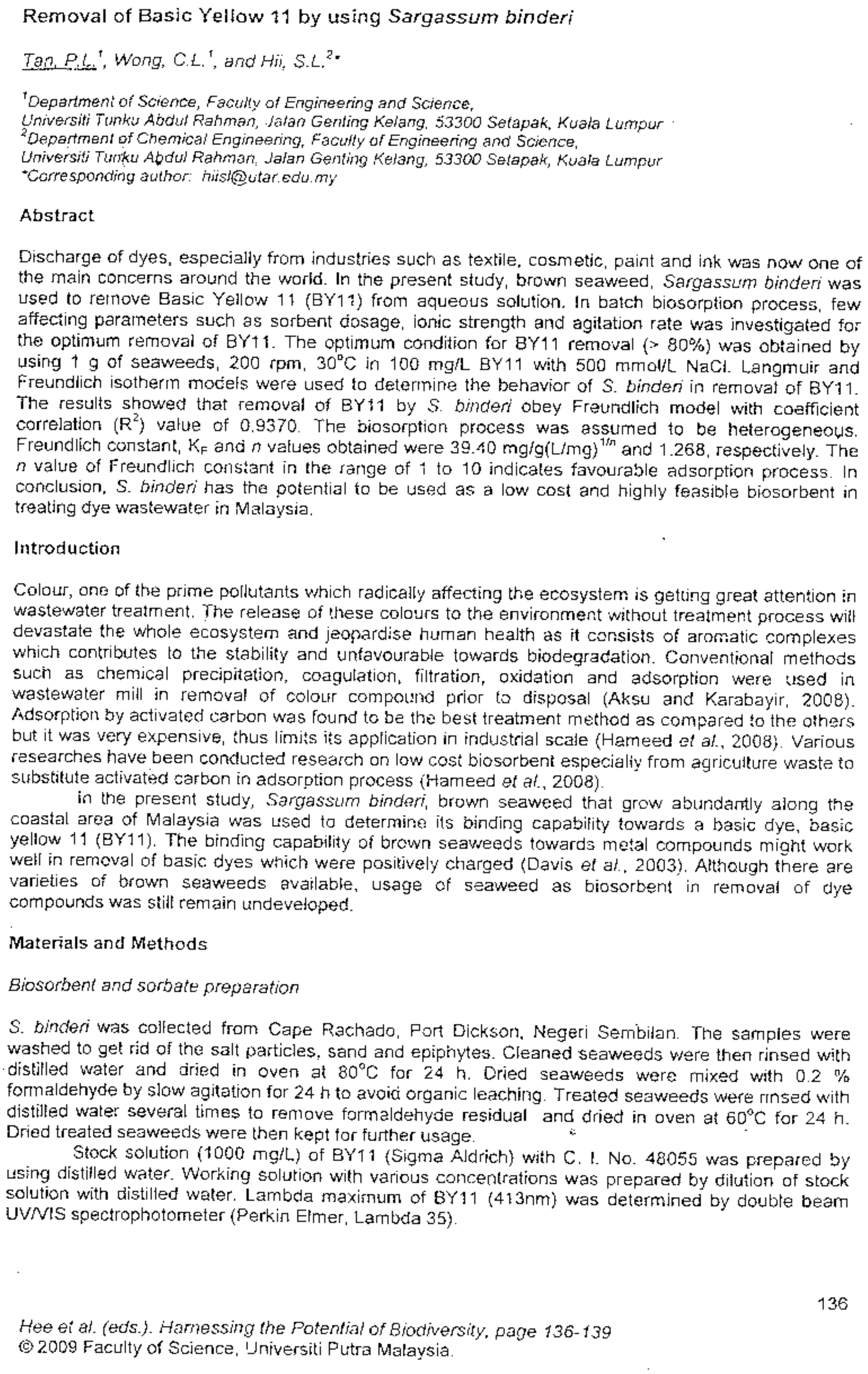
2Department of Chemical Engineering, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur
Tel: +603-41079802, Fax: -603-41079803, Email: hiisl@utar.edu.my
**Corresponding author*

Abstract

Water pollution is one of the prime pollution occurring in Malaysia. Thus, research on removal of dye compound using low cost and effective biosorbent is extensively conducted. Upon this, binding capability of two seaweeds, namely *Sargassum binderi* (phaeophyceae) and *Caulerpa lentilifera* (Chlorophyceae), in uptake of one basic dye, Basic Yellow 11 (BY11) was studied. Selected operating parameters (sorbent dosage, initial concentration and ionic strength) were investigated in determination pf the optimum uptake conditions of BY11. Both seaweeds exhibited high performance in removal of BY11 (almost 90 %) by using 1 g of sorbent dosage in 100 mg/L dye concentration with 100 mmol/L NaCl. Isotherm models (Langmuir and Freundlich model) were applied in determination of sorption behavior for both seaweeds. The results indicated that both isotherm models could be accepted (R2>0.9) where homogenous and heterogeneous adsorption occurred simultaneously. The ability of *S. binderi* and *C. lentilifera* in removal of BY11 was promising. Hence, both seaweeds have the potential to be effective adsorbents for industrial scale application.

APPENDIX J

Extended Abstract for Symposium Biology Malaysia, 2009



Removal of Basic Yellow 11 by using *Sargassum binderi*

Tan, P.L.[1], *Wong, C.L.*[1], *and Hii, S.L.*[2*]

[1]*Department of Science, Faculty of Engineering and Science,*
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur
[2]*Department of Chemical Engineering, Faculty of Engineering and Science,*
Universiti Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur
**Corresponding author: hiisl@utar.edu.my*

Abstract

Discharge of dyes, especially from industries such as textile, cosmetic, paint and ink was now one of the main concerns around the world. In the present study, brown seaweed, *Sargassum binderi* was used to remove Basic Yellow 11 (BY11) from aqueous solution. In batch biosorption process, few affecting parameters such as sorbent dosage, ionic strength and agitation rate was investigated for the optimum removal of BY11. The optimum condition for BY11 removal (> 80%) was obtained by using 1 g of seaweeds, 200 rpm, 30°C in 100 mg/L BY11 with 500 mmol/L NaCl. Langmuir and Freundlich isotherm models were used to determine the behavior of *S. binderi* in removal of BY11. The results showed that removal of BY11 by *S. binderi* obey Freundlich model with coefficient correlation (R^2) value of 0.9370. The biosorption process was assumed to be heterogeneous. Freundlich constant, K_F and *n* values obtained were 39.40 mg/g(L/mg)$^{1/n}$ and 1.268, respectively. The *n* value of Freundlich constant in the range of 1 to 10 indicates favourable adsorption process. In conclusion, *S. binderi* has the potential to be used as a low cost and highly feasible biosorbent in treating dye wastewater in Malaysia.

Introduction

Colour, one of the prime pollutants which radically affecting the ecosystem is getting great attention in wastewater treatment. The release of these colours to the environment without treatment process will devastate the whole ecosystem and jeopardise human health as it consists of aromatic complexes which contributes to the stability and unfavourable towards biodegradation. Conventional methods such as chemical precipitation, coagulation, filtration, oxidation and adsorption were used in wastewater mill in removal of colour compound prior to disposal (Aksu and Karabayir, 2008). Adsorption by activated carbon was found to be the best treatment method as compared to the others but it was very expensive, thus limits its application in industrial scale (Hameed *et al.*, 2008). Various researches have been conducted research on low cost biosorbent especially from agriculture waste to substitute activated carbon in adsorption process (Hameed *et al.*, 2008).

In the present study, *Sargassum binderi*, brown seaweed that grow abundantly along the coastal area of Malaysia was used to determine its binding capability towards a basic dye, basic yellow 11 (BY11). The binding capability of brown seaweeds towards metal compounds might work well in removal of basic dyes which were positively charged (Davis *et al.*, 2003). Although there are varieties of brown seaweeds available, usage of seaweed as biosorbent in removal of dye compounds was still remain undeveloped.

Materials and Methods

Biosorbent and sorbate preparation

S. binderi was collected from Cape Rachado, Port Dickson, Negeri Sembilan. The samples were washed to get rid of the salt particles, sand and epiphytes. Cleaned seaweeds were then rinsed with distilled water and dried in oven at 80°C for 24 h. Dried seaweeds were mixed with 0.2 % formaldehyde by slow agitation for 24 h to avoid organic leaching. Treated seaweeds were rinsed with distilled water several times to remove formaldehyde residual and dried in oven at 60°C for 24 h. Dried treated seaweeds were then kept for further usage.

Stock solution (1000 mg/L) of BY11 (Sigma Aldrich) with C. I. No. 48055 was prepared by using distilled water. Working solution with various concentrations was prepared by dilution of stock solution with distilled water. Lambda maximum of BY11 (413nm) was determined by double beam UV/VIS spectrophotometer (Perkin Elmer, Lambda 35).

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Biosorption process.

Biosorption process was carried out by agitating a fixed amount of treated seaweed with 150 mL of synthetic dye solution at 130 rpm 30°C for 4 h. A small volume of dye solutions were drawn at predetermined time interval. Determination of dye solution concentration was conducted by using double beam UV/VIS spectrophotometer. Sorption capacity, qe (mg/g) was determined by using Equation (1)

$$qe = \frac{(C_o - C_e)V}{W} \qquad \text{(Equation 1)}$$

C_o (mg/L) indicates initial concentration, while C_e (mg/L) is the concentration at equilibrium. W (g) signifies the weight of biosorbent used while V (L) is the volume of working solution.

Percentage of uptake was calculated by Equation (2)

$$\text{\% of uptake} = \frac{C_o - C_e}{C_o} \; x \quad 100\% \qquad \text{(Equation 2)}$$

Effect of sorbent dosage, agitation rate and ionic strength

The effect of sorbent dosage was determined by contacting the dye solution with a series of biosorbent dosage (0.1g to 2.0 g. To study the agitation speed, seaweeds (0.5 g) were agitated at various agitation rate (50 rpm, 100 rpm, 150 rpm, 200 rpm, and 250 rpm) at 30°C for 4 h. In order to determine the effects of ionic strength, various concentrations of ionic salt compound (NaCl) were applied into dye solutions at 30°C for 4 h.

Isotherm analysis

Isotherm analysis (Langmuir and Freundlich) was conducted by comparing the correlation coefficient values (R^2) derived from each respective models.

Results and Discussion

Effect of sorbent dosage

Percentage of BY11 uptake increased (from 91.78% to 99.37%) with the increasing of sorbent dosage (0.1 to 2.0 g) (Figure 1). This phenomena might be due to increasing in exposed surface area, thus contributed to increase in available binding sites (Liew *et al.*, 2005). No significant uptake of BY11 was recorded with sorbent dosage higher than 0.5 g, hence, the optimal dosage of seaweed in removal of BY11 was found to be at 0.5 g in 150 ml of dye solution.

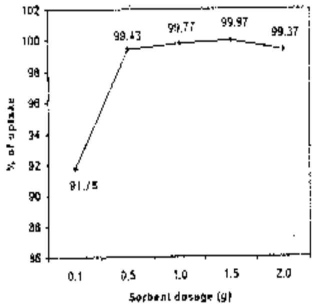

Figure 1: Effect of sorbent dosage in removal of BY11 by *S. binderi.*

Effect of agitation rate

The removal of BY11 by *S. binderi* was almost constant (approximate 98% of uptake) with the increasing of agitation rate from 50 to 250 rpm as shown in Table 1. Time for the system to achieve equilibrium decreased with the increase of agitation rate.

Table 1: Effect of agitation rate in removal of BY11 by *S. binderi*.

Agitation rate (rpm)	Equilibrium time (min)	% of removal
50	90	98.11
100	60	98.54
150	45	98.96
200	45	98.46
250	30	98.76

Effect of Ionic Strength

Generally, wastewater from textile industries contained high concentration of salt compounds and might contribute to high ionic strength. Figure 2 shows the sorption capacity of *S. binderi* in removal of BY11 with presence of NaCl in series of concentrations. Sorption capacity of *S. binderi* decreased with increasing of ionic strength from 29.08 to 25.40 mg/g. Percentage of uptake decreased with increasing of ionic strength concentrations from 96.94% to 84.66% (Figure 3). These phenomena might be attributed by competition of available binding sites between positively charged dye compounds and ionic compounds (Sumanjit *et al.*, 2008).

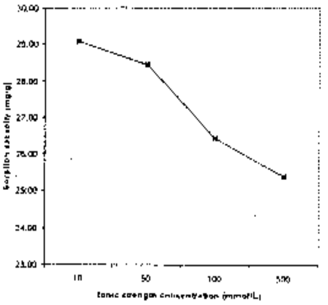

Figure 2: Sorption capacity of *S. binderi* in removal of BY11 with various ionic strength concentrations.

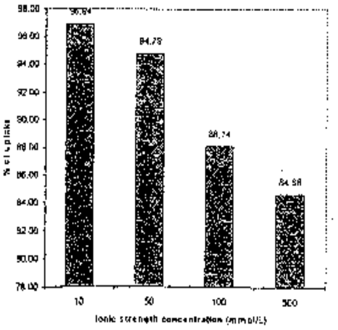

Figure 3: Effect of ionic strength in removal of BY11 by *S. binderi*

Isotherm analysis

Langmuir and Freundlich isotherm models were applied in determination of sorption efficiencies of *S. binderi*.

Langmuir isotherm model assumes that adsorption occurs homogeneously and monolayer adsorption takes place within biosorbent (Nwabanne and Mordi, 2009). Linearised Langmuir adsorption was represented by Equation (3).

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \qquad \text{(Equation 3)}$$

where Q_o and b was Langmuir constant derived from linear plot of $1/q_e$ versus $1/C_e$.

On the other hand, Freundlich proposed that adsorption occurs heterogeneously and was given by linearised equation (4) (Nwabanne and Mordi, 2009).

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \qquad \text{(Equation 4)}$$

K_F (sorption capacity) and n values were derived from linear plot of $\ln q_e$ versus $\ln C_e$.

Parameter constants derived from both Langmuir and Freundlich isotherm model were shown in Table 2. The adsorption system follow the Freundlich isotherm with high R^2 value (R^2=0.9370) as compared to Langmuir isotherem (R^2=0.7773). Thus, the adsorption of BY11 by *S. binderi* occurred heterogeneously. Freundlich constant, K_F and n were 39.40 (mg/g(L/mg)$^{1/n}$ and 1.268, respectively. Fruendlich adsorption indicator, n value was more than 1 which indicated removal of BY11 by favourable condition towards adsorption process (Tan *et al.*, 2009).

Table 2: Comparison between Langmuir and Freundlich isotherm constant.

Langmuir isotherm			Freundlich Isotherm		
Q_o (mg/g)	b (L/mg)	R^2	K_F (mg/g(L/mg)$^{1/n}$	n	R^2
43.29	1.974	0.7773	39.40	1.268	0.9370

Conclusion

In conclusion, % uptake of BY11 increased with increasing of sorbent dosage, and decreased with increasing of ionic strength concentration. Agitation speed possessed no significant effect on the uptake of BY11 by *S. binderi*. The adsorption of BY11 by *S. binderi* occurred heterogeneously as according to Freundlich isotherm model. Thus, *S. binderi* could be identified as potential biosorbent in removal of BY11.

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