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จุฬาลงกรณ์มหาวิทยาลัย

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REMOVAL OF WATER-SOLUBLE DYES BY ADSORPTION USING CHITOSAN



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สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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จากการทดลองพบว่า ตัวดูดซับไคโตซานทั้ง 3 ชนิด สามารถกำจัดสีย้อมทั้ง 4 ชนิดได้ โดยปริมาณการดูดซับสีย้อมทั้ง 4 ชนิดขึ้นกับชนิดของสีย้อม พีเอชเริ่มต้น อุณหภูมิ ร้อยละของการลดหมู่อะซีทิลของไคโตซาน ความเข้มข้นเริ่มต้นของสีย้อม และขนาดอนุภาคของตัวดูดซับ ความสามารถในการดูดซับสีแอสซิด สีไดเร็กต์ และสีรีแอกทีฟในสภาวะเป็นกรด (พีเอชต่ำ) ดีกว่าสภาวะเป็นกลางและเบส ส่วนสีเบสิกนั้นที่สภาวะเป็นเบสดีกว่าที่สภาวะเป็นกลางและกรด สำหรับผลของอุณหภูมิ อุณหภูมิไม่มีผลต่อความสามารถในการดูดซับสีแอสซิด ความสามารถในการดูดซับสีไดเร็กต์เพิ่มขึ้นเมื่ออุณหภูมิสูงขึ้น แต่สีเบสิกนั้นถูกดูดซับได้น้อยลง สีแอสซิด สีไดเร็กต์ และสีรีแอกทีฟถูกดูดซับด้วยไคโตซานที่มีร้อยละของการลดหมู่อะซีทิลต่ำได้ดีกว่า (ร้อยละ 79) ตรงข้ามกับสีเบสิกจะถูกดูดซับโดยไคโตซานที่มีร้อยละของการลดหมู่อะซีทิลสูงได้ดีกว่า (ร้อยละ 95) ไคโตซานสามารถดูดซับสีย้อมทั้ง 4 ชนิดได้ดีขึ้น เมื่อความเข้มข้นเริ่มต้นของสีย้อมมีค่าเพิ่มขึ้น และขนาดอนุภาคของตัวดูดซับมีขนาดอนุภาคเล็กลง

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ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....  
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# #4370279721: MAJOR CHEMICAL ENGINEERING DEPARTMENT

KEY WORD: WATER-SOLUBLE DYES/ CHITOSAN/ ADSORPTION/  
DEACETYLATION/ REMOVAL

CHOTIROS EIAMSA-ARD: REMOVAL OF WATER-SOLUBLE DYES BY  
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In this study, removal of water-soluble dyes from aqueous solution by adsorption was investigated. Adsorbents were chitosan having degree of deacetylation of 79%, 87% and 95%. A set of experiments was conducted at atmospheric pressure initial solution pH of 5, 7 and 9, and temperatures of 30°C, 40°C and 50°C. Water-soluble dyes in this study are acid, direct, reactive and basic dyes. Each type of dye was dissolved in distilled water to obtain feedstock solution having initial concentration of 100 milligram per liter.

The results show that all three types of chitosan can be used to remove all types of dye from aqueous solution. Removal of water-soluble dye depends on type of dye, initial pH, temperature, degree of deacetylation of chitosan, initial dye concentration, and particle size of adsorbent. Acid, direct, and reactive dyes can be adsorbed on chitosan better in acidic solution (low pH value) and basic dye can be adsorbed better in alkaline solution. Adsorption ability of acid dye is independent of temperature. Adsorption ability of direct dye increases with increasing operating temperature but adsorption ability of basic dye decreases with increasing operating temperature. Acid, direct, and reactive dyes can be adsorbed on chitosan better at low degree of deacetylation (79%DD) and basic dye can be adsorbed better at high degree of deacetylation (95%DD). Adsorption ability of each type of dye slightly increases with increasing of initial concentration and decreases with increasing particle size of chitosan.

Department.....Chemical Engineering.....Student's signature.....  
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สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## CONTENTS

	PAGE
ABSTRACT (IN ENGLISH).....	iv
ABSTRACT (IN THAI).....	v
ACKNOWLEDGEMENT.....	vi
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
CHAPTER	
I. INTRODUCTION.....	1
1.1 State of the problem.....	1
II LITERATURE REVIEWS.....	4
2.1 Textile Industry.....	4
2.1.1 Sources and Characteristics of Textile Wastewater.....	5
2.2 Colorants.....	5
2.2.1 Color of Dyes.....	6
2.2.2 Classification of Dyes.....	8
2.3 Wastewater Treatment.....	15
2.3.1 Color Removal.....	18
2.4 Adsorption.....	23
2.4.1 Adsorption Theory.....	23
2.4.2 Mechanisms of Adsorption onto Porous Adsorbent.....	26
2.5 Chitosan.....	26
2.5.1 Structure of Chitin and Chitosan.....	26
2.5.2 Physicochemical Properties of Chitosan.....	29
2.5.3 Application of Chitosan.....	31
2.5.4 Application of Chitosan for Wastewater Treatment.....	31
2.5.5 Factor Effecting of Dye Adsorption Using Chitosan.....	34
2.6 Related Literatures.....	36

## CONTENTS (continued)

	PAGE
III EXPERIMENTAL AND ANALYTICAL TECHNIQUES.....	40
3.1 Materials.....	40
3.1.1 Adsorbent.....	40
3.1.2 Water-Soluble Dyes.....	40
3.1.3 Chemical.....	40
3.2 Equipments.....	43
3.2.1 Sieving Machine and Sieves.....	43
3.2.2 Analytical Balance.....	43
3.2.3 pH Meter.....	43
3.2.4 Ultraviolet-Visible Spectrophotometer (UV/VIS).....	43
3.2.5 Surface Area Analyzer.....	43
3.3 Experimental Procedure.....	44
3.3.1 Adsorbent Preparation.....	44
3.3.2 Feed Preparation.....	44
3.3.3 Adsorption Procedure.....	45
3.3.4 Desorption Procedure.....	46
3.4 Analysis Technique and Errors of Experiments.....	47
3.4.1 Surface Area and Pore Volume.....	47
3.4.2 Dye Concentration.....	47
3.4.3 Calculation of Amount of Adsorbed Dye on the Adsorbent.....	48
3.4.4 Calculation of Amount of Desorbed Dye from the Adsorbent.....	48
3.4.5 Experimental and Analysis Error.....	49
IV RESULTS AND DISCUSSIONS.....	56
4.1 Experimental Procedure and Preliminary Experimental Results	57



## CONTENTS (continued)

	PAGE
4.1.1 Adsorption Experiment.....	57
4.1.2 Effect of Adsorbent Weight and Effect of Contacting Time on Adsorption.....	57
4.2 Experimental Results.....	60
4.2.1 Adsorption Behavior of Dye on Chitosan.....	61
4.2.2 Effect of pH on Dye Adsorption.....	63
4.2.3 Effect of temperature on Dye Adsorption.....	66
4.2.4 Effect of Degree of Deacetylation of Chitosan on Dye Adsorption.....	69
4.2.5 Effect of Initial Dye Concentration on Dye Adsorption....	72
4.2.6 Effect of Particle Size on Adsorbent on Dye Adsorption..	73
4.3 Dye Desorption.....	77
4.3.1 Effect of pH on Dye Desorption.....	77
4.3.2 Effect of Temperature on Dye Desorption.....	77
V CONCLUSIONS AND RECOMMENDATIONS.....	80
5.1 Conclusion.....	80
5.2 Recommendation.....	81
REFERENCES.....	82
APPENDIX.....	86
Appendix A.....	87
Appendix B.....	99
Appendix C.....	104
VITA.....	116

## LIST OF TABLES

Table	PAGE
2.1 Characteristic of textile wastewater.....	5
2.2 Relationship between wavelength of absorbed light and hue.....	6
2.3 Dye classification by methods of application to the fiber types.....	12
2.4 Estimate degree of fixation for different dye/fiber combination.....	15
2.5 Textile wastewater treatment removal efficiencies of the different unit operation and unit processes.....	17
2.6 Distinction between physical adsorption and chemical adsorption.....	25
2.7 Ideal monomer, the official name and general formula of chitin and chitosan.....	27
2.8 Comparison of bond strengths.....	34
3.1 The empirical formula and molecular weight of dye.....	43
3.2 $\lambda_{\text{max}}$ of each dye solutions.....	44
3.3 Slope value of the dye solution at specified wavelength.....	45
3.4 Average concentration and error of experiment at various temperature of acid dye.....	50
3.5 Average concentration and error of experiment at various temperature of basic dye.....	51
3.6 Average concentration and error of experiment at various temperature of direct dye .....	52
3.7 Average concentration and error of experiment at various temperature of reactive dye.....	53
4.1 Surface area and pore diameter of chitosan.....	56
4.2 Operating conditions of dye adsorption experiments.....	60
4.3 Operating conditions of dye desorption experiments.....	61
A1 Conditions and results of adsorption experiments.....	87
A2 Conditions and results of desorption experiments.....	98

## LIST OF TABLES (continued)

Table	PAGE
B1 Properties of chitosan 79% degree of deacetylation.....	99
B2 Properties of chitosan 87% degree of deacetylation.....	100
B3 Properties of chitosan 95% degree of deacetylation.....	101
B4 Properties of hydrochloric acid.....	102
B5 Properties of sodium hydroxide.....	103
C1 Calibration curve of Acid Orange 7 at 450 nm.....	104
C2 Calibration curve of Direct Green 26 at 617 nm.....	107
C3 Calibration curve of Reactive Violet 5 at 555 nm.....	110
C4 Calibration curve of Basic Yellow 2 at 444 nm.....	113



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## FIGURE CONTENTS

Figure	PAGE
2.1 Overall structure of Thai textile industry.....	4
2.2 Some auxochrome groups and color observed from dye structure.....	8
2.3 Monoazo dyes.....	9
2.4 Carbonyl dyes.....	9
2.5 Antraquinones dyes.....	10
2.6 Fluorescent carbonyl dyes.....	10
2.7 Benzodifurannodes dyes.....	11
2.8 Indigoid dyes.....	11
2.9 Phthalocyanides dyes.....	11
2.10 Adsorption operation with solid-particle sorbents.....	23
2.11 Structure of chitin, chitosan, and cellulose (ideal).....	27
2.12 IR spectra of (A) chitin and (B) chitosan.....	28
2.13 NMR spectra of chitin and chitosan by CP-MAS method.....	29
2.14 Hydrogen Bond between Cellulose and Dye.....	33
3.1 Chemical structure of C.I. Acid Orange 7.....	41
3.2 Chemical structure of C.I. Direct Green 26.....	41
3.3 Chemical structure of C.I. Reactive Violet 5.....	42
3.4 Chemical structure of C.I. Basic Yellow 2.....	42
3.5 Schmatic diagram of the experimental apparatus.....	46
3.6 Amount of adsorbed dye for acid dye at various temperature.....	50
3.7 Amount of adsorbed dye for direct dye at various temperature.....	51
3.8 Amount of adsorbed dye for reactive dye at various temperature.....	52
3.9 Amount of adsorbed dye for basic dye at various temperature.....	53
3.10 Dye concentration for blank test at various pHs and 30°C.....	55
3.11 Dye concentration for blank test at various temperatures and pH 5.....	56
4.1 Amount of adsorbed dye at various of adsorbent weight at 30°C .....	58
4.2 Amount of adsorbed dye at various of contact time 30°C.....	59

## FIGURE CONTENTS (continued)

Figure	PAGE
4.3 Effect of pH on the adsorption of Acid Orange 7.....	64
4.4 Effect of pH on the adsorption of Direct Green 26.....	64
4.4 Effect of pH on the adsorption of Reactive Violet 5.....	65
4.6 Effect of pH on the adsorption of Basic Yellow 2.....	65
4.7 Effect of temperature on the adsorption of Acid Orange 7.....	76
4.8 Effect of temperature on the adsorption of Direct Green 26.....	67
4.9 Effect of temperature on the adsorption of Reactive Violet 5.....	68
4.10 Effect of temperature on the adsorption of Basic Yellow 2.....	68
4.11 Effect of degree of deacetylation of adsorbent on the adsorption of Acid Orange 7.....	70
4.12 Effect of degree of deacetylation of adsorbent on the adsorption of Direct Green 26.....	70
4.13 Effect of degree of deacetylation of adsorbent on the adsorption of Reactive Violet 5.....	71
4.14 Effect of degree of deacetylation of adsorbent on the adsorption of Basic Yellow 2.....	71
4.15 Effect of initial of dye concentration of Acid Orange 7, Basic Yellow 2, Direct Green 26, and Reactive Violet 5 on dye adsorption.....	73
4.16 Effect of particle size on the adsorption of Acid Orange 7.....	74
4.17 Effect of particle size on the adsorption of Direct Green 26.....	74
4.18 Effect of particle size on the adsorption of Reactive Violet 5.....	75
4.19 Effect of particle size on the adsorption of Basic Yellow 2.....	75
4.20 Effect of pH on dye desorption of Acid Orange 7, Basic Yellow 2, Direct Green 26, and Reactive Violet 5.....	78
4.21 Effect of temperature on dye desorption of Acid Orange 7, Basic Yellow 2, Direct Green 26, and Reactive Violet 5 .....	79

## FIGURE CONTENTS (continued)

Figure	PAGE
C1 Calibration curve of Acid Orange 7 at pH 5.....	105
C2 Calibration curve of Acid Orange 7 at pH 7.....	105
C3 Calibration curve of Acid Orange 7 at pH 9.....	106
C4 Calibration curve of Direct Green 26 at pH 5.....	108
C5 Calibration curve of Direct Green 26 at pH 7.....	108
C6 Calibration curve of Direct Green 26 at pH 9.....	109
C7 Calibration curve of Reactive Violet 5 at pH 5.....	111
C8 Calibration curve of Reactive Violet 5 at pH 7.....	111
C9 Calibration curve of Reactive Violet 5 at pH 9.....	112
C10 Calibration curve of Basic Yellow 2 at pH 5.....	114
C11 Calibration curve of Basic Yellow 2 at pH 7.....	114
C12 Calibration curve of Basic Yellow 2 at pH 9.....	115



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

# CHAPTER I

## INTRODUCTION

### 1.1 State of the problem

Textile industry in Thailand is continuously growing both in its number of factories and production capacity. It plays an important role in Thai economic growth due to the increasing of gross national product, export value and employment. Last year Thailand earned more than 5.5 billion US dollars from this industry.

Although the textile industry makes great benefit, it consumes large quantities of water and consequently produces large amounts of wastewater, which containing various pollutants. Nature of textile wastewater has already been reviewed in terms of process chemicals used and in terms of classical parameters (BOD, COD, TSS, and TS) including the contents of nitrogen, phosphorus, heavy metal, organic matter, solid oil and grease and dyes. Even when dyes impart only small fractions of the total organic load in wastewater, their high degree of color is easily recognizable and damages the aesthetic nature of the environment. Thailand does not have certain limits for quantities of color in the effluent, but have only announced that the color of effluent must not be undesirable.

Dyes do not only add pollution problems to the water, but they are also difficult to remove since many of them are biologically non-degradable. Hence, color removal from such effluent is a major environmental problem. Primary and secondary treatments are not enough to efficiently removal all contaminants. Then tertiary treatment is often needed to remove color before discharge into a municipal sewer or into natural stream. Unless properly treated, the dyestuffs present in wastewater can significantly affect photosynthesis activity due to reduction of light penetration and may also be toxic to certain forms of aquatic life due to the presence of substitute metals and chlorine. Recent research indicated that some dyes are human carcinogens.

There are many techniques used in treating aqueous effluents but chemical and biological methods have their own limitations towards wastewater treatment, that is why adsorption is preferred and this method is becoming increasingly popular. The most efficient and commonly used of adsorbent for color removal is activated carbon but it has limits because of its high cost and regenerability. These problems lead many researchers to find more effective and cheaper substitutes such as coal, peat, wood, Fuller's earth, fired clay, fly ash, silica gel, bentonite clay, baggage pith, maize cob, coconut shells, rice husk, chitin and chitosan. Of these alternatives, chitosan, the derivatived of chitin, appears to be more attractive since chitin is the second most abundant biopolymer in nature next to cellulose.

Chitosan is a partially acetylated glucosamine polymer and produced by the deacetylation of chitin, which is a natural biopolymer extracted from the shells of arthropods such as lobster, shrimps, crabs and squids. Since such arthropods are abundantly available, chitosan can be produced from them at low cost. Chitosan is harmless to human, It may be utilized for ion-exchangers and adsorbents in the food and pharmaceutical industries. Chitosan is economically attractive because it can be regenerated (Annadurai 2000).

Chitosan has many useful features such as hydrophilicity, biocompatibility, biodegradability and anti-bacterial property. This biopolymer is also a known sorbent, effective in the uptake of transition metals since the amine and hydroxy groups on chitosan chains can serve as coordination and interaction site (Wu et.al. 2001). Furthermore, the sorption performance of chitosan can be enhanced by simple modifications.

A large number of equilibrium and kinetic studies on the adsorption of dyes using chitin, chitosan, and its derivatives have been carried out (McKay et.al. 1982, Juang et.al.1997, Wu et.al. 2001). Only few researchers compared the results with degree of deacetylation of chitosan but none had studied at high degree of deacetylation. Hence, the objectives of this experiment are to study effectiveness of high degree of deacetylation of chitosan in the removal of water-soluble dyes. In



addition, this research also studies the effects of pH of solution, operating temperature, initial dye concentration and particle size range of chitosan that affect the adsorbents in removal dyes.

In this study, chitosan having degree of 79%, 87%, and 95% are used as adsorbent. Four types of water-soluble dyes, acid, basic, direct and reactive dyes are dissolved in demineralized water and used as the initial solution. The experiments are conducted in agitated-batch system at atmospheric pressure and at operating temperatures of 30°C, 40°C, and 50°C.

After adsorption, liquid and spent adsorbent is separated by filter paper. Liquid samples are measured by UV/VIS spectrophotometer. Spent adsorbents are washed several times to remove unadsorbed dye and kept in dry place for desorption study.

Desorption experiments are conducted to study the effects of pH and operating temperature on desorption of adsorbed dye from the adsorbent.



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## CHAPTER II

### LITERATURE REVIEWS

#### 2.1 Textile Industry

The structure of textile industry can be divided into three main sub-industries, which consists of upstream industry, midstream industry and downstream industry. Upstream industry is the first part of textile industry involving the process of manufacturing natural fiber and man-made fiber. Midstream industry consists of many complicated activities that concern with the process of spinning, weaving, knitting, dyeing and printing. Garment industry is in downstream industry. Figure 2.1 shows the structure of Thai textile industry. Basically, the textile products from any previous industry will become the raw material in the next industry.

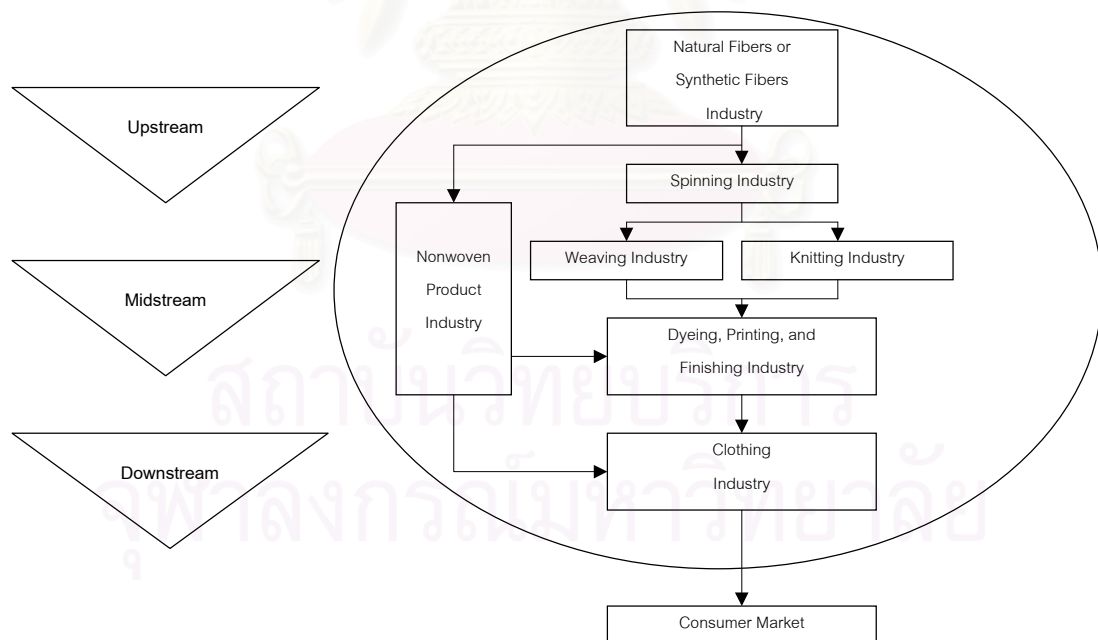


Figure 2.1 Overall Structure of Thai Textile Industry (Udomkitdecha 2000)

### 2.1.1 Sources and Characteristics of Textile Wastewater (langphasuk 1997)

Textile industry is involved in the manufacture of fabric from both natural and man-made fibers. There are various types of manufacturing processes depending on the raw materials and textile products. Textile mill operations consist of slashing, desizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing. Except of slashing and finishing step, water is a major constituent of desizing through printing step. Therefore, a large amount of wastewater is generated from these operations.

The main sources of wastewater generated the textile wet-processing industry originate from washing (scouring) and bleaching of natural fibers and from dyeing and finishing steps. Given the great variety of fibers, dyes, process aids and finishing products in use, these process generate wastewater of great chemical complexity and diversity which are not adequately treated in conventional wastewater treatment plant. Characteristics of textile wastewater are shown in Table 2.1.

Table 2.1 Characteristics of Textile Wastewater

Parameter	Value (Thailand) (Milintalake 1994)	Value (Foreign) (Gaeta et.al. 1991)	Unit
Temperature	About 50	10 – 90	Degree of Celsius
Color	High	Observe	-
PH	9 – 12	2 – 12	-
COD	500 – 1200	80 – 4000	milligram/liter
BOD	100 – 1000	50 – 2000	milligram/liter
TSS	High	20 – 500	milligram/liter

## 2.2 Colorants

Desired color of textile is generally achieved by incorporation of colored compounds referred to as *dyes* and *pigments* into fiber. The term colorant is frequently used to encompass both types of coloring materials. Dyes and pigments are both commonly supplied by the manufactures as colored powders. However, they are distinctly

different in their properties and especially in the way they are used and they are distinguished on the basis of their solubility characteristics: essentially, dyes are soluble, pigments are insoluble.

Dyes are almost invariably applied to textile materials from an aqueous medium, so that they are generally required to dissolve in water. Examples of water-soluble dye are acid, basic, direct, and reactive dye. Vat dyes, an important application class of dyes for cellulose fibers, are completely insoluble materials but they are converted by a chemical reduction process from that into a water-soluble and then can be applied to the fiber.

### 2.2.1 Color of Dyes

Physiological sensation of color arises when an object does not reflect all the incident white light falling on it. Some of the light energy is absorbed and the remainder is reflected and perceived as color. The perceived color of the object is determined by the wavelength(s) of the absorbed light. The extent of absorption at a given wavelength is known as the absorbance. Light of the remaining wavelengths is transmitted, perceived by the eye and interpreted by the brain as color. The principle is illustrated in Table 2.2, which summarizes the hues produced by the selective absorption of particular wavelengths.

Table 2.2 Relationship between wavelength of absorbed light and hue (Ingamells 1993)

Absorbed wavelength (nm)	Hue of absorbed light	Perceived hue
400-440	Violet	Greenish-yellow
440-480	Blue	Yellow
480-510	Blue-green	Orange
510-540	Green	Red
540-570	Yellow-green	Purple
570-580	Yellow	Blue
580-610	Orange	Greenish-blue
610-700	Red	Blue-green

Dye molecule can consider to be structured from two components, the dye chromophore and dye functional group (auxochrome)

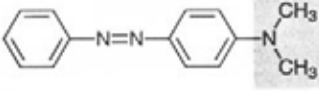
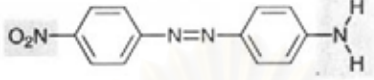
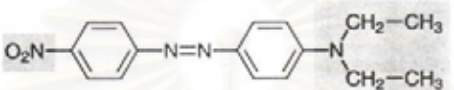
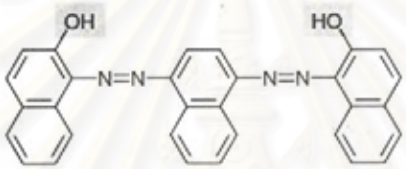
Chromophore is an unsaturated functional group in organic compound which can cause absorption in ultraviolet-visible range due to  $n \rightarrow \pi^*$  and/or  $\pi \rightarrow \pi^*$  transitions. Each chromophore has its adsorption maxima affected by solvent and structural detail of the molecule containing the chromophore such as the conjugation in molecule (Skoog 1992).

There are seven groups of chromophore in dye as follow:

- nitroso group:  $-\text{NO}$  or  $=\text{N-OH}$
- nitro group:  $-\text{NO}_2$  or  $=\text{NO.OH}$
- azo group:  $-\text{N}=\text{N}-$
- ethylene group:  $>\text{C}=\text{C}<$
- carbonyl group:  $>\text{C}=\text{O}$
- carbonyl-nitrogen group:  $>\text{C}=\text{NH}$  or  $>\text{CH}=\text{NH}$
- sulfur group:  $>\text{C}=\text{S}$  or  $-\text{C-S-S-C}$

The color of the molecule may be modified and increased in intensity of color by introducing a variety of smaller groups into molecule, example of which are shown in Figure 2.2, such group are called auxochrome

In addition, other groups that have no influence on the color can be added to change the insoluble molecule to a water-soluble dye. Thus compounds may be synthesized to produce all colors of the visible spectrum by suitable choice of auxochrome such as  $-\text{SO}_3-\text{Na}^+$ ,  $-\text{NH}_2\text{HCl}$ ,  $-\text{OH}$ ,  $-\text{NH}_2\text{SO}_2$ , and  $-\text{NH}_2$ .

Structure	Colour observed
	Yellow-green
	Yellow
	Red
	Blue


 - Auxochrome

Figure 2.2 Some auxochrome groups and color observed from dye structures (Ingamells 1993)

### 2.2.2 Classification of Dyes

Dyes may be classified according to chemical structure or according to their method of application. Classification of dye according to chemical structure is most useful to dye chemist who may be interested dye synthesis and relationship between chemical structure and properties of dye. Classification according to method of application is most useful to technologist concerned with coloration of textile products.

### 2.2.2.1 Classification of Dyes by Chemical Structure

Dyes are grouped according to certain common chemical structural features. The most important organic dyes, in roughly decreasing order of importance, belong to:

#### 1) Azo dyes

Azo dyes constitute by far the most important chemical class of commercial organic colorant. They account for around 60-70% of the dyes used in traditional textile applications. Azo colorants contain as their common structure feature the azo (-N=N-) group. Usually, although not exclusively, the azo group links two aromatic ring systems. The majority of the commercially important azo colorants contain a single azo group and are therefore referred to as monoazo dyes, but there are many which contain two (diazo), three (triazazo) or more such groups. See in Figure 2.3

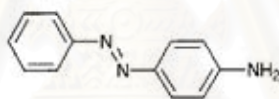


Figure 2.3 Monoazo dyes

#### 2) Carbonyl dyes

This chemical class of colorants which is second in importance to azo dyes is characterized by the presence of a carbonyl (C=O) group, which may be regarded as the essential chromophoric unit. The vast majority of carbonyl dyes contain two or more carbonyl groups, as illustrated in Figure 2.4, are linked to one another through a conjugated system, frequently an aromatic ring system.

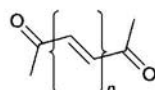


Figure 2.4 Carbonyl dyes

Carbonyl dyes are capable of providing a wide range of color, essentially covering the entire visible spectrum and giving long wavelength absorption bands with relatively short conjugated system. This feature applied especially to anthraquinone and indigo derivatives, which are thus of particular importance in the blue shade area.

The characteristic structure features of the most important types of carbonyl colorants are review in the following:

- Anthraquinones dyes

A common arrangement of the carbonyl groups in colored molecules gives rise to a group of compounds known as quinones. These may be dedined as cyclohexadienediones. The simplest quinones are *o*- and *p*-benzoquinones, Figures 2.5

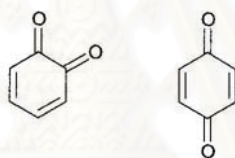


Figure 2.5 Anthraquinones dyes

- Fluorescent carbonyl dyes

One of the most important groups of fluorescent brightening agent dyes is based on the coumarin ring system, as shown in Figure 2.6

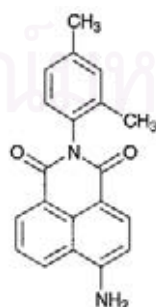


Figure 2.6 Fluorescent carbonyl dyes



- Benzodifurannones dyes

They were launched commercially in the late 1980s by ICI as disperse dyes for polyester application. Figure 2.7 shows a representative example of these dyes. They are capable of providing a range of color but the most important are red.

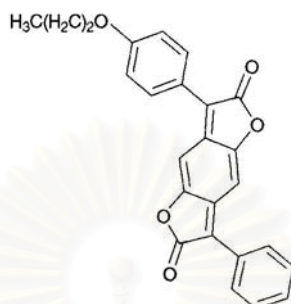


Figure 2.7 Benzodifurannones dyes

- Indigoid dyes

Indigo (Figure 2.8), the parent system of this group of colorants, is one of the oldest known natural dyes.

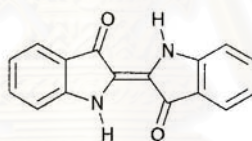


Figure 2.8 Indigoid dyes

3) Phthalocyanines dyes

Phthalocyanines are aromatic molecules. They have emerged as one of the most extensive studied classes of compounds, because of their intense, bright color, their high stability and their unique molecular structure. Figure 2.9 is almost certainly the first preparation of M-phthalocyanines. When M is a metal, that often be Cu.

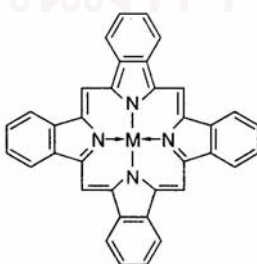


Figure 2.9 Phthalocyanines dyes

In addition, there are many other chemical types of dyes that do not fall into the category previously mentioned such as polymethines, arcarbonium ion colorants, dioxazines, sulfur dyes, nitro dyes and etc.

#### 2.2.2.2 Classification of Dyes by Methods of Application to the Fiber Types

Table 2.3 lists ten of the most frequently used dye classes classified in terms of their method of application to fiber types. The table also lists the attachment mechanisms, method of application and chemicals used. The dye characteristics, which are important in selecting a color removal technology, are also provided.

Table 2.3 Dyes classification by methods of application to the fiber types (Buckley 1992)

Dye class	Characteristics	Typical associated fiber	Dye-fiber attachment mechanism	Typical method of application
Acid	Anionic highly water soluble poor wet fastness	Nylon, Wool	Ionic bond	Fiber placed in acidified aqueous media pH 3-5 Fiber assumes a positive charge dye added and temperature to 50 - 110 °C
Metal complex acid dye (dye molecule is complex with chromium, Cobalt)	Anionic low water solubility good wet fastness	Nylon, Wool	Ionic bond	As with acid dyes pH 5-7

Table 2.3 (continued)

Dye class	Characteristics	Typical associated fiber	Dye-fiber attachment mechanism	Typical method of application
Direct	Anionic highly water soluble poor wet fastness	Cotton, Viscose	Ionic bond	Fiber placed in dyebath slightly alkaline Add dye electrolyte (NaCl, Na <sub>2</sub> SO <sub>4</sub> ) to displace dye to fiber, temperature to 98 °C
Basic or cationic	Cationic highly water soluble	Acrylics	Ionic bond	Fiber placed in acidified aqueous dyebath at pH 4 to 6 dye added temperature increase from 100 to 105 °C , dye diffuses into fiber
Dispersed	Colloidal dispersion very low water solubility good wet fastness	Polyester, nylon, acrylic, cellulose acetate	Colloidal impregnation, adsorption	Fiber placed in acidified dyebath pH 4.5 Dye added temperature to 130 °C causes dye migration into fiber
Reactive	Anionic highly water soluble good wet fastness	Cotton, Viscose, Wool	Covalent bonds	Fiber placed in aqueous dye solution add salt to displace dye to fiber add alkali to cause reaction between dye and fiber

Table 2.3 (continued)

Dye class	Characteristics	Typical associated fiber	Dye-fiber attachment mechanism	Typical method of application
Sulphur	Colloidal after reaction in fiber insoluble wet fast	Cotton, Viscose	Dye precipitated in-situ in fiber	Fiber placed in dyebath dye dissolves in alkaline sodium sulphur Dye displaced to fiber with electrolyte dye precipitated in-situ with air or peroxide
Vat	As per sulphur dye	Cotton, Viscose	Dye precipitated in-situ in fiber	As with sulphur dye
Azoic	As per sulphur dye	Cotton, Viscose	Dye precipitated in-situ in fiber	Fiber placed in dyebath coupler applied to fiber dye chrome added boiled to precipitate
Mordant or chrome	Anionic water soluble good wet fastness	wool	Fiber-Chrome- dye complex	Fiber placed in acidified dyebath add sodium dichromate Add dye temperature at 98 °C

One of the major factors determining the release of a dye to the environment is its degree of fixation on the substrate. Table 2.4 represents the summary of the data available.

Table 2.4 Estimate degree of fixation for different dye/fiber combinations (Cooper 1995)

Dye class	Fiber	Degree of fixation (%)	Loss to effluent (%)
Acid	Polyamide	80-95	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

The problem of color effluent has become identified particularly with the dyeing of cellulose fibers (notably cotton, which accounts for almost 50% of the total fiber consumed by the textile industry worldwide), and in particular with the use of reactive dyes. It can be seen from Table 2.4 that as much as 50% of reactive dye used may be lost to the effluent.

### 2.3 Wastewater Treatment (Black 1977)

Most conventional sewage treatment plants are designed to merely remove or reduce the organic materials and thus decrease the BOD of the wastewater. There are three basic types of treatment that may be used in treating sewage: primary, secondary, and tertiary. These terms refer to the quality of effluent released rather than the actual treatment process employed. The processes employed in the various types of tertiary treatment may vary widely, depending on the type of tertiary plant constructed.

Primary treatment includes process such as screening, neutralization, equalization, and gravity sedimentation. Purpose of primary treatment is to remove suspended matter, including oil and grease, and to achieve uniform flows and concentrations, as the suspended matter is removed, BOD and COD is also reduced.

Secondary treatment involves the use of biological methods (trickling filters and/or activated sludge) in addition to the usual methods employed in primary treatment. These biological methods approximate the natural purification processes that wastewater would be subjected to in a natural waterway in a shorter time period and reduced amount of physical space.

In tertiary treatment the sewage is subjected to one or more additional processes, either prior to or after receiving conventional primary and secondary treatment. This additional specific for a given area, such as the removal of certain industrial chemicals, dissolved metals, phosphates, or nitrates. Tertiary treatment very depending upon the actual wastewater generated or anticipated to be generated in particular area. The treatment of wastewater containing industrial waste, trace metal, and so on, will be considered under industrial wastewater treatment.

Wastewater from the textile industry is a serious pollution problem because it is high in both color and organic content. A combination of several processes is generally necessary to achieve adequate removal of all contaminants. Table 2.5 describes treatment processes and shows the range of removal efficiencies of contaminants.



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Table 2.5 Textile wastewater treatment removal efficiencies of the different unit operation and unit processes

Treatment Process Unit	Range of Removal Efficiency in (%)				
	BOD <sub>5</sub>	COD	TSS	Grease	Color
<b>Primary Treatment</b>					
-Screening	0-5	-	5-20	-	-
-Equalization	0-20	-	-	-	-
-Neutralization	-	-	-	-	-
-Chemical Coagulation (remove varies with chemicals and dosage used)	40-70	40-70	30-90	90-97	0-70
-Flotation	30-50	20-40	50-60	90-98	-
<b>Secondary Treatment</b>					
-Conventional Activated Sludge and Clarification	70-95+	50-70	85-95	0-15	20% color removal for biological treatment units
-Extended Aeration and Clarification	70-94+	50-70	85-95	0-15	
-Aerobic lagoon and Clarification	60-90	45-60	85-95	0-10	
-Aerobic Lagoon	50-80	35-60	50-80	0-10	
-Packed Tower	40-70	20-40	-	-	
-Roughing Filter	40-60	20-30	-	-	
<b>Tertiary Treatment</b>					
-Chemical Coagulation	40-70	40-70	30-90	90-97	0-70
-Mixed Media Filtration	25-40	25-40	80	-	-
-Carbon Adsorption	25-40	25-60	25-40	-	80-90
-Chlorination	0-5	0-5	-	0-5	0-5
-Ozonation	-	30-40	50-70	-	70-80
<b>Advanced Treatment</b>					
-Spray Irrigation	90-95	80-90	95-98	-	-
-Evaporation	98-99	95-98	99	-	-
-Reverse Osmosis	95-99	90-95	95-98	-	-

Source: UNEP (1994)

Common methods employed in the tertiary treatment are chemical coagulation and filtration, carbon adsorption, chemical oxidation, ammonia stripping, and advanced biological treatment.

### 2.3.1 Color Removal

Conventional water processes such as oxidation, coagulation, and filtration are effective in removing color. Adsorption and ion exchange can also be employed. In practice, color is usually removed to acceptable levels by normal water treatment operations. Each of these color removal processes is briefly discussed as follows. (Qasim 2000)

#### - Oxidation

Such oxidizing chemicals as potassium permanganate, chlorine, chlorine compounds, and ozone can remove color. Color removal is most effective when followed by coagulation and other conventional treatment processes. Potassium permanganate can oxidize color-causing compounds but is normally used for disinfection or for taste and odor control.

Ozone is a more powerful oxidant than chlorine, and removes color better than chlorine. It has the added benefit that it does not depress the pH level as much-nor does it produce trihalomethanes (THMs). The cost of ozone is usually not justified merely for color removal, but ozone is frequently employed for taste and odor removal.

#### - Coagulation

Conventional coagulation, as part of the overall water treatment process, effectively removes some color in addition to turbidity; however, the mechanism of color removal appears to be different from that for turbidity removal. With enhanced coagulation, many dissolved solids also precipitate out of solution, like the coagulation, and may adsorb color-causing compounds on the growing floc. The quality of raw water, charge difference, and degree of ionization of the suspended and dissolved solids appear to account for the distinct responses during coagulation. Because of the varied nature and origins of color, jar tests and pilot testing can help to identify the best color removal strategy.



#### - Filtration

Filters remove suspended solids that cause turbidity and color. In a conventional treatment process of coagulation and flocculation followed by sedimentation, the solids removed in the filter consist of the lightest portion of floc that did not settle in the sedimentation basin. Thus, the filters remove most of the apparent color due to turbidity and some of the true color captured during the prior treatment processes. Filtered water is low in turbidity; most color remaining in the water is attributed to the dissolved solids and is measured as true color.

#### - Ion Exchange

Ion Exchange processes remove ionic species by employing resins and electrical charge methods. The expense of ion exchange, however, inhibits its widespread application to remove color or even taste and odor.

#### - Adsorption

Activated carbon is the most widely used as adsorbent for dye removal. Since it is high cost that lead many researchers to search for more effective and cheaper materials. Many adsorbents have been investigated for removal of water-soluble dye in synthesis wastewater and from textile effluent. Examples of these adsorbents are described as follow.

##### 1) Activated carbon

Activated carbon is the original adsorbent used to adsorb dye molecules and removal color. The activated carbon can be granulated (GAC) or powdered (PAC). GAC is normally used in columns, through which effluent is passed. PAC is usually dosed as a slurry into effluent stream for subsequent removal and disposal. Surface area of its is about  $600-1,000 \text{ m}^2/\text{g}$ .

McKay (1979) investigated the adsorption of Victoria Blue dye (Basic Blue 26) on activated carbon. He found that the rate of color removal from the bulk solution is

increased with increasing degree of agitation and initial dye concentration but decreased when the particle size is increased.

McKay (1982) studied the ability of one activated carbon to remove dyestuffs from aqueous solutions. The factors affecting the rate of dye removal with four important classes of dyestuffs, acid, basic, direct, and disperse dyes. For basic, acid, and disperse dyes carbon was an excellent adsorbent and trends observed for the different variables were similar. The rate of adsorption increased with increasing temperature, initial dye concentration, mass of adsorbent, concentration of sodium sulphate salt in solution and agitation but decreased when particle size of adsorbent increase. The pH of solution has little or no influence on the adsorption of acid dye but for the basic dye the adsorption is enhanced by acidic solutions.

Ivo *et. al.* (1997) prepared activated carbon, magnetic charcoal, by entrapment of fine charcoal particles into the structure of magnetic iron oxides. This adsorbent can efficiently adsorb a variety of organic compounds. For the adsorption experiments water soluble organic dyes belonging to the triphenylmethane, heteropolycyclic, and azodye groups were used as model compounds. Maximum adsorption capacities ranged between 10 and 20 mg of dyes per 1 cm<sup>3</sup> of the sedimented adsorbent; this corresponds to 132.5 -265 mg of dyes per 1 g of dried adsorbent.

## 2) Clays

Dyes can be adsorbed on to several low-cost natural materials and special materials based on inorganic particulate synthetic clay have been developed for the adsorption of dye waste. Surface area of these materials is about 50-200 m<sup>2</sup>/g.

McKay *et. al.* (1985) studied the adsorption of Basic Blue 69 and Acid Blue 25 used Fuller's earth and fired clay as adsorbent. The adsorption capacity of Basic Blue 69 and Acid Blue 25 on fired clay are 7 and 40 mg/g, respectively, indicating its use in treating dyehouse effluents is of little or only very limited significance. Fuller's earth has considerable adsorption capacities, 220 and 1200 mg/g for Basic Blue 69 and Acid Blue 25, respectively. Certain variables, which influence the kinetic of adsorption process, have been

investigated. Increased agitation increased the rate of dye adsorption. Increasing the initial dye concentration increased the treated effluent outlet concentration for a given mass of adsorbent. Decreasing particle size increases the rate of dye adsorption and increased temperature increase the initial rate of adsorption.

Osathanugrah (1994) investigated the adsorption property of clay-minerals, bentonite and kaolinite clays, and the mixture of clay-minerals and chemical coagulants, on removal of dyestuffs; disperse, direct, and reactive dye, from 6 dyes prepared solution and 5 samples of the textile effluent. It was found that bentonite clay is the best adsorbent and alum are more effective coagulant than the others when they reach the optimum pH. But pH has no effect to bentonite adsorption.

Lee *et. al.* (1997) used Hexane – Extracted Spent Bleaching Earth (HSBE), a waste material from the palm oil industry, for removal of some organic dyes (Acid Blue 25, Acid Blue 29, Basic Blue 3, Methylene Blue, Reactive Blue 2, and Reactive Yellow 2). Sorption capacity increased with increasing pH, initial dye concentration, temperature, sorbent dosage and agitation rate in the batch process.

### 3) Bioadsorbent

Bioadsorbents are naturally occurring polymers, which are biodegradable. Adsorb species within their structure act as ion-exchanges. Surface area of them are about 30-200 m<sup>2</sup>/g. Most of them obtain from plants and waste of agriculture products such as maize cob, sawdust, fly ash and etc.

Asfour *et. al.* (1985) studied the adsorption of basic blue dye on hardwood sawdust. The capacity of hardwood for the adsorption of basic dye was found to increase by decreasing the particle size and increasing the temperature. In comparison between the adsorptive capacity (for standard values) of hardwood sawdust and activated carbon, as standard adsorption, under identical conditions that the relative cost of hardwood adsorbent is on 8.4 % that of activated carbon. In addition, based on the low cost of the sawdust compared to activated carbon, there is no need to recover the sawdust and the exhausted wood can be used as a fuel.

Khare *et. al.* (1987) used fly ash for the removal of Victoria Blue from aqueous solution at different concentrations and pHs. The removal of Victoria Blue decreases with increasing the initial dye concentration but increases when pH of solution increased. This can be explained on the basis of hydroxylation of oxides present in adsorbent. The hydroxylated oxide surface become positively charged at lower pH which is not suitable for adsorption of dye cations. At higher pH, the association of dye anions with negatively charged oxide surface take place.

El-Geundi *et. al.* (1991) studied the adsorption of 2 basic dyes and 2 acid dyes onto maize cob. Maize cob as an adsorbent has high adsorption capacity for basic dyes but low capacity for acid dyes. The effects of the system variables on the adsorption of dye onto maize cob has been reported, increasing the rate of agitation and the maize cob mass increases the rate of dye adsorption. Increasing particle size decreases the adsorption rate.

Phumkacha (1996) studied of color removal of textile wastewater by using three different kinds of process as follow 1) coagulation by alum 2) batch adsorption by adsorbent; granular activated carbon, fly ash and 3) color removal by using both alum and adsorbents. The experiment consisted of 2 part. First, the experiment was done with four synthetic wastewater; acid dyes, direct dyes, reactive dyes, and basic dyes. Acid dyes, direct dyes, and reactive dyes have negative charge except basic dyes which have positive charge. The efficiency of color removal by alum coagulation was more than 80% for all types of dyes except basic dyes. Color removal by granular activated carbon was effective for positive dyes. Fly ash effectively remove in all types of dyes. The efficiency of alum-granular activated carbon and alum-fly ash combination were more than that the alum only. The second experiment for real textile wastewater, the color removal efficiency by alum were in the range of 67.7-72.8%, the COD reduction in the range of 56.0-65.1%, the cost of alum coagulation in the range of 5.0-7.5 bahts/m<sup>3</sup>.

Semrat (2000) investigated the color removal efficiency for textile mill wastewater by activated carbon and agricultural waste as carbon as sorbent, coconut shell carbon and bagasse carbon. In order to increase adsorption efficiency of agricultural waste

carbon, sodium chloride solution was used. The results reveal that coconut shell carbon is unable to use as adsorbent by considering from adsorption isotherm test. Activated carbon and bagasse carbon are feasible because of its longer breakthrough time. Breakthrough time of activated carbon, activated carbon mixed bagasse carbon, and bagasse carbon are 2-12, 2-9, and 2-6 respectively and COD reduction ranging from 84-99% and 54-58%, 50-98% and 44-75%, and 51-59% and 15-73%, respectively.

## 2.4 Adsorption (Kenneth 1992, Alley 2000)

Adsorption is mass transfer process that can generally be defined as the accumulation of materials at the interface between two phases. These phases can be any of the following combination: liquid-liquid, liquid-solid, gas-liquid and gas-solid. In the adsorption process, molecules, as shown in Figure 2.10, or atom or ions in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. The adsorbed solutes are referred to as *adsorbate*, whereas the solid material is the *adsorbent*.

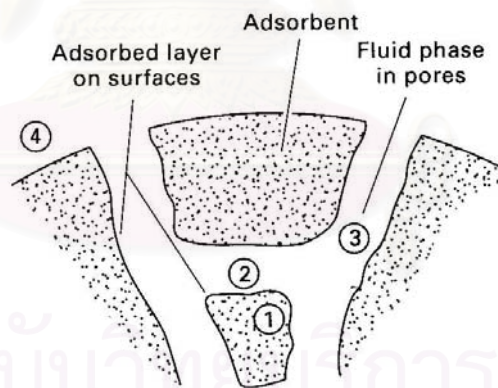


Figure 2.10 Adsorption operation with solid-particle sorbents

### 2.4.1 Adsorption Theory

Thermodynamic system of the adsorption in which the various compounds are striving for equilibrium. The process of adsorption occurs in both steady-state and unsteady-state conditions. The primary force driving the interaction between the adsorbate and the adsorbent is the electrostatic attraction and repulsion between molecules of the

adsorbate and the adsorbent. These driving forces can be either physical or chemical. In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involved only relatively weak intermolecular forces, and chemical adsorption, which involve essentially the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Table 2.6 was shown some difference between physical adsorption and chemical adsorption.

#### 2.4.1.1 Physical Adsorption

Physical adsorption is a result of intermolecular forces that interact between the adsorbate and the adsorbent. These physical electrostatic forces include the van der Waals force, consisting of weak attraction and repulsion through dipole-dipole interactions and dispersing interactions, and hydrogen bonding. Dipole-dipole interactions are the result of polar compounds orienting themselves so that their charges result in a lower combined free energy. Dispersing interactions are the result of attractive forces between electrons and nuclei of molecular systems. If the molecules come too close to each other, repulsive forces can push the molecules apart. Hydrogen bonding is a special case of dipole-dipole interaction in which the hydrogen atom in molecule has a partial positive charge, attracting another atom or molecule with a partial negative charge. For liquid phase systems, the van der Waals force is the primary physical force driving adsorption. Physical adsorption is a readily reversible reaction and includes both mono- and multilayer coverage. Because physical adsorption does not involve the sharing of electrons, it generally has low adsorption energy, and is not site specific. The heat of adsorption for the reaction is on the order of 40 Btu/lb. per mole of the adsorbate. When the intermolecular forces between a chemical molecule in a liquid stream and a solid (the adsorbent) are greater than the forces between the molecules of the liquid stream, the chemical is adsorbed onto the adsorbent surface.

### 2.4.1.2 Chemical Adsorption

Chemical adsorption (Chemisorption), like physical adsorption, is also based upon electrostatic forces. The mechanisms of chemical adsorption are similar to those of physical adsorption, yet are often stronger (approaching the adsorption energies of chemical bonds). The transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent produce chemical adsorption. It may be an irreversible reaction and have high adsorption energies. The heat of adsorption is significantly greater than for physical adsorption, ranging from 80 to 400 Btu/lb. mole. It is not unusual for the adsorbate to have chemically changed due to the reaction. Chemical adsorption involves only monolayer coverage, and is a site specific reaction, occurring at specific functional group locations. Functional groups are distinctive arrangements of atoms in organic compounds that give that compound its specific chemical and physical properties.

Table 2.6 Distinction between physical adsorption and chemical adsorption

Physical adsorption	Chemical adsorption
-Low heat of adsorption (<2 or 3 times latent heat of evaporation)	-High heat of adsorption (>2 or 3 times latent heat of evaporation)
-Non specific	-Highly specific
-Monolayer or multilayer	-Monolayer only
-No dissociation of adsorbed species	-May involve dissociation
-Only significant at relatively low temperatures	-Possible over a wide range of temperatures
-Rapid, non-activated, reversible	-Activated, may be slow and irreversible
-No electron transfer although polarization of sorbate may occur	-Electron transfer leading to bond formation between sorbate and surface

Adsorption onto solid adsorbent has great environmental significance, since it can effectively remove pollutants from both aqueous streams. Due to the high degree of purification that can be achieved, this process is often used at the end of a treatment sequence.

#### 2.4.2 Mechanism of Adsorption onto the Porous Adsorbent (McKay et.al. 1980)

For the adsorption of a solute onto the porous surface of an adsorbent, these are essentially four stages in the adsorption process, the following steps are required:

- (1) transport of dye from the bulk of solution to the exterior surface of the adsorbent;
- (2) movement of dye across the interface and adsorption onto external surface sites;
- (3) migration of dye molecules within the pores of the adsorbent, and
- (4) interaction of dye molecules with the available sites on the interior surfaces, bounding the pore and capillary spaces of the adsorbent.

#### 2.5 Chitosan (Muzzarelli 1977)

Chitosan is an all natural product which is obtained by deacetylated chitin. It is harmless to human and has many useful features; biodegradability, biocompatibility, hydrophilicity, anti-bacterial activity, and protein affinity. It is used as a potential bioseparator in agricultural, food, and pharmacy process.

##### 2.5.1 Structure of Chitin and Chitosan

Chitin is a high molecular weight linear biopolymer. It is highly insoluble in common solvents, resembling cellulose in its solubility and low chemical reactivity. It may be regarded as cellulose with hydroxyl at position C-2 having been replaced by an acetamido group ( $-\text{NH}-\text{CO}-\text{CH}_3$ ), which in chitosan is replaced by an amino group ( $-\text{NH}_2$ ). All of these structures are shown in Figure 2.11. Like cellulose, it naturally functions as a structural polysaccharide. It is most abundant in crustaceans, insects, and fungi. It is present in commercial quantities in the shells of lobsters, crabs and shrimp. The skeletal shells of these crustaceans contain approximately 75% calcium carbonate and 15-20% chitin.



Table 2.7 Ideal monomer, the official name and general formula of chitin and chitosan

	Chitin	Chitosan
Monomer (ideal)	2-acetamido-2-deoxy- $\beta$ -D-glucose	2-amino-2-deoxy- $\beta$ -D-glucose
The official name	(1 $\rightarrow$ 4) -2-acetamido-2-deoxy- $\beta$ -D-glucan (fully acetylated product)	(1 $\rightarrow$ 4) -2-amino-2-deoxy- $\beta$ -D-glucan (completely deacetylated product)
General formula	$(C_8H_{13}NO_5)_n$	$(C_6H_{11}NO_4)_n$

In chitin the amino group is acetylated, thus chitin is an amide of acetic acid; in chitosan the amino group is free and therefore chitosan is a primary amine. But chitin can not be sharply distinguished from chitosan, because fully acetylated and fully deacetylated chitin do not normally occur in nature and are difficult to prepare.

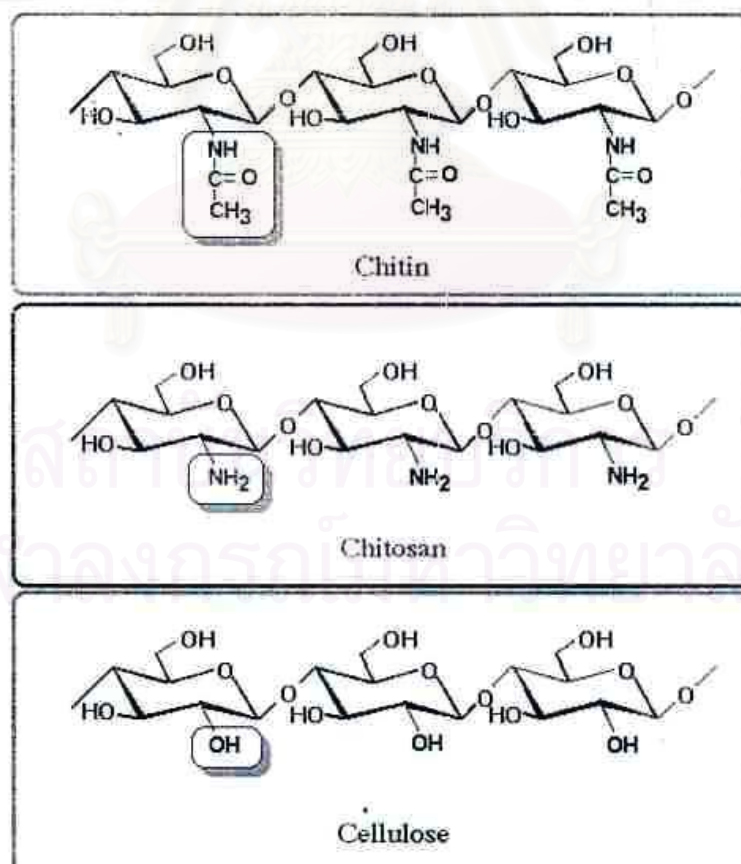


Figure 2.11 Structure of Chitin, Chitosan and Cellulose (ideal)

The term chitin currently refers to a polymer of N-acetylglucosamine where a minority of the acetyl groups has been lost, while the term chitosan currently refers to a deacetylation product obtained from chitin, where most of the acetyl groups have been removed. Experimentally, chitosan can be distinguished from chitin because of its solubility in dilute acetic or formic acid; chitin is also a product that contain less than 7% nitrogen, while chitosan contains 7% or more nitrogen.

The difference between chitin and chitosan lies in the degree of deacetylation. Generally, the reaction of deacetylating chitin in an alkaline solution cannot reach completion even under harsh treatment. The degree of deacetylation usually ranges from 70% to 95%, depending on the method used.

The difference of IR spectra and NMR spectra of chitin and chitosan structure were shown in Figure 2.12 and Figure 2.13, respectively.

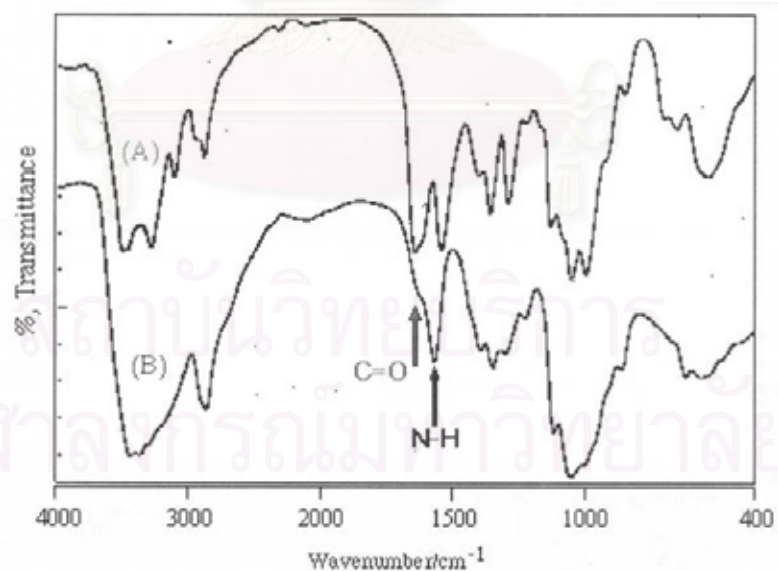


Figure 2.12 IR spectra of (A) Chitin and (B) Chitosan

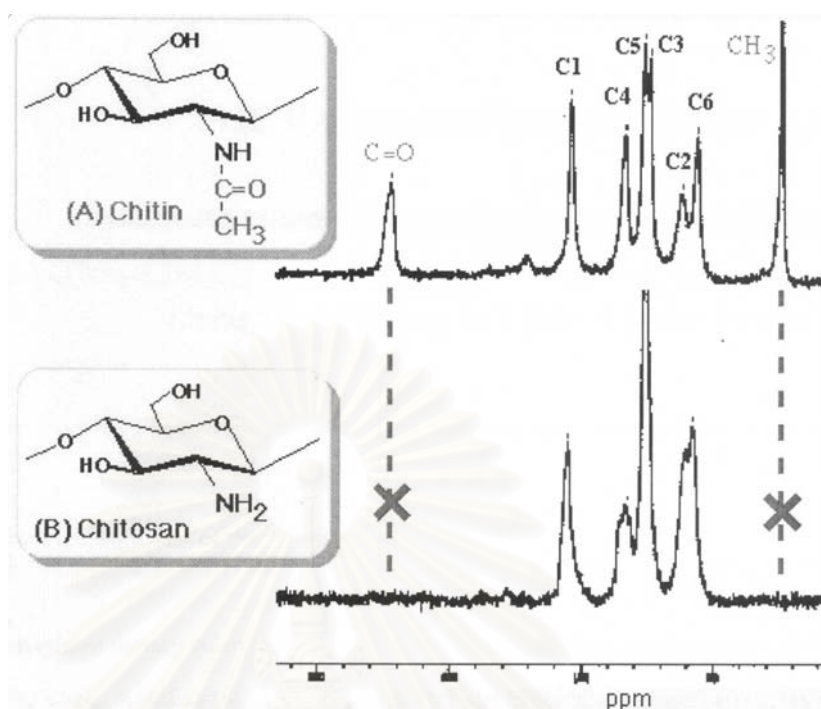


Figure 2.13 NMR spectra of Chitin and Chitosan by CP-MAS method

## 2.5.2 Physicochemical Properties of Chitosan

### 2.5.2.1 Solubility

Chitosan is insoluble in water, alkali, and organic solvents but is soluble in most solutions of organic acids when the pH of solution is less than 6. Acetic and formic acids are two of the most widely used acids for dissolving chitosan. Some dilute inorganic acids, such as nitric acid, hydrochloric acid, perchloric acid, and phosphoric acid, can also be used to prepare a chitosan solution but only after prolonged stirring and warming.

### 2.5.2.2 Viscosity

The viscosity of chitosan in solution is influenced by many factors, such as the degree of deacetylation, molecular weight, concentration, ionic strength, pH, and temperature. In general, as the temperature rises, the viscosity of the polymer solution

decrease. However, a pH change in the polymer solution may give different results depending on the type of acids employed. With acetic acid, the viscosity of chitosan tends to increase with decreasing pH, whereas with hydrochloric acid the viscosity decreases when the pH is lowered. These indicated that the intrinsic viscosity of chitosan was a function of the degree of ionization as well as ion strength.

#### 2.5.2.3 Molecular weight

The molecular weight of native chitin is usually larger than 1,000,000 while commercial chitosan products fall between 100,000 and 1,200,000. During the manufacturing process, harsh conditions and lead to degradation of the chitosan product. For example, with the Horowitz method, after a 30-minute treatment at 180 °C, a chitosan sample with a chain length of only twenty units was obtained. In generally, factors such as dissolved oxygen, high temperature, and shear stress, can cause the further degradation of chitosan products.

#### 2.5.2.4 Degree of deacetylation (DD)

The degree of deacetylation is one of the most important chemical characteristics of chitosan. This determines the content of free amino groups in the polysaccharide. Since chitin and chitosan are co-polymer of 2 monomers between D-glucosamine and N-acetyl-D-glucosamine when the ratio of the first monomer is higher than the other monomer, the value of the degree of deacetylation is high, this polymer will present the advantage feature of chitosan.

#### 2.5.2.5 Coagulating Ability

Chitosan is a good coagulating agent and flocculant due to the high density of amino groups, which can interact with negatively charged substances, such as proteins, solids, dyes, and polymers. However, chitosan behaves quite differently with respect to transition metal ions. The nitrogen in the amino group of the chitosan molecule

acts as an electron donor and is presumably responsible for selective chelating with metal ions.

### 2.5.3 Application of Chitosan

The industrial production and use of chitosan has been steadily increasing since the 1970s. The major applications of chitosan were centered on sludge dewatering, food processing and metal ion chelation. The present trend, in industrial applications, however, is toward producing high value products, such as cosmetics, drug carriers, feed additives, semi-permeable membranes, and pharmaceuticals. The difference in value between the products and the low-cost polymer is one of the main driving forces pushing studies on new application of chitosan. Biotechnology is currently attempting large-scale production of high value bioproducts like monoclonal antibodies. Immobilization techniques have been proven to be an effective way to increase cell density, product concentration, and hence, productivity in a culturing system. Chitosan membranes and gels have great potential for use in immobilized cell culture systems.

### 2.5.4 Application of Chitosan for Wastewater Treatment

The powerful adsorption capabilities of chitosan towards most of persistent toxic found in aquatic environment make it one of the most suitable polymers to be used for elimination of non-biodegradable toxic. Chitosan is capable of lowering transitional metal ions concentrations to part per billion concentrations, is widely available and is environmentally safe. Another attractive feature is that it possesses a number of different functional groups to which other chemical moieties can be reacted and which can increase the efficiency of metal ion uptake and/or the chemical loading possible. Moreover, it is possible to regenerate them, *in situ*, by simply exposing the metal laden materials to aqueous acid solution, when desired.

#### 2.5.4.1 Heavy Metal Removal

Chitosan and derivatives function effectively to chelate metals, including lead, iron, mercury, cadmium, copper, nickel, manganese, zinc, cobalt, chromium, and silver. Trace radioactive elements such as uranium or plutonium can also be removed. Chitosan is a suitable adsorbent for the removal of copper and chromium from aqueous solution, as both kinetics and capacity are highly favorable.

#### 2.5.4.2 Flocculant

Chitosan can be used to flocculate the suspended solids from a variety of wastewater. Use of both chitosan and an anionic polymer in flocculation of sewage sludge can result in a sludge cake with 5% lower moisture content.

#### 2.5.4.3 Petroleum Sorbent

Chitin and chitosan powder could be sprayed onto petroleum or related products to remove them from salt or fresh water. Recovered products could be burned as a fuel.

#### 2.5.4.4 PCB Removal

The sorption abilities of chitosan are more efficient than those of other tested organic substances. Up to 84% of the PCB present in water adsorbed by 100 mg of chitosan. Chitin had relatively good adsorption properties towards PCB but the reproducibility was poor.

#### 2.5.4.5 Role of Intermolecular Forces in Dye Adsorption

Various attractive forces have the potential of binding dyes to chitosan, adsorbent, and often more than one type of chemical bonding can operate with the same



will react with sodium hydroxide to form the sodium salt of the dye as shown in Equation (2.1)



#### 4) Covalent Bonds

This bonding involves the sharing of electron, thus each atom has two electrons in its valence shell. Covalent bonding is stronger than salt link, hydrogen bond and van der Waals force, respectively. The relative strengths of different bonds is given in Table 2.8

Table 2.8 Comparison of bond strengths

Bond type	Relative strength
Van der Waals	1.0
Hydrogen	3.0
Salt link	7.0
Covalent	30.0

#### 2.5.5 Factors Effecting of Dye Adsorption Using Chitosan

As a generalization, the adsorptive capacity of a given adsorbent material is proportional to the surface area available. However, there are a number of other factors that affect adsorption.

##### 2.5.6.1 Characteristic of Chitosan

The structure of chitosan is cellulose based and the surface of cellulose in contact with water is negatively charged. Most dyes are ionized in solution many being salts or sulphonic or carboxylic acids. While others contain acidic phenolic groups. Acid Blue 25 is an example of a dye that ionizes to an anionic colored component  $\text{D}^-$  and a cation of  $\text{Na}^+$ . Basic Blue 69 is an example of a dye that will ionize to give the colored cationic dye base. These ions will undergo attraction on approaching the chitosan structure.



#### 2.5.6.2 Surface Area and Pore Size Distribution

One of the major considerations when selecting the adsorbent is the surface area of the material. Adsorbent materials used for wastewater treatment are highly porous. The majority of the surface area of chitosan is provided by the pore structure. Another surface area property affecting adsorption is the distribution of pore size diameters.

Pore size distribution is a measurement of the percent of the space of a particle occupied by micropores (pore diameter < 2 Angstroms), mesopores (pore diameter >20 Angstroms and < 500 Angstroms), and macropores (pore diameter > 500 Angstroms). A molecule cannot penetrate into a pore smaller than a given minimum diameter (depending upon the size of the molecule).

#### 2.5.6.3 pH of Dye Solution

Value of pH of dye solution is an important factor in the sorption of certain dyes onto chitosan because, at low pH, chitosan free amino groups are protonated, causing them to attract anionic dyes.

#### 2.5.6.4 Temperature of Dye Solution

Increasing the temperature must increase the mobility of the large dye ion. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling large dyes to penetrate further.

#### 2.5.6.5 Agitation

The increase in the rate of color removal by agitation may be attributed to the decrease in the diffusion layer thickness surrounding the adsorbent particles, then dye molecule can through pass the film to penetrate on the adsorbent.

## 2.6 Related Literatures

Chitosan is an excellent natural adsorbent with much higher selectivity than usual commercial chelating resins and high loading capacity. The excellent adsorption behaviors of chitosan as such was considered to be attributable to the following factors:

1. high hydrophilicity of chitosan owing to large number of hydroxyl groups,
2. large number of primary amino groups with high activity as adsorption sites,
3. flexible structure of polymer chain of chitosan which enables to take suitable configuration of the complexation with dye molecules.

Muzzarelli (1977) reported that the kinetics of the reaction of Procion Yellow RS with the amino groups of chitosan were studied by Kri chevskii and Sadov. Dichlorotriazine dye reacts with amino groups of chitin and chitosan in both alkaline and acidic media, the hydroxyl groups take part in the reaction in alkaline media only.

The adsorption of sulfonated dyes by chitin can be regarded as an ion exchange process at the cationic site; the reaction with a dye in sulfuric acid medium can be written as equation (2.2)



McKay et al. (1982) determined the Langmuir and Freundlich constant and the effect of chitin particle size and solution temperature on the adsorption of 4 dyes; Acid Blue 25, Acid Blue 158, Mordant Yellow 5, and Direct Red 84. The results indicated chitin particle size has a little or no influence on its ability to adsorb Acid Blue 25, Acid Blue 158, and Mordant Yellow 5. These dyes could completely penetrate the internal pore structure of chitin and saturate the particle. The results show 2 completely different effects. The adsorption of Acid Blue 158, the adsorption capacity decreases with increasing temperature. This phenomenon is quite common and is due to the enhanced magnitude of reverse (desorption) step in mechanism as the temperature increase. But the adsorption capacity of chitin for Direct Red 84 increases with decreasing temperature. Consequently, increasing the temperature must increase the mobility of large dye ions and may produce a

swelling effect with in the internal structure of the chitin enabling the large dyes to penetrate further.

Kim et al. (1997) determined the effects of degree of deacetylation (DD) of chitin on dye removal from textile effluents. DDs were varied from 10.7% to 67.2 % and the pHs were varied from pH 3 to pH 7. The sorption capacity of dyes; Acid Blue 193, Acid Blue 40, Direct Yellow 44, and Direct Blue 78, increases with increasing of deacetylation of chitin, but decreases with increasing of pH. This is mainly due to increase quaternary amine groups ( $-\text{NH}_3^+$ ) of chitin with a high deacetylation and low pH.

Annadurai et al. (1999) studied the adsorption and desorption of reactive dye (Verofix Red) by used chitin as the adsorbent. Reactive dye solution of 40 mg/L was treated with adsorbent in batch processing and constant stirring. The different parameters studied were as follow; chitin concentration, pH, temperature, and particle size. The adsorption increases with increasing pH and temperature but decreases when the particle size increased. The results of desorption were opposed to the adsorption.

Juang et al. (1997) studied the capacity of the use of chitosan for removing vinyl sulfone and chlorotiazine reactive dyes from aqueous solutions. They observed that the adsorption capability of dye decreases with increasing particle size of the chitosan. At a chitosan particle size 250-420  $\mu\text{m}$  at 303 K give the maximum adsorption capability of Reactive Red 222, Reactive Yellow 145, and Reactive Blue 222 are about 380, 179, and 87 g/kg, respectively. The present results are significantly greater than those obtained previous using adsorbents such as activated carbon, natural clays, bagasse pith, maize cob and etc., in which the capacity for reactive dyes is often less than 30 g/kg.

Chamnanmanoontham (1999) investigated the effects of various parameters on the adsorption of 4 dyes on three adsorbents. The adsorption of acid dye, reactive dye and direct dye was highly effective in acidic solution at pH 5 or less, of which chitosan could adsorb more than chitin and shrimp shells. On the contrary, the amounts of basic dye adsorbed on adsorbents were very effective in alkaline solutions at pH 10 or higher, especially on shrimp shells. The amounts of adsorbed dye increased with increasing adsorption time and initial dye concentration but decreased with increasing particle size.

The adsorbed amounts of all dyes except the basic dye increased with increasing degree of deacetylation. The ionic interaction was the main force that involved in the dye adsorption on adsorbent. Desorption of dyes from adsorbents was highly effective at 80 °C and  $\text{pH} \geq 10$  except the basic dye which highly desorbed at  $\text{pH} \leq 3$ .

Wu et al. (2000) compared the adsorption capacities and rates of Copper (Cu) and a commercial reactive dye (Reactive Red 222) on flake- and bead-types of chitosans which prepared from three fishery wastes (shrimps, crab, and lobster shells). It was shown that all equilibrium isotherms could be well fitted by the Langmuir equation. The adsorption capacity of Cu(II) on flake- and bead-types of chitosans appeared to be comparable, but the adsorption capacity of Reactive Red 222 on bead type was much higher larger than that on flake type by a factor of 2.0-3.8.

Yoshida et al. (1991) found that the adsorption of direct dye acid dye on chitosan fiber appeared technically and economically feasible. The amount of adsorption of Brilliant Yellow, direct dye, and Acid Orange 2 on chitosan fiber was much larger than on the activated carbon fiber, through the dyes adsorbed well on the activated carbon fiber too. The amount of adsorption of these dyes increases with increasing initial concentration of the dyes and decreases with increasing temperature. For Crystal Violet, basic dye, was adsorbed on the chitosan fiber very little but on activated carbon fiber well.

Yoshida et al. (1993) studied the adsorption of Acid Orange 2 by using chitosan fiber (ChF) and cross-linked chitosan fiber using Denokol EX841, chitosan fiber A (ChF-A) and chitosan fiber B (ChF-B) which have Denokol are 4.76 and 17.6% by weight, respectively. The concentration of amino group in the adsorbent phase was 3 to 5 times larger than that of the commercial weak-base ion exchanger and decreased with increasing degree of cross-linking. The maximum amounts of the dye adsorbed on ChF, ChF-A, and ChF-B were about 10, 6, and 3.2 mol/kg, respectively, for initial liquid-phase concentration of the dye  $C_0 = 1 \text{ mol/m}^3$  at 298 K. These values are much larger than the corresponding values for activated carbon fiber. The amount of the dye adsorbed increases with increasing initial dye concentration and decreases with increasing temperature. Since ChF dissolved in acetic acid solution but ChF-A, and ChF-B did not, then new cross-linked

chitosan fibers may be useful for the recovery of acid dyes not only from neutral solutions but also from organic acid solutions.

Kittikorn (2000) modified chitosan by graft polymerization using acrylamide monomer. The final product that convert acrylamide group into free amino groups and carboxylic groups to be the vinylamine-co-acrylic acid-co-chitosan. The results of potentiometric titration showed that the final product contained an increase in amount of free amino groups, which was expected to enhance the performance of removal capacity of anionic dye and heavy metal ion. The assessment of removal capacity of anionic dyes by modified chitosan indicated that an increase in free amino groups of modified chitosan led to an increase dye removal capacity. However, its dye removal capacity was much lower than those of virgin chitosan. It was found that the molecular weight of the modified chitosan was significantly lower than that of virgin chitosan due to the degradation of chitosan backbone during Hofmann degradation treatment. This indicated that the molecular weight of chitosan played an important role in anionic dye removal



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## CHAPTER III

### EXPERIMENTAL PROCEDURE AND ANALYSIS METHODS

This chapter consists of description in experimental procedure and analytic method. It is divided into four sections. First section concerns with materials, which consists of adsorbent, dyes, and chemicals. Second section reviews all equipment that used in the experiments. Third section describes the experimental apparatus, adsorption procedure, and desorption procedure. The last section refers to analysis techniques and errors of the experiments.

#### 3.1 Materials

##### 3.1.1 Adsorbent

Adsorbent was composed of chitosan flake degree of deacetylation 79%, 87%, and 95% that supplied by Seafresh Chitosan (Lab) Co., Ltd. (Thailand). Specifications of these chitosans were shown in Appendix B.

##### 3.1.2 Water-soluble dyes

Four types of water-soluble dyes were obtained from Tung Ti Hua Heng. C.I. generic names were C.I. Acid Orange 7, C.I. Basic Yellow 2, C.I. Direct Green 26, and C.I. Reactive Violet 5. Chemical structures of these dyes are shown in Figures 3.1 to 3.4. Table 3.1 shows the empirical formula and molecular weight of each dye.

##### 3.1.3 Chemical

Hydrochloric acid (37% w/v) and Sodium hydroxide were supplied by SR-Lab. 0.1M HCl and 0.1M NaOH were prepared to adjust the pH of the dye solution to pH 5, pH 7 and pH 9. Specifications of these chemicals were shown in Appendix B.

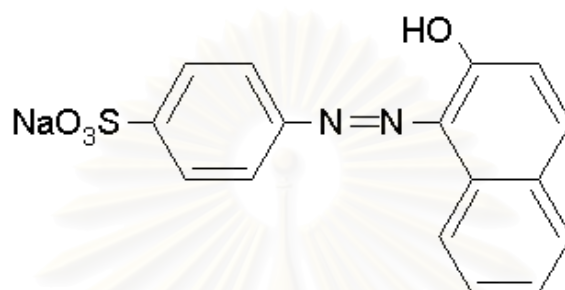


Figure 3.1 Chemical structure of C.I. Acid Orange 7

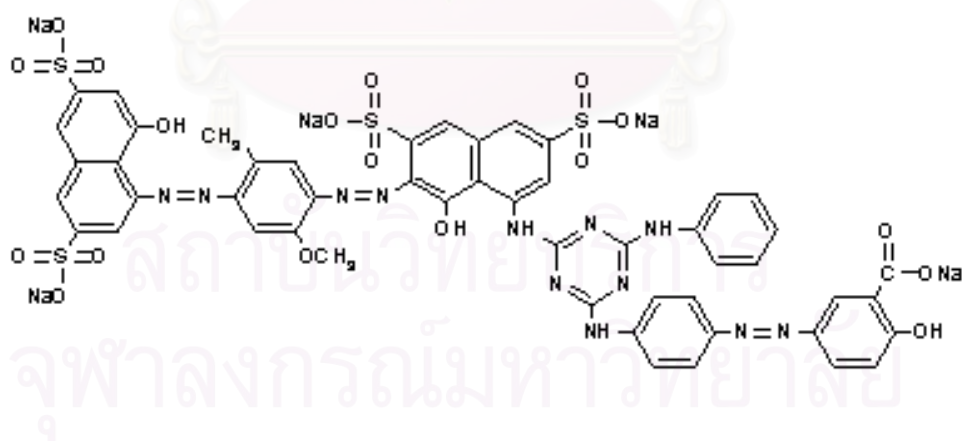


Figure 3.2 Chemical structure of C.I. Direct Green 26

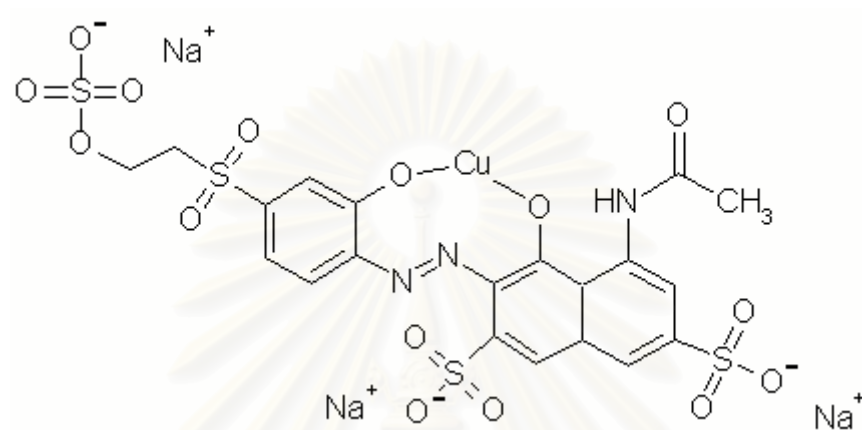


Figure 3.3 Chemical structure of C.I. Reactive Violet 5

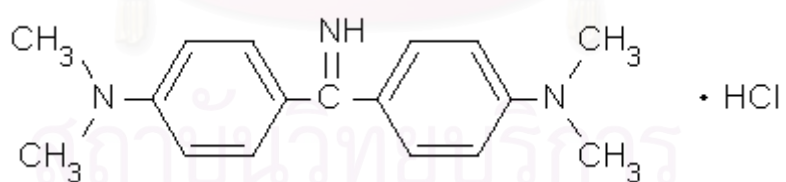


Figure 3.4 Chemical structure of C.I. Basic Yellow 2



Table 3.1 The empirical formula and molecular weight of dye

C.I. generic name	C.I. Number	Chemical Class	Empirical Formula	Molecular Weight
C.I. Acid Orange 7	15510	Monoazo	$C_{16}H_{11}N_2NaO_4S$	350.3
C.I. Basic Yellow 2	41000	Diphenylmethane	$C_{17}H_{21}N_3 \cdot HCl$	303.8
C.I. Direct Green 26	34045	Triazo	$C_{50}H_{33}N_{12}Na_5O_{18}S_4$	735.6
C.I. Reactive Violet 5	18097	Monoazo	$C_{20}H_{16}N_3Na_3O_{15}S_4$	1333.07

### 3.2 Equipment

#### 3.2.1 Sieving Machine and Sieves

A sieving machine type Vibro and sieves from Retsch, 5657 HAAN, Germany were used for classification of particle sizes of adsorbents.

#### 3.2.2 Analytical Balance

Adsorbent was weighted by using BP210s, Sartorius.

#### 3.2.3 pH Meter

The pH values of solutions were obtained on an HI 8424, microcomputer pH merter, Hanna.

#### 3.2.4 Ultraviolet-Visible Spectrophotometer (UV/VIS)

An 6405 UV/VIS spectrophotometer, Jenway, was used for qualitative and quantitative analysis of dye adsorption and desorption at wavelengths.

#### 3.2.5 Surface Area Analyzer

The specific BET (Brunauer-Emmett-Teller) surface area was determined by using a surface area analyzer, ASAP 2000.

### 3.3 Experimental Procedures

#### 3.3.1 Adsorbent Preparation

Chitosan produced from crab shell wastes was offered as flake from Seafresh Chitosan (Lab) Co., Ltd., Thailand, without further purification. Three types of chitosan with different degree of deacetylation were sieved to three particle size ranges, 0.150-0.300, 0.300-0.425, and 0.425-0.600 mm. Specifications of these chitosan are shown in Appendix B. Particle size at 0.425-0.600 mm of chitosan was fixed for subsequent study.

#### 3.3.2 Feed Preparation

For all type of dye, aqueous dye solutions were prepared at pH 5, pH 7 and pH 9, which adjusted by using 0.1M HCl or 0.1 M NaOH. The  $\lambda_{\max}$  values of the dye solution were determined by scanning at wavelength 190-900 nm using UV/VIS spectrophotometer. The  $\lambda_{\max}$  values of each dye solutions are shown in Table 3.2.

Table 3.2  $\lambda_{\max}$  of each dye solutions

Dye Types	$\lambda_{\max}$ (nm)
Acid Orange 7	450
Basic Yellow 2	444
Direct Green 26	617
Reactive Violet 5	555

##### 3.3.2.1 Preparation of Calibration Curve of Dye Solution at Various pH

Several concentrations of the aqueous dye solutions were prepared at pH 5, pH 7, and pH 9. The absorbance of each dye concentration was recorded at its  $\lambda_{\max}$  using UV/VIS spectrophotometer. The collection curve was plotted between dye concentration and absorbance. Calibration curve of each dye at pH 5, pH 7, and pH 9 are shown in Appendix C.

Table 3.3 shows the slope values obtained from the calibration curves plotted between the absorbance of dye solutions and their concentration.

Table 3.3 Slope values of the dye solutions at specified wavelength

Dye Types	Wavelength (nm)	Slope Value
Acid Orange 7	450	0.0221
Basic Yellow 2	444	0.0228
Direct Green 26	617	0.0162
Reactive Violet 5	555	0.0127

### 3.3.2.2 Effect of Various pH on Dye Stability

The aqueous dye solutions (100 mg/L) were prepared at pH 5, pH 7, and pH 9. The amount of 150 ml of each dye solution was stirred in oil bath at 30°C, 40°C, and 50°C for 12 hours. The absorbance of each dye remained in the supernatant after 0 h and 12 h stirred was calculated from Equation (3.1) and plotted against the pH.

$$Q_s = \frac{A_s}{S} \quad (3.1)$$

When  $Q_s$  = amount of dye in supernatant after 0 h or 12 h (mg/L)

$A_s$  = absorbance of dye in supernatant after 0 h or 12 h

$S$  = slope value from calibration curve of dye concentration and absorbance

### 3.3.3 Adsorption Procedure

Figure 3.5 shows the apparatus of adsorption experiment. Fifty milligrams of chitosan flakes were added into a 250-ml Erlenmeyer flask. The flask was vacuumed by vacuum pump. Approximately 0.5 ml of demineralized water dropped in the flask to fill pore of chitosan and slowly shake the flask for well mixed between deionized water and the adsorbent. Approximately 150 ml of aqueous dye solution with initial concentration of 100

mg/L, which adjusted to pH 5, pH 7, and pH 9, was poured into the flask. The pH of the system were adjusted by using 0.1M HCl or 0.1M NaOH. The suspension was stirred for 12 hours in oil bath at various temperatures (30°C, 40°C, and 50°C). After that, the suspension was separated by filter paper. The absorbances of the residual dye in solution were determined by using UV/VIS spectrophotometer at  $\lambda_{\text{max}}$  of each dye. The spent adsorbents were wash several times with demineralizes water to remove the unadsorbed dyes. The dye-sorbed adsorbents obtained were dried in vacuum oven at ambient temperature, kept away from light and collected in closed container for desorption study. Blanked used in the experiment were demineralizes water with the same pH corresponding to the dye solution.

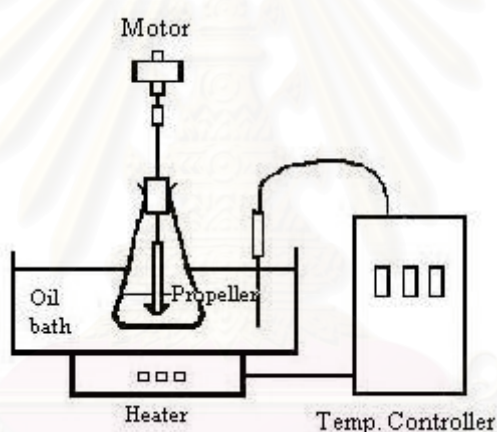


Figure 3.5 Schematic diagram of the experimental apparatus

#### 3.3.4 Desorption Procedure

Desorption of each dye-sorbed adsorbent approximately 50 mg was carried out in 150 ml of demineralizes water at pH varied to pH 5, pH 7, and pH 9. Demineralizes water was adjusted pH by using 0.1M HCl or 0.1M NaOH. The temperatures were set at 30°C, 40°C, and 50°C. The suspensions were stirred for 12 hours. The supernatant was separated by filter paper. The absorbances of desorbed dye in the supernatant were determined by using UV/VIS spectrophotometer at  $\lambda_{\text{max}}$  of each dye.

### 3.4 Analysis Technique and Errors of Experiments

This section is described analytic techniques and errors of experiments. UV/VIS spectrophotometer used for determined the residual dye in solution. The adsorbents were analyzes characteristic such as surface area and pore volume of adsorbents. Analytic procedure are described below but analytical result were shown in Chapter IV

#### 3.4.1 Surface Area and Pore Volume

A micromeritics model ASAP 2000 was used to determine surface area, pore volume, and pore size distribution of adsorbent. The instrument detects the volume of adsorbed nitrogen gas on surface at various relative pressures. There are two operating steps, degassing step and analysis step.

Firstly, the adsorbent was heated and placed under vacuum to remove moisture and other contaminants. Temperature of degassing was carried out at 150°C and vacuum until pressure dropped to 10 mmHg. After that, the sample was weighed and then the degassed sample was transfer from the degas port to the analysis port.

At the analysis port, the sample was analyzed at vacuum pressure of 15 mmHg and liquid nitrogen was used as a coolant. The nitrogen gas was used as analysis gas. The volume of adsorbed nitrogen on sample will relate with relative pressure ( $P/P_0$ ). The volumes of adsorbed nitrogen and relative pressure were plotted the graph. The Y-intercept and slope of the graph was calculated BET surface area of sample.

#### 3.4.2 Dye Concentration

Dye exhaustion or amount of dye adsorbed is usually defined in terms of difference between the initial and final dye concentrations. UV/VIS spectrophotometer is the most commonly used technique for quantitative determination of dye concentration. Usually the Beer-Lambert law is employed to determine the concentration of dye in solution from a measurement of absorbance at wavelength of maximum absorption dye.

$$\text{Absorbance} = \log \left( \frac{I_0}{I} \right) = acl \quad (3.2)$$

Where  $I_0$  = intensity of light incident optical cell holding the dye solution

$I$  = intensity of light transmitted through the cell

$a$  = absorptivity or extinction coefficient (L/g.cm) of dye

$c$  = concentration of dye solution in the cell (g/L)

$l$  = path length through the cell (cm)

### 3.4.3 Calculation of amount of adsorbed dye on the adsorbent

The amounts of adsorbed dyes were calculated from Equation (3.3), which was derived from Beer's law as follow:

$$Q_a = \frac{[C - (A_a - A_{bl})/S] \times V}{W \times 100} \quad (3.3)$$

Where  $Q_a$  = Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

$C$  = Initial concentration of dye (mg/L)

$A_a$  = Absorbance of unadsorbed dye after adsorption

$A_{bl}$  = Absorbance of blank

$S$  = Slope value from calibration curve of dye concentration and absorbance

$V$  = Volume of dye solution (mL)

$W$  = Weight of adsorbent (g)

### 3.4.3 Calculation of amount of desorbed dye from the adsorbent

The amount of desorbed dye were calculated from Equation (3.4), which was derived from Beer's law as follow:

$$Q_d = \frac{A_d \times V \times 100}{S \times Q_a \times W \times 1000} \quad (3.4)$$

Where  $Q_d$  = Amount of desorbed dye (%w/w)

$Q_a$  = Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

$A_d$  = Absorbance of desorbed dye

$S$  = Slope value from calibration curve of dye concentration and absorbance

$V$  = Volume of dye solution (mL)

$W$  = Weight of adsorbent (g)

### 3.4.5 Experimental and Analysis Error

#### 3.4.5.1 Experimental Error

In this section, experiments are conducted to verify repeatability, an average and a standard deviation value of the experiment. Equation (3.5) and Equation (3.6) define an average value and percent deviation.

$$\text{Average value} \quad \bar{X} = \frac{\sum x}{n} \quad (3.5)$$

$$\text{Percent deviation from average value} = \frac{\sqrt{(X - \bar{X})^2}}{X} \times 100 \quad (3.6)$$

After each experiment, the solution, feed, and spent adsorbents were separated. The solutions were analyzed to find the residual dye concentration in its by using UV/VIS spectrophotometer. The experiments were repeatedly adsorbed at the same condition for 5 times. The results of the experimental error were shown in Figures 3.6 to 3.9 Average concentration of dye and percent error are calculated and shown in Tables 3.4 to 3.7.

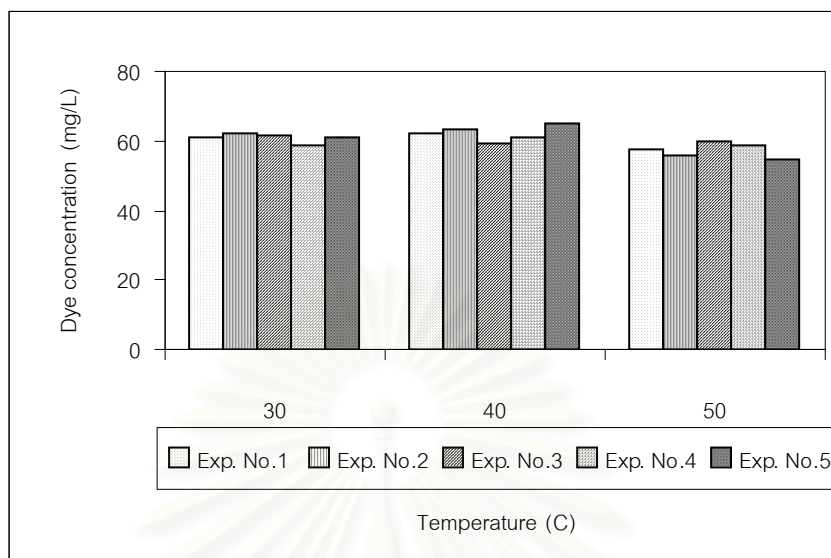


Figure 3.6 Amount of adsorbed dye for acid dye at various temperatures

Table 3.4 Average concentration and error of experiment at various temperatures of acid dye

Dye type	Acid dye		
	30	40	50
Temperature (°C)	30	40	50
Average concentration (mg/L)	60.81	62.06	57.37
Maximum error (%)	2.09	4.35	4.52
Minimum error (%)	3.24	4.65	4.72



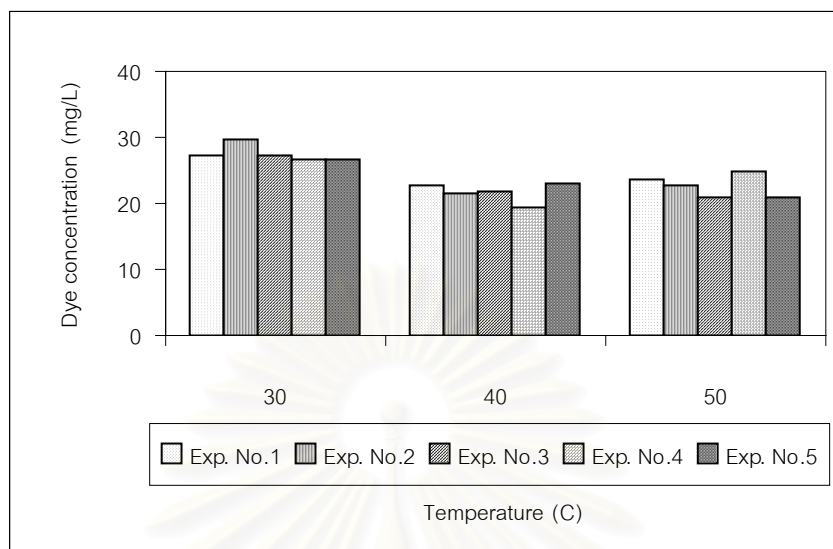


Figure 3.7 Amount of adsorbed dye for basic dye at various temperatures

Table 3.5 Average concentration and error of experiment at various temperatures of basic dye

Dye type	Basic dye		
Temperature (°C)	30	40	50
Average concentration (mg/L)	27.60	21.68	22.63
Maximum error (%)	7.50	10.02	10.76
Minimum error (%)	2.92	11.47	8.12

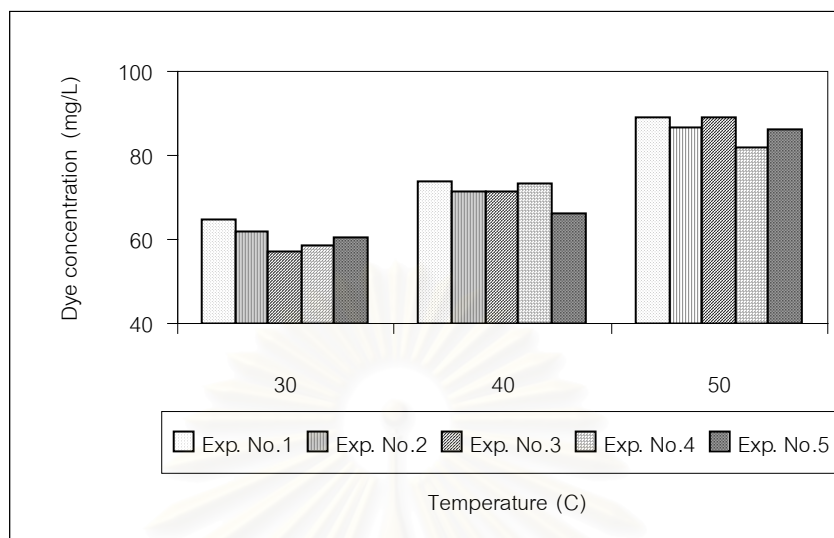


Figure 3.8 Amount of adsorbed dye for direct dye at various temperatures

Table 3.6 Average concentration and error of experiment at various temperatures of direct dye

Dye type	Direct dye		
	30	40	50
Temperature (°C)	30	40	50
Average concentration (mg/L)	60.59	71.21	86.52
Maximum error (%)	6.57	3.74	2.81
Minimum error (%)	5.48	6.77	5.40

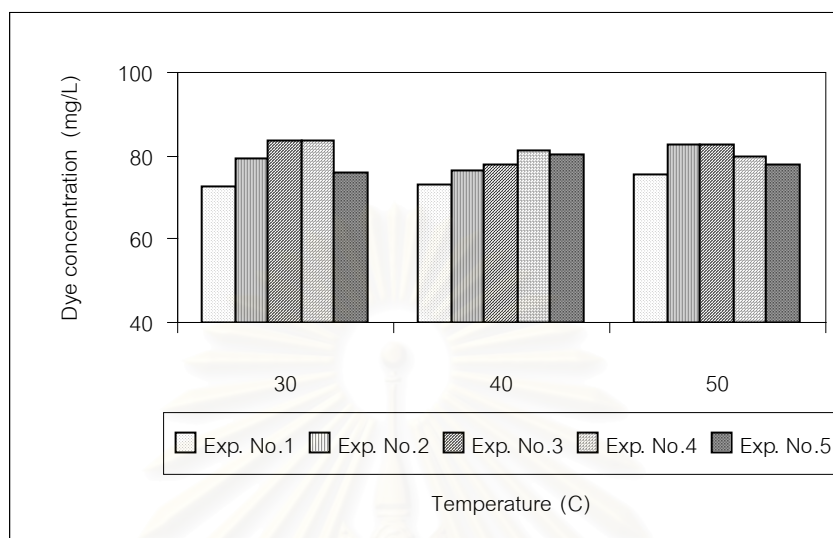


Figure 3.9 Amount of adsorbed dye for reactive dye at various temperatures

Table 3.7 Average concentration and error of experiment at various temperatures of reactive dye

Dye type	Reactive dye		
	30	40	50
Temperature (°C)	30	40	50
Average concentration (mg/L)	79.15	77.80	79.78
Maximum error (%)	6.06	4.59	3.94
Minimum error (%)	8.13	6.22	5.17

Table 3.4 shows average concentration and percent error in study of acid dye adsorption. Average concentration of dye is 60.81, 62.06, and 57.37 mg/L at 30°C, 40°C, and 50°C, respectively. Percent error of this experiment is in range of 2.09 to 4.72%. Average concentration and percent error in study of basic are shown in Table 3.5. Percent error has range from 2.92 to 11.47%. Table 3.6 and Table 3.7 show the result of direct dye and reactive dye, respectively. They found that percent error is in range of 3.74 to 6.77% and 3.94 to 8.13% for direct dye and reactive dye, respectively.

#### 3.4.5.2 Instrument Error

This experiment was conducted to verify instrumental error, average and deviation of experiments. The same sample was analyzed for 5 times by the instrument at the same condition. From analysis, the maximum percent deviation was in range of 3% for all dyes.

#### 3.4.5.3 Blank Test

The experiments conducted in this section are aimed to verify any possibility of dyes to be adsorbed on the glassware as well as their decomposition. Each dye is prepared at an initial concentration of 100 mg/L and at pH 5, 7, and 9. The temperatures used for the experiments are 30°C, 40°C, and 50°C and the time is 12 hours. Figures 3.6 to 3.7 show the results of this study. It is found that the concentration of all dyes remains constant at the end of 12 hours. So it can be concluded that dye is neither adsorbed on the glassware nor decomposed in this study

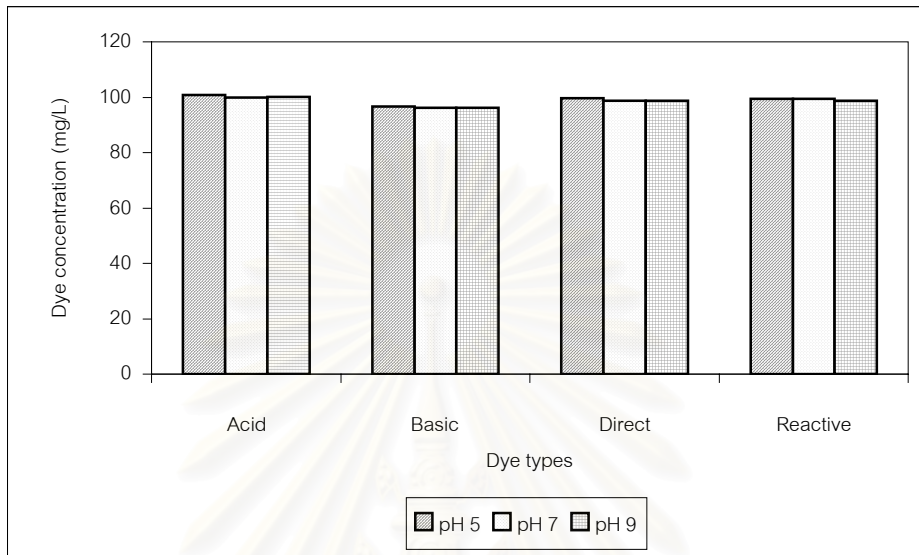


Figure 3.10 Dye concentration for blank test at various pH and 30°C

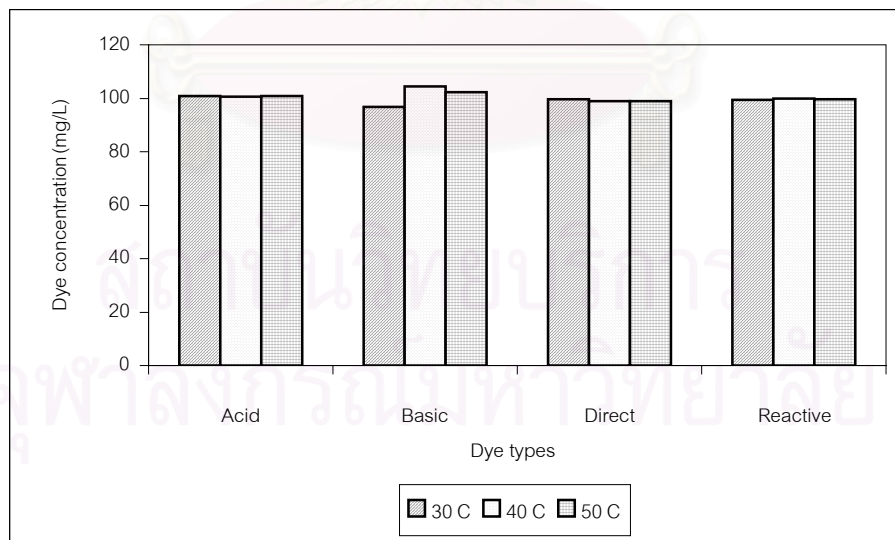


Figure 3.11 Dye concentration for blank test at various temperatures and pH 5

## CHAPTER IV

### RESULTS AND DISCUSSIONS

Experimental results and discussions on adsorption of water-soluble dyes by chitosan are presented in this chapter. Dyes can be classified by their application methods to fiber as acid, basic, direct, and reactive dyes. These dyes are water-soluble dyes. Experiments in this study are categorized into three parts:

Part 4.1: Preliminary experiments are conducted in order to find suitable quantity of adsorbent and contacting time.

Part 4.2: Adsorption experiments are conducted to study effects of aqueous solutions such as pH, temperature, initial dye concentration, particle size range, and degree of deacetylation.

Part 4.3: Desorption experiments are conducted to study effects of pH and temperature.

Three types of chitosan with different degree of deacetylation manufactured by Seafreash Chitosan (Lab) Co., Ltd., are used in this study. Surface area of chitosan was determined by BET surface analyzer which shown in Table 4.1.

Table 4.1 Surface area and pore diameter of chitosan

Degree of deacetylation (%)	Particle size (mm)	Surface area (m <sup>2</sup> /g)	Pore diameter (Å)
79	0.150-0.300	1.9012	60.4677
	0.300-0.425	1.6248	60.9734
	0.425-0.600	1.4876	60.2375
87	0.150-0.300	1.8348	118.9756
	0.300-0.425	1.7645	105.9288
	0.425-0.600	1.3527	129.8745
95	0.150-0.300	1.9195	128.4570
	0.300-0.425	1.7562	123.9007
	0.425-0.600	1.3106	103.2003

## 4.1 Experimental Procedure and Preliminary experimental results

This section describes adsorption experiment briefly and preliminary experimental results. Preliminary experiments were conducted in order to find effect of weight of adsorbent and contacting time on adsorption of dyes.

### 4.1.1 Adsorption Experiment

A 250-ml stirred batch is used for studying adsorption of water-soluble dyes by chitosan. In each experiment, chitosan is added to 150 ml of aqueous dye solution and stirred at constant temperature. After each experiment liquid and spent adsorbent are separated by filter paper (Whatman no.1). The spent adsorbents are washed several times with demineralized water to remove the unadsorbed dye. The dye-sorbed adsorbents obtained are dried in oven and kept in close container to avoid light for desorption study. Experimental results are shown in Appendix A.

The liquid products are analyzed by UV/VIS spectrophotometer to find the dye concentration. Instead of presenting the results in dye concentration, adsorbed dye is calculated using Equation 3.3 and is used for further discussion.

### 4.1.2 Effect of Adsorbent Weight and Effect of Contacting Time on Adsorption

The objectives of this section are to find suitable quantity of adsorbent and suitable length of time required for each subsequent experiment. The experiments are conducted at an ambient temperature (30°C) and an atmospheric pressure. Chitosan having degree of deacetylation of 79% and 0.300-0.425 mm in particle size is used as adsorbent. Initial concentration of each dye is 100 mg/L.

### Effect of Adsorbent Weight on Adsorption of Dyes

A set of experiments is conducted to find the effect of adsorbent weight on adsorption of dyes. The adsorbent weights vary from 0.02 gram to 0.1 gram while the contact time is kept at 12 hours. Effect of adsorbent weight on adsorption of dyes is shown in Figure 4.1. Efficiency of dye removal is considered from remaining dye or concentration of dye in liquid product. If remaining dye is high, efficiency is low. On the other hand, high efficiency is obtained when amount of dye in liquid product is low. The results indicate that content of acid, direct, and reactive dyes decrease linearly with amount of adsorbent used at low quantity of adsorbent, 0.02 gram to 0.06 gram. At high value of adsorbent weight, 0.06 gram to 0.1 gram, the quantity of dye adsorbed are almost the same. Quantity of basic dye removal is dose not change when adsorbent weight increases. The weight of adsorbent chosen for further study is 0.05 gram for all types of dyes.

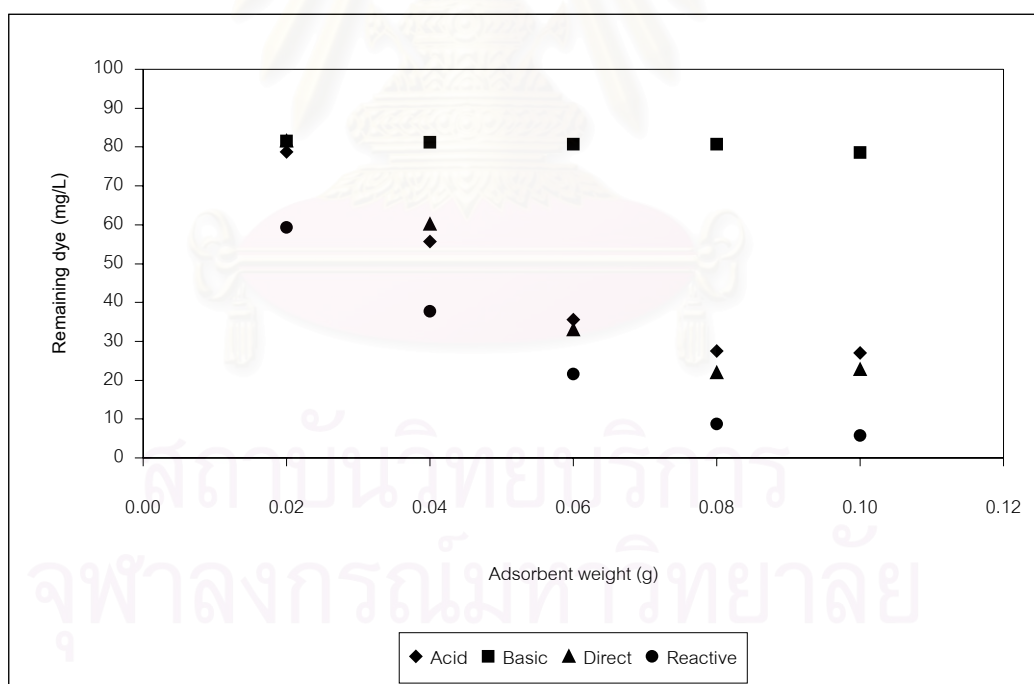


Figure 4.1 Amount of adsorbed dye at various of adsorbent weight at 30°C



### Effect of Contact Time on Adsorption of Dyes

A set of experiments is conducted to find the effect of contact time on adsorption of dyes. Contact time between adsorbent and liquid feed are varied from 3 to 18 hours. The results, shown in Figure 4.2, indicate that the ability of dye removal depends on the length of contact time for acid, direct, and reactive dyes.

The concentration curve of acid dye can be divided into two parts. In first period, 3 to 9 hours, dye in the bulk can be adsorbed rapidly on the adsorbent because of high dye concentration in the bulk solution. In final period, 12 to 18 hours, the concentration of dye in bulk is lower than the initial period and deposited dye retards transferring of dye from the bulk to adsorbent surface. Thus, rate of dye deposition on adsorbent is very slow and the concentration curve is nearly constant. From this set of experiments, the suitable constant time is considered. It indicated that the suitable time should be 12 hours because at this time, the removal of dye is so high and constant enough for studying in this thesis.

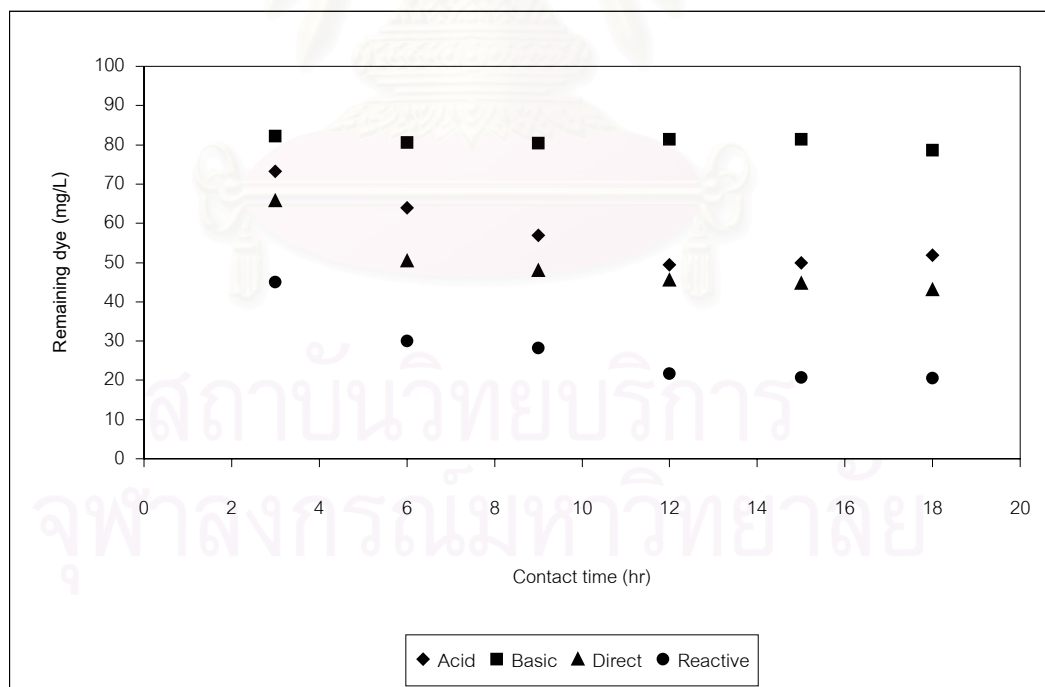


Figure 4.2 Amount of adsorbed dye various of contact time at 30°C and 1 atm

From the preliminary study, it can be summarized that suitable adsorbent weight is 0.05 gram, and contact time is 12 hours. This condition is used to study the others effect of dye adsorption experiment such as pH, temperature, initial dye concentration, particle size range of adsorbent and degrees of deacetylation of chitosan which are discussed in Section 4.2.

#### 4.2 Experimental results

This section describes adsorption behavior of chitosan with dye and results of effects of pH, temperature, initial dye concentration, particle size range and degree of deacetylation of chitosan. Table 4.2 shows all operating conditions of adsorption of each dye.

Table 4.2 Operating conditions of dye adsorption experiments

Adsorbent weight (mg)	50
Feed solution (ml)	150
Feed concentration (mg/L)	100
Time (hours)	12
Pressure (atm)	1
Dye types	Acid Orange 7 Basic Yellow 2 Direct Green 26 Reactive Violet 5
Initial pH of feed	5, 7, 9
Temperature (°C)	30, 40, 55
Initial dye concentration (mg/L)	100, 250, 500
Particle size (mm)	0.150-0.300 0.300-0.425 0.425-0.600
Degree of deacetylation (%)	79, 87, 95

Desorption experiments of selected spent adsorbents were also conducted using conditions shown in Table 4.3. The results of adsorption and desorption experiments are shown in Appendix A.

Table 4.3 Operating conditions of dye desorption experiments

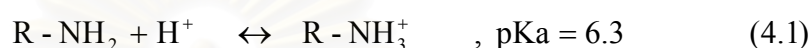
Adsorbent weight (mg)	50
Feed solution (ml)	150
Time (hours)	12
Pressure (atm)	1
Dye types	Acid Orange 7 Basic Yellow 2 Direct Green 26 Reactive Violet 5
Initial pH of feed	5, 7, 9
Temperature (°C)	30, 50

#### 4.2.1 Adsorption Behavior of Dye on Chitosan

Adsorption of dye takes place when dye transfers from solution to the adsorbent. Interaction between the dye and the adsorbent can be considered by their chemistry to be similar to that in dyeing process. The dyes are attracted to the adsorbent because of chemical interactions between the dye molecules and the adsorbent. Chemical structure of the dye consists of two important components, chromophore and auxochrome. Chromophore is a functional group which absorb and reflect color at different wavelength. Different colors observed are the results of wavelength of chromophore absorb and reflect. Auxochrome is a smaller group added to increase intensity of color and changes insoluble molecule to a water-soluble molecule. Water-soluble dyes contain at least one solubilising group, most commonly a sulphonic acid group ( $-\text{SO}_3^-$ ). The three most important of these dyes are acid, direct, and reactive dyes. Acid Orange 7, Direct Green 26 and Reactive Violet 5, used in the

experiments, contain sulphonic group in their chemical structures. The chemical structures of acid, direct, and reactive are shown in Figures 3.1 to 3.3.

Chitosan is a known effective adsorbent in the adsorption of metal ions and dyes because the amino ( $\text{NH}_2$ ) and hydroxy ( $\text{OH}$ ) groups on its chains can serve as coordination and electrostatic interactions. In aqueous solution, the amino group of chitosan ( $\text{R-NH}_2$ ) can be protonated to  $\text{R-NH}_3^+$  according to Equation 4.1. (WU et al. 1999, 2001)



Previous studies, Wu et al. 2001, indicated that the uptake of transition metals (positive charge) on chitosan is mainly effected via coordinated with their unprotonated amino groups ( $\text{R-NH}_2$ ). For anionic compounds, the uptake of them on chitosan occurs via electrostatic interaction with their protonated amino groups ( $\text{R-NH}_3^+$ ).

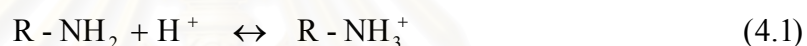
The different mechanisms of interaction between cation on unprotonated amino groups and anion on protonated amino groups of chitosan can be experimentally supported from pH changes after the adsorption experiments.

Initial pH of solution was adjusted to pH 5, pH 7, and pH 9 using 0.1M HCl or 0.1M NaOH. After each adsorption experiments, the pH of the solution was measured. At initial pH 5, pH 7, and pH 9, the pH value after adsorption experiment change to 6.26-7.18, 6.75-7.19, and 6.95-7.57, respectively. The different pH value after adsorption experiments can be explained by using Equation 4.1. Behavior of chitosan is the same as buffer. Equilibrium of Equation 4.1 shift to pKa which equalize 6.3. When the initial pH of solution is less than 6.3 such pH 5, after adsorption experiments it is found that the pH of solution increases. When the initial pH of solution is higher than 6.3, after adsorption experiments it is found that the pH of solution decreases. The results indicate an agreement with Equation 4.1.

#### 4.2.2 Effect of pH on Dye Adsorption

A set of experiments is conducted to study the effects of pH on adsorption of dyes. Initial pH of dye solutions in this study are 5, 7, and 9. The comparisons of adsorption ability of each dye on chitosan at various initial pH are illustrated in Figures 4.3 to 4.6. It is shown that ability of chitosan on adsorption of each type of dyes strongly depend on initial pH of the solution at all operating temperatures. Acid, direct, and reactive dyes can be adsorbed on chitosan better in acidic solution (low pH value) and basic dye can be adsorbed better in alkaline solution.

Previous studies (Wu et al. 1999, 2001, Yoshida et al. 1993) indicated that adsorption of metal ions and dyes occurred on amino group ( $\text{NH}_2$ ) of chitosan. In aqueous solution, amino group of chitosan may be protonated as the following equation



The positive charge of amino group ( $\text{NH}_3^+$ ) of chitosan can react with negative charges of adsorbate.

When acid, direct, and reactive dyes are dissolved in water. They are dissociated into anionic compounds. These dyes can be adsorbed by the electrostatic attraction between anionic ions and  $\text{RNH}_3^+$ .

In acidic solution, excess of  $\text{H}^+$  can react with amino groups ( $\text{RNH}_2$ ) of chitosan and  $\text{RNH}_3^+$  occurs. This amino group ( $\text{RNH}_3^+$ ) can react with anionic dyes which results in high adsorption ability of chitosan and anionic dyes in acidic solutions.

In alkaline solution,  $\text{H}^+$  does not exist in large quantity.  $\text{RNH}_3^+$  exist in small quantity. Thus in alkaline solution, acid, direct, and reactive dyes can be adsorbed by chitosan is less quantity than in acidic solution.

Basic dye is a cationic compound when it is dissolved in water. It can be adsorbed by amino groups ( $\text{RNH}_2$ ) of chitosan in a similar manner as  $\text{H}^+$ .

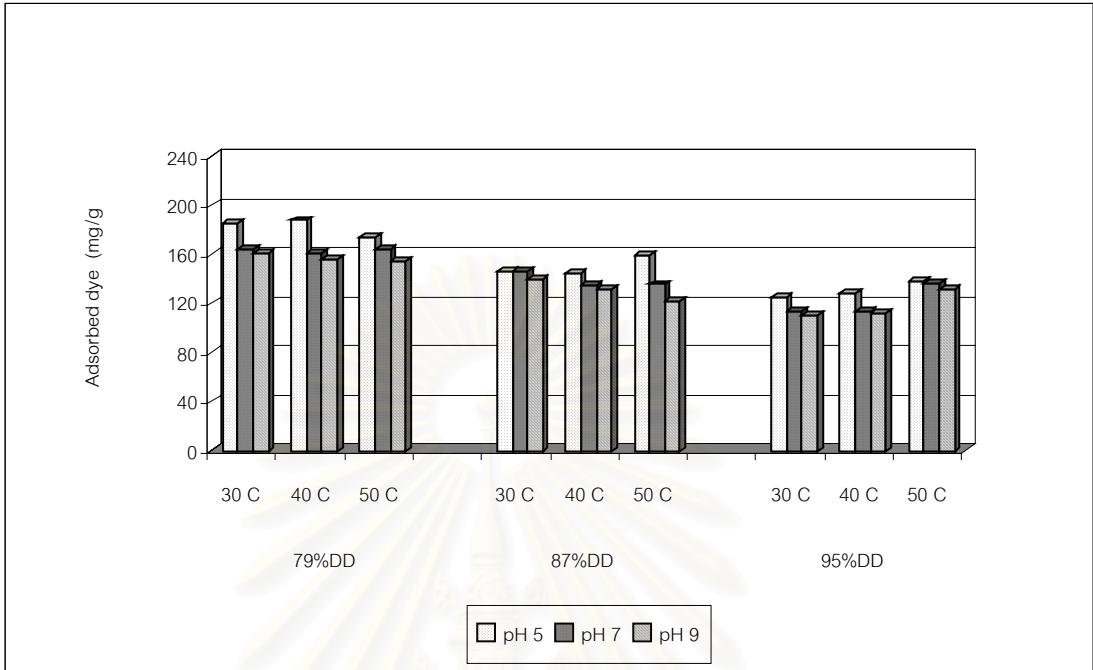


Figure 4.3 Effect of pH on the adsorption of Acid Orange 7

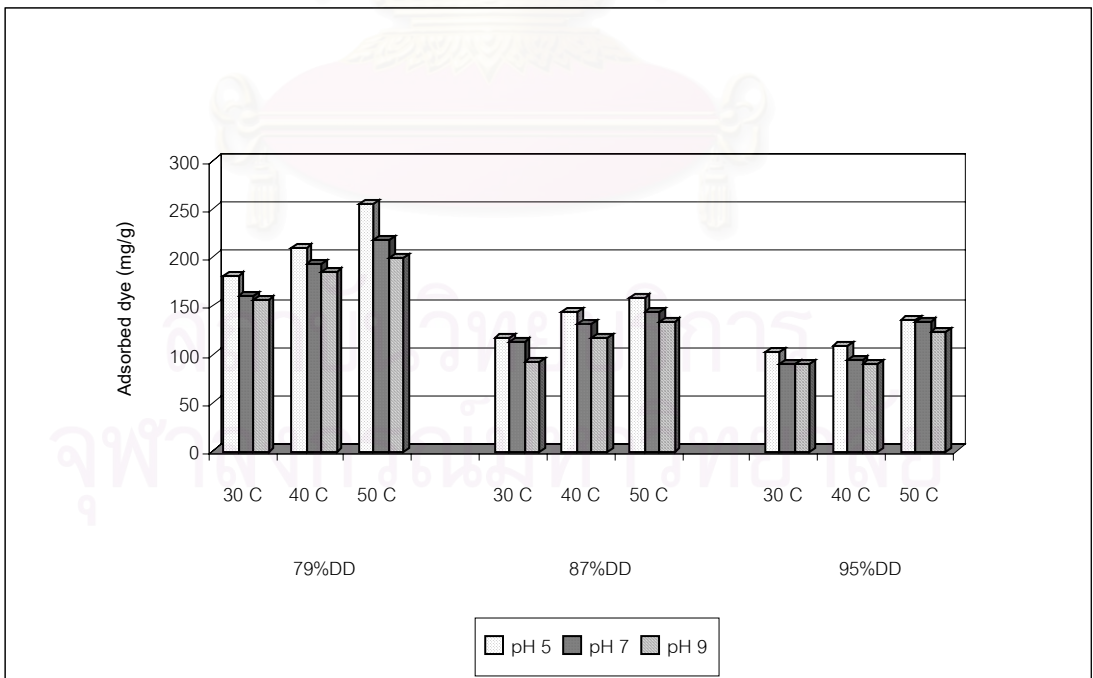


Figure 4.4 Effect of pH on the adsorption of Direct Green 26

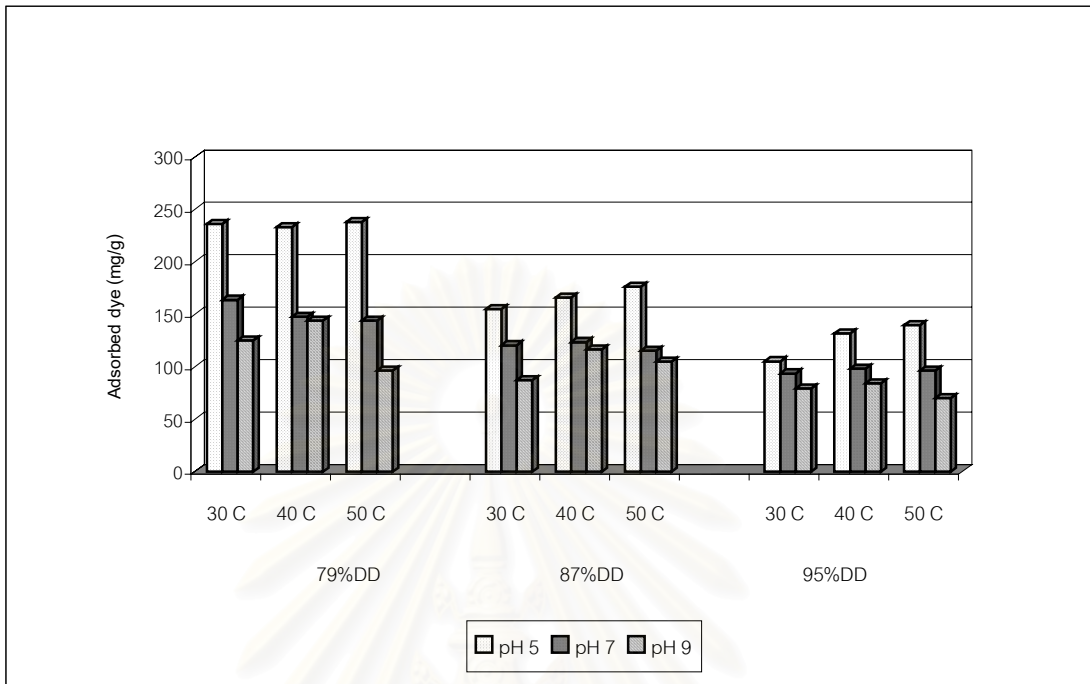


Figure 4.5 Effect of pH on the adsorption of Reactive Violet 5

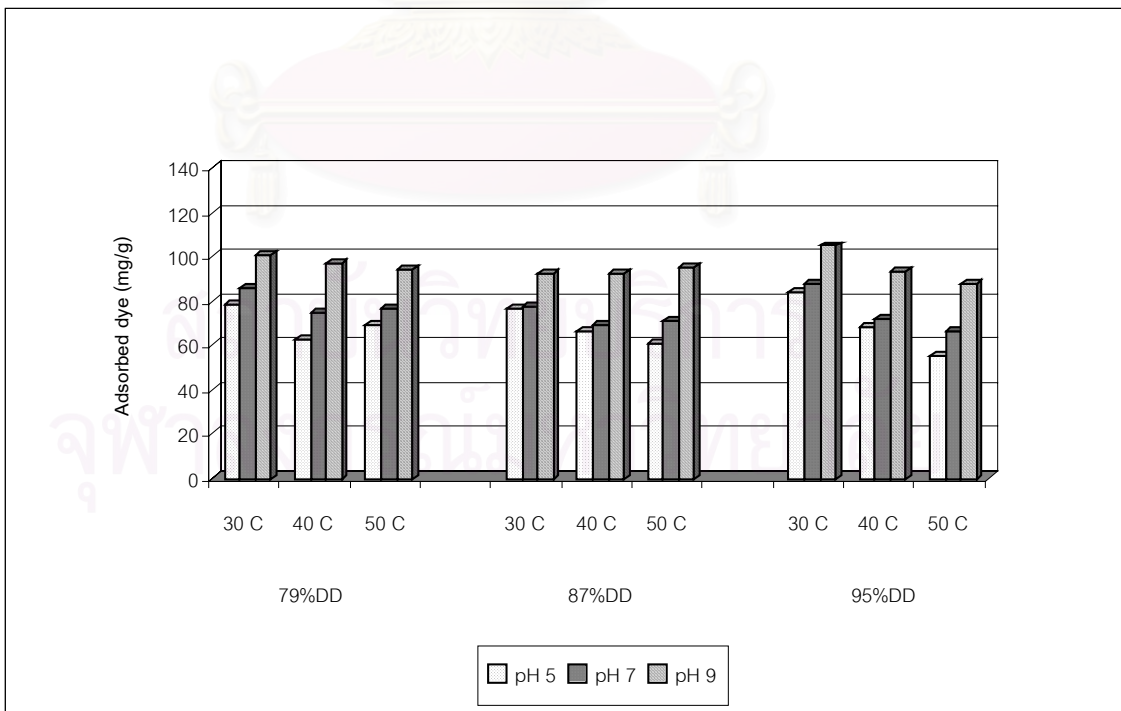


Figure 4.6 Effect of pH on the adsorption of Basic Yellow 2

In acidic solution, large quantity of  $H^+$  exists in the solution, so there is an adsorption competition between  $H^+$  and cation of basic dye onto  $RNH_2$ . Thus adsorption ability of basic dye on chitosan in acidic solution is lower than in alkaline solution.

In alkaline solution,  $H^+$  does not exist in large quantity. It does not have adsorption competition of  $H^+$  and cation of basic dye, so basic dye can be adsorbed by amino group ( $RNH_2$ ) higher quantity than in acidic solution.

#### 4.2.3 Effect of Temperature on Dye Adsorption

In this section, the experiments are conducted at various temperatures in order to study the effect of operating temperature on dye adsorption. Figures 4.7 to 4.10 show the results that plotted amount of adsorbed dyes and temperatures. It is shown that adsorption ability of acid dye nearly constant when temperature increased. So, it may be conclude that adsorption ability of acid dye independent with temperature. Adsorption ability of direct dye increases with increasing operating temperature. When temperature increased adsorption ability of reactive dye change but it cannot be observed their trend. So, it cannot be concluded. Adsorption ability of basic dye slightly decreases with increasing operating temperature.

Adsorption of dye is mass transfer of dye to the adsorbent. Mass transfer resistance, including external and intraparticle mass transfer resistance, are the function of the diffusivity coefficient according of Stokes-Einstein equation (James R, Welty, 1984) as follow

$$D_{AB} = kT/6 \pi r \mu_B$$

Where  $D_{AB}$  = Diffusivity

$k$  = Boltzmann constant

$T$  = Temperature



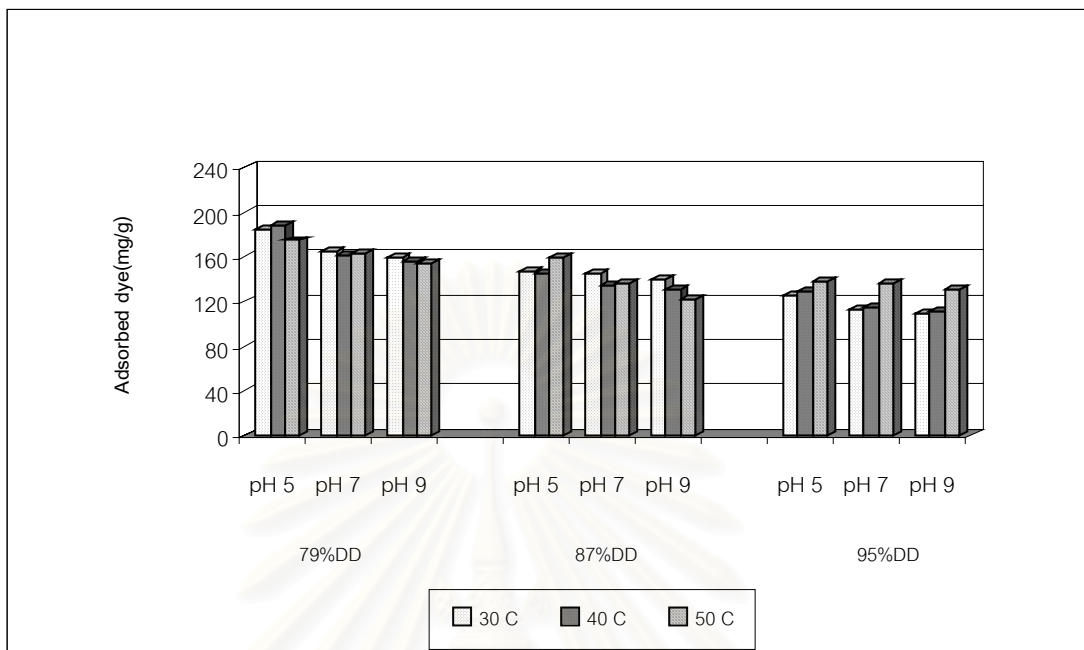


Figure 4.7 Effect of temperature on the adsorption of Acid Orange 7

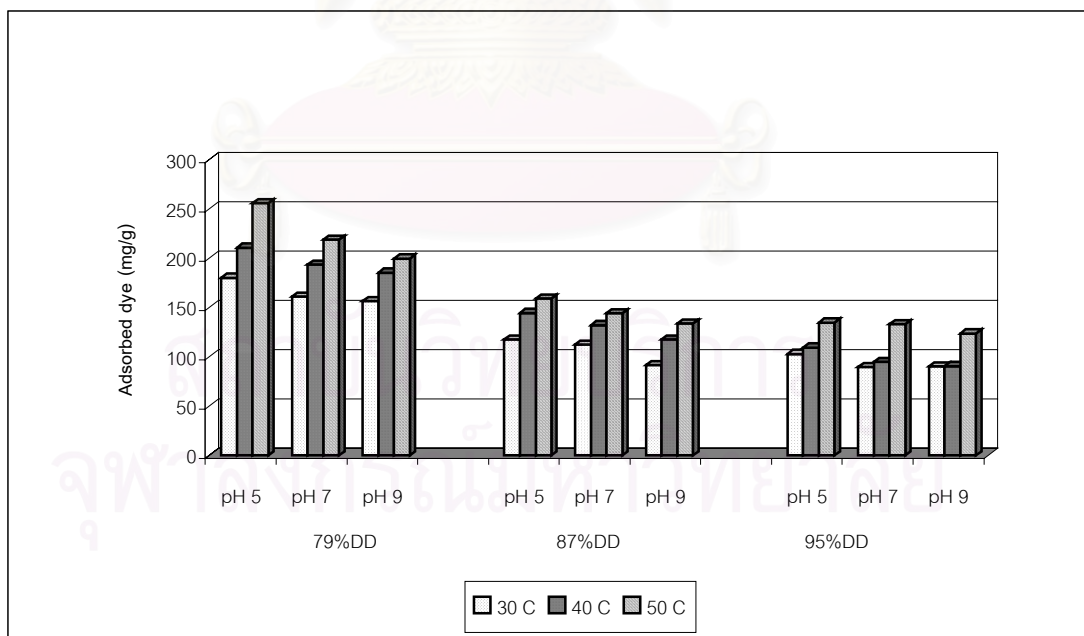


Figure 4.8 Effect of temperature on the adsorption of Direct Green 26

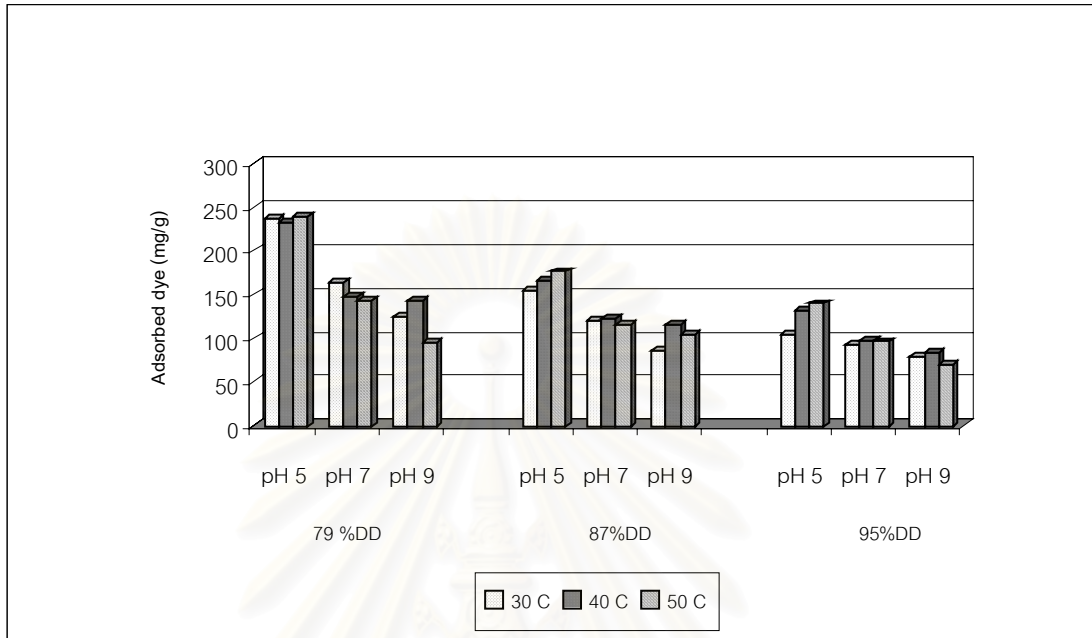


Figure 4.9 Effect of temperature on the adsorption of Reactive Violet 5

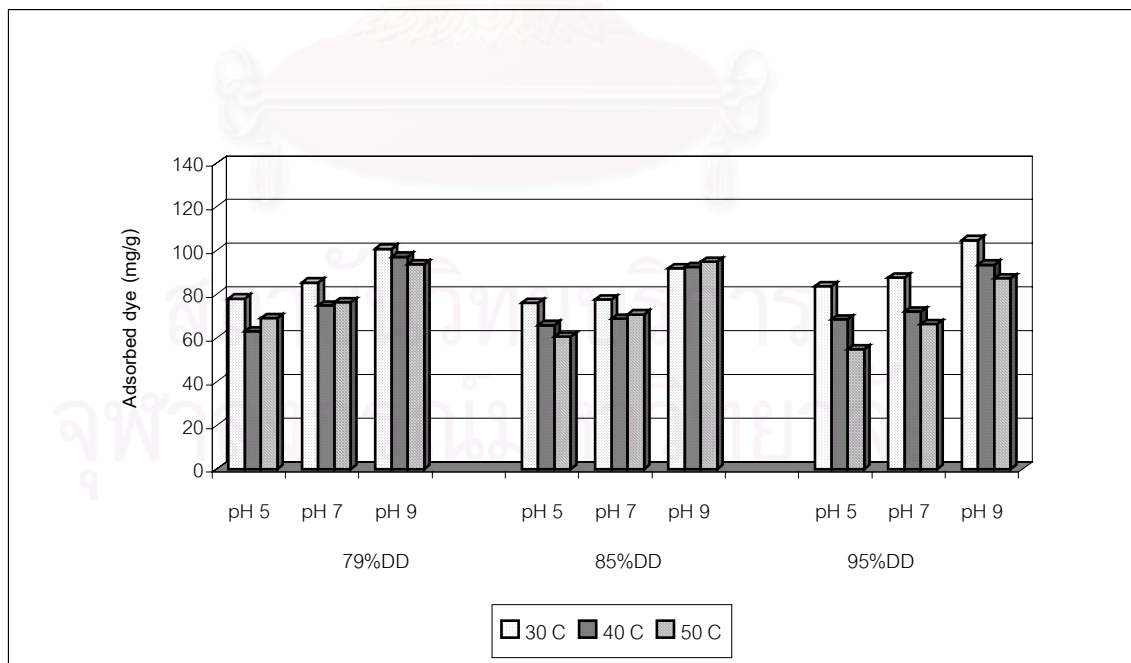


Figure 4.10 Effect of temperature on the adsorption of Basic Yellow 2

$r$  = solute particle radius

$\mu_B$  = solvent viscosity

Diffusivity coefficient increases with increasing temperature result in adsorption ability of direct dye increase with increasing operating temperature.

Adsorption ability of Basic Yellow 2 slightly decreases when temperature increased. This may since a rise in temperature increases the escaping tendency of dye molecules from an interface of adsorbent. The bond formed between chitosan and dye might be quite reversible in this case. Thereby, Basic Yellow 2 can penetrate onto chitosan at high temperature less quantity than at low temperature.

#### 4.2.4 Effect of Degree of Deacetylation of Chitosan on Dye Adsorption

A set of experiments is conducted to study effect of degree of deacetylation of chitosan on adsorption of dyes. Chitosan is classified on the basis of their degree of deacetylation (DD). Degree of deacetylation in this study is 79%, 87%, and 95%. Figures 4.11 to 4.14 show the comparison of degree of deacetylation of chitosan on adsorption of acid, direct, reactive, and basic, respectively. It is shown that acid, direct, and reactive dyes can be adsorbed on chitosan better at low degree of deacetylation (79%DD) and basic dye can be adsorbed better at high degree of deacetylation (95%DD).

The results do not agree with previous studied. Kim et al. (1997) found that the adsorption ability of chitosan on adsorption of Acid Blue 40, Acid Blue 193, Direct Yellow 44, and Direct Blue 78 increased with increasing of degree of deacetylation of chitosan from 10.7% to 46.8% but when degree of deacetylation of chitosan increase to 67.2% the adsorption ability slightly decreased.

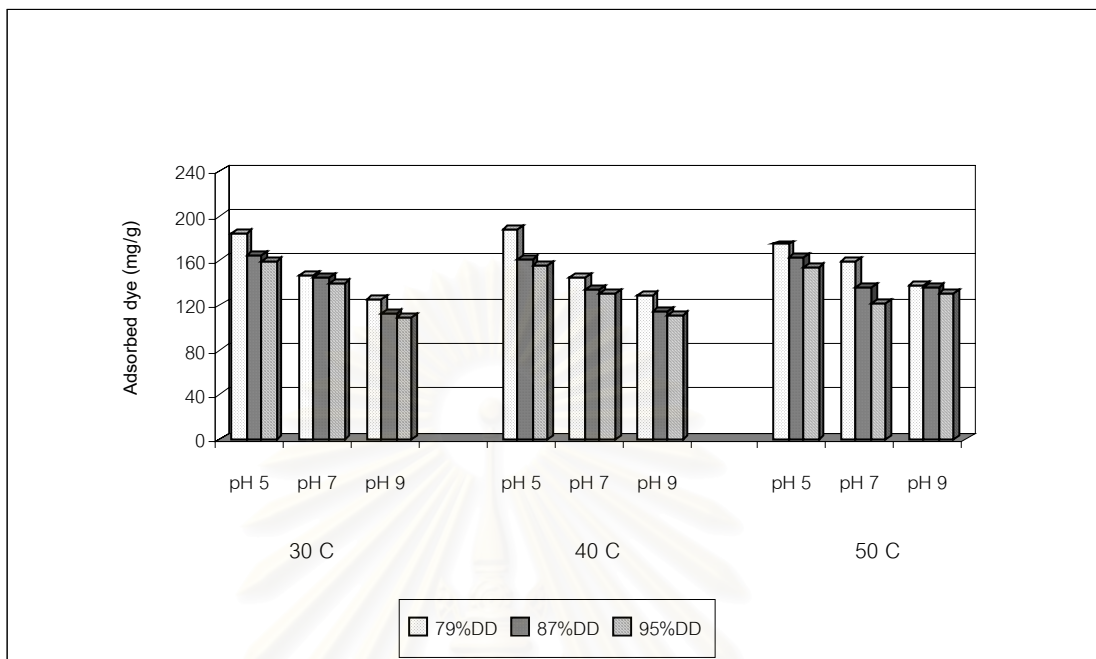


Figure 4.11 Effect of degree of deacetylation of adsorbent on adsorption of Acid Orange 7

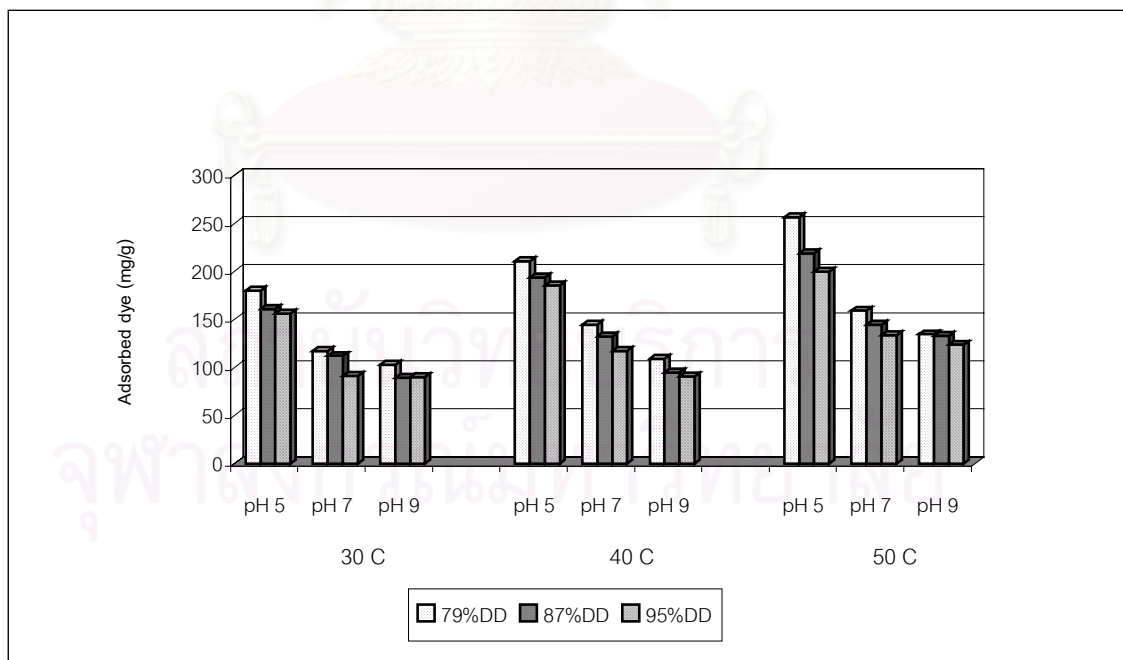


Figure 4.12 Effect of degree of deacetylation of adsorbent on adsorption of Direct Green 26

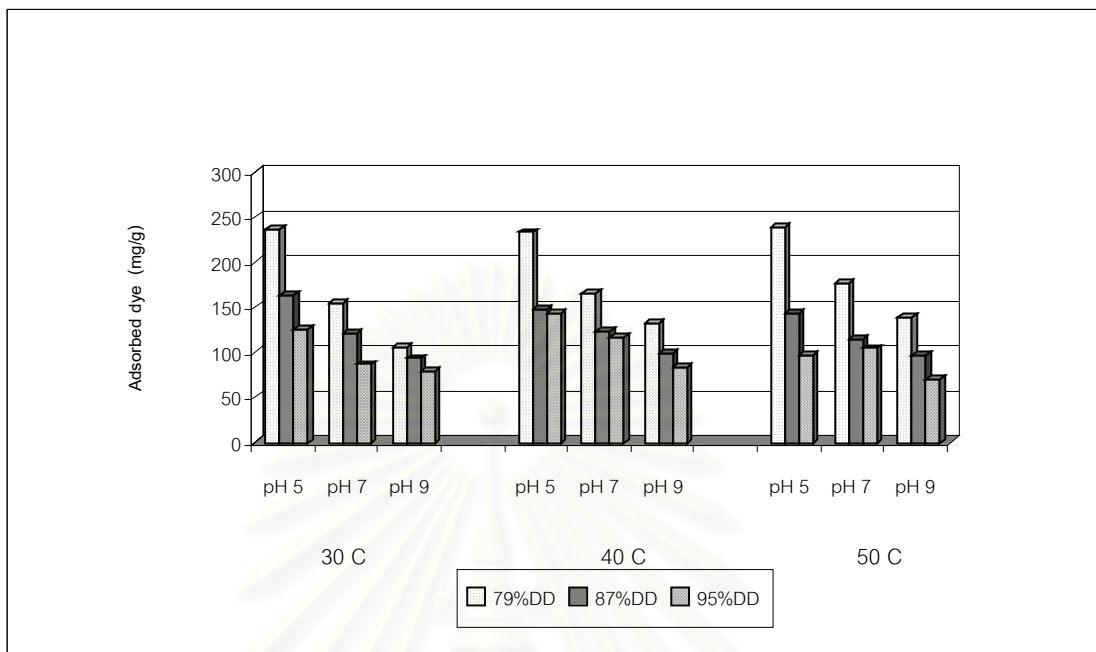


Figure 4.13 Effect of degree of deacetylation of adsorbent on adsorption of Reactive Violet 5

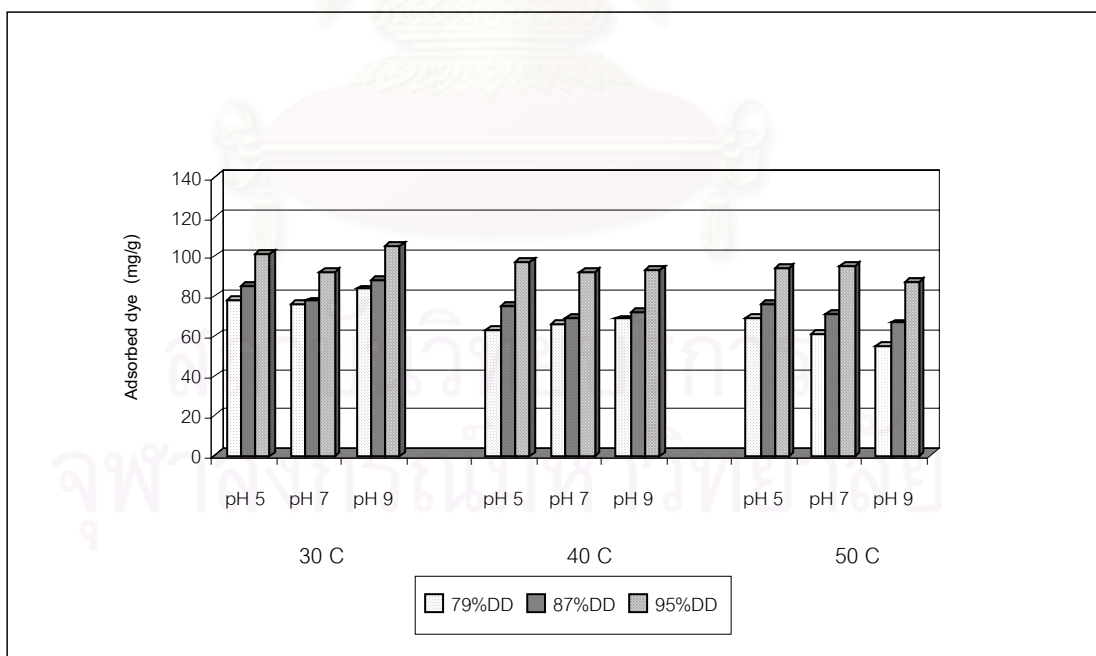


Figure 4.14 Effect of degree of deacetylation of adsorbent on adsorption of Basic Yellow 2

Chamnanmanoontham (1999) also found that the adsorption ability increased with increasing degree of deacetylation on adsorption of Acid Red 360, Direct Red 80, and Reactive Red 158 and the highest amount of adsorbed dyes was not from the highest degree of deacetylation of chitosan (79.55%) used in her experiments. The highest amounts of adsorbed dyes are obtained for chitosan with 71.08%DD for acid and direct dye and 60.71% for reactive dye. For basic dye, the amount of adsorbed dye is rather constant with increasing %DD and the highest amount of adsorbed dye is from the lowest %DD used. This mainly due to the increase of amino group in chitosan, thus it can interact with dye ions higher.

But this reason cannot be used to explain in high degree of deacetylation as the same as in this experiment (79-95%DD). It can be concluded that when adsorption ability of each dye reached to maximum efficiency the amount of adsorbed dye on chitosan independent with amount of amino group on chitosan. This may suggest that high degree of deacetylation does not need to adsorb dye for high efficiency.

#### 4.2.5 Effect of Initial Dye Concentration on Dye Adsorption

A set of experiment is conducted to study effect of initial dye concentration on adsorption of dye by chitosan. Concentrations of each dye are varied at the varied of 100, 250, and 500 mg/L. 79%DD chitosan is used as adsorbent. Temperature is fixed at 30°C and contact time is 12 hours. Acid, direct, and reactive dyes are adjusted to pH 5 and basic dye is adjusted to pH 9 due to that pH show the highest adsorption ability of each dye. The results of the effect of initial dye concentration of acid, basic, direct, and reactive dyes are shown in Figure 4.15. Amount of adsorbed dye of acid, direct, reactive, and basic dyes slightly increase with increasing of initial concentration of each dye.

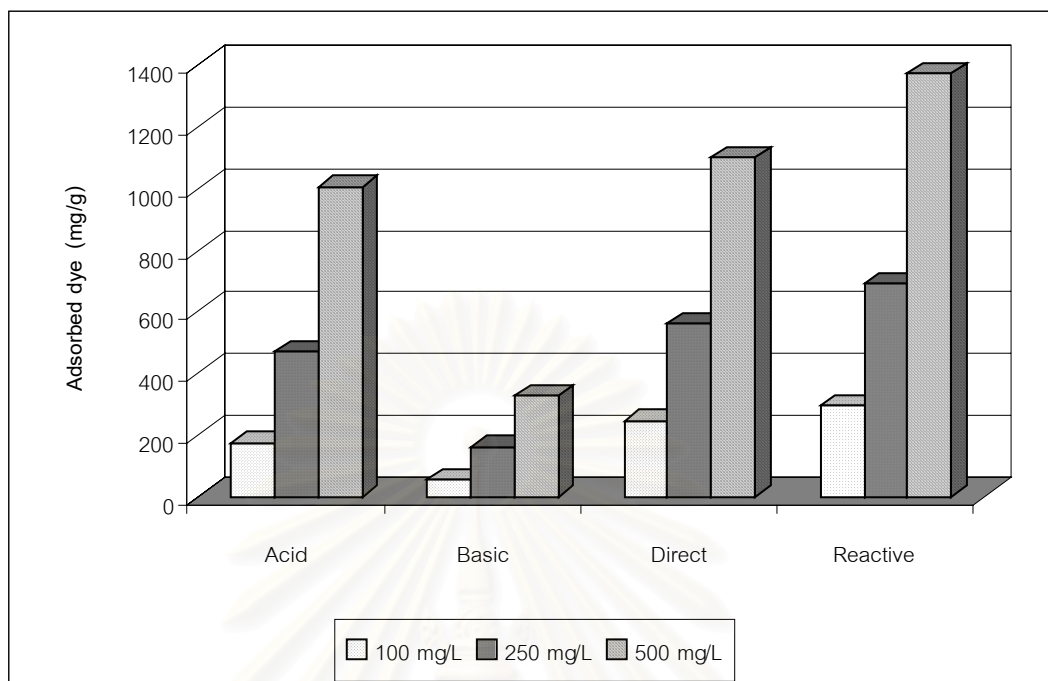


Figure 4.15 Effect of initial dye concentration of Acid Orange 7, Basic Yellow 2, Direct Green 26, and Reactive Violet 5 on dye adsorption.

At high concentration, dye ions exist in large quantity. They can be adsorbed by chitosan are higher quantity than in low concentration

#### 4.2.6 Effect of Particle Size of Adsorbent on Dye Adsorption

A set of experiments is conducted to study effect of particle size of adsorbent on adsorption of each dye. Figures 4.16 to 4.19 show the effect of particle size of adsorbent on dye adsorption at 30°C at specified pH and contact time. It is shown that four types of dyes are similar trends. The adsorption ability of acid, basic, direct, and reactive dyes decreases with increasing particle size of all types of chitosan.

Chitosan are sieved into three particle size ranges. Surface area of adsorbent determined by BET surface area analyzer. Table 4.1 shows surface area and

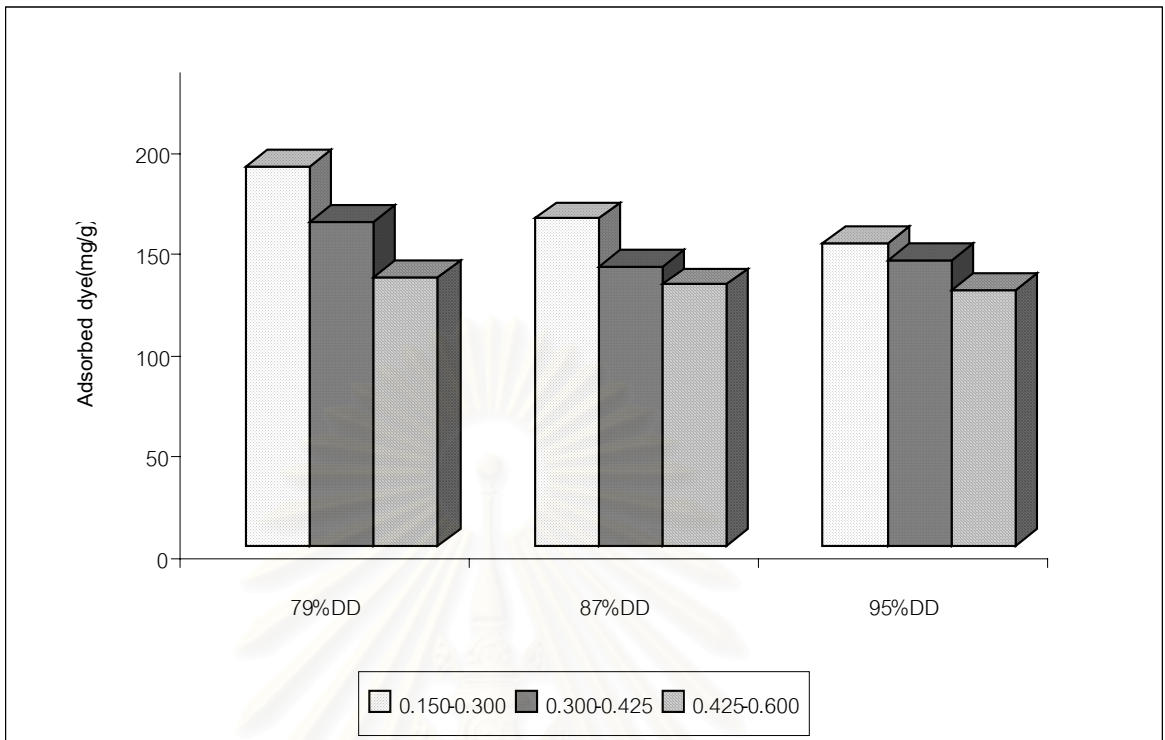


Figure 4.16 Effect of particle sizes of adsorbents on adsorption of Acid Orange 7

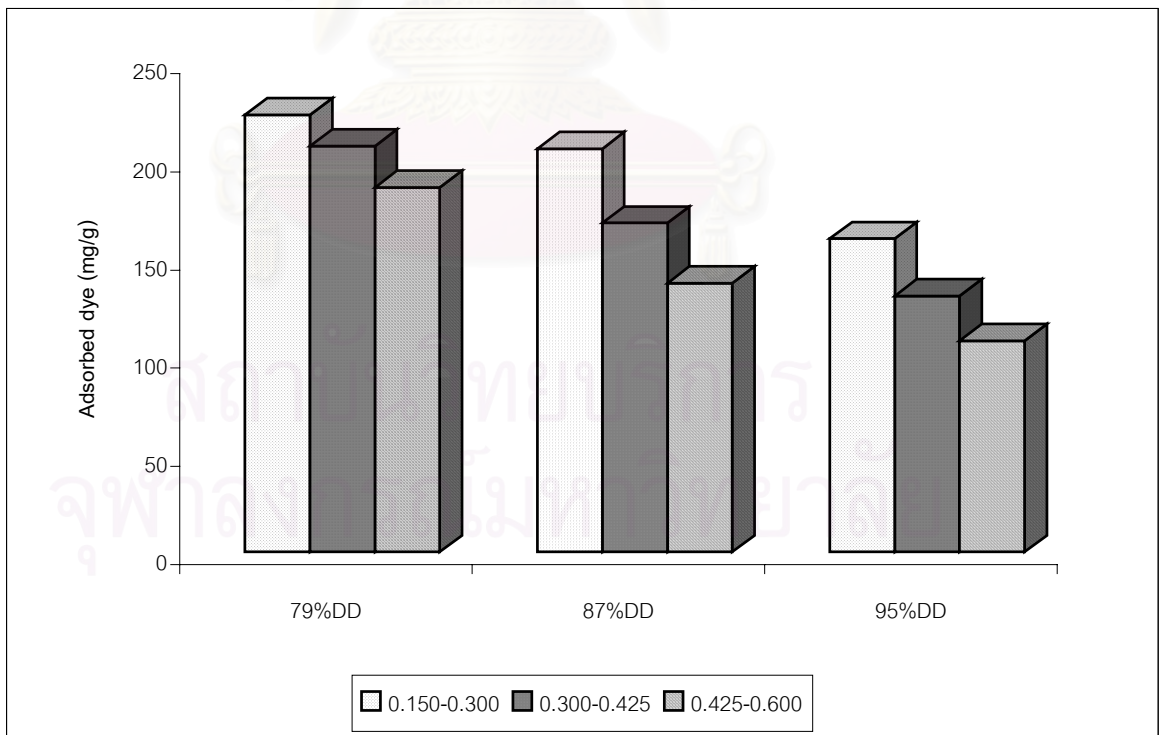


Figure 4.17 Effect of particle sizes of adsorbents on adsorption of Direct Green 26



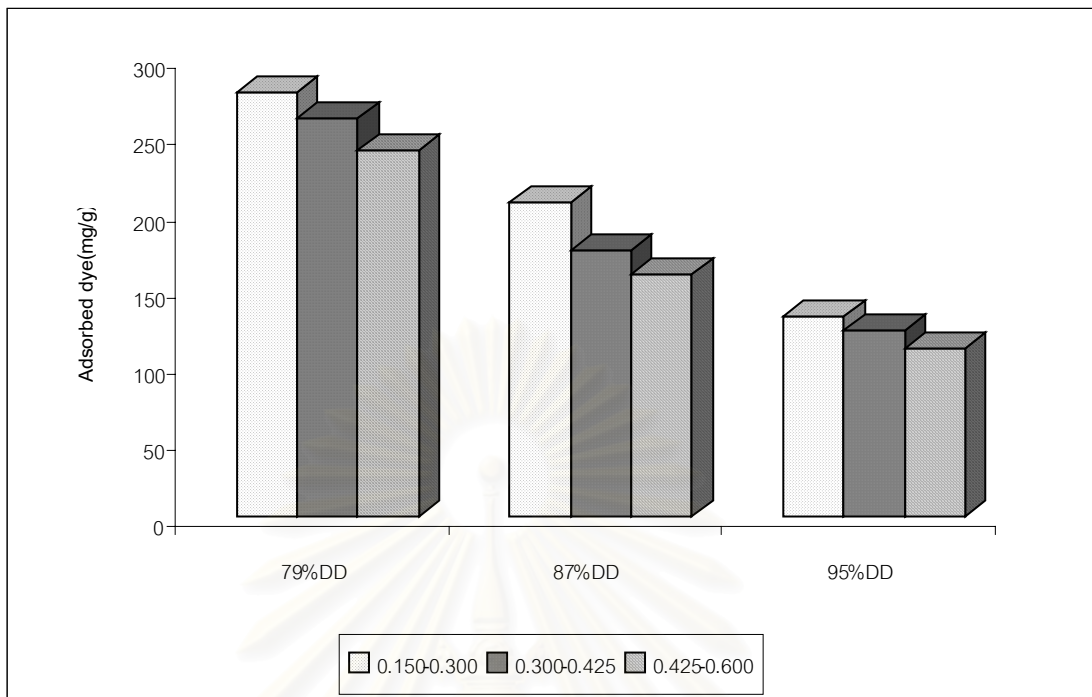


Figure 4.18 Effect of particle sizes of adsorbents on adsorption of Reactive Violet 5

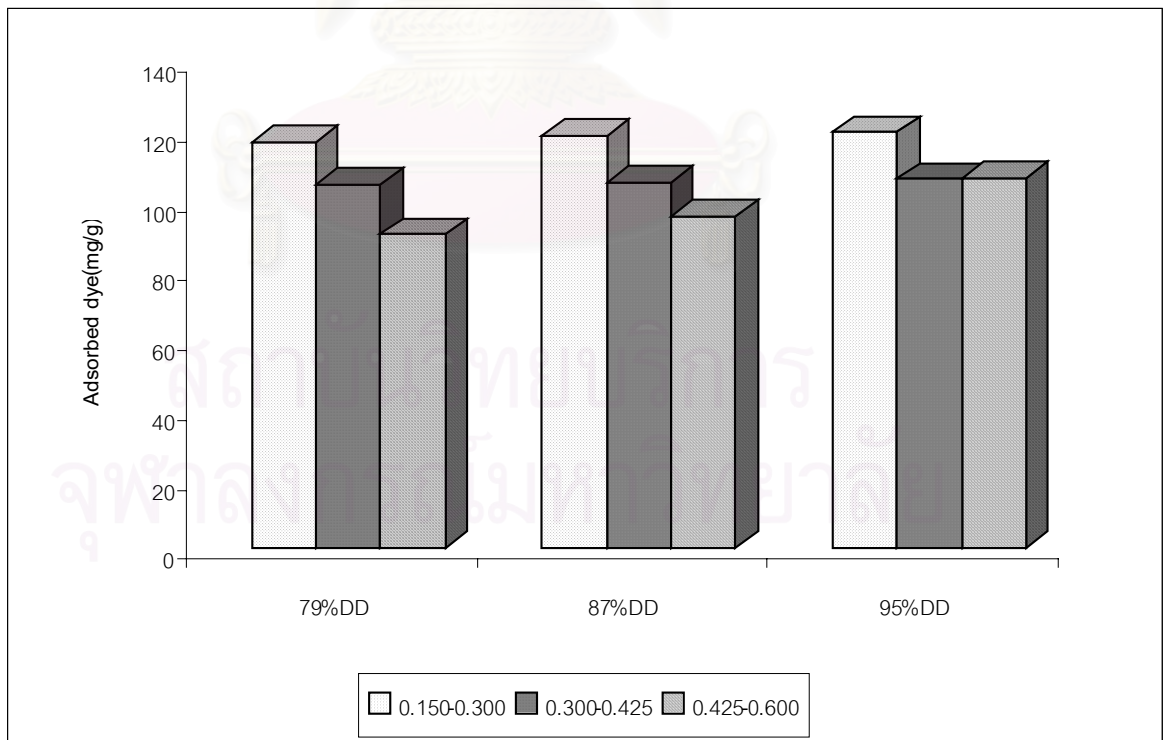


Figure 4.19 Effect of particle sizes of adsorbents on adsorption of Basic Yellow 2

pore diameter of each particle size range of adsorbent. It is found that the smallest particle size range has the highest surface area. So, the dye ions can be adsorbed on surface area of the smallest particle size range higher quantity than medium, and the highest particle size range.

Similar to previous studies, Juang et al. (1997) studied adsorption of three reactive dyes on chitosan. Similar trend for all dye, an increases in capacity with decreasing particle size mainly suggests that the dye do not completely penetrate the particle or partly that the dyes preferentially adsorb near the outer surface of the particle.

McKay et al. (1982) found that chitin particle size has little or no influence on its ability to adsorb Mordant Yellow 5 and Acid Blue 158. In case of the large Direct Red 84 dye molecule, a particle size effect can be observed.

Annadurai et al. (1999) observed that as the particle size decreased, the adsorption of reactive dye increases. Such an effect is probably due to the ability of the large dye ion molecules to penetrate more of the internal pore structure of chitin and similar phenomenon is reported previously (McKay et al., 1982, 1983), for the adsorption of certain dyes on chitin and activated carbon.

### 4.3 Dye Desorption

This set of experiments is conducted to study effect of pH and temperature on dye desorption. The operating condition of dye desorption is shown Table 4.3. The operating conditions of dye desorption are in range of dye adsorption. Results of these factors are described as follow.

#### 4.3.1 Effect of pH on Dye Desorption

A set of experiments is conducted in order to study effect of pH on dye desorption. Results of acid, direct, reactive, and basic are presented in Figure 4.20. It is shown that percent of dye desorption from the adsorbent is very low for all types of dye in operating pH test.

Previous studies, Kim et al. (1997) found that the dye desorption from the deacetylated chitin is almost negligible up to pH 9 at 25°C, but it increase considerably at pHs higher than 10. Increasing pH could results in reduction of  $\text{NH}_3^+$  ions from the deacetylated chitin, facilitating desorption of the dyes from the adsorbent.

Chamnanmanoontham (1999) found that percent of basic dye desorption from chitosan increases with decreasing pH. At pH3, percent of basic dye desorption shows the highest quantity.

In this experiment, percent of dye desorption from the adsorbent is very low for all types of dye in operating pH test. Thus, it can neglect the dye desorption occurring.

#### 4.3.2 Effect of temperature on Dye Desorption

A set of experiments is conducted in order to study effect of temperature on dye desorption. Results of acid, direct, reactive, and basic are presented in Figure 4.21. Percent of dye desorption slightly increases with increasing temperature from 30°C to 50°C.

Kim et al. (1997) suggested that synergistic swelling effects of chitosan caused by high temperature, resulting in easy desorption.

A rise of temperature will damage the bond between the adsorbed-dye and the adsorbent. It increases the escaping tendency of the adsorbed-dye from interface of the adsorbent. Then, the adsorbed-dye can be desorbed easily when the temperature increase.

From the results of pH and temperature on dye desorption in this experiment, it can be concluded that the dye desorption can be neglected since it vary low values.

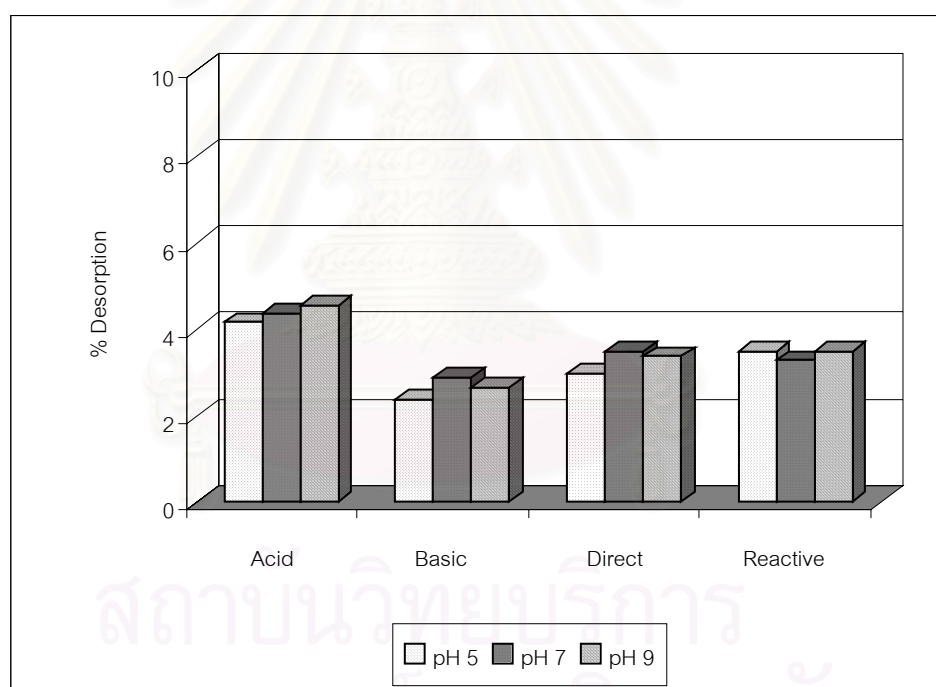


Figure 4.20 Effect of pH on dye desorption

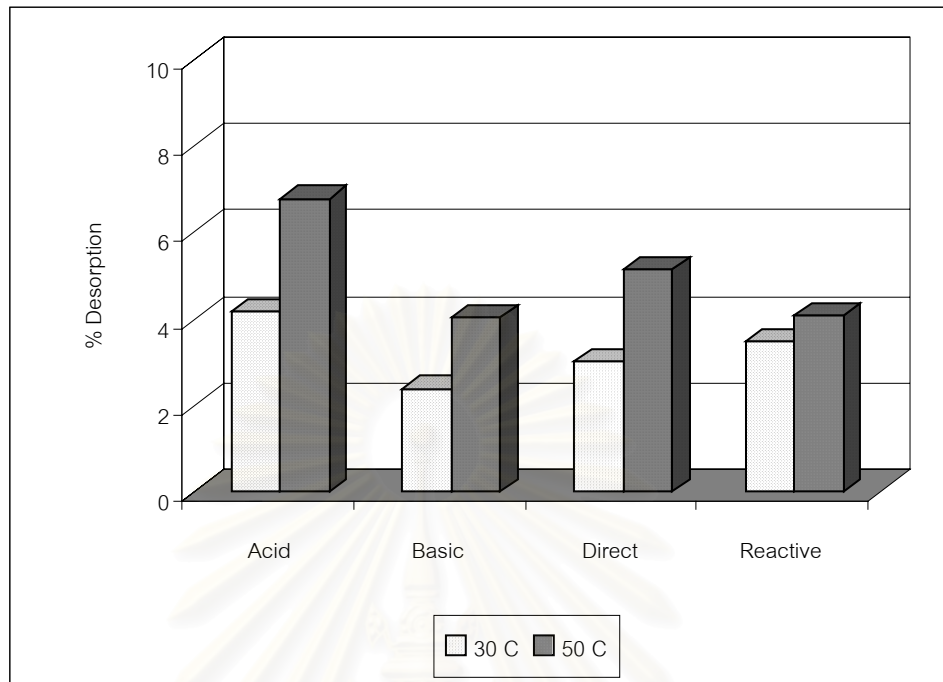


Figure 4.21 Effect of temperature on dye desorption

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## CHAPTER V

### CONCLUSIONS

#### 5.1 Conclusions

The following conclusions are drawn from the study:

1. All three types of chitosan can be used to remove acid, direct, reactive, and basic dyes.
2. Removal of water-soluble dyes using chitosan depends on type of water-soluble dyes.
3. Adsorption ability of each type of dye depends on initial pH solution. Acid, direct, and reactive dyes can be adsorbed on chitosan better in acidic solution (low pH value) and basic dye can be adsorbed better in alkaline solution.
4. Adsorption ability of some type of dye depends on operating temperature. Adsorption ability of acid dye is independent of temperature. Adsorption ability of direct dye increases with increasing operating temperature and decreases with increasing operating temperature for basic dye. For reactive dye, it cannot be concluded.
5. Adsorption ability of each type of dye depends on degree of deacetylation of chitosan. Acid, direct, and reactive dyes can be adsorbed on chitosan better at low degree of deacetylation (79%DD) and basic dye can be adsorbed better at high degree of deacetylation (95%DD).
6. Adsorption ability of each type of dye depends on initial concentration of dye. Adsorption ability of acid, direct, reactive, and basic dyes slightly increases with increasing initial concentration of each dye.

7. Adsorption ability of each type of dye depends on particle size of chitosan. Adsorption ability of acid, direct, reactive, and basic dyes decreases with increasing of particle size of chitosan.

8. Desorption of each type of dye independent with pH range in this study.

9. Desorption of each type of dye depends on temperature. Percent desorption of each type of dye slightly increases with increasing temperature.



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APPENDICES

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## Appendix A

Table A1 Conditions and results of adsorption experiments

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
1	Acid	79%DD	0.300-0.425	0.02	100.77	7	12	30	164.60
2	Acid	79%DD	0.300-0.425	0.04	100.77	7	12	30	168.84
3	Acid	79%DD	0.300-0.425	0.06	100.77	7	12	30	162.90
4	Acid	79%DD	0.300-0.425	0.08	100.77	7	12	30	137.28
5	Acid	79%DD	0.300-0.425	0.10	100.77	7	12	30	110.70
6	Basic	79%DD	0.300-0.425	0.02	99.06	7	12	30	130.78
7	Basic	79%DD	0.300-0.425	0.04	99.06	7	12	30	67.03
8	Basic	79%DD	0.300-0.425	0.06	99.06	7	12	30	46.01
9	Basic	79%DD	0.300-0.425	0.08	99.06	7	12	30	34.42
10	Basic	79%DD	0.300-0.425	0.10	99.06	7	12	30	30.63
11	Direct	79%DD	0.300-0.425	0.02	101.01	7	12	30	195.08
12	Direct	79%DD	0.300-0.425	0.04	101.01	7	12	30	178.09
13	Direct	79%DD	0.300-0.425	0.06	101.01	7	12	30	186.32
14	Direct	79%DD	0.300-0.425	0.08	101.01	7	12	30	160.46
15	Direct	79%DD	0.300-0.425	0.10	101.01	7	12	30	127.35
16	Reactive	79%DD	0.300-0.425	0.02	99.98	7	12	30	299.85
17	Reactive	79%DD	0.300-0.425	0.04	99.98	7	12	30	233.49
18	Reactive	79%DD	0.300-0.425	0.06	99.98	7	12	30	195.85
19	Reactive	79%DD	0.300-0.425	0.08	99.98	7	12	30	171.07
20	Reactive	79%DD	0.300-0.425	0.10	99.98	7	12	30	141.35
21	Acid	79%DD	0.300-0.425	0.05	101.27	7	3	30	83.31
22	Acid	79%DD	0.300-0.425	0.05	101.27	7	6	30	110.86
23	Acid	79%DD	0.300-0.425	0.05	101.27	7	9	30	131.99
24	Acid	79%DD	0.300-0.425	0.05	101.27	7	12	30	154.76
25	Acid	79%DD	0.300-0.425	0.05	101.27	7	15	30	153.26

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
26	Acid	79%DD	0.300-0.425	0.05	101.27	7	18	30	147.67
27	Basic	79%DD	0.300-0.425	0.05	99.57	7	3	30	51.87
28	Basic	79%DD	0.300-0.425	0.05	99.57	7	6	30	57.00
29	Basic	79%DD	0.300-0.425	0.05	99.57	7	9	30	57.53
30	Basic	79%DD	0.300-0.425	0.05	99.57	7	12	30	54.63
31	Basic	79%DD	0.300-0.425	0.05	99.57	7	15	30	54.63
32	Basic	79%DD	0.300-0.425	0.05	99.57	7	18	30	62.66
33	Direct	79%DD	0.300-0.425	0.05	100.22	7	3	30	123.07
34	Direct	79%DD	0.300-0.425	0.05	100.22	7	6	30	168.99
35	Direct	79%DD	0.300-0.425	0.05	100.22	7	9	30	176.59
36	Direct	79%DD	0.300-0.425	0.05	100.22	7	12	30	183.62
37	Direct	79%DD	0.300-0.425	0.05	100.22	7	15	30	186.40
38	Direct	79%DD	0.300-0.425	0.05	100.22	7	18	30	191.22
39	Reactive	79%DD	0.300-0.425	0.05	100.94	7	3	30	167.70
40	Reactive	79%DD	0.300-0.425	0.05	100.94	7	6	30	212.58
41	Reactive	79%DD	0.300-0.425	0.05	100.94	7	9	30	218.02
42	Reactive	79%DD	0.300-0.425	0.05	100.94	7	12	30	237.62
43	Reactive	79%DD	0.300-0.425	0.05	100.94	7	15	30	240.69
44	Reactive	79%DD	0.300-0.425	0.05	100.94	7	18	30	241.17
45	Acid	79%DD	0.425-0.600	0.05	100.28	5	12	30	187.84
46	Acid	79%DD	0.425-0.600	0.05	100.28	5	12	30	185.46
47	Acid	79%DD	0.425-0.600	0.05	100.28	5	12	30	183.28
48	Acid	79%DD	0.425-0.600	0.05	100.28	5	12	30	183.15
49	Acid	79%DD	0.425-0.600	0.05	100.28	5	12	30	177.31
50	Basic	79%DD	0.425-0.600	0.05	99.76	9	12	30	88.227

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
51	Basic	79%DD	0.425-0.600	0.05	99.76	5	12	30	81.52
52	Basic	79%DD	0.425-0.600	0.05	99.76	5	12	30	81.25
53	Basic	79%DD	0.425-0.600	0.05	99.76	5	12	30	79.68
54	Basic	79%DD	0.425-0.600	0.05	99.76	5	12	30	79.68
55	Direct	79%DD	0.425-0.600	0.05	100.89	5	12	30	196.56
56	Direct	79%DD	0.425-0.600	0.05	100.89	5	12	30	188.78
57	Direct	79%DD	0.425-0.600	0.05	100.89	5	12	30	184.52
58	Direct	79%DD	0.425-0.600	0.05	100.89	5	12	30	178.04
59	Direct	79%DD	0.425-0.600	0.05	100.89	5	12	30	174.34
60	Reactive	79%DD	0.425-0.600	0.05	99.12	5	12	30	248.94
61	Reactive	79%DD	0.425-0.600	0.05	99.12	5	12	30	248.70
62	Reactive	79%DD	0.425-0.600	0.05	99.12	5	12	30	234.76
63	Reactive	79%DD	0.425-0.600	0.05	99.12	5	12	30	225.55
64	Reactive	79%DD	0.425-0.600	0.05	99.12	5	12	30	215.63
65	Acid	79%DD	0.425-0.600	0.05	100.79	5	12	40	196.76
66	Acid	79%DD	0.425-0.600	0.05	100.79	5	12	40	191.74
67	Acid	79%DD	0.425-0.600	0.05	100.79	5	12	40	188.61
68	Acid	79%DD	0.425-0.600	0.05	100.79	5	12	40	185.90
69	Acid	79%DD	0.425-0.600	0.05	100.79	5	12	40	179.79
70	Basic	79%DD	0.425-0.600	0.05	98.89	5	12	40	68.62
71	Basic	79%DD	0.425-0.600	0.05	98.89	5	12	40	65.09
72	Basic	79%DD	0.425-0.600	0.05	98.89	5	12	40	61.67
73	Basic	79%DD	0.425-0.600	0.05	98.89	5	12	40	61.28
74	Basic	79%DD	0.425-0.600	0.05	98.89	5	12	40	55.55
75	Direct	79%DD	0.425-0.600	0.05	100.5	5	12	40	223.17

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	PH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
76	Direct	79%DD	0.425-0.600	0.05	100.5	5	12	40	221.50
77	Direct	79%DD	0.425-0.600	0.05	100.5	5	12	40	215.20
78	Direct	79%DD	0.425-0.600	0.05	100.5	5	12	40	215.20
79	Direct	79%DD	0.425-0.600	0.05	100.5	5	12	40	200.57
80	Reactive	79%DD	0.425-0.600	0.05	99.44	5	12	40	242.34
81	Reactive	79%DD	0.425-0.600	0.05	99.44	5	12	40	239.27
82	Reactive	79%DD	0.425-0.600	0.05	99.44	5	12	40	231.71
83	Reactive	79%DD	0.425-0.600	0.05	99.44	5	12	40	227.93
84	Reactive	79%DD	0.425-0.600	0.05	99.44	5	12	40	217.30
85	Acid	79%DD	0.425-0.600	0.05	99.95	5	12	50	179.71
86	Acid	79%DD	0.425-0.600	0.05	99.95	5	12	50	176.05
87	Acid	79%DD	0.425-0.600	0.05	99.95	5	12	50	171.98
88	Acid	79%DD	0.425-0.600	0.05	99.95	5	12	50	168.18
89	Acid	79%DD	0.425-0.600	0.05	99.95	5	12	50	163.83
90	Basic	79%DD	0.425-0.600	0.05	98.97	5	12	50	71.778
91	Basic	79%DD	0.425-0.600	0.05	98.97	5	12	50	68.094
92	Basic	79%DD	0.425-0.600	0.05	98.97	5	12	50	64.805
93	Basic	79%DD	0.425-0.600	0.05	98.97	5	12	50	59.805
94	Basic	79%DD	0.425-0.600	0.05	98.97	5	12	50	59.542
95	Direct	79%DD	0.425-0.600	0.05	99.98	5	12	50	266.79
96	Direct	79%DD	0.425-0.600	0.05	99.98	5	12	50	266.42
97	Direct	79%DD	0.425-0.600	0.05	99.98	5	12	50	259.57
98	Direct	79%DD	0.425-0.600	0.05	99.98	5	12	50	259.20
99	Direct	79%DD	0.425-0.600	0.05	99.98	5	12	50	245.50
100	Reactive	79%DD	0.425-0.600	0.05	99.71	5	12	50	247.87



Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
101	Reactive	79%DD	0.425-0.600	0.05	99.71	5	12	50	247.63
102	Reactive	79%DD	0.425-0.600	0.05	99.71	5	12	50	238.42
103	Reactive	79%DD	0.425-0.600	0.05	99.71	5	12	50	232.28
104	Reactive	79%DD	0.425-0.600	0.05	99.71	5	12	50	226.14
105	Acid	79%DD	0.425-0.600	0.05	100.90	5	12	30	185.14
106	Acid	79%DD	0.425-0.600	0.05	100.90	7	12	30	163.97
107	Acid	79%DD	0.425-0.600	0.05	100.90	9	12	30	160.03
108	Acid	87%DD	0.425-0.600	0.05	100.90	5	12	30	146.86
109	Acid	87%DD	0.425-0.600	0.05	100.90	7	12	30	145.64
110	Acid	87%DD	0.425-0.600	0.05	100.90	9	12	30	139.13
111	Acid	95%DD	0.425-0.600	0.05	100.05	5	12	30	124.75
112	Acid	95%DD	0.425-0.600	0.05	100.05	7	12	30	112.80
113	Acid	95%DD	0.425-0.600	0.05	100.05	9	12	30	109.55
114	Acid	79%DD	0.425-0.600	0.05	100.50	5	12	40	187.74
115	Acid	79%DD	0.425-0.600	0.05	100.50	7	12	40	160.73
116	Acid	79%DD	0.425-0.600	0.05	100.50	9	12	40	155.98
117	Acid	87%DD	0.425-0.600	0.05	100.50	5	12	40	144.44
118	Acid	87%DD	0.425-0.600	0.05	100.50	7	12	40	134.53
119	Acid	87%DD	0.425-0.600	0.05	100.50	9	12	40	130.73
120	Acid	95%DD	0.425-0.600	0.05	100.14	5	12	40	128.43
121	Acid	95%DD	0.425-0.600	0.05	100.14	7	12	40	113.90
122	Acid	95%DD	0.425-0.600	0.05	100.14	9	12	40	111.05
123	Acid	79%DD	0.425-0.600	0.05	100.82	5	12	50	174.59
124	Acid	79%DD	0.425-0.600	0.05	100.82	7	12	50	163.59
125	Acid	79%DD	0.425-0.600	0.05	100.82	9	12	50	153.55

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
126	Acid	87%DD	0.425-0.600	0.05	100.82	5	12	50	159.79
127	Acid	87%DD	0.425-0.600	0.05	100.82	7	12	50	135.49
128	Acid	87%DD	0.425-0.600	0.05	100.82	9	12	50	121.92
129	Acid	95%DD	0.425-0.600	0.05	100.29	5	12	50	137.84
130	Acid	95%DD	0.425-0.600	0.05	100.29	7	12	50	135.67
131	Acid	95%DD	0.425-0.600	0.05	100.29	9	12	50	130.92
132	Basic	79%DD	0.425-0.600	0.05	98.70	5	12	30	78.07
133	Basic	79%DD	0.425-0.600	0.05	98.70	7	12	30	85.31
134	Basic	79%DD	0.425-0.600	0.05	98.70	9	12	30	100.84
135	Basic	87%DD	0.425-0.600	0.05	98.70	5	12	30	76.10
136	Basic	87%DD	0.425-0.600	0.05	98.70	7	12	30	77.55
137	Basic	87%DD	0.425-0.600	0.05	98.70	9	12	30	91.89
138	Basic	95%DD	0.425-0.600	0.05	99.35	5	12	30	83.58
139	Basic	95%DD	0.425-0.600	0.05	99.35	7	12	30	87.66
140	Basic	95%DD	0.425-0.600	0.05	99.35	9	12	30	104.76
141	Basic	79%DD	0.425-0.600	0.05	99.31	5	12	40	62.93
142	Basic	79%DD	0.425-0.600	0.05	99.31	7	12	40	74.90
143	Basic	79%DD	0.425-0.600	0.05	99.31	9	12	40	97.14
144	Basic	87%DD	0.425-0.600	0.05	99.31	5	12	40	65.96
145	Basic	87%DD	0.425-0.600	0.05	99.31	7	12	40	68.85
146	Basic	87%DD	0.425-0.600	0.05	99.31	9	12	40	92.54
147	Basic	95%DD	0.425-0.600	0.05	99.55	5	12	40	68.52
148	Basic	95%DD	0.425-0.600	0.05	99.55	7	12	40	72.07
149	Basic	95%DD	0.425-0.600	0.05	99.55	9	12	40	93.52
150	Basic	79%DD	0.425-0.600	0.05	100.40	5	12	50	69.09

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
151	Basic	79%DD	0.425-0.600	0.05	100.40	7	12	50	76.46
152	Basic	79%DD	0.425-0.600	0.05	100.40	9	12	50	93.70
153	Basic	87%DD	0.425-0.600	0.05	100.40	5	12	50	60.67
154	Basic	87%DD	0.425-0.600	0.05	100.40	7	12	50	70.81
155	Basic	87%DD	0.425-0.600	0.05	100.40	9	12	50	94.88
156	Basic	95%DD	0.425-0.600	0.05	98.77	5	12	50	54.86
157	Basic	95%DD	0.425-0.600	0.05	98.77	7	12	50	66.44
158	Basic	95%DD	0.425-0.600	0.05	98.77	9	12	50	87.23
159	Direct	79%DD	0.425-0.600	0.05	99.42	5	12	30	180.11
160	Direct	79%DD	0.425-0.600	0.05	99.42	7	12	30	161.04
161	Direct	79%DD	0.425-0.600	0.05	99.42	9	12	30	156.41
162	Direct	87%DD	0.425-0.600	0.05	99.42	5	12	30	117.52
163	Direct	87%DD	0.425-0.600	0.05	99.42	7	12	30	112.15
164	Direct	87%DD	0.425-0.600	0.05	99.42	9	12	30	91.41
165	Direct	95%DD	0.425-0.600	0.05	99.78	5	12	30	103.04
166	Direct	95%DD	0.425-0.600	0.05	99.78	7	12	30	89.53
167	Direct	95%DD	0.425-0.600	0.05	99.78	9	12	30	90.27
168	Direct	79%DD	0.425-0.600	0.05	98.99	5	12	40	210.67
169	Direct	79%DD	0.425-0.600	0.05	98.99	7	12	40	193.64
170	Direct	79%DD	0.425-0.600	0.05	98.99	9	12	40	185.30
171	Direct	87%DD	0.425-0.600	0.05	98.99	5	12	40	144.38
172	Direct	87%DD	0.425-0.600	0.05	98.99	7	12	40	132.16
173	Direct	87%DD	0.425-0.600	0.05	98.99	9	12	40	117.53
174	Direct	95%DD	0.425-0.600	0.05	98.87	5	12	40	109.39
175	Direct	95%DD	0.425-0.600	0.05	98.87	7	12	40	94.94

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
176	Direct	95%DD	0.425-0.600	0.05	98.87	9	12	40	90.68
177	Direct	79%DD	0.425-0.600	0.05	98.80	5	12	50	256.03
178	Direct	79%DD	0.425-0.600	0.05	98.80	7	12	50	218.81
179	Direct	79%DD	0.425-0.600	0.05	98.80	9	12	50	199.55
180	Direct	87%DD	0.425-0.600	0.05	98.80	5	12	50	159.18
181	Direct	87%DD	0.425-0.600	0.05	98.80	7	12	50	144.36
182	Direct	87%DD	0.425-0.600	0.05	98.80	9	12	50	133.81
183	Direct	95%DD	0.425-0.600	0.05	99.03	5	12	50	134.68
184	Direct	95%DD	0.425-0.600	0.05	99.03	7	12	50	133.20
185	Direct	95%DD	0.425-0.600	0.05	99.03	9	12	50	123.76
186	Reactive	79%DD	0.425-0.600	0.05	99.56	5	12	30	236.08
187	Reactive	79%DD	0.425-0.600	0.05	99.56	7	12	30	163.80
188	Reactive	79%DD	0.425-0.600	0.05	99.56	9	12	30	124.82
189	Reactive	87%DD	0.425-0.600	0.05	99.56	5	12	30	155.06
190	Reactive	87%DD	0.425-0.600	0.05	99.56	7	12	30	120.33
191	Reactive	87%DD	0.425-0.600	0.05	99.56	9	12	30	87.03
192	Reactive	95%DD	0.425-0.600	0.05	98.88	5	12	30	105.07
193	Reactive	95%DD	0.425-0.600	0.05	98.88	7	12	30	93.49
194	Reactive	95%DD	0.425-0.600	0.05	98.88	9	12	30	79.08
195	Reactive	79%DD	0.425-0.600	0.05	99.90	5	12	40	233.09
196	Reactive	79%DD	0.425-0.600	0.05	99.90	7	12	40	147.57
197	Reactive	79%DD	0.425-0.600	0.05	99.90	9	12	40	144.03
198	Reactive	87%DD	0.425-0.600	0.05	99.90	5	12	40	166.00
199	Reactive	87%DD	0.425-0.600	0.05	99.90	7	12	40	123.48
200	Reactive	87%DD	0.425-0.600	0.05	99.90	9	12	40	116.63

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
201	Reactive	95%DD	0.425-0.600	0.05	99.14	5	12	40	131.83
202	Reactive	95%DD	0.425-0.600	0.05	99.14	7	12	40	98.29
203	Reactive	95%DD	0.425-0.600	0.05	99.14	9	12	40	83.88
204	Reactive	79%DD	0.425-0.600	0.05	99.61	5	12	50	238.12
205	Reactive	79%DD	0.425-0.600	0.05	99.61	7	12	50	144.11
206	Reactive	79%DD	0.425-0.600	0.05	99.61	9	12	50	96.15
207	Reactive	87%DD	0.425-0.600	0.05	99.61	5	12	50	176.23
208	Reactive	87%DD	0.425-0.600	0.05	99.61	7	12	50	115.05
209	Reactive	87%DD	0.425-0.600	0.05	99.61	9	12	50	104.66
210	Reactive	95%DD	0.425-0.600	0.05	99.37	5	12	50	139.61
211	Reactive	95%DD	0.425-0.600	0.05	99.37	7	12	50	96.38
212	Reactive	95%DD	0.425-0.600	0.05	99.37	9	12	50	69.92
213	Acid	79%DD	0.425-0.600	0.05	100	5	12	30	176.47
214	Acid	79%DD	0.425-0.600	0.05	250	5	12	30	469.55
215	Acid	79%DD	0.425-0.600	0.05	500	5	12	30	1004.93
216	Basic	79%DD	0.425-0.600	0.05	100	5	12	30	54.30
217	Basic	79%DD	0.425-0.600	0.05	250	5	12	30	159.91
218	Basic	79%DD	0.425-0.600	0.05	500	5	12	30	326.20
219	Direct	79%DD	0.425-0.600	0.05	100	5	12	30	246.65
220	Direct	79%DD	0.425-0.600	0.05	250	5	12	30	560.36
221	Direct	79%DD	0.425-0.600	0.05	500	5	12	30	1099.95
222	Reactive	79%DD	0.425-0.600	0.05	100	5	12	30	295.79
223	Reactive	79%DD	0.425-0.600	0.05	250	5	12	30	690.41
224	Reactive	79%DD	0.425-0.600	0.05	500	5	12	30	1371.45
225	Acid	79%DD	0.150-0.300	0.05	100.58	5	12	30	186.90

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
226	Acid	79%DD	0.300-0.425	0.05	100.58	5	12	30	160.29
227	Acid	79%DD	0.425-0.600	0.05	100.58	5	12	30	132.46
228	Acid	87%DD	0.150-0.300	0.05	100.58	5	12	30	161.51
229	Acid	87%DD	0.300-0.425	0.05	100.58	5	12	30	138.03
230	Acid	87%DD	0.425-0.600	0.05	100.58	5	12	30	128.93
231	Acid	95%DD	0.150-0.300	0.05	100.58	5	12	30	149.70
232	Acid	95%DD	0.300-0.425	0.05	100.58	5	12	30	141.42
233	Acid	95%DD	0.425-0.600	0.05	100.58	5	12	30	126.22
234	Basic	79%DD	0.150-0.300	0.05	99.81	9	12	30	116.54
235	Basic	79%DD	0.300-0.425	0.05	99.81	9	12	30	101.04
236	Basic	79%DD	0.425-0.600	0.05	99.81	9	12	30	89.82
237	Basic	87%DD	0.150-0.300	0.05	99.81	9	12	30	118.11
238	Basic	87%DD	0.300-0.425	0.05	99.81	9	12	30	104.96
239	Basic	87%DD	0.425-0.600	0.05	99.81	9	12	30	95.22
240	Basic	95%DD	0.150-0.300	0.05	99.81	9	12	30	119.17
241	Basic	95%DD	0.300-0.425	0.05	99.81	9	12	30	105.75
242	Basic	95%DD	0.425-0.600	0.05	99.81	9	12	30	106.14
243	Direct	79%DD	0.150-0.300	0.05	101.26	5	12	30	222.67
244	Direct	79%DD	0.300-0.425	0.05	101.26	5	12	30	206.74
245	Direct	79%DD	0.425-0.600	0.05	101.26	5	12	30	185.63
246	Direct	87%DD	0.150-0.300	0.05	101.26	5	12	30	205.26
247	Direct	87%DD	0.300-0.425	0.05	101.26	5	12	30	167.48
248	Direct	87%DD	0.425-0.600	0.05	101.26	5	12	30	136.93
249	Direct	95%DD	0.150-0.300	0.05	101.26	5	12	30	159.52
250	Direct	95%DD	0.300-0.425	0.05	101.26	5	12	30	130.45

Table A1 (continued)

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	Int. Conc. (mg/L)	pH	Time (h)	Temp (°C)	Adsorbed dye (mg/g)
251	Direct	95%DD	0.425-0.600	0.05	101.26	5	12	30	107.48
252	Reactive	79%DD	0.150-0.300	0.05	100.34	5	12	30	276.69
253	Reactive	79%DD	0.300-0.425	0.05	100.34	5	12	30	260.15
254	Reactive	79%DD	0.425-0.600	0.05	100.34	5	12	30	238.89
255	Reactive	87%DD	0.150-0.300	0.05	100.34	5	12	30	204.64
256	Reactive	87%DD	0.300-0.425	0.05	100.34	5	12	30	173.46
257	Reactive	87%DD	0.425-0.600	0.05	100.34	5	12	30	157.40
258	Reactive	95%DD	0.150-0.300	0.05	100.34	5	12	30	130.00
259	Reactive	95%DD	0.300-0.425	0.05	100.34	5	12	30	120.78
260	Reactive	95%DD	0.425-0.600	0.05	100.34	5	12	30	109.45

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Table A2 Conditions and results of desorption experiments

Exp. No.	Type of dye	Type of chitosan	Particle size (mm)	Adsorbent weight (g)	pH	Time (h)	Temp (°C)	Desorbed dye (%)
261	Acid	79%DD	0.425-0.600	0.05	5	12	30	4.17
262	Acid	79%DD	0.425-0.600	0.05	7	12	30	4.39
263	Acid	79%DD	0.425-0.600	0.05	9	12	30	4.54
264	Basic	79%DD	0.425-0.600	0.05	5	12	30	2.39
265	Basic	79%DD	0.425-0.600	0.05	7	12	30	2.89
266	Basic	79%DD	0.425-0.600	0.05	9	12	30	2.64
267	Direct	79%DD	0.425-0.600	0.05	5	12	30	3.00
268	Direct	79%DD	0.425-0.600	0.05	7	12	30	3.50
269	Direct	79%DD	0.425-0.600	0.05	9	12	30	3.38
270	Reactive	79%DD	0.425-0.600	0.05	5	12	30	3.48
271	Reactive	79%DD	0.425-0.600	0.05	7	12	30	3.28
272	Reactive	79%DD	0.425-0.600	0.05	9	12	30	3.48
273	Acid	79%DD	0.425-0.600	0.05	5	12	50	6.78
274	Basic	79%DD	0.425-0.600	0.05	5	12	50	4.03
275	Direct	79%DD	0.425-0.600	0.05	5	12	50	5.13
276	Reactive	79%DD	0.425-0.600	0.05	5	12	50	4.08

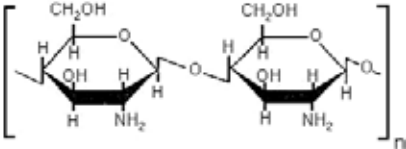
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## Appendix B

Table B1 Properties of Chitosan 79 % Degree of Deacetylation \*

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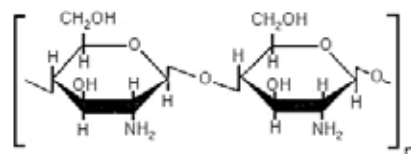
Structure		
Chemical Name	poly (1→4)-2-amino-2-deoxy-β-D-glucan	
Appearance		Yellowish
Particle Size		Mesh No.18
Ash Content		0.55%
Moisture Content		9.0%
Deacetylation		79%
Solution (1% in 1% acetic acid)		
Insoluble		0.93%
Viscosity		696 cps
Heavy Metal		0 ppm
Microbial Content		
Total Plate Count		50 cfu/g
Yeast & Mold		10 cfu/g
E.coli & Salmonella		Nil

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\* From Seafresh Chitosan (Lab) Co., Ltd.

Table B2 Properties of Chitosan 87 % Degree of Deacetylation \*

Structure



Chemical Name

poly (1→4)-2-amino-2-deoxy-β-D-glucan

Appearance

Yellowish

Particle Size

Mesh No.18

Ash Content

0.18%

Moisture Content

9.0%

Deacetylation

87%

Solution (1% in 1% acetic acid)

Insoluble

0.37%

Viscosity

852 cps

Heavy Metal

0 ppm

Microbial Content

Total Plate Count

50 cfu/g

Yeast &amp; Mold

20 cfu/g

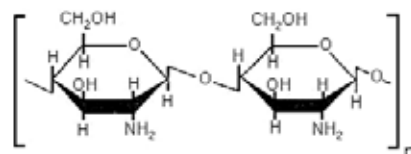
E.coli &amp; Salmonella

Nill

\* From Seafresh Chitosan (Lab) Co., Ltd.

Table B3 Properties of Chitosan 95 % Degree of Deacetylation \*

Structure



Chemical Name

poly (1→4)-2-amino-2-deoxy-β-D-glucan

Appearance

Yellowish

Particle Size

Mesh No.18

Ash Content

0.15%

Moisture Content

9.0%

Deacetylation

95%

Solution (1% in 1% acetic acid)

Insoluble

0.4%

Viscosity

648 cps

Heavy Metal

0 ppm

Microbial Content

Total Plate Count

10 cfu/g

Yeast &amp; Mold

10 cfu/g

E.coli &amp; Salmonella

Nill

\* From Seafresh Chitosan (Lab) Co., Ltd.

Table B4 Properties of Hydrochloric Acid \*

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Formula	HCl
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	- 15.35
Melting Point (°C)	- 83
Specific Gravity	5.44
Solubility	Soluble in Water and Alcohol
Purity	37%
Supplier	Merck

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\* From Encyclopedia of Chemical Engineering.

Table B5 Properties of Sodium Hydroxide \*

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Formula	NaOH
Chemical Name	Sodium Hydroxide
Physical Properties	
Molecular Weight	40.01
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	1390
Melting Point (°C)	318
Specific Gravity	2.13
Solubility	Soluble in Water
Purity	48 - 51%
Supplier	Carlo Erba

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\* From Encyclopedia of Chemistry

## APPENDIX C

## Calibration Curve of Dye Solution at Various pHs

Average slope value obtained from the calibration curve plotted between the absorbance of the dye solutions and the dye concentrations are shown in Tables C1 to C4.

Table C1 Calibration curve of Acid Orange 7 at 450 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R <sup>2</sup>
5	0	0	0.0221	0.9986
	20	0.427		
	40	0.910		
	60	1.358		
	80	1.716		
	100	2.218		
7	0	0	0.0220	0.9988
	20	0.432		
	40	0.916		
	60	1.350		
	80	1.719		
	100	2.210		
9	0	0	0.0221	0.9988
	20	0.433		
	40	0.918		
	60	1.354		
	80	1.722		
	100	2.211		

Average slope of Acid Orange 7 is 0.0221. Figures C1 to C3 show the calibration curve of Acid Orange 7 at pH 5, pH 7, and pH 9, respectively.

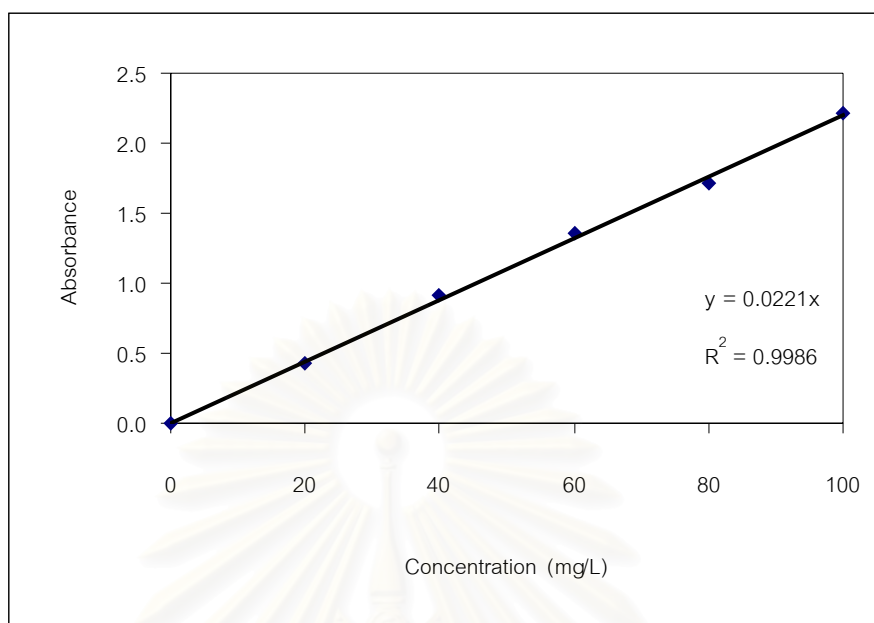


Figure C1 Calibration curve of Acid Orange 7 at pH 5

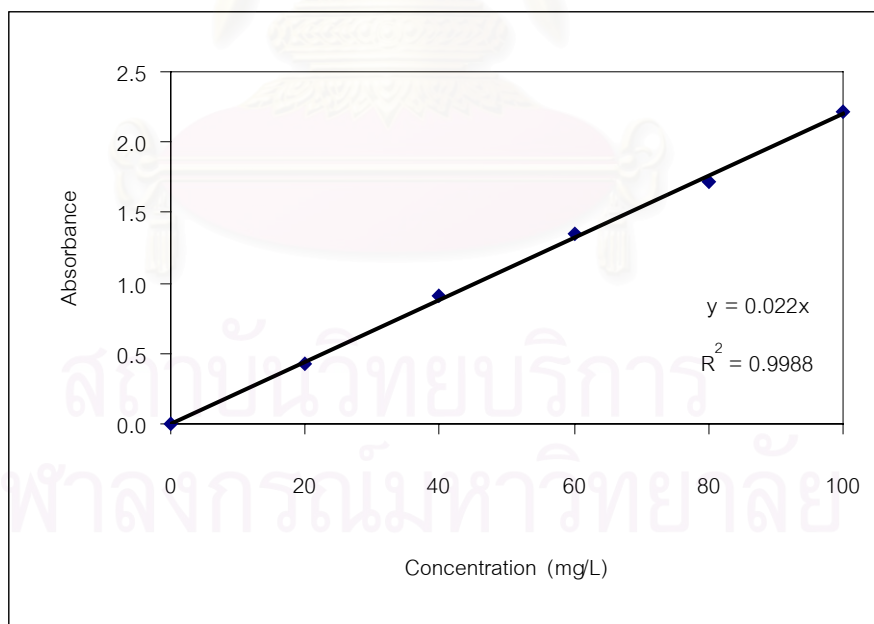


Figure C2 Calibration curve of Acid Orange 7 at pH 7

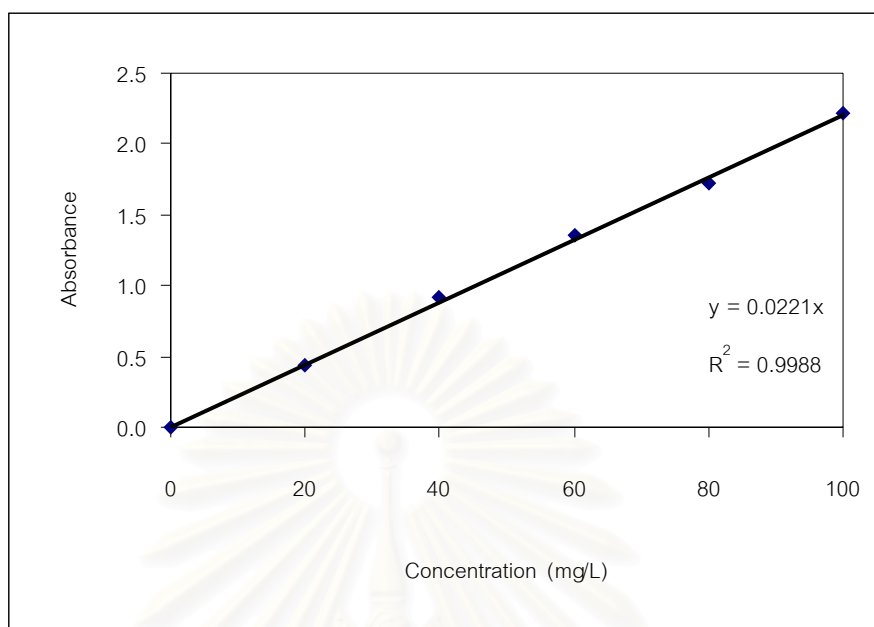


Figure C3 Calibration curve of Acid Orange 7 at pH 9

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Table C2 Calibration curve of Direct Green at 617 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R <sup>2</sup>
5	0	0	0.0162	0.9984
	20	0.344		
	40	0.676		
	60	1.002		
	80	1.280		
	100	1.597		
7	0	0	0.0162	0.9983
	20	0.352		
	40	0.678		
	60	0.999		
	80	1.282		
	100	1.601		
9	0	0	0.0162	0.9982
	20	0.351		
	40	0.683		
	60	1.002		
	80	1.283		
	100	1.603		

Average slope of Direct Green 26 is 0.0162. Figures C4 to C6 show the calibration curve of Direct Green 26 at pH 5, pH 7, and pH 9, respectively.

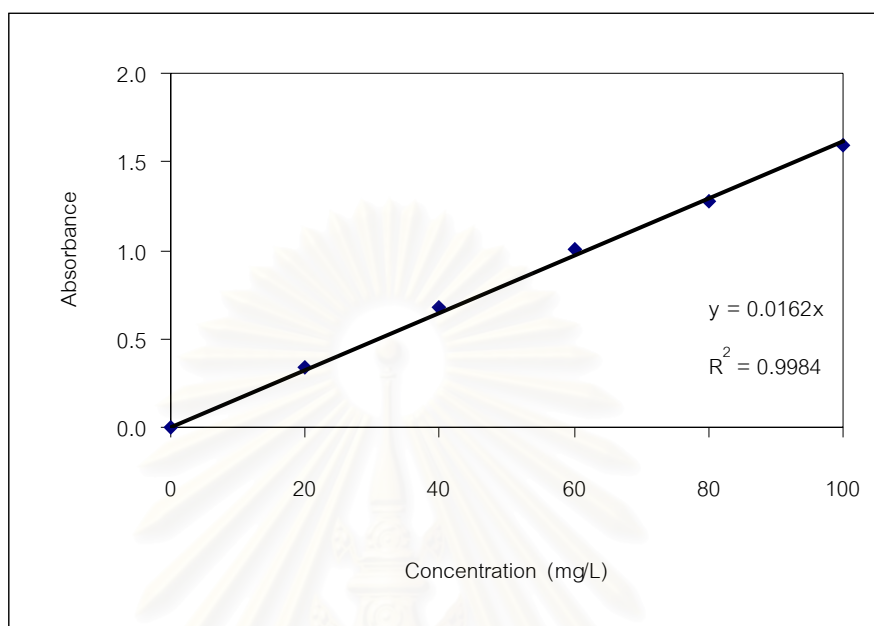


Figure C4 Calibration curve of Direct Green 26 at pH 5

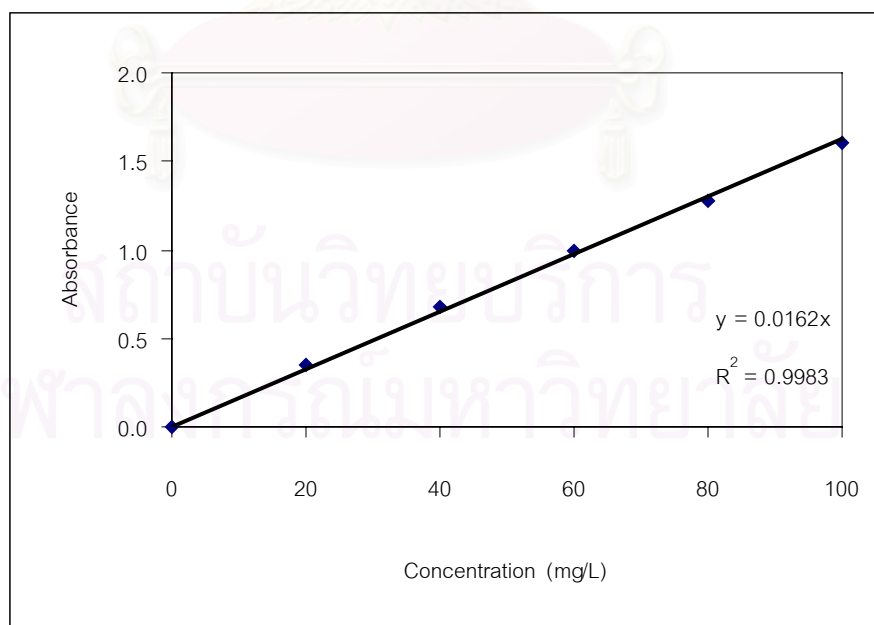


Figure C5 Calibration curve of Direct Green 26 at pH 7

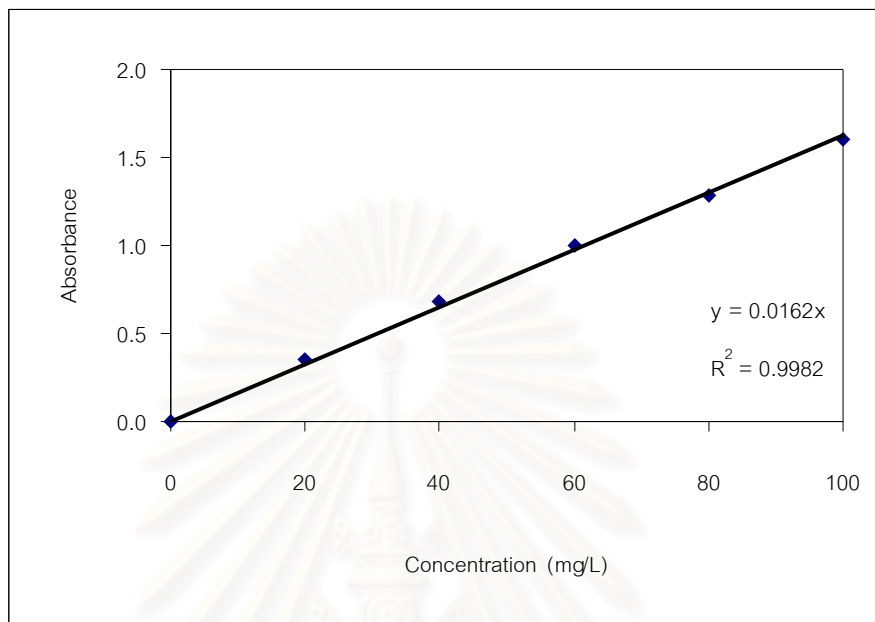


Figure C6 Calibration curve of Direct Green 26 at pH 9

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จุฬาลงกรณ์มหาวิทยาลัย

Table C3 Calibration curve of Reactive Violet 5 at 555 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R <sup>2</sup>
5	0	0	0.0127	0.9996
	20	0.266		
	40	0.523		
	60	0.764		
	80	1.025		
	100	1.263		
7	0	0	0.0127	0.9998
	20	0.259		
	40	0.515		
	60	0.766		
	80	1.026		
	100	1.264		
9	0	0	0.0127	0.9999
	20	0.257		
	40	0.516		
	60	0.772		
	80	1.019		
	100	1.268		

Average slope of Reactive Violet 5 is 0.0127. Figures C7 to C9 show the calibration curve of Reactive Violet 5 at pH 5, pH 7, and pH 9, respectively.

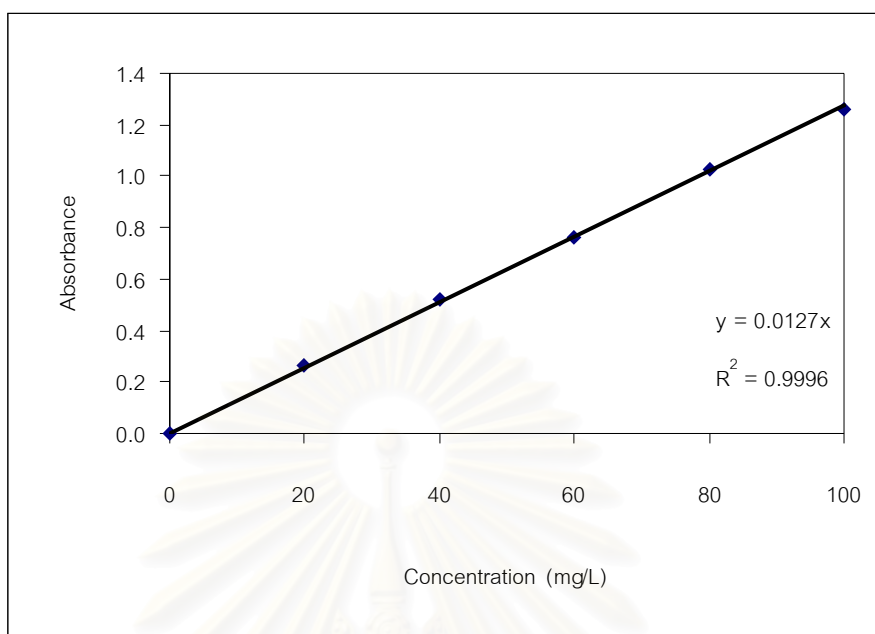


Figure C7 Calibration curve of Reactive Violet 5 at pH 5

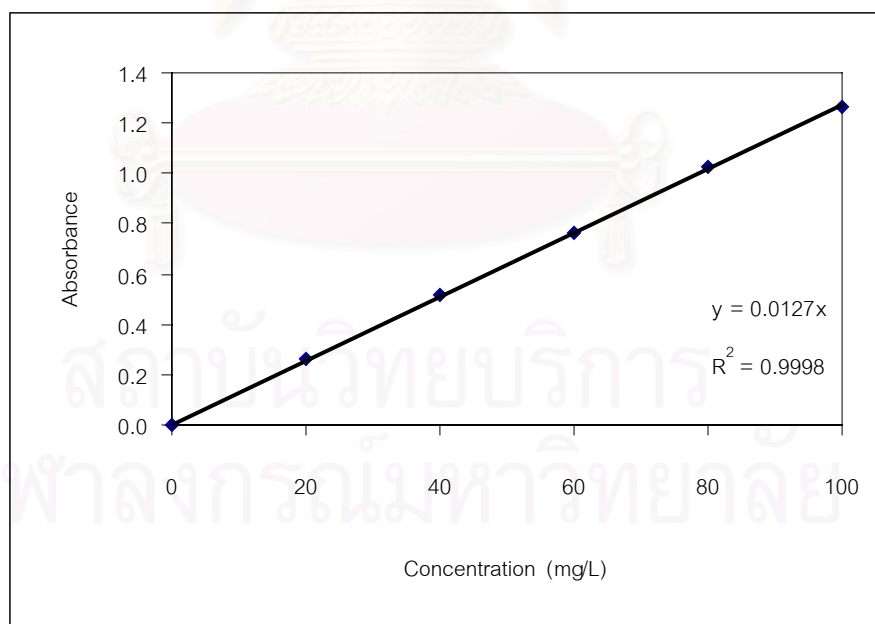


Figure C8 Calibration curve of Reactive Violet 5 at pH 7

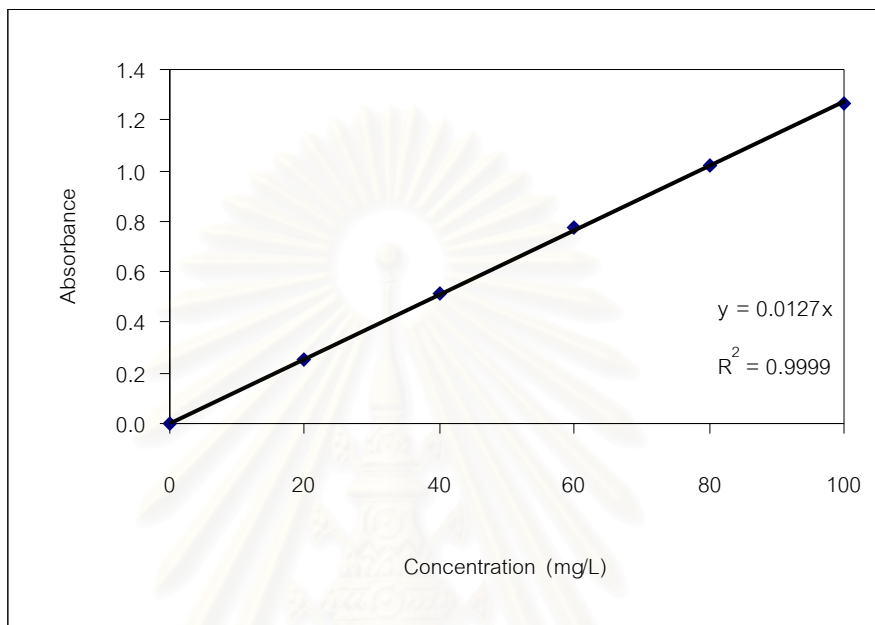


Figure C9 Calibration curve of Reactive Violet 5 at pH 9

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Table C4 Calibration curve of Basic Yellow 2 at 444 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R <sup>2</sup>
5	0	0	0.0228	0.9930
	20	0.552		
	40	0.985		
	60	1.418		
	80	1.810		
	100	2.202		
	7	0		
20		0.559		
40		0.989		
60		1.415		
80		1.815		
100		2.195		
9		0	0	0.0228
	20	0.562		
	40	0.993		
	60	1.411		
	80	1.814		
	100	2.199		

Average slope of Basic Yellow 2 is 0.0228. Figures C10 to C12 show the calibration curve of Basic Yellow 2 at pH 5, pH 7, and pH 9, respectively.

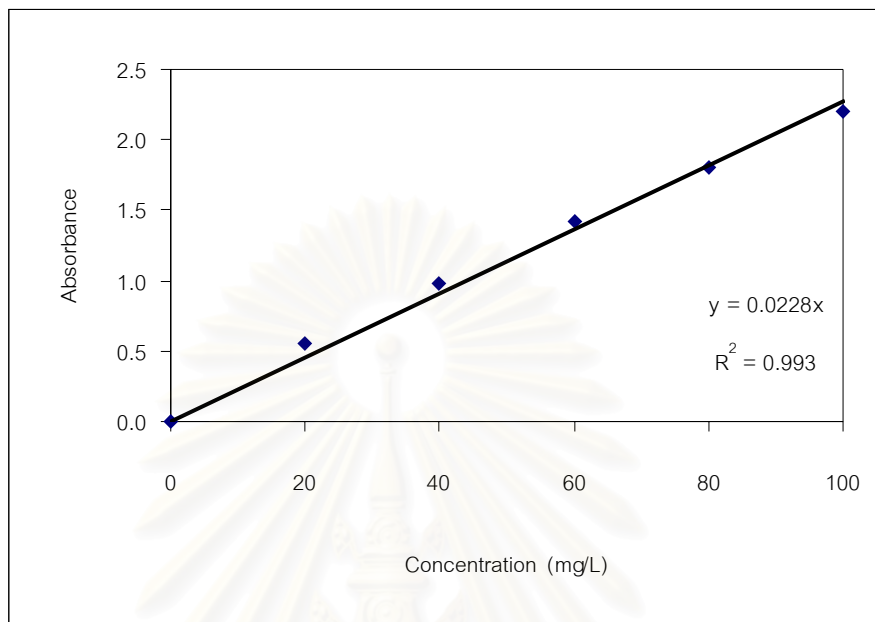


Figure C10 Calibration curve of Basic Yellow 2 at pH 5

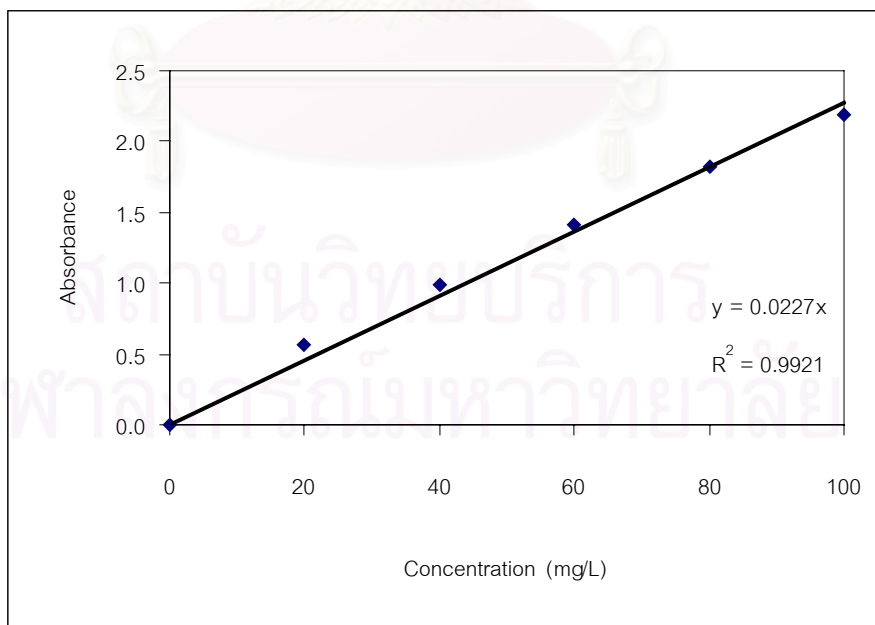


Figure C11 Calibration curve of Basic Yellow 2 at pH 7



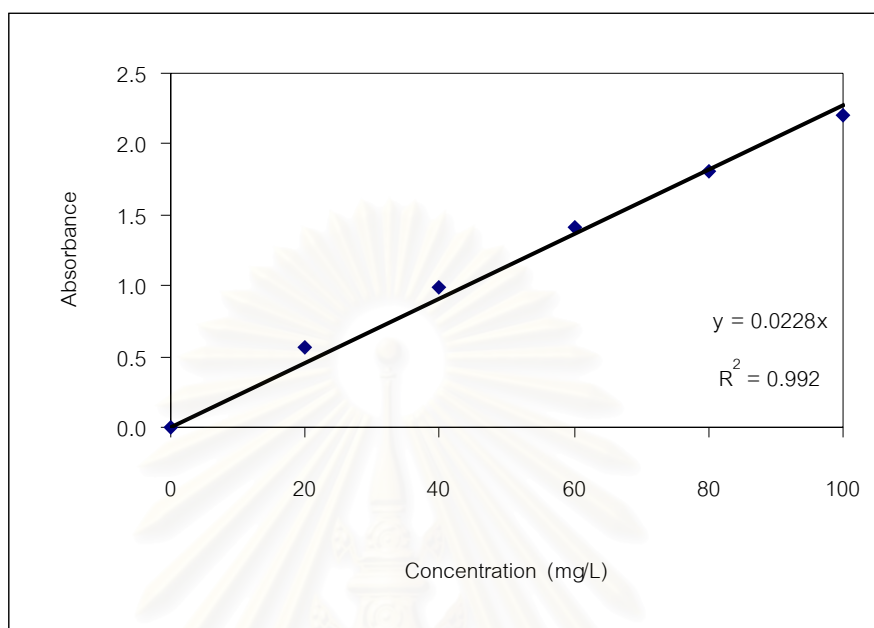


Figure C12 Calibration curve of Basic Yellow 2 at pH 9

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## VITA

Miss Chotiros Eiamsa-ard was born on June 26, 1979 in Bangkok, Thailand. Education levels are high school in 1993-1996 from Suankularb Wittayalai Nonthaburi School, Nonthaburi, and Bachelor Degree in Chemical Engineering from Srinakharinwirot University, Bangkok in 1996-2000. The last education is studying in Master Degree in Chemical Engineering, Chulalongkorn University that began in 2000.



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