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REMOVAL OF BASIC DYES BY BIOSORPTION

Mr. Pimol Punjongharn

A Thesis Submitted in Partial Fulfillment of the Requirements

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Department of Chemical Engineering

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Thesis Title	REMOVAL OF BASIC DYES BY BIOSORPTION
By	Mr. Pimol Punjongharn
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Thesis Advisor	Associate Professor Prasert Pavasant, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

.....Chairman
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.....Member
(Varun Taepaisitphongse, Ph.D.)

.....Member
(Vorapot Kanokkantapong, Ph.D.)

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สาหร่ายช่อพริกไทยหรือ *Caulerpa lentillifera* สามารถดูดซับสีเบสิค, Astrazon Blue FGRL, Astrazon Red GTLN, and Astrazon Golden Yellow GL-E งานวิจัยนี้ใช้ความเข้มข้นเริ่มต้นของสีอยู่ในช่วง 100-1800 มก/ลิตร สาหร่ายช่อพริกไทยจะถูกอบแห้งและแบ่งขนาดออกเป็น 3 ขนาดดังนี้ S (0.1-0.84 มม.), M (0.84-2.0 มม.) และ L (2.0 มม.ขึ้นไป) การทดลองทั้งหมดในงานวิจัยนี้ทำการดูดซับแบบกึ่งปฏิกรณ์และควบคุมอุณหภูมิที่ 25 องศาเซลเซียส การดูดซับจะเข้าสู่สมดุลภายใน 1 ชม. ค่าจลศาสตร์ของการดูดซับเป็นไปตามโมเดลของ pseudo second order โดยค่า k_2 จะเพิ่มขึ้นเมื่อลดขนาดของตัวดูดซับ สมดุลของการดูดซับเป็นไปตามทั้งโมเดลของ Langmuir และ Freundlich โดยตัวดูดซับขนาด S จะมีค่าการดูดซับที่สูงสุดตามด้วย M และ L การลดขนาดของตัวดูดซับจะเพิ่มพื้นที่ผิวและปริมาตรของรูพรุนในการดูดซับสีเบสิคของตัวดูดซับทำให้ค่าการดูดซับเพิ่มขึ้น ค่าการดูดซับของสี AB จะลดลงที่สภาพความเป็นกรดสูงเนื่องจากการรับโปรตอนของหมู่ฟังก์ชั่นที่พื้นผิวของตัวดูดซับ ส่วนค่าการดูดซับของสี AR และ AY ไม่ค่อยเปลี่ยนแปลงตามความเป็นกรดหรือเบสเนื่องจากกลไกการดูดซับโดยใช้การดูดกันโดยใช้กระแสไฟฟ้าสถิตซึ่งกลไกนี้จะไม่ค่อยมีผลต่อค่าการเปลี่ยนแปลงของกรดหรือเบส การเพิ่มความเค็มของระบบการดูดซับจะส่งผลให้ค่าการดูดซับลดลงโดยมีสาเหตุมาจากการแข่งขันกันของไอออน Na^+ และไอออนบวกของสีเบสิคที่พื้นผิวของตัวดูดซับ ยิ่งไปกว่านั้นการเพิ่มความเค็มจะส่งผลให้เกิดชั้นของกระแสไฟฟ้าที่พื้นผิวของตัวดูดซับซึ่งจะ ขัดขวางอนุภาคประจุบวกของสีเบสิคไม่ให้เข้าสู่พื้นผิวของตัวดูดซับ

ภาควิชา วิศวกรรมเคมี
สาขาวิชาวิศวกรรมเคมี
ปีการศึกษา 2549

ลายมือชื่อนิสิต.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....

4870554721 : MAJOR CHEMICAL ENGINEERING
KEY WORD: TEXTILE DYE/ ADSORPTION/ DECOLORIZATION/ GREEN ALGAE/ KINETICS/ ISOTHERMS/ SALT CONCENTRATION

PIMOL PUNJONGHARN: REMOVAL OF BASIC DYES BY BIOSORPTION. THESIS ADVISOR: ASSOC. PROF. PRASERT PAVASANT, Ph.D., 76 pp.

Green macroalga *Caulerpa lentillifera* was found to have adsorption capacity for basic dyes, Astrazon Blue FGRL, Astrazon Red GTLN, and Astrazon Golden Yellow GL-E. The initial dye concentration was in the range from 100-1800 mg l^{-1}. The dried algal sorbent was ground and sieved into 3 sizes: S (0.1-0.84 mm), M (between 0.84-2.0 mm), and L sizes (larger than 2.0 mm). For all conditions examined in this work (at 25°C in batch systems), the adsorption reached equilibrium within the first hour. The kinetic data corresponded well with the pseudo second-order kinetic model where the rate constant, k_2, decreased as the sorbent size increased for all dyes. The adsorption isotherms followed both Langmuir and Freundlich models. Among three sorbent sizes, S size gave the highest adsorption capacity followed by M and L sizes, respectively. A reduction of sorbent size increased the specific surface area for mass transfer, and also increased the total pore volume, thus providing more active sites for adsorption. The adsorption of AB was adversely influenced by the protonation of algal surface at low pH. On the other hand, the adsorption of AR and AY could be due to weak electrostatic interaction, which was not significantly affected by pH. Increasing salinity of the system caused a decrease in adsorption capacity possibly due to the competition between Na^+ ions and the dye cations for the binding sites on algal surface. Moreover, an increase in salinity generated a compressed electrical double layer on the algal surface which exerted repulsive force, retarding the adsorption of positive charged molecules such as the basic dyes.

Department Chemical Engineering Student's signature.....
Field of study Chemical Engineering Advisor's signature.....
Academic year 2006

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NOMENCLATURE

Symbol	*Description*
b	Langmuir isotherm constant (l mg^{-1})
c	concentration of electrolyte (mole)
C_e	liquid phase dye concentration at equilibrium (mg l^{-1})
e	electron volt (1.6×10^{-19} J)
k	boltzmann constant (1.38×10^{-23} J K^{-1})
k_1	equilibrium rate constant of first order model (min^{-1})
k_2	equilibrium rate constant of pseudo second order model (g $mg^{-1}min^{-1}$)
K_F	Freundlich isotherm constant (l g^{-1})
m	mass of sorbent used (g)
n	Freundlich isotherm exponent
N_A	Avogadro's constant (6.02×10^{23} mol^{-1})
q	amount of dye adsorbed at time (mg g^{-1})
q_e	amount of dye adsorbed at equilibrium time (mg g^{-1})
q_m	maximum adsorption capacity of sorbent (mg g^{-1})
R^2	linear regression coefficient of determination
t	time (min)
T	temperature (ºC, K)
z	electrolyte charge number
ΔG	Free energy of activation (kJ mol^{-1})
δ	Thickness of electrical double layer
$\in$	permittivity constant (c^2 $J^{-1}m^{-1}$)

σ_0	charge density (c m^{-2})
Ψ_0	potential of algae surface (J c^{-1})

CHAPTER I

INTRODUCTION

1.1 Motivations

Cationic dyes are synthetic pigments commonly known as basic dyes and are widely used in textile industry. Basic dyes are used in several processes such as acrylic, nylon, silk, and wool dyeing. The efficiency of dyeing process is often poor resulting in an escape of a large quantity of dyes through wastewater. This un-reacted color when emitted to the environment becomes wastewater which may cause serious environmental problems because the colored wastewater could reduce the light penetration through the water surface and decrease photosynthetic activity of aquatic organisms. Moreover, the heavy metal in the basic dyes could accumulate in the environment and may cause serious long term effects to ecosystem. To date, there are many technologies both physical and chemical methods for the removal of basic dyes such as the use of fenton reagent, photochemical, adsorption, membrane filtration, etc. Adsorption using activated carbon is also well known and widely used in several processes for the removal of basic dyes and heavy metals. Activated carbon is often of high efficiency particularly for low strength wastewater but it is generally very expensive. Recently, the use of biosorbent for dye removal has gained increasing attention (Pakdeepan, 2001 and Marungrueng and Pavasant, 2006) and our recent research demonstrated that the macroalga *Caulerpa lentillifera* could also be used effectively for the removal basic dyes and some heavy metals in basic dyes (Apiratikul and Pavasant, 2006, Marungrueng and Pavasant, 2006). One of the main factors influencing the effectiveness of the biosorption is the type of basic dyes as different dyes could have different attraction to the sorbent surface. In addition, there are several controlling factors for the removal of basic dyes, such as pH, initial dye concentration, adsorbent dosage, particle size, temperature. This work intended to extend the horizon regarding the fundamentals of the biosorption of basic dyes using the dried *Caulerpa lentillifera* from the work of Marungrueng and Pavasant (2006) and therefore was set out to investigate the effect of sorbent size and adsorbent dosage on the adsorption of basic dyes. In certain cases, the wastewater containing dye could have high salt concentration and this may interfere with the biosorption characteristics

which is the situation likely to occur in actual wastewaters. Hence, one of the main focuses of this work was to examine the effect of salt on the sorption of basic dyes.

1.2 Objectives

The main objective of this work was to examine the performance of the biosorption of basic dyes with dried biomass of *Caulerpa lentillifera*. This included the determinations/examinations of:

- adsorption kinetics of the adsorption of basic dyes,
- adsorption isotherms of the adsorption of basic dyes,
- the effect of sorbent size on the adsorption of basic dyes,
- the effect of pH on the adsorption of basic dyes,
- the effect of salt concentration on the adsorption of basic dyes.

1.3 Scopes of the study

- The model basic dyes investigated in this work included commercial dyes namely Astrazon® Golden Yellow GL-E (AY), Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR).
- The sorbent size for this experiment was divided to 3 sizes S (0.1-0.84 mm), M (0.84-2 mm) and L (> 2mm).
- The initial dye concentration was 100-1800 mg l^{-1}.
- The pH investigated in this work was in the range from 2 to 6.
- Salt concentration range was from 0 – 20 % w/v.

CHAPTER II

BACKGROUNDS & LITERATURE REVIEW

2.1 Chemical structure of basic dyes

The basic dyes examined in this work include Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), and Astrazon® Golden Yellow GL-E (AY), all supplied by Dystar Thai Co., Ltd. Astrazon® Blue FGRL consists of two main components, which are C.I. basic blue 159 and C.I. basic blue 3. The ratio of the two components is approximately 5:1 by weight, respectively. Astrazon® Red GTLN also consists of two main components, which are C.I. basic red 18:1 and C.I. basic yellow 28. The ratio of the two components is approximately 40:1 by weight, respectively. Astrazon® Golden Yellow GL-E has only one main component, which is C.I. basic yellow 28. All chemical structures are shown in Fig. 2.1. Physical and chemical properties of these dyes are shown in Table 2.1.

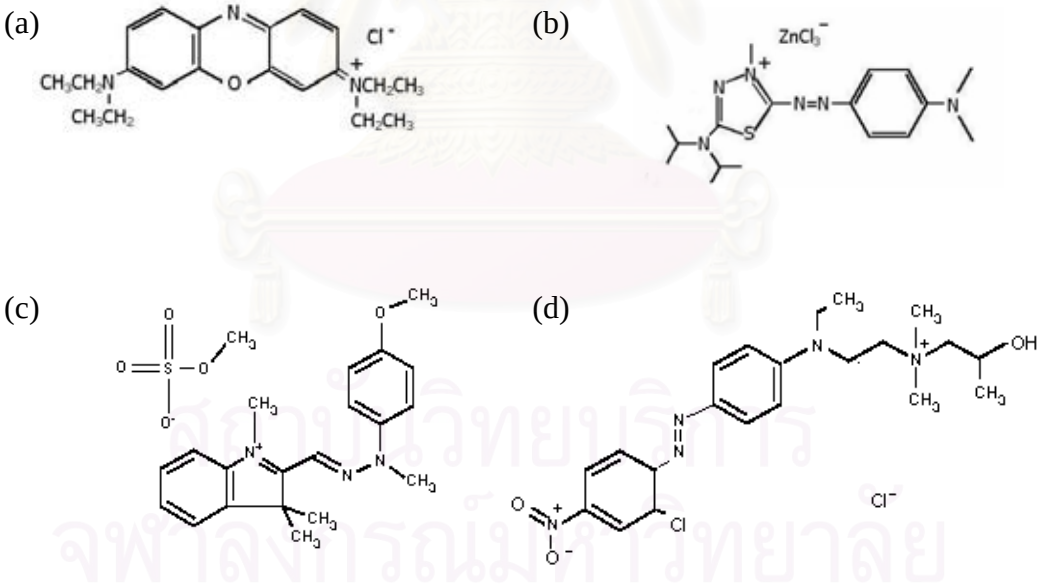


Fig. 2.1 Chemical structures of (a) C.I. Basic Blue 159, (b) C.I. Basic Blue 3, (c) C.I. Basic Yellow 28, and (d) C.I. Basic Red 18:1

Table 2.1 Physical and chemical properties, stability, toxiciological, and ecological information of the three modeled basic dyes (from MSDS)

Parameters	AB	AR	AY
Form	Powder	Powder	Powder
Color	Blue	Red	Yellow
Odor	Odorless	Odorless	Weak odor
Melting temperature	N/A	Approx. 180 °C	N/A
Solubility in water	10 g l^{-1}	60 g l^{-1}	60 g l^{-1}
pH value	6.0-7.0	5.5-7.0	3.5-6.0
Thermal decomposition	>170 °C	N/A	N/A
Acute oral toxicity	LD_{50} 206 mg kg^{-1} (rat)	LD_{50} >100 mg kg^{-1} (rat)	LD_{50} 560 mg kg^{-1} (rat)
Irritant effect on eyes	Irritant (rabbit eye)	Serious irritant (rabbit eye)	Irritant (rabbit eye)
Biodegradability	N/A	N/A	<20%
Fish toxicity	LC_{50} 10-100 mg l^{-1}	LC_{50} 10-100 mg l^{-1}	LC_{50} >100mg l^{-1}

N/A = Not available

2.2 *Caulerpa lentillifera*

Caulerpa lentillifera (Fig. 2.2) is a green macroalga classified in

Phylum: *Protista*

Division: *Chlorophyta* (Green algae group)

Class: *Chlorophyceae*

Order: *Caulerpales*

Family: *Caulerpaceae*

Genus: *Caulerpa*

Species: *Lentillifera.*

This seaweed commonly grows rapidly in rainfed agricultural areas, thus becomes unwanted material. It can tolerate a salinity range of 30-35 ppt. The characteristics of this algae are siphonous form with septum cover cell to produce gaemetangium in reproducing period. Generally *Caulerpa lentillifera* is found growing on rocks, and sand at shallow water near coral. The branch height, looked just like a bunch of

pepper, is 1-6 cm which consists of small green ramulous, spherical in shape with a diameter of around 1.5 – 2 mm.

Caulerpa lentillifera is often used to treat wastewater containing nitrogen compounds. Its rapid growth makes it common for the farmers to discard the excess biomass. Previous work has shown that this alga, unwanted agricultural material, could well be employed as an effective biosorbent for heavy metals (Sungkhum, 2003, Apiratikul and Pavasant, 2006) and basic dyes (Marungrueng and Pavasant, 2006).

Fig. 2.2 Sea grapes or green caviar (*Caulerpa lentillifera*)

2.3 Biosorption

2.3.1 Mechanism of biosorption

The kinetics of adsorbate uptake by green alga can be divided into two categories.

1. The first is called “biosorption”. This category is the passive transport mechanism, which is fast (less than 5-10 minutes), reversible and metabolism-independent surface reaction. The example of this category includes physical sorption or ion-exchange of the sorbate species at the cell surface.
2. The second is called “bioaccumulation”. This category is the active transport mechanism, which involves the uptake of the adsorbates into the living or dead cells, which is slower binding process, irreversible and metabolism-dependence.

Bacteria, cyanobacteria, algal, fungi, and yeasts are able to remove pollutants from their surrounding environment by both mechanisms. Metabolism-independent adsorption of adsorbate to cell wall (biosorption) which is polysaccharides or other materials occurs in living and non-living cells and is generally rapid. Metabolism-

dependent intracellular uptake or transport occurs in living cell (bioaccumulation) usually at a much slower rate than adsorption, although greater amount of adsorbate may be accumulated by this mechanism.

2.3.2 Biosorption of basic dyes

Biosorption is the passive process that biomass sequesters adsorbates (the dye molecules) by its external cell components. Biosorption depends on environmental factors and the degree of affinity resulting in different type of bindings between adsorbates and active site of a particular molecular structure of the cell wall. An important feature of biosorption is that it can bind and accumulate adsorbates even when the biomass is dead because it is independent of metabolism activities. Biosorption is caused by a number of different physicochemical mechanisms mainly electrostatic attractions between functional groups on the biomass surface and charges on the adsorbate.

The search for new technologies involving the removal of toxic substances from wastewater has directed towards biosorption. The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998):

- Low cost;
- High efficiency;
- Minimization of chemical and/or biological sludge

2.3.3 Comparison between inorganic and organic materials

Many investigators have examined the possibilities in employing inorganic and organic materials for the sorption of basic dyes. Inorganic sorbent mostly gives high efficiency for removal of basic dyes but often at high price. This is a major constraint for the use of such sorbents. Organic sorbents or biosorbents, on the other hand, have lower cost than inorganic sorbents, and this makes the use of such material economically attractive. Examples of various inorganic sorbents and their capacities for the removal of basic dyes are shown in Table 2.2 whereas Table 2.3 summarizes advantages and disadvantages of the use of biosorbents.

Table 2.2 Examples of inorganic adsorbents and its adsorption capacity.

Inorganic adsorbent	Dye	Operation conditions		Adsorption capacity, q_m (mg g^{-1})	References
		T (^oC)	pH		
Carbon	Basic Red 22	25	-	790	Nassar and Magdy, 1997
Carbon	Basic Blue 3	25	-	649	Nassar and Magdy, 1997
Carbon	Basic Yellow 21	25	-	600	Nassar and Magdy, 1997
Activated tyres	Methylene blue	-	-	130	Sainz-Diaz and Griffiths, 2000
Activated sewage char	Methylene blue	-	-	120	Sainz-Diaz and Griffiths, 2000
Amorphous silica	Methylene blue	-	5.0	26.5	Woolard et al., 2002
Zeolite	Methylene blue	-	5.0	12.7	Woolard et al., 2002

Table 2.3 Example of biosorbent for removal of basic dyes

Biosorbent	Dye	Operation conditions		Biosorption capacity,	References
		T (^oC)	pH	q_m (mg g^{-1})	
Palm-fruit bunch	Basic Red 18	-	-	242	Nassar et al., 1995
Orange peel	Congo Red	29	7.7	22.4	Namasivayam et al., 1996
Orange pee	Rhodamine B	29	7.7	3.23	Namasivayam et al., 1996
Linseed cake	Basic Blue 41	30	-	573	Liversidge et al., 1997
Palm-fruit bunch	Basic Blue 3	25	-	92.3	Nassar and Magdy, 1997

Palm-fruit bunch	Basic Red 22	25	-	180	Nassar and Magdy, 1997
Palm-fruit bunch	Basic Yellow 21	25	-	327	Nassar and Magdy, 1997
Peat	Basic Blue 69	80	-	226	Ho and McKay, 1998
Wood	Basic Blue 69	-	-	71.9	Ho and McKay, 1998
Sugar-industry mud	Basic Red 22	-	-	519	Magdy and Daifullah, 1998
Cotton waste	Safranine	-	-	875	McKay et al., 1999
Rice husk	Methylene blue	-	-	312	McKay et al., 1999
Cotton waste	Methylene blue	-	-	278	McKay et al., 1999
Bark	Methylene blue	-	-	915	McKay et al., 1999
Rice husk	Safranine	-	-	838	McKay et al., 1999
Aspergillus niger	Basic Blue 9	-	-	18.5	Fu and Virarahavan, 2000
Bagasse pith	Basic Blue 69	-	-	158	McKay et al., 2003
Giant duckweed	Methylene blue	25	9.0	145	Waranusantigul et al., 2003
Bagasse pith	Basic Red 22	-	-	77.0	McKay et al., 2003
Tree fern	Basic Red 13	40	5.0	408	Ho et al., 2005
Caulerpa lentillifera	Astrazon Blue FGRL	27	7.0	37.17	Marungrueng and Pavasant, 2006

Cyclodextrin-based	Basic Green 4 (Malachite Green)	25	-	91.9	Crini et al., 2007

2.3.4 Advantages and disadvantages of current technologies

There are currently a number of technologies both physical and chemical methods for the remove of basic dyes. Table 2.4 summarizes on such technologies and provides information regarding the advantages and disadvantages of the various treatment methods.

Table 2.4 Advantages and disadvantages of various treatment methods for the removal of dyes

Physical/chemical methods	Advantages	Disadvantages
Adsorption: activated carbon	Good removal of wide variety of dyes	Very expensive
Adsorption: peat	Good adsorbent due to the cellular structure	Specific surface area for adsorption are lower than activated carbon
Adsorption: silica gel	Effective for basic dye removal	Side reaction prevent commercial application
Adsorption: wood chips	Good sorption capacity or acid dyes	Requires long retention times
Electrokinetic coagulation	Economically feasible	High sludge production
Fenton reagent	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot o dissolved oxygen
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines

Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-product

2.4 Adsorption fundamentals

2.4.1 Adsorption kinetics

There are many models for characterizing the kinetic behavior of a reaction. Largegren's kinetics equation or first-order equation (Largegren, 1898) is the equation for determination how the rate of reaction varies as the reaction progresses. This equation is widely used to determine the solute adsorption on various adsorbent. Largegren's kinetics equation is described below:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{2.1}$$

where q is the amount adsorbed dye on the adsorbent (mg g^{-1}) q_e is the amount of adsorbed dye at equilibrium (mg g^{-1}). And k_1 is the rate constant of first-order biosorption (min^{-1}). After integrating and applying the boundary condition, when t=0 to t=t and q=0 to q=q, Eq (2.1) becomes

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{2.2}$$

A pseudo second order is another equation used to determine the rate of reaction (Ho and McKay, 1999). This takes the following expression:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{2.3}$$

where q and q_e is the amount of adsorbed dye on the adsorbent and amount of adsorbed dye at equilibrium, respectively, and k_2 is the rate constant of pseudo second order biosorption with a unit of g mg^{-1} min^{-1}. After integrating and applying boundary condition, when t=0 to t=t and q=0 to q=q, Eq (2.3) becomes

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \tag{2.4}$$

Eq (2.4) is rearranged to linear form as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2.5}$$

Some literature reviews on the kinetic model of various adsorption systems are shown in Table 2.5.

Table 2.5 Literature reviews on the kinetic model of various adsorption systems

Adsorbent/dyes	Kinetic model	References
Coir pith/ rhodamine B	First order (T=30°C, pH=6.5,initial dye concentration=125 mg l^{-1} and sorbent 4.0 g l^{-1})	Namasivayam et al., 2001
Aspergillus niger/ Congo Red	First order (initial pH=6)	Fu and Viraraghavan, 2002
Date pits/ Methylene blue	Pseudo-second order (Date pits activated at 500, 900 °C initial dye concentration ranged from 20-400 mg l^{-1}, sorbent = 5 mg ml^{-1})	Banat et al., 2003
Giant duckweed/ Methylene blue	First order (T=25°C, pH=7, initial dye concentration= 300,500 mg l^{-1}, 100 mL and sorbent 0.5 g)	Waranusantikul et al., 2003
Enteromorpha prolifera/ Acid red 337 and Acid blue 324	Pseudo-second order (T=20,25,30,40 ºC)	Özer et al., 2005
Neem leaf powder/ Methylene blue	First order (T=27°C, pH=7, initial dye concentration= 50 mg l^{-1} and sorbent 2-10 g l^{-1})	Bhattacharyya and Sharma, 2005
Dicranella varia/ Acid red 274	Pseudo-second order (T=30 ºC, pH=3,initial dye concentration=700 mg l^{-1}, sorbent =0.5 g l^{-1})	Gonul and Özer, 2005
Chlorella vulgaris/ Remazol black B, remazol red and remazol golden yellow	Pseudo-second order (T=25-55 ºC, pH=2, initial dye concentration=80, 240 mg l^{-1}, sorbent=1 g l^{-1} at 150 rpm)	Aksu and Tezer, 2005

Spirogyrarhizopus/Acid blue 290 and Acid blue 324	Pseudo-second order (Acid blue 290 : T=30 ºC, pH 2.0, biosorbent=1 g l^{-1} at 150 rpm Acid blue 324 : T=25ºC, pH 3.0, biosorbent=1 g l^{-1} at 150 rpm)	Özer et al., 2006a
Caulerpa lentillifera/Astrazon Blue	Pseudo-second order (T=27°C, pH=7, initial dye concentration=20,40,80,160,320, 640,1280 mg l^{-1}, sorbent 0.5 g/ 30 ml at 130 rpm)	Marungrueng and Pavasant, 2006
Corynebacterium glutamicum/ anionic dye Reactive black 5	Pseudo-second order (T=25 ºC, pH=3, initial dye concentration=500 mg l^{-1}, sorbent=0.4 g/80ml at 160 rpm)	Won et al., 2006
Dead *streptomyces rimosus/* Methylene blue	Pseudo-second order (T=20 ºC, initial dye concentration=50,100,150 mg l^{-1}, sorbent=0.45g/100ml)	Nacera and Aicha, 2006
Anaerobic sludge/ cationic dye, rhodamine B and anionic dye	Pseudo-second order (T=20-60 ºC, pH=7, initial dye concentration= 50 µmol l^{-1},sorbent =3.0 g l^{-1})	Wang et al., 2006

2.4.2 Adsorption isotherm

Sorption isotherm is the relationship between concentration and adsorption capacity at the adsorbing temperature. An adsorption isotherm explains the equilibrium relationship between the uptake capacity and the concentration in the fluid stream and therefore can be used to determine the maximum adsorbed dye. Good adsorbents must have a large surface area per unit weight of biomass. From this hypothesis, maximum sorption increases when sorbent size decreases as this will enhance the surface area and subsequently increase the active sites for adsorption. Langmuir and Freundlich equations are the two most employed isotherms for the adsorption systems and they are shown below:

Langmuir isotherm: $$q = \frac{x}{m} = \frac{q_m b C_e}{1 + b C_e} \quad (2.6)$$

Freundlich isotherm: $$q = \frac{x}{m} = K_f C_e^{1/n} \quad (2.7)$$

where

x	=	Adsorbed mass = $V(C_i - C_e)$
V	=	Solution volume
C_i	=	initial dye concentration
C_e	=	equilibrium dye concentration
m	=	adsorbent mass
q	=	adsorbed dye quantity per gram of biomass at any time
q_m	=	the maximum adsorption capacity
b	=	Langmuir constants
K_f, n	=	Freundlich constants

2.5 Controlling factors for biosorption

There are a number of controlling factors that have impacts on the biosorption. They are described below.

2.5.1 pH

The pH value is an important parameter for the adsorption process. The optimal pH may cause high efficiency for adsorption and this depends on the dye and adsorbent surface chemistries. The difference in adsorption capacity at different pH value results from:

- The competition between cationic dyes and protons for the binding site at low pH.
- The change in functional groups on the cell wall.

In most cases, the adsorption of cationic dye should decrease at a lower pH. This may be due to the occurrence of positive charge on the surface of an adsorbent in an acidic medium. Examples of the findings on the effects of pH are given in Table 2.6.

Table 2.6 Effect of pH on various adsorption systems

Adsorption system	Concluding results	References
Coir pith/ Rhodamine-B	Maximum sorption increased at pH=3 (q_m=42.5 mg g^{-1})	Namasivayam et al., 2001
Date pits/ Methylene blue	Low uptake at acidic condition	Banat et al.,2003
Giant duckweed/ Methylene blue	Minimum sorption at pH=2 (q_m= 27 mg g^{-1}) and constant sorption at pH=3 (q_m=126 mg g^{-1})	Waranusantikul, 2003
Indian Rosewood sawdust/ Methylene blue	Constant sorption at any pH (q_m=62.5 mg g^{-1})	Garg et al., 2004
Neem leaf powder/ Methylene blue	Constant sorption at neutral pH (q_m=30.66 mg g^{-1})	Bhattacharyya and Sharma, 2005
Dicranella varia/ Acid red 274	Maximum sorption at pH 3 (q_m=450 mg g^{-1})	Akkaya and Özer, 2005
Chlorella vulgaris/ Remazol black B, remazol red and remazol golden yellow	Maximum sorption at pH 2 (q_m=54 mg g^{-1}, 55 mg g^{-1} and 34 mg g^{-1}) respectively	Aksu and Tezer, 2005
Enteromorpha prolifera/ Acid red 337 and Acid blue 324	Maximum sorption at pH 2 (q_m=52 mg g^{-1} and 49 mg g^{-1}) respectively	Özer et al., 2005
Spirogyra rhizopus/Acid blue 274	Maximum sorption at pH 3 (q_m= 104 mg g^{-1})	Özer et al., 2006a
Spirogyra rhizopus/ Acid blue 290 and Acid blue 324	Maximum sorption at pH 2 and 3 (q_m=66 mg g^{-1} and 48 mg g^{-1}) respectively	Özer et al., 2006a
Corynebacterium glutamicum/ anionic dye Reactive black 5	Maximum sorption at pH 3 (q_m=51 mg g^{-1})	Won et al., 2006

2.5.2 Initial dye concentration

The studies on the effects of initial dye concentration have been done on various adsorption systems. The adsorption capacity often was found to increase with an increase in initial dye concentration. As the amount of dye being adsorbed on to the sorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the sorbent, the solution with a higher initial concentration required a slightly longer time than lower initial concentration. The effects of initial dye concentration on various adsorption systems are shown in Table 2.7.

Table 2.7 Effects of initial dye concentration on various adsorption systems

Adsorption system	Concluding results	References
Diatomaceous clay/ Methylene blue	Sorption capacity increased at high concentration (initial dye concentration = 150 mg l^{-1} and 300 mg l^{-1} $C_{(t)}/C_0$ = 0.05 and 0.56 respectively)	Shawabkeh and Tutunji, 2003
Sawdust/ Methylene blue	Sorption capacity increased at high concentration (initial dye concentration = 25 mg l^{-1} : q_e =11.63 mg g^{-1} = 70 mg l^{-1} : q_e =30.66 mg g^{-1})	Garg et al., 2004
Neem leaf powder/ Methylene blue	Sorption capacity increased at high concentration (initial dye concentration = 25 mg l^{-1} : q_e =11.63 mg g^{-1} = 70 mg l^{-1} : q_e =30.66 mg g^{-1})	Bhattacharyya and Sharma, 2005
Enteromorpha prolifera/ Acid red 337 and Acid blue 324	Sorption capacity increased at high concentration (AR 337 ; initial dye concentration = 100 mg l^{-1} : q_e = 60 mg g^{-1} = 200 mg l^{-1} : q_e = 135 mg g^{-1} AB 324 ; initial dye concentration = 100 mg l^{-1} : q_e = 40 mg g^{-1}	Özer et al., 2005

	= 200 mg l^{-1} : q_e= 105 mg g^{-1})	
Chlorella vulgaris/ Remazol black B, remazol red and remazol golden yellow	Sorption capacity increased at high concentration (RB; initial dye concentration = 18.0 mg l^{-1} : q_e = 14.9 mg g^{-1} = 79.3 mg l^{-1} : q_e = 55.3 mg g^{-1} RR; initial dye concentration = 17.7 mg l^{-1} : q_e = 14.2 mg g^{-1} = 75.1 mg l^{-1} : q_e = 55.2 mg g^{-1} RGY; initial dye concentration = 10.2 mg l^{-1} : q_e = 6.2 mg g^{-1} = 80.6 mg l^{-1} : q_e = 35.0 mg g^{-1})	Aksu and Tezer, 2005
Dicranella varia/ Acid red 274	Sorption capacity increased at high concentration (initial dye concentration = 300 mg l^{-1} : q_e = 530 mg g^{-1} = 900 mg l^{-1} : q_e = 910 mg g^{-1})	Akkaya and Özer, 2005
Spirogyra rhizopus/ Acid blue 290 and Acid blue 324	Sorption capacity increased at high concentration (AB 290 ; initial dye concentration = 500 mg l^{-1} : q_e = 340 mg g^{-1} = 1000 mg l^{-1} : q_e = 600 mg g^{-1} AB 324 ; initial dye concentration = 500 mg l^{-1} : q_e = 200 mg g^{-1} = 1000 mg l^{-1} : q_e= 370 mg g^{-1})	Özer et al., 2006
Spirogyra rhizopus/ Acid blue 274	Sorption capacity increased at high concentration (initial dye concentration = 1000 mg l^{-1} : q_e = 1000 mg g^{-1} = 750 mg l^{-1} : q_e = 750 mg g^{-1})	Özer et al., 2006

Caulerpa lentillifera/ Astrazon Blue FGRL	Sorption capacity increased at high concentration (initial dye concentration = 40 mg l^{-1} : q_e = 2.19 mg g^{-1} = 640 mg l^{-1} : q_e = 37.8 mg g^{-1})	Marungrueng and Pavasant, 2006
Dead *streptomyces rimosus*/ Methylene blue	Sorption capacity increased at high concentration (initial dye concentration = 50 mg l^{-1} : q_e = 7.7 mg g^{-1} = 150 mg l^{-1} : q_e = 24.0 mg g^{-1})	Nacera and Aicha, 2006
Anaerobic sludge/ cationic dye, rhodamine B and anionic dye	Sorption capacity increased at high concentration (initial dye concentration = 50 µmol l^{-1} : q_e = 14 mg g^{-1} = 100 µmol l^{-1} : q_e = 27 mg g^{-1})	Wang et al., 2006

2.5.3 Adsorbent dosage

The increase in the amount of adsorbent increases the adsorbent surface area and availability of adsorption sites. Although the adsorption increased by increasing the adsorbent dosage, the amount of dye adsorbed per unit mass of adsorbent was often found to decrease. With an increase in the adsorbent dosage, the residual concentration of the dye in solution decreased due to equilibrium limitations. Subsequently the uptake capacity of dye at low concentration often was lower than at high concentration. Literature reviews on the effects of adsorbent dosage are shown in Table 2.8.

Table 2.8 Effect of adsorbent dosage on various adsorption systems

Adsorption system	Concluding results	References
Water hyacinth roots / Methylene blue	Total adsorption increased when adsorbent dosage was increased but the amount of dye adsorbed per unit decreased Dosage 0.2 g ; q_e = 95 mg g^{-1} 1.0 g ; q_e = 30 mg g^{-1}	Low et al., 1995
Date pits/ Methylene blue	No effected on sorption when increase adsorbent dosage	Banat et al., 2003
Giant duckweed / Methylene blue	Total adsorption increased when adsorbent dosage was increased but the amount of dye adsorbed per unit decreased Dosage 0.1 g ; q_e = 250 mg g^{-1} 0.4 g ; q_e = 65 mg g^{-1}	Waranusantikul et al., 2003
Sawdust treated with sulfuric acid (SDC), sawdust treated with formaldehyde (SD) / Methylene blue	Total adsorption increased and equilibrium time decreased when adsorbent dosage was increased but the amount of dye adsorbed per unit decreased SDC 0.2 g ; q_e = 56.4 mg g^{-1} 1.0 g ; q_e = 24.3 mg g^{-1} SD 0.2 g ; q_e = 31.1 mg g^{-1} 1.0 g ; q_e = 22.8 mg g^{-1}	Garg et al., 2004

2.5.4 Adsorbent particle size

The adsorption capacity usually increases with decreasing size of adsorbent. In contrast, the equilibrium time decreases with decreasing the size. The decrease in adsorbent size usually affects the surface area of adsorbent. Past researches on the effect of sorbent size are shown in Table 2.9.

Table 2.9 Effects of adsorbent particle size on various adsorption systems

Adsorption system	Concluding results	References
Diatomaceous earth/ Methylene blue	Sorption capacity increased when surface area of particle was increased. D = 250-500 µm ; q_e = 170 mg g^{-1} 106-250 µm ; q_e = 185 mg g^{-1} < 106 µm ; q_e = 210 mg g^{-1} (Diatomite 0.5 g, V=50 ml, 48 h, T=20°C at 125 rpm)	Al-Ghouti et al., 2003
Date pits/ Methylene blue	Sorption capacity increased when surface area of particle was increased. D = 0.700-1.000 µm ; q_e = 7.9 mg g^{-1} 0.500-0.700 µm ; q_e = 8.4mg g^{-1} 0.212-0.500 µm ; q_e = 8.8 mg g^{-1} 0.125-0.212 µm ; q_e = 9.6 mg g^{-1} (adsorbent concentration 5 mg ml^{-1})	Banat et al., 2003
Waste carbon slurries/ Basic Red	Equilibrium time decreased 50% when surface area of particle was increased.	Gupta et al., 2003
Pine sawdust/ metal complex dyes	Sorption capacity increased when surface area of particle was increased. D = 500-710 µm ; q_e = 16.0 mg g^{-1} 355-500 µm ; q_e = 18.0 mg g^{-1} 250-355 µm ; q_e = 20.5 mg g^{-1} 150-250 µm ; q_e = 23.0 mg g^{-1} 90-150 µm ; q_e = 25.0 mg g^{-1} (dose=1g l^{-1}, pH 7.5, initial dye concentration=100 mg l^{-1})	Özacar and Şengil, 2005

Tree fern / Basic red 13	Sorption capacity increased when surface area of particle was increased. D = 101-124 µm ; q_e = 0.778 mg g^{-1} 74–88 µm ; q_e = 0.844 mg g^{-1} 61-74 µm ; q_e = 0.894 mg g^{-1} 38-45 µm ; q_e = 1.01 mg g^{-1} T=30°C, initial dye concentration 0.25-1.8 mmol l^{-1})	Ho et al., 2005
Powder peanut hull / Amaranth(Am), sunset yellow(SY),fast green FCF(FG)	Sorption capacity increased when surface area of particle was increased. Am : D = 20-40 mesh ; q_e = 5.6 mg g^{-1} 40-60 mesh ; q_e = 7.2 mg g^{-1} 60-80 mesh ; q_e = 9.0 mg g^{-1} 80-100 mesh ; q_e = 9.5 mg g^{-1} SY : D = 20-40 mesh ; q_e = 5.2 mg g^{-1} 40-60 mesh ; q_e = 6.3 mg g^{-1} 60-80 mesh ; q_e = 8.2 mg g^{-1} 80-100 mesh ; q_e = 9.2 mg g^{-1} FG : D = 20-40 mesh ; q_e = 6.2 mg g^{-1} 40-60 mesh ; q_e = 7.5 mg g^{-1} 60-80 mesh ; q_e = 9.0 mg g^{-1} 80-100 mesh ; q_e = 9.5 mg g^{-1} (dye concentration=50 mg l^{-1} dose=5g l^{-1} contact time=36 ,pH 2.0)	Gong et al., 2005

2.5.5 Temperature

The increase and decrease in temperature can also influence the biosorption capacity but its effect is difficult to generalize. For chemisorption mechanism, the rise in

temperature increases in number of molecules acquiring sufficient energy to undergo chemical reaction (endothermic reaction). However, the extremely high temperature can lead to the destruction of cell surface which can alter the binding site on the alga surface. Being an exothermic reaction, on the other hand, the adsorption capacity can be enhanced by decreasing temperature. Different adsorption mechanisms have been investigated as shown in Table 2.10.

Table 2.10 Effect of temperature on various adsorption systems

Adsorption system	Concluding results	References
Neem leaf powder/ Methylene blue	Endothermic (optimum condition T=67°C, q_m=11.63 mg g^{-1})	Bhattacharyya and Sharma, 2005
Tree fern / Basic red 13	Endothermic (optimum condition T=40°C, q_m=0.88 mmol g^{-1})	Ho et al., 2005
Silica/ Basic Blue	Exothermic (optimum condition T=20°C, q_m=4.12 mg g^{-1})	Ahmed and Ram, 1992
Activated sludge biomass/ Basic Yellow 24	Exothermic (optimum condition T=20°C, q_m=56.98 mg g^{-1})	Chu and Chen, 2002
Date pits/ Methylene blue	Exothermic (optimum condition T=25°C, q_m=80.29 mg g^{-1})	Banat et al., 2003
Enteromorpha prolifera/ Acid red 337 and Acid blue 324	Exothermic (optimum condition T=25°C, q_m=160.59 mg g^{-1})	Özer et al., 2005
Dicranella varia/ Acid red 274	Exothermic (optimum condition T=30°C, q_m=190 mg g^{-1})	Akkaya and Özer, 2005
Chlorella vulgaris/ Remazol black B, remazol red and remazol golden yellow	Exothermic (optimum condition RB: T=35°C, q_m=63 mg g^{-1} RR: T=25°C, q_m=56 mg g^{-1} RGY: T=35°C, q_m=34 mg g^{-1})	Aksu and Tezer, 2005
Spirogyra rhizopus/ Acid blue 290 and Acid blue 324	Exothermic (optimum condition T=30°C and 25°C, q_m=72 mg g^{-1} and 48 mg/g respectively)	Özer et al., 2006
Spirogyra rhizopus/ Acid blue 274	Exothermic (optimum condition T=30°C)	Özer et al., 2006

Dead *streptomyces rimosus*/ Methylene blue	Exothermic (optimum condition T=20°C, q_m=8.2 mg g^{-1})	Nacera and Aicha, 2006
Anaerobic sludge/ cationic dye, rhodamine B and anionic dye	Exothermic (optimum condition T=20°C, q_m=5.91 mg g^{-1})	Wang et al., 2006

2.5.6 Pretreatment

A number of chemical substances can be used to pre-treat the adsorbent to alter its adsorptive power. Examples of these chemicals are formaldehyde, sulfuric acid, chitosan, calcium chloride, etc. The pretreatment is the method often used to enhance the maximum capacity of adsorbent. When sorbent is treated with any chemical substance, the porosity of sorbent is possibly changed and may incorporate several additional functional groups on the cell wall. Example of the effect of pretreatment of sorbent with chemical substance on adsorption systems are shown in Table 2.11.

Table 2.11 Effect of pretreatment of sorbent with chemical substance

Adsorption system	Concluding results	References
Caulerpa lentillifera/Cu, Cd and Pb treated with 0.5 N of NaOH (1h), $CaCO_3$(24h),Na_2SO_4(24h), Na_2CO_3(24h),$NaNO_3$(24h)	The maximum sorption is changed when treated with different pretreatment techniques Cu: pretreatment techniques Untreated q_m = 0.0819 mmol g^{-1} NaOH q_m = 0.0946 mmol g^{-1} $CaCO_3$ q_m = 0.1059 mmol g^{-1} Na_2SO_4 q_m = 0.0796 mmol g^{-1} Na_2CO_3 q_m = 0.0727 mmol g^{-1} Cd: pretreatment techniques Untreated q_m = 0.0367 mmol g^{-1} $CaCO_3$ q_m = 0.0654 mmol g^{-1} $NaNO_3$ q_m = 0.0301 mmol g^{-1} Na_2CO_3 q_m = 0.0420 mmol g^{-1} Pb: pretreatment techniques Untreated q_m = 0.0363 mmol g^{-1}	Suthiparinyanont et al., 2003

	NaOH q_m = 0.0607 mmol g^{-1} (contact time 60 min, concentration of heavy metal=100 mg l^{-1})	
Sawdust treated with sulfuric acid (SDC), sawdust treated with formaldehyde (SD) / Methylene blue	The maximum sorption of the sawdust for removal of methylene blue is changed when treated with sulfuric acid and treated with formaldehyde. SDC q_m = 56.4 mg g^{-1} SD q_m = 31.1 mg g^{-1}	Garg et al., 2004

2.5.7 Salt concentration

In certain cases, the wastewater containing dye can have high salt concentration. This may interfere with the biosorption characteristics. In general, the adsorption capacity usually decreases with an increase in salt concentration. This is because salt increases the ionic strength, which subsequently reduces the activity of active sites on cationic dye. This is because ionic strength can influence the aqueous phase equilibrium. According to surface chemistry theory, when two phases are in contact in aqueous solution, they are bound to be surrounded by an electrical double layer owning to electrostatic interaction. If the adsorption mechanism is significantly controlled by this electrical layer then the electrostatic attraction adsorption decreases with an increase in ionic strength. Examples of the effect of salt concentration on adsorption system are shown in Table 2.12.

Table 2.12 Effect of salt concentration on various adsorption systems

Adsorption system	Concluding results	References
Dunaliellia species/ Chromium(VI)	The maximum sorption decreased when salt concentration was increased. (NaCl) 0% NaCl q_m = 37.7 mg g^{-1} 5% NaCl q_m = 24.5 mg g^{-1} 15% NaCl q_m = 18.2 mg g^{-1}	Donmez and Aksu, 2002

	20% NaCl q_m = 13.4 mg g^{-1} (pH 2.0, T=25°C, dose 1 g l^{-1},C_0 = 56.6 mg l^{-}1 at 125 rpm	
Chaff/ Methylene blue	The maximum sorption decreased when salt concentration was increased. (NaCl and $CaCl_2$) NaCl : 0.00 mol l^{-1} q_m = 0.625 mg g^{-1} 0.05 mol l^{-1} q_m = 0.600 mg g^{-1} 0.10 mol l^{-1} q_m = 0.585 mg g^{-1} 0.20 mol l^{-1} q_m = 0.556 mg g^{-1} $CaCl_2$: 0.00 mol $l^{-1}$$q_m$ = 0.575 mg g^{-1} 0.05 mol $l^{-1}$$q_m$ = 0.513 mg g^{-1} 0.10 mol $l^{-1}$$q_m$ = 0.475 mg g^{-1} 0.20 mol l^{-1} q_m = 0.465mg g^{-1} (initial concentration 30 mg l^{-1}, dose 8 g l^{-1})	Han et al., 2006
Corynebacterium glutamicum/ Anionic dye reactive black 5	No effect on sorption when salt concentration (NaCl) was increased.	Won et al., 2006

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

- Astrazon® Blue FGRL (AB)
- Astrazon® Red GTLN (AR)
- Astrazon® Golden Yellow GL-E (AY)
- *Caulerpa lentillifera*

3.2 Equipment

- Screen Fabric Filter
- Spectrophotometer, Spectronic® UV/VIS Helios Alpha Spectrophotometer with Vision 32 software –v.125
- Rotary Shaker
- Refrigerator
- pH-meter Hanna HI 98240
- Blender
- Dessicator

3.3 Glassware

- Volumetric flasks
- Pipette
- Beakers
- Test tubes
- Cylinder
- Funnels

3.4 Procedure

3.4.1 Algal collection

Caulerpa lentillifera is collected from Banchong Farm, Chachoengsao Province, Thailand.

3.4.2 Algal sorbent preparation

1. Wash the algae with water.
2. Dry the algae at room temperature for 1 night to remove excess water.
3. Grind the algae with blender.
4. Sieve the ground algae to S, M, and L sizes where
    a. S is for the size range of 0.1 mm to 0.84 mm
    b. M is for the size range of 0.84 mm to 2 mm
    c. L is for the size range of larger than 2 mm
5. Store the algae in dessicator.

3.4.3 Determination of λ_{max}

1. Prepare 100 mg l^{-1} of the AB solution by diluting the stock solution
2. Scan for the wavelength of maximum light absorption using scan mode of the Spectrophotometer.
3. Repeat Steps 1-2 with AR and AY.

3.4.4 Calibration curves

1. Prepare 30 ml solution with the initial AB dye concentration 0, 2.5, 5, 6.25, 10, 12.5, 20, 25, 40, 50, 100 mg l^{-1}.
2. Measure the light absorbance of the solution with spectrophotometer.
3. Pour the solution to Screen fabric filter and measure the light absorbance of the solution with spectrophotometer.
4. Repeat Steps 1-3 with AR, AY.
5. Plot the concentration (x-axis) vs. the light absorbance (y-axis).

3.4.5 Determination of sorption kinetics

1. Prepare 30 ml solution with the initial AB dye concentrations of 100 mg l^{-1} (9 flasks).
2. Add 0.5 g of S-size algae in the solutions.
3. Mix the solutions slowly with a rotary shaker at a rate of 130 rpm.
4. Collect the sample and separate solid phase with screen fabric filter (at 1, 3, 5, 10, 20, 30, 60, 120, 180 min) in the test tubes.
5. Keep the sample in the refrigerator for 20-24 hours.

6. Measure the light absorbance of the sample with spectrophotometer.
7. Triplicate the experiments.
8. Repeat Steps 1-7 with AR, AY and change the alga to M and L-size.

3.4.6 Determination of sorption isotherms

1. Prepare 30 ml solution of AB with initial dye concentrations of 100, 200, 400, 600, 800, 1000, 1200, 1500, 1800 mg l^{-1} (9 flasks).
2. Add 0.5 g of S-size algae in the solutions.
3. Mix the solutions slowly with a rotary shaker at a rate of 130 rpm.
4. Wait until equilibrium is reached before collecting the sample and separating the solid phase with screen fabric filter.
5. Keep the sample in the refrigerator for 20-24 hours.
6. Measure the light absorbance of the sample with spectrophotometer.
7. Triplicate the experiments.
8. Repeat Steps 1-7 with AR, AY and change algae to M and L-size.

3.4.7 Determination of effect of pH

1. Prepare 30 mL solution of AB with initial dye concentrations of 100, 200, 400, 600, 800, 1000, 1200, 1500, 1800 mg l^{-1} and control at pH = 2.
2. Add 0.5 g of S-size alga in the solution.
3. Mix the solutions slowly with a rotary shaker at a rate of 130 rpm.
4. Collect the sample and separate solid phase with screen fabric filter at 90 min.
5. Keep the sample in the refrigerator for 20-24 hours.
6. Measure the light absorbance of the sample with spectrophotometer.
7. Triplicate the experiments.
8. Repeat Steps 1-7 with AR, AY.
9. Change pH to be 4 and 6.

3.4.8 Determination for effect of salt concentration

1. Prepare 30 mL solution of AB with initial dye concentrations of 100, 200, 400, 600, 800, 1000, 1200, 1500, 1800 mg l^{-1}.
2. Add 0.5 g of S-size alga in the solution.

3. Add 5 % NaCl (w/v) in the solution.
4. Mix the solutions slowly with a rotary shaker at a rate of 130 rpm.
5. Keep the sample in the refrigerator for 20-24 hours.
6. Measure the light absorbance of the sample with spectrophotometer.
7. Triplicate the experiments.
8. Repeat Steps 1-7 with AR, AY.
9. Add salt (NaCl) concentration of 10%, 15%, and 20% (w/v).

3.5 Analytical Measurement

3.4.1 Determination of dye concentration

After finishing each batch, the algal mass was separated from the solution by filtration through the screen fabric filter. The filtrates were analyzed for the concentration using Spectronic® UV/VIS Helios Alpha Spectrophotometer with Vision 32 software – v.125. The absorbance was measured at the wavelength of maximum light absorbance for each dye and the calibration curve was generated from the standards with the following concentrations: 2.5, 5, 6.25, 10, 12.5, 20, 25, 40, 50, 100 mg l^{-1}.

3.4.2 Determination of adsorption capacity

The adsorption capacity, *q*, is calculated from the difference between initial and equilibrium concentrations as shown in Eq (3.1)

$$q = \frac{V(C_i - C_e)}{1000W} \tag{3.1}$$

where *q* is the uptake (mg g^{-1}), C_i the initial dye concentration (mg l^{-1}), C_e the dye concentration remaining in the solution at equilibrium (mg l^{-1}), *W* the adsorbent dosage (g), and *V* the solution volume (ml).

3.4.3 Determination of rate constant of biosorption (*k*)

The *k* value from the Lagergren's kinetics equation (first order) and the pseudo second-order equation can be estimated according to the following instructions.

3.4.3.1 Lagergren's kinetics equation (first order)

The first order kinetic constant can be found from the slope of the plot between log (q_e-q) (y-axis) and t (x-axis) as shown in Eq.(3.2):

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \qquad (3.2)$$

where q_e is the adsorption capacity at the equilibrium (mg g^{-1}).

3.4.3.2 Pseudo second-order equation

The pseudo second-order equation is shown in Eq. (3.3):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3.3)$$

where q_e is the adsorption capacity found from the slope of graph between t/q (y-axis) and t (x-axis). Therefore the second order kinetic constant can be calculated from the interception on y-axis by linear equation.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of algal sorbent

Recent works (Marungrueng and Pavasant, 2006) on the examination of the functional groups of the dried *Caulerpa lentillifera* were done using Fourier Transform Infrared (FT-IR) technique (Perkin Elmer, 1760X). The results showed that the most abundant functional groups in dried alga *C. lentillifera* were hydroxyl (O-H), carboxyl (COOH), amine (NH_2), and sulfonyl (S=O) (Marungrueng and Pavasant, 2006) and the pK_a of these functional groups were 9.5-13, 1.7-4.7, 8-11 and 1.3, respectively (Apiratikul and Pavasant, 2006). The effect of pH on the dissociation of functional groups could be explained in terms of pH_{zpc} (pH of zero-point charge) of the adsorbent. In this research, the pH_{zpc} of *C. lentillifera* was at the pH of 0.3. The surface areas, total pore volume, and pore diameter of the alga sizes L, M, and S (from the standard BET procedure, N_2 adsorption) are shown in Table 4.1. For brevity purposes, in the following text, the alga size L is represented by "L", size M by "M" and size S by "S". Specific surface area and total pore volume of M was greater than those of S and L, respectively. On the other hand, pore diameter of S was greater than those of L and M, respectively.

4.2 Kinetics of basic dyes

To investigate the mechanism of adsorption, two kinetic models are generally employed. Largergren pseudo first order kinetics has been widely used to determine the solute adsorption on various adsorbents. This pseudo first order kinetics equation can be written in a linear form as:

$$\log\left(q_e - q\right) = \log q_e - \frac{k_1}{2.303}t \tag{4.1}$$

The pseudo second order kinetic equation was proposed by Ho and McKay (1999) where:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4.2}$$

For all sizes of alga, the adsorptions of the three dyes revealed that equilibriums were reached within the first hour. At initial dye concentration of 100 mg l^{-1}, the adsorption capacity (q_e) of AB obtained from the kinetic experiments were 5.4 , 5.2, and 5.1 mg g^{-1} for adsorbent sizes S, M, L, respectively, and q_e for AR were 5.4, 5.3, and 5.2 mg g^{-1} whereas q_e for AY were 4.7, 4.4, and 3.7 mg g^{-1}, respectively.

The kinetic plots for the adsorption of the three basic dyes with *Caulerpa lentillifera* were shown in Fig. 4.1-4.3. The parameter fittings demonstrated that the data fitted better with the pseudo second order than the pseudo first order models. The second order rate constants from the pseudo second order model are reported in Table 4.2. This finding was similar to the results of other studies on the biosorption of several other basic dyes. For instance, the pseudo second order kinetics were successfully applied for the biosorption of Rhodamine B on anerobic sludge (Wang et. al, 2006), the adsorption of Remazol black B, red and golden yellow on *Chlorella vulgaris* (Aksu, 2005), and basic green 4 (Malachite Green) on cyclodextrin-based (Crini et. al, 2006).

Azizian (2004) suggested that the pseudo second order kinetic model was best used to describe the adsorption at low initial concentration (when compared to the weight of sorbent) which could be the case for this work. It is better to explain the derivation for this kinetic model before moving further with the discussion. The pseudo first order and pseudo second order models for sorption processes from solutions were derived by a general and different method. This would allow the selection between the uses of the first-order or second-order models and also identified the real meaning of their observed rate coefficients. The mechanism of the adsorption for solute A in the solution is assumed to follow Eq. (4.3):

$$A + * \underset{k_d}{\overset{k_a}{\leftrightarrows}} A_{(a)} \tag{4.3}$$

where k_a and k_d are the adsorption and desorption rate constants and * represents the vacant site. The adsorption and desorption rates are

$$v_a = k_a C(1-\theta) \tag{4.4}$$

$$v_d = k_d \theta \tag{4.5}$$

where θ is the coverage fraction ($0 \leq \theta \leq 1$) and C is the molar concentration of solute at any time. The overall rate equation is

$$\frac{d\theta}{dt} = v_a - v_d \tag{4.6}$$

$$\frac{d\theta}{dt} = k_a C(1-\theta) - k_d\theta \tag{4.7}$$

The adsorption of solute from solution onto the surface of sorbent decreases the concentration of solute in solution, and the concentration of solute at any time:

$$C = C_0 - \beta\theta \tag{4.8}$$

where C_0 is the initial molar concentration of solute, C is its molar concentration at any time and β is

$$\beta = \frac{m_c q_m}{M_w V} \tag{4.9}$$

where m_c is the mass (g) of sorbent, q_m the maximum sorption capacity of sorbent, M_w the molar weight of solute (g/mol), and V the volume of solution (L). One can rewrite β as

$$\beta = \frac{C_0 - C_e}{\theta_e} \tag{4.10}$$

where C_e is the equilibrium molar concentration of solute and Θ_e the equilibrium coverage fraction. By inserting Eq.(4.8) into Eq.(4.7),

$$\frac{d\theta}{dt} = k_a(C_0 - \beta\theta)(1-\theta) - k_d\theta \tag{4.11}$$

Eq.(4.11) is the general equation, which is used at different conditions for derivation of various kinetics models of sorption. If the experimental conditions appear such that the initial concentration of solute is very high compared to $\beta\theta$ ($C_0 >> \beta\theta$), then one can ignore the $\beta\theta$ term in Eq.(4.11) and therefore

$$\frac{d\theta}{dt} = k_a C_0 - (k_a C_0 + k_a)\theta \tag{4.12}$$

By mathematical method and integrating Eq(4.12) so we can obtain pseudo first order kinetic model which was derived by Lagergren with a different method. The relationship between rate constant of first-order (k_1) and initial concentration of solute are shown by

$$k_1 = k_a C_0 + k_d \tag{4.13}$$

If the initial concentration of solute is not too high for the $\beta\theta$ term in Eq.(4.11) to be ignored. By rearrangement of Eq.(4.11) we obtain

$$\frac{d\theta}{dt} = k_a \beta \theta^2 - \left(\beta + C_0 + \frac{1}{K} \right) k_a \theta + k_a C_0 \qquad (4.14)$$

Again after intergration and mathematical manipulation as approximate, Eq.(4.14) is changed to pseudo second order kinetic model which was derived by different method. From derivation of Eq.(4.14) we can observed rate constant (k_2) is a complex function of the initial concentration of solute (C_0). Table 4.2 also illustrates that the adsorption capacity and k_2 slightly increased when the alga was ground to smaller size. This could be due to two reasons. Firstly the smaller alga had more binding sites available for adsorption or secondly the binding sites in the small alga were easier to access. This was explained in more detail in the next section.

4.3 Adsorption isotherms

Sorption isotherm is the relationship between concentration and adsorption capacity at each particular temperature. In this study, Langmuir and Freundlich isotherm equations were employed to describe the isotherm of the adsorption of basic dyes where:

Langmuir isotherm: $$q = \frac{x}{m} = \frac{q_m b C_e}{1 + b C_e} \qquad (4.15)$$

Freundlich isotherm: $$q = \frac{x}{m} = K_f C_e^{1/n} \qquad (4.16)$$

Different adsorbent sizes (S, M, and L) were studied for the effect of sorbent size on the adsorption isotherms. Langmuir and Freundlich plots are shown in Fig. 4.4-4.6 and their corresponding isotherm parameters are summarized in Table 4.3. The high R^2 for both models suggested that the equilibrium data were well represented by both equilibrium models. The applicability of these models to this dye-algal sorbent system implied the possibility that both monolayer biosorption and heterogenous surface condition could exist under the experimental condition (Dönmez and Aksu, 2002) This could be also be because the initial dye concentration was low. However, a dye concentration above 1800 mg l^{-1} was far beyond the level found in industrial effluent, which was only approximately 100 mg l^{-1} (U.S. EPA, 1996). Hence, increasing initial concentrations above this point was not included in the scope of this work. In addition, the dye solution at above 1,000 mg l^{-1} was highly viscous and quite difficult to handle. The maximum adsorption capacities (q_m) calculated by Langmuir model for AB, using the L, M, and S size adsorbent, were 68.0, 70.4, and 80.7 mg g^{-1}; AR 78.4,

76.9, and 113.6 mg g^{-1}; AY 26.9, 27.4 and 35.5 mg g^{-1}, respectively. The results showed that smaller sized alga gave more adsorption capacity to the removal of basic dyes than the alga of larger sizes.

The free energy change (ΔG) for the adsorption at 25°C was also calculated using the following equation:

$$\Delta G = -RT \ln b \tag{4.17}$$

where b is a Langmuir isotherm constant, R the gas constant (8.314 J mol^{-1} K^{-1}), and T the temperature (Kelvin). The calculated ΔG was between -2.7 to -4.8 kJ mol^{-1} (as shown in Table 4.3) indicating a spontaneous nature of adsorption.

From the BET analysis reported in Table 4.1, the alga with size M, unexpectedly, had the largest surface area and total pore volume, followed by S and L. However, the pore diameter of alga size M was the lowest among the three. The effects of sorbent size on the adsorption capacity could then be discussed as follows. Firstly, the smaller particle, M and S size sorbents, had more surface area and total pore volume available for the removal of basic dyes than the larger ones. L had lower surface area and total pore volume than the other two. As a result, the adsorption capacity acquired from the L-size sorbent was the lowest in all experimental conditions. Secondly, the pore diameter was believed to also exert significant impacts on adsorption capacity where a larger pore diameter allowed an easier access of the dye molecule into the sorbent structure resulting in a higher adsorption capacity. For the sorbent of S size, it was shown that this did not only possess high surface area, but also had the largest pore diameter. Consequently, it gave the highest adsorption capacity. In case of M size, the sorbent had the largest surface area, but smallest pore diameter. Therefore, basic dyes molecules could hardly enter the pore and the access to the binding sites inside the pore became difficult. It was also possible that there was a clog in the pore. The adsorption capacity was therefore controlled by two contradicting mechanisms, one was the surface area and the other was the pore diameter. The fact that the alga with size M had lower adsorption capacity for removal of basic dye than the S size suggested that the effect of pore diameter was more significant than the effect of surface area.

4.4 Effect of pH

pH is an important factor influencing the adsorption of basic dyes on the algal biomass. It had been proven that the adsorption system depended on the degree of ionization of the dye solution and the dissociation of functional groups on the active sites of the adsorbent which varied at different pH. In most cases, the adsorption of basic dyes decreased at lower pH due to the occurrence of proton in acidic mediums (Kumar et al., 2005; Crini et al., 2006). To search for the optimal adsorption pH, the adsorptions of basic dyes (AB, AR and AY) were conducted at various pH levels from 2, 4, 6, and uncontrolled at pH 7±1 (unctrl). There were no attempts to examine the adsorption at basic conditions (pH > 7) as the dyes could not be dissolved completely. The results in Fig. 4.7 represent the adsorption isotherms of AB, AR, and AY at various pH conditions and the isotherm parameters are summarized in Table 4.4.

The maximum adsorption capacities (q_m) at pH 2, 4, and 6, and at the uncontrolled pH conditions, estimated from Langmuir model for AB were 74.1, 94.3, 93.5, and 80.7 mg g^{-1}; AR 97.1, 100.0, 105.3, and 113.6 mg g^{-1}; and AY 31.9, 30.4, 32.9, and 35.5 mg g^{-1}, respectively. From the results, the conditions at pH of 6 and at uncontrolled pH seemed to give the highest adsorption capacity for the removal of all basic dyes, and in most cases, the adsorption capacity decreased with a drop in pH. For AB and AR, the effect of pH was significant and the adsorption capacity could drastically change from 74.1 to 93.5 mg g^{-1} and 97.1-113.6 mg g^{-1} with an increase in the pH from 2 to 6. However, the effects on the adsorptions of AY were not quite strong and the adsorption capacity only varied in a narrow range with a change in pH from 2 to 6. As error from the measurement by spectrophotometer was about ±2.5% and therefore the differences in q_m of AY which were less than 5 % as reported in this table was considered not at all significant.

The pH_{zpc} (zero point charge) of the adsorbent is the pH where the surface charge remains neutral. The surface charge of the adsorbent is positive when the media pH is below the pH_{zpc} value while it is negative at pH greater than pH_{zpc}. In this research *Caulerpa lentillifera* had pH_{zpc} of 0.3 and the negative zeta potential increased at pH higher than pH_{zpc}, and remained constant after pH 7. Therefore, the alga had less negative charges on its surface at acidic medium and had the highest negative charges at neutral pH due to the protonation in acidic solution. From the results in Section 4.1, the possible functional group that could change the charge

within the pH range from 2 to 6 was carboxyl which had the pK_a at around 1.7-4.7. At pH higher than 1.7-4.7, carboxyl became deprotonated and therefore attracted positive charged compounds such as basic dye. However, pH only did have significant effect on the adsorption of AB and AR, therefore this carboxyl group was expected to be mainly responsible for the adsorption of AB and AR. The adsorption mechanisms for AY should be different from AB and AR, and none of the functional groups examined above could be reasonably responsible for such adsorption. In case of AY, the adsorption mechanism for the cationic dyes and adsorbent might be due to a weak electrostatic interaction between dyes and electron-rich sites of the surface of algae which might not be affected significantly from the change in pH.

4.5 Effect of salt concentration

The effect of salt was studied using NaCl solution. The NaCl concentration ranged from 0 to 10 %w/v. Langmuir and Freundlich models were used to describe adsorption isotherms of the basic dyes. The effect of salt concentration on the adsorption of AB and AY using initial dye concentration of 100-1800 mg l^{-1} are shown in Fig. 4.8. It was noted that AR could not be dissolved in saline water and therefore was not investigated here. The results clearly demonstrated that increasing in salt concentration from 0 to 10% (w/v) led to a significant decrease in adsorption capacity of AB. The maximum adsorption capacity (q_m) of AB at 0, 5, and 10% salt concentration were 80.7, 78.7 and 38.3 mg g^{-1}, respectively. This corresponded to an almost 50% decrease in the adsorption capacity for the range of salft examined here. The isotherm parameters of Langmuir and Freundlich models were shown in Table 4.5. The results suggested that with increasing NaCl concentration, q_m decreased. The same finding was found for the adsorption of AY. However, the solubility of AY at high salt concentration (10% w/v NaCl) was relatively low and therefore the experiment could not be conducted in such condition. The maximum adsorption capacities (q_m) of AY at 0 and 5% salt concentrations were 35.5 and 27.9 mg g^{-1}, respectively.

The results demonstrated clearly that salinity had significant impact on the adsorption of basic dyes. Past research showed that an increase in salinity or ionic strength (Na^+ to Ca^{2+}) of the solution could cause a sharp decrease in maximum adsorption capacity of methylene blue on chaff (Han et al., 2006). This could be attributed to the competition between ions of similar charge. For the case of this work,

the decrease in adsorption capacity might be due to the competition of basic dyes (which also possessed cationic properties) and Na^+ ions for the adsorption sites on algal surface. In addition, the presence of salinity generated the electrical double layer (Gong et al., 2006; Eren and Afsin, 2006; Anirudhan and Ramachandran, 2006). According to surface chemistry theory (Shaw, 1980), most substances acquired a surface electric charge when brought into contact with a polar medium in aqueous phase. This surface charge influenced the distribution of nearby ions in the polar medium. Ions of opposite charge (counter-ions) were attracted towards the surface and (less important) ions of like charge (co-ions) were repelled away from the surface. At this point, they were surrounded by an "electrical double layer" owning to electrostatic interaction.

If the adsorption mechanism was significantly influenced by the electrostatic attraction, adsorption decreases with an increase in salt concentration and ionic strength (Han et al., 2006). The theory of the electrical double layer deals with the distribution of ions on the surface of the adsorbent where δ is the thickness of the charged layer and (Shaw, 1980):

$$\frac{1}{\delta} = \left(\frac{2e^2 N_A c z^2}{\in kT} \right)^{1/2} \tag{4.18}$$

where N_A is Avogadro's constant (6.02×10^{23} mol^{-1}), c the electrolyte concentration, z electrolyte charged number, $\in$ the permittivity constant, e the electron volt (1.6×10^{-19} Joule), k the boltzmann constant (1.38×10^{-23} Joule/Kelvin), and T the temperature (Kelvin). For an aqueous solution of a symmetrical electrolyte at 25^0C, Eq.(6) become

$$\frac{1}{\delta} = 0.329 \times 10^{10} \left(\frac{cz^2}{mol.dm^{-3}} \right)^{1/2} m^{-1} \tag{4.19}$$

The thicknesses (δ) at 5, 10 %w/v NaCl were 3.29×10^{-10} and 2.32×10^{-10} m. This equation showed that an increase in salt concentration or ionic strength caused a compression of electrical double layer. At this point, the charge density (σ_0) at the surface increased according to the Poisson-Boltzmann distribution where, at low potential at 25^0C,

$$\sigma_0 = \frac{\in \psi_0}{\delta} \tag{4.20}$$

where $\in$ the permittivity constant (approximately 4.56×10^{-13} c^2 $J^{-1}m^{-1}$ for an aqueous solution of a symmetrical electrolyte at $25\ ^0$C), Ψ_0 the potential of algae at pH 7 which

was 60×10^{-3} J c^{-1}. The charge density values of 5, 10 %w/v NaCl at algal surface approximately 8.32×10^{-5} and 11.77×10^{-5} c m^{-2}.

From the above description, two causes of the decrease of adsorption capacity due to the increase in salt concentration might be introduced, (i) the competition with Na^+ with the dye cations to access the binding site on algal surface, and as a result, reduced the electric potential at the surface of adsorbent: (ii) Secondly, the increase in NaCl concentration or ionic strength (*c* or *z*) led to the compression of electric double layer at 25 ^oC (δ decreased from Eq. 4.19) which propels away the positive charged dye molecules. Both effects deteriorated the removal efficiency of the basic dyes. These effects could be described diagrammatically as shown in Fig. 4.9.

Table 4.1 BET surface areas, total pore volume, and average pore diameter for adsorbent particles with different sizes

Algae size	Surface area ($m^2\ g^{-1}$)	Total pore volume ($ml\ g^{-1}$)	Average pore diameter (Å)
L (> 2 mm)	3.2	6.2×10^{-3}	77.1
M (0.84-2 mm)	8.7	14.6×10^{-3}	44.8
S (0.1-0.84 mm)	5.0	11.6×10^{-3}	105.0

Table 4.2 Pseudo second order rate constants for all basic dyes at initial dye concentration of 100 mg l^{-1}

Basic dyes	Particle size	$q_{e,exp}$ ($mg\ g^{-1}$)	Pseudo second order rate constants		
			k_2 ($g\ mg^{-1}min^{-1}$)	$q_{e,cal}$ ($mg\ g^{-1}$)	R^2
AB	L	5.1	7.8×10^{-2}	5.2	0.9999
	M	5.2	8.3×10^{-2}	5.3	0.9999
	S	5.4	11.9×10^{-2}	5.5	0.9999
AR	L	5.2	14.0×10^{-2}	5.3	0.9999
	M	5.3	15.0×10^{-2}	5.3	0.9999
	S	5.4	16.3×10^{-2}	5.4	0.9999
AY	L	3.7	10.0×10^{-2}	3.8	0.9985
	M	4.4	12.5×10^{-2}	4.5	0.9999
	S	4.7	15.7×10^{-2}	4.7	0.9997

Table 4.3 Constants of Langmuir and Freundlich isotherms

Basic dye	Sorbent size	Langmuir constants			Freundlich constants			ΔG
		q_m (mg g^{-1})	b (l mg^{-1})	R^2	K_f	n	R^2	(kJ mol^{-1})
AB	L	68.0	4.0×10^{-3}	0.9256	0.6	1.4	0.9736	-3.4
	M	70.4	3.9×10^{-3}	0.9752	0.8	1.5	0.9915	-3.4
	S	80.7	5.8×10^{-3}	0.9689	0.9	1.4	0.9776	-4.4
AR	L	78.7	3.4×10^{-3}	0.9584	0.6	1.2	0.8634	-2.7
	M	76.9	7.0×10^{-3}	0.8997	1.6	1.5	0.7899	-4.8
	S	113.6	4.6×10^{-3}	0.9139	0.3	1.4	0.8952	-4.0
AY	L	26.9	4.5×10^{-3}	0.9124	0.7	1.9	0.9457	-4.0
	M	27.4	4.1×10^{-3}	0.9573	0.8	2.0	0.9434	-3.4
	S	35.5	7.4×10^{-3}	0.9164	2.1	2.4	0.8977	-4.8

Table 4.4 Constants of Langmuir and Freundlich isotherms for the adsorption of basic dyes with S size algae

Basic dye	pH	Langmuir constants			Freundlich constants		
		q_m (mg g^{-1})	b (l mg^{-1})	R^2	K_f	n	R^2
AB	2	74.1	7.0×10^{-3}	0.9693	1.5	1.6	0.9823
	4	94.3	3.8×10^{-3}	0.9711	0.7	1.3	0.9916
	6	93.5	4.9×10^{-3}	0.9731	0.8	1.3	0.9771
	unctrl	80.7	5.8×10^{-3}	0.9689	0.9	1.4	0.9776
AR	2	97.1	6.4×10^{-3}	0.9302	0.2	0.7	0.8966
	4	100.0	4.2×10^{-3}	0.9357	0.2	0.8	0.9138
	6	105.3	3.9×10^{-3}	0.9186	0.2	0.8	0.9186
	unctrl	113.6	4.6×10^{-3}	0.9139	0.3	1.4	0.8952
AY	2	31.9	3.0×10^{-3}	0.9381	0.6	1.9	0.9579
	4	30.4	4.6×10^{-3}	0.9795	1.2	2.2	0.9642
	6	32.9	5.1×10^{-3}	0.9530	1.1	2.1	0.9638
	unctrl	35.5	7.4×10^{-3}	0.9164	2.1	2.4	0.8977

Table 4.5 Constants of Langmuir and Freundlich isotherms of basic dyes at various salt concentrations by using algal S size

Basic dye	NaCl (%w/v)	Langmuir constants			Freundlich constants		
		q_m (mg g^{-1})	b (l mg^{-1})	R^2	K_f	n	R^2
AB	0	80.7	5.8×10^{-3}	0.9689	0.9	1.4	0.9796
	5	78.7	3.8×10^{-3}	0.9333	0.45	1.3	0.9606
	10	38.3	11.2×10^{-3}	0.9839	2.0	2.1	0.9803
AY	0	35.5	7.4×10^{-3}	0.9164	2.1	2.4	0.8977
	5	27.9	5.4×10^{-3}	0.9745	1.2	2.2	0.9852

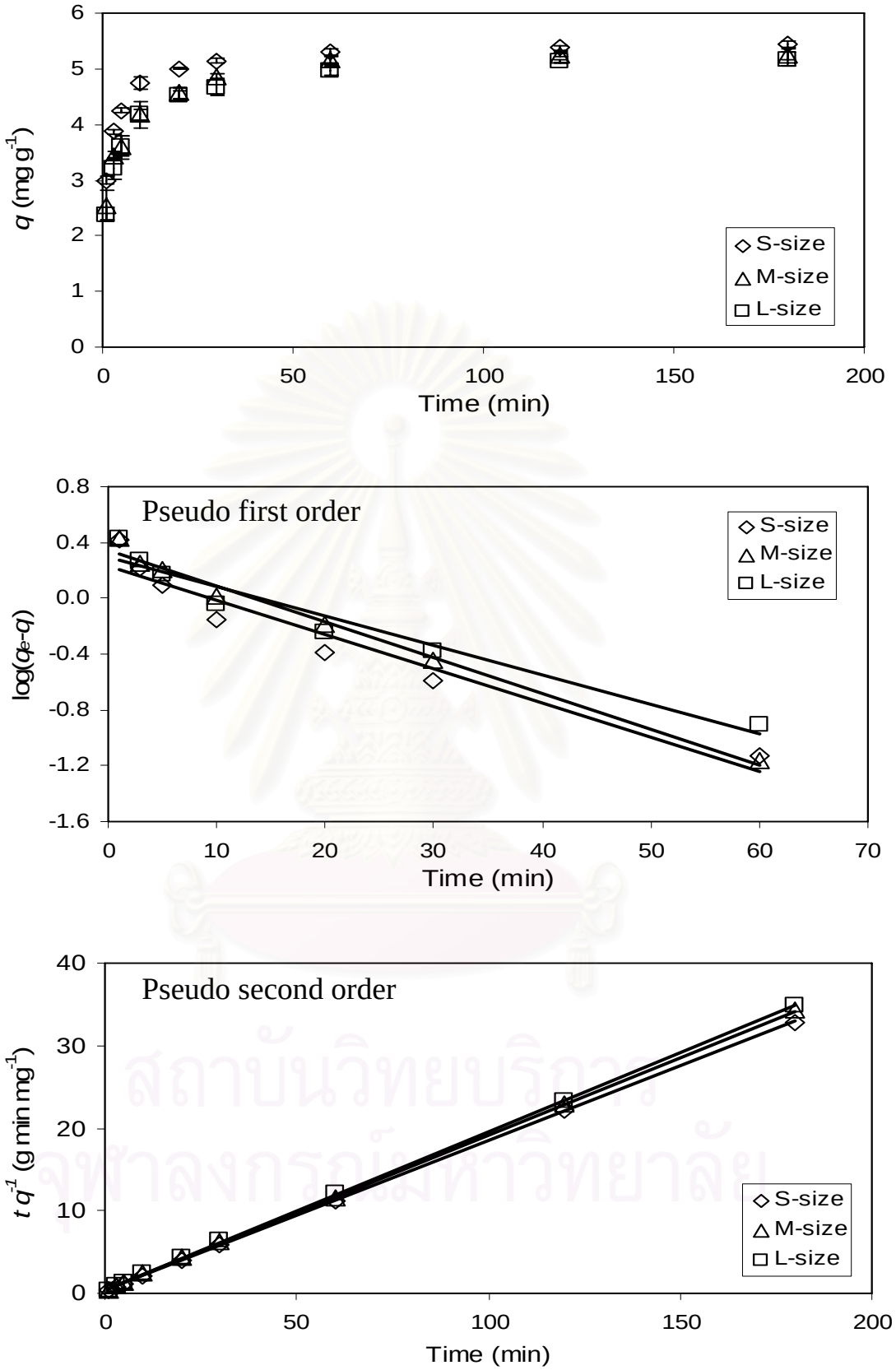


Fig. 4.1 Kinetics plots of AB (adsorbent dose=0.5 g, initial pH=7.0,130 rpm, T=25^{0}C)

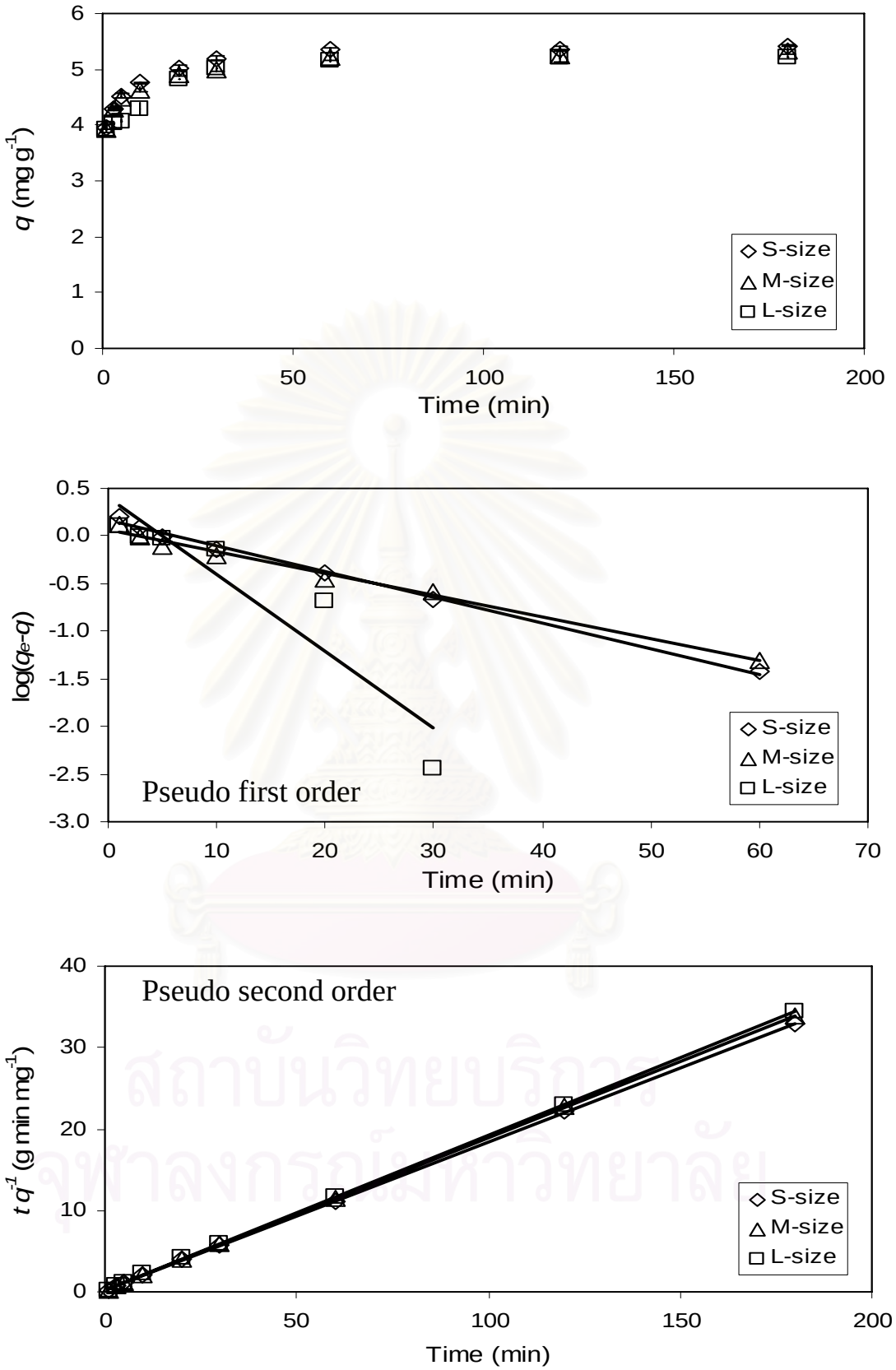


Fig. 4.2 Kinetics plots of AR (adsorbent dose=0.5 g, initial pH=7.0,130 rpm, T=25^{0}C)

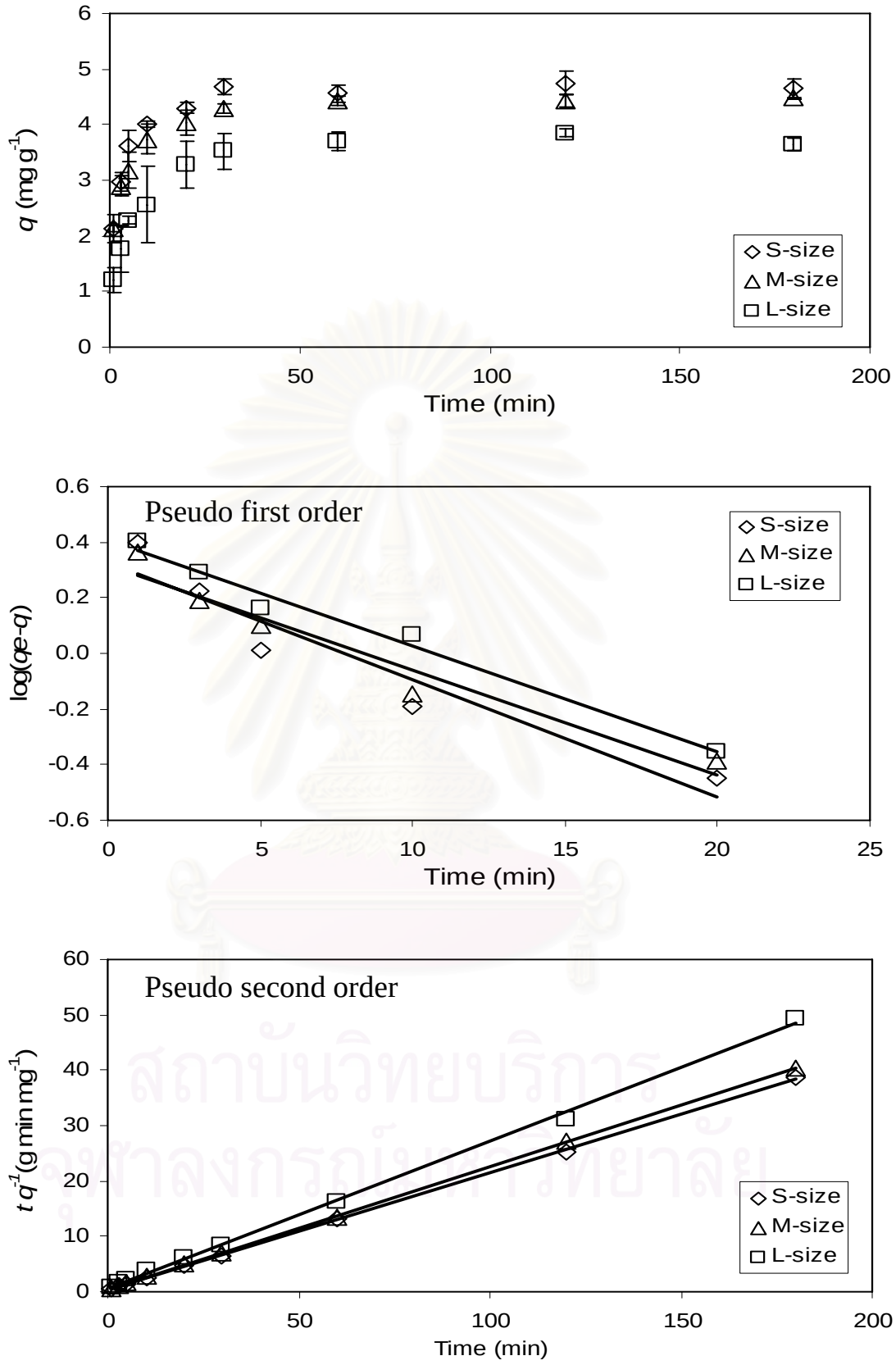


Fig. 4.3 Kinetics plots of AY (adsorbent dose=0.5 g, initial pH=7.0,130 rpm, T=25^{0}C)

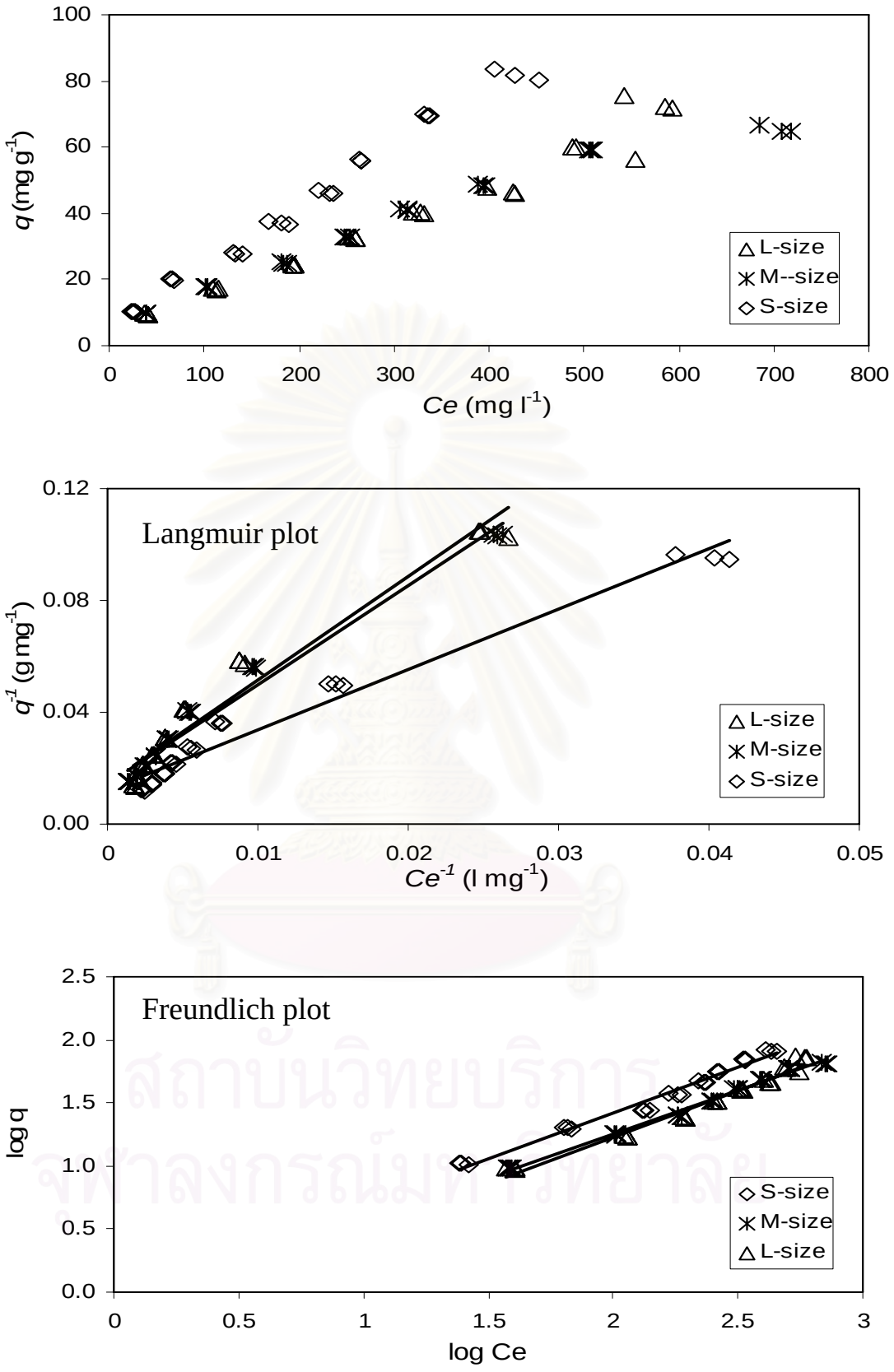


Fig 4.4 Isotherm plots of AB (adsorbent dose=0.5 g, initial pH=7.0, 130 rpm,T=25^{0}C)

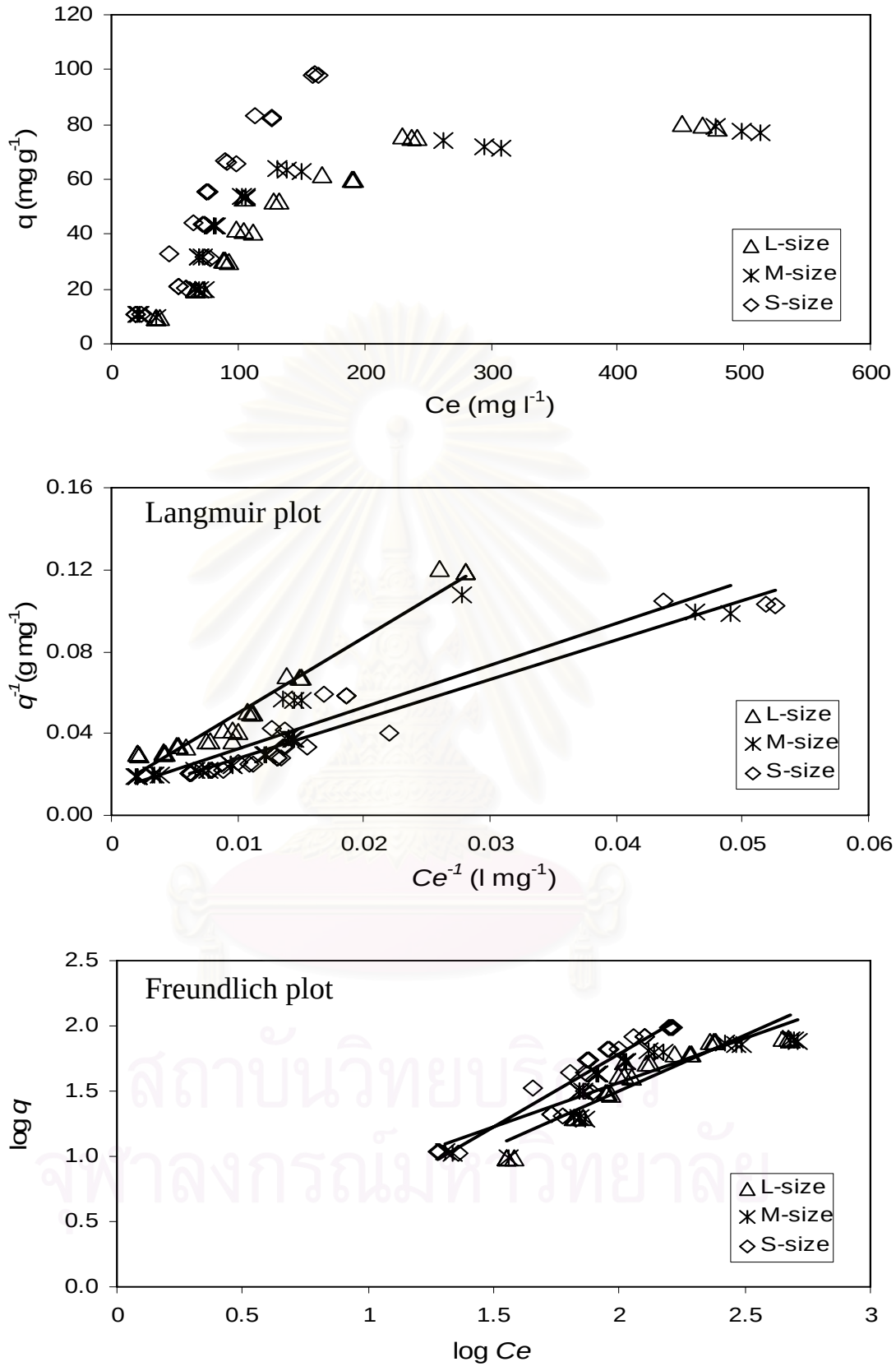


Fig 4.5 Isotherm plots of AR (adsorbent dose=0.5 g, initial pH=7.0, 130 rpm,T=25^{0}C)

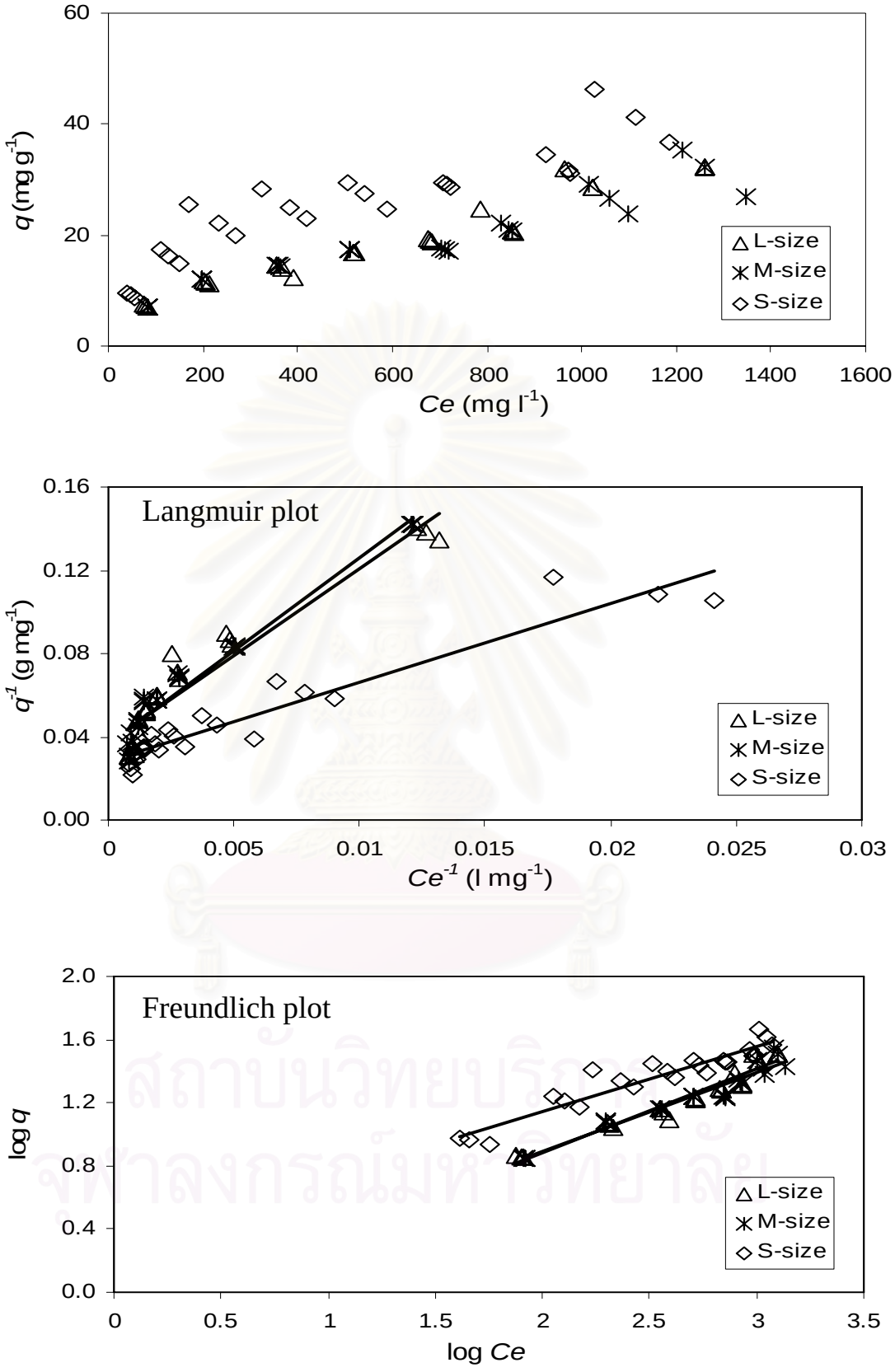


Fig 4.6 Isotherm plots of AY (adsorbent dose=0.5 g, initial pH=7.0, 130 rpm,T=25^0C)

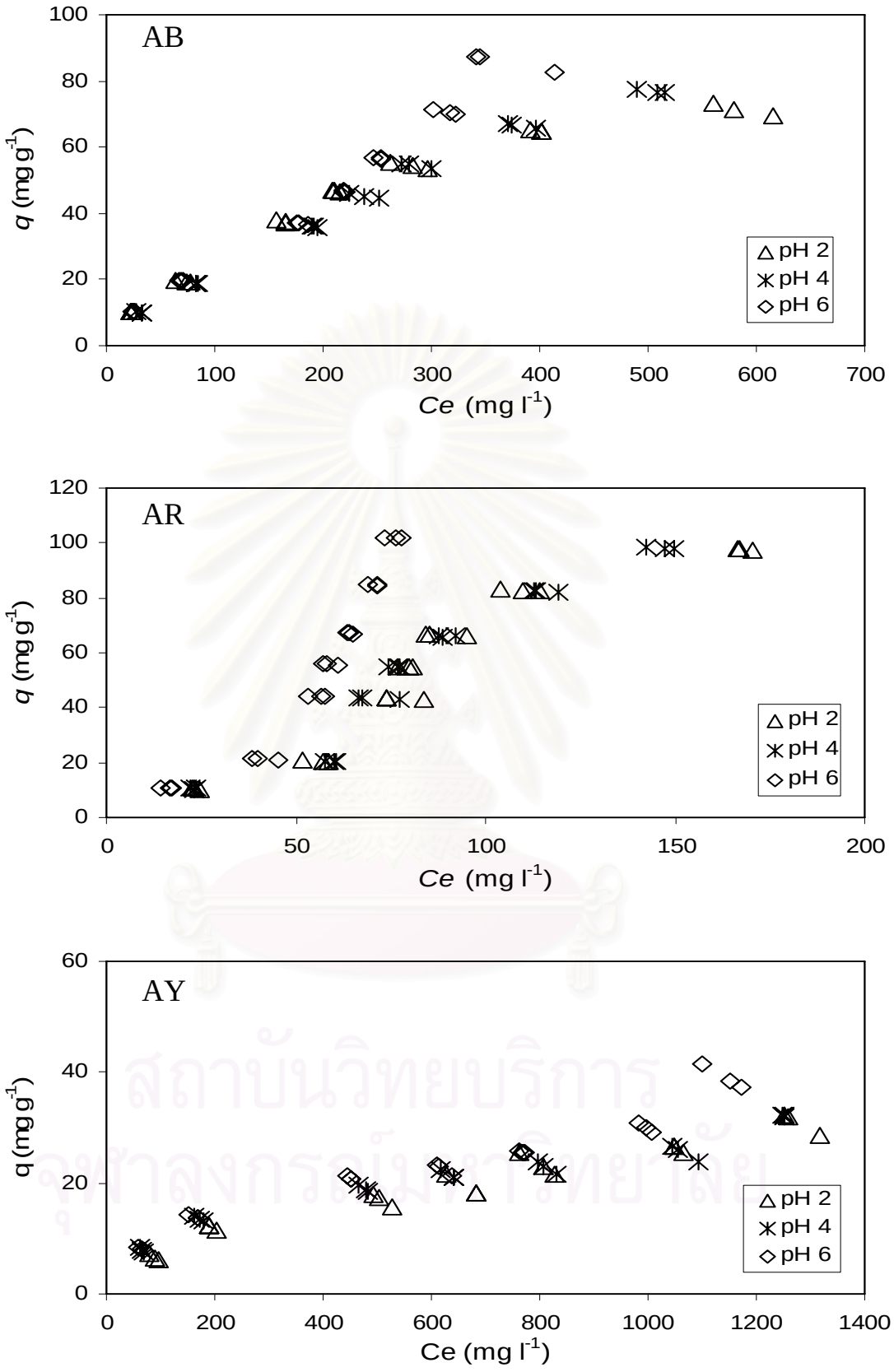


Fig. 4.7 Isotherms plots of the adsorption of basic dyes with *Caulerpa lentillifera* (adsorbent dose = 0.5 g, initial pH = 7.0, at 130 rpm, T = 25^0 C)

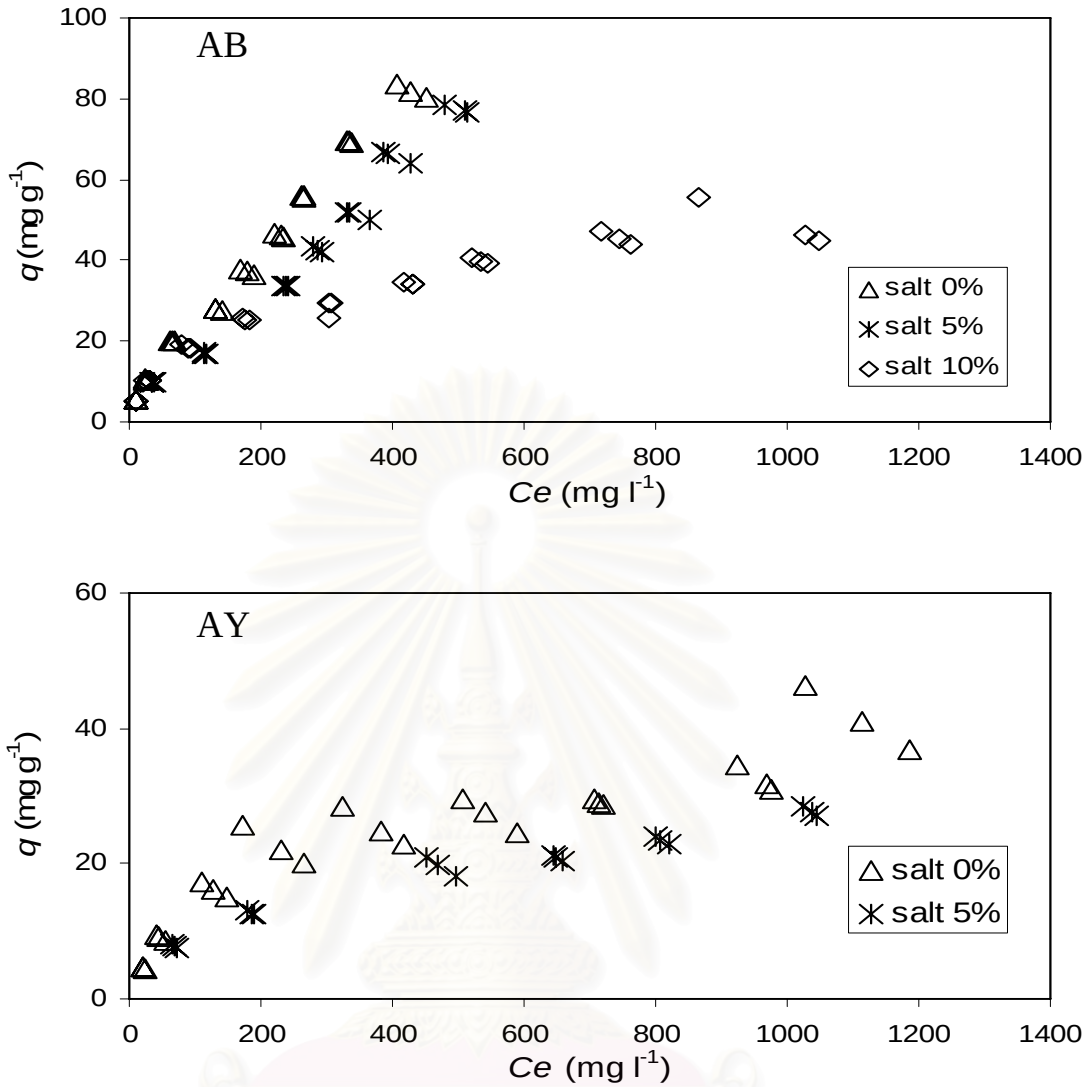


Fig. 4.8 Isotherms plots of the adsorption of basic dyes with *Caulerpa lentillifera* (adsorbent dose = 0.5 g, initial pH = 7.0, at 130 rpm, T = 25^0C)

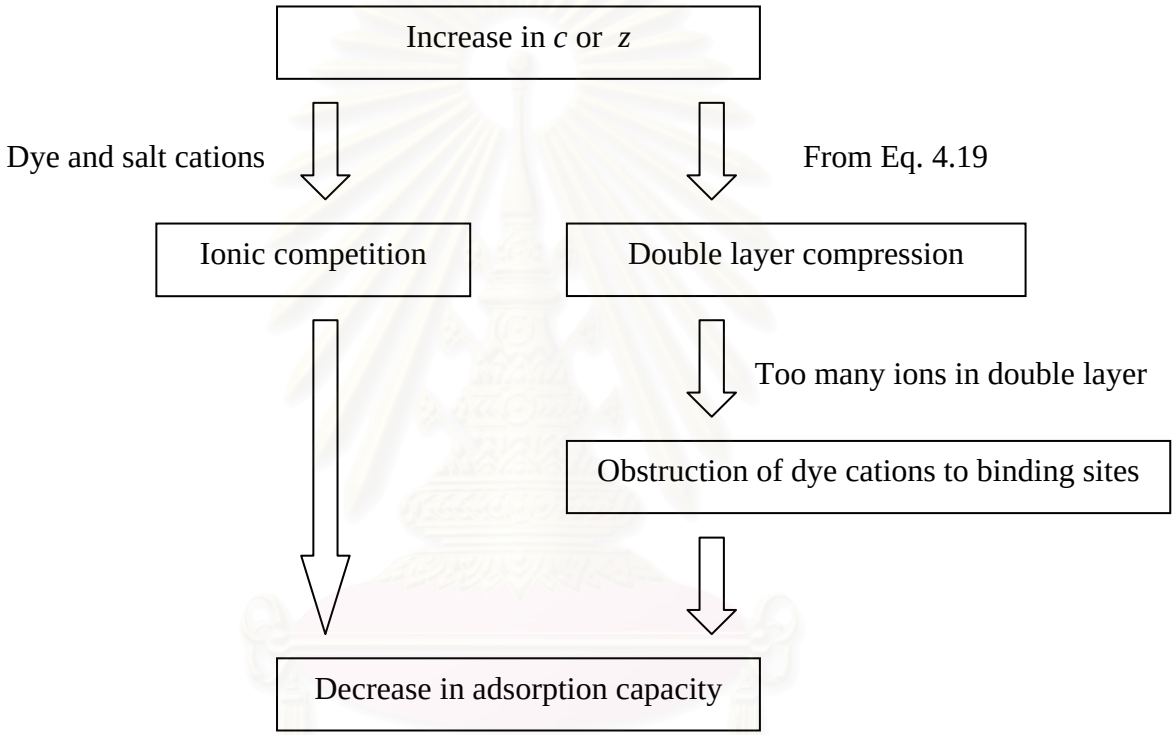


Fig. 4.9 Effect of salt concentration and ionic strength to adsorption capacity

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The investigation in this work led to the following conclusions:

1. The adsorption capacity reached equilibrium within the first 60 min.
2. A better fit of experimental data with the pseudo second order equation indicated that the adsorption took place quite rapidly. The rate constant tended to increase with a decrease of sorbent size.
3. The adsorption isotherms of basic dyes fitted both Langmuir and Freundlich models. The maximum sorption capacity was obtained from algae S size.
4. The adsorption capacity was the highest at neutral pH and decreased at lower pH (for AB and AR). This was because, at lower pH, the negatively charged sites on adsorbent decreased (from protonation of carboxyl groups) and the presence of excess H^+ ions competed with dye cations for the adsorption sites. In case of AY, pH was not significant for the adsorption capacity. This might be due to a weak electrostatic interaction between dyes and electron-rich sites of the surface of algae.
5. The effect of salt concentration had impact on the sorption capacity. Increasing salt concentration led to decreasing maximum sorption capacity. The cause of this effect might be due to the competition of basic dye cations and Na^+ ions for the sorption sites and properties of the electrical double layer on the surface of the adsorbent.

5.2 Contributions

The management of waste has been a subject of concerns particularly in this new era where the consumption of natural resources is perhaps greater than the sustainable rate. Turning wastes into something useful is one of the potential alternatives capable of reducing the resource depletion rate. Comparison between the adsorption capacities of this alga with other sorbents as given in Table 5.1 emphasized that the alga had a

reasonably high adsorption capacities for the basic dyes. This validates the application of this alga for the color removal especially in textile industry.

5.3 Recommendations / Future works

This work is among the series of work on the use of *Caulerpa lentillifera* biomass as an adsorbent for positive charged contaminants such as basic dyes and heavy metals. The next step towards the actual application of such technology is to evaluate the adsorption in pilot scale. This is to examine whether the biosorbent could last a long term operation. In addition, the treatment of loaded adsorbent should also be investigated, e.g. regeneration or final disposal.

Table 5.1 Maximum adsorption capacity of various types of basic dyes by natural adsorbents

Adsorbent	Adsorbate	q_m (mg g^{-1})	Reference
Macroalga *C. lentillifera*	Astrazon Blue FGRL Astrazon Red GTLN Astrazon Golden Yellow GL-E	94.34 113.64 35.46	This study
Raw date pits	Methylene Blue	80.29	Banat et al., 2003
Giant duck-weed (*Spirodela polyrrhiza*)	Methylene Blue	129.87	Waranusantigul et al., 2003
Neam (*Azadirachta indica*) leaf powder	Methylene Blue	8.76	Bhattacharyya and Sharma, 2005
Fresh water algae *Pithophora sp.*	Malachite Green	117.65	Kumar et al., 2005
Cationic surfactant-modified bentonite clay	Tannin	69.80	Anirudhan and Ramachandran, 2006
Wheat bran	Astrazon Yellow 7GL	69.06	Sulak et al., 2006
Cyclodextrin-based	C.I. Basic Green 4 (Malachite Green)	91.90	Crini et al., 2007
Phosphoric acid modified rice straw	Basic Blue 9 Basic Red 5	208.33 188.68	Gong et al., 2007

REFERENCES

Ahmed, M. and Ram, R., 1992. Removal of basic dye from wastewater using silica as an adsorbent. Environmental Pollution. 77(1): 79-86.

Akkaya, G. and Özer, A., 2005. Biosorption of Acid Red 274 (AR 274) on *Dicranella varia*: Determination of equilibrium and kinetic model parameters. Process Biochemistry. 40: 3559-3568.

Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. Process Biochemistry. 40(3-4): 997-1026.

Akzu, Z. and Tezer, S., 2005. Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. Process Biochemistry. 40: 1347-1361.

Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J., andAhmad, M.N., 2003. The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. Journal of Environmental Management. 69(3): 229-238.

Anirudhan, T.S. and Ramachandran, M., 2006. Adsorptive removal of tannin from aqueous solutions by cationic surfactant-modified bentonite clay. Journal of Colloid and Interface Science. 299: 116-124.

Apiratikul, R. and Pavasant, P., 2006. Sorption isotherm model for binary component sorption of copper, cadmium and lead ions using dried green macroalga, *Caulerpa lentillifera*.Chemical Engineering Journal 119: 135-145.

Arunima S., Krishna G. Bhattacharyya, 2005. *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium. Journal of hazardous Materials B125: 102-112.

Azizian, S., 2004. Kinetic models of sorption: a theoretical analysis. Journal of Colloid and Interface Science 276: 47-52.

Banat, F., Al-asheh, S. and Al-Makhadmeh, L., 2003. Evalution of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Biochemistry. 39 (2): 193-202.

Banat, I.M., McMullan, G., Meehan, C., Kirby, N., Nigam, P., Smyth, W.F., Marchant, R., 1999. Microbial decolorization of textile dyes. Proceedings of the Industrial Waste Technical Conference, Indianapolis, USA: 1-16.

Bhattacharyya K.G. and Sharma A., 2005. Kinetics and thermodynamics of Methylene Blue adsorption on Neem *(Azadirachta indica)* leaf powder. Dyes and Pigments (1): 51-59.

Choy, K.K.H., McKay, G., Porter, J.F., 1999. Sorption of acid dyes from effuents using activated carbon. Resource Conserve Recycle. 27(1-2): 57-71.

Chu, H.C. and Chen, K.M., 2002. Reuse of activated sludge biomass: II The rate processes for the adsorption of basic dyes on biomass. Process Biochem. 37(10): 1129-1134.

Crini, G. Peindy, H.N., Gimbert, F, and Robert, C., 2006. Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. Separation and Purification Technology 53: 97-110.

Doğan, M., Özdemir, Y., and Alkan, M. 2006. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. Dyes and Pigments xx: 1-13.

Eren, E. and Afsin, B., 2006. Investigation of a basic dye adsorption from aqeous solution onto raw and pre-treated sepiolite surfaces. Dyes and Pigments 73: 162-167.

Fu, Y. and Viraraghavan, T., 2002. Dye biosorption sites in *Aspergillus niger*. Bioresource Technology. 82: 139-145.

Garg, V.K., Kumar, R. and Gupta, R., 2004. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria. Dyes and Pigments. 62 (1): 1-10.

Gong, R., Jin, Y., Chen, J., Hu, Y., and Sun, J. Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. Dyes and Pigments 73, 332-337.

Gonul D., Zumriye A., 2002. Removal of chromium(VI) from saline wastewaters by *Dunaliella* species. Process Biochemistry 38: 751-762.

Gupta, V.K., Ali, I., Suhas, Mohan, D., 2003. Equilibrium uptake and sorption dynamic for the removal of a basic dye (basic red) using low-cost adsorbents. Journal of Colloid and Interface Science 265: 257-264.

Han, R., Wang, Y., Han, P., Shi, J., Yang, J., Lu, Y. 2006. Removal of methylene blue from aqueous solution by chaff in batch mode. Journal of Hazardous Materials B137: 550-557.

Ho, Y.S., Chiang T.H., and Hsueh Y.M., 2005. Removal of basic dye from aqueous solution using tree fern as a biosorbent. Process Biochem. 40(1): 119-124.

Ho, Y.S. and McKay, G., 1998. Kinetic model for the sorption of dye from aqueous solution by wood. Process Saf Environ Protect. 76(B2): 183-191.

Kratochvil, D., and Volesky, B., 1998. Advances in the biosorption of heavy metals. Trends in Biotechnology. 16: 291-300.

Kumar, K., Sivanesan, S. and Ramamurthi, V., 2005. Adsorption of malachite green onto *Pithophora sp*., a fresh water algae: Equilibrium and kinetic modeling. Process Biochemistry 40: 2865-2872.

Lagergren, S., 1898. Zur Theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar, Band 24, No. 4.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc. 40(9): 1361-1403.

Liversidge, R.M., Lloyd, G.J., Wase, D.A.J., Forster, C.F., 1997. Removal of Basic Blue 41 Dye from Aqueous solution by Linseed Cake. Process Biochemistry. 32(6): 473-477.

Low, K.S., Lee, C.K., Tan, K.K., 1995. Biosorption of basic dyes by water hyacinth roots. Bioresource Technology 52: 79-83.

Magdy, Y.H. and Daifullah, A.A.M., 1998. Adsorption of a Basic Dye from Aqueous Solutions onto Sugar-Industry-Mud in Two Modes of Operations. Waste Manage. 18(4): 219-226.

Marungrueng, K. and Pavasant, P., 2006. Removal of basic dye (Astrazon Blue FGRL) using macroalga *Caulerpa lentillifera.* Journal of Environmental Manage: 1-7.

McKay, G., Porter, J.F., and Prasad, G.R., 1999. The Removal of Dye Colours from Aqueous Solutions by Adsorption on Low-Cost Materials. Water, Air, & Soil Pollution. 114(3-4): 423-438.

McKay, G., El-Geundi, M., and Nassar, M.M., 2003. Equilibrium Studies during the Removal of Dyestuffs from Aqueous Solutions using Bagasse Pith. Water Research. 21(12): 1513-1520.

Namasivayam, C., Radhika, R., Suba, S., 2001. Uptake of dyes by a promising locally available argricultural solid waste: cor pith. Waste Management 21: 381-387.

Namasivayam, C. and Sumithra, S., 2005. Removal of direct red 12B and methylene blue from water by adsorption onto Fe(III)/Cr(III) hydroxide, an industrial solid waste. Journal of Environmental Management. 74(3): 207-215.

Nacera, Y., and Aicha, B., 2006. Equilibrium and kinetic modeling of methylene blue biosorption by pretreated dead *streptomyces rimosus*: Effect of temperature. Chemical Engineering Journal 119: 121-125.

Nassar, M.M., and Magdy, Y.H., 1997. Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. Chemical Engineering Journal 66: 223-226.

Özacar, M. and Şengil, I.A., 2005. Adsorption of metal complex dyes from aqeous solutions by pine sawdust. Bioresource Technology. 96(7): 791-795.

Özer, A., Akkaya, G., Turabik, M., 2005. The biosorption of Acid red 337 and Acid blue 324 on *Enteromorpha prolifera*: The application of nonlinear regression analysis to dye biosorption. Chemistry Engineering Journal 112: 181-190.

Özer, A., Akkaya, G., Turabik, M., 2006a. Biosorption of Acid Blue 290 (AB 290) and Acid Blue 324 (AB 324) dyes on *Spirogyra rhizophus.* Journal of hazardous materials B135: 355-364.

Özer, A., Akkaya, G., Turabik, M., 2006b. The removal of Acid Red 274 from wastewater : Combined biosorption and biocoagulation with *Spirogyra rhizophus.* Dyes and Pigments 71: 83-89.

Sainz-Diaz, C.I. and Griffiths, A.J., 2000. Activated carbon from solid wastes using a pilot-scale batch flaming pyrolyser. Fuel 79: 1863-1871.

Shawabkeh, A. and Tutunji, M.F., 2003. Experimental study and modeling of basic dye sorption by diatomaceous clay. Appl Clay Sci. 24(1-2): 111-120.

Sulak, M.T., Demirbas, E., and Kobya, M., 2006 Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran. Bioresource Technology xxx, xxx-xxx.

Sungkhum, V., 2003. Biosorption of Heavy Metals by Green Macroalga, Caulerpa lentillifera. M.Sc. Thesis, Environmental Science, Inter-department of Environmental Science, Graduate School, Chulalongkorn University.

US EPA, 1996. Best management pratice for pollution prevention in the textile industry. EPA/625/R-96/004, Ohio.

Wang, Y., Mu, Y., Zhao, Q.B., Yu, H.Q., 2006. Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge. Separation and Purification Technology 50: 1-7.

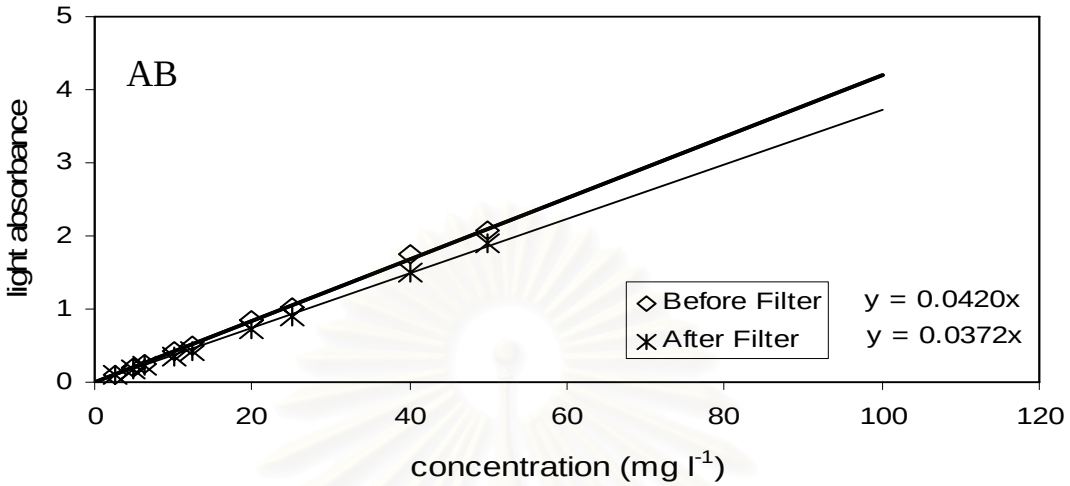
Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M. and Upatham, E.S., 2003. Kinetic of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environental Pollution. 125 (3): 385-392.

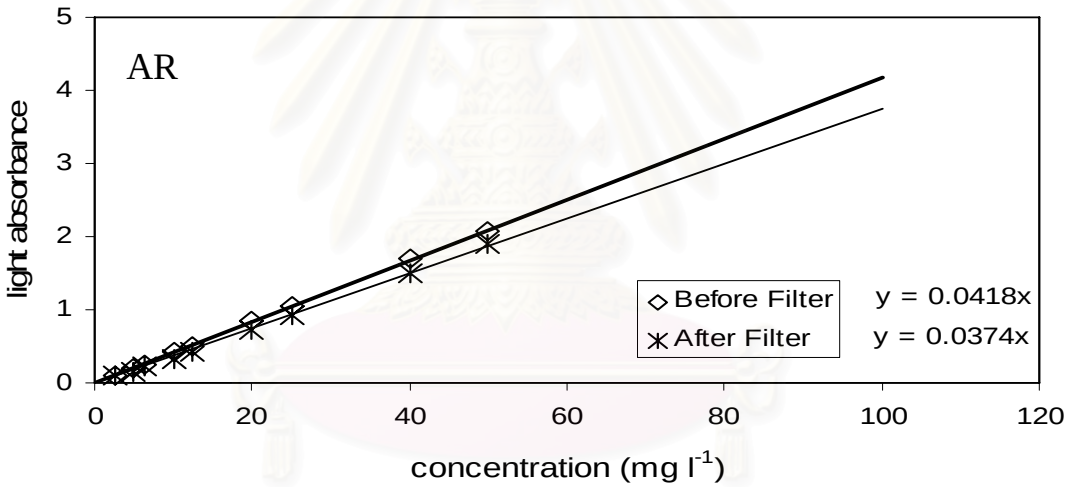
Won, S., Kim, H.J., Choi, S.H., Chung, B., Kim, K., Yun, Y., 2006. Perfomance kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low cost biosorbent. Chemical Engineering Journal. 121: 37-43.

Woolard, C.D., Strong, J., Erasmus, C.R., 2002. Evaluation of the use of modified coal-ash as a potential sorbent for organic waste stream. Applied Geochemistry. 17: 1159-1164.

APPENDICES

Appendix A


AB
light absorbance
concentration (mg l-1)
Before Filter
After Filter
y = 0.0420x
y = 0.0372x


AR
light absorbance
concentration (mg l-1)
Before Filter
After Filter
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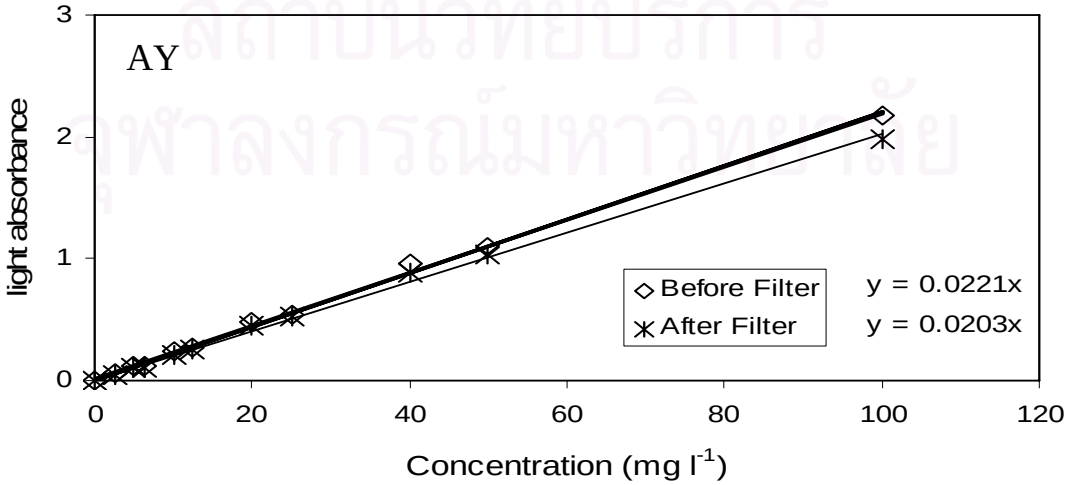
y = 0.0374x


AY
light absorbance
Concentration (mg l-1)
Before Filter
After Filter
y = 0.0221x
y = 0.0203x

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2006

"SEE 2006" Secretariat,
The Joint Graduate School of Energy and Environment,
King Mongkut's University of Technology Thonburi,
126 Pracha-Uthit Road, Bangmod, Tungkru,
Bangkok 10140 Thailand

26 April 2007

Mr. Pimol Punjongharn,
Faculty of Engineering,
Department of Chemical Engineering,
Chulalongkorn University,
Bangkok, 10330, Thailand

CERTIFICATE OF PARTICIPATION

It is hereby certified that Mr. Pimol Punjongharn, student at Chulalongkorn University, Faculty of Engineering, Department of Chemical Engineering, has participated to the International Conference on Sustainable Energy and The Environment: Technology and Policy Innovations (SEE 2006), held in Bangkok during 21-23 November 2006.
He has presented a research paper on "Effect of Sorbent Size on the Sorption of Basic Dyes by Using *Caulerpa lentillifera*" in the poster session of the conference.

Yours sincerely,

Assoc. Prof. Dr. Bundit Fungtammasan
Director of JGSEE
Chairman of the Conference Organizing Committee

BIOGRAPHY

Mr. Pimol Punjongharn was born on 16th October, 1983 in Bangkok. He finished his secondary course from Suankularbwittayalai School in March, 2001. After that, he received his Bachelor's degree in the major of Chemical Engineering in Faculty of Engineering at Srinakarinwirot University in March 2005. In 2005, he continued his further study for Master's degree in Chemical Engineering at Chulalongkorn University. He participated in the Environmental Engineering Research Group.