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ADSORPTION OF WATER-SOLUBLE DYES ON CHITIN AND CHITOSAN

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จากการศึกษาปัจจัยต่างๆ ที่มีผลต่อการดูดซับของสีย้อม 4 ชนิดบนตัวดูดซับ 3 ชนิด พบว่าตัวดูดซับทุกชนิดสามารถดูดซับสีแอซิด สีรีแอคทีฟ และสีไดเร็คได้ดีในสารละลายกรดที่มีค่าพีเอช 5 หรือต่ำกว่า โดยไคโตแซนจะดูดซับสีย้อมดังกล่าวได้ในปริมาณที่สูงกว่าไคตินและเปลือกกุ้ง ตรงข้ามกับสีเบสิกจะถูกดูดซับได้ดีในสารละลายด่างที่มีค่าพีเอช 10 หรือสูงกว่า โดยเปลือกกุ้งจะดูดซับสีเบสิกได้ในปริมาณที่สูงกว่าไคตินและไคโตแซนมาก ปริมาณสีย้อมที่ถูกดูดซับจะเพิ่มขึ้นเมื่อระยะเวลาที่ใช้ในการดูดซับและความเข้มข้นของสารละลายสีย้อมเพิ่มขึ้น แต่จะลดลงเมื่ออนุภาคของตัวดูดซับมีขนาดเพิ่มขึ้น ปริมาณของสีทุกชนิดที่ถูกดูดซับยกเว้นสีเบสิก จะเพิ่มขึ้นเล็กน้อยเมื่อค่าดีกรีออฟดีอะเซทิลเลชันของไคโตแซนเพิ่มขึ้น แรงปฏิกิริยาระหว่างประจุเป็นแรงสำคัญที่สุดที่เกี่ยวข้องในการดูดซับของสีย้อมบนตัวดูดซับ

นอกจากนี้ยังมีการศึกษาการคายการดูดซับของสีย้อมที่ค่าพีเอชและอุณหภูมิต่างๆกัน สีย้อมสามารถคายการดูดซับจากตัวดูดซับได้ดีที่อุณหภูมิ 80 องศาเซลเซียส และค่าพีเอช 10 หรือสูงกว่า ยกเว้นสีเบสิกจะคายการดูดซับได้ดีในสารละลายที่มีค่าพีเอช 3 หรือต่ำกว่า สีรีแอคทีฟจะคายการดูดซับได้น้อยที่สุด ในการกำจัดสีย้อมออกจากน้ำทิ้งของโรงงานฟอกย้อมสิ่งทอก็ให้ผลในทำนองเดียวกันกับการกำจัดสีย้อมออกจากสารละลายของสีย้อมที่สังเคราะห์ขึ้น ไคโตแซนสามารถดูดซับสีแอซิด สีรีแอคทีฟ และสีไดเร็ค ได้ในปริมาณสูงสุดเกือบถึง 72% 61% และ 94% ตามลำดับ ส่วนเปลือกกุ้งสามารถดูดซับสีเบสิกจากน้ำทิ้งได้ในปริมาณสูงถึง 43% ปริมาณสีย้อมที่กำจัดได้จะขึ้นอยู่กับชนิดของสีย้อมในน้ำทิ้ง

ภาควิชา.......หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต..
สาขาวิชา......ปิโตรเคมี..	ลายมือชื่ออาจารย์ที่ปรึกษา..
ปีการศึกษา...2542..	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม Ratana Rujiravanit

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KEYWORD: WATER-SOLUBLE DYE / ADSORPTION / DESORPTION / DYE REMOVAL / TEXTILE EFFLUENT / BIOADSORBENT / CHITIN / CHITOSAN / SHRIMP SHELLS

JINTANA CHAMNANMANOONTHAM : ADSORPTION OF WATER-SOLUBLE DYE ON CHITIN AND CHITOSAN. THESIS ADVISOR : ASSO. PROF. KUNCHANA BUNYAKIAT, THESIS COADVISOR : RATANA RUJIRAVANIT, Ph.D. 157 pp. ISBN 974-334-485-3.

Effects of various parameters on the adsorption of four dyes on three adsorbents were investigated. The adsorption of acid dye, reactive dye and direct dye was highly effective in acidic solutions 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 adsorbents.

Desorption of dyes at different pHs and temperatures was also studied. Desorption of dyes from adsorbents was highly effective at 80 °C and pH $\geq$ 10 except the basic dye which highly desorbed at pH $\leq$ 3. The least desorption was found in the reactive dye. The removal of dyes from textile effluents was shown similar tendency to those from the synthetic dye solutions. The amounts of acid dye, reactive dye and direct dye adsorbed on chitosan reach almost 72%, 61% and 94%, respectively, shrimp shells could adsorb basic dye from effluents up to 43 %. The amounts of dye removal depend on the type of dyes in effluents.

ภาควิชา........หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต..
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CHAPTER I

INTRODUCTION

Water pollution has become serious problems for many countries due to There are many types of effluents from many factories passed into the rivers such as domestic, industrial, and agricultural wastewaters. Among these, textile effluent is one of major contributions[1].

A large fraction of textile effluents is discharged in strong acidic solutions with intense color that are harmful to aquatic animals and microorganism due to decrease in oxygen and increase in COD and BOD. Although most of water-soluble dyes are non-toxic at the concentration discharged into the rivers but the color they impart is very undesirable to the water users. Hence, color removal from such effluents is a major environmental problem because of the difficulty of treatment by conventional chemical coagulation, flocculation and biological treatments [2-6].

Dyes are organic compounds containing conjugated double bond and composing of the color producing groups called chromophores and the groups affecting to the color intensity called auxochromes. Dyes are classified into two classes according to their solubilities and application, water-insoluble and water-soluble dyes [7-9]. The latter such as acid, reactive, direct, and basic dyes cause more effects to the effluents Because it is very difficult to remove them from water by chemical and biological treatments.

Liquid-phase adsorption wastewater has been shown to be effective for removing water-soluble dyes, suspended solids, odor, organic matter, and oils from aqueous streams. Activated carbon is the most widely used adsorbent for this process, nevertheless, it has a rather low capacity for reactive dyes. In addition, the use of activated carbon is sometimes limited because of its high cost. This leads many workers to search for more effective and cheaper substitutes such as coal, fly ash, wood, silica gel, bentonite clay, bagasse pith, maize cob, coconut shell, rice husk, chitin and chitosan. Among these alternatives, chitin and its derivative, chitosan, appear to be more attractive since chitin is the second most abundant biopolymer in nature next to cellulose.

Chitin is a polysaccharide containing acetamido groups in its molecules. It is mostly found in shells of crustaceans such as shrimp, lobster, crabs and squids. Shrimp shells contain about 15-20 % chitin, 25-40 % protein and 40-55 % calcium carbonate. Chitosan is a partially acetylated glucosamine polymer. Chitosan can be prepared by deacetylation of chitin. Chitosan has many useful features such as its hydrophilicity, biocompatibility, biodegradability. Chitin and chitosan are known as biosorbents, effective in the uptake of dyes and metals since the acetamido and the amino groups of chitin and chitosan can serve as chelation sites for dyes and metals. In contrast to chitin, the ability of complexation and adsorption of metals with chitosan is superior due to its higher content of amino functions. Furthermore, the sorption performance of chitosan can be enhanced by simple modifications [(10-12)].

A large number of equilibrium and kinetic studies on the adsorption of dyes using chitin, chitosan, and its derivatives have been carried out [(13-19)] but none had compared the results with shrimp shell wastes which is another interesting aspect. Hence this present work will focus on three parts as follows :

1. To study the effects of adsorption parameters on dye adsorption by chitin, chitosan and shrimp shells. The parameters studied were pH of solution, degree of deacetylation, particle size of adsorbents, adsorption time, initial dye concentration.
2. To investigate the optimum pH and temperature on the desorption of dyes from chitin, chitosan and shrimp shells.
3. The effectiveness of the three adsorbents on dye removal from textile effluents was also studied.

CHAPTER II
LITERATURE REVIEW

2.1 Role of Intermolecular Forces in Dye Adsorption [8, 11]

Van der Waals forces

These forces are weak interactions between the nuclei of the constituent atoms of one molecule with the electrons of another. The van der Waals forces increase with increasing of the molecular size. They operate only when dyes and adsorbent moleculcs are in close proximity to each other, when they can become dominant force of attraction.

Hydrogen bonds

The hydrogen atom is the smallest of all the atoms; in organic compounds it normally forms a single covalent bond only. Often, however, a neighbouring atom may have a higher affinity for electrons than does the hydrogen atom, causing a drift of the electrons shared by the hydrogen towards the larger atom. This leaves a slight positive charge on the hydrogen atom, which in turn encourages bond formation between it and nearby atoms such as nitrogen or oxygen as below. Such bonds are readily broken and re-formed and they are one of the factors involved when substances are dissolved by water.

$\delta^{-}\delta^{+}$

Cellulose – O H - - NH_2

Dye

Ionic bonding or salt link

This attraction force is caused by electron transfer from one atom to another. The resulting ions have opposite charges, like the acidic and basic groups react together to form salt links. An acidic group in a dye molecule will dissociate similarly, and will react with a basic compound. For example, the sulphonic acid group in a dye molecule will react with sodium hydroxide to form the sodium salt of the dye as shown in equation (2.1)

$$D-SO_3H \quad + \quad NaOH \longrightarrow D-SO_3Na + H_2O \qquad (2.1)$$

Covalent bonding

This bonding involves the sharing of electrons, thus each atom has two electrons in its valence shell. Covalent bonding is stronger than salt link, hydrogen bond and van der Waal force, respectively as shown in Table 2.1

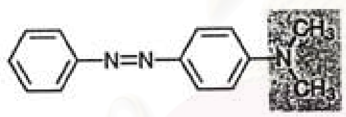
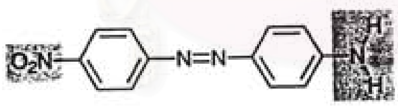
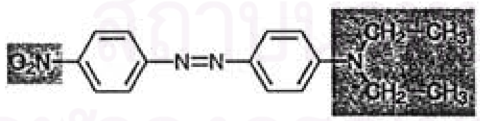
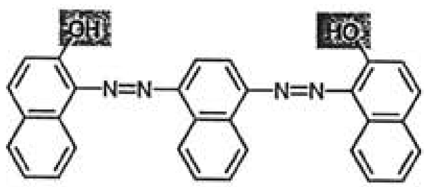
Table 2.1 Comparison of bond strength

Bond type	Relative strength
Van der Waals	1.0
Hydrogen bond	3.0
Ionic bond	7.0
Covalent bond	30.0

2.2 Water–soluble Dyes

All dye molecules contain aromatic ring structures. One of the most widespread functional group in dye is azo group (- N = N -). It will react with other aromatic molecules to form the azo compound that are widely distributed in several different classes of dye. The simplest azo molecule is phenylazobenzene (azobenzene) which is called the chromophore group of azo dyes and the colour of the molecule may be modified and increase in intensity of colour by introducing a variety of small group into the molecule, exmples of which are shown in Table 2.1. Such groups are called auxochromes. Approximately 50 % of the available commercial contain at least one azo chromophoric group.

Table 2.2 Color of some azo compounds

Structure	Color observed
	Yellow-green
	Yellow
	Red
	Blue
	– Auxochrome

Water-soluble dye are classified by application into two classes which are anionic and cationic dyes [7]. Anionic dye contains the chromophore with negative charge of anion such as acid dye, reactive dye, direct dye etc. Cationic dye contains the chromophore with positive charge of cation such as basic dye.

Acid dyes [7-8]

These water-soluble anionic dyes are applied to wool, silk, modified acrylic fiber and leather. All acid dye molecules have certain features in common. They all possess at least one group of atoms that imparts solubility in water to the large coloured component of the molecule. This is usually the sodium salt of a sulphonic acid group, $-SO_3Na$. Nature of acid dye molecules are presented in Figure 2.1 The sulphonic acid group is also important in linkage the dye to the fiber by reacting with a basic group in the wool molecule and form a salt likage. Other factors in the attraction between fiber and dye include hydrogen bonds and van der Waal forces which depend directly on the size of the dye molecule.

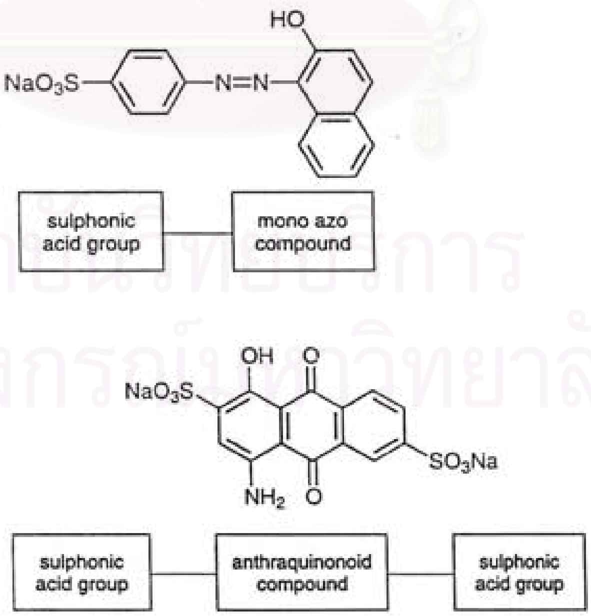


Figure 2.1 Nature of acid dye molecules

Reactive dyes [7-8]

These water-soluble anionic dyes contain $-SO_3Na$ and the reactive group in molecules that can form ionic attraction and covalent bond with substrate, respectively. The type of reactive group determines the level of its reactivity, whilst its substantivity is governed by the chromophore. These dyes are applied for cellulose, cotton, wool, silk and nylon. The leaving group on the reactive group may be Cl, F or Br. The characteristic features of a reactive dye are shown in Figure 2.2.

Reactive dyes can react with compounds containing amino groups, amide groups, mercapto groups and hydroxyl groups in molecules by forming covalent bonds with the reactive group as shown in Figure 2.3. Those compounds are amino acid, protein, wool, silk, nylon and cellulose [9].

Direct dyes [7-8]

These water-soluble anionic dyes contain $-SO_3Na$ group. The principal use is the dyeing of cotton, regenerated cellulose, paper, leather and nylon. They conform to the general formula $R_1 - N = N - X - N = N - R_2$. It is their larger size that distinguishes them from acid dyes and makes them substantive to cellulose. Their attachment is through both hydrogen bonds and van der Waals forces, and the intensity of the latter increase with increasing of the molecular size. An example of this dye is shown in Figure 2.4

Basic dyes [7-8]

These water-soluble cationic dyes contain positive charge of ammonium salt, sulfonium or oxonium. They are applied to acrylic fiber, silk, wool, modified nylon and modified polyester. Basic dyes are held on to the fiber by formation of salt links with anionic groups deliberately built into the fiber to provide dye sites. Examples of basic dyes are shown in Figure 2.5

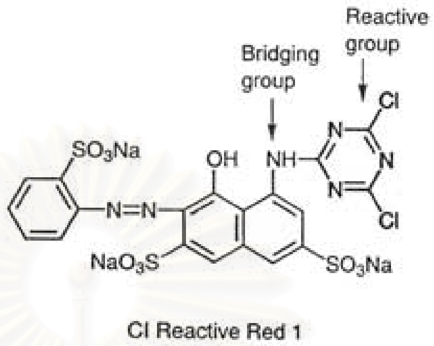


Figure 2.2 Nature of reactive dyes

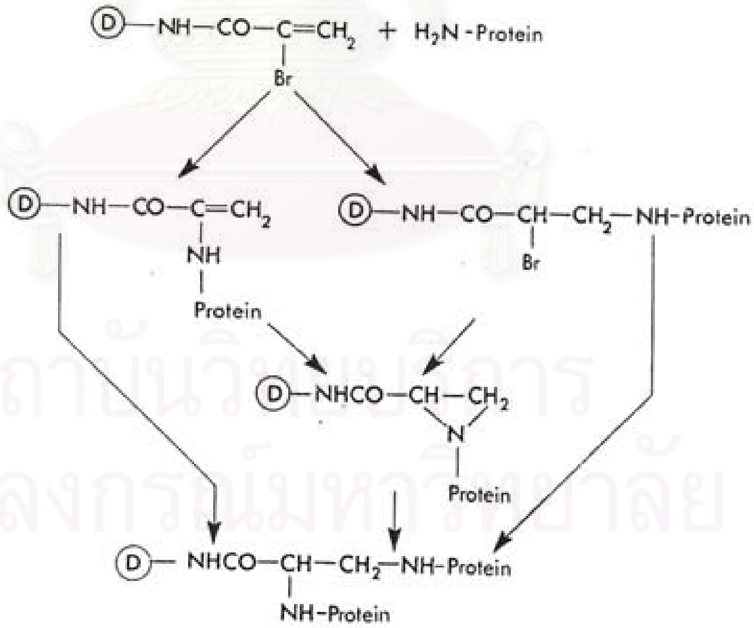


Figure 2.3 Reactions of reactive dye and protein

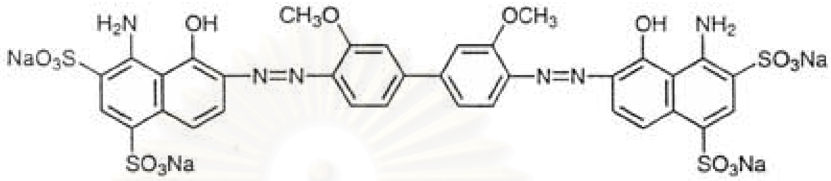


Figure 2.4 Nature of direct dye

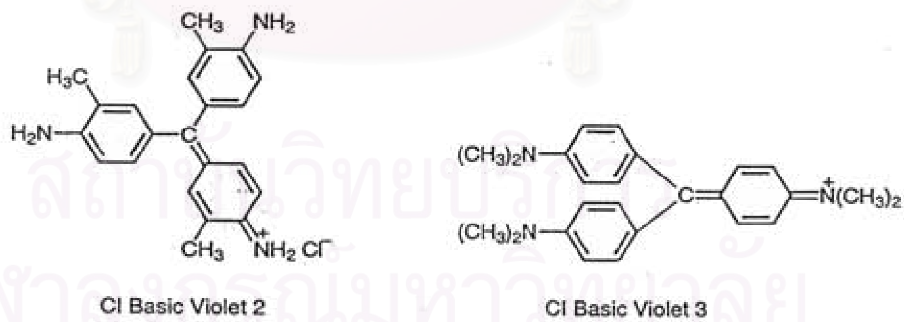
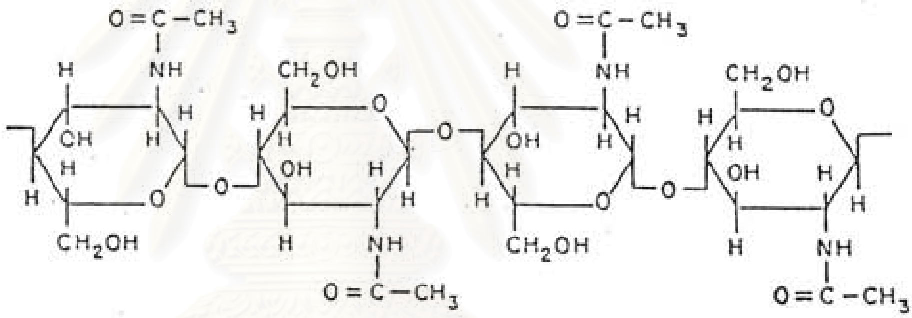


Figure 2.5 Basic dyes

2.3 Chitin and Chitosan [10]

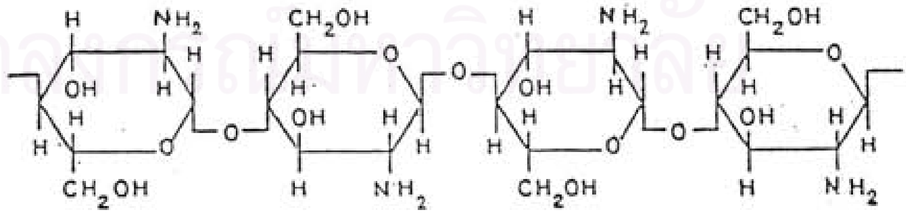
Chitin is a polysaccharide biopolymer. Its structure, chemical name and general forrmula are shown in Figure 2.6. In chitin the amino group is acetylated to be acetamido group (-NH-CO-CH_3) attached to the second carbon atom at which the acetyl group (-CO-CH_3) can be replaced easily. Chitin is mostly found in the exoskeleton of arthopods, cell walls of fungi, bacteria and yeast.

Chitosan is a derivative of chitin obtained from deacetylation reaction, Its structure, chemical name and general formula are shown in Figure 2.7. The acetyl group in chitin is replaced by hydrogen atom to become amino group (-NH_2) on the second carbon atom.



Poly-β(1,4)-2-acetamido-2-deoxy D-glucose ; $(C_8H_{13}NO_5)_n$

Figure 2.6 Structure, chemical name and general formula of chitin



Poly-β(1,4)-2-amido-2-deoxy D-glucose ; $(C_6H_{11}NO_4)_n$

Figure 2.7 Structure, chemical name and general formula of chitosan

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 obtain from chitin, where most of the acetyl groups have been removed. In chitin the amino group is deacetylated, thus chitin is an amide of acetic acid; in chitosan the amino group is free and therefore chitosan is a primary amine. The amino groups of chitin and chitosan are exceptionally stable in 50 % NaOH, even at 160 °C, at which most amines liberate ammonia or yield degradation products.

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. Several authors have estimated that chitin contains 82.5 % of acetylglucosamine, 12.5 % of glucosamine and 5 % water.

Chitin and chitosan possess many interesting and useful properties such as biocompatibility, biodegradability, antibacterial properties, metal chelating and binding abilities with protein and organic compound.

HCl binding capacity on chitin at pH 3 and pH 4 were 3800 and 450 mmol/kg, respectively. Chitosan also shows the acid binding ability. The reactions are reversible as shown in equation (2.2) and (2.3)

Chitin, $$\text{R-NHCOCH} + \text{H}^+\text{X}^- \rightleftharpoons \text{R-NH}_2^+\text{COCH}_3\text{X}^- \qquad (2.2)$$

Chitosan, $$\text{R-NH}_2 + \text{H}^+\text{X}^- \rightleftharpoons \text{RNH}_3^+\text{X}^- \qquad (2.3)$$

2.4 Shrimp shells

One of the most important source of chitin is shrimp shells which is the by product of frozen shrimp industries. Thailand is one of the biggest frozen shimp exporters. A typical composition of shrimp shell (on a dry basis) is 15-20 % chitin, 25-40 % protein and 40-55 % calcium carbonate. Blue crab wastes (on a dry basis) has approximately 15 % chitin, 35 % protein and 50 % calcium carbonate [10].

Protein [11] is biopolymer of α-amino acids. The physical and chemical properties of a protein are determined by its constituent amino acids and joined with amide linkages called peptide bonds. The general structure of protein is shown in Figure 2.8

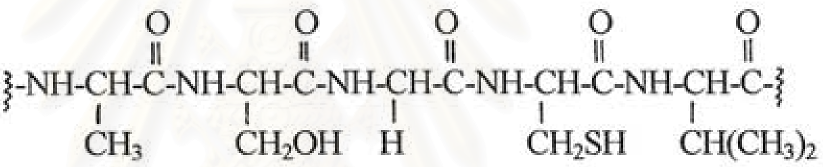


Figure 2.8 General structure of protein

Amino acid [11] is a molecule that contains both an amino group ($-NH_2$) and a carbonyl group (-COOH). The general structure of amino acid is shown in Figure 2.9

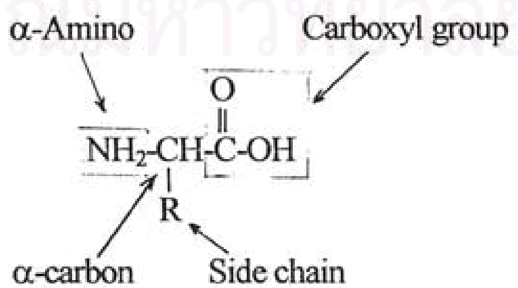


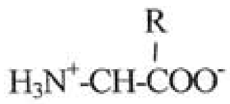
Figure 2.9 General structure of amino acid

Dipolar ion (zwitterion) is an amino acid structure with an overall charge of zero but having a positively charge substituent and a negatively charged substituent. Most amino acids exist in dipolar ionic form as shown in equation (2.4)

(2.4)

Uncharged structure	Dipolar ion or zwitterion
(minor component)	(major component)

R-COOH R-NH_2



carboxyl group	basic amino group	ammonium ion	carboxylate ion
$Pk_a = 5$	$pk_b = 4$	$pk_a = 10$	$pk_b = 12$

Acidic part is $-NH^+_3$ group not -COOH group

Basic part is $-COO^-$ group not $-NH_2$ group

Amphoteric property is the characteristic of an amino acid which contains both acidic and basic groups in molecule.

The acidic group is $-NH^{+3}$

The basic group is $-COO^-$

The predominant form of amino acid depends on the pH of solution.

In basic solution $-NH^+_3$ is deprotonated to a free $-NH_2$ group and the molecule is overall negative group. In acid solution $-COO^-$ is protonated to a free $-COOH$ group and the molecule is overall positive.

$$\underset{\text{R}}{H_2N\text{-}CH\text{-}COO^-} \underset{-OH}{\overset{H^+}{\rightleftharpoons}} \underset{\text{R}}{H_3N^+\text{-}CH\text{-}COO^-} \underset{-OH}{\overset{H^+}{\rightleftharpoons}} \underset{\text{R}}{H_3N^+\text{-}CH\text{-}COOH}$$

Anionic in base	Neutral	Cationic in acid
(High pH)	(Isoelectric pH)	(Low pH)
glyeine, pH > 9.6	pH 6.0	pH < 2.3

2.5 Related literatures

The removal of soluble azo dye in effluents containing azo reactive dyes are very difficult to treat in environmental systems, due to the sulphonic acid groups, which make the dyes very water soluble and polar.

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 (2.5) [10].

$$R\text{-}N^+H_2COCH_3\ ½\,SO_4^{2-} + NaDye \rightleftharpoons R\text{-}N^+H_2COCH_3Dye^- + ½Na_2SO_4 \quad (2.5)$$

Muzzarelli [10] 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 react with the amino groups of chitin and chitosan in both alkaline and acidic media, the hydroxyl groups take part in the reaction in alkaline media only.

Lin[13] investigated the effectiveness of powdered activated carbon (PAC) on the removal of color and chemical oxygen demand (COD) of disperse dye and the effect of PAC particle size on the treatment efficiency. Experimental results showed that a PAC dosage of 15 g dm^{-3} was sufficient to achieve an efficiency of 95 % COD removal and the effect of PAC particle size on COD removal did not appear to be large, being within 10 %.

Shimizu et al. [14] studied on the effect of added metal ions on the interaction of chitin and partially deacetylated chitin with an azo dye carrying two hydroxyl groups. The metal ions used were, Zn^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}. It was observed that the degree of adsorption increased with the increasing of Cu^{2+}. This might be attributed to the formation of the polymer - copper - dye coordination linkage.

Reife and Freeman[15] studied the adsorption of dyes and selected intermediates by using activated carbon adsorption columns developed by several pilot plants in commercial scale systems. Three acid dyes, four direct dyes and seven reactive dyes were investigated. Sodium hydrosulfite was also used to decolorize the dyes before carbon adsorption. It was found that many factors involved the adsorption efficiency such as choice of activated carbon, temperature, pH, contact time and optimum dosage of activated carbon and sodium hydrosulfite.

PhumKacha [16] studied of color removal from textile wastewater by using three differente kinds of processes. It was found that dye removal by using alum is highly effective without readjusting the pH, for acid dyes, reactive dyes and direct dyes excecpt the basic dye. Activated carbon was also highly effective for all dyes, as well as fly ash except the Levafix Navy Blue. Dye removal from textile wastewater was also satisfied with alum and fly ash.

Khachonkeittikun [17] investigated of COD reduction and color removal from textile wastewater by using activated carbon (AC) and sawdust as adsorbents in the adsorption columns. The result showed that the adsorption by AC and sawdust at the same column height decreased in order as follows: basic dye, direct dye, reactive dye and acid dye. The adsorption capacity per unit weight of both adsorbent were compared in term of color removal and COD reduction the sawdust gave 1.55 - 2.89 times and 1.18 – 2.38 times, respectively.

Juang *et al.* [18] studied the capability of chitosan to remove vinyl sulfone and chlorotriazine reactive dyes from aqueous solutions using Reactive Red 222 (RR222), Reactive Yellow 145 (RY145), and Reactive Blue 222 (RB 222) with varying concentrations of 50-500 g/m^3. He found that the amount of adsorbed dye decreased with increasing particle size of the chitosan. The maximum adsorption capacities of chitosan with particle size of 250-420 μm were 380, 179 and 87 g/kg for RR 222, RY 145, and RB 222, respectively.

Kim *et al.* [19] 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. It was found that the dye adsorption increased with increasing of DD of deacetylated chitin for each pH. He concluded that the deacetylated chitin with 36.3 and 46.8 % DDs were generally most effective DD in removal of four dyes and chromium ions at pH 3 and pH 4, respectively.

CHAPTER III
METHODOLOGY

3.1 Materials

3.1.1 Water-soluble Dyes

Four types of water-soluble dyes were obtained from DyStar Thai Co., Ltd. and used without further purification. The C.I. generic names were C.I. Acid Red 360, C.I. Reactive Red 158, C.I. Direct Red 80 and C.I. Basic Red 24. Commercial names and characteristics of these dyes are presented in Table 3.1. The chemical structures of C.I. Direct Red 80 and C.I. Basic Red 24 are shown in Figure 3.1. However, the structures of C.I. Acid Red 360 and C.I. Reactive Red 158 are not revealed by the manufacturer and are not published by the Sociely of Dyers and Colourists [20-21]. The aqueous solution of each dye was prepared by dissolving dyes in deionized water to the desired concentrations (200-2,600 mg/L).

3.1.2 Shrimp shells

Shrimp shell wastes were kindly supplied by Surapon Foods Public Co.,Ltd. After washing and drying, shrimp shells were ground to 2-3 mm particle size, packed in plastic bags and kept in dry clean plastic pail with cover at ambient temperature until use.

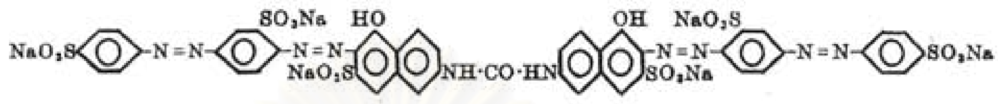
3.1.3 Chemicals

Hydrochloric acid (37% w/v) and sodium hydroxide solution (50% w/v) were supplied by Witcorp Chemicals Co.,Ltd. Sodium borohydride and lithium chloride were purchased from Ajax Chemicals. Hydrochloric acid, sodium hydroxide, glacial acetic acid, sodium chloride and urea were obtained from Carlo Erba. N,N-dimethylacetamide was purchased from Lab-Scan.

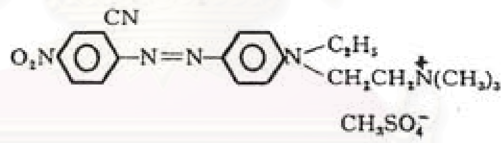
Table 3.1 Characteristics of water-soluble dyes

C.I. generic name	Commercial name	Chemical class	Active ingredient (%w/w)	Solubility in water at 25°C(g/L)	pH in water (100 g/L)
C.I. Acid Red 360	Telon Fast Red AFG	Azo	92-97	30	6.5 – 8.0
C.I. Reactive Red 158	Levafix Brilliant Red E-4BA	Azo	45 – 55	60	6.0 – 7.0
C.I. Direct Red 80	Sirius Red F3B	Polyazo	92-97	50	9.5 – 11.0
C.I. Basic Red 24	Astrazon Red 5BL 200%	Monoazo	100	< 1	2.0 – 2.5

DyStar Thai Co., Ltd.



C.I. Direct Red 80



C.I. Basic Red 24

Figure 3.1 Chemical structures of C.I. Direct Red 80 and C.I. Basic Red 24

3.2 Equipments

3.2.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained on an Equinox 55 spectrometer, Bruker, USA. A frequency range of 4000 – 400 cm^{-1} was observed with 32 scans at a resolution of 8 cm^{-1} using a deuterated triglycine sulfate detector (DTGS).

3.2.2 Ultraviolet-Visible Spectrophotometer (UV/VIS)

An UV/VIS spectrophotometer, Lambda 10 from Perkin Elmer, USA was used for qualitative and quantitative analysis of dye adsorption and desorption at various wavelengths.

3.2.3 Shaking Water Bath

A thermostatic shaking water bath, GFL 1086 was used for shaking and controlling temperature of adsorption and desorption experiments.

3.2.4 pH Meter

pH values of solutions were obtained on an 920A pH meter, Orion, USA.

3.2.5 High Speed Centrifuge

A Sorval® Super T21 High Speed Centrifuge, Du Pont, USA, was used for separation of the supernatant.

3.2.6 Viscometer

Ubbelohde viscometer no. 75 and 150, Cannon, USA, were used for determination of viscosity of chitosan and chitin respectively.

3.2.7 Sieving Machine and Sieves

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

3.2.8 Surface Area Analyzer

The specific BET (Brunauer-Emmett-Teller) surface area was determined by using a surface area analyzer, Autosorb-1, Quantachrome, USA.

3.3 Experimental Procedures

3.3.1 Production of Chitin

Shrimp shells were demineralized by immersing in 1M HCl with intermittently stirring at ambient temperature overnight. The demineralized product was washed with water several times until neutral to pH paper, filtered and dried in hot air oven at 100 °C. The reaction occurred as shown in equation (3.1)

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3 \qquad (3.1)$$

After demineralization, the product was deproteinized by heating in 1M NaOH solution at 80-90 °C for 2 h and cool. The deproteinized products were washed with water until neutral to pH paper, filtered and dried at 100 °C in hot air oven. The product obtained was chitin.

3.3.2 Production of Chitosan (22)

Deacetylation of chitin to obtain chitosan was accomplished by reacting with concentrated sodium hydroxide at high temperature with the ratio of 10 g of chitin, 0.5 g of sodium borohydride and 100 mL of 20-50 %w/w NaOH at 110 °C for varying time in order to get the required degree of deacetylation (DD). The chitosan product was cooled, washed with water until neutral to pH paper, filtered and dried at 100 °C in hot air oven. The step of chitin and chitosan production is shown in Figure 3.2

3.3.3 Preparation of Adsorbents

Prior to use, the shrimp shells, chitin and chitosan flakes were ground, sieved into three sizes, namely 0.212-0.425, 0.425-0.710 and 0.710-1.00 mm by using sieving machine and kept in dried, clean and closed containers.

3.3.4 Determination of Degree of Deacetylation of Chitin and Chitosan

The degrees of deacetylation(DD) of chitin and chitosan were determined by the modified method of Sannan *et al.* [23]

I.R. measurement was carried out as follow. The samples (53 μm) were dried at 60 °C for 12 h under reduced pressure. The mixed powder of 1 mg of sample and 30 mg of KBr was mechanically blended. The I.R. spectra of samples were recorded with FTIR spectrometer. The intensity of maxima of the I.R. absorption bands was determined by the baseline method. The degrees of deacetylation of chitin and chitosan were calculated from equation (3.2).

$$DD\,(\%) = 98.03 - 34.68\,[A_{1550}/A_{2878}] \quad (3.2)$$

Where A_{1550} and A_{2878} were the absorbances of the amide II band and the C-H band at 1550 and 2878 cm^{-1}, respectively.

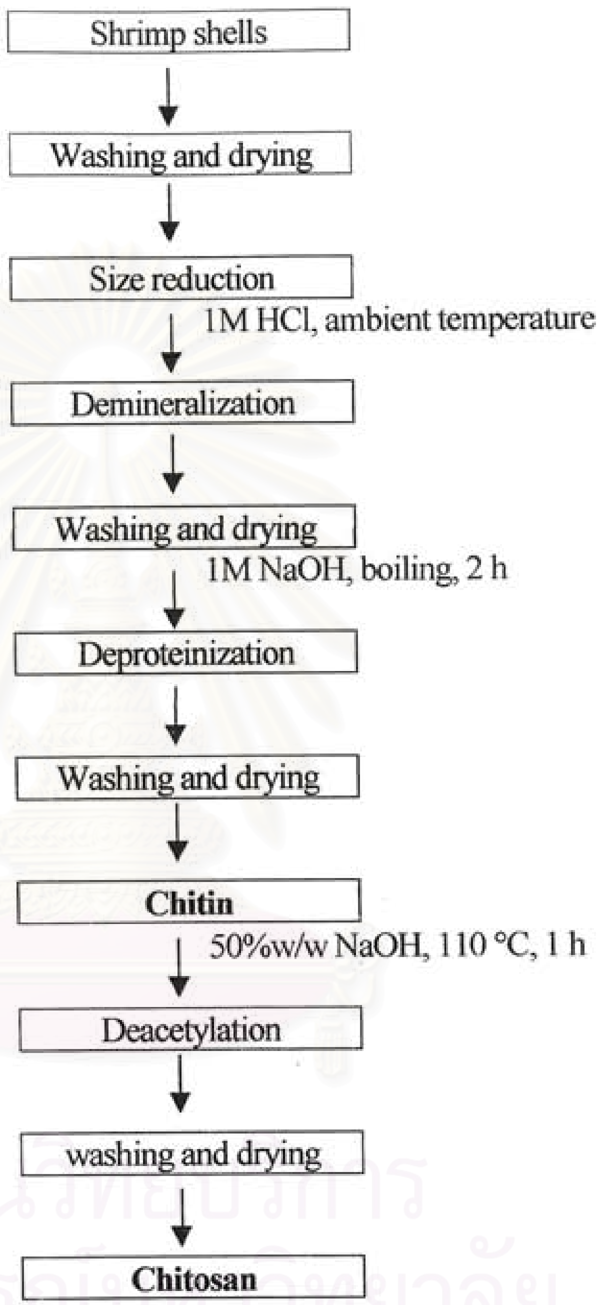


Figure 3.2 Chitin and chitosan production from shrimp shells

3.3.5 Determination of Molecular Weight of Chitin [24] and Chitosan [25]

This method is based on viscometry. In this method, viscometric constants for chitosan are applied, because those for chitin are not yet available. Various concentrations of chitin and chitosan solutions were prepared as follows.

Chitin powder (0.053–0.212 mm) was weighed and completely dissolved in 5%w/v lithium chloride in N, N-dimethylacetamide to prepare stock solution (0.08 g/100 mL). Various concentrations of chitin were diluted from the stock solution with the same solvent. Viscosity of each solution is measured at 30 °C with a Cannon-Ubbelohde viscometer no. 150.

Chitosan powder (0.053–0.212 mm) was weighed and completely dissolved in 0.2M acetic acid-0.1M NaCl-4M urea aqueous solution to prepare stock solution (0.40 g/100 mL). Various concentrations of chitosan were diluted from the stock solution with the same solvent. Viscosity of each solution is measured at 25 °C with a Cannon-Ubbelohde viscometer no. 75.

Intrinsic viscosities of chitin and chitosan were determined graphically by plotting the viscosity data against concentration. The molecular weight of chitin and chitosan were calculated from equation (3.3)

$$[\eta] = kM^a \qquad (3.3)$$

Where $[\eta]$: Intrinsic viscosity

M : Molecular weight of chitin or chitosan

k : Mark-Houwink constant (8.93×10^{-4})

a : Mark-Houwink exponent (0.71)

3.3.6 Determination of Specific Surface Area of Adsorbents

The adsorbents used in this study were shrimp shells, chitin and chitosan. The particle size ranges of these adsorbents were 0.212-0.425, 0.425-0.710 and 0.710-1.000 mm. After drying at 100 °C for at least 3 h, suitable amounts of samples (0.2-0.3 g) were weighed and the specific BET (Brunauer-Emmett-Teller) surface areas were automatically determined by using surface area analyzer from nitrogen adsorption isotherms and equation (3.4)

$$S = \frac{Wm \times N \times Acs}{M} \quad (3.4)$$

Where S : Total surface area of adsorbent (m^2/g)

W_m : Weight of adsorbate monolayer (g)

N : Avogadro's number (6.023×10^{23})

Acs : Molecular cross-sectional area of the adsorbate molecule (m^2) (16.2 $Å^2$ for nitrogen monolayer at 77 °K)

M : Molecular weight of adsorbate

3.3.7 Determination of λmax of Dye Solutions at Various pHs

The optimum concentrations of each dye were prepared at pH 3 to pH 12. The λmax values of the dye solutions were determined by scanning at wavelength 900–190 nm using UV/VIS spectrophotometer.

3.3.8 Preparation of Calibration Curve of Dye Solutions at Various pHs

Several concentrations of the aqueous dye solutions were prepared at pH 3 to pH 12. The absorbance of each dye concentration was recorded at its λmax using UV/VIS spectrophotometer. The calibration curve was plotted between dye concentration and absorbance.

3.3.9 Effect of Various pHs on Dye Stability

The aqueous dye solutions (200 mg/L) were prepared at pH 3 to pH 12. The amount of 25 mL of each dye solution was shaken in shaking water bath at 80 rpm for 0 h and 24 h at ambient temperature and centrifuged at 15000 rpm for 10 min. The absorbance of each supernatant was recorded at its λmax using UV/VIS spectrophotometer. The amount of each dye remained in the supernatant after 0 h and 24 h shaking was calculated from equation (3.5) and plotted against the pH.

$$Qs = \frac{As}{S} \qquad (3.5)$$

Where Qs : Amount of dye in supernatant after 0 h or 24 h (mg/L)

As : Absorbance of dye in supernatant after 0 h or 24 h

S : Slope value from calibration curve of dye concentration and absorbance

3.3.10 Preparation of Dye-sorbed Adsorbents

Aqueous dye solutions (400 mg/L) were prepared at specified pHs as follows: C.I. Acid Red 360 at pH 4, C.I. Reactive Red 158 at pH 3, C.I. Direct Red 80 at pH 3 and C.I. Basic Red 24 at pH 10.

Five grams of each adsorbent (0.425-0.710 mm) were added to 150 mL of each dye solution. The dye solution were shaken in shaking water bath at 120 rpm for 24 h at ambient temperature and filtered. The adsorbents were wash several times with deionized water to remove the unadsorbed dyes. The filtrate was collected and diluted to 250 mL in volumetric flask. 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. The absorbances of the residual dye in supernatant were determined by using UV/VIS spectrophotometer at λmax of each dye. Blanks used in the experiment were deionized water with the same pH corresponding to the dyes solutions. The amounts of dye adsorbed were calculated from equation (3.6) which was derived from the Beer's law [26-27] as follows:

$$Qa = \frac{(C \times 150) - [(Aa\text{-}Abl) \times 250] / S}{W \times 1000} \quad (3.6)$$

Where Qa : Amount of dye adsorbed on the adsorbent (mg/g)

C : Initial concentration of dye solution (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

W : Weight of adsorbent (g)

3.3.11 Effects of Various Parameters on Dye Adsorption

Four types of water-soluble dyes, namely C.I. Acid Red 360, C.I. Reactive Red 158, C.I. Direct Red 80 and C.I. Basic Red 24, as well as three types of adsobents, namely shrimp shells, chitin of 21.64 %DD and chitosan of 79.55 %DD were used in all experiments. The particle size range of each adsorbent used was between 0.425-0.710 mm.

Fifty milligrams of the adsorbents were suspended in 25 mL of aqueous dye solution with initial concentration of 200 mg/L. The pHs of the system were adjusted from pH 3 to pH 11 by using 0.1M NaOH or 0.1M HCl. The suspensions were shaked in shaking water bath at 80 rpm for 24 h (otherwise stated) at ambient temperature (25 °C). The supernatant was separated by centrifugation at 15000 rpm for 10 min. The absorbances of the residual dye in supernatant were determined by using UV/VIS spectrophotometer at λmax of each dye. Blanks used in the experiment were deionized water with the same pH corresponding to the dyes solutions. Adsorption parameters such as degree of deacetylation of chitosan, adsorption time, particle size of the adsorbents and dye concentration, were also varied to study effects of these parameters on dye adsorption. The amounts of adsorbed dyes were calculated from equation (3.7) and (3.8) which was derived from the Beer's law [26-27] as follows :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000} \quad (3.7)$$

$$Ec = \frac{Qa \times W \times 10^5}{C \times V} \quad (3.8)$$

Where Qa : Amount of adsorbed dye(mg of adsorbed dye per g of adsorbent)

C : Initial concentration of dye (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : 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)

Ec : Adsorption efficiency of dye on adsorbent over concentration (% w/w)

3.3.12 Effects of pH and Temperature on Dye Desorption from the Adsorbents

Desorption of each dye-sorbed adsorbent (50 mg) was carried out in 50 mL of deionized water at pHs varied from pH 4 to pH 12 adjusted by using 0.1M NaOH or 0.1M HCl. The temperatures were set at 30 °C and 80 °C. The suspensions were shaken at 120 rpm for 24 h. The supernatant was separated by centrifugation at 15,000 rpm for 10 min. The absorbances of the desorbed dye in the supernatant were determined by using UV/VIS spectrophotometer at λmax of each dye. The amounts of desorbed dyes were calculated from equation (3.9) which was derived from the Beer's law [26-27] as follows :

$$Qd = \frac{Ad \times V \times 100}{S \times Qa \times W \times 1000} \quad (3.9)$$

Where Qd : Amount of desorbed dye (% w/w)

Qa : Amount of adsorbed dye (mg of dye per g of dye-sorbed adsorbent)

Ad : Absorbance of desorbed dye

V : Volume of deionized water at pH tested (mL)

S : Slope value from calibration curve of dye concentration and absorbance.

W : Weight of dye-sorbed adsorbent (g)

3.3.13 Dye Removal from Textile Effluents

Nine samples of dye effluents from dyebath drainages after dyeing were obtained from Asia Fiber Co.,Ltd., Tanakul Textile Printing and Dyeing Co.,Ltd., Sinsaenee Co.,Ltd., and Golden Thai Industries Co.,Ltd., respectively. These samples were used for studying on dye removal from the effluents. Authorized person of each factory confirmed the specified type of dye in each effluent.

The dye effluents were measured the initial pH and then adjusted to pH 4 for acid dye, reactive dye and direct dye, and to pH 10 for basic dye by using HCl or NaOH solutions. The dye solutions were centrifuged to remove undissolved particles. Fifty milligrams of each adsorbent were suspended in 25 mL of each dye supernatant and the further adsorption procedures were followed those described in section 3.3.11. The amount of dye removal was calculated from equation (3.10), which was derived from the Beer's law [26-27].

$$Qr = \frac{[Ab - (Aa - Abl)] \times 100}{Ab} \quad (3.10)$$

Where Qr = Amount of dye removal (%w/w)

Ab = Absorbance of dye before adsorption

Aa = Absorbance of dye after adsorption

Abl = Absorbance of blank

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Production of Chitin

Six batches of chitin, obtained from shrimp shells by demineralization with 1M HCl for 24 h and deproteinization with 1M NaOH at 80-90 °C for 2 h, were produced for further chitosan preparation. Another batch with 21.64% of degree of deacetylation (DD) carried out by the same procedure was prepared for dye adsorption and desorption studies. The conversion of shrimp shells to chitin was about 26-30 % (w/w). Mazzarelli reported that the yield of chitin obtained by the method of Whistler and BeMiller was about 20 % [10].

4.2 Production of Chitosan

Five batches of chitosan were produced from chitin by deacetylation in 50% w/v NaOH solution at 110 °C for 1 h. Degree of deacetylation of chitosan obtained was about 79.3-79.8% and the production yield was about 78-85% based on chitin. Three batches of those with 79.55% DD were mixed well and kept for further dye adsorption and desorption studies.

FTIR spectra of shrimp shell, chitin and chitosan are demonstrated in Figure 4.1. The absorption bands at 1655, 1550 and 1310 cm^{-1}, which are characteristic bands of chitin have been reported to be the amide I, II, and III bands, respectively. The sharp band at 1378 cm^{-1} has been assigned to the CH_3 symmetrical deformation mode. All these bands are known to become very weak in the IR spectrum of chitosan [23].

The degrees of deacetylation (DD) of chitosan obtained from chitin by using various NaOH concentrations and various reaction times were determined and the results are shown in Table 4.1. The DD of original chitin before the hydrolysis was 20.85%. Peak intensities of chitosan at 1550 cm^{-1} decreased and the DDs increased

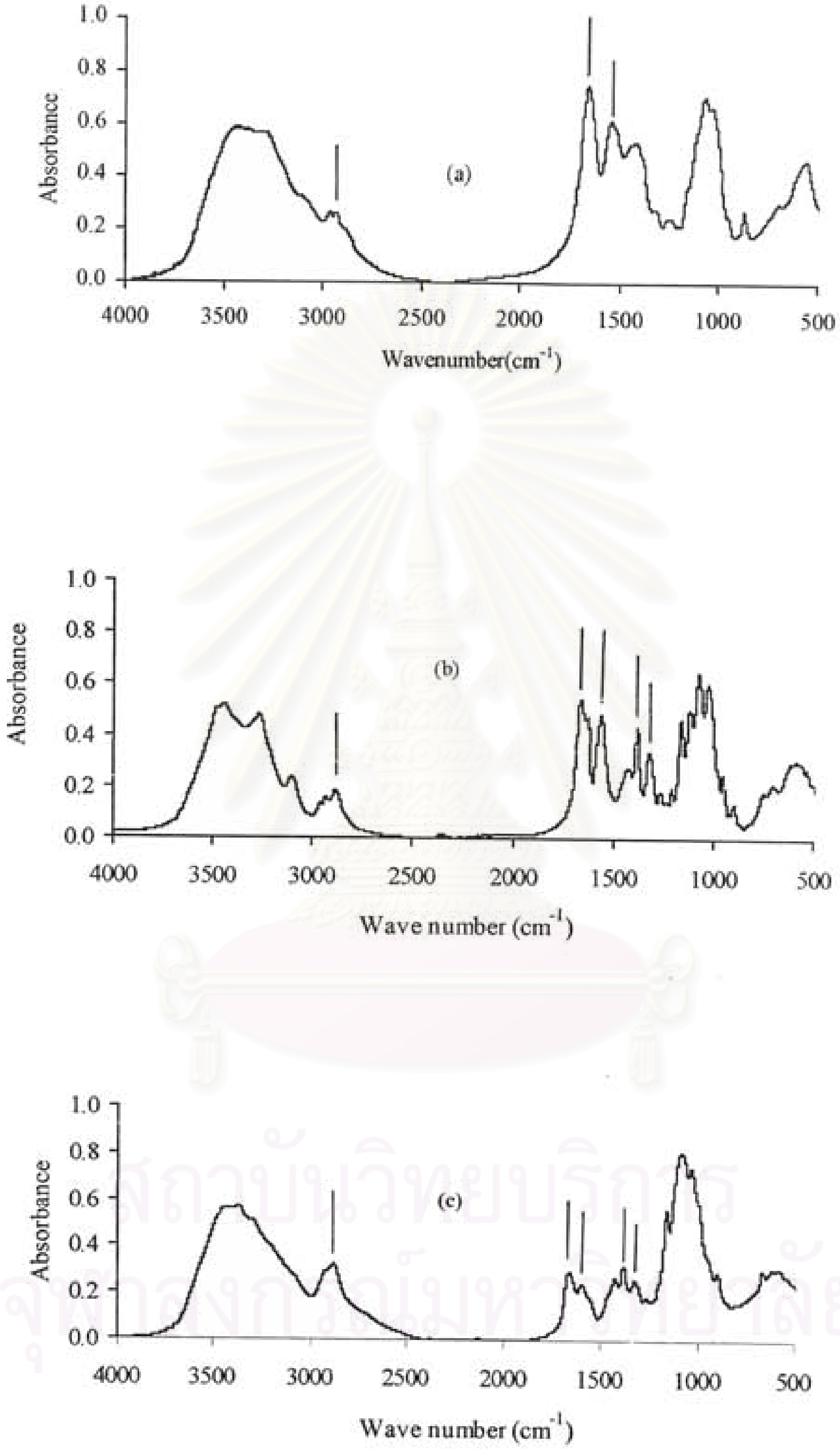


Figure 4.1 FTIR spectra (a) shrimp shell (b) chitin (DD=21.64%) (c) chitosan (DD=79.55%)

with the increase of NaOH concentration and reaction time. In addition, it is also possible that the treatment could cause a discrepancy in the heterogeneity of the sample deacetylated in 35% w/v NaOH at 110°C for 40 min.

Table 4.1 Degree of deacetylation of chitosan obtained from chitin at various conditions

NaOH concentration (%w/v)	Reaction time (min)	Degree of deacetylation (%)
20	20	21.62
	40	23.80
	60	24.48
30	30	34.06
	60	34.88
35	20	36.54
	40	49.20
	60	45.12
	90	47.36
37	30	52.98
	60	60.71
38	60	72.68
40	10	69.33
	30	71.08
	60	73.54
50	60	79.55

4.3 Molecular Weight of Chitin and Chitosan

Figure 4.2 was the relationships between viscosity and concentration of chitin and chitosan. The molecular weights (MW) of chitin and chitosan were 2.05×10^6 and 5.73×10^5, respectively. The remarkable difference between the MW of chitin and chitosan indicated that chain scission of chitin occurred during deacetylation reaction due to the severity of reaction conditions. Muzzaulli[10] reported that the molecular weight of β-chitin and chitosan obtained by Lee were as follows : chitin 2.5×10^6, chitosan A, 7.25×10^5; chitosan B, 4.92×10^5 and chitosan C, 2.35×10^5.

4.4 Specific Surface Area of Adsorbents

Table 4.2 shows the specific BET surface area of three adsorbents analyzed by using surface area analyzer. The surface area decreased as particle size of the adsorbents increased. The specific surface areas of chitin and chitosan of the same size were about two times higher than that of shrimp shells.

Table 4.2 Specific surface area of the adsorbents

Type of adsorbents	Particle size (mm)	Specific BET Surface area (m^2/g)
Shrimp shells	0.212-0.425	10.02
	0.425-0.710	8.96
	0.710-1.00	8.59
Chitin	0.212-0.425	23.24
	0.425-0.710	17.64
	0.710-1.00	17.27
Chitosan	0.212-0.425	20.09
	0.425-0.710	17.39
	0.710-1.00	12.03

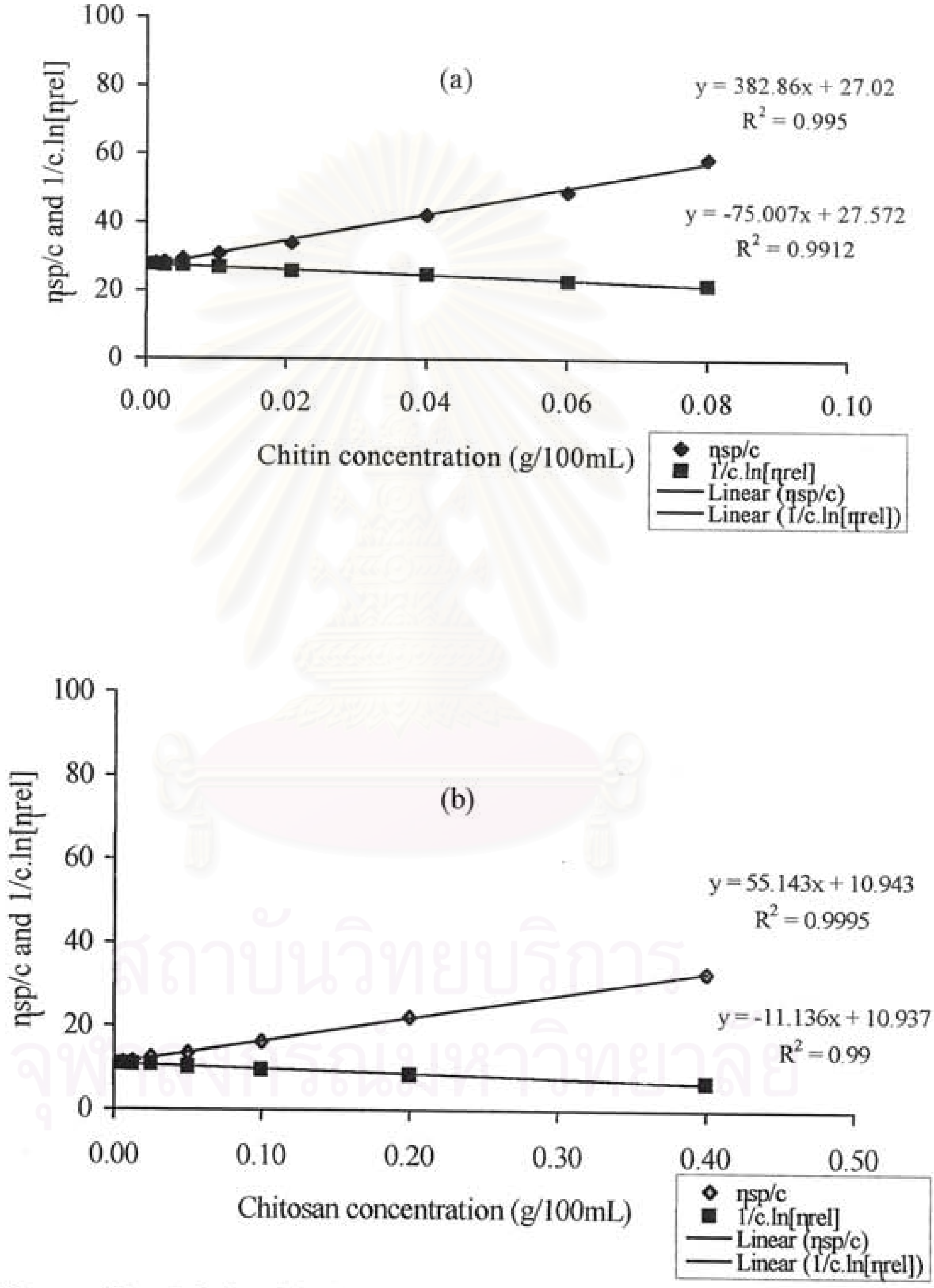


Figure 4.2 Relationships between viscosity and concentration
(a) chitin (b) chitosan

4.5 λmax of Dye Solutions at Various pHs

Adsorption spectra of dye solution (20 mg/L) at pH 4 scanned from wavelength 900-190 mm on UV/VIS spectrophotometer are demonstrated in Figure 4.3. The λ max values of each dye solution are shown in Table 4.3. The effect of pH on the λ max of the dye solution was investigated by varying the pHs of the dye solutions from pH 3 to pH 12. It was found that the λ max of each dye solution did not change when the pH of the dye solution was varied from pH 3 to pH 12.

Table 4.3 λmax of dye solutions

Type of dye	λmax (nm)
C.I. Acid Red 360	535
C.I. Reactive Red 158	512
C.I. Direct Red 80	526
C.I. Basic Red 24	512

4.6 Effect of Various pHs on Dye Stability

The effects of pH on stability of each dye solution were shown in figures 4.4 – 4.7. The pHs of the dye solutions were varied from pH 3 to pH 8, execpt for basic dye that the pHs were varied from pH 3 to pH 11. After standing for 24 h, the changes in dye concentrations were determined. It was found that all dye solutions were stable for the whole pH range tested, except for the acid dye which was partially precipitated at pH 3.

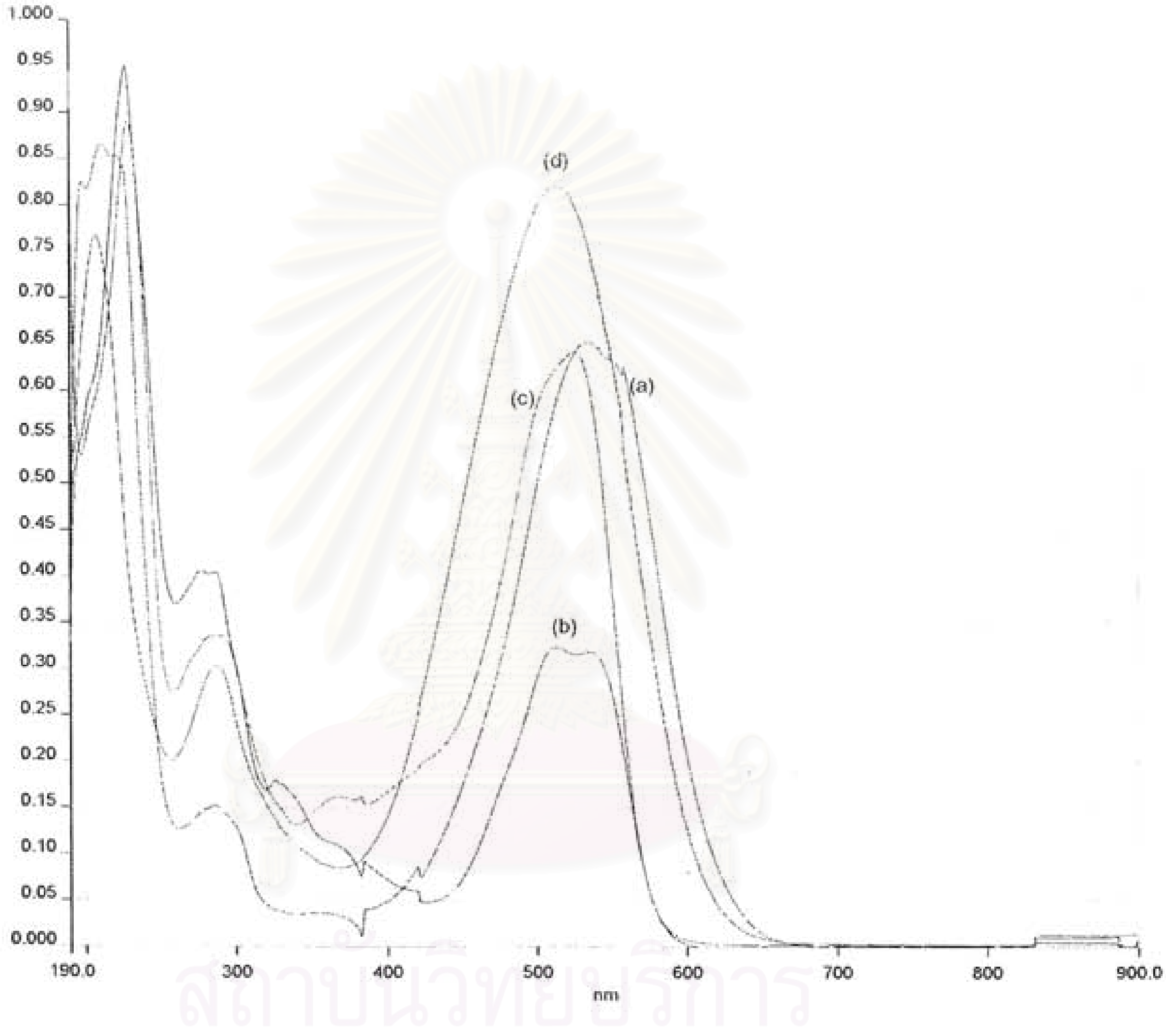


Figure 4.3 UV/VIS spectra of dye solutions with concentration of 20 mg/L at pH 4:
(a) C.I. Acid Red 360 (b) C.I. Reactive Red 158
(c) C.I. Direct Red 80 (d) C.I. Basic Red 24

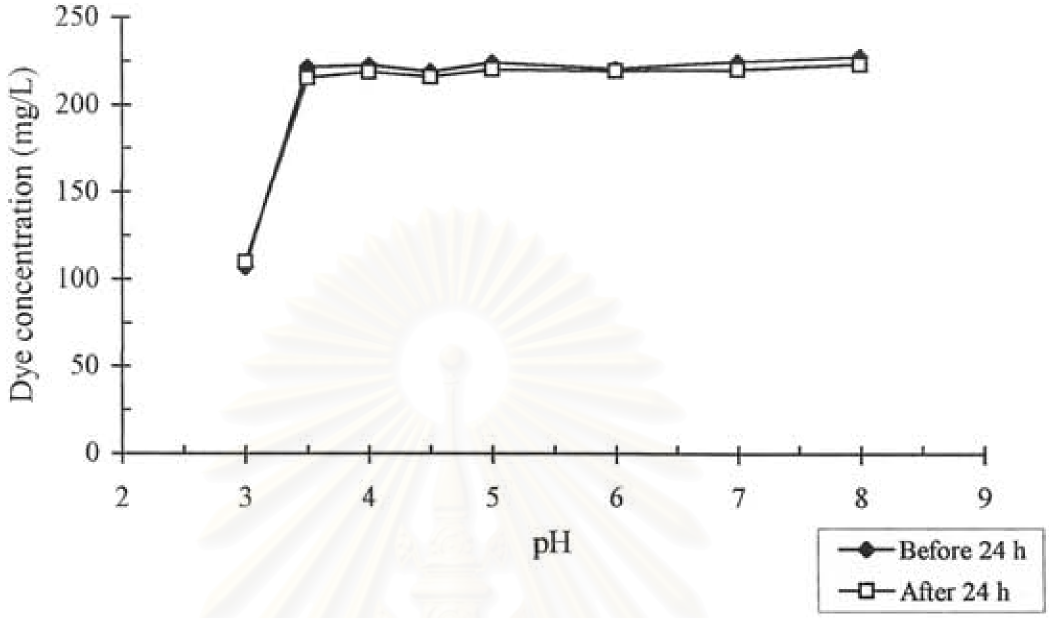


Figure 4.4 Stability of C.I. Acid Red 360 at various pHs

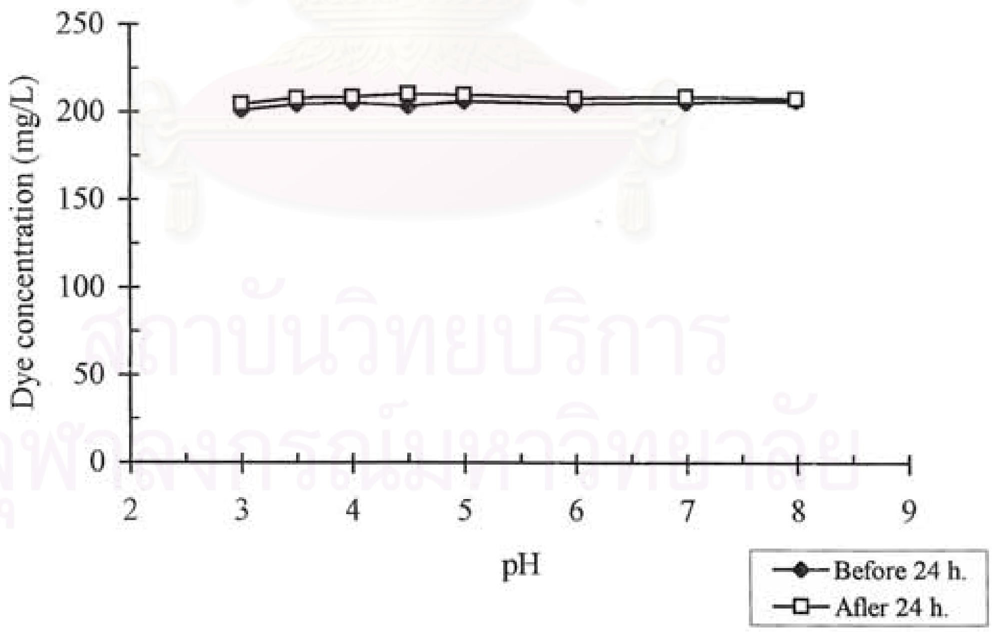


Figure 4.5 Stability of C.I. Reactive Red 158 at various pHs

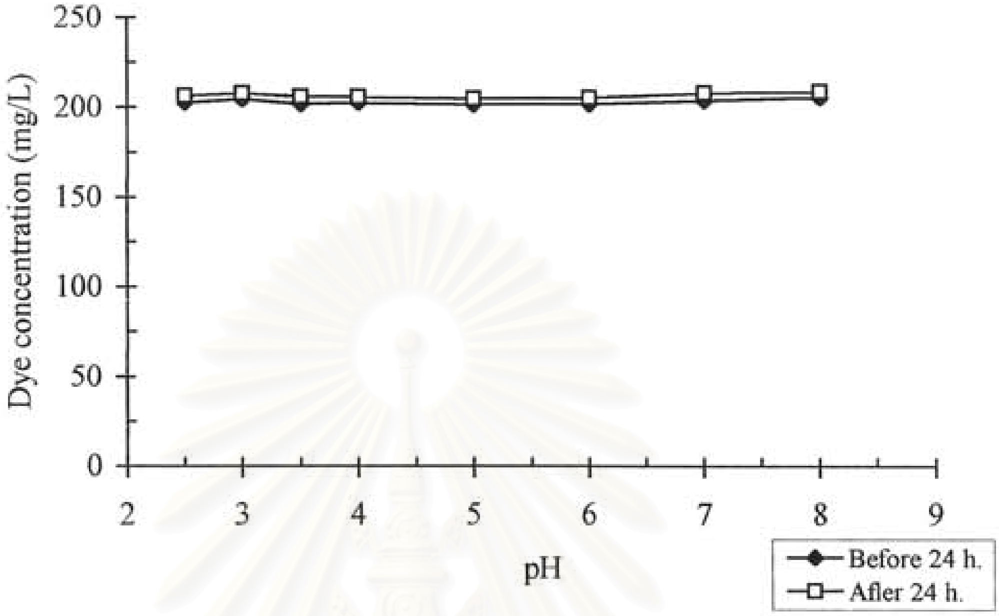


Figure 4.6 Stability of C.I. Direct Red 80 at various pHs

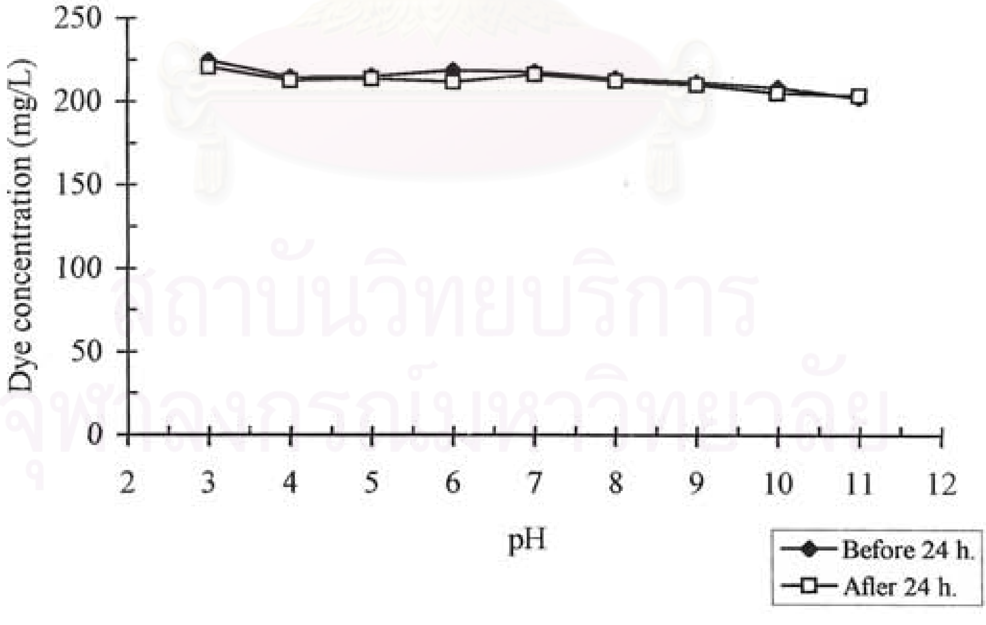


Figure 4.7 Stability of C.I. Basic Red 24 at various pHs

4.7 Calibration Curve of Dye Solutions at Various pHs

Table 4.4 shows the average slope values obtained from the calibration curves plotted between the absorbance of the dye solutions and their concentrations measured at pH 3 to pH 12, except for the acid dye that was determined at pH 4 to pH 11. There was little difference between the slope value determined at different pH of which the standard deviation was not more than 0.001. These average slope values of the dye solutions would be used to calculate the amounts of dye in all solutions throughout this research.

Table 4.4 Average slope values of the dyes at specified wavelength

Type of dyes	Wavelength (nm)	Average slope value
C.I. Acid Red 360	535	0.0326
C.I. Reactive Red 158	512	0.0160
C.I. Direct Red 80	526	0.0310
C.I. Basic Red 24	512	0.0446

4.8 Dye-sorbed Adsorbents

The dye–sorbed adsorbents were prepared for the dye desorption studies. The amount of dye adsorbed on shrimp shells, chitin and chitosan in the unit of milligrams of dye per gram of adsorbent is shown in Table 4.5. The amount of each dye adsorbed on each adsorbent was slightly different except the basic dye of which chitin and chitosan could notably adsorb less than shrimp shells.

Table 4.5 Amounts of dyes adsorbed on adsorbents at specified pH at 25 °C

Type of dye	pH	Adsorbed dye (mg/g)		
		Shrimp shell	Chitin	Chitosan
C.I. Acid Red 360	4	11.84	11.43	11.83
C.I. Reactive Red 158	3	11.97	12.00	12.00
C.I. Direct Red 80	3	11.80	12.00	11.99
C.I. Basic Red 24	10	11.79	3.62	1.99

4.9 Dye Adsorption

4.9.1 Effect of pH on Dye Adsorption

Figures 4.8-4.11 show adsorption behaviors of each dye solution on shrimp shells, chitin and chitosan. For acid dye and reactive dye shown in Figures 4.8 – 4.9, chitosan, chitin and shrimp shells could adsorb the dye at acidic pH better than at alkaline pH. When the pHs of dye solutions increased from pH 3 to pH 8, the adsorbed dye tended to decreased. Especially, when the pH changed from pH 5 to pH 6, the amounts of adsorbed dyes sharply decreased. From pH3 to pH 5 and from pH 6 to pH 8, the changes in the amounts of adsorbed dyes were relatively small as compared to the change between pH 5 and pH 6. Among the three adsorbents, chitosan gave the highest amount of adsorbed dyes followed by chitin and shrimp shells.

Acid dye showed very high adsorption on chitin, chitosan and shrimp shells at acidic pH because the negative charge of sulphonic acid groups ($-SO_3^-$) reacted with basic amino groups ($-NH_3^+$) present in shrimp shells, chitin and chitosan resulting in the ionic interaction, formation of between the dyes and the adsorbents. In alkaline pH, the adsorption of acid dye on each adsorbent was low as compared to the adsorption in acidic pH because there was a repulsion force between negative charges of sulphonic acid groups and positive charges of basic amino groups.

Reactive dye, besides the sulphonic acid groups, also contains the reactive group in the molecule, of which its type determines the level of its reactivity [8]. Very high adsorption of reactive dye occurred on the three adsorbents in acidic pH solutions. This due to the ionic interactions between the sulphonic acid groups of the dye and the basic amino groups in adsorbents, similar to acid dye, and the covalent bond which may be formed between reactive groups of the dye and acetamido and basic amino groups of the adsorbents [9-10]. The adsorption of reactive dye in alkaline solution was lower than that in acidic pH.

Direct dye is a polyazo dye containing sulphonic acid groups. The molecular structure of direct dye is similar to acid dye and reactive dye but the molecular size is larger. The important interaction forces between direct dye and the adsorbents are ionic bonding, hydrogen bonds and van der Waals forces [8]. The adsorption of direct dye on chitosan shown in Figure 4.10 increased sharply at pH less than 3.5. The similar trend was obtained for the dye adsorption on chitin and shrimp shells but the amounts of adsorbed dye were lower than that obtained for chitosan. The difference in adsorption ability of the adsorbents for direct dye may be due to ionic bond formation between amino groups of chitosan and sulphonic acid groups of direct dye. Chitin also contains amino groups in its molecules but the number of amino groups in chitin is less than chitosan. At pH higher than 4, the amounts of adsorbed dye were rather constant for all types of adsorbent.

However, the use of chitosan as an adsorbent at pH less than 3 could be severely limited because chitosan can dissolve at these pHs. Moreover the experimental result in Figure 4.8 showed that some part of C.I. Acid Red 360 existed in solution as large molecule clusters, also called dye aggregates, at pH less than 3.5. For these reasons, the optimum pH for further adsorption studied of C.I. Acid Red 360, C.I. Reactive Red 158 and C.I. Direct Red 80 is at pH 4.

Figure 4.11, shrimp shells could adsorb C.I. Basic Red 24 much better than chitin and chitosan for the whole pH range. C.I. Basic Red 24 contains positive charges of trimethyl-ammonium groups ($-N^+(CH_3)_3$) in its molecules. Shrimp shell contains 15-20% chitin, 25-40% protein and 40-55% calcium carbonate. In alkaline solutions, the carboxylic groups ionize to form negative ions leaving the shrimp shells a net negative charge ($RCOO^-$) which forms ionic interaction with positive ion of basic dye.

In acidic solutions, the situation was reversed, protonation of amino groups of chitin and protein in shrimp shells occurred resulting in the formation of a positive charge (RNH^+_3). Consequently, the repulsion force occurred between positive charge of basic dye and positive charge of chitin and protein containing in shrimp shells.

Contrarily, the adsorption of basic dye on chitin and chitosan containing positive charges of ammonium group ($-NH_3^+$) was very low due to the repulsion between positive charges of dye and adsorbents.

However, the adsorption of dye on three adsorbents could also be attributed to many other different interactions [(8)] between the adsorbate and adsorbent molecules. Those interactions may be ionic bonding, covalent bonding, hydrophobic interaction, hydrogen bonding and van der Waals forces.

4.9.2 Effect of Degree of Deacetylation of Chitosan

The effect of degree of deacetylation (DD) of chitosan on adsorption capacity is shown in Figure 4.12. Adsorption of acid dye, reactive dye, and direct dye on the adsorbents was held at pH 4 for 1, 5 and 24 h, respectively, due to the ease of adsorption. Basic dye was adsorbed at pH 10 for 24 h.

For acid dye and direct dye, the highest amounts of adsorbed dyes were obtained for chitosan with 71.08% DD. For reactive dye and basic dye, those were obtained for chitosan with 60.71% DD and 24.48% DD, respectively.

However, the amounts of adsorbed dyes were slightly increased as the DD increased due to an increase in ionic bonding sites. For basic dye the amount of adsorbed dye was rather constant as the DD increased due to the repulsion of positive charges of the dye and the adsorbents.

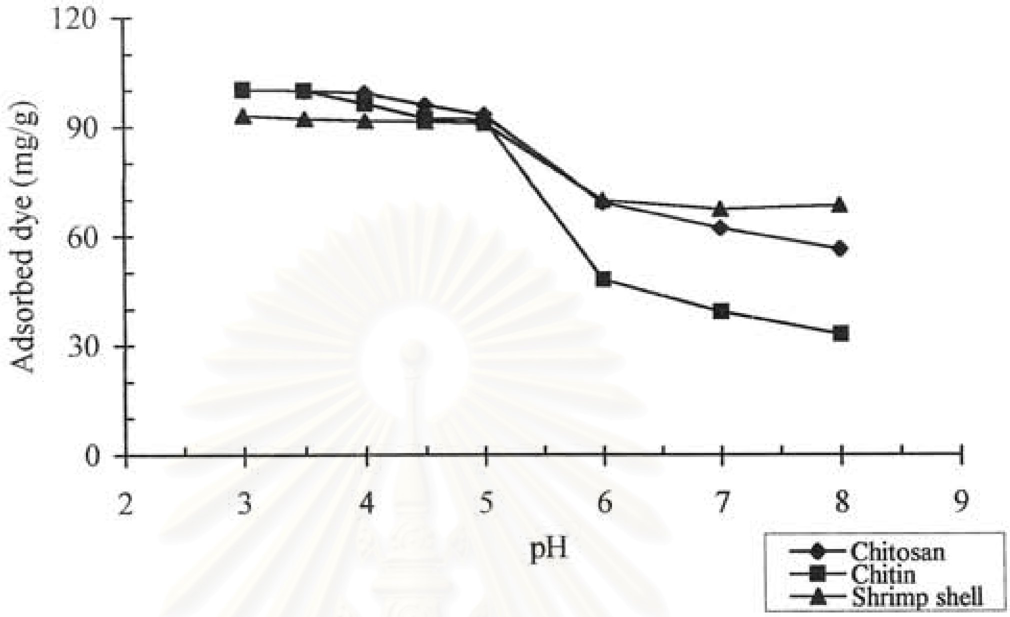


Figure 4.8 Effect of pH on the adsorption of C.I. Acid Red 360 at 25 °C

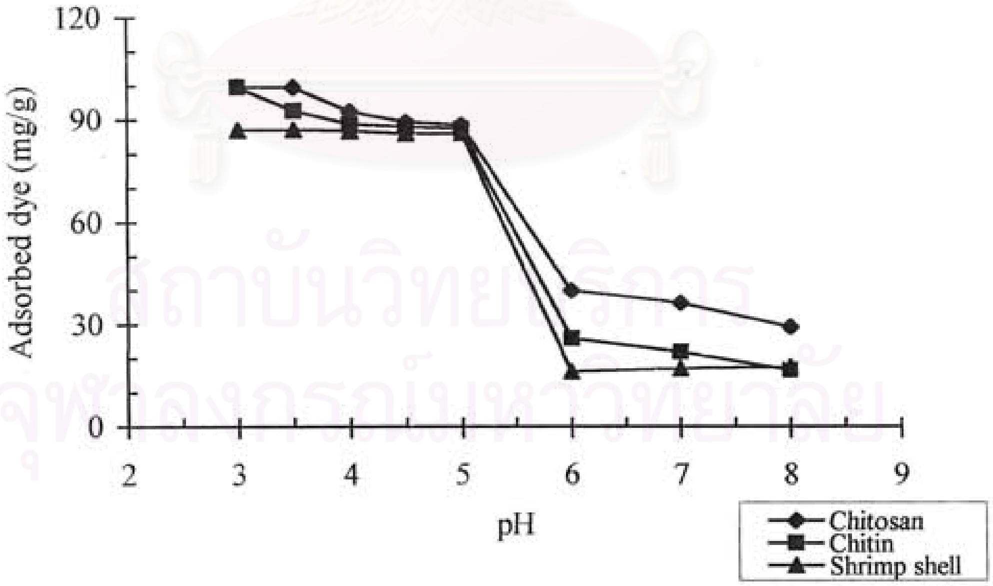


Figure 4.9 Effect of pH on the adsorption of C.I. Reactive Red 158 at 25 °C

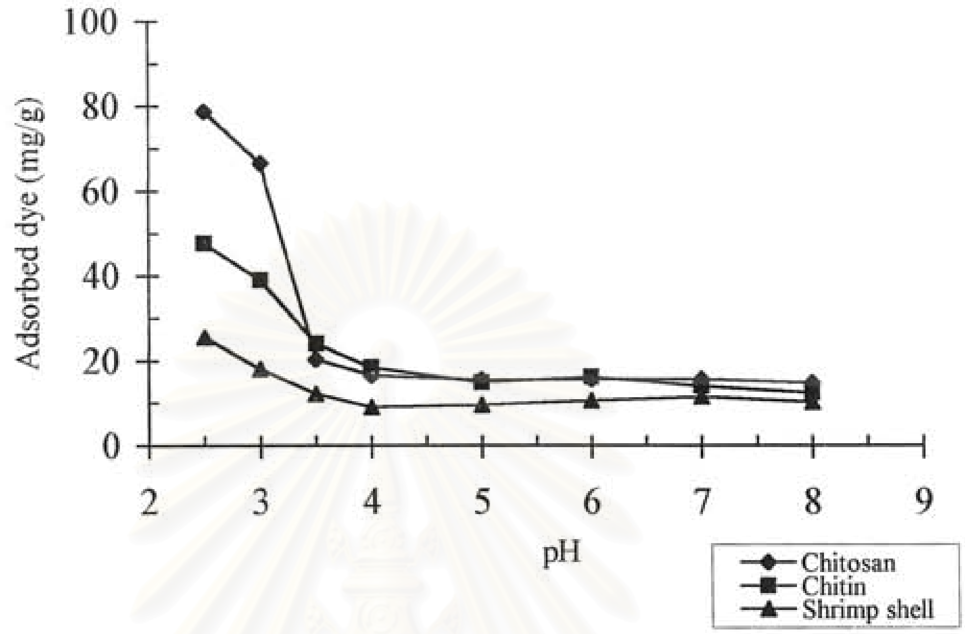


Figure 4.10 Effect of pH on the adsorption of C.I. Direct Red 80 at 25 °C

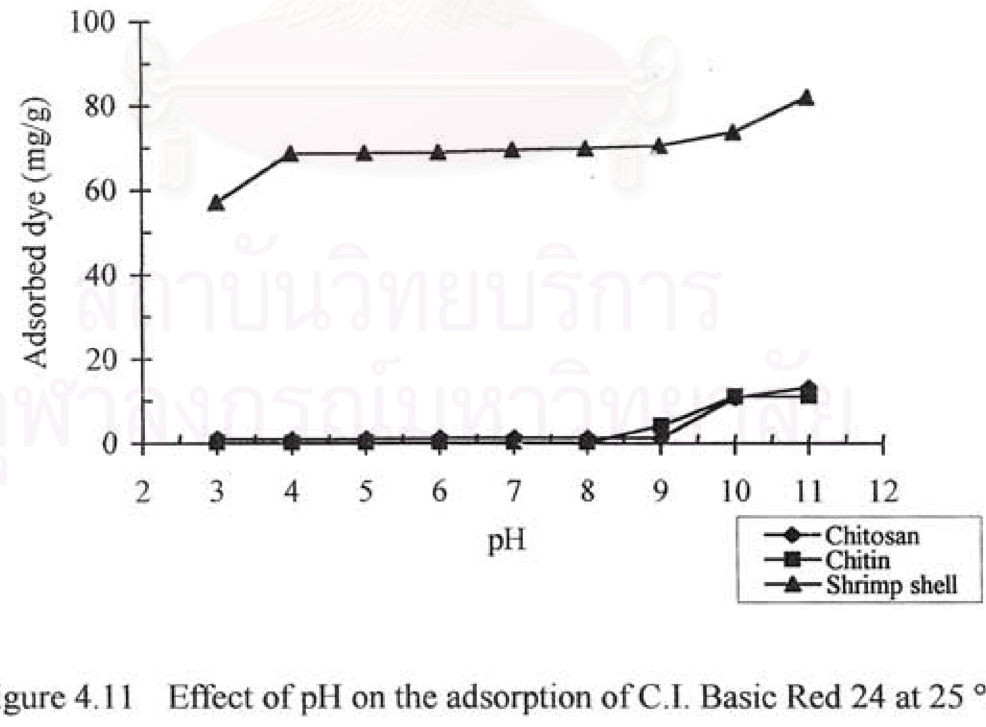


Figure 4.11 Effect of pH on the adsorption of C.I. Basic Red 24 at 25 °C

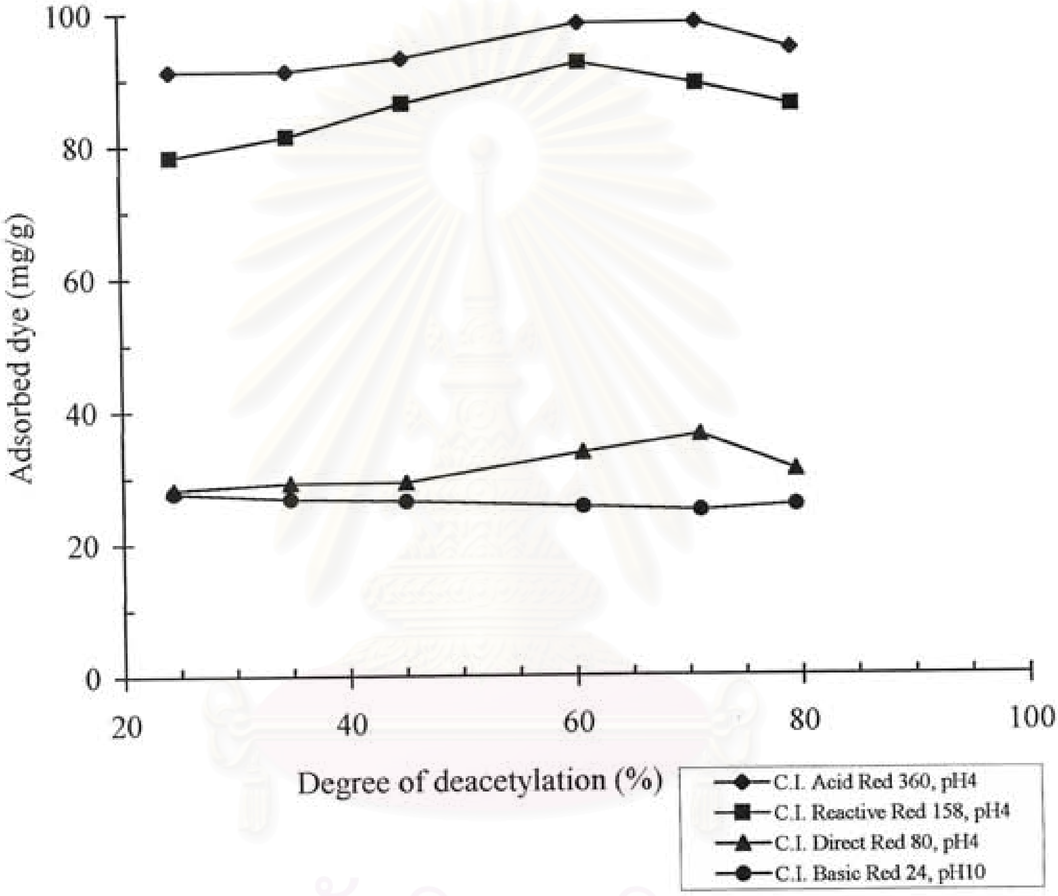


Figure 4.12 Effect of degree of deacetylation of chitosan on dye adsorption at 25 °C

4.9.3 Effect of Time on Dye Adsorption

The effect of time on dye adsorption of chitin, chitosan and shrimp shells at specified pH and 25°C is shown in Figures 4.13-4.16.

At pH 4, the adsorption of C.I. Acid Red 360 on chitosan and chitin reached equilibrium very fast and nearly constant within 18 h, while the rate of dye adsorption on shrimp shells was slower than chitin and chitosan. The adsorption rate of C.I. Reactive Red 158 on chitin and chitosan increased very fast within 3 h and very slightly increased after that, while the rate of dye adsorption on shrimp shells was slower than chitin and chitosan. The adsorption rate of C.I. Direct Red 80 at pH 4 and C.I. Basic Red 24 at pH 10 on all adsorbents increased very fast within 1 h and 3 h, respectively, and increased very slowly after that. It was observed that shrimp shells used as adsorbent tended to ferment after incubation in dye solutions longer than 24 h. The contact time used for other adsorption and desorption studies was 24 h (otherwise stated).

4.9.4 Effect of Particle Size of Adsorbents on Dye Adsorption

Figures 4.17-4.20 show the effect of particle size of adsorbents on dye adsorption at 25 °C at specified pH and contact time due to the ease of adsorption. Four types of dyes showed similar trends that the adsorption capacity of the adsorbents was very slightly decreased with increasing particle size of shrimp shells, chitin and chitosan. The adsorbents with 0.425-0.710 mm particle size were used for further adsorption and desorption studies.

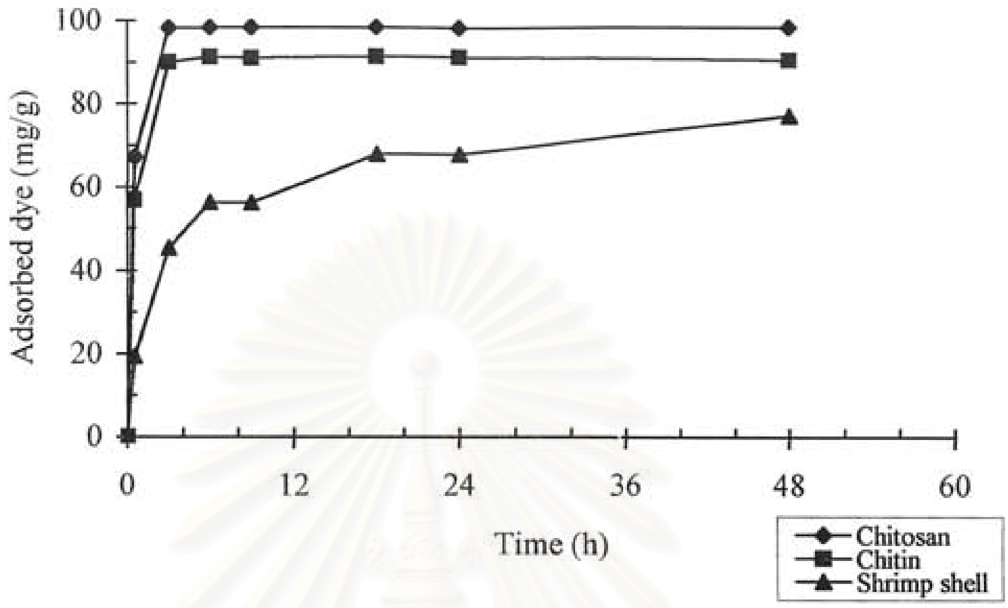


Figure 4.13 Effect of adsorption time of C.I. Acid Red 360 on adsorbents at pH 4 and 25 °C

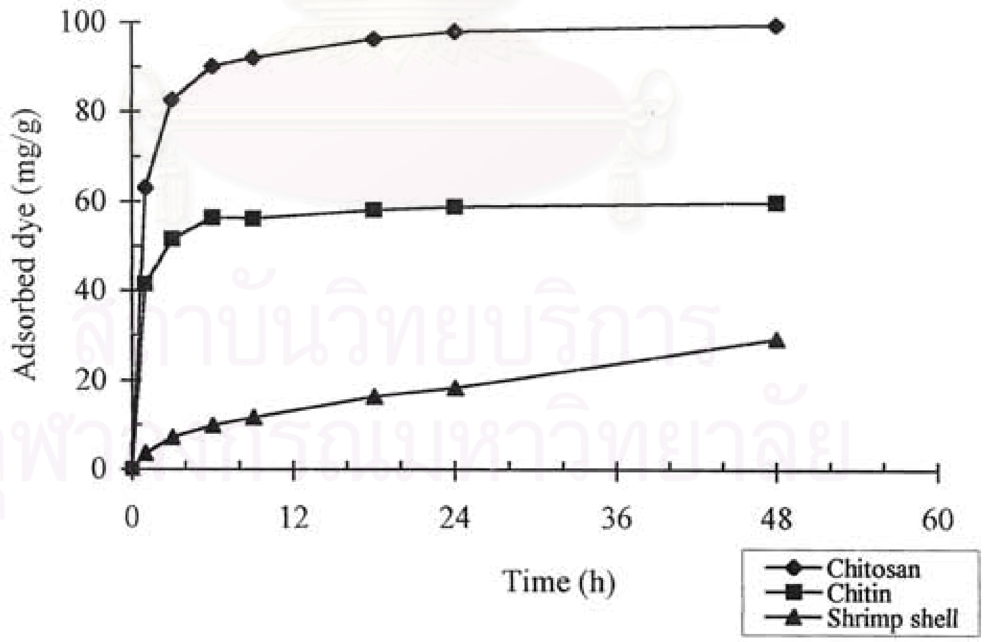


Figure 4.14 Effect of adsorption time of C.I. Reactive Red 158 adsorbents at pH 4 and 25 °C

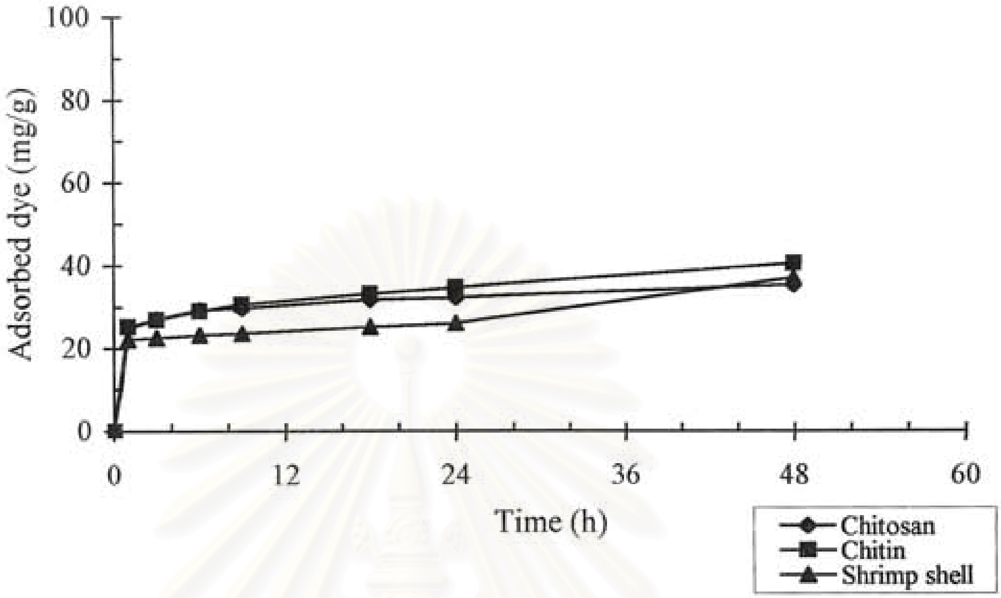


Figure 4.15 Effect of adsorption time of C.I. Direct Red 80 on adsorbents at pH 4 and 25 °C

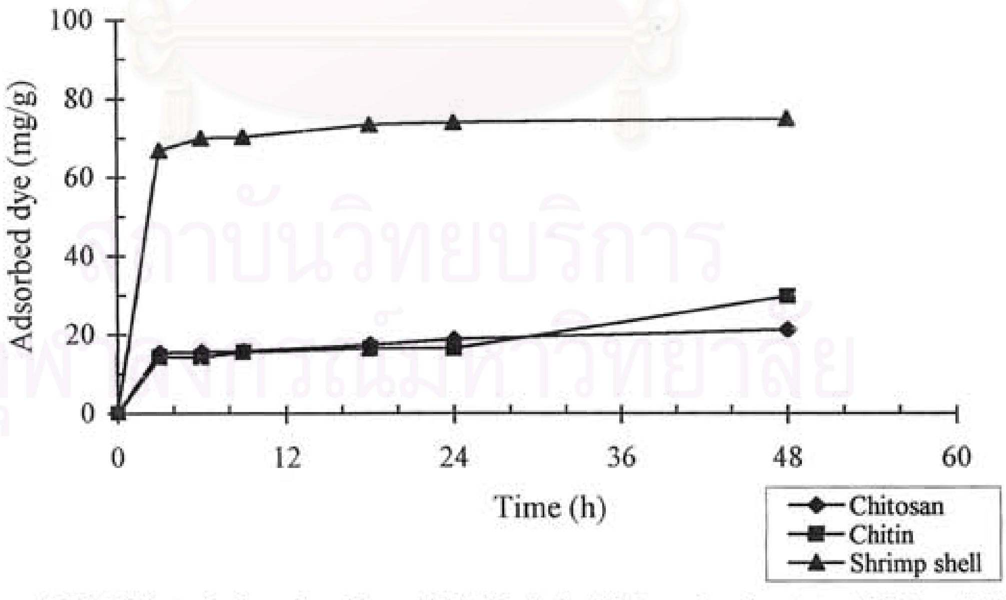


Figure 4.16 Effect of adsorption time of C.I. Basic Red 24 on adsorbents at pH 10 and 25 °C

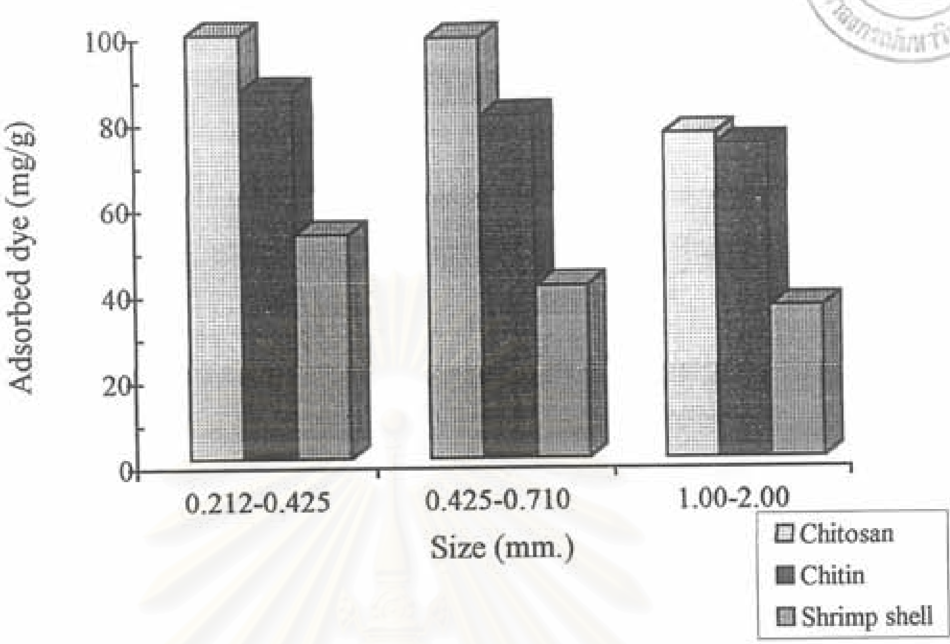


Figure 4.17 Effect of particle sizes of adsorbents on adsorption of C.I. Acid Red 360 for 1 h at pH 4 and 25 °C

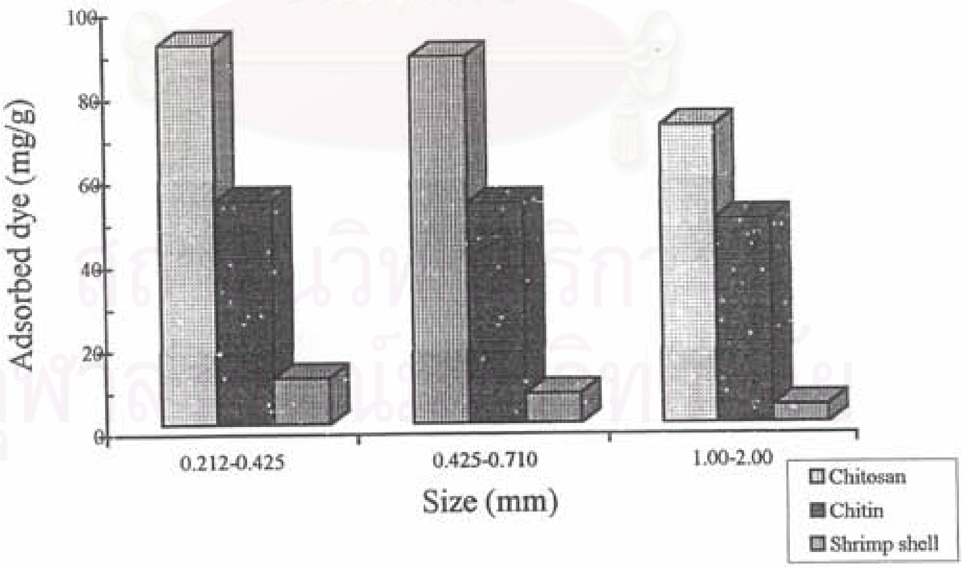


Figure 4.18 Effect of particle sizes of adsorbents on adsorption of C.I. Reactive Red 158 for 5 h at pH 4 and 25 °C

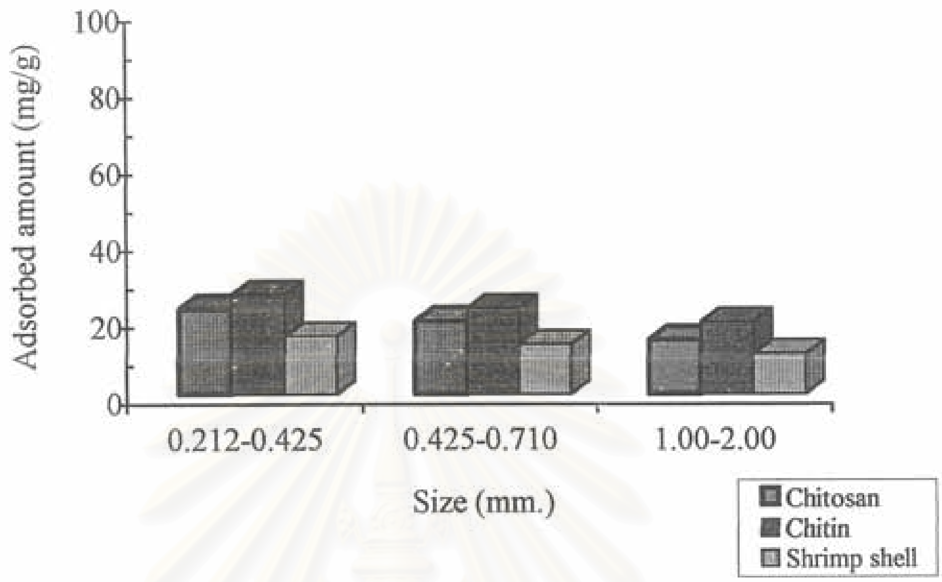


Figure 4.19 Effect of particle sizes of adsorbents on adsorption of C.I. Direct Red 80 for 24 h at pH 4 and 25 °C

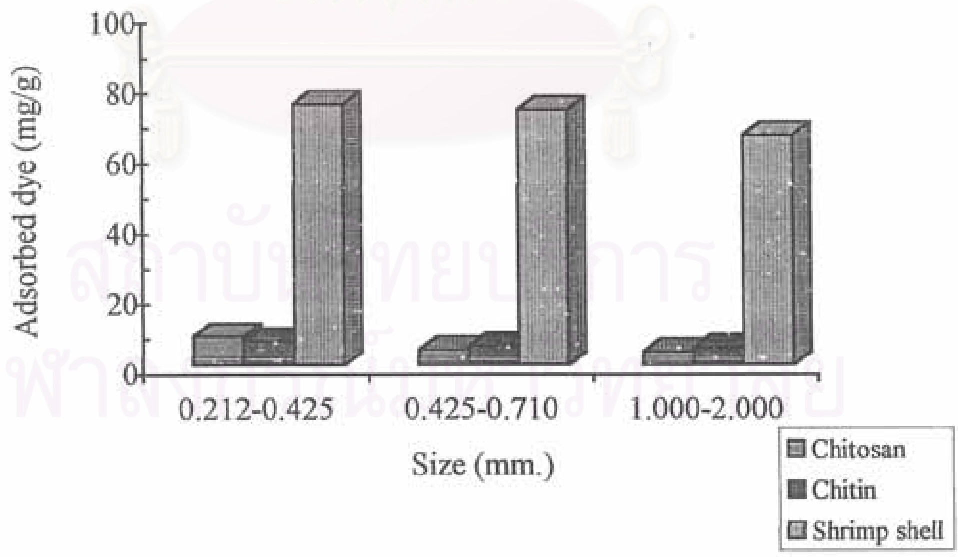


Figure 4.20 Effect of particle sizes of adsorbents on adsorption of C.I. Basic Red 24 for 24 h at pH 10 and 25 °C

4.9.5 Effect of Initial Dye Concentration

The effect of initial dye concentrations on dye adsorption of chitin, chitosan and shrimp shells is shown in Figures 4.21–4.32. The amounts of C.I. Acid Red 360 adsorbed on chitin and chitosan at pH 4 increased with increasing of initial dye concentrations from 0 to 800 mg/L (Figure 4.21). For the initial dye concentration higher than 800 mg/L, the amounts of the adsorbed dye become constant. In case of dye adsorption on shrimp shells, the amount of adsorbed dye increased linearly as initial dye concentrations increased from 0 to 2600 mg/L. The dye adsorption efficiency on shrimp shells was higher than chitin and chitosan when the initial dye concentrations were higher than 800 mg/L.

At pH 4, the adsorption amount and of C.I. Reactive Red 158 on chitosan increased with increasing dye concentrations. Adsorption efficiency of dye on chitosan was higher than chitin and shrimp shells, respectively. It was observed that the adsorption pattern of reactive dye on these adsorbents at pH 3 was higher than at pH 4.

Adsorption amount and efficiency of C.I. Direct Red 80 in solutions at pH 4 were rather low on all adsorbents and obviously distinct from that at pH 3. Amount of dye adsorbed on shrimp shells increased with increasing dye concentrations at pH 3, similar to that on chitin. While that on chitosan was decreased after dye concentration was more than 400 mg/L.

At pH 10, C.I. Basic Red 24 showed similar adsorption trends to acid dye and reactive dye. The distinct difference was that adsorption amount and efficiency of this dye on shrimp shells were much higher than that on chitin and chitosan.

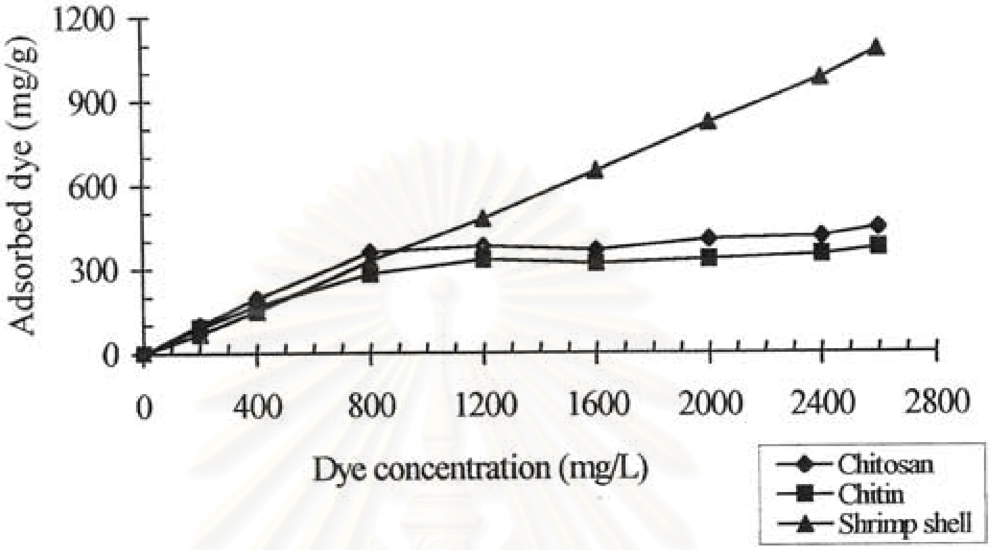


Figure 4.21 Effect of initial concentrations of C.I. Acid Red 360 on dye adsorption at pH 4 and 25 °C

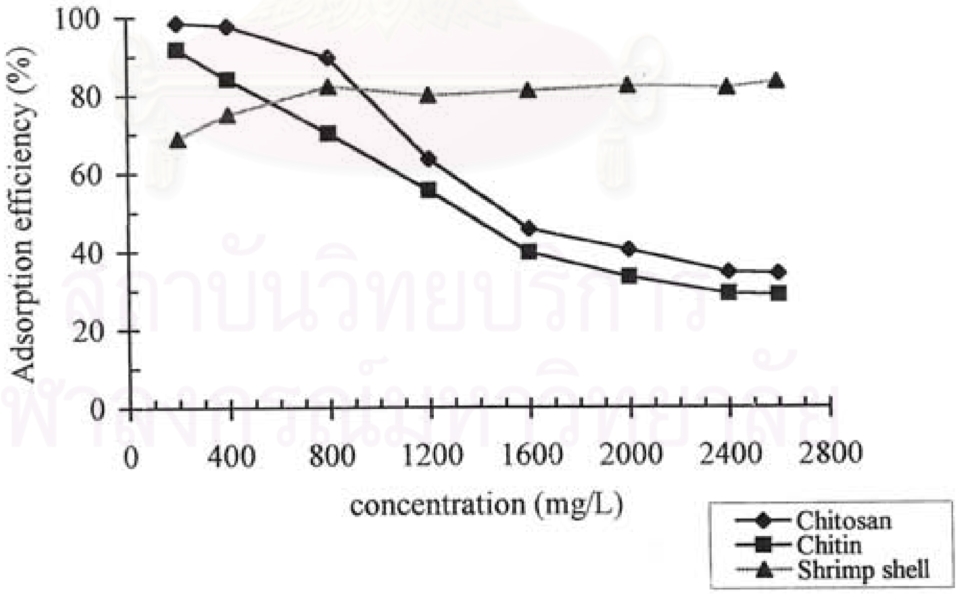


Figure 4.22 Effect of initial concentrations of C.I. Acid Red 360 on dye adsorption efficiency at pH 4 and 25 °C

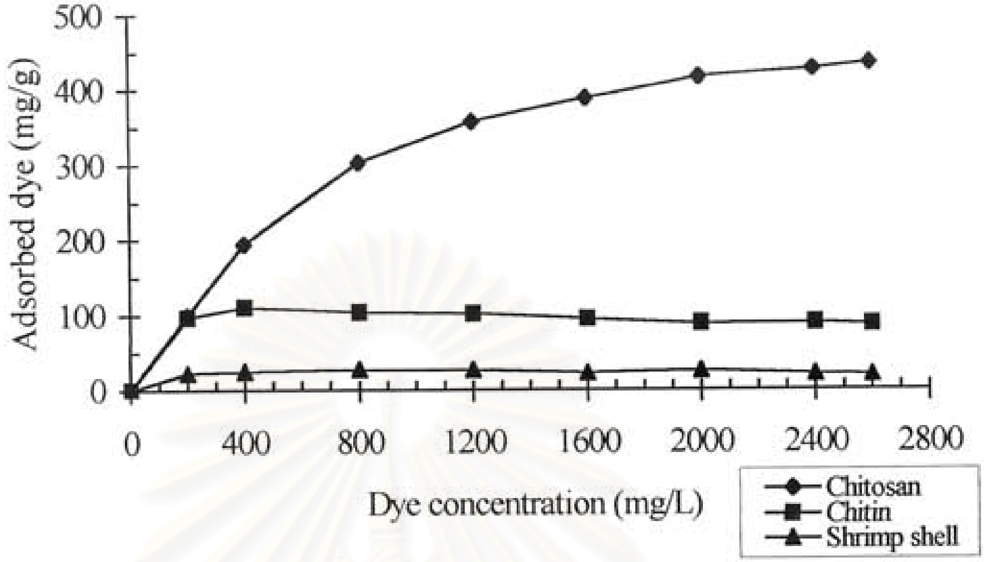


Figure 4.23 Effect of initial concentrations of C.I. Reactive Red 158 on dye adsorption at pH 3 and 25 °C

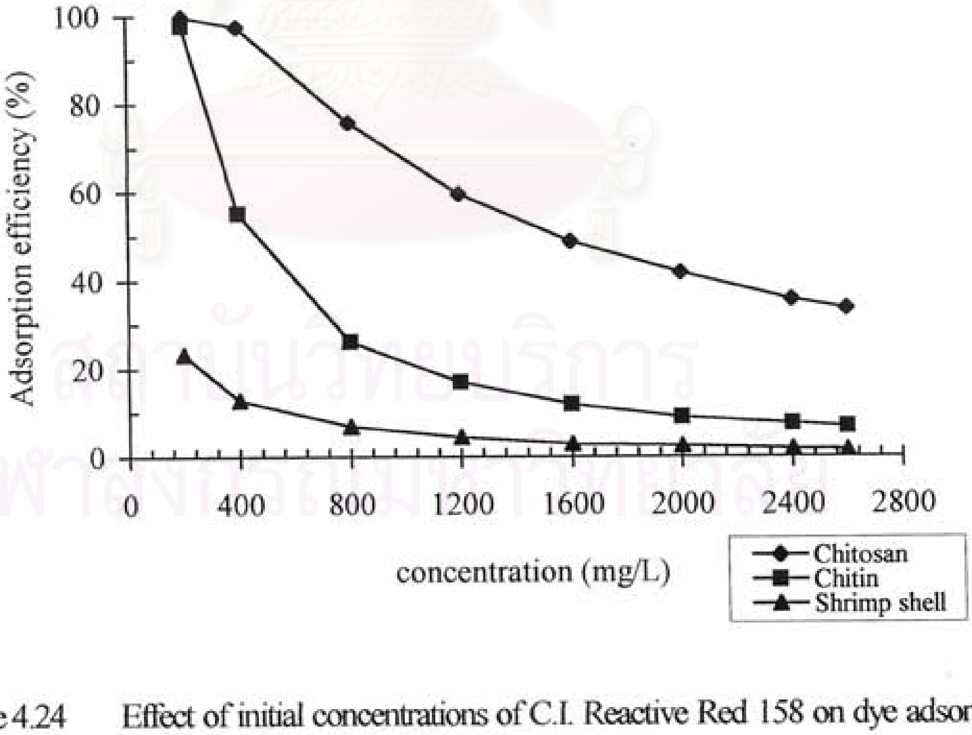


Figure 4.24 Effect of initial concentrations of C.I. Reactive Red 158 on dye adsorption efficiency at pH 3 and 25 °C

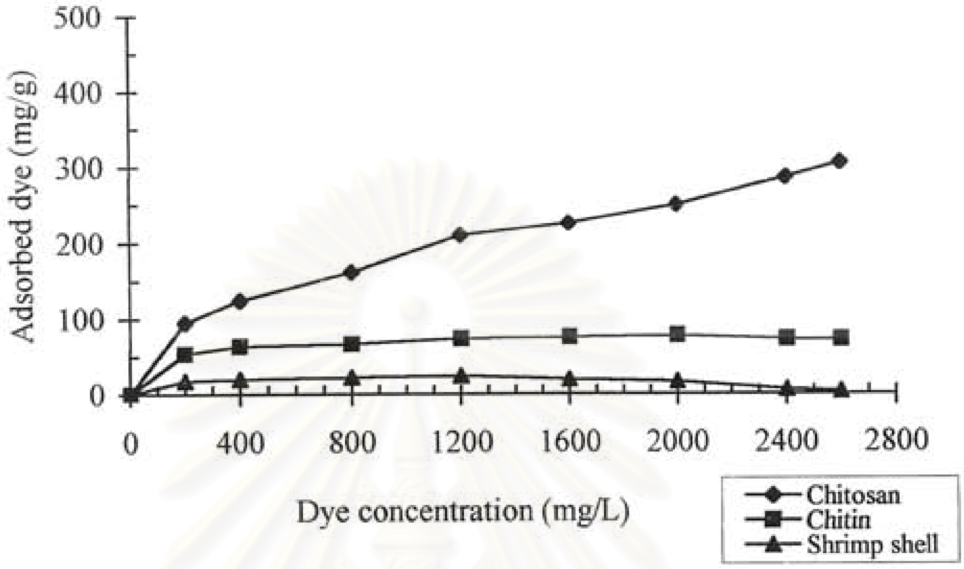


Figure 4.25 Effect of initial concentrations of C.I. Reactive Red 158 on dye adsorption at pH 4 and 25 °C

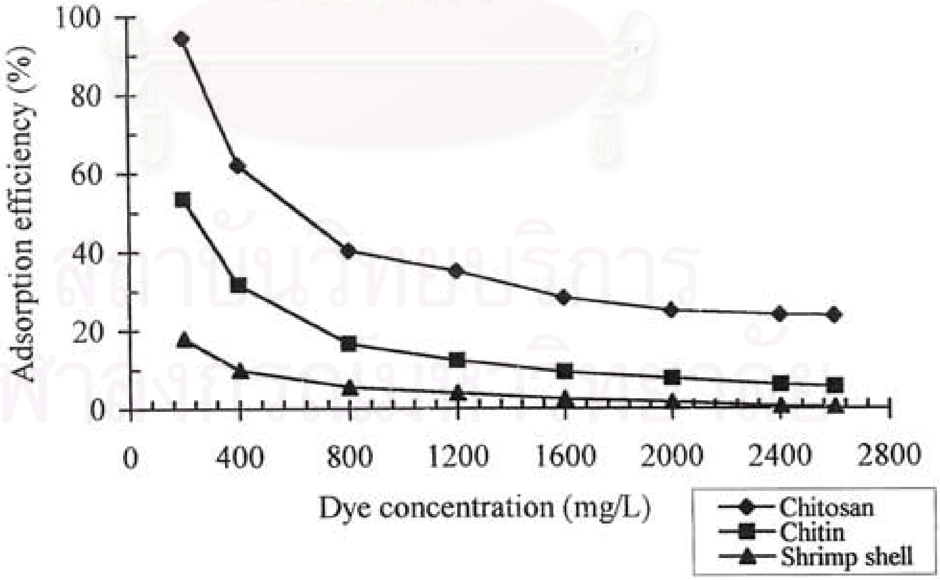


Figure 4.26 Effect of initial concentrations of C.I. Reactive Red 158 on dye adsorption efficiency at pH 4 and 25 °C

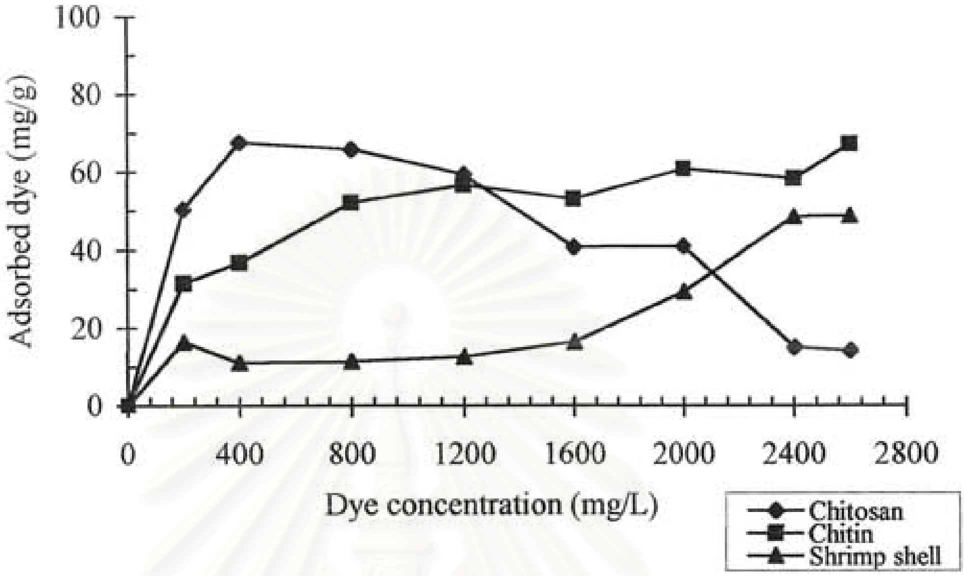


Figure 4.27 Effect of initial concentrations of C.I. Direct Red 80 on dye adsorption at pH 3 and 25 °C

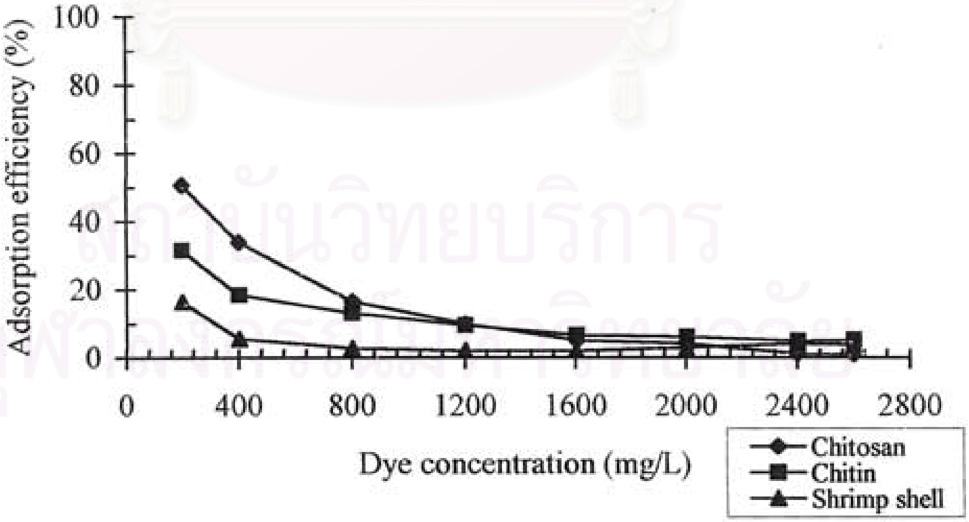


Figure 4.28 Effect of initial concentrations of C.I. Direct Red 80 on dye adsorption efficiency at pH 3 and 25 °C

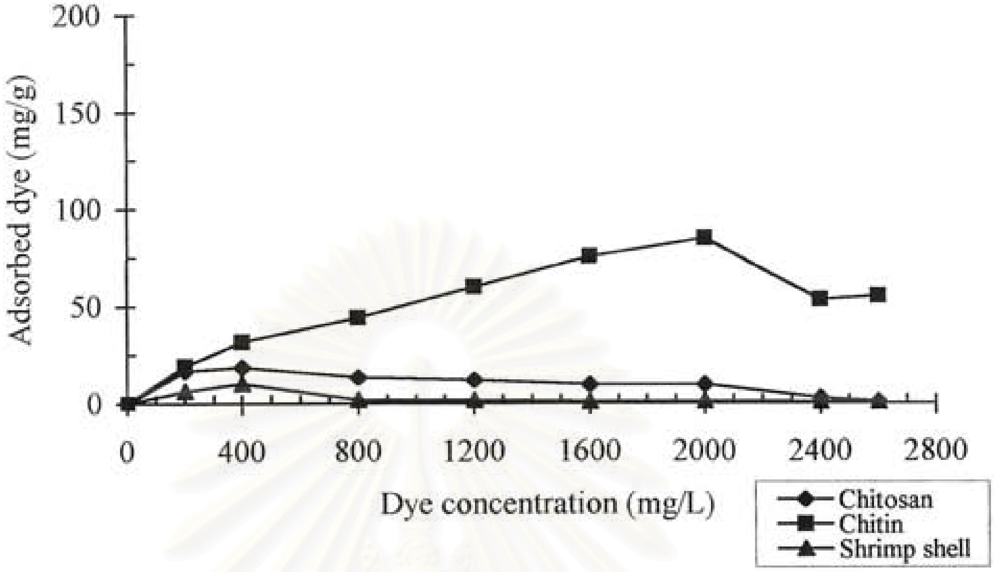


Figure 4.29 Effect of initial concentrations of C.I. Direct Red 80 on dye adsorption at pH 4 and 25 °C

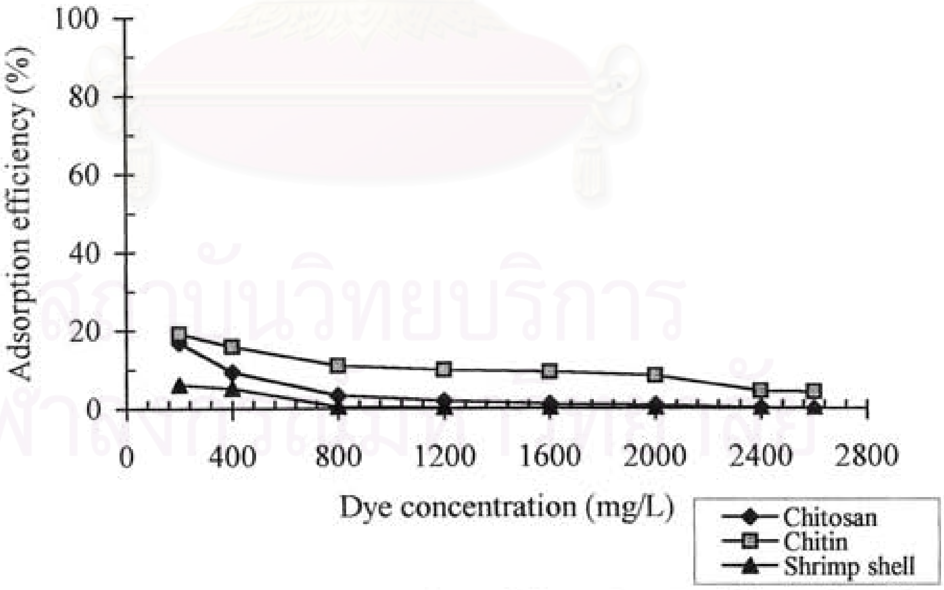


Figure 4.30 Effect of initial concentrations of C.I. Direct Red 80 on dye adsorption efficiency at pH 4 and 25 °C

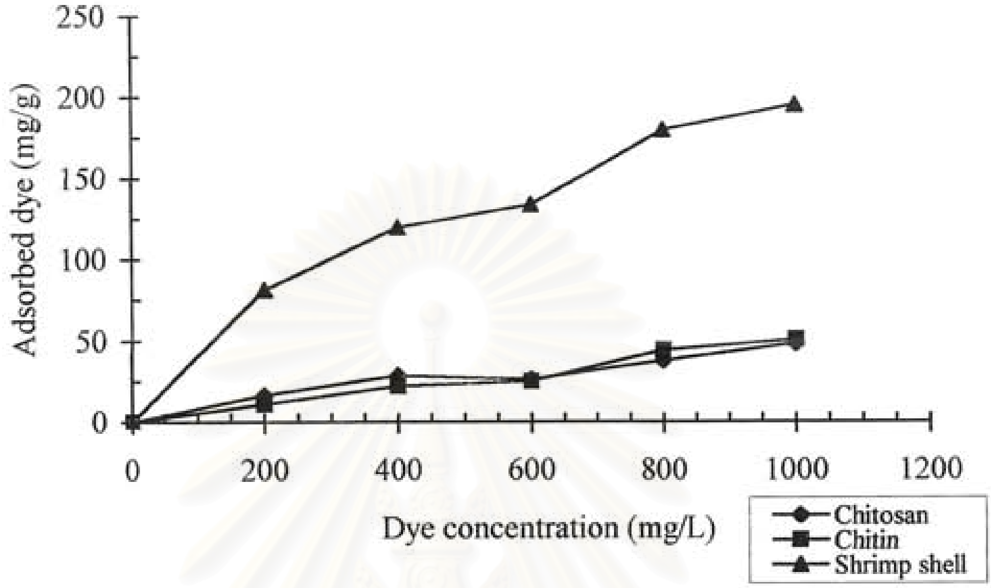


Figure 4.31 Effect of initial concentrations of C.I. Basic Red 24 on dye adsorption at pH 10 and 25 °C

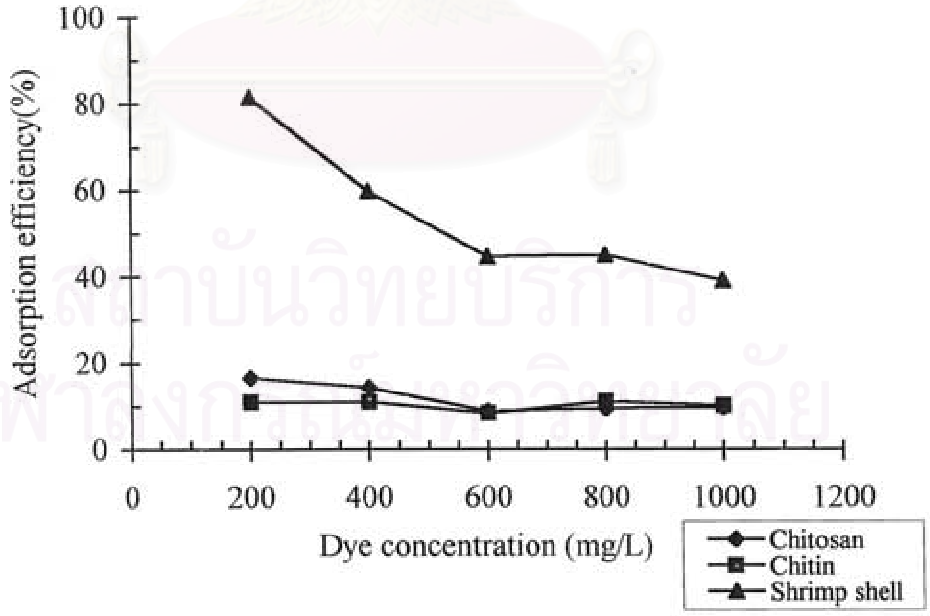


Figure 4.32 Effect of initial concentrations of C.I. Basic Red 24 on dye adsorption efficiency at pH 10 and 25 °C

4.10 Dye Desorption

4.10.1 Effect of pH on Dye Desorption

The effect of pH on dye desorption from the adsorbents is shown in Figures 4.33–4.36. Dye desorption from all adsorbents except basic dye was almost negligible up to pH 10 at 30°C. However dye desorption increased considerably at pHs higher than 10. This was because increasing the pH could reduce the amount of $-NH_3^+$ groups in shrimp shells, chitin and chitosan, resulting in facilitating desorption of the dyes from the adsorbents[19].

It should be noted that C.I. Acid Red 360, which showed the highest adsorption, was also obtained for the highest desorption. On the other hand, C.I. Reactive Red 158 also showed the lowest desorption, revealing a relative stability of nonionic bonding at different pHs. It should be noted that the desorbed dye from chitosan at pH 3 was higher than expected. This may be due to the dissolution of chitosan at pH 3, resulting in the releasing dye into the solution.

4.10.2 Effect of Temperature on Dye Desorption

The effect of temperatures on dye desorption from the adsorbents is shown in Figures 4.37-4.40. The increase of the temperature from 30 °C to 80 °C substantially enhanced efficiency of desorption. This suggested synergetic swell effects of the adsorbents caused by high temperature and pH, resulting in easy desorption [19].

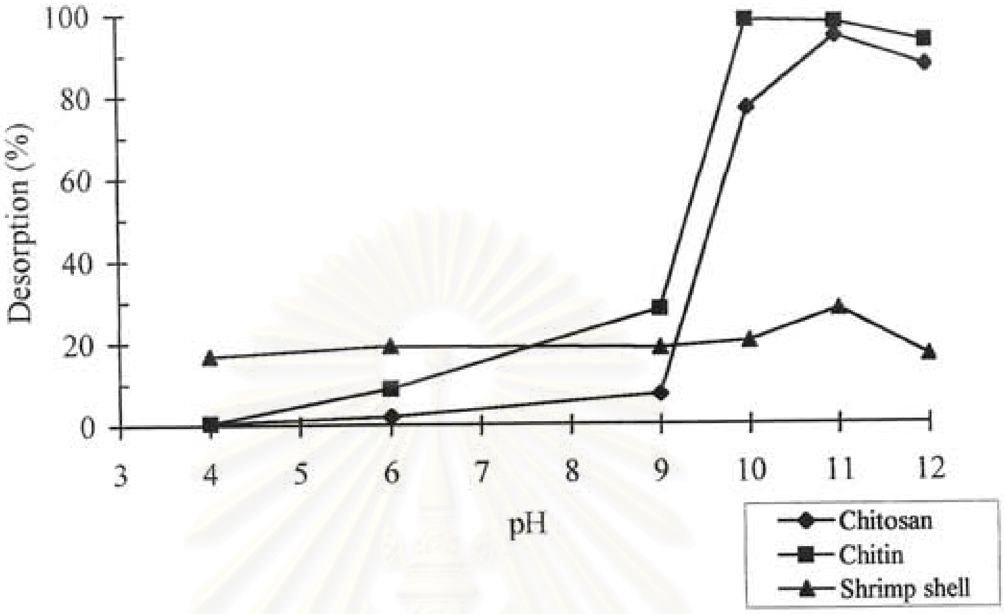


Figure 4.33 Effect of pH on the desorption of C.I. Acid Red 360 at 30 °C

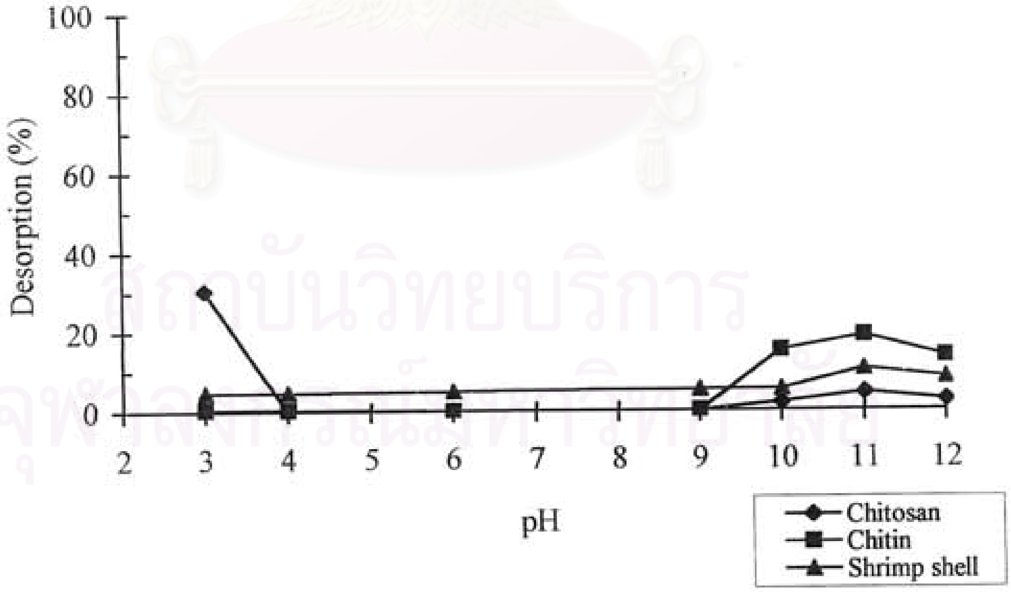


Figure 4.34 Effect of pH on the desorption of C.I. Reactive Red 158 at 30 °C

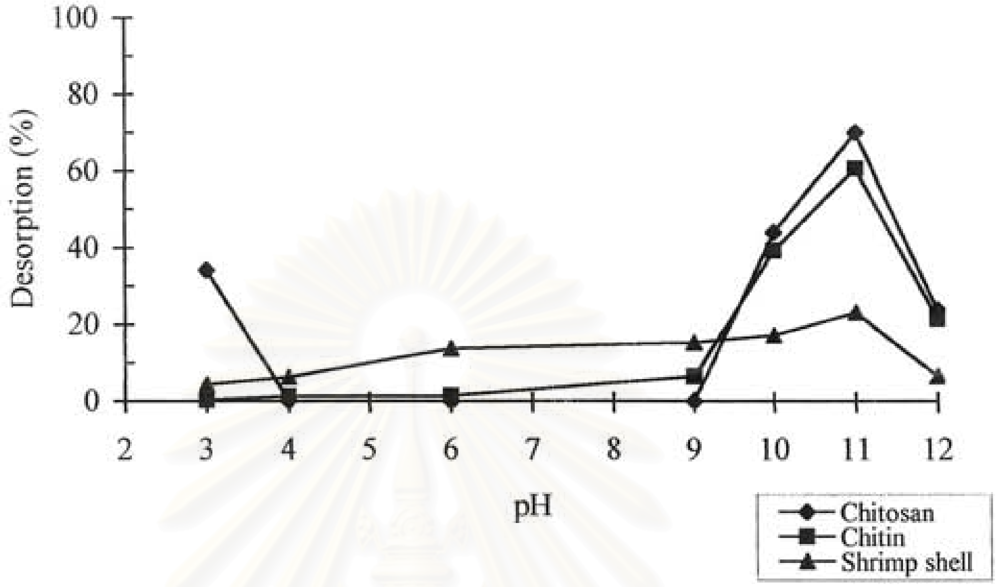


Figure 4.35 Effect of pH on the desorption of C.I. Direct Red 80 at 30 °C

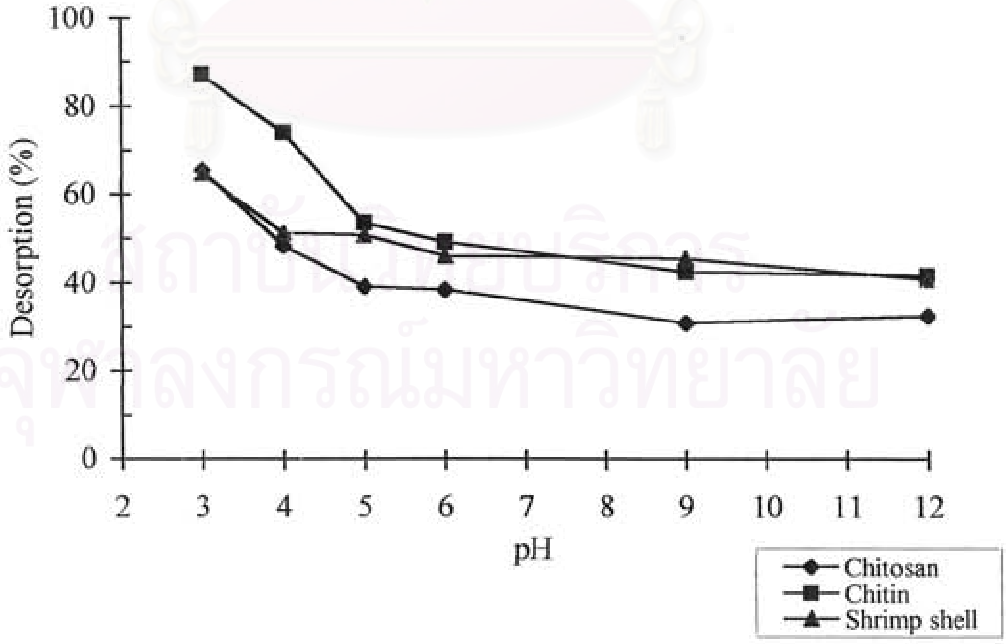


Figure 4.36 Effect of pH on the desorption of C.I. Basic Red 24 at 30 °C

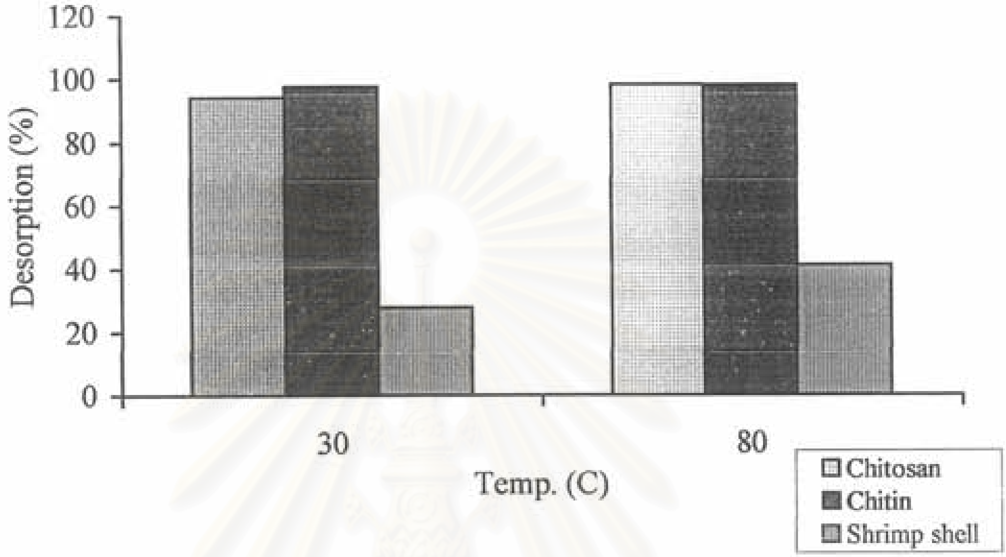


Figure 4.37 Effect of temperature on the desorption of C.I. Acid Red 360 at pH 11

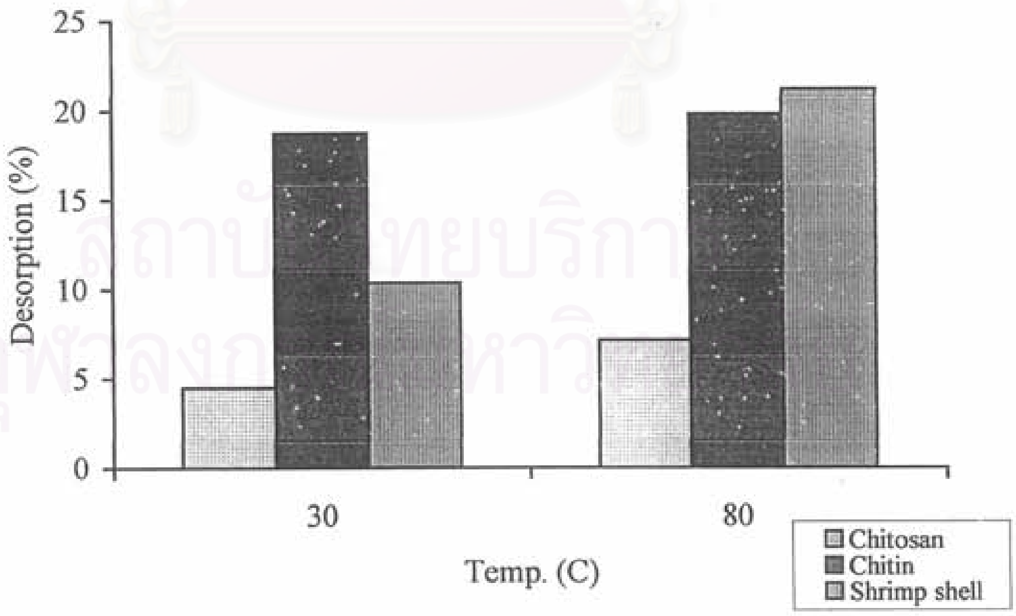


Figure 4.38 Effect of temperature on the desorption of C.I. Reactive Red 158 at pH 11

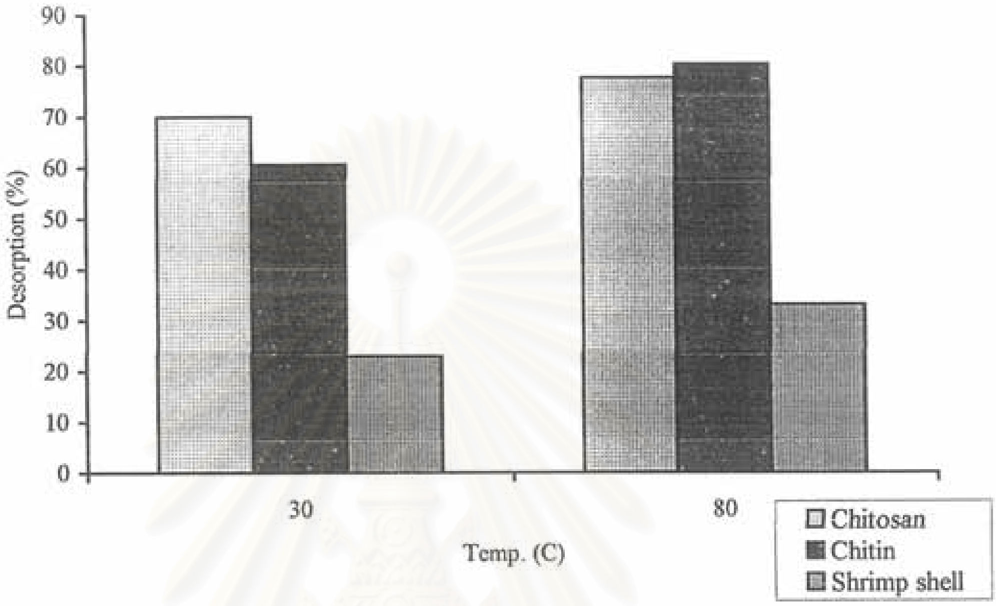


Figure 4.39 Effect of temperature on the desorption of C.I. Direct Red 80 at pH 11

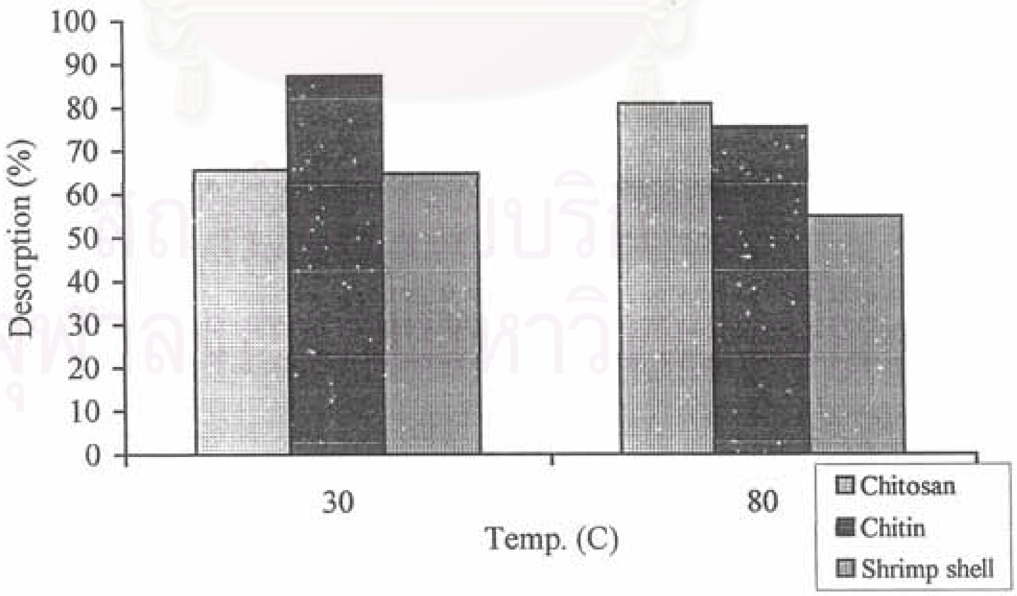


Figure 4.40 Effect of temperature on the desorption of C.I. Basic Red 24 at pH 3

4.11 Dye Removal from Textile Effluents

Nine samples of the effluents of acid dye, reactive dye, direct dye, and basic dye were obtained from the dyebath drainages of four factories, namely Asia Fiber Co., Ltd., Tanakul Textile Printing and Dyeing Co., Ltd., Sinsaenee Co., Ltd., and Golden Thai Industries Co., Ltd., respectively. UV/VIS spectra of the dye effluents are shown in Figures 4.41–4.44. The λmax and initial pH of the effluents is listed in Table 4.6. The dye removal measured at individual λmax of effluent is demonstrated in Table 4.7.

It was observed that the same type of dye showed different λmax, indicating difference in chromophore. Acid dye and basic dye effluents were acidic solutions but reactive dye and direct dye effluents were alkaline solutions. The results of dye removal from effluents conform to those in laboratory experiments. Acid dye No. 1AF and 2AF, reactive dye No. 1TK and 2TK, and direct dye No. 1SN were adsorbed best by chitosan with the amounts of 71.94, 16.50, 61.16, 60.76 and 94.04 % w/w, respectively. Maximum adsorption of reactive dye No. 3TK and 4TK were obtained by chitin with the amounts of 82.12 and 59.39 % w/w, respectively. Basic dye No. 1GT and 2GT were adsorbed best by shrimp shells with the amounts of 43.09 and 21.87% w/w, respectively. Under comparable conditions, the amount of dye removal decreases in the following order :

Acid dye, sample nos. 1, 2	chitosan >chitin > shrimp shells
Reactive dye, sample nos. 1, 2	chitosan >chitin > shrimp shells
3, 4	chitin >chitosan > shrimp shells
Direct dye, sample no. 1	chitosan >chitin > shrimp shells
Basic dye, sample nos. 1, 2	shrimp shells >chitin > chitosan

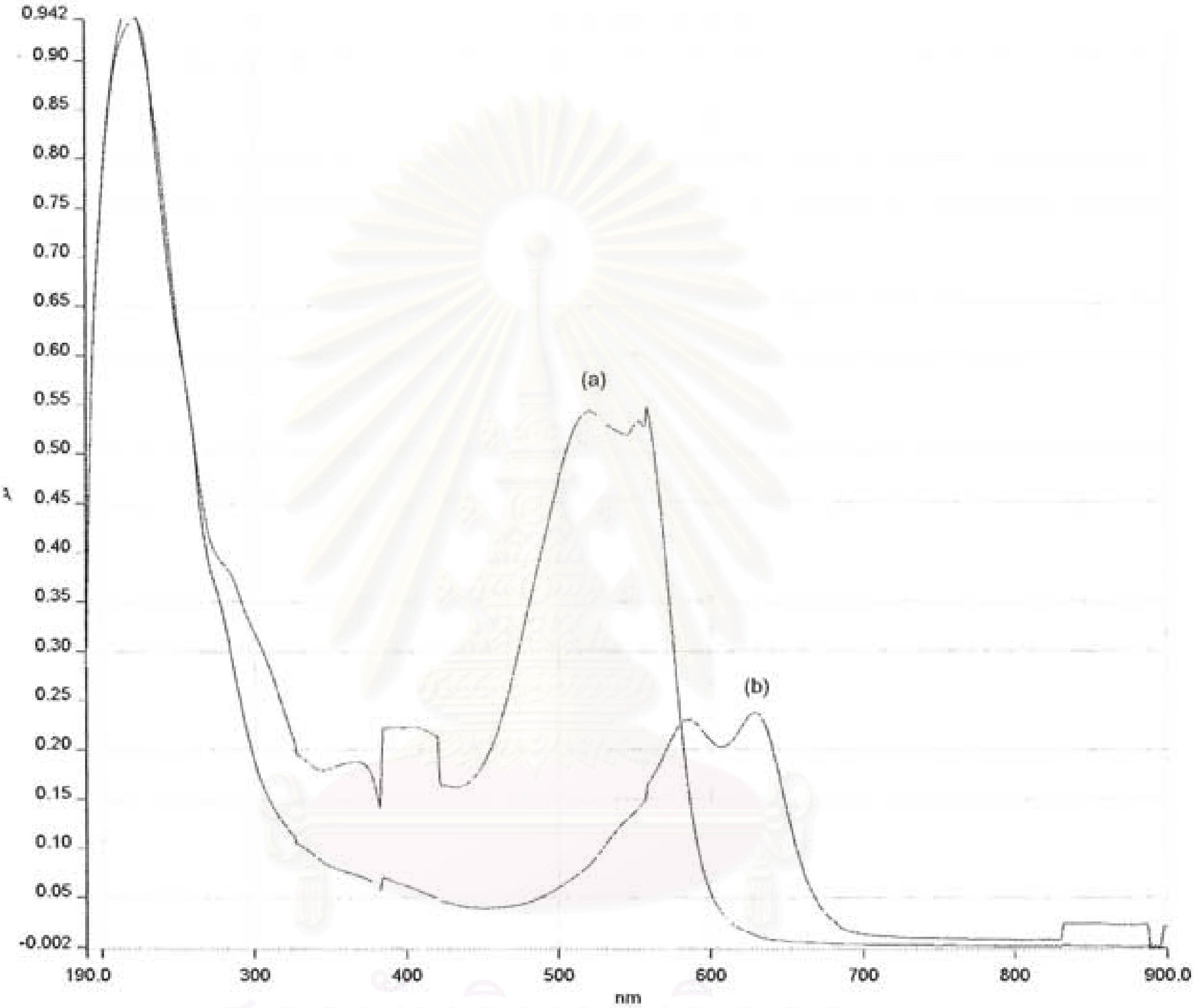


Figure 4.41 UV/VIS spectra of acid dye in textile effluents obtained from Asia Fiber Co., Ltd. : (a) 1 AF (b) 2 AF

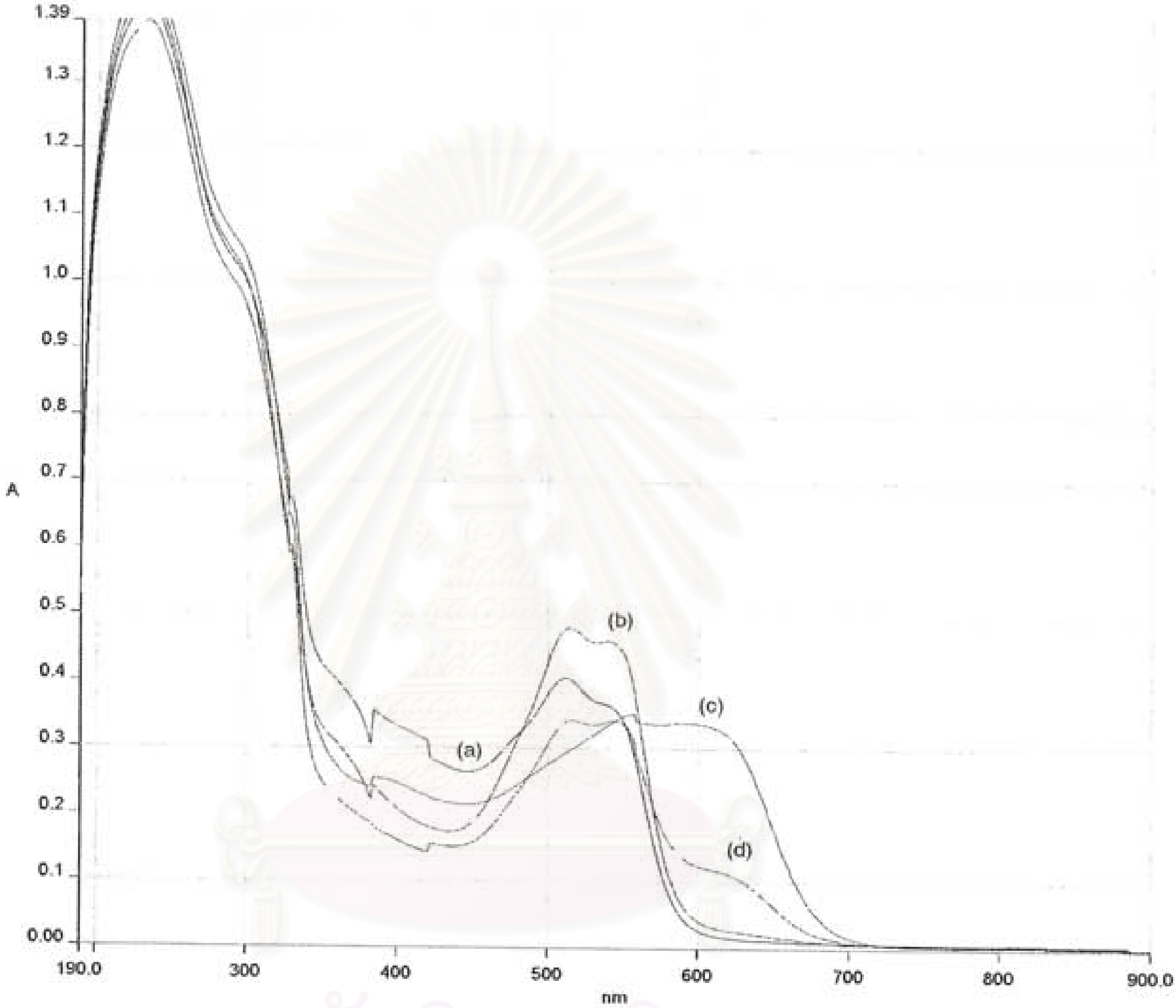


Figure 4.42 UV/VIS spectra of reactive dye in textile effluents obtained from Tanakul Textile Printing and Dyeing Co., Ltd. : (a) 1TK (b) 2TK (c) 3 TK (d) 4 TK

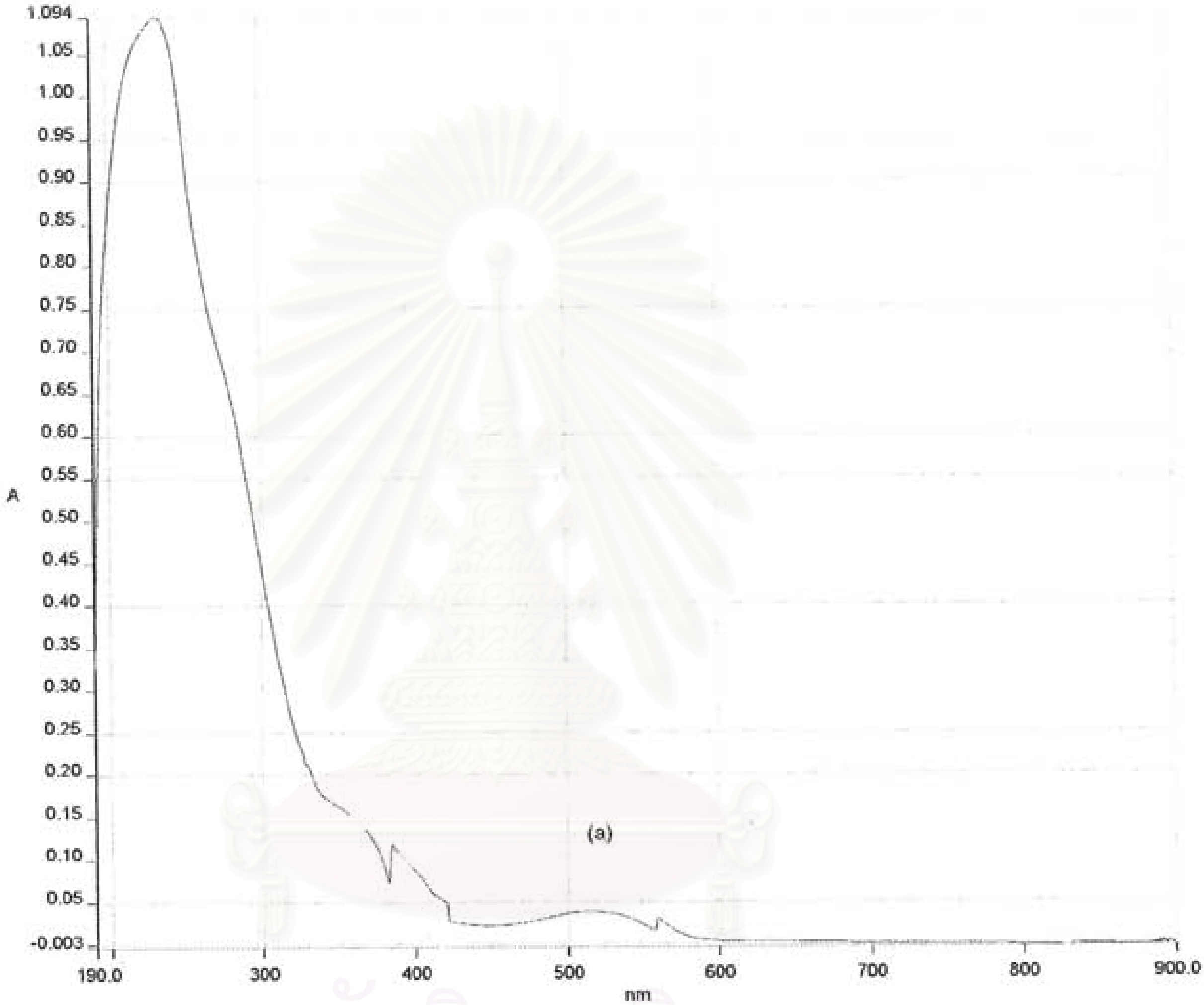


Figure 4.43 UV/VIS spectra of direct dye in textile effluents obtained from Sinsaenee Co., Ltd. : (a) 1SN

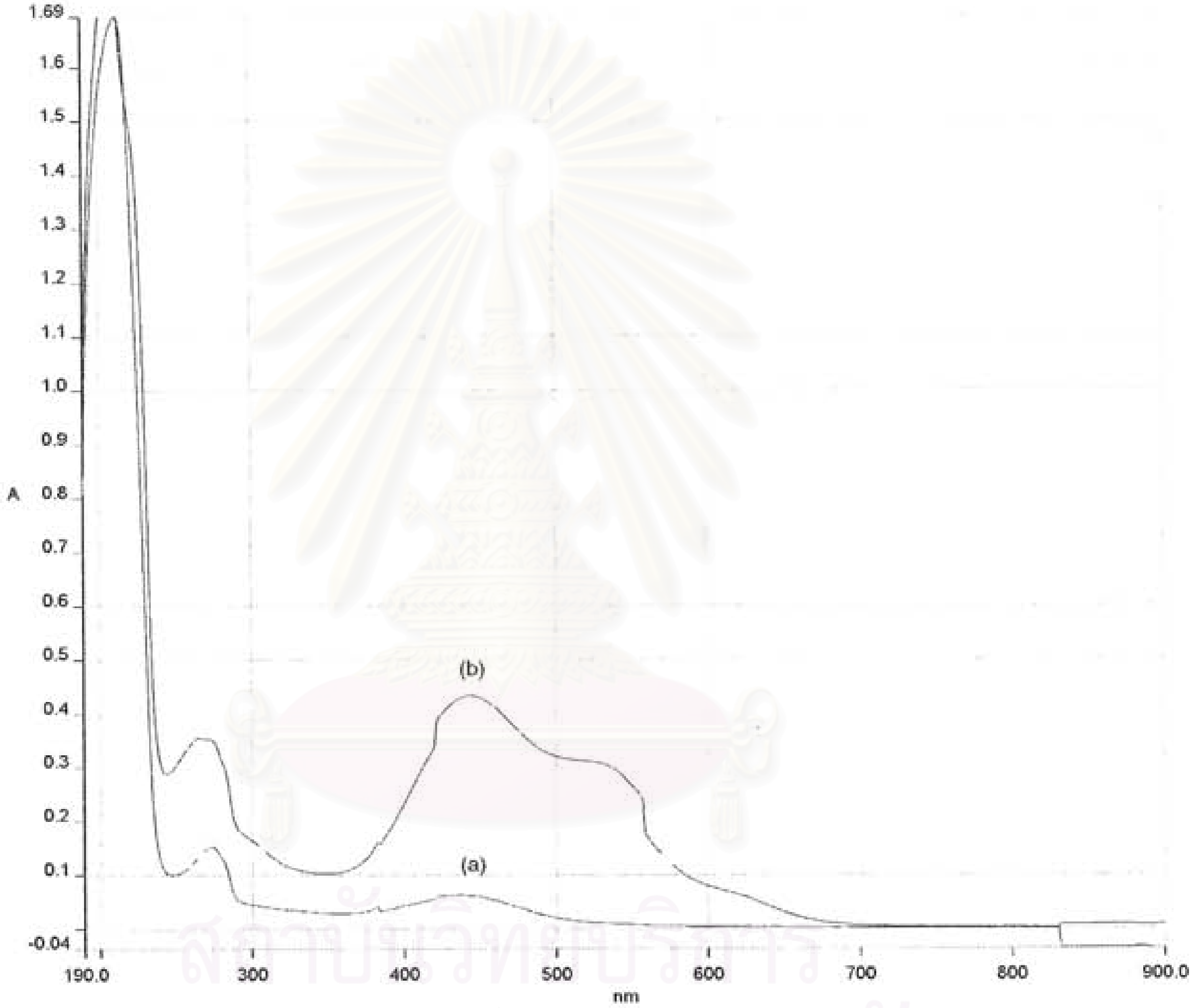


Figure 4.44 UV/VIS spectra of basic dye in textile effluents obtained from Golden Thai Industries Co., Ltd. : (a) 1GT (b) 2GT

Table 4.6 λ max and initial pH of textile effluents

Type of dye	Sampling date	Sample no.	λmax (nm)	Initial pH	Appearance
Acid dye*		1 AF	522	4.64	Deep red turbid solution
		2 AF	630	4.89	Sky blue nearly clear solution
Reactivedye**		1 TK	514	10.51	Deep red turbid solution
		2 TK	512	10.54	Deep orange-red turbid solution
		3 TK	516	10.40	Deep violet turbid solution
		4 TK	556	10.31	Deep blue turbid solution
Direct dye***		1 SN	516	9.93	Light orange turbid solution
Basic dye†		1 GT	434	4.95	Deep orange red turbid solution
		2 GT	444	4.53	Dark blue turbid solution

* Asia Fiber Co.,Ltd.

** Tanakul Textile Printing and Dyeing Co.,Ltd.

*** Sinsaenee Co.,Ltd.

† Golden Thai Industries Co.,Ltd.

Table 4.7 Amount of dyes removed from textile effluents by adsorbents

Type of dye	Sample no.	Dye removal (% w/w)		
		Shrimp shells	Chitin	Chitosan
Acid dye	1 AF	13.54	12.93	71.94
	2 AF	4.29	0.90	16.50
Reactive dye	1 TK	20.88	59.76	61.16
	2 TK	20.72	58.31	60.76
	3 TK	31.58	82.12	71.25
	4 TK	20.16	59.39	41.28
Direct dye	1 SN	51.77	80.63	94.04
Basic dye	1 GT	43.09	26.91	19.19
	2 GT	21.87	9.71	8.50

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Chitosan was the most effective adsorbent for C.I. Acid Red 360. The maximum adsorption could be achieved at acidic pH 5 or less by using chitosan with 71.08 % DD. The dye concentration should not be more than 800 mg/L. The rate of dye adsorption increased very fast within 3 h. The desorption of dye from chitin and chitosan which occurred at 80 °C and pH 10 or higher was about 98 %. The amounts of dye removed by chitosan from effluent No. 1AF and 2AF was 72 and 16 %, respectively which was higher than the amount of dye removed by chitin and shrimp shells.

For C.I. Reactive Red 158, the best adsorbent was also chitosan with 60.71 % DD. Optimum conditions were at acidic pH 5 or less, adsorption time was not less than 9 h and dye concentration could be higher up to 2600 mg/L. Very low desorption occurred from all adsorbents even at 80 °C and pH 11. Dye removal from effluent No. 1TK and 2TK, best by chitosan, was equal about 61 % and No. 3TK and 4TK, best by chitin, was about 82 and 59 %, respectively.

Chitosan with 71.08 %DD could highly adsorb C.I. Direct Red 80 at pH 3 or less. The dye concentration could be higher up to 2000 mg/L. Dye desorption from chitosan at 80 °C and pH 11 was about 77 %. The direct dye removal from effluent was highly achieved by chitosan about 94 %.

Shrimp shells were the best adsorbent for C.I. Basic Red 24. High adsorption was achieved at pH 10 or higher. The adsorption rate increases very fast within 3 h. The dye concentration could be higher up to 2600 mg/L. The dye desorption from chitin was higher than chitosan and shrimp shells, about 75 % at 80 °C and pH 3. Shrimp shells were also the best for basic dye removal from effluents. The amounts of dye removed from sample No. 1GT and 2GT were about 43 and 21 %, respectively.

The results were shown that the amounts of all dyes adsorbed on all adsorbents increased slightly with a decrease in particle size.

In conclusion, each adsorbent could effectively removes dye from the textile effluents and its efficiency depended on the type of dyes in effluents.

Recommendations

Although the application of chitin, chitosan and shrimp shells used as bioadsorbents in this research may probably be possible to apply in real situations, many points of interest need further studies.

The morphological characterization of chitin, chitosan and shrimp shells should be determined by scanning electron microscope (SEM) in order to evaluate the effects of their surface, shape and porosity on dye adsorption and desorption.

Eventhough the operation cost of dye adsoption and desorption using chitin, chitosan and shrimp shells may be very low, the adsorbent recycling should be studied.

Finally and importantly, the removal of dye from effluents by continuous process should also be studied in order to investigate the practical application in plant scale.

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APPENDICES

APPENDIX A

Production of Chitin

Table A.1 Yields of chitin produced from shrimp shells

Chitin batch no.	Weight of shrimp shells (g)	Weight of chitin (g)	Yield (% W/W)
1	600	163	27.2
2	800	242.5	30.3
3	1000	279	27.9
4	1000	283	28.3
5	1000	276	27.6
6	1000	287	28.7
7	1000	268	26.8

Production of Chitosan

Table A.2 Conversion of chitosan from chitin

Chitosan batch no.	Weight of chitin (g)	Weight of chitosan Obtained (g)	Conversion (% W/W)
1	85	66.3	78.0
2	242.5	189.5	78.1
3	279	239	85.7
4	283	215	76.0
5	276	218	79.0

Determination of Degree of Deacetylation (DD)

IR spectrum of chitosan is shown in Figure A.1. Its intensity of maxima of the absorption bands by baseline method at 1550 and 2878 cm^{-1} were 0.1450 and 0.2700, respectively. The DD of chitosan was calculated as follow :

An example of calculation

$$\begin{aligned} DD &= (98.03) - (34.68)\,(A_{1550} / A_{2878}) \\ &= (98.03) - (34.68)\,(0.1450 / 0.2700) \\ &= 79.40 \ \% \end{aligned}$$

Table A.3 Degree of deacetylation of chitin

Batch no.	A1550 / A2878			DD (%)				S.D
	1	2	3	1	2	3	Average	
6	0.30/0.14	0.505/0.23	0.345/0.152	23.72	21.88	19.32	21.64	2.21
7	0.31/0.14	0.412/0.185	0.38/0.17	21.24	20.80	20.51	20.85	0.37

Table A.4 Degree of deacetylation of chitosan

Batch no.	A1550 / A2878			DD (%)				S.D
	1	2	3	1	2	3	Average	
1	0.146/0.272	0.18/0.335	0.17/0.32	79.42	79.40	79.61	79.47	0.12
2	0.125/0.228	0.12/0.225	0.17/0.316	79.02	79.53	79.37	79.31	0.26
3	0.17/0.313	0.15/0.28	0.145/0.27	79.19	79.45	79.41	79.35	0.14
4	0.11/0.205	0.132/0.25	0.15/0.28	79.42	79.72	79.45	79.53	0.16
5	0.15/0.285	0.14/0.265	0.15/0.285	79.78	79.71	79.78	79.75	0.04

Determination of Molecular Weight of Chitin and Chitosan

Molecular weight (MW) of chitin and chitosan could be determined from its intrinsic viscosity obtained from the intercept of the plot between its concentrations and specific viscosities as follows:

$$[\eta] = kM^{a}$$

$$\eta_{rel} = t/t_{s}$$

$$\eta_{sp} = (t/t_{s}) - 1$$

$$\eta_{red} = n_{sp}/c$$

$$\eta] = [\eta_{red}]_{c=0}$$

Where $[\eta]$	:	Intrinsic viscosity	=	$[\eta_{red}]_{c=0}$
M	:	Molecular weight of chitosan		
k	:	Mark-Houwink constant	=	8.93×10^{-4}
a	:	Mark-Houwink exponent	=	0.71
η_{rel}	:	Relative viscosity		
η_{sp}	:	Specific viscosity		
η_{red}	:	Reduced viscosity		
t	:	Running time of chitosan solution (second)		
t_{s}	:	Running time of solvent (second)		

MW of Chitin

Running times of solvent and chitin solutions were measured by using Ubbelohde viscometer, Cannon type no. 150 at 30 °C. The calculated viscosity of chitin is shown in Table A.5. The intrinsic viscosity of chitin obtained from the intercept of the plot between its concentrations and specific viscosities is shown in Figure 4.2 (a). Then the MW of chitin was determined from the above formulae.

Table A.5 Determination of viscosity of chitin

Conc. (g/100 ml)	Time					η_{rel}	η_{sp}	η_{red}	1/c. ln[η_{rel}]
	1	2	3	4	Average				
0.00	83.27	83.38	83.24	83.25	83.29				
0.0013	86.26	86.28	86.36	86.42	86.33	1.0366	0.0366	28.12	27.62
0.0026	89.20	89.46	89.50	89.52	89.42	1.0737	0.0737	28.33	27.35
0.0052	95.98	96.07	96.04	95.96	96.01	1.1528	0.1528	29.39	27.35
0.0104	110.00	110.06	109.94	110.08	110.02	1.3210	0.3210	30.87	26.77
0.0208	142.00	142.03	142.12	141.92	142.02	1.7052	0.7052	33.90	25.66
0.0400	224.00	223.93	224.09	223.96	224.00	2.6895	1.6895	42.24	24.74
0.0600	327.44	327.23	327.26	327.31	327.31	3.9300	2.9300	48.83	22.81
0.0800	475.09	475.37	475.57	474.73	475.19	5.7056	4.7056	58.82	21.77

Calculation of MW of chitin

$M^a = [n]/k = 27.02 \times 10000 / 8.93 = 30257.5588$

$a \log M = \log [30257.5588] = 4.4808$

$\log M = 4.4808 / 0.71 = 6.3110$

$M = 10^{6.3110} = 2{,}046{,}444$

The MW of chitin was about 2.50×10^6.

MW of Chitosan

Running times of solvent and chitosan solutions were measured by using Ubbelohde viscometer, Cannon type no. 75 at 25 °C. The calculated viscosity of chitosan is shown in Table A.6. The intrinsic viscosity of chitosan obtained from the intercept of the plot between its concentrations and specific viscosities is shown in Figure 4.2 (b). Then the MW of chitosan was calculated from the above formulae.

Table A.6 Determination of viscosity of chitosan

Conc. (g/100 ml)	Time					η_{rel}	η_{sp}	η_{red}	1/c. ln[η_{rel}]
	1	2	3	4	Average				
0	125.06	124.92	124.97	125.03	125.00				
0.00625	133.78	133.99	134.09	133.56	133.86	1.0709	0.0709	11.34	10.96
0.0125	143.07	142.89	143.09	142.93	143.00	1.1440	0.1440	11.52	10.76
0.0250	164.02	163.99	163.86	164.14	164.00	1.3121	0.3121	12.48	10.86
0.0500	210.18	209.83	209.96	210.01	210.00	1.6800	0.6800	13.60	10.38
0.1000	328.14	327.91	327.89	328.07	328.00	2.6241	1.6241	16.24	9.65
0.2000	682.05	682.13	681.97	681.86	682.00	5.4562	4.4562	22.28	8.48
0.4000	1770.02	1769.56	1770.24	1770.88	1770.18	14.1620	13.1620	32.90	6.63

Calculation of MW of chitosan

$M^a = [\eta]/k = 10.943 \times 10000 / 8.93 = 12254.1993$

$a \log M = \log [12254.1993] = 4.0883$

$\log M = 4.0883 / 0.71 = 5.7582$

$M = 10^{5.7582} = 573{,}060$

The MW of chitosan was about 5.73×10^5.

APPENDIX B

Calibration Curve of Dye Solutions at Various pHs

The average slope value obtained from the calibration curve plotted between the absorbance of the dye solutions and the dye concentrations are shown in Tables B.1–B.4. The standard deviations (S.D.) of C.I. Acid Red 360, C.I. Reactive Red 158, C.I. Direct Red 80 and C.I. Basic Red 24 were 0.0010, 0.0005, 0.0011 and 0.0010, respectively.

Table B.1 Calibration curve of C.I. Acid Red 360 at 535 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
3 *	0.00	0.0000	0.0150	0.9827
	5.01	0.0840		
	10.02	0.1788		
	15.04	0.2574		
	20.05	0.3039		
	25.06	0.3658		
	30.07	0.4301		
4	0.00	0.0000	0.0325	0.9989
	5.01	0.1795		
	10.01	0.3366		
	15.02	0.4965		
	20.02	0.6554		
	25.03	0.8184		
	30.04	0.9605		
5	0.00	0.0000	0.0337	0.9987
	5.02	0.1799		
	10.04	0.3536		
	15.05	0.5212		
	20.07	0.6707		
	25.09	0.8559		
	30.11	0.9971		
6	0.00	0.0000	0.0340	0.9990
	5.02	0.1817		
	10.05	0.3537		
	15.07	0.5298		
	20.10	0.6798		
	25.12	0.8509		
	30.14	1.0115		
7	0.00	0.0000	0.0338	0.9987
	5.00	0.1879		
	10.00	0.3487		
	15.01	0.5243		
	20.01	0.6816		
	25.01	0.8418		
	30.01	1.0011		

* C.I. Acid Red 360 partially precipitated at pH 3.

Table B.1 (continued)

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
8	0.00	0.0000	0.0319	0.9982
	5.02	0.1752		
	10.03	0.3331		
	15.05	0.5000		
	20.06	0.6386		
	25.08	0.7783		
	30.10	0.9597		
9	0.00	0.0000	0.0317	0.9984
	5.02	0.1679		
	10.04	0.3309		
	15.07	0.4879		
	20.09	0.6293		
	25.11	0.7715		
	30.13	0.9666		
10	0.00	0.0000	0.0314	0.9983
	5.01	0.1666		
	10.01	0.3345		
	15.02	0.4855		
	20.02	0.6229		
	25.03	0.7657		
	30.04	0.9489		
11	0.00	0.0000	0.0316	0.9977
	5.02	0.1619		
	10.04	0.3201		
	15.07	0.4817		
	20.09	0.6116		
	25.11	0.7741		
	30.13	0.9681		
12	0.00	0.0000	0.0327	0.9971
	5.01	0.1875		
	10.02	0.3440		
	15.02	0.5193		
	20.03	0.6554		
	25.04	0.8194		
	30.05	0.9620		

Table B.2 Calibration curve of C.I. Reactive Red 158 at 512 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
3	0.00	0.0000	0.0155	0.9994
	10.00	0.1624		
	20.00	0.3197		
	30.00	0.4748		
	40.00	0.6275		
	50.00	0.7745		
	60.00	0.9213		
4	0.00	0.0000	0.0156	0.9994
	10.03	0.1640		
	20.06	0.3231		
	30.10	0.4761		
	40.13	0.6315		
	50.16	0.7807		
	60.19	0.9249		
5	0.00	0.0000	0.0154	0.9988
	10.00	0.1637		
	20.00	0.3226		
	30.00	0.4771		
	40.00	0.6262		
	50.00	0.7667		
	60.00	0.9122		
6	0.00	0.0000	0.0154	0.9999
	10.01	0.1514		
	20.02	0.3097		
	30.04	0.4669		
	40.05	0.6217		
	50.06	0.7716		
	60.07	0.9190		
7	0.00	0.0000	0.0154	0.9998
	10.05	0.1512		
	20.10	0.3101		
	30.14	0.4674		
	40.19	0.6222		
	50.24	0.7724		
	60.29	0.9194		

Table B.2 (continued)

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
8	0.00	0.0000	0.0165	1.0000
	10.00	0.1664		
	20.00	0.3308		
	30.00	0.4945		
	40.00	0.6593		
	50.00	0.8236		
	60.00	0.9913		
9	0.00	0.0000	0.0166	1.0000
	10.03	0.1692		
	20.06	0.3338		
	30.10	0.5006		
	40.13	0.6670		
	50.16	0.8318		
	60.16	1.0044		
10	0.00	0.0000	0.0165	1.0000
	10.02	0.1692		
	20.03	0.3321		
	30.05	0.4971		
	40.06	0.6611		
	50.08	0.8252		
	60.10	0.9936		
11	0.00	0.0000	0.0165	1.0000
	10.04	0.1684		
	20.08	0.3315		
	30.12	0.4960		
	40.16	0.6586		
	50.20	0.8235		
	60.24	0.9944		
12	0.00	0.0000	0.0163	1.0000
	10.01	0.1670		
	20.02	0.3292		
	30.04	0.4922		
	40.05	0.6555		
	50.06	0.8179		
	60.07	0.9788		

Table B.3 Calibration curve of C.I. Direct Red 80 at 526 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
3	0.00	0.0000	0.0314	1.0000
	5.02	0.1598		
	10.04	0.3154		
	15.05	0.4741		
	20.07	0.6291		
	25.09	0.7863		
	30.11	0.9480		
4	0.00	0.0000	0.0322	0.9999
	5.02	0.1642		
	10.04	0.3255		
	15.07	0.4854		
	20.09	0.6432		
	25.11	0.8073		
	30.13	0.9740		
5	0.00	0.0000	0.0318	0.9999
	5.02	0.1634		
	10.04	0.3225		
	15.05	0.4818		
	20.07	0.6422		
	25.09	0.7969		
	30.11	0.9502		
6	0.00	0.0000	0.0321	0.9995
	5.03	0.1749		
	10.06	0.3338		
	15.09	0.4905		
	20.12	0.6464		
	25.15	0.8040		
	30.18	0.9650		
7	0.00	0.0000	0.0321	0.9994
	5.03	0.1748		
	10.06	0.3342		
	15.09	0.4917		
	20.12	0.6478		
	25.15	0.8039		
	30.18	0.9595		

Table B.3 (continued)

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
8	0.00	0.0000	0.0303	1.0000
	5.00	0.1508		
	10.00	0.3046		
	15.01	0.4546		
	20.01	0.6064		
	25.01	0.7571		
	30.01	0.9131		
9	0.00	0.0000	0.0304	1.0000
	5.01	0.1513		
	10.02	0.3049		
	15.02	0.4595		
	20.03	0.6099		
	25.04	0.7598		
	30.05	0.9111		
10	0.00	0.0000	0.0301	1.0000
	5.00	0.1525		
	10.01	0.3040		
	15.01	0.4545		
	20.02	0.6048		
	25.02	0.7504		
	30.02	0.9055		
11	0.00	0.0000	0.0299	1.0000
	5.02	0.1510		
	10.05	0.3024		
	15.07	0.4515		
	20.10	0.5992		
	25.12	0.7482		
	30.14	0.9030		
12	0.00	0.0000	0.0294	0.9997
	5.00	0.1536		
	10.01	0.3011		
	15.01	0.4471		
	20.02	0.5912		
	25.02	0.7330		
	30.02	0.8744		

Table B.4 Calibration curve of C.I. Basic Red 24 at 512 nm

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
3	0.00	0.0000	0.0432	0.9985
	5.00	0.2224		
	10.00	0.4347		
	15.00	0.6369		
	20.00	0.8258		
	25.00	1.0914		
	30.00	1.3119		
4	0.00	0.0000	0.0432	0.9983
	5.01	0.2229		
	10.02	0.4354		
	15.03	0.6385		
	20.04	0.8251		
	25.05	1.0948		
	30.06	1.3164		
5	0.00	0.0000	0.0438	0.9989
	5.01	0.2238		
	10.02	0.4254		
	15.04	0.6367		
	20.05	0.8585		
	25.06	1.1015		
	30.07	1.3385		
6	0.00	0.0000	0.0443	0.9987
	5.00	0.2247		
	10.01	0.4313		
	15.01	0.6296		
	20.02	0.8784		
	25.02	1.1212		
	30.02	1.3443		
7	0.00	0.0000	0.0445	0.9992
	5.01	0.2268		
	10.02	0.4351		
	15.03	0.6395		
	20.04	0.8978		
	25.05	1.1254		
	30.06	1.3459		

Table B.4 (continued)

pH of dye	Concentration (mg/L)	Absorbance	Slope	R^2
8	0.00	0.0000	0.0452	0.9993
	5.03	0.2224		
	10.06	0.4486		
	15.08	0.6767		
	20.11	0.8948		
	25.14	1.1259		
	30.17	1.3898		
9	0.00	0.0000	0.0452	0.9989
	5.01	0.2220		
	10.02	0.4454		
	15.02	0.6671		
	20.03	0.8795		
	25.04	1.1267		
	30.05	1.3859		
10	0.00	0.0000	0.0451	0.9991
	5.02	0.2188		
	10.05	0.4510		
	15.07	0.6714		
	20.10	0.8784		
	25.12	1.1387		
	30.14	1.3787		
11	0.00	0.0000	0.0459	0.9992
	5.00	0.2344		
	10.01	0.4562		
	15.01	0.6840		
	20.02	0.8930		
	25.02	1.1423		
	30.02	1.3995		
12	0.00	0.0000	0.0458	0.9984
	5.01	0.2498		
	10.02	0.4621		
	15.04	0.6661		
	20.05	0.8865		
	25.06	1.1578		
	30.07	1.3945		

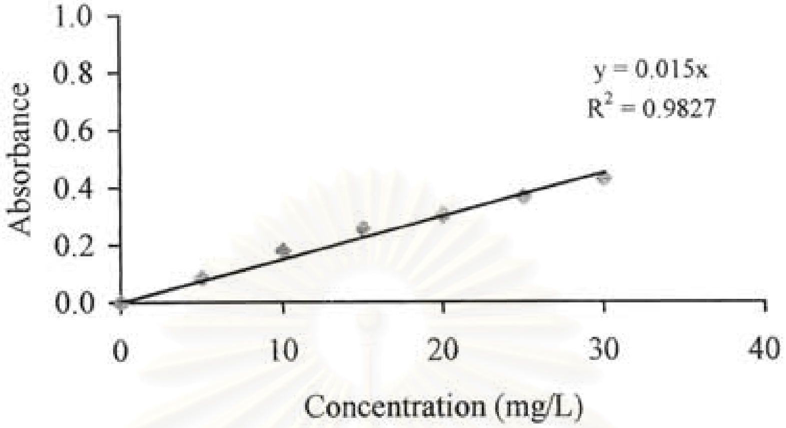

Figure B.1 Calibration curve of C.I. Acid Red 360 at pH 3

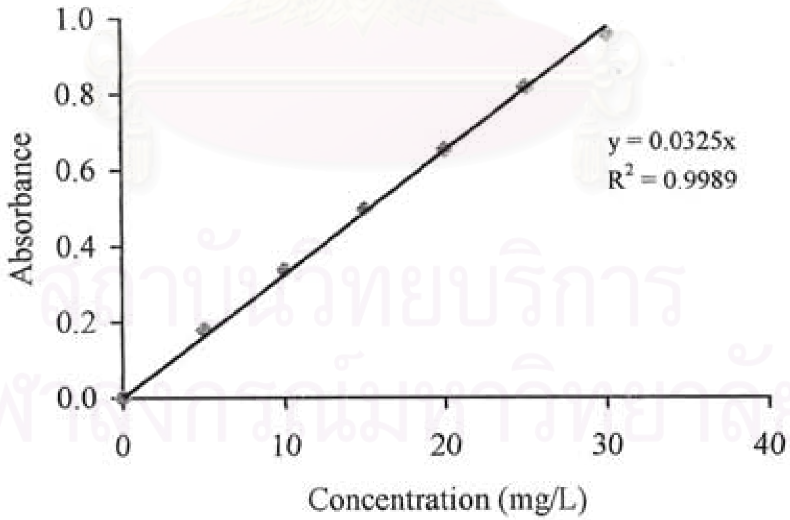

Figure B.2 Calibration curve of C.I. Acid Red 360 at pH 4

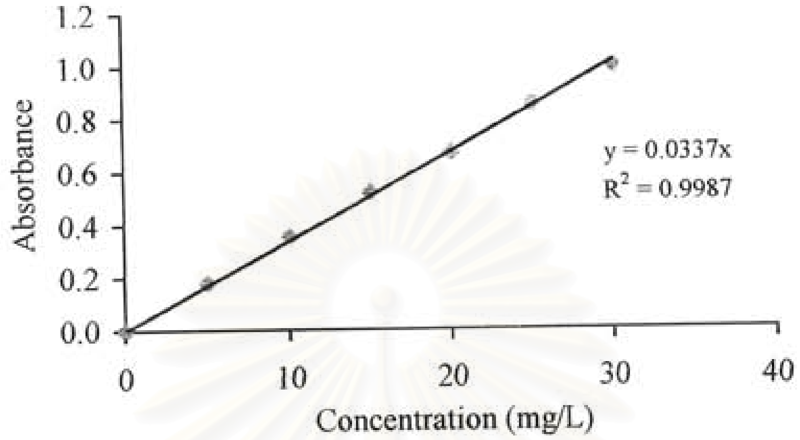

Figure B.3 Calibration curve of C.I. Acid Red 360 at pH 5

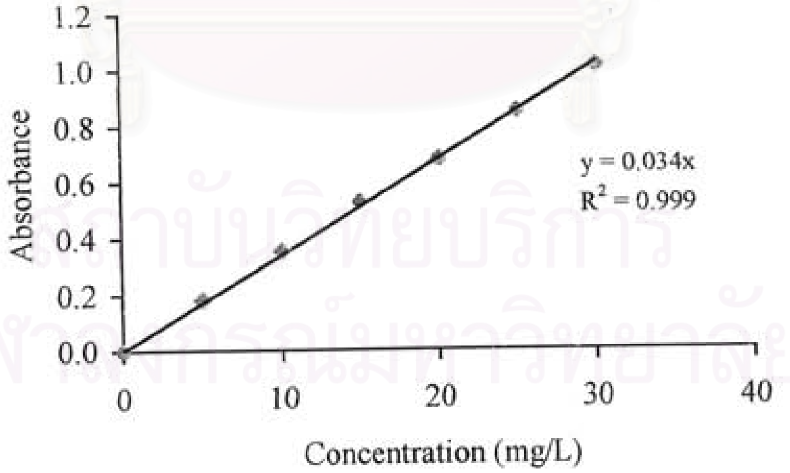

Figure B.4 Calibration curve of C.I. Acid Red 360 at pH 6

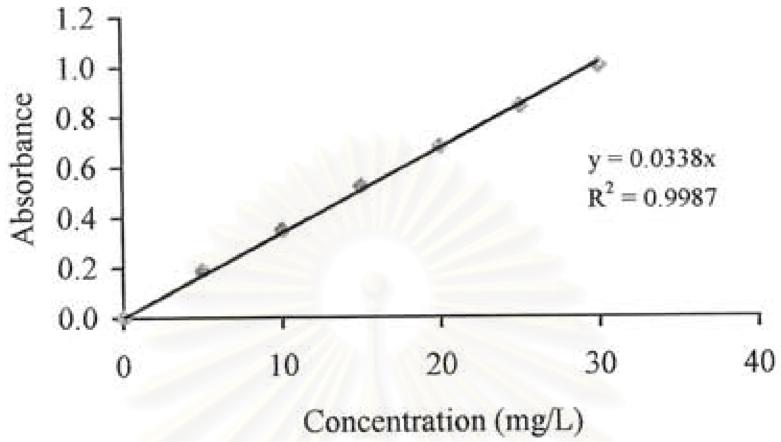

Figure B.5 Calibration curve of C.I. Acid Red 360 at pH 7

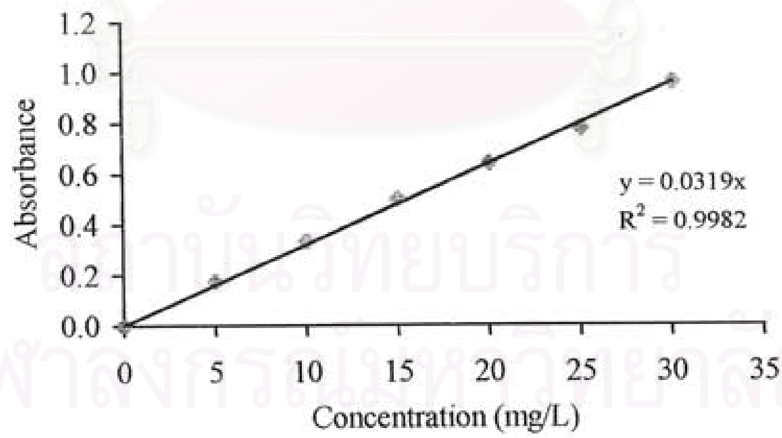

Figure B.6 Calibration curve of C.I. Acid Red 360 at pH 8

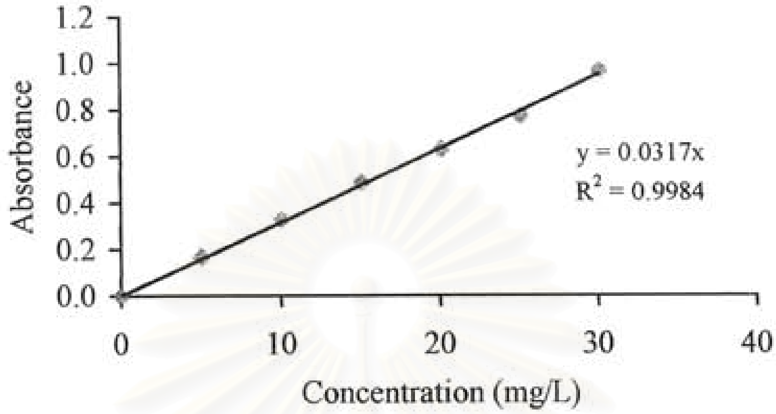

Figure B.7 Calibration curve of C.I. Acid Red 360 at pH 9

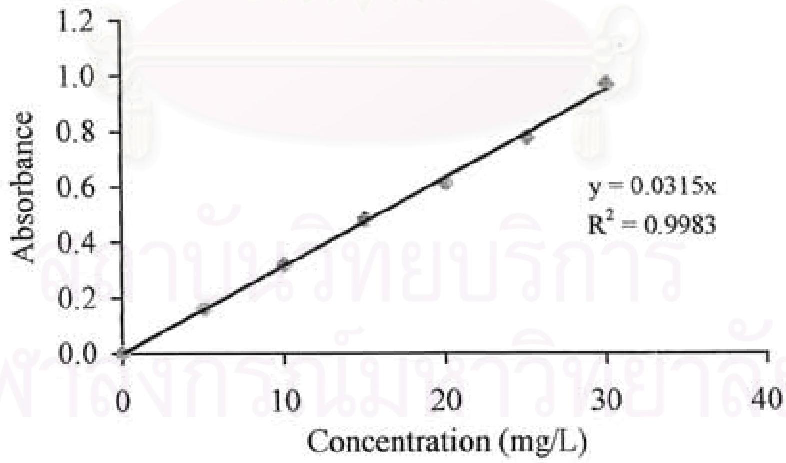

Figure B.8 Calibration curve of C.I. Acid Red 360 at pH 10

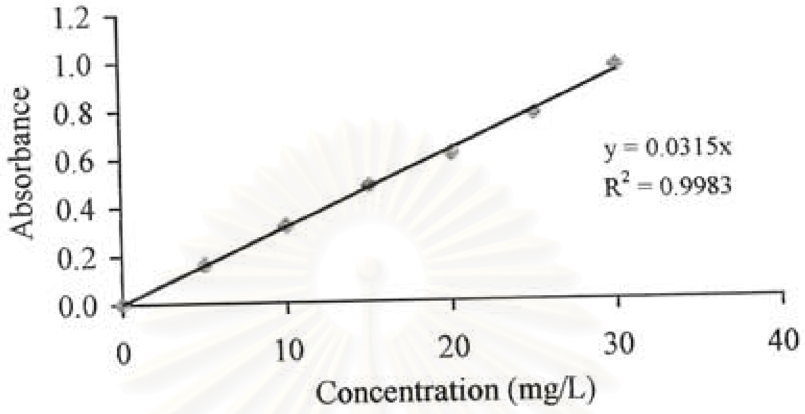

Figure B.9 Calibration curve of C.I. Acid Red 360 at pH 11

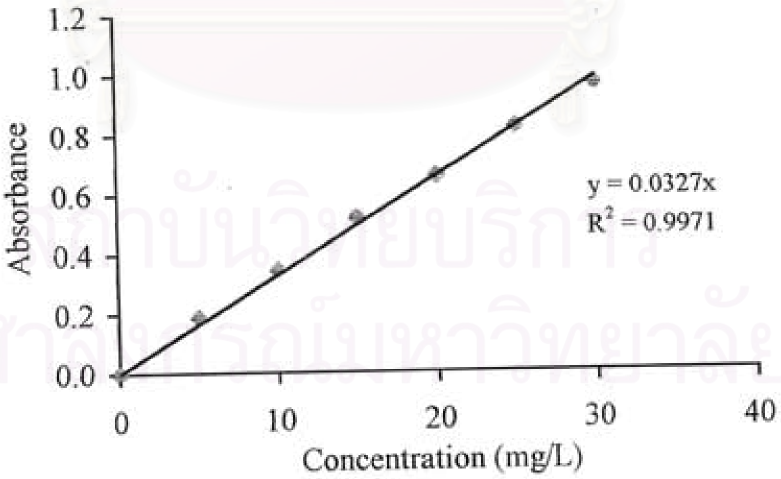

Figure B.10 Calibration curve of C.I. Acid Red 360 at pH 12

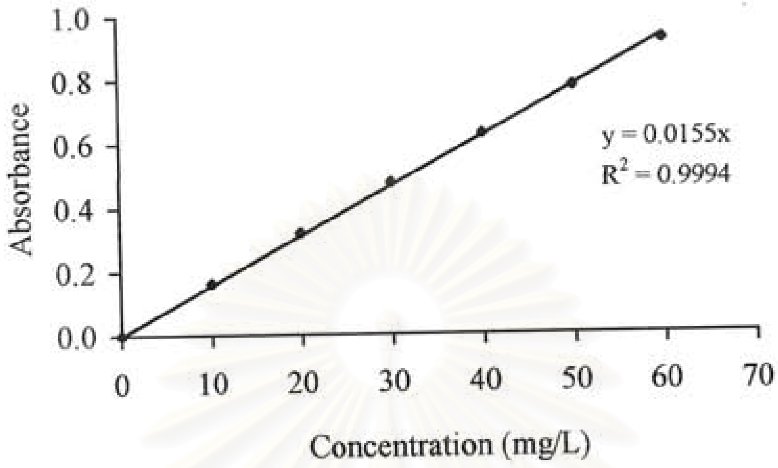

Figure B.11 Calibration curve of C.I. Reactive Red 158 at pH 3

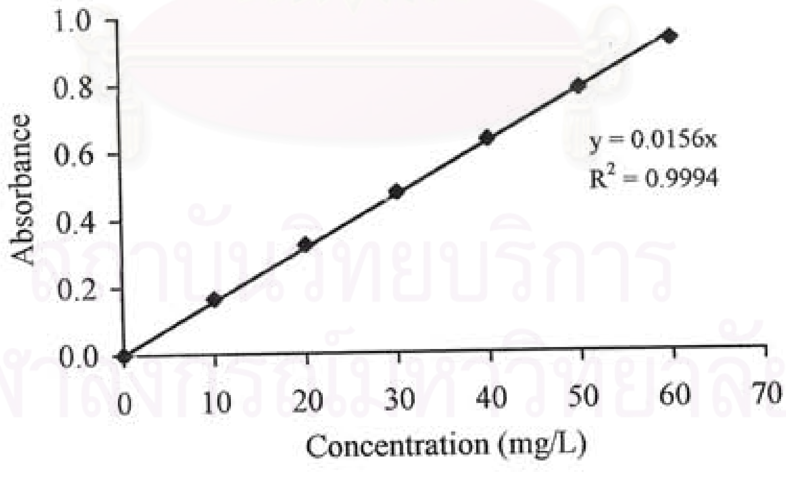

Figure B.12 Calibration curve of C.I. Reactive Red 158 at pH 4

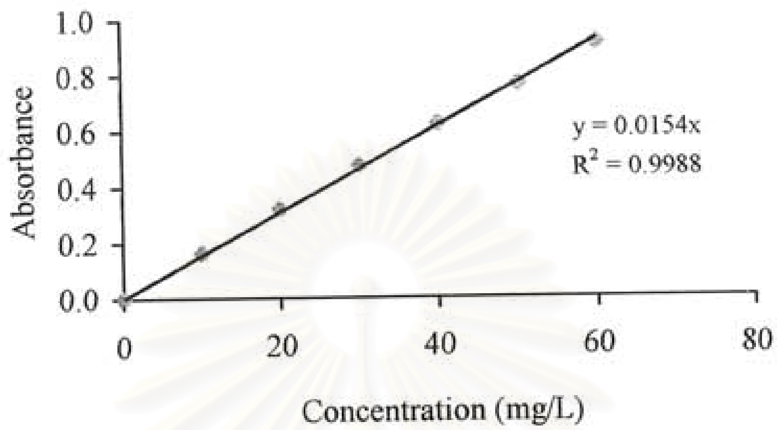

Figure B.13 Calibration curve of C.I. Reactive Red 158 at pH 5

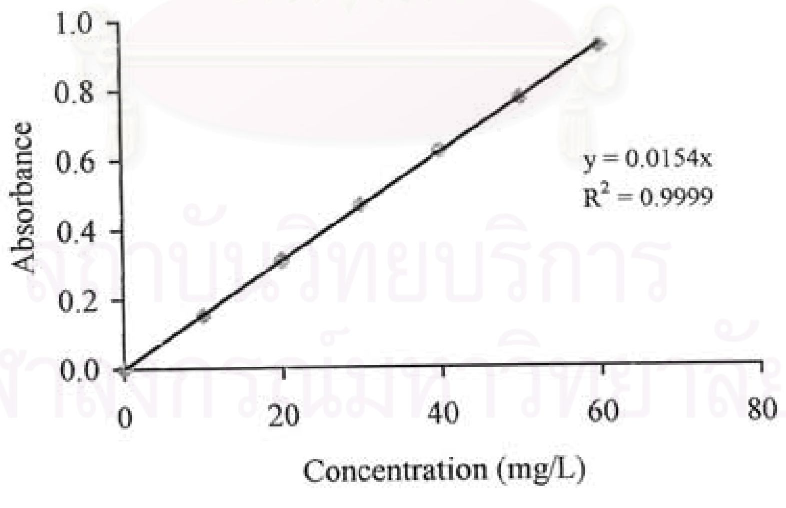

Figure B.14 Calibration curve of C.I. Reactive Red 158 at pH 6

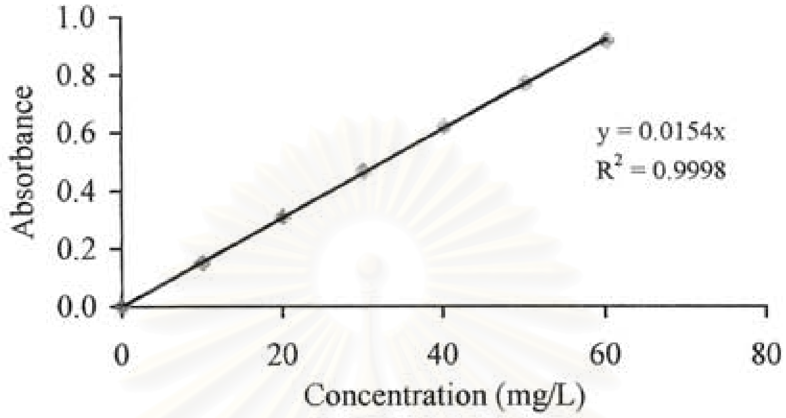

Figure B.15 Calibration curve of C.I. Reactive Red 158 at pH 7

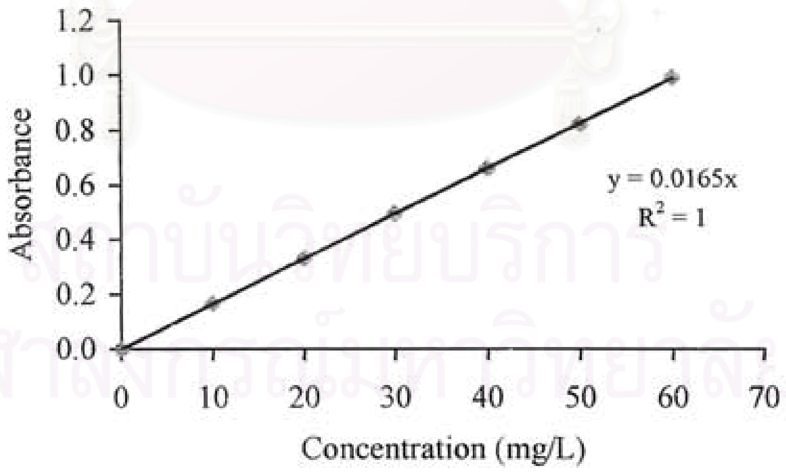

Figure B.16 Calibration curve of C.I. Reactive Red 158 at pH 8

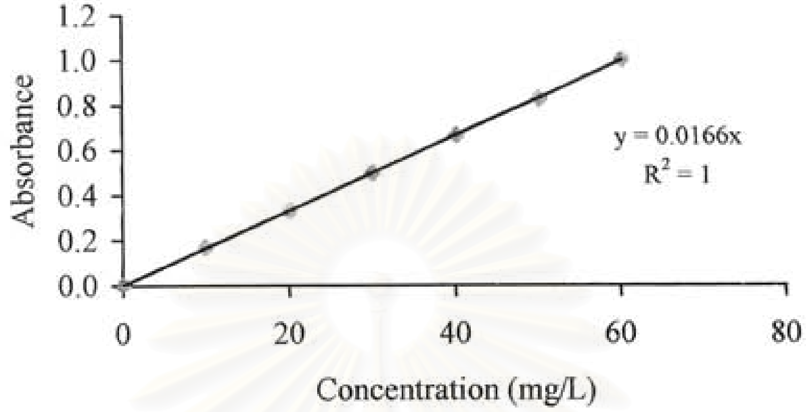

Figure B.17 Calibration curve of C.I. Reactive Red 158 at pH 9

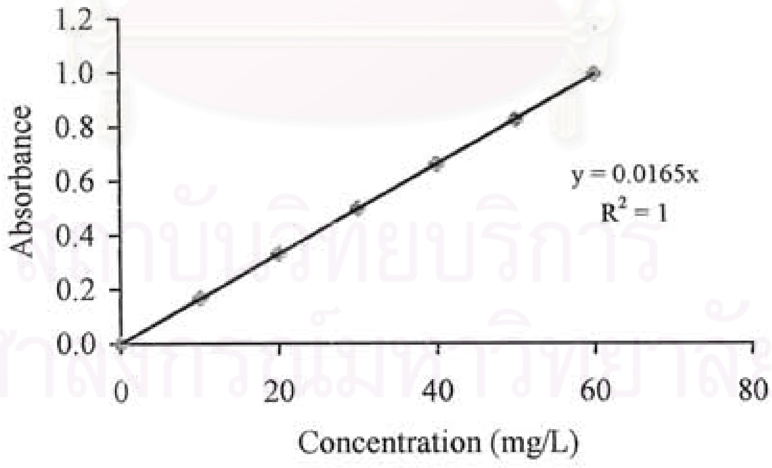

Figure B.18 Calibration curve of C.I. Reactive Red 158 at pH 10

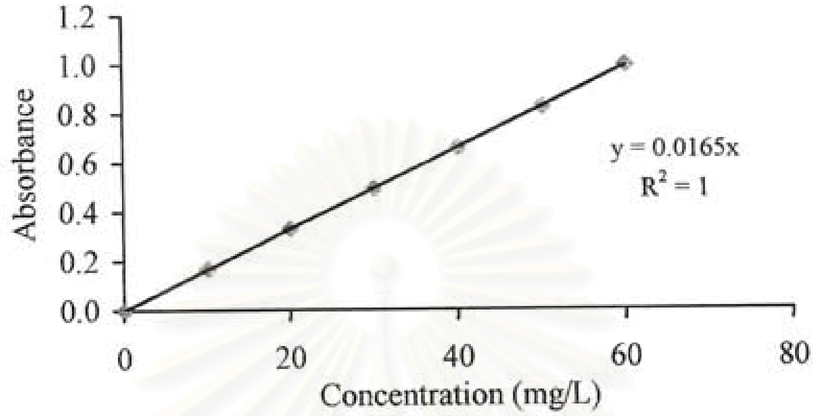

Figure B.19 Calibration curve of C.I. Reactive Red 158 at pH 11

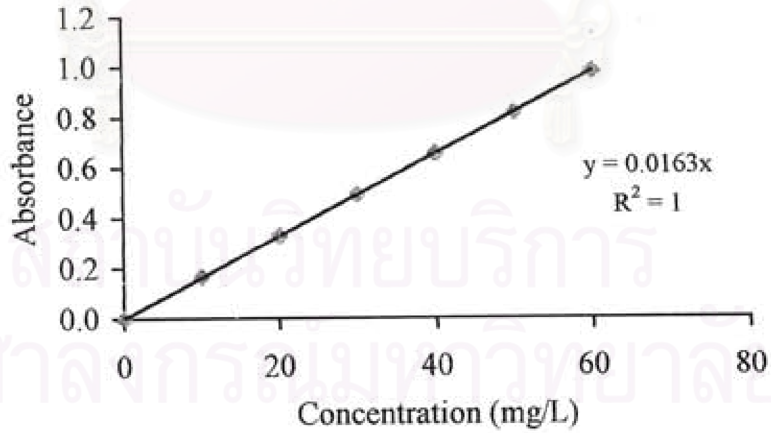

Figure B.20 Calibration curve of C.I. Reactive Red 158 at pH 12

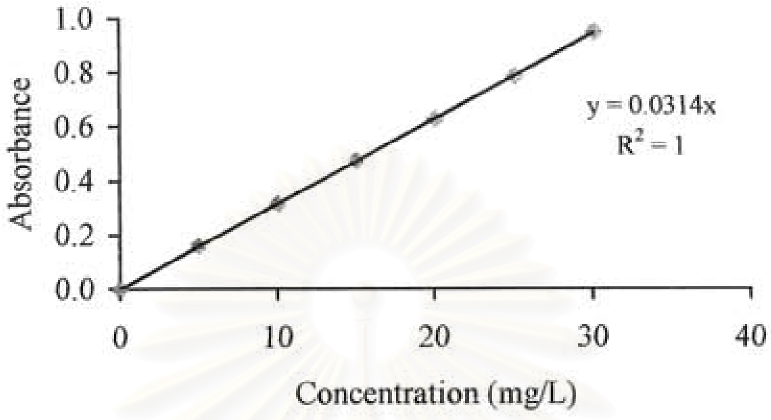

Figure B.21 Calibration curve of C.I. Direct Red 80 at pH 3

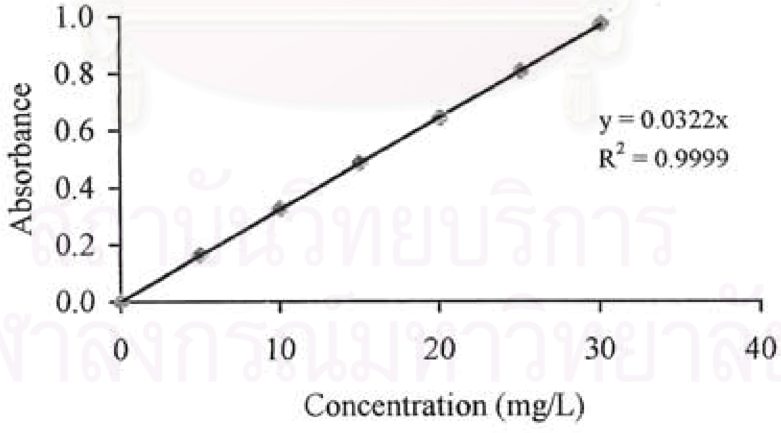

Figure B.22 Calibration curve of C.I. Direct Red 80 at pH 4

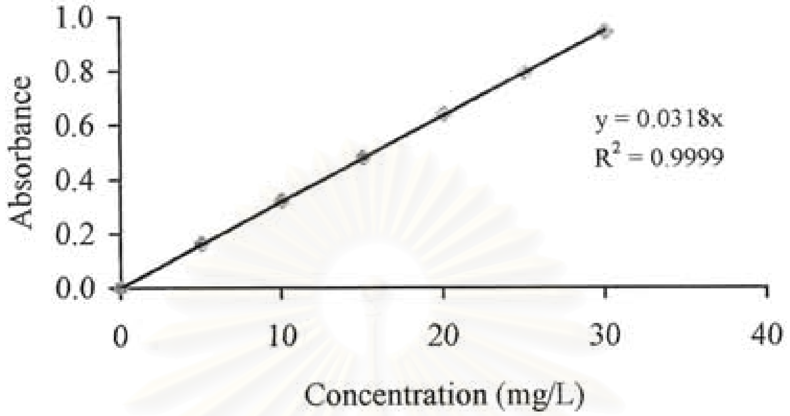

Figure B.23 Calibration curve of C.I. Direct Red 80 at pH 5

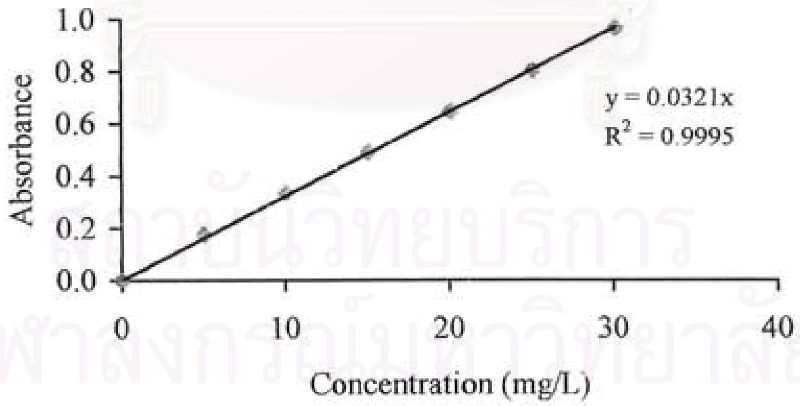

Figure B.24 Calibration curve of C.I. Direct Red 80 at pH 6

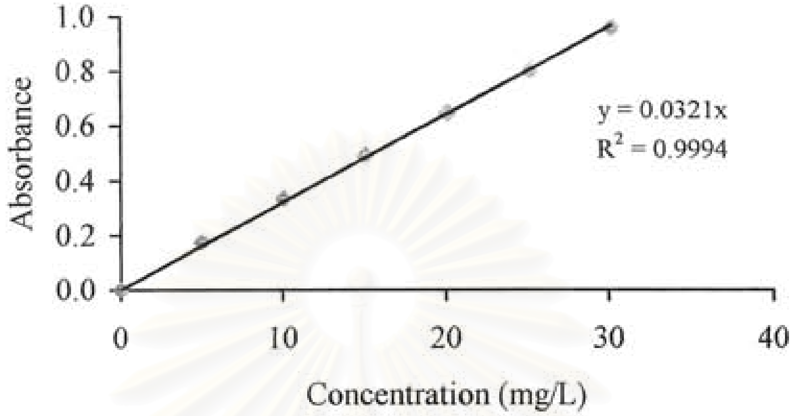

Figure B.25 Calibration curve of C.I. Direct Red 80 at pH 7

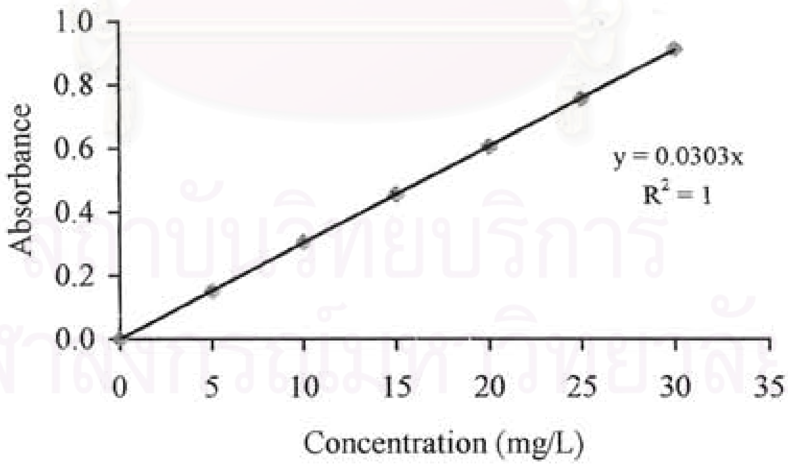

Figure B.26 Calibration curve of C.I. Direct Red 80 at pH 8

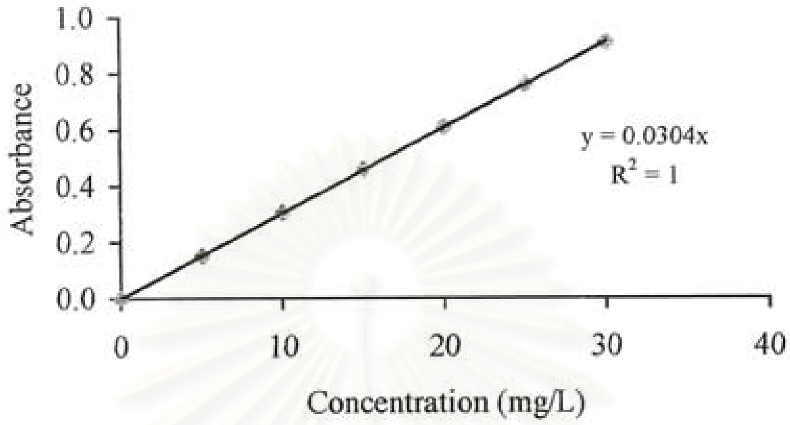

Figure B.27 Calibration curve of C.I. Direct Red 80 at pH 9

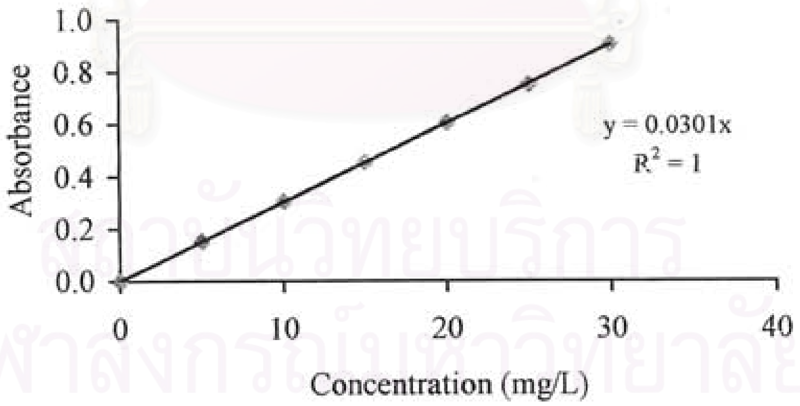

Figure B.28 Calibration curve of C.I. Direct Red 80 at pH 10

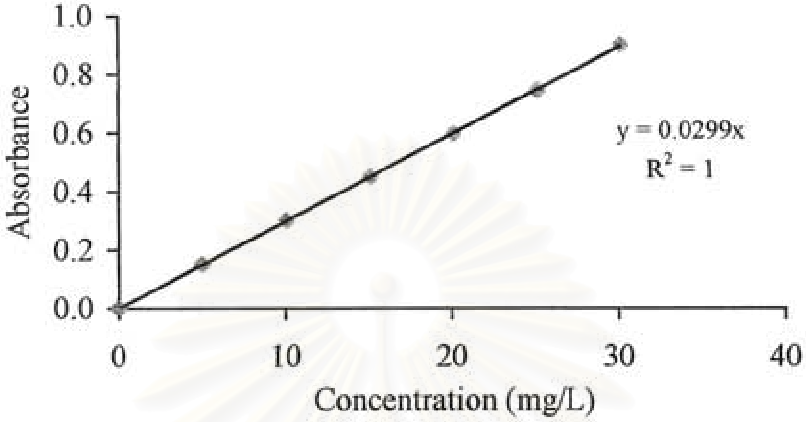

Figure B.29 Calibration curve of C.I. Direct Red 80 at pH 11

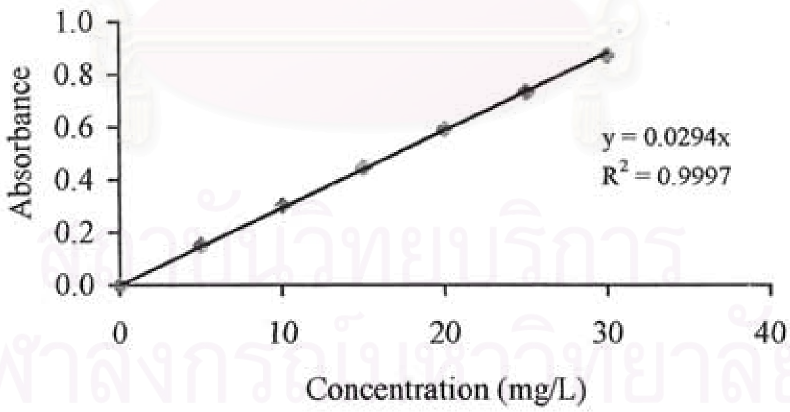

Figure B.30 Calibration curve of C.I. Direct Red 80 at pH 12

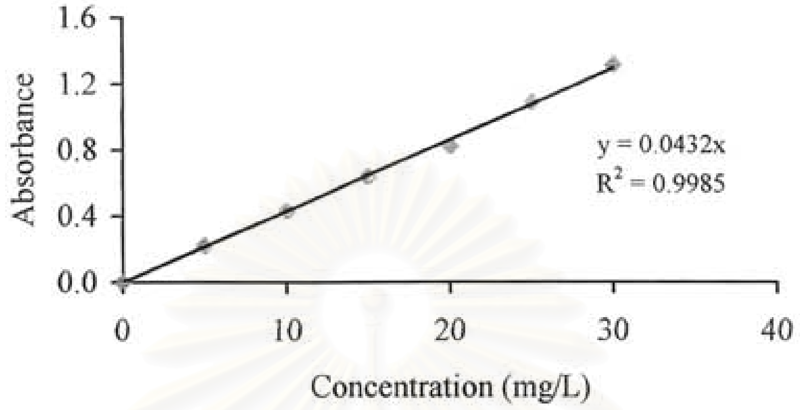

Figure B.31 Calibration curve of C.I. Basic Red 24 at pH 3

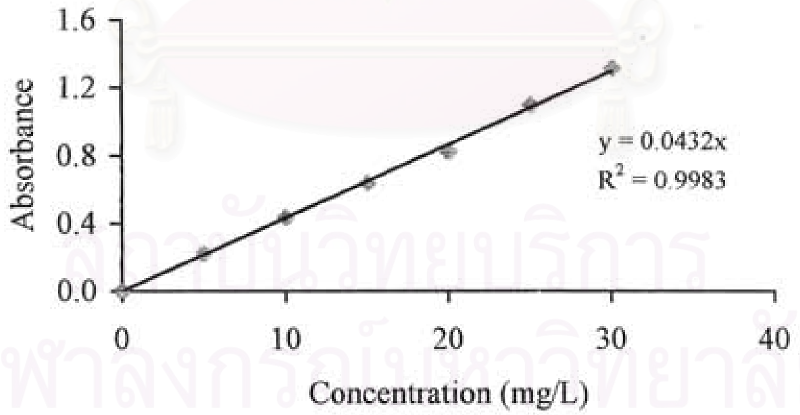

Figure B.32 Calibration curve of C.I. Basic Red 24 at pH 4

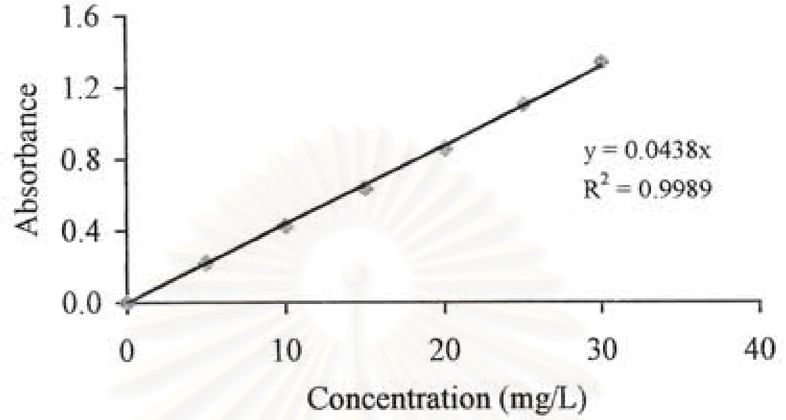

Figure B.33 Calibration curve of C.I. Basic Red 24 at pH 5

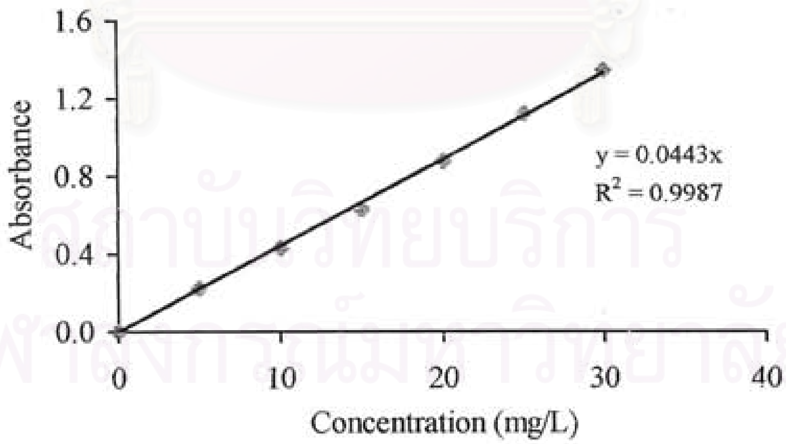

Figure B.34 Calibration curve of C.I. Basic Red 24 at pH 6

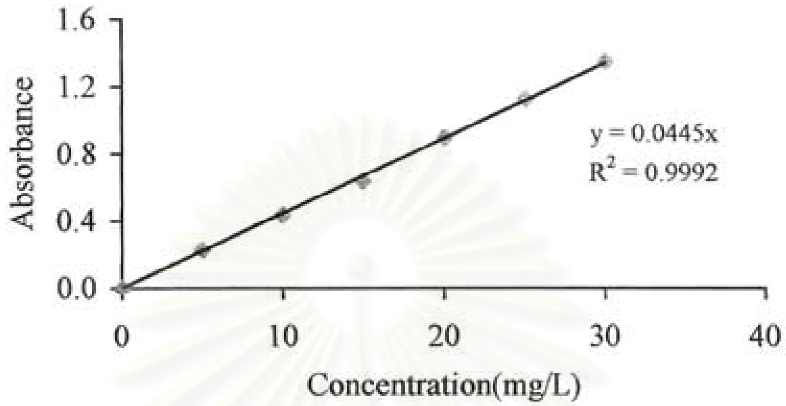

Figure B.35 Calibration curve of C.I. Basic Red 24 at pH 7

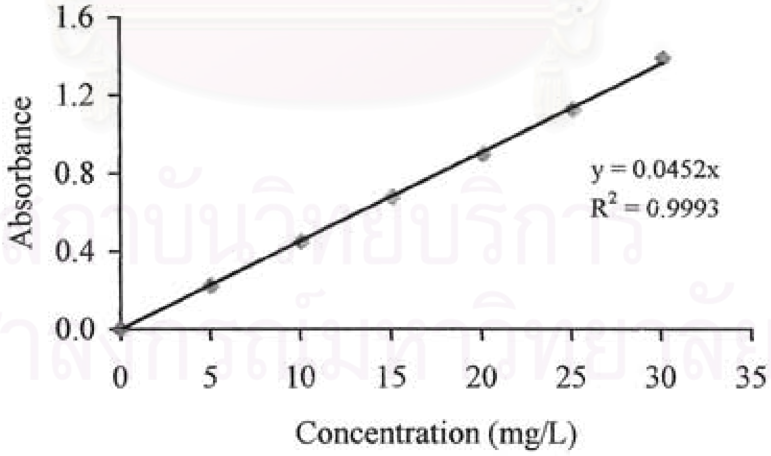

Figure B.36 Calibration curve of C.I. Basic Red 24 at pH 8

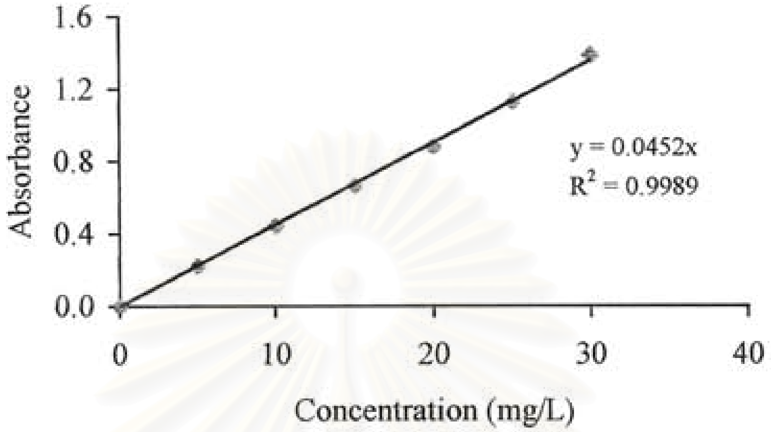

Figure B.37 Calibration curve of C.I. Basic Red 24 at pH 9

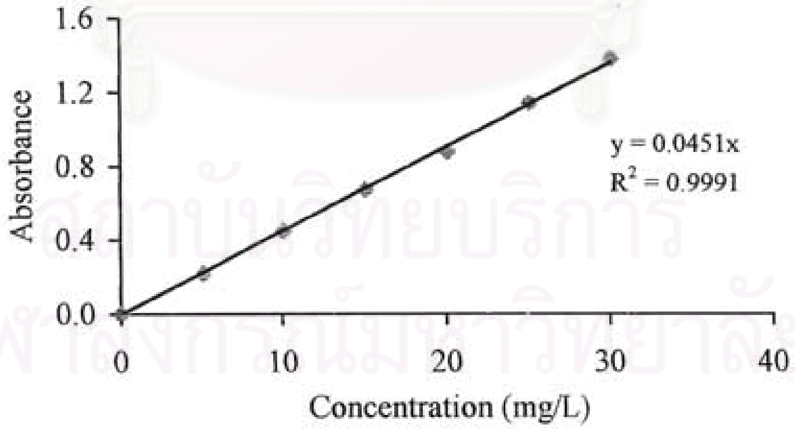

Figure B.38 Calibration curve of C.I. Basic Red 24 at pH 10

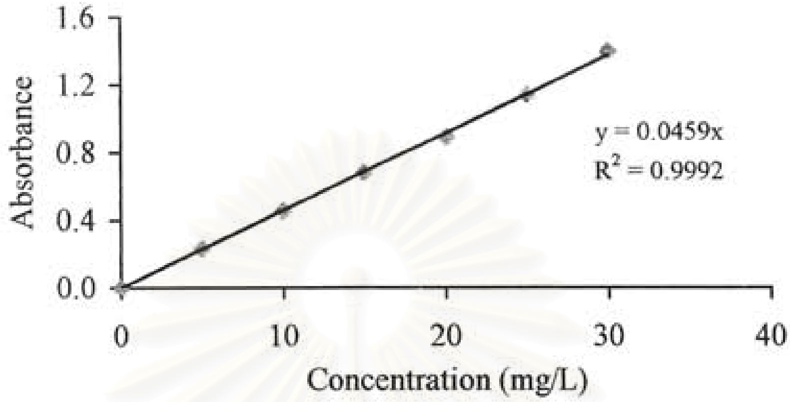

Figure B.39 Calibration curve of C.I. Basic Red 24 at pH 11

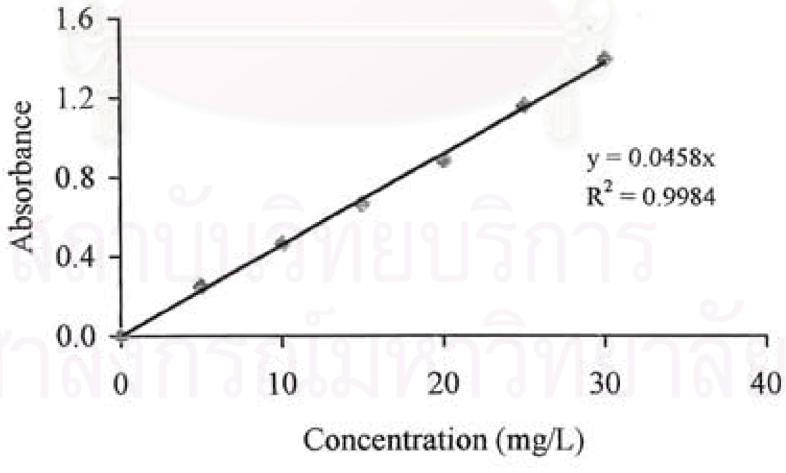

Figure B.40 Calibration curve of C.I. Basic Red 24 at pH 12

APPENDIX C

Effect of Various pHs on Dye Stability

The amounts of dyes adsorbed on adsorbents were calculated from the following equation :

$$Q_s \quad = \quad A_s/S$$

Where Q_s : Amount of dye in supernatant after 0 and 24 h (mg/L)

A_s : Absorbance of dye in supernatant after 0 and 24 h

S : Slope value from calibration curve of dye concentration and absorbance

<u>Test conditions</u>

Dye concentration		:	200.00 mg/L
Dye volume		:	25.0 mL
Shaking		:	80 rpm, 0 and 24 h, 25°C
Centrifuging		:	15000 rpm, 10 min, 25°C
C.I. Acid Red 360	S	=	0.0326
C.I. Reactive Red 158	S	=	0.0160
C.I. Direct Red 80	S	=	0.0310
C.I. Basic Red 24	S	=	0.0446

<u>An example of calculation</u>

Amount of C.I. Acid Red 360 after 0 h at pH 4,

$$Q_0 = A_0 / S$$
$$= (7.2660) / (0.0326)$$
$$= 222.88 \text{ mg/L}$$

Amount of C.I. Acid Red 360 after 24 h at pH 4,

$$Q_{24} = A_{24} / S$$
$$= (7.1240) / (0.0326)$$
$$= 218.53 \text{ mg/L}$$

Table C.1 Stability of C.I. Acid Red 360 at various pHs before and after 24 h shaking

pH of dye	A_0		A_{24}		Q_0			Q_{24}		
	1	2	1	2	1	2	Average	1	2	Average
3.0 *	3.4700	3.5120	3.5880	3.5800	106.44	107.73	107.09	110.06	109.82	109.94
3.5	7.236	7.2140	7.0180	7.0200	221.96	221.29	221.63	215.28	215.34	215.31
4.0	7.2660	7.2680	7.1240	7.1340	222.88	222.94	222.91	218.53	218.83	218.68
4.5	7.1500	7.1500	7.0400	7.0520	219.33	219.33	219.33	215.95	216.32	216.13
5.0	7.3140	7.3500	7.1940	7.2020	224.36	225.46	224.91	220.67	220.92	220.80
6.0	7.1960	7.2000	7.1600	7.1680	220.74	220.86	220.80	219.63	219.88	219.75
7.0	7.3340	7.3260	7.1840	7.1820	224.97	224.72	224.85	220.37	220.31	220.34
8.0	7.4180	7.4320	7.2780	7.2920	227.55	227.98	227.76	223.25	223.68	223.47

* Dye precipitated after adjusting pH to pH 3.

Table C.2 Stability of C.I. Reactive Red 158 at various pHs before and after 24 h shaking

pH of dye	A_0		A_{24}		Q_0			Q_{24}		
	1	2	1	2	1	2	Average	1	2	Average
3.0	3.2160	3.2190	3.2760	3.2780	201.00	201.19	201.09	204.75	204.88	204.81
3.5	3.2680	3.2730	3.3260	3.3290	204.25	204.56	204.41	207.88	206.06	207.97
4.0	3.2870	3.2840	3.3400	3.3400	205.44	205.25	205.34	208.75	208.75	208.75
4.5	3.2560	3.2580	3.3640	3.3700	203.50	203.63	203.56	210.25	210.63	210.44
5.0	3.3000	3.2990	3.3570	3.3560	206.25	206.19	206.22	209.81	209.75	209.78
6.0	3.2710	3.2750	3.3290	3.3270	204.44	204.69	204.56	208.06	207.94	208.00
7.0	3.2890	3.2910	3.3430	3.3450	205.56	205.69	205.63	208.94	209.06	209.00
8.0	3.3050	3.3060	3.220	3.3250	206.56	206.63	206.59	207.63	207.81	207.72

Table C. 3 Stability of C.I. Direct Red 80 at various pHs before and after 24 h shaking

pH of dye	A_0		A_{24}		Q_0			Q_{24}		
	1	2	1	2	1	2	Average	1	2	Average
2.5	6.2800	6.2820	6.4000	6.4000	202.58	202.65	202.61	206.45	206.45	206.45
3.0	6.3320	6.3320	6.4320	6.4380	204.26	204.26	204.26	207.48	207.68	207.58
3.5	6.2480	6.2560	6.3760	6.3860	201.55	201.81	201.68	205.68	206.00	205.84
4.0	6.2680	6.2800	6.3820	6.3840	202.19	202.58	202.39	205.87	205.94	205.90
5.0	6.2580	6.2520	6.3480	6.3520	201.87	201.68	201.77	204.77	204.90	204.84
6.0	6.2520	6.2560	6.3600	6.3560	201.68	201.81	201.74	205.16	205.03	205.10
7.0	6.3160	6.3200	6.4400	6.4440	203.74	203.87	203.81	207.74	207.87	207.81
8.0	6.3560	6.3600	6.4620	6.4720	205.03	205.16	205.10	208.45	208.77	208.61

Table C.4 Stability of C.I. Basic Red 24 at various pHs before and after 24 h shaking

pH of dye	A_0		A_{24}		Q_0			Q_{24}		
	1	2	1	2	1	2	Average	1	2	Average
3.0	10.030	10.040	9.8300	9.8550	224.89	225.11	225.00	220.40	220.96	220.68
4.0	9.5850	9.5650	9.4750	9.4800	214.91	214.46	214.69	212.44	212.56	212.50
5.0	9.6150	9.5950	9.5250	9.5300	215.58	215.13	215.36	213.57	213.68	213.62
6.0	9.7400	9.7600	9.4250	9.4500	218.39	218.83	218.61	211.32	211.88	211.60
7.0	9.7150	9.7150	9.6350	9.6600	217.83	217.83	217.83	216.03	216.59	216.31
8.0	9.5300	9.5550	9.4750	9.4700	213.68	214.24	213.96	212.44	212.33	212.39
9.0	9.4500	9.4400	9.3700	9.3700	211.88	211.66	211.77	210.09	210.09	210.09
10.0	9.2950	9.2850	9.1500	9.1600	208.41	208.18	208.30	205.16	205.38	205.27
11.0	9.0300	9.0250	9.0650	9.0850	202.47	202.35	202.41	203.25	203.70	203.48

APPENDIX D

Preparation of Dye–sorbed Adsorbents

The amounts of dyes on dye-sorbed adsorbents were calculated from the following equation :

$$Qa = \frac{(C \times 150) - [(Aa - Abl) \times 250] / S}{W \times 1000}$$

Where Qa : Amount of dye adsorbed on adsorbent (mg/g)

C : Initial concentration of dye solution (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

W : Weight of adsorbent (5.00 g)

An example of calculation

Amount of C.I. Acid Red 360 adsorbed on chitosan,

$$Qa = \frac{(400.14)(150) - [(0.1189 - 0.0034)(250)] / (0.0326)}{(5.00)(1000)}$$

$$= 11.83 \text{ mg/g}$$

Table D. 1 Amount of dyes on dye-sorbed shrimp shells

Type of dye	C (mg/L)	S	Aa	Abl	Qa (mg/g)
C.I. Acid Red 360	400.14	0.0326	0.1252	0.0164	11.84
C.I. Reactive Red 158	400.00	0.0160	0.0243	0.0148	11.97
C.I. Direct Red 80	400.22	0.0310	0.1443	0.0154	11.80
C.I. Basic Red 24	400.14	0.0446	0.2047	0.0164	11.79

Table D. 2 Amount of dyes on dye-sorbed chitin

Type of dye	C (mg/L)	S	Aa	Abl	Qa (mg/g)
C.I. Acid Red 360	400.14	0.0326	0.3792	0.0035	11.43
C.I. Reactive Red 158	400.00	0.0160	0.0026	0.0027	12.00
C.I. Direct Red 80	400.22	0.0310	0.0041	0.0030	12.00
C.I. Basic Red 24	400.14	0.0446	7.4800	0.0027	3.62

Table D. 3 Amount of dyes on dye-sorbed chitosan

Type of dye	C (mg/L)	S	Aa	Abl	Qa (mg/g)
C.I. Acid Red 360	400.14	0.0326	0.1189	0.0034	11.83
C.I. Reactive Red 158	400.00	0.0160	0.0035	0.0029	12.00
C.I. Direct Red 80	400.22	0.0310	0.0114	0.0037	11.99
C.I. Basic Red 24	400.14	0.0446	8.9313	0.0028	1.99

APPENDIX E

Effect of pH over Dye Adsorption on Adsorbents

The amounts of dye adsorbed on adsorbents were calculated from the following equation :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000}$$

Where Qa	:	Amount of adsorbed dye (mg of adsorbed dye per g of Adsorbent)
C	:	Initial concentration of dye (mg/L)
Aa	:	Absorbance of unadsorbed dye after adsorption
Abl	:	Absorbance of blank
S	:	Slope value from calibration curve of dye concentration and Absorbance
V	:	Volume of dye solution (25.0 mL)
W	:	Weight of adsorbent (g)

Test conditions

Adsorption temperature		:	25 °C
C.I. Acid Red 360	S	=	0.0326
C.I. Reactive Red 158	S	=	0.0160
C.I. Direct Red 80	S	=	0.0310
C.I. Basic Red 24	S	=	0.0446

An example of calculation

Adsorption amount of C.I. Acid Red 360 on chitosan at pH 4,

$$Qa = \frac{[(200.32) - (0.0322 - 0.0034) / (0.0326)] (25.0)}{(0.0501) (1000)}$$

$$= 99.52 \quad mg/g$$

Table E.1 Effect of pH on the adsorption of C.I. Acid Red 360 on shrimp shells

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	201.40	0.0503	0.0502	0.4774	0.4783	0.0148	0.0148	93.05	93.22	93.13
3.5	200.16	0.0501	0.0500	0.5208	0.5289	0.0142	0.0144	92.13	92.19	92.16
4.0	200.32	0.0500	0.0503	0.5545	0.5558	0.0113	0.0115	91.83	91.26	91.55
4.5	200.68	0.0503	0.0502	0.5602	0.5378	0.0120	0.0122	91.38	91.91	91.65
5.0	200.92	0.0502	0.0503	0.5957	0.5914	0.0181	0.0185	91.24	91.13	91.18
6.0	200.40	0.0500	0.0500	1.9550	2.0400	0.0134	0.0136	70.42	69.12	69.77
7.0	200.40	0.0503	0.0501	2.0360	2.2500	0.0144	0.0149	68.78	65.79	67.28
8.0	200.92	0.0500	0.0503	2.0080	2.1440	0.0121	0.0126	69.59	67.11	68.35

Table E.2 Effect of pH on the adsorption of C.I. Acid Red 360 on chitin

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	201.40	0.0503	0.0502	0.0098	0.0035	0.0065	0.0067	100.05	100.35	100.20
3.5	200.16	0.0500	0.0502	0.0032	0.0041	0.0050	0.0052	100.11	99.70	99.90
4.0	200.32	0.0500	0.0502	0.2367	0.2513	0.0033	0.0036	96.58	95.98	96.28
4.5	200.68	0.0502	0.0501	0.4887	0.5025	0.0032	0.0036	92.52	92.50	92.51
5.0	200.92	0.0500	0.0501	0.5340	0.5390	0.0032	0.0035	92.32	92.06	92.19
6.0	200.40	0.0502	0.0503	3.2910	3.4900	0.0037	0.0038	49.58	46.45	48.02
7.0	200.40	0.0500	0.0502	3.8500	4.1020	0.0033	0.0031	41.20	37.18	39.19
8.0	200.92	0.0502	0.0502	4.3430	4.4400	0.0046	0.0047	33.78	32.30	33.04

Table E.3 Effect of pH on the adsorption of C.I. Acid Red 360 on chitosan

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	201.40	0.0503	0.0502	0.0137	0.0063	0.0033	0.0038	99.94	100.26	100.10
3.5	200.16	0.0502	0.0500	0.0014	0.0000	0.0034	0.0033	99.71	100.13	99.92
4.0	200.32	0.0501	0.0503	0.0322	0.0323	0.0034	0.0033	99.52	99.12	99.32
4.5	200.68	0.0503	0.0502	0.2313	0.2081	0.0032	0.0030	96.26	96.20	96.23
5.0	200.92	0.0501	0.0502	0.4195	0.4317	0.0030	0.0028	93.73	93.36	93.55
6.0	200.40	0.0500	0.0501	2.0217	2.0060	0.0023	0.0022	69.15	69.33	69.24
7.0	200.40	0.0501	0.0502	2.4290	2.5050	0.0022	0.0023	62.85	61.57	62.21
8.0	200.92	0.0503	0.0502	2.8220	2.8860	0.0022	0.0023	56.87	56.01	56.44

Table E.4 Effect of pH on the adsorption of C.I. Reactive Red 158 on shrimp shells

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
3.0	200.40	0.0502	0.0502	0.4253	0.4310	0.0164	0.0163	87.07	86.89	86.98
3.5	200.48	0.0500	0.0502	0.4353	0.4115	0.0135	0.0137	87.06	87.46	87.26
4.0	200.60	0.0500	0.0500	0.4423	0.4463	0.0123	0.0125	86.86	86.74	86.80
4.5	200.64	0.0502	0.0502	0.4597	0.4640	0.0130	0.0135	86.02	85.90	85.96
5.0	200.64	0.0500	0.0500	0.4686	0.4828	0.0206	0.0202	86.32	85.86	86.09
6.0	200.00	0.0501	0.0502	2.7050	0.6940	0.0152	0.0154	15.91	16.23	16.07
7.0	200.16	0.0501	0.0500	2.6860	2.6590	0.0158	0.0159	16.60	17.48	17.04
8.0	200.32	0.0502	0.0501	2.6610	2.6550	0.0138	0.0138	17.37	17.59	17.48

Table E.5 Effect of pH on the adsorption of C.I. Reactive Red 158 on chitin

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
3.0	200.40	0.0500	0.0502	0.0173	0.0157	0.0076	0.0077	99.90	99.55	99.72
3.5	200.48	0.0502	0.0501	0.2315	0.2393	0.0045	0.0042	92.78	92.71	92.74
4.0	200.60	0.0502	0.0502	0.3409	0.3799	0.0038	0.0040	89.41	88.20	88.80
4.5	200.64	0.0501	0.0501	0.3805	0.4018	0.0040	0.0041	88.38	87.72	88.05
5.0	200.64	0.0502	0.0501	0.4118	0.4114	0.0041	0.0040	87.23	87.41	87.32
6.0	200.00	0.0502	0.0500	2.3730	2.3800	0.0044	0.0045	25.88	25.77	25.82
7.0	200.16	0.0500	0.0502	2.5020	2.5060	0.0039	0.0041	22.01	21.81	21.91
8.0	200.32	0.0502	0.0500	2.6890	2.6730	0.0052	0.0054	16.23	16.80	16.51

Table E.6 Effect of pH on the adsorption of C.I. Reactive Red 158 on chitosan

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
3.0	200.40	0.0502	0.0502	0.0000	0.0000	0.0027	0.0029	99.88	99.89	99.89
3.5	200.48	0.0502	0.0502	0.0112	0.0087	0.0030	0.0029	99.59	99.66	99.62
4.0	200.60	0.0501	0.0501	0.2401	0.2474	0.0032	0.0033	92.71	92.49	92.60
4.5	200.64	0.0501	0.0502	0.3417	0.3485	0.0030	0.0031	89.56	89.17	89.36
5.0	200.64	0.0502	0.0502	0.3620	0.3783	0.0028	0.0030	88.74	88.24	88.49
6.0	200.00	0.0502	0.0501	1.9210	1.9220	0.0029	0.0031	39.90	39.95	39.93
7.0	200.16	0.0502	0.0500	2.0390	2.0500	0.0030	0.0031	36.31	36.11	36.21
8.0	200.32	0.0500	0.0500	2.2740	2.2730	0.0033	0.0032	29.20	29.23	29.21

Table E.7 Effect of pH on the adsorption of C.I. Direct Red 80 on shrimp shells

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
2.5	200.40	0.0503	0.0501	4.6470	4.6320	0.0160	0.0158	25.35	25.69	25.52
3.0	200.52	0.0501	0.0501	5.0940	5.1220	0.0154	0.0154	18.31	17.86	18.09
3.5	200.60	0.0503	0.0500	5.4830	5.4650	0.0145	0.0143	12.03	12.39	12.21
4.0	200.00	0.0500	0.0500	5.6520	5.6620	0.0127	0.0126	9.04	8.88	8.96
5.0	200.00	0.0501	0.0501	5.6420	5.6150	0.0189	0.0193	9.29	9.73	9.51
6.0	200.08	0.0502	0.0502	5.5440	5.5730	0.0144	0.0146	10.81	10.35	10.58
7.0	200.08	0.0502	0.0502	5.4950	5.5130	0.0153	0.0153	11.61	11.32	11.47
8.0	200.44	0.0500	0.0502	5.6090	5.5810	0.0140	0.0138	9.98	10.38	10.18

Table E.8 Effect of pH on the adsorption of C.I. Direct Red 80 on chitin

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
2.5	200.40	0.0500	0.0500	3.2500	3.2900	0.0080	0.0083	47.91	47.27	47.59
3.0	200.52	0.0502	0.0501	3.7990	3.8010	0.0078	0.0078	38.96	39.00	38.98
3.5	200.60	0.0502	0.0500	4.7200	4.7360	0.0045	0.0043	24.15	23.98	24.06
4.0	200.00	0.0500	0.0502	5.0500	5.0630	0.0039	0.0041	18.61	18.33	18.47
5.0	200.00	0.0501	0.0500	5.2800	5.2900	0.0040	0.0041	14.87	14.74	14.81
6.0	200.08	0.0502	0.0500	5.2100	5.1960	0.0045	0.0046	16.02	16.31	16.16
7.0	200.08	0.0502	0.0500	5.3530	5.3230	0.0039	0.0042	13.71	14.25	13.98
8.0	200.44	0.0501	0.0500	5.4380	5.4650	0.0054	0.0051	12.57	12.61	12.31

Table E.9 Effect of pH on the adsorption of C.I. Direct Red 80 on chitosan

pH of dye	C (mg/L)	W(g)		Aa		Abl		Qa(mg/g)		
		1	2	1	2	1	2	1	2	Average
2.5	200.40	0.0502	0.0503	1.3220	1.2900	0.0040	0.0042	78.63	78.99	78.81
3.0	200.52	0.0502	0.0500	2.0790	2.0920	0.0037	0.0038	66.52	66.58	66.55
3.5	200.60	0.0500	0.0502	4.9600	4.9580	0.0035	0.0036	20.36	20.31	20.33
4.0	200.00	0.0502	0.0502	5.1650	5.1900	0.0034	0.0038	16.68	16.29	16.48
5.0	200.00	0.0502	0.0500	5.2230	5.2560	0.0029	0.0030	15.74	15.27	15.51
6.0	200.08	0.0500	0.0501	5.2290	5.2430	0.0032	0.0031	15.75	15.49	15.62
7.0	200.08	0.0501	0.0500	5.2490	5.2300	0.0032	0.0034	15.40	15.74	15.57
8.0	200.44	0.0500	0.0501	5.2910	5.3060	0.0032	0.0032	14.93	14.66	14.80

Table E.10 Effect of pH on the adsorption of C.I. Basic Red 24 on shrimp shells

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	200.28	0.0502	0.0501	3.8275	3.8500	0.0164	0.0163	57.19	57.05	57.12
4.0	200.20	0.0502	0.0501	2.7950	2.8000	0.0123	0.0125	68.63	68.71	68.67
5.0	200.08	0.0500	0.0502	2.7900	2.7875	0.0206	0.0202	68.99	68.74	68.87
6.0	200.16	0.0500	0.0502	2.7800	2.7750	0.0152	0.0154	69.08	68.87	68.98
7.0	200.20	0.0500	0.0500	2.7525	2.7475	0.0158	0.0159	69.42	69.48	69.45
8.0	200.08	0.0500	0.0500	2.7150	2.7075	0.0138	0.0138	69.76	69.84	69.80
9.0	200.20	0.0501	0.0501	2.6450	2.6450	0.0164	0.0164	70.49	70.49	70.49
10.0	200.12	0.0500	0.0500	2.3675	2.3775	0.0205	0.0208	73.75	73.64	73.69
11.0	200.12	0.0500	0.0500	1.6250	1.6350	0.0145	0.0152	82.01	81.90	81.95

Table E.11 Effect of pH on the adsorption of C.I. Basic Red 24 on chitin

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	200.28	0.0502	0.0500	8.9250	8.9225	0.0076	0.0077	0.17	0.20	0.18
4.0	200.20	0.0502	0.0501	8.9150	8.9175	0.0038	0.0040	0.20	0.17	0.19
5.0	200.08	0.0500	0.0502	8.9200	8.9150	0.0041	0.0040	0.09	0.14	0.11
6.0	200.16	0.0500	0.0500	9.9225	8.9150	0.0044	0.0045	0.10	0.19	0.14
7.0	200.20	0.0501	0.0502	8.9175	8.9225	0.0039	0.0041	0.17	0.12	0.14
8.0	200.08	0.0501	0.0501	8.9150	8.9275	0.0052	0.0054	0.15	0.02	0.09
9.0	200.20	0.0500	0.0501	8.5525	8.5575	0.0064	0.0064	4.29	4.23	4.26
10.0	200.12	0.0500	0.0500	7.9475	7.9425	0.0089	0.0090	11.06	11.12	11.09
11.0	200.12	0.0500	0.0500	7.9275	7.9375	0.0090	0.0088	11.29	11.17	11.23

Table E.12 Effect of pH on the adsorption of C.I. Basic Red 24 on chitosan

pH of	C	W(g)		Aa		Abl		Qa(mg/g)		
dye	(mg/L)	1	2	1	2	1	2	1	2	Average
3.0	200.28	0.0503	0.0500	8.8250	8.8300	0.0027	0.0029	1.23	1.18	1.20
4.0	200.20	0.0502	0.0500	8.8325	8.8400	0.0032	0.0033	1.11	1.03	1.07
5.0	200.08	0.0500	0.0501	8.8250	8.8225	0.0028	0.0030	1.14	1.16	1.15
6.0	200.16	0.0502	0.0502	8.8175	8.8200	0.0029	0.0031	1.26	1.23	1.24
7.0	200.20	0.0502	0.0501	8.8150	8.8175	0.0030	0.0031	1.31	1.28	1.29
8.0	200.08	0.0501	0.0502	8.8150	8/.8125	0.0033	0.0032	1.25	1.28	1.26
9.0	200.20	0.0500	0.0501	8.8150	8.8250	0.0034	0.0036	1.32	1.20	1.26
10.0	200.12	0.0500	0.0500	7.9650	7.9650	0.0054	0.0055	10.83	10.83	10.83
11.0	200.12	0.0500	0.0500	7.7450	7.7550	0.0050	0.0049	13.29	13.18	13.23

APPENDIX F

Effect of Degree of Deacetylation (DD) on Dye Adsorption

The amounts of dye adsorbed on chitosan with different DDs were calculated from the following equation :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000}$$

Where Qa : Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

C : Initial concentration of dye (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

V : Volume of dye solution (25.0 mL)

W : Weight of adsorbent (0.0500g)

Test conditions

Adsorption temperature : 25 °C

C.I. Acid Red 360	C = 200.04	S = 0.0326	pH 4
C.I. Reactive Red 158	C = 200.32	S = 0.0160	pH 4
C.I. Direct Red 80	C = 200.16	S = 0.0310	pH 4
C.I. Basic Red 24	C = 200.16	S = 0.0446	pH 10

An example of calculation

Adsorption amount of C.I. Acid Red 360 on chitosan of 79.55%DD at pH 4,

$$Qa = \frac{[(200.04) - (0.3665 - 0.0034) / (0.0326)] (25.0)}{(0.0500)(1000)}$$

$$= 94.45 \quad mg/g$$

Table F.1 Effect of DD on the adsorption of C.I. Acid Red 360

DDs	Aa		Abl		Qa (mg/g)		
(%)	1	2	1	2	1	2	Average
24.48	0.5799	0.5784	0.0032	0.0036	91.17	91.20	91.19
34.88	0.5721	0.5784	0.0033	0.0032	91.30	91.20	91.25
45.12	0.4547	0.4611	0.0030	0.0031	93.09	93.00	93.04
60.71	0.1112	0.1119	0.0033	0.0034	98.37	98.36	98.36
71.08	0.1085	0.1096	0.0032	0.0033	98.40	98.39	98.40
79.55	0.3665	0.3693	0.0034	0.0033	94.45	94.41	94.43

Table F.2 Effect of DD on the adsorption of C.I. Reactive Red 158

DDs	Aa		Abl		Qa (mg/g)		
(%)	1	2	1	2	1	2	Average
24.48	0.6972	0.7075	0.0038	0.0040	78.49	78.18	78.33
34.88	0.6003	0.6067	0.0037	0.0036	81.52	81.31	81.41
45.12	0.4457	0.4491	0.0036	0.0035	86.34	86.24	86.29
60.71	0.2523	0.2534	0.0033	0.0034	92.38	92.35	92.36
71.08	0.3544	0.3567	0.0032	0.0033	89.19	89.12	89.15
79.55	0.4581	0.4614	0.0034	0.0033	85.95	85.84	85.90

Table F.3 Effect of DD on the adsorption of C.I. Direct Red 80

DDs (%)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
24.48	4.4090	4.5150	0.0039	0.0041	29.03	27.32	28.18
34.88	4.3950	4.4040	0.0040	0.0038	29.26	29.11	29.18
45.12	4.3980	4.4020	0.0037	0.0037	29.20	29.14	29.17
60.71	4.1120	4.1340	0.0035	0.0033	33.81	33.46	33.63
71.08	3.9410	3.9740	0.0034	0.0032	36.57	36.03	36.30
79.55	4.2800	4.2960	0.0034	0.0033	31.10	30.84	30.97

Table F.4 Effect of DD on the adsorption of C.I. Basic Red 24

DDs (%)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
24.48	6.4410	6.5010	0.0089	0.0090	27.97	27.30	27.64
34.88	6.5160	6.5760	0.0080	0.0082	27.12	26.45	26.79
45.12	6.5610	6.6020	0.0076	0.0074	26.61	26.15	26.38
60.71	6.6670	6.6560	0.0052	0.0054	25.40	25.52	25.46
71.08	6.7040	6.7380	0.0053	0.0054	24.98	24.60	24.79
79.55	6.6100	6.6880	0.0054	0.0055	26.04	25.16	25.60

APPENDIX G

Effect of Adsorption Time of Dyes on Adsorbents

The amounts of dye adsorbed on adsorbents were calculated from the following equation :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000}$$

Where Qa : Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

C : Initial concentration of dye (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

V : Volume of dye solution (25.0 mL)

W : Weight of adsorbent (0.0500g)

Test conditions

Adsorption temperature : 25 °C

C.I. Acid Red 360	C = 200.00	S = 0.0326	pH 4
C.I. Reactive Red 158	C = 200.02	S = 0.0160	pH 4
C.I. Direct Red 80	C = 200.00	S = 0.0310	pH 4
C.I. Basic Red 24	C = 200.16	S = 0.0446	pH 10

An example of calculation

Adsorption amount of C.I. Acid Red 360 on chitosan for 24 h,

$$Qa = \frac{[(200.00) - (0.0939 - 0.0034) / (0.0326)]\,(25.0)}{(0.0500)\,(1000)}$$

$$= 98.61 \quad \text{mg/g}$$

Table G.1 Effect of adsorption time of C.I. Acid Red 360 on shrimp shells

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
0.5	5.2475	5.2625	0.0078	0.0080	19.64	19.41	19.52
3	3.5725	3.5725	1.0085	0.0087	45.34	45.34	45.34
6	2.8500	2.8550	0.0091	0.0090	56.43	56.35	56.39
9	2.8525	2.8675	0.0098	0.0095	56.40	56.17	56.28
18	2.1000	2.1025	0.0106	0.0108	6.95	67.92	67.94
24	2.0950	2.1050	0.0113	0.0115	68.04	67.89	67.97
48	1.5775	1.4100	0.0116	0.0115	75.98	78.55	77.27

Table G.2 Effect of adsorption time of C.I. Acid Red 360 on chitin

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
0.5	2.8020	2.8120	0.0023	0.0022	57.06	56.90	56.98
3	0.6543	0.6579	0.0024	0.0025	90.00	89.95	89.97
6	0.5666	0.5686	0.0025	0.0024	91.35	91.32	91.33
9	0.5816	0.5912	0.0029	0.0030	91.12	90.98	91.05
18	0.5676	0.5585	0.0032	0.0031	91.34	91.48	91.41
24	0.5621	0.5643	0.0036	0.0033	91.43	91.40	91.41
48	0.6071	0.6099	0.0036	0.0035	90.74	90.70	90.72

Table G.3 Effect of adsorption time of C.I. Acid Red 360 on chitosan

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
0.5	2.1330	2.1400	0.0020	0.0022	67.32	67.21	67.26
3	0.1121	0.1127	0.0023	0.0025	98.32	98.31	98.31
6	0.1082	0.1084	0.0026	0.0024	98.38	98.37	98.38
9	0.1069	0.1072	0.0029	0.0027	98.40	98.40	98.40
18	0.0933	0.0933	0.0030	0.0031	98.62	98.62	98.62
24	0.0939	0.0945	0.0034	0.0033	98.61	98.60	98.61
48	0.0924	0.0928	0.0036	0.0035	98.64	98.63	98.63

Table G.4 Effect of adsorption time of C.I. Reactive Red 158 on shrimp shells

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	3.0900	3.1000	0.0099	0.0102	3.76	3.45	3.61
3	2.9740	2.9900	0.0105	0.0110	7.40	6.92	7.16
6	2.8890	2.9040	0.0109	0.0112	10.07	9.61	9.84
9	2.8300	2.8470	0.0115	0.0116	11.93	11.40	11.67
18	2.6810	2.6940	0.0118	0.0117	16.60	16.19	16.39
24	2.6190	2.6340	0.0123	0.0125	18.55	18.09	18.32
48	2.2730	2.2800	0.0125	0.0129	29.37	29.16	29.27

Table G.5 Effect of adsorption time of C.I. Reactive Red 158 on chitin

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	1.8680	1.8820	0.0023	0.0025	41.71	41.28	41.49
3	1.5480	1.5580	0.0028	0.0030	51.72	51.42	51.57
6	1.3930	1.4040	0.0033	0.0032	56.58	56.24	56.41
9	1.4030	1.4110	0.0034	0.0033	56.27	56.02	56.15
18	1.3430	1.3510	0.0036	0.0035	58.15	57.90	58.03
24	1.3210	1.3280	0.0038	0.0040	58.85	58.64	58.74
48	1.2870	1.2950	0.0042	0.0041	59.92	59.67	59.80

Table G.6 Effect of adsorption time of C.I. Reactive Red 158 on chitosan

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	1.1790	1.1850	0.0022	0.0021	63.24	63.04	63.14
3	0.5534	0.5581	0.0026	0.0029	82.80	82.66	82.73
6	0.3171	0.3198	0.0030	0.0031	90.19	90.11	90.15
9	0.2581	0.2600	0.0032	0.0031	92.04	91.98	92.01
18	0.1233	0.1239	0.0032	0.0033	96.26	96.24	96.25
24	0.0696	0.0692	0.0032	0.0033	97.94	97.95	97.94
48	0.0196	0.0194	0.0034	0.0033	99.50	99.51	99.51

Table G.7 Effect of adsorption time of C.I. Direct Red 80 on shrimp shells

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	4.8240	4.8440	0.0080	0.0083	22.32	22.00	22.16
3	4.8110	4.8200	0.0088	0.0087	22.55	22.40	22.47
6	4.7610	4.7800	0.0092	0.0094	23.36	23.05	23.21
9	4.7430	4.7580	0.0098	0.0100	23.66	23.42	23.54
18	4.6480	4.6560	0.0116	0.0114	25.22	25.09	25.15
24	4.5950	4.5980	0.0127	0.0126	26.09	26.04	26.07
48	3.9100	3.9380	0.0127	0.0129	37.14	36.69	36.92

Table G.8 Effect of adsorption time of C.I. Direct Red 80 on chitin

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	4.6200	4.6460	0.0025	0.0023	25.52	25.10	25.31
3	4.5070	4.5480	0.0024	0.0023	27.35	26.68	27.01
6	4.3920	4.4080	0.0026	0.0027	29.20	28.95	29.08
9	4.3040	4.3110	0.0027	0.0028	30.62	30.51	30.57
18	4.1360	4.1580	0.0033	0.0036	33.34	32.99	33.17
24	4.0360	4.0540	0.0039	0.0041	34.97	34.68	34.82
48	3.6860	3.7000	0.0040	0.0043	40.61	40.39	40.50

Table G.9 Effect of adsorption time of C.I. Direct Red 80 on chitosan

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
1	4.5950	4.7040	0.0021	0.0020	25.92	24.16	25.04
3	4.5200	4.5230	0.0025	0.0023	27.14	27.09	27.11
6	4.3790	4.3850	0.0026	0.0024	29.41	29.31	29.36
9	4.3530	4.3720	0.0027	0.0026	29.83	29.53	29.68
18	4.2310	4.2330	0.0030	0.0033	31.81	31.78	31.79
24	4.1980	4.2100	0.0034	0.0033	32.35	32.15	32.25
48	4.0130	4.0210	0.0035	0.0033	35.33	35.20	35.26

Table G.10 Effect of adsorption time of C.I. Basic Red 24 on shrimp shells

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
3	2.9640	2.9940	0.0188	0.0185	67.06	66.72	66.89
6	2.6920	2.7210	0.0190	0.0190	70.11	69.79	69.95
9	2.6680	2.6900	0.0198	0.0196	70.39	70.14	70.27
18	2.3940	2.4160	0.0201	0.0200	73.47	73.22	73.34
24	2.3430	2.3620	0.0205	0.0208	74.04	73.83	73.94
48	2.2560	2.2700	0.0208	0.0210	75.02	74.87	74.94

Table G.11 Effect of adsorption time of C.I. Basic Red 24 on chitin

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
3	7.6400	7.6700	0.0056	0.0060	14.49	14.16	14.33
6	7.6150	7.6850	0.0063	0.0066	14.78	14.00	14.39
9	7.5200	7.5750	0.0072	0.0075	15.86	15.24	15.55
18	7.4350	7.4800	0.0082	0.0081	16.82	16.31	16.57
24	7.4450	7.4900	0.0089	0.0090	16.72	16.21	16.46
48	6.2550	6.3200	0.0092	0.0090	30.06	29.33	29.69

Table G.12 Effect of adsorption time of C.I. Basic Red 24 on chitosan

Time	Aa		Abl		Qa (mg/g)		
(h)	1	2	1	2	1	2	Average
3	7.5150	7.6950	0.0026	0.0025	15.86	14.96	15.41
6	7.4950	7.5600	0.0028	0.0030	16.09	15.36	15.72
9	7.4900	7.5600	0.0035	0.0033	16.15	15.36	15.76
18	7.3400	7.4050	0.0040	0.0042	17.84	17.11	17.47
24	7.2300	7.2650	0.0054	0.0055	19.09	18.70	18.89
48	7.0000	7.0650	0.0056	0.0054	21.67	20.94	21.30

APPENDIX H

Effect of Particle Size on Dyes Adsorption

The amounts of dye adsorbed on adsorbents were calculated from the following equation :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000}$$

Where Qa : Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

C : Initial concentration of dye (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

V : Volume of dye solution (25.0 mL)

W : Weight of adsorbent (0.0500g)

Test conditions

Adsorption temperature : 25 °C

C.I. Acid Red 360	C = 200.00	S = 0.0326	pH 4	time 1 h
C.I. Reactive Red 158	C = 200.02	S = 0.0160	pH 4	time 5 h
C.I. Direct Red 80	C = 200.00	S = 0.0310	pH 4	time 24 h
C.I. Basic Red 24	C = 200.16	S = 0.0446	pH 10	time 24 h

An example of calculation

Amount of C.I. Acid Red 360 adsorbed on chitosan with 0.212-0.425 mm size,

$$Qa = \frac{[(200.00) - (0.0952\text{-}0.0030) / (0.0326)]\,(25.0)}{(0.0500)\,(1000)}$$

$$= 98.59 \quad \text{mg/g}$$

Table H.1 Effect of particle size of shrimp shells on the adsorption of C.I. Acid Red 360

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	3.0875	3.1775	0.0115	0.0114	52.82	51.44	52.13
0.425-0.710	3.8550	3.9625	0.0113	0.0115	41.05	39.40	40.22
0.710-1.000	4.1775	4.3000	0.0112	0.0114	36.10	34.22	35.16

Table H.2 Effect of particle size of chitin on the adsorption of C.I. Acid Red 360

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	0.9280	0.9520	0.0033	0.0032	85.82	85.45	85.63
0.425-0.710	1.2970	1.3250	0.0033	0.0036	80.16	79.73	79.95
0.710-1.000	1.7530	1.8070	0.0033	0.0033	73.16	72.34	72.75

Table H.3 Effect of particle size of chitosan on the adsorption of C.I. Acid Red 360

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	0.0952	0.0963	0.0030	0.0031	98.59	98.57	98.58
0.425-0.710	0.3109	0.3226	0.0034	0.0033	95.28	95.10	95.19
0.710-1.000	1.5820	1.6300	0.0032	0.0033	75.79	75.05	75.42

Table H.4 Effect of particle size of shrimp shells on the adsorption of C.I. Reactive Red 158

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	2.8520	2.8650	0.0125	0.0124	11.28	10.87	11.07
0.425-0.710	2.9810	2.9900	0.0123	0.0125	7.24	6.96	7.10
0.710-1.000	3.0740	3.0860	0.0122	0.0124	4.33	3.96	4.14

Table H.5 Effect of particle size of chitin on the adsorption of C.I. Reactive Red 158

Particle size	Aa		Abl		Qa (mg/g)		
(mm)	1	2	1	2	1	2	Average
0.212-0.425	1.4960	1.5060	0.0040	0.0039	53.39	53.07	53.23
0.425-0.710	1.5100	1.5150	0.0038	0.0040	52.94	52.79	52.87
0.710-1.000	1.6570	1.6480	0.0038	0.0036	48.35	48.62	48.49

Table H.6 Effect of particle size of chitosan on the adsorption of C.I. Reactive Red 158

Particle size	Aa		Abl		Qa (mg/g)		
(mm)	1	2	1	2	1	2	Average
0.212-0.425	0.3075	0.3093	0.0033	0.0035	90.50	90.45	90.48
0.425-0.710	0.4040	0.4057	0.0032	0.0033	87.49	87.44	87.46
0.710-1.000	0.9380	0.9370	0.0030	0.0031	70.79	70.83	70.81

Table H.7 Effect of particle size of shrimp shells on the adsorption of C.I. Direct Red 80

Particle size	Aa		Abl		Qa (mg/g)		
(mm)	1	2	1	2	1	2	Average
0.212-0.425	5.2780	5.2860	0.0128	0.0127	15.21	15.08	15.14
0.425-0.710	5.4110	5.4150	0.0126	0.0127	13.06	13.00	13.03
0.710-1.000	5.5710	5.5660	0.0125	0.0124	10.48	10.56	10.52

Table H.8 Effect of particle size of chitin on the adsorption of C.I. Direct Red 80

Particle size	Aa		Abl		Qa (mg/g)		
(mm)	1	2	1	2	1	2	Average
0.212-0.425	4.5870	4.5950	0.0040	0.0042	26.21	26.08	26.15
0.425-0.710	4.8210	4.8250	0.0039	0.0041	22.43	22.37	22.40
0.710-1.000	5.0440	5.0480	0.0040	0.0040	18.84	18.78	18.81

Table H.9 Effect of particle size of chitosan on the adsorption of C.I. Direct Red 80

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	4.8340	4.8450	0.0035	0.0034	22.22	22.04	22.13
0.425-0.710	5.0330	5.0430	0.0034	0.0035	19.01	18.85	18.93
0.710-1.000	5.3310	5.3470	0.0033	0.0034	14.20	13.94	14.07

Table H.10 Effect of particle size of shrimp shells on the adsorption of C.I. Basic Red 24

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	2.3200	2.3300	0.0206	0.0205	74.30	74.19	74.25
0.425-0.710	2.4620	2.4670	0.0205	0.0208	72.71	72.66	72.68
0.710-1.000	3.1140	3.1210	0.0204	0.0205	65.40	65.32	65.36

Table H.11 Effect of particle size of chitin on the adsorption of C.I. Basic Red 24

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	8.3175	8.3450	0.0090	0.0088	6.94	6.62	6.78
0.425-0.710	8.4500	8.4600	0.0090	0.0089	5.45	5.34	5.39
0.710-1.000	8.4950	8.5200	0.0088	0.0090	4.94	4.67	4.80

Table H.12 Effect of particle size of chitosan on the adsorption of C.I. Basic Red 24

Particle size (mm)	Aa		Abl		Qa (mg/g)		
	1	2	1	2	1	2	Average
0.212-0.425	8.2050	8.2275	0.0055	0.0054	8.16	7.90	8.03
0.425-0.710	8.5450	8.5575	0.0054	0.0055	4.34	4.21	4.28
0.710-1.000	8.5900	8.6125	0.0053	0.0054	3.84	3.59	3.71

APPENDIX I

Effect of Concentration over Dyes Adsorption on Adsorbents

The amounts of dye adsorbed on adsorbents and adsorption efficiency were calculated from the following equation :

$$Qa = \frac{[C - (Aa - Abl) / S] \times V}{W \times 1000}$$

$$Ec = \frac{Qa \times W \times 10^5}{C \times V}$$

Where Qa : Amount of adsorbed dye (mg of adsorbed dye per g of adsorbent)

C : Initial concentration of dye (mg/L)

Aa : Absorbance of unadsorbed dye after adsorption

Abl : Absorbance of blank

S : Slope value from calibration curve of dye concentration and absorbance

V : Volume of dye solution (25.0 mL)

W : Weight of adsorbent (0.0500g)

Ec : Adsorption efficiency of dye on adsorbent (% w/w)

<u>Test conditions</u>

Adsorption temperature	: 25 °C	time 24 h
C.I. Acid Red 360	S = 0.0326	pH 4
C.I. Reactive Red 158	S = 0.0160	pH 4
C.I. Direct Red 80	S = 0.0310	pH 4
C.I. Basic Red 24	S = 0.0446	pH 10

An example of calculation

Adsorption amount of C.I. Acid Red 360 (200.08 mg/L) on chitosan,

$$Qa = \frac{[(200.08) - (0.0998 - 0.0034) / (0.0326)] (25.0)}{(0.0500) (1000)}$$

$$= 98.56 \quad mg/g$$

Adsorption efficiency of C.I. Acid Red 360 (200.08 mg/L) on chitosan,

$$Ec = \frac{[(98.56) (0.0500) (100000)}{(200.08) (25.0)}$$

$$= 98.52 \quad \%w/w$$

Table I.1 Adsorption of C.I. Acid Red 360 on shrimp shells and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0113	0.0115	0.00	0.00	0.00			
200.08	2.0140	2.0390	68.91	68.67	68.79	68.88	68.64	68.76
400.16	3.2640	3.2870	150.19	149.84	150.02	75.07	74.89	74.98
800.20	4.6170	4.6520	328.15	328.93	328.54	82.02	82.21	82.11
1200.32	7.8650	7.9100	479.71	479.02	479.36	79.93	79.81	79.87
1600.32	9.9150	9.9950	646.97	647.04	647.00	80.86	80.86	80.86
2000.00	11.6300	11.7000	821.80	820.73	821.26	82.18	82.07	82.13
2400.00	14.3600	14.4600	980.17	978.64	979.40	81.66	81.54	81.60
2600.04	14.3300	14.4000	1080.41	1079.34	1079.87	83.11	83.02	83.07

Table I.2 Adsorption of C.I. Acid Red 360 on chitin and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0033	0.0036	0.00	0.00	0.00			
200.08	0.5059	0.5087	91.78	91.92	91.85	91.75	91.89	91.82
400.16	2.0660	2.0800	168.11	168.23	168.17	84.02	84.08	84.05
800.20	7.7450	7.8000	280.80	280.52	280.66	70.18	70.11	70.15
1200.32	17.3800	17.4850	333.65	332.04	332.84	55.59	55.32	55.46
1600.32	31.4200	31.6400	318.31	314.94	316.62	39.78	39.36	39.57
2000.00	43.3500	43.7400	335.18	329.19	332.18	33.52	32.92	33.22
2400.00	55.2700	55.8100	352.59	343.62	348.11	29.38	28.63	29.00
2600.04	60.2200	60.8100	376.45	367.40	371.93	28.96	28.26	28.61

Table I.3 Adsorption of C.I. Acid Red 360 on chitosan and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0034	0.0033	0.00	0.00	0.00			
200.08	0.0998	0.1007	98.56	98.55	98.55	98.52	98.51	98.51
400.16	0.2991	0.3014	195.54	195.51	195.53	97.73	97.72	97.72
800.20	2.7175	2.7300	358.47	358.28	358.38	89.60	89.55	89.57
1200.32	14.2150	14.3150	382.19	380.66	381.42	63.68	63.43	63.55
1600.32	28.3400	28.4600	365.55	363.71	364.63	45.68	45.45	45.57
2000.00	38.7900	39.0800	405.11	400.66	402.89	40.51	40.07	40.29
2400.00	51.0000	51.5100	418.08	410.26	414.17	34.83	34.18	34.51
2600.04	55.0100	56.6600	456.36	431.05	443.71	35.10	33.16	34.13

Table I.4 Adsorption of C.I. Reactive Red 158 on shrimp shells and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0164	0.0163	0.00	0.00	0.00			
200.00	2.4830	2.4600	22.92	23.64	23.28	22.92	23.64	23.28
400.04	5.6050	5.5800	25.37	26.16	25.77	12.69	13.08	12.88
800.00	11.9250	11.9500	27.85	27.07	27.46	6.96	6.77	6.87
1200.08	18.3400	18.3600	27.43	26.80	27.11	4.57	4.47	4.52
1600.08	24.8900	24.8800	22.74	23.05	22.89	2.84	2.88	2.86
2000.00	31.2550	31.1150	23.79	28.17	25.98	2.38	2.82	2.60
2400.12	37.7600	37.7150	20.57	21.98	21.27	1.71	1.83	1.77
2600.28	40.9850	40.9600	19.87	20.65	20.26	1.53	1.59	1.56

Table I.5 Adsorption of C.I. Reactive Red 158 on chitin and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0076	0.0077	0.00	0.00	0.00			
200.00	0.0894	0.0771	97.45	97.83	97.64	97.45	97.83	97.64
400.04	2.8570	2.8940	110.98	109.82	110.40	55.48	54.91	55.19
800.00	9.5100	9.4250	103.05	105.71	104.38	25.76	26.43	26.09
1200.08	15.9450	15.9600	102.00	101.53	101.76	17.00	16.92	16.96
1600.08	22.5650	22.5850	95.12	94.50	94.81	11.89	11.81	11.85
2000.00	29.1600	29.1600	88.99	88.99	88.99	8.90	8.90	8.90
2400.12	35.6300	35.4350	86.86	92.96	89.91	7.24	7.75	7.49
2600.28	38.9100	38.7200	84.44	90.38	87.41	6.49	6.95	6.72

Table I.6 Adsorption of C.I. Reactive Red 158 on chitosan and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0027	0.0029	0.00	0.00	0.00			
200.00	0.0100	0.0092	99.78	99.80	99.79	99.78	99.80	99.79
400.04	0.1794	0.1590	194.50	195.14	194.82	97.24	97.56	97.40
800.00	3.0650	3.1260	304.31	302.40	303.35	76.08	75.60	75.84
1200.08	7.9550	7.5750	351.53	363.41	357.47	58.59	60.56	59.57
1600.08	13.3550	12.8800	382.78	397.63	390.21	47.85	49.70	48.77
2000.00	18.5050	18.7350	421.81	414.62	418.21	42.18	41.46	41.82
2400.12	24.4050	25.0500	437.49	417.34	427.41	36.46	34.78	35.62
2600.28	27.7600	27.5950	432.73	437.88	435.31	33.28	33.68	33.48

Table I.7 Adsorption of C.I. Reactive Red 158 on shrimp shells and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0123	0.0125	0.00	0.00	0.00			
200.00	2.6350	2.6410	18.04	17.86	17.95	18.04	17.86	17.95
400.00	5.7650	5.7950	20.23	19.29	19.76	10.12	9.65	9.88
800.00	12.1150	12.1100	21.79	21.95	21.87	5.45	5.49	5.47
1200.00	18.4500	18.4300	23.83	24.45	24.14	3.97	4.08	4.02
1600.00	24.9750	24.9950	19.92	19.29	19.61	2.49	2.41	2.45
2000.00	31.4600	31.5000	17.26	16.01	19.64	1.73	1.60	1.66
2401.44	38.2300	38.2550	6.42	5.64	6.03	0.53	0.47	0.50
2600.96	41.5000	41.5550	3.99	2.27	3.13	0.31	0.17	0.24

Table I.8 Adsorption of C.I. Reactive Red 158 on chitin and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0038	0.0040	0.00	0.00	0.00			
200.00	104920	1.4930	53.50	53.47	53.48	53.50	53.47	53.48
400.00	4.3810	4.3840	63.22	63.12	63.17	31.61	31.56	31.58
800.00	10.6850	10.6700	66.22	66.68	66.45	16.55	16.67	16.61
1200.00	16.8350	16.8600	74.03	73.25	73.64	12.34	12.21	12.27
1600.00	23.1950	23.2150	75.28	74.65	74.97	9.41	9.33	9.37
2000.00	29.5450	29.5500	76.84	76.68	76.76	7.68	7.67	7.68
2401.44	36.1200	36.1350	72.09	71.62	71.86	6.00	5.97	5.98
2600.96	39.3650	39.2950	70.45	72.63	71.54	5.42	5.59	5.50

Table I.9 Adsorption of C.I. Reactive Red 158 on chitosan and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0032	0.0033	0.00	0.00	0.00			
200.00	0.1782	0.1785	94.53	94.52	94.53	94.53	94.52	94.53
400.00	2.4340	2.4260	124.04	124.29	124.16	62.02	62.14	62.08
800.00	7.6550	7.6450	160.88	161.20	161.04	40.22	40.30	40.26
1200.00	12.4850	12.4550	209.95	210.88	210.41	34.99	35.15	35.07
1600.00	18.3800	18.4000	225.73	225.10	225.41	28.22	28.14	28.18
2000.00	24.0150	24.0200	249.63	249.48	249.55	24.96	24.95	24.96
2401.44	29.2650	29.2800	286.29	285.82	286.06	23.84	23.80	23.82
2600.96	31.8550	31.8400	305.11	305.58	305.35	23.46	23.50	23.48

Table I.10 Adsorption of C.I. Direct Red 80 on shrimp shells and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0154	0.0154	0.00	0.00	0.00			
200.12	5.1980	5.2120	16.47	16.24	16.36	16.46	16.23	16.35
400.08	11.7250	11.7400	11.18	10.93	11.05	5.59	5.47	5.53
800.28	24.0700	24.1800	12.20	10.43	11.32	3.05	2.61	2.83
1200.16	36.4800	36.3900	11.94	13.39	12.67	1.99	2.23	2.11
1600.24	48.5900	48.6200	16.66	16.17	16.42	2.08	2.02	2.05
2000.80	60.2300	60.2200	29.20	29.36	29.28	2.92	2.93	2.93
2400.84	71.1900	71.6700	52.44	44.70	48.57	4.37	3.72	4.05
2600.80	77.6800	77.5400	47.75	50.00	48.87	3.67	3.85	3.76

Table I.11 Adsorption of C.I. Direct Red 80 on chitin and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0078	0.0078	0.00	0.00	0.00			
200.12	4.1230	4.3950	33.69	29.30	31.49	33.67	29.28	31.47
400.08	10.2700	9.9900	34.52	39.04	36.78	17.26	19.51	18.39
800.28	21.5000	21.6700	53.53	50.79	52.16	13.38	12.69	13.03
1200.16	33.7400	33.6400	56.01	57.63	56.82	9.33	9.60	9.47
1600.24	46.2300	46.4100	54.60	51.70	53.15	6.82	6.46	6.64
2000.80	58.2400	58.2700	61.17	60.69	60.93	6.11	6.07	6.09
2400.84	71.0400	70.5800	54.74	62.16	58.45	4.56	5.18	4.87
2600.80	76.8000	76.1200	61.82	72.78	67.30	4.75	5.60	5.18

Table I.12 Adsorption of C.I. Direct Red 80 on chitosan and adsorption efficiency at pH 3 and 25 °C as a function of dye concentrations

C (mg/L)	Aa		Qa (mg/g)			Ec (% w/w)		
	1	2	1	2	Average	1	2	Average
0.00	0.0037	0.0038	0.00	0.00	0.00			
200.12	3.0930	.00340	50.23	51.19	50.71	50.20	51.15	50.68
400.08	8.2500	8.1700	67.04	68.33	67.68	33.51	34.16	33.83
800.28	20.3800	21.0800	71.53	60.24	65.89	17.87	15.05	16.46
1200.16	33.6600	33.3700	57.24	61.91	59.58	9.54	10.32	9.93
1600.24	47.1400	47.0200	39.86	41.79	40.83	4.98	5.22	5.10
2000.80	59.4700	59.5000	41.27	40.78	41.03	4.13	4.08	4.10
2400.84	73.5900	73.4100	13.54	16.45	15.00	1.13	1.37	1.25
2600.80	79.6500	79.8600	15.78	12.40	14.09	1.21	0.95	1.08

Table I.13 Adsorption of C.I. Direct Red 80 on shrimp shells and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C (mg/L)	Aa		Qa (mg/g)			Ec (% w/w)		
	1	2	1	2	Average	1	2	Average
0.00	0.013	0.013	0.00	0.00	0.00			
200.28	5.8225	5.8500	6.43	5.99	6.21	6.42	5.98	6.20
400.00	11.7700	11.7750	10.37	10.28	10.33	5.18	5.14	5.16
800.44	24.6800	24.7300	2.36	1.55	1.96	0.59	0.39	0.49
1200.52	37.1100	37.1500	1.92	1.27	1.59	0.32	0.21	0.27
1600.40	49.5600	49.5900	1.05	0.57	0.81	0.13	0.07	0.10
2000.60	61.9300	62.0000	1.63	0.50	1.07	0.16	0.05	0.11
2400.64	74.4100	74.3900	0.36	0.69	0.52	0.03	0.06	0.04
2601.52	80.6100	80.6300	0.80	0.48	0.64	0.06	0.04	0.05

Table I.14 Adsorption of C.I. Direct Red 80 on chitin and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0039	0.0041	0.00	0.00	0.00			
200.28	5.0175	5.0150	19.28	19.32	19.30	19.25	19.29	19.27
400.00	10.4225	10.4425	31.96	31.64	31.80	15.98	15.82	15.90
800.44	22.0600	22.1200	44.48	43.51	43.99	11.11	10.87	10.99
1200.52	33.5000	33.4900	60.00	60.16	60.08	10.00	10.02	10.01
1600.40	44.9200	44.9500	75.75	75.26	75.51	9.47	9.41	9.44
2000.60	56.7600	56.7500	84.88	85.04	84.96	8.49	8.50	8.49
2400.64	71.1200	71.1200	53.29	53.29	53.29	4.44	4.44	4.44
2601.52	77.1800	77.2800	55.99	54.37	55.18	4.30	4.18	4.24

Table I.15 Adsorption of C.I. Direct Red 80 on chitosan and adsorption efficiency at pH 4 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0034	0.0038	0.00	0.00	0.00			
200.28	5.1750	5.1575	16.73	17.01	16.87	16.71	16.99	16.85
400.00	11.2250	11.2525	19.01	18.57	18.79	9.50	9.28	9.39
800.44	24.0100	23.9600	13.02	13.83	13.42	3.25	3.45	3.35
1200.52	36.4600	36.4800	12.25	11.93	12.09	2.04	1.99	2.01
1600.40	49.0200	49.0300	9.61	9.45	9.53	1.20	1.18	1.19
2000.60	61.4000	61.4400	10.04	9.39	9.71	1.00	0.94	0.97
2400.64	74.2200	74.2900	3.28	2.15	2.72	0.27	0.18	0.23
2601.52	80.6100	80.5900	0.66	0.98	0.82	0.05	0.08	0.06

Table I.16 Adsorption of C.I. Basic Red 24 on shrimp shells and adsorption efficiency at pH 10 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0227	0.0242	0.00	0.00	0.00			
200.00	1.6680	1.6840	81.56	81.38	81.47	81.56	81.38	81.47
400.08	7.1650	7.2425	119.98	119.11	119.54	59.98	59.54	59.76
600.36	14.8000	14.9350	134.52	133.01	133.77	44.81	44.31	44.56
800.16	19.5600	19.7900	181.06	178.48	179.77	45.26	44.61	44.93
1000.08	27.0350	27.3800	197.22	193.35	195.29	39.44	38.67	39.05

Table I.17 Adsorption of C.I. Basic Red 24 on chitin and adsorption efficiency at pH 10 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0072	0.0074	0.00	0.00	0.00			
200.00	7.9200	7.9900	11.29	10.51	10.90	11.29	10.51	10.90
400.08	15.7900	15.9900	23.10	20.86	21.98	11.55	10.43	10.99
600.36	24.4300	24.6900	26.38	23.47	24.93	8.79	7.82	8.30
800.16	31.6000	31.9200	45.90	42.31	44.11	11.47	10.58	11.02
1000.08	39.5700	40.6500	56.51	44.40	50.46	11.30	8.88	10.09

Table I.18 Adsorption of C.I. Basic Red 24 on chitosan and adsorption efficiency at pH 10 and 25 °C as a function of dye concentrations

C	Aa		Qa (mg/g)			Ec (% w/w)		
(mg/L)	1	2	1	2	Average	1	2	Average
0.00	0.0032	0.0034	0.00	0.00	0.00			
200.00	7.4000	7.4950	17.08	16.01	16.54	17.08	16.01	16.54
400.08	15.2000	15.4050	29.67	27.38	28.52	14.83	13.68	14.26
600.36	24.2500	24.6000	28.36	24.43	26.39	9.45	8.14	8.79
800.16	32.1300	32.5400	39.92	35.32	37.62	9.98	8.83	9.40
1000.08	40.0200	40.6000	51.42	44.92	48.17	10.28	8.98	9.63

APPENDIX J

Effect of pH on Dye Desorption

The amount of dye desorbed from each adsorbent was calculated from the following equation :

$$Qd = \frac{Ad \times V \times 100}{S \times Qa \times W \times 100}$$

Where	Qd	:	Amount of desorbed dye (% w/w)
	Qa	:	Amount of adsorbed dye (mg of dye per g of dye-sorbed adsorbent)
	Ad	:	Absorbance of desorbed dye
	V	:	Volume of deionized water at pH tested (mL)
	S	:	Slope value from calibration curve of dye concentration and absorbance
	W	:	Weight of dye-sorbed adsorbent (g)

<u>Test condition</u>

Desorption temperature	:	30°C
Desorption pH	:	pH 3 to pH 12
V for each dye	:	50.0 mL
W for each dye	:	0.0500 g
S for each dye	:	obtained from Table 4.4
Qa for each dye	:	obtained from Table 4.5

<u>An example of calculation</u>

The amount of C.I. Acid Red 360 desorbed from chitosan at pH 11,

$$Qd = \frac{(0.3633)(50.0)(100)}{(0.0326)(11.83)(0.0500)(1000)}$$

$$= 94.20 \text{ mg/g}$$

Table J.1 Effect of pH on the desorption of C.I. Acid Red 360 from shrimp shells

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
4	0.0651	0.0649	16.87	16.81	16.84
6	0.0739	0.0738	19.15	19.12	19.13
9	0.0713	0.0714	18.47	18.50	18.49
10	0.0777	0.0779	20.13	20.18	20.16
11	0.1072	0.1074	27.77	27.82	27.80
12	0.0638	0.0641	16.53	16.61	16.57

Table J.2 Effect of pH on the desorption of C.I. Acid Red 360 from chitin

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
4	0.0021	0.0023	0.56	0.62	0.59
6	0.0330	0.0328	8.86	8.80	8.83
9	0.1043	0.1047	27.99	28.10	28.04
10	0.3660	0.3662	98.22	98.28	98.25
11	0.3634	0.3640	97.53	97.69	97.61
12	0.3457	0.3463	92.78	92.94	92.86

Table J.3 Effect of pH on the desorption of C.I. Acid Red 360 from chitosan

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
4	0.0022	0.0019	0.57	0.49	0.53
6	0.0076	0.0077	1.97	2.00	1.98
9	0.0276	0.0278	7.16	7.21	7.18
10	0.2961	0.2964	76.78	76.86	76.82
11	0.3633	0.3633	94.20	94.20	94.20
12	0.3356	0.3362	87.02	87.18	87.10

Table J.4 Effect of pH on the desorption of C.I. Reactive Red 158 from shrimp shells

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0090	0.0092	4.70	4.80	4.75
4	0.0090	0.0090	4.70	4.70	4.70
6	0.0096	0.0097	5.01	5.06	5.04
9	0.0102	0.0103	5.33	5.38	5.35
10	0.0103	0.0103	5.38	5.38	5.38
11	0.0201	0.0196	10.49	10.23	10.36
12	0.0157	0.0158	8.20	8.25	8.22

Table J.5 Effect of pH on the desorption of C.I. Reactive Red 158 from chitin

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0010	0.0009	0.52	0.47	0.49
4	0.0009	0.0008	0.47	0.42	0.44
6	0.0000	0.0000	0.00	0.00	0.00
9	0.0006	0.0001	0.31	0.05	0.18
10	0.0291	0.0291	15.16	15.16	15.16
11	0.0358	0.0360	18.65	18.75	18.70
12	0.0260	0.0256	13.54	13.33	13.44

Table J.6 Effect of pH on the desorption of C.I. Reactive Red 158 from chitosan

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0586	0.0585	30.52	30.47	30.49
4	0.0000	0.0000	0.00	0.00	0.00
6	0.0000	0.0000	0.00	0.00	0.00
9	0.0002	0.0004	0.10	0.21	0.16
10	0.0039	0.0040	2.03	2.08	2.06
11	0.0088	0.0085	4.58	4.43	4.51
12	0.0051	0.0048	2.66	2.50	2.58

Table J.7 Effect of pH on the desorption of C.I. Direct Red 80 from shrimp shells

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0161	0.0163	4.40	4.46	4.43
4	0.0231	0.0230	6.31	6.29	6.30
6	0.0502	0.0502	13.72	13.72	13.72
9	0.0564	0.0563	15.42	15.39	15.40
10	0.0629	0.0629	17.20	17.20	17.20
11	0.0842	0.0841	23.02	22.99	23.00
12	0.0236	0.0235	6.45	6.42	6.44

Table J.8 Effect of pH on the desorption of C.I. Direct Red 80 from chitin

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0011	0.0008	0.30	0.22	0.26
4	0.0046	0.0044	1.24	1.18	1.21
6	0.0054	0.0053	1.45	1.42	1.44
9	0.0239	0.0244	6.42	6.56	6.49
10	0.1463	0.1462	39.33	39.30	39.31
11	0.2254	0.2253	60.59	60.56	60.58
12	0.0796	0.0794	21.40	21.34	21.37

Table J.9 Effect of pH on the desorption of C.I. Direct Red 80 from chitosan

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.1272	0.1268	34.22	34.11	34.17
4	0.0007	0.0005	0.19	0.13	0.16
6	0.0000	0.0000	0.00	0.00	0.00
9	0.0000	0.0000	0.00	0.00	0.00
10	0.1639	0.1638	44.10	44.07	44.08
11	0.2599	0.2607	69.92	70.14	71.03
12	0.0884	0.0884	23.78	23.78	23.78

Table J.10 Effect of pH on the desorption of C.I. Basic Red 24 from shrimp shells

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.3405	0.3406	64.75	64.77	64.76
4	0.2689	0.2695	51.14	51.25	51.19
5	0.2666	0.2669	50.70	50.76	50.73
6	0.2418	0.2418	45.98	45.98	45.98
9	0.2383	0.2388	45.32	45.41	45.37
12	0.2138	0.2141	40.66	40.72	40.69

Table J.11 Effect of pH on the desorption of C.I. Basic Red 24 from chitin

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.1407	0.1409	87.15	87.27	87.21
4	0.1195	0.1195	74.02	74.02	74.02
5	0.0870	0.0861	53.89	53.33	53.61
6	0.0793	0.0795	49.12	49.24	49.18
9	0.0682	0.0685	42.24	42.43	42.33
12	0.0672	0.0669	41.62	41.44	41.53

Table J.12 Effect of pH on the desorption of C.I. Basic Red 24 from chitosan

pH	Ad		Qd (mg/g)		
	1	2	1	2	Average
3	0.0584	0.0580	65.80	65.35	65.57
4	0.0429	0.0430	48.34	48.45	48.39
5	0.0345	0.0349	38.87	39.32	39.10
6	0.0337	0.0345	37.97	38.87	38.42
9	0.0273	0.0275	30.76	30.98	30.87
12	0.0299	0.0276	33.69	31.10	32.39

APPENDIX K

Effect of Temperature on Dye Desorption

The amounts of dye desorbed from adsorbent at each temperature were calculated from the same equation as in APPENDIX J and are shown in Table K.1–K. 12

<u>Test condition</u>

Desorption temperature	:	30 and 80°C
V for each dye	:	50.0 mL
W for each dye	:	0.0500 g
S for each dye	:	obtained from Table 4.4
Qa for each dye	:	obtained from Table 4.5

Table K.1 Effect of temperature on the desorption of C.I. Acid Red 360 from shrimp shells at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.1072	0.1074	27.77	27.82	27.80
80	0.1582	0.1586	40.99	41.09	41.04

Table K.2 Effect of temperature on the desorption of C.I. Acid Red 360 from chitin at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.3634	0.3640	97.53	97.69	97.61
80	0.3652	0.3650	98.01	97.96	97.98

Table K.3 Effect of temperature on the desorption of C.I. Acid Red 360 from chitosan at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.3633	0.3633	94.20	94.20	94.20
80	0.3783	0.3786	98.09	98.17	98.13

Table K.4 Effect of temperature on the desorption of C.I. Reactive Red 158 from shrimp shells at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.0201	0.0196	10.49	10.23	10.36
80	0.0406	0.0404	21.20	21.09	21.15

Table K.5 Effect of temperature on the desorption of C.I. Reactive Red 158 from chitin at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.0358	0.0360	18.65	18.75	18.70
80	0.0379	0.0380	19.74	19.79	19.77

Table K.6 Effect of temperature on the desorption of C.I. Reactive Red 158 from chitosan at pH 11

Temperature (°C)	Ad		Qd (mg/g)		
	1	2	1	2	Average
30	0.0088	0.0085	4.58	4.43	4.51
80	0.0138	0.0136	7.19	7.08	7.14

Table K.7 Effect of temperature on the desorption of C.I. Direct Red 80 from shrimp shells at pH 11

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.0842	0.0841	23.02	22.99	23.00
80	0.1208	0.1212	33.02	33.13	33.08

Table K.8 Effect of temperature on the desorption of C.I. Direct Red 80 from chitin at pH 11

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.2254	0.2253	60.59	60.56	60.58
80	0.2984	0.2988	80.22	80.32	80.27

Table K.9 Effect of temperature on the desorption of C.I. Direct Red 80 from chitosan at pH 11

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.2599	0.2607	69.92	70.14	70.03
80	0.2882	0.2885	77.54	77.62	77.58

Table K.10 Effect of temperature on the desorption of C.I. Basic Red 24 from shrimp shells at pH 3

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.3405	0.3406	64.75	64.77	64.76
80	0.2880	0.2882	54.77	54.81	54.79

Table K.11 Effect of temperature on the desorption of C.I. Basic Red 24 from chitin at pH 3

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.1407	0.1409	87.15	87.27	87.21
80	0.1216	0.1217	75.32	75.38	75.35

Table K.12 Effect of temperature on the desorption of C.I. Basic Red 24 from chitosan at pH 3

Temperature	Ad		Qd (mg/g)		
(°C)	1	2	1	2	Average
30	0.0584	0.0580	65.80	65.35	65.57
80	0.0718	0.0716	80.90	80.67	80.79

APPENDIX L

Dye Removal from Textile Effluents

The amounts of dyes removed from nine samples of textile effluents were calculated at individual λ max of each sample from the following equation :

$$Qr = \frac{[Ab - (Aa - Abl)] \times 100}{Ab}$$

Where	Q1	:	Amount of dye removal (% w/w)
	Ab	:	Adsorbance of dye before adsorption
	Aa	:	Adsorbance of dye after adsorption
	Abl	:	Adsorbance of blank

<u>An example of calculation</u>

The amount of acid dye no. 1AF removed from the effluent by chitosan at pH 4,

$$Qr = \frac{[(18.4425) - (5.1575 - 0.0032)]\,(100)}{(18.4425)}$$

$$= 72.05\ \%\ w/w$$

Table L.1 Dye removal from textile effluents by shrimp shells

Type of dye	Sample no.	Ab	Aa		Abl		Qr (% w/w)		
			1	2	1	2	1	2	Average
Acid dye	1 AF	18.4425	15.9175	16.0000	0.0132	0.0131	13.76	13.32	13.54
	2 AF	0.2608	0.2556	0.2570	0.0067	0.0067	4.56	4.03	4.29
Reactive dye	1 TK	5.1660	4.0940	4.1080	0.0134	0.0136	21.01	20.74	20.88
	2 TK	4.3960	3.4930	3.5020	0.0123	0.0125	20.82	20.62	20.72
	3 TK	1.7590	1.2140	1.2185	0.0127	0.0127	31.71	31.45	31.58
	4 TK	3.5370	2.8310	2.8410	0.0120	0.0118	20.30	20.01	20.16
Direct dye	1 SN	0.0679	0.0452	0.0457	0.0127	0.0127	52.14	51.40	51.77
Basic dye	1 GT	0.0615	0.0665	0.0670	0.0317	0.0318	43.50	42.68	43.09
	2 GT	0.3781	0.3244	0.3252	0.0294	0.0294	21.98	21.77	21.87

Table L.2 Dye removal from textile effluents by chitin

Type of dye	Sample no.	Ab	Aa		Abl		Qr (% w/w)		
			1	2	1	2	1	2	Average
Acid dye	1 AF	18.4425	16.0275	16.0975	0.0043	0.0046	13.12	12.74	12.93
	2 AF	0.2608	0.2607	0.2601	0.0015	0.0024	0.79	1.02	0.90
Reactive dye	1 TK	5.1660	2.0800	2.0860	0.0038	0.0044	59.82	59.70	59.76
	2 TK	4.3960	1.8345	1.8385	0.0038	0.0040	58.36	58.27	58.31
	3 TK	1.7590	0.3180	0.3179	0.0033	0.0035	82.11	82.12	82.12
	4 TK	3.5370	1.4490	1.4320	0.0042	0.0041	59.15	59.63	59.39
Direct dye	1 SN	0.0679	0.0165	0.0166	0.0033	0.0035	80.71	80.56	80.63
Basic dye	1 GT	0.0615	0.0575	0.0580	0.0127	0.0129	27.32	26.50	26.91
	2 GT	0.3781	0.3524	0.3521	0.0107	0.0110	9.67	9.75	9.71

Table L.3 Dye removal from textile effluents by chitosan

Type of dye	Sample no.	Ab	Aa		Abl		Qr (% w/w)		
			1	2	1	2	1	2	Average
Acid dye	1 AF	18.4425	5.1575	5.1975	0.0032	0.0036	72.05	71.84	71.94
	2 AF	0.2608	0.2594	0.2604	0.0014	0.0014	1.84	1.46	1.65
Reactive dye	1 TK	5.1660	2.0065	2.0140	0.0035	0.0038	61.23	64.08	61.16
	2 TK	4.3960	1.7255	1.7310	0.0032	0.0033	60.82	60.70	60.76
	3 TK	1.7590	0.5083	0.5098	0.0032	0.0033	71.29	71.20	71.25
	4 TK	3.5370	2.0790	2.0830	0.0040	0.0040	41.33	41.22	41.28
Direct dye	1 SN	0.0679	0.0071	0.0075	0.0032	0.0033	94.33	93.73	94.04
Basic dye	1 GT	0.0615	0.0569	0.0583	0.0078	0.0080	20.33	18.05	19.19
	2 GT	0.3781	0.3525	0.3527	0.0067	0.0066	8.53	8.48	8.50

CURRICULUM VITAE

Mrs. Jintana Chamnanmanoontham was born on June 13, 1957 in Bangkok. She received her Diploma in Analytical Chemistry, Chulalongkorn University in 1979, and her Bachelor's degree of Science in General Science, Faculty of Science, Chulalongkorn University in 1981. She continued in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 1997, and completed the program in 1999. At present she works at Petroleum and Petrochemical College, Chulalongkorn University.