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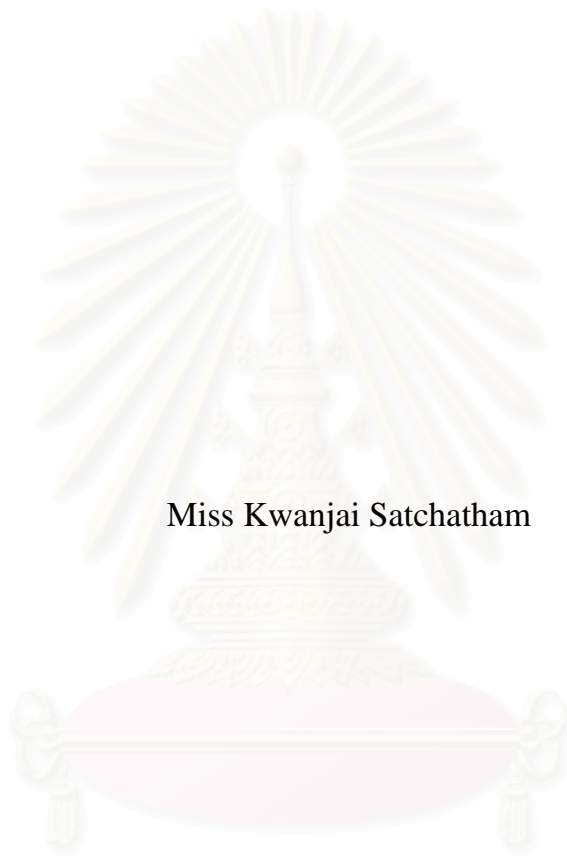
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

DECOLORIZATION OF DYEING WASTEWATER BY CHITOSAN  
FROM DRIED SHRIMP SHELL



Miss Kwanjai Satchatham

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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**By** Miss Kwanjai SATCHATHAM  
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**Thesis Advisor** Sangobtip PONGSTABODEE, Ph.D.  
**Thesis Co-advisor** Prof. Pattarapan PRASASSARAKICH, Ph.D.

---

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

..... Dean of the Graduate School  
(Prof. Suchada Kiranandana, Ph.D.)

**THESIS COMMITTEE**

.....Chairman  
(Asst. Prof. Sutha Khaodhiar, Ph.D.)

.....Thesis Advisor  
(Sangobtip Pongstabodee, Ph.D.)

.....Thesis Co-advisor  
(Prof. Pattarapan Prasassarakich, Ph.D.)

..... Member  
(Prof. Somsak Danronglerd, Ph.D.)

..... Member  
(Assoc. Prof. Tharapong Vitidsant. , Ph.D.)

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งานวิจัยนี้เป็นการศึกษาความสามารถของไคโตซานที่เตรียมจากเปลือกกุ้งแห้งในการกำจัดสีย้อมแอสซิดและสีย้อมรีแอคทีฟโดยกระบวนการดูดซับ การดำเนินการทดลองแบ่งเป็น 2 ส่วนคือ แบบชุดและแบบต่อเนื่อง ความสามารถในการดูดซับสีย้อมรีแอคทีฟ (RR120) และสีย้อมแอสซิด (AB 129) ของไคโตซานในรูปแบบแบบเกล็ด เม็ด และ เม็ดที่ผ่านกระบวนการเชื่อมขวางทางโครงสร้าง ได้ถูกเปรียบเทียบในการศึกษาครั้งนี้ ซึ่งจากการทดลองพบว่าที่ค่าความเป็นกรด-ด่างเท่ากับ 7 และความเข้มข้นของน้ำสีเท่ากับ 30 มิลลิกรัมต่อลิตร ไคโตซานในรูปแบบเม็ดที่ผ่านกระบวนการเชื่อมขวางทางโครงสร้างมีประสิทธิภาพในการกำจัดสีได้สูงที่สุดตามมาด้วยไคโตซานในรูปแบบแบบเม็ดและเกล็ดตามลำดับ จากการศึกษาทางสมดุลในการดูดซับพบว่าผลการทดลองสามารถอธิบายได้ด้วยสมการ Langmuir และประสิทธิภาพในการกำจัดสีย้อมของไคโตซานจะเพิ่มขึ้นเมื่อค่าความเป็นกรด-ด่างของสารละลายลดลงหรือเมื่อความเข้มข้นของสีมากขึ้น สำหรับการศึกษากำจัดสีย้อมของไคโตซานในการทดลองแบบต่อเนื่องพบว่าประสิทธิภาพสูง และความสามารถในการดูดซับสีย้อมของไคโตซานนั้นขึ้นอยู่กับความสูงของคอลัมน์และอัตราการไหลของน้ำเสียในระบบ

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สาขาวิชาการจัดการสิ่งแวดล้อม

ปีการศึกษา 2546

ลายมือชื่อนิสิต.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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The possibility for removal of dyestuffs contaminant from an effluent by dried-shrimp shell chitosan adsorbent was investigated in batch and continuous modes. The chitosan was prepared in three forms such a flake, bead and crosslinked bead. Reactive dye RR 120 and acid dye AB 129 were chosen. Comparing ability of decolorization of chitosan in each form when concentration was 30 mg/l at pH 7, the results showed that the percentage of dyestuffs removal obtained from crosslinked chitosan bead was higher than that of non-crosslinked bead and flake forms, respectively. The experimental results also showed that the initial dye concentration and the pH of dyeing wastewater played an important role for decolorization. The removal of dye increased when decrease in pH or increase in initial dye concentration. All equilibrium isotherms could be well fitted by Langmuir equation. In the column studies, the results showed that the decolorization was strongly deepened on flow rate and bed height of packed column.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

Field of Study Environmental Management

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Student.....

Advisor .....

Co-advisor.....

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# CHAPTER I

## Introduction

### 1.1 Introduction and Motivation

In modern industrial society, dyes are used in everywhere to get an attractive product, in particular the dyestuff manufacturing and consuming in textile industry. Therefore, the large amount of wastewater contaminated a proportion of dyes are generated and discharged to the surrounding. The dyes impart color to a natural waterway and then an aesthetic value is reduced.

Textile industry is one of the most important industries in Thailand. It contributes large proportion of earnings to the country. According to the report of Ministry of Industry, there are 4,654 factories in Thailand (Udomkichecha, 2001). Although it provides such economic value to Thailand, but in term of environmental aspect it causes some major problems, especially from dyeing wastewater. The total dye consumption of the textile industry worldwide is in excess of  $10^7$  kg/year and an estimated 9% of this is discharged into waste stream by the textile industry (Pereira et al., 2003; Wong et al., 2003).

In dyeing wastewater, a large variety of dyes can be found. The presence of dyes in effluent even though in very low concentration is undesirable. These dyes can reduce light penetration through the water and then lead to less potentially inhibiting photosynthesis. Due to their complex structure and synthetic origin, dyes are resistant to fading on exposure to light, water and chemical. Many of them are biological non-degradable (Albanis et al., 2000; Kadirvelu et al., 2000; Robinson et al., 2001; Bhattacharyya and Sarma, 2003). Previous studies

have shown that many of dyes are toxic and have carcinogenic, mutagenic and detrimental effect to aquatic life and human (Ghoreishi and Haghghi, 2003). Therefore, it is necessary for dye-containing effluents to be treated before being discharged into natural waterways. To remove dyes from the wastewater in an economic fashion remains a major problem for the textile industry, in the past municipal sewage systems are used for purification of textile dye effluents but it is found to be ineffective (Figueiredo et al., 2000; Robinson et al., 2002).

While many physical and chemical methods including adsorption, coagulation, precipitation, filtration and oxidation have been used for the treatment of dye-containing effluent, adsorption appears to offer the best prospects overall other treatments (Annadurai et al., 2002). The advantages of adsorption over other conventional treatment are less land area requirement, lower sensitivity to diurnal variation, none effect from toxic chemical, and greater flexibility in design and operation (McKay et al., 1999). The most widely used adsorbent for industrial application is activated carbon, but their use is usually limited due to high cost. Moreover, there are many problems involving with the regeneration of used activated carbon (Wu et al., 2000; Ho and Chiang, 2001).

Chitosan, a natural biopolymer of N-deacetylated derivative of chitin, shells of crustacean such as crab and shrimp are the main sources of chitin because this latter can be found in big quantities. Chitosan has been reported for the high potentials of the adsorption of dyes. Other useful features of chitosan include non-toxicity, hydrophilicity, biocompatibility, biodegradability, and anti-bacteria property. In addition, chitosan appears to be economically attractive because chitin is the second-most abundant polymer in nature next to cellulose (Wu et al., 2001; Chiou and Li, 2003). In this research, chitosan will be used as an adsorbent to decolorize dyestuffs from wastewater. Furthermore, after adsorption process, adsorbed dyes can be desorbed and reuse in dyeing process (Maetakanon et al., 2002).

In Asian countries such as Thailand, Japan and China, fishery wastes such as shrimp, lobster and crab shells have been developed into one of the promising options to produce chitosan. These wastes could be obtained from local fishery industries. Since such wastes are abundantly available, chitosan may be produced at low cost. Additionally, chitosan offers a lot of benefits for wastewater treatment application today (Babel and Kurniawan, 2003).

For Thailand, not only the fishery waste from seafood industry has a big quantity, but also the waste from dried-shrimp industry. This waste is used only for animal feed and fertilizer, but the chitin can be isolated. The chitin, which is the main component of the waste, could generate the value-added products such as and chitosan. As mentioned above, this leads the study on the decolorization of dyeing wastewater by chitosan from dried-shrimp shell.

## **1.2 Objective**

The main objective of this study is to decolorize dyeing wastewater by using chitosan prepared from dried shrimp shell. The specific objectives are as follows:

1. To determine an optimal condition for dyeing removal by chitosan.
2. To evaluate a capacity of chitosan to remove dye from wastewater.
3. To investigate an equilibrium time of dye removal by using chitosan.

### 1.3 Scope of the Investigation

The research was conducted to decolorize the synthetic dyeing wastewater and determine the efficiency of the adsorbents. The following points of the research were studied.

1. Chitosan flake, non- cross-linked chitosan bead, and cross-linked chitosan bead was used as an adsorbent and compare the efficiency of these three adsorbents.
2. Reactive and acid dyestuffs were used in this study.
3. Studied on the decolorization of dyeing wastewater in static-batch mode and in a continuous packed-bed reactor.
4. Synthetic dyeing wastewater's concentration was done at 30 and 100 mg/l and pH was varied from 3-9.
5. Glutaraldehyde was used as a cross-linking agent.



## CHAPTER II

### Background and Literature Review

#### 2.1 Wastewater from Textile Industry

Textile manufacturing is one of the largest industries produced wastewater. The problems associated with the discharge of color from textile industry have concerned both industrial and academic scientists for at least four decades, not only in Thailand but also in most industrialized countries.

Wastewaters from dyeing processes are extremely variable in composition, due to the large number of dyes and other chemicals used in dyeing processes. These may originate from the dyes themselves or derive from auxiliary chemicals such as salt, surfactant, levelers, lubricants, and alkalinity (Reife and Freeman, 1996).

The main source of dyeing wastewater is from after-washing operations, since the unfixed dye is washed out and causes colored wastewater. Each fiber type has affinity for specific classes through ionic bonding, hydrogen bonding, and van der Waal forces or by simple solubility effects. Specific dyeing condition and auxiliary chemicals are required for the application of the various classes of dyes to particular substrates as shown in **Table 2.1**.

In a review of the data available on fish toxicity, it is found that 98% of dyes have an  $LC_{50}$  value greater than 1 mg/l, and that 59% have an  $LC_{50}$  value greater than 100 mg/l (Easton, 1995). The data are shown in **Table 2.2**.

**Table 2.1:** Dye Classes and Fibers (Smith, 2003)

Dye Class	Fibers Applied to	Chemicals Used	Mechanism	Pollution Concern
Acid	Wool (hair) Nylon Silk	Acetic acid	Affinity by ionic bonds	Color pH
Azoic (Naphthol)	Cellulose	Diazotization	Coupling within the fiber	Color pH
Basic	Acrylic Cationic polyester	Acetic acid	Affinity by ionic bonds	Aquatic toxicity pH
Direct	Cellulose	Salt, alkali	Affinity by weak interaction	Color Salt
Disperse	Polyester Acetate, triacetate Other synthesis	Dispersant	Simple solubility	Color Organics Antimony
Fiber reactive	Cellulose Wool (hair)	Salt, alkali	Reaction with fiber	Salt pH
Mordant	Natural fiber	Heavy metals	Binding to sorbed metal	Metals
Pigment	All	Latex	Binding to surface film	Suspended solids Color
Solvent	Synthetic	Organic solvents	Simple solubility	Organics
Sulfur	Cellulose	Redox reagents	Insolubilizing by oxidation	Sulfide Redox chemicals Color
Vat	Cellulose	Redox reagents	Insolubilizing by oxidation	Redox chemicals Color

**Table 2.2:** Fish Toxicity Level of Dyes (Easton, 1995)

LC <sub>50</sub> <sup>a</sup> value (mg/l)	Proportion of dyes (%)
<1	2
1-10	10
10-100	27
100-500	31
>500	38

<sup>a</sup>LC<sub>50</sub>: Lethal Concentration 50%, a statically derived concentration at which 50% of the individuals will be expected to die.

As a result, many governments have established environmental restrictions with regard to the quality of colored effluents and have forced the dye houses to decolorize their effluents before discharging. In Thailand, there is no regulation about dye containing effluents. The standard for the textile or dye manufacturing is still unclear, unlike other parameters (**Table 2.3**).

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**Table 2.3:** Standard Value of Wastewater from Textile Manufacturing

Parameter	Standard values
1. pH value	5.5-9.0
2. TDS	Not more than 3,000 mg/l
3. Suspended Solids	Not more than 50 mg/l
4. Temperature	Not more than 40 °C
5. Color or Odor	Unobjectionable
6. Sulfide as H <sub>2</sub> S	Not more than 1.0 mg/l
7. Cyanide as HCN	Not more than 0.2 mg/l
8. Formaldehyde	Not more than 1.0 mg/l
9. Phenol	Not more than 1.0 mg/l
10. Fat, oil and Grease	Not more than 5.0 mg/l
11. Free Chlorine	Not more than 1.0 mg/l
12. Pesticide	None
13. Biochemical Oxygen Demand (BOD)	Not more than 60 mg/l
14. Total Kjeldahl Nitrogen (TKN)	Not more than 100 mg/l
15. Chemical Oxygen Demand (COD)	Not more than 600 mg/l
16. Heavy Metal	
1. Zn	Not more than 5.0 mg/l
2. Hexavalent Chromium	Not more than 0.25 mg/l
3. Trivalent Chromium	Not more than 0.75 mg/l
4. Cu	Not more than 2.0 mg/l
5. Cd	Not more than 0.03 mg/l
6. Ba	Not more than 1.0 mg/l
7. Pb	Not more than 0.2 mg/l
8. Ni	Not more than 1.0 mg/l
9. Mn	Not more than 5 mg/l
10. As	Not more than 0.25 mg/l
11. Hg	Not more than 0.005 mg/l

Source: Ministry of Science Technology and Environment (1996)

## 2.2 Dyes

Dyes used by the textile industry are generally synthetic organic aromatic compound, which is embodied with various functional groups and heavy metal. Some naturally occurring dyes, derived from animal or plant sources, are also used but are relatively unimportant commercially. Textiles are dyed using many different colorants, which may be classified in several ways. It is classified by their solubility, there are two main categories; water-soluble dyes and water insoluble dyes (Amornsri, 2003).

### 2.2.1 Classification of dyes

#### a) Water soluble dyes

This class of dyes presents in form of sodium salt, which give an anionic charge when being dissolved. This category includes acid dye, reactive dye, and direct dye.

Another categories of the water-soluble dyes, which give a cationic charge when being dissolved, are cationic dyes or basic dyes.

#### b) Water insoluble dyes

Water insoluble dyes can be divided into five groups; (1) dyes soluble in the substrate such as disperse dyes and solvent-soluble dyes, (2) temporarily solubilized dyes such as vat dyes and sulfur dyes, (3) poly condensation dyes, (4) dyes formed within the fiber, and (5) pigments.

Furthermore, dyes may be classified by their chromogenic systems, and the American Association of Textile Chemists and Colorists have achieved this in the Color Index (C.I.) published. The Color Index is the most comprehensive and authoritative reference work in the field. Technical information relating to fastness properties and methods of synthesis is provided. The classification in which dyes are identified by C.I. structure numbers according to chromogen cross-refer to a further classification in which the dyes are collected into groups according to use (Rys and Zollinger, 1972; Rattee, 1995).

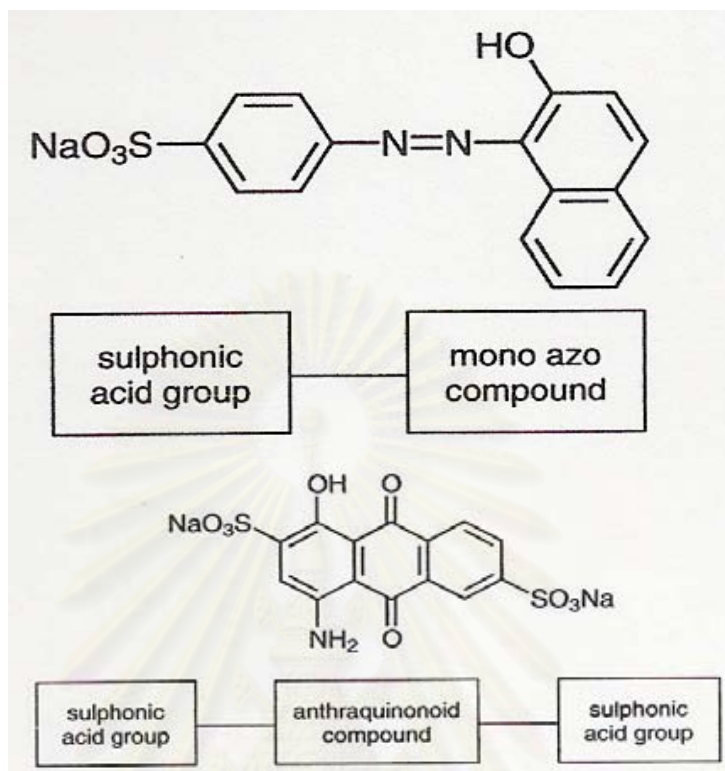
Among many types of dyes, reactive and acid dyes are the most problematic (Robinson et al., 2001; Pereira et al., 2003). Therefore, both of them are considered in this work.

### 2.2.2 Acid dyes

Acid dyes are water-soluble anionic compounds, used for coloring nylon, wool, and certain other natural polymers. They are fairly low molecular weight, typically 300-500 g/mol (Cooper, 1978; Smith, 2003).

Acid dye molecules provide a wide range of colors covering several different chromophonic systems, based on anthraquinone, azo, triarylmethane and azine structures. 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 colored component of the molecule. This is usually, but not always, the sodium salt of a sulphonic acid group,  $-\text{SO}_3\text{Na}$  (Ingamells, 1993), typical acid dyes structures are shown in **Figure 2.1**.

Acid dyes are typically applied in batch processes from acidic baths (pH 3 -7), with high bath exhaustion. These dyes are very water soluble, making machine cleaning fairly easy and not requiring much in the way of chemicals (Smith, 2003).

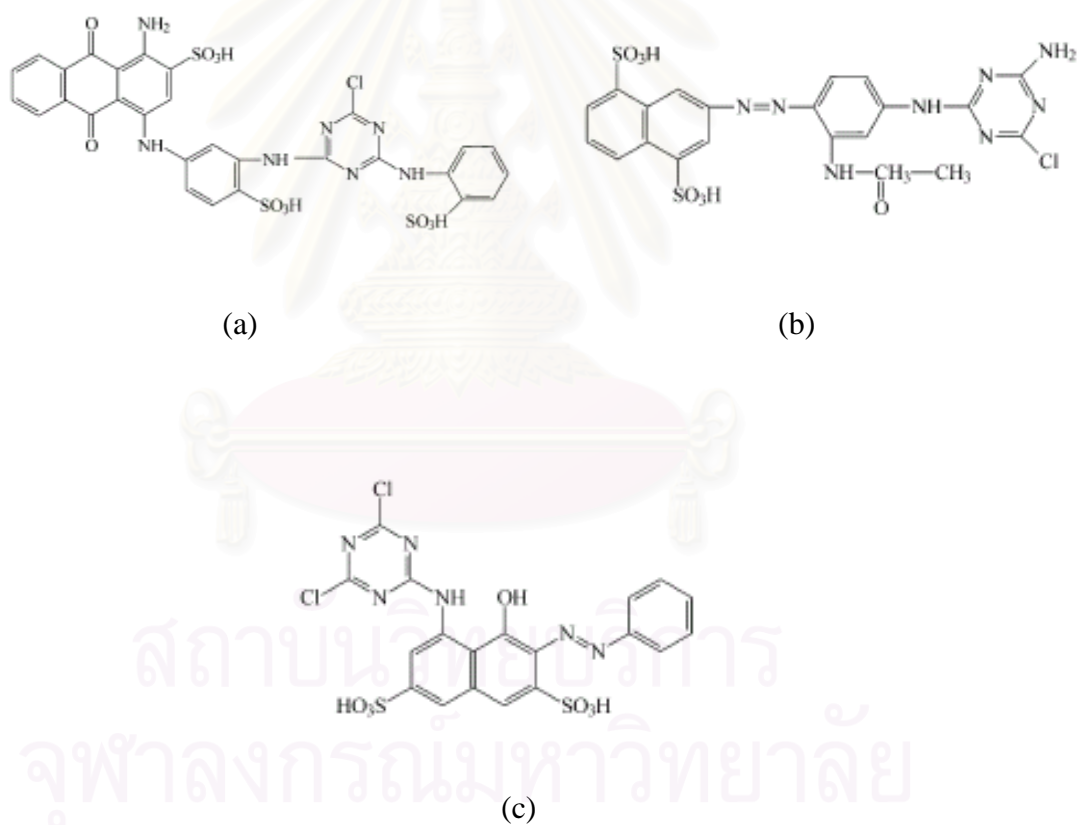


**Figure 2.1:** The general structure of Acid Dyes (Ingamells, 1993)

### 2.2.3 Reactive dyes

All of dyes classes, reactive dyes have been the fastest growing and the most popular over the last 30 years. They give an exceptionally large shade range with brilliant colors possible in all hues, and the fastness is outstanding. But, as currently constituted and applied, the pollution potential of these is perhaps the greatest of all dye classes. They require huge amounts of salt, and the fixation efficiency is poor, with most fiber-reactive batch dyeings utilizing only one half to two thirds of the available color. The rest is discharged as colored wastewater (Smith, 2003).

Reactive dyes are water-soluble anionic dyes, which mainly used for dyeing cellulosic fibers such as cotton and rayon but are also sometimes used for wool, silk, nylon, and leather. The structure of reactive dyes consists of three parts; a chromophore which is the color-bearing group, a reactive group that usually a heterocyclic carbon-nitrogen ring system, and a leaving group which is part of the carbon-nitrogen group which is generally a halogen compound (Druding, 1982). The example of reactive dyes structure as presented in **Figure 2.2**.



**Figure 2.2:** The structure of Reactive Dyes: (a) Reactive Blue 2,

(b) Reactive Yellow 86, and (c) Reactive Red 2



## **2.3 Current Methods for Color Removal**

A practical and cost-effective method to eliminate dye-containing effluent has been sought for over 25 years. Among the vast array of available options which exist, none has emerged as a compelling, simple, cost effective, or universally applicable method (Easton, 1995). From the rational and practically available color removal possibilities, there are essentially six primary groups of methods. These methods include:

### **2.3.1 Biotreatment**

Biological treatment processes used in the textile industry are generally unsuccessful in significant color removal. One reason is that dyes are designed to be biological non-degradable. The evolution of long retention times for conventional textile extended-aeration systems, which generally operate at 2-3 days or more. This is also the reason why municipal treatment systems are much less successful at color removal.

A major advantage of biological treatment over certain physical or chemical treatment methods is the production of biogas. Biogas can be reused to provide heat and power, and will reduce energy costs (Robinson et al., 2001).

### **2.3.2 Coagulation**

Coagulation is one of the oldest practiced methods of wastewater treatment. This is an economically feasible method of dye removal, which is relatively rapid and significant reduction of COD (Easton, 1995). But the disadvantage of this method is the production of large amounts of sludge occurs, and this results in high disposal costs (Robinson et al., 2001).

### **2.3.3 Membrane technologies**

The use of various membrane technologies such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration to clean effluent from textile industries offer the appeal of recovering and reusing chemicals and dyes, and producing reusable water. However, the concentrated residue left after separation poses disposal problems, and high capital cost and the possibility of clogging, and membrane replacement is its disadvantages (Robinson et al., 2001).

### **2.3.4 Electrochemical destruction**

This is a relatively new technique, which was developed in the mid 1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge buildup. The breakdown metabolites are generally not hazardous leaving it safe for treated wastewater to be released back into waterways. It shows efficient and economical removal of dyes and a high efficiency for color removal and degradation of recalcitrant pollutants. But the drawback of this method is the high cost of electricity and chemicals (Robinson et al., 2001).

### **2.3.5 Oxidation**

In respect to oxidation methods, it was described earlier how modern dyes are resistant to mild oxidation conditions, such as exist in biological treatment systems. Suitable color removal, therefore, must be accomplished by more powerful oxidizing methods, such as chlorine, ozone, Fenton's reagent (peroxide and ferrous sulfate), UV/peroxide, UV/ozone, or other oxidizing techniques or combinations. The problem associated with oxidation lies in the unknown nature of the products formed and the risk that some of these may be even more harmful to the environment

than the initial components of the effluent. Nevertheless, the advantage of this method is the process can be made extremely rapid, so minimizing equipment size and cost (Easton, 1995).

### **2.3.6 Adsorption Techniques**

Adsorption techniques have gained favor recently due to their higher efficiency in the removal of pollutants compared with conventional methods. Adsorption produces a high quality product, and is a process, which is economically feasible. Decolorization is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. This technique is chosen to study in this work.



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## 2.4 Adsorption

Adsorption is a process by which material accumulates at the interface between two phases. These phases can be any of the following combinations: liquid-liquid, liquid-solid, gas-liquid, and gas-solid. The adsorbing phase is called the adsorbent, and any substance being adsorbed is termed as an adsorbate (Noll et al., 1992).

### 2.4.1 Equilibrium Isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Therefore, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems (Wong et al., 2003). In this study, the experimental data were compared by two isotherm equations namely, Langmuir and Freundlich.

#### a) Langmuir Isotherm

Langmuir's model of adsorption is originally developed to represent chemisorption; this model depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. This isotherm equation further assumes that adsorption take place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent (Mantell, 1951; Noll et al., 1992; Ray, 1995). Langmuir adsorption isothermal model can be expressed as

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (2.1)$$

where  $q_e$  is solid phase sorbate concentration at equilibrium (mg/g),  $Q$  (mg/g) is the maximum amount of the dye per unit weight of chitosan to form complete monolayer coverage on the surface bound at high equilibrium dye concentration  $C_e$ .  $b$  are the Langmuir constants related to the affinity of binding sites (l/g).

Therefore, a plot of  $1/q_e$  versus  $1/C_e$  gives a straight line of slope  $b$  and intercept  $1/Q$ , a linear expression of Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \left(\frac{1}{C}\right) \quad (2.2)$$

### b) Freundlich Isotherm

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterised by the heterogeneity factor  $1/n$ . Hence, the empirical equation can be written:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.3)$$

where  $q_e$  is solid phase sorbate concentration in equilibrium (mg/g),  $C_e$  is liquid phase sorbate concentration in equilibrium (mg/l),  $K_F$  is Freundlich constant (l/g) and  $1/n$  is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of Equation (2.3).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2.4)$$

Therefore, a plot of  $\ln q_e$  versus  $\ln C_e$  enables the constant  $K_F$  and exponent  $1/n$  to be determined. This isotherm is represented the physical adsorption. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich equation predicts that the dye concentrations on the adsorbent will increase as long as there is an increased in the dye concentration in the liquid (Mantell, 1951; Noll et al., 1992; Ray, 1995) .

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

The most widely used adsorbent for industrial application is activated carbon, but their use is usually limited due to high cost. Moreover, there are many problems involving with the regeneration of used activated carbon (Wu et al., 2000; Ho and Chiang, 2001). Extensive investigations are being carried out to search for alternative cheap adsorbents capable of removing significant quantities of dyes.

Chitosan is obviously desirable because it is readily available and is a renewable and sustainable resource that has been reported for the high potentials of the adsorption of dyes.

## 2.5 Chitin and Chitosan

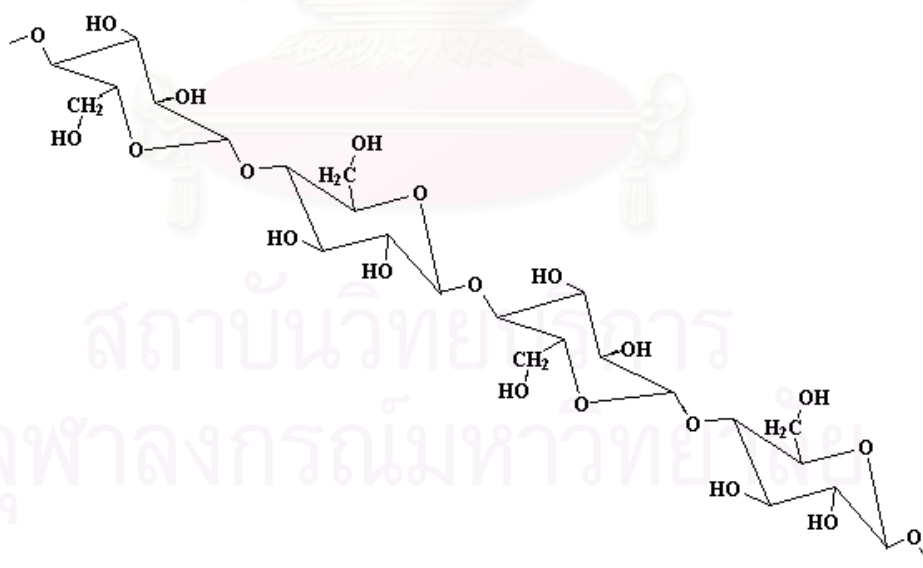
Chitin is the polysaccharides, it is widely distributed both in animal and plant kingdom. Among the polysaccharides, chitin is the second-most abundant biopolymer in nature next to cellulose. In animals, the most readily associated sources are in the shells of crustaceans and mollusks, and backbone of squids and insects' exoskeletons. Chitin's role in the shell and cuticle is as a structural component that contributes strength and protection to the organisms. In crustaceans or more specifically shellfish, chitin is found as a constituent of a complex network with proteins onto which calcium carbonate deposits to form the rigid shell. In the plant kingdom, chitin is present in the algae, commonly known as marine diatoms, protozoa and the cell wall of several fungal species (Khor, 2001). The name chitin is derived from the Greek word chiton, meaning a coat of mail. Chitin was reportedly first discovered by Bradcoccot in 1811 (Shahidi et al., 1999).

Chitosan is not native to animal sources and normally obtained by the deacetylation of chitin. The discovery of chitosan is attributed to Rouget in 1859 when he boiled chitin in a concentrated potassium hydroxide solution (Goosen, 1997).

Since the biodegradation of chitin is very slow in crustacean shell waste, loading up of large quantities of dispossess from processing of crustaceans. It has become a major concern in the seafood processing industry. The total global annual estimate of it is around  $5.118 \times 10^6$  metric tons. Out of the different species of crustaceans, shrimp and crab shell wastes have been widely used for the isolation of chitin. Therefore, production of value-added products such as chitin, chitosan and their derivatives and application of products in different fields is of utmost interest (Shahidi et al., 1999).

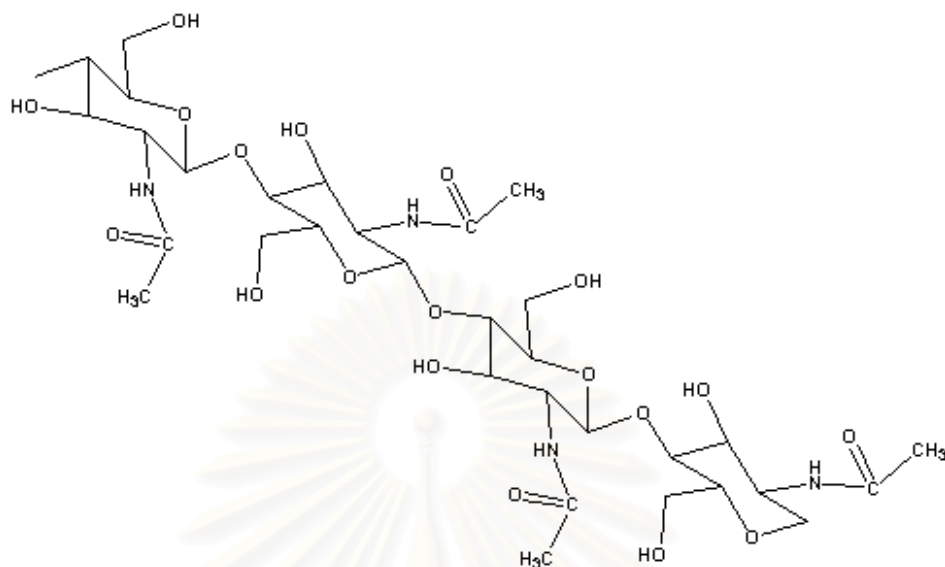
### 2.5.1 Structure of Chitin and Chitosan

Chitin and chitosan are chemically similar to cellulose, differing only in R group attached to carbon 2 of the general carbohydrate structure (Monteiro and Airoidi, 1999; Anjus et al., 2002). The ideal structure of chitin is a linear polysaccharide of  $\beta$ -(1-4)-2-acetamido-2-deoxy-D-glucopyranose where all residues are comprised entirely of N-acetyl-glucosamine residues or chitin jargon, fully acetylated. Likewise, the ideal structure of chitosan is a linear polymer of  $\beta$ -(1-4)-2-amino-2-deoxy-D-glucopyranose where all residues are comprised entirely of N-acetyl-glucosamine residues or fully deacetylated (Kubota and Kikuchi, 1998; Khor, 2001). The structures of cellulose, chitin and chitosan are shown in **Figure 2.3, 2.4** and **2.5**, respectively.

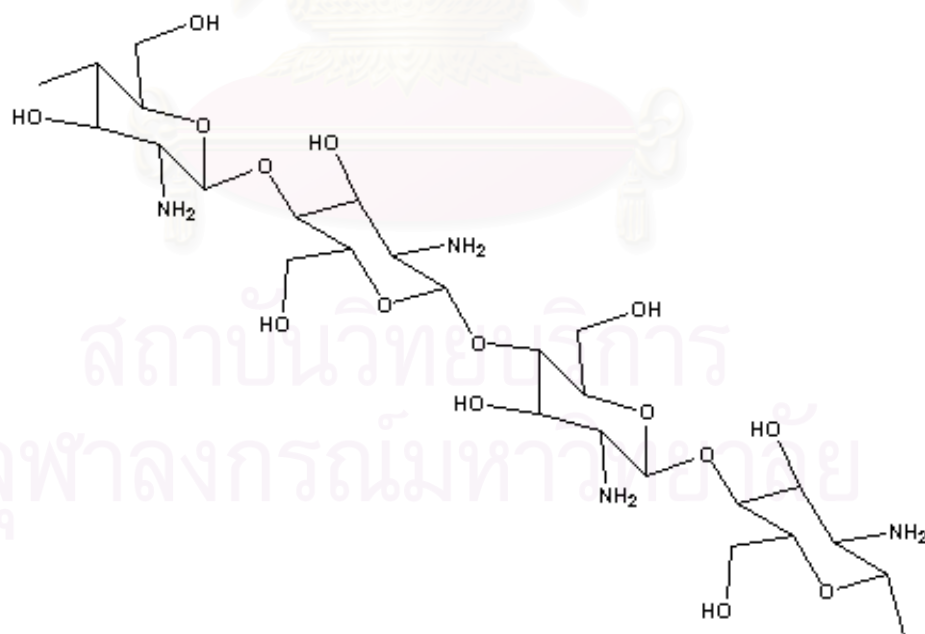


**Figure 2.3:** The structure of cellulose (Khor, 2001)





**Figure 2.4:** The structure of chitin (Khor, 2001)



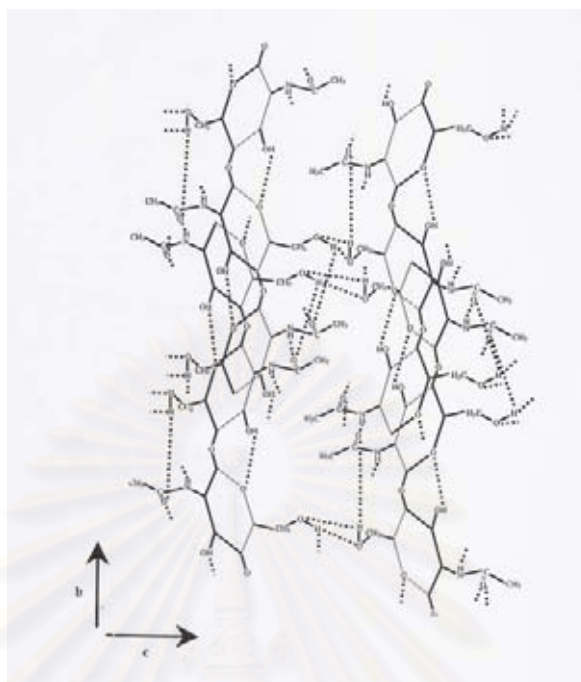
**Figure 2.5:** The structure of chitosan (Khor, 2001)

The difference between chitin and chitosan lies in their respective acetyl content. When the number of acetamido groups is more than 50%, the biopolymer is termed chitin. In chitin terminology, the number of acetamido groups is termed the degree of acetylation (DA). On the other hand, when the degree of deacetylation (DD) or the amino groups is predominant, the biopolymer is termed chitosan (Goosen, 1997; Khor, 1999).

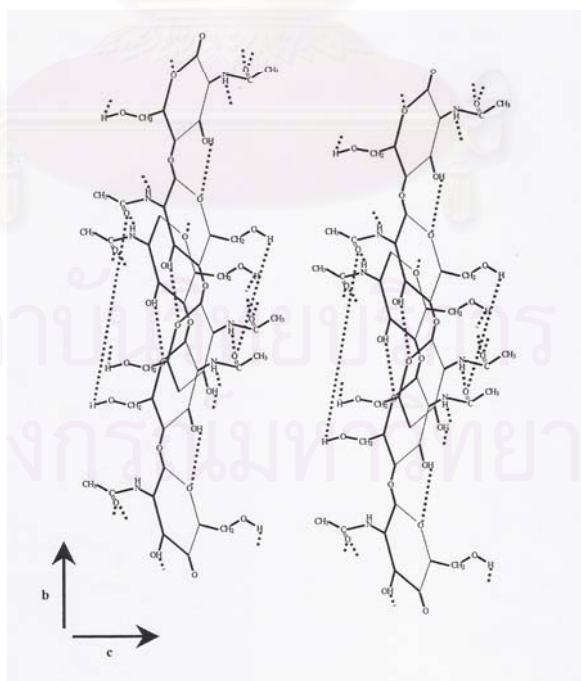
Chitin has three crystalline forms,  $\alpha$ -,  $\beta$ - and  $\gamma$ -chitin.  $\alpha$ -Chitin is the most abundant form, found in shellfish and also in fungal cell wall. In the solid state, adjacent  $\alpha$ -chitin chains are organized in an anti-parallel configuration in the c direction (**Figure 2.6**). It has been suggested that the conformation of chitosan was similar to that of  $\alpha$ -chitin (Goosen, 1997).

$\beta$ -Chitin (**Figure 2.7**) is found in chitin extracted from the diatom spines and squid pens.  $\beta$ -Chitin is packed in a parallel arrangement that does not favor the inter-chain hydrogen bonding between the C-6 hydroxyl groups along the c-axis, in other respects, existing in  $\alpha$ -chitin (Muzzarelli and Muzzarelli, 1998).

$\gamma$ -Chitin is a mixture of  $\alpha$ - and  $\beta$ -chitin, with two parallel chains and for every anti-parallel stack that leads to water swelling properties intermediate between  $\alpha$ - and  $\beta$ -chitin (Knoh, 1999).



**Figure 2.6:** The structure of  $\alpha$ -chitin (Khor, 2001)



**Figure 2.7:** The structure of  $\beta$ -chitin (Khor, 2001)

## 2.5.2 Physical and Chemical Characterization of Chitin and Chitosan

### a) Degree of N-Acetylation/Deacetylation

The degree of deacetylation (%DD) or degree of acetylation (%DA) is one of the most important characteristics of chitin and chitosan. The degree of deacetylation determines the content of free amino groups in chitosan, and degree of acetylation is the number of glucopyranose units in chitin. This is a key property that must be determined as it influences the physical and chemical properties of chitin and chitosan such as solubility, chemical reactivity, and biodegradability and therefore their applications (Goosen, 1997; Khor, 1999; Kumar, 2000).

There are various methods for determination of this important parameter, including titration, circular dichroism, infrared (IR) spectroscopy, high performance liquid chromatography (HPLC), ultraviolet (UV) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. The most widely adopted methods are the first derivative UV spectrophotometry and <sup>1</sup>H NMR (Muzzarelli and Peter, 1997).

### b) Molecular Weight

While the degree of deacetylation (or acetylation) identifies the biopolymer as chitin or chitosan, the molecular weight determines the viscosity and rate of degradation. The weight-average molecular weight of chitin is  $1.03 \times 10^6$  to  $2.5 \times 10^6$ , but the N-deacetylation reaction reduces this to  $1 \times 10^5$  to  $5 \times 10^5$  (Kumar, 2000).

The molecular weight of chitin and chitosan can be determined by methods such as laser light-scattering spectrometry, viscometry, and gel permeation chromatography. Among these, the most accurate and complete information can be obtained by gel permeation chromatography (Muzzarelli and Peter, 1997).

### **c) Solubility**

Chitin is highly hydrophobic and is insoluble in water and most organic solvents. It is soluble in hexafluoroisopropanol, hexafluoroacetone, chloroalcohols in conjugation with aqueous solution of mineral acids and dimethylacetamide containing 5% lithium chloride. Whereas chitosan, the deacetylated product of chitin is insoluble in alkali and organic solvent but is soluble in most solutions of dilute organic acids such as acetic acid, formic acid, etc. (Kumar, 2000).

Due to its solubility in dilute organic acid chitosan can be processed into different geometrical configurations including membranes, fibers, hollow fibers, capsules, and beads (Edwards et al., 1999).

### **2.5.3 Isolation of Chitosan**

The process of isolating chitosan from shellfish begins with the selection of shells. Cleaning and drying of the shells followed by thorough crushing in the next step in the process.

### **a) Deproteinization**

In deproteinization, covalent chemical bonds have to be destroyed between the chitin-protein complex. Chemical methods were the first approach used in deproteinization. A wide range of chemicals have been tried as deproteinization reagents including NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, KOH, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S, Ca(OH)<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub>, NaHSO<sub>3</sub>, CaHSO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub>. NaOH is the preferred reagent and used with variations in the temperature and duration of treatment parameters.

### **b) Demineralization**

The demineralization process is the removal of minerals, primarily calcium carbonate (CaCO<sub>3</sub>). Demineralization is readily achieved because it involves the decomposition of calcium carbonate into water-soluble calcium salt with the release of carbon dioxide. The most used reagent is dilute hydrochloric acid (HCl) that produces water-soluble calcium chloride (CaCl<sub>2</sub>).

### **c) Deacetylation of Chitin to Chitosan**

The removal of these two major components, proteins and calcium carbonate gives raw chitin. The deacetylation of chitin into chitosan is usually achieved by treating chitin with 50% NaOH at 95°C for 3 hours, cooling down decanting off the NaOH and washing with water until neutral pH.

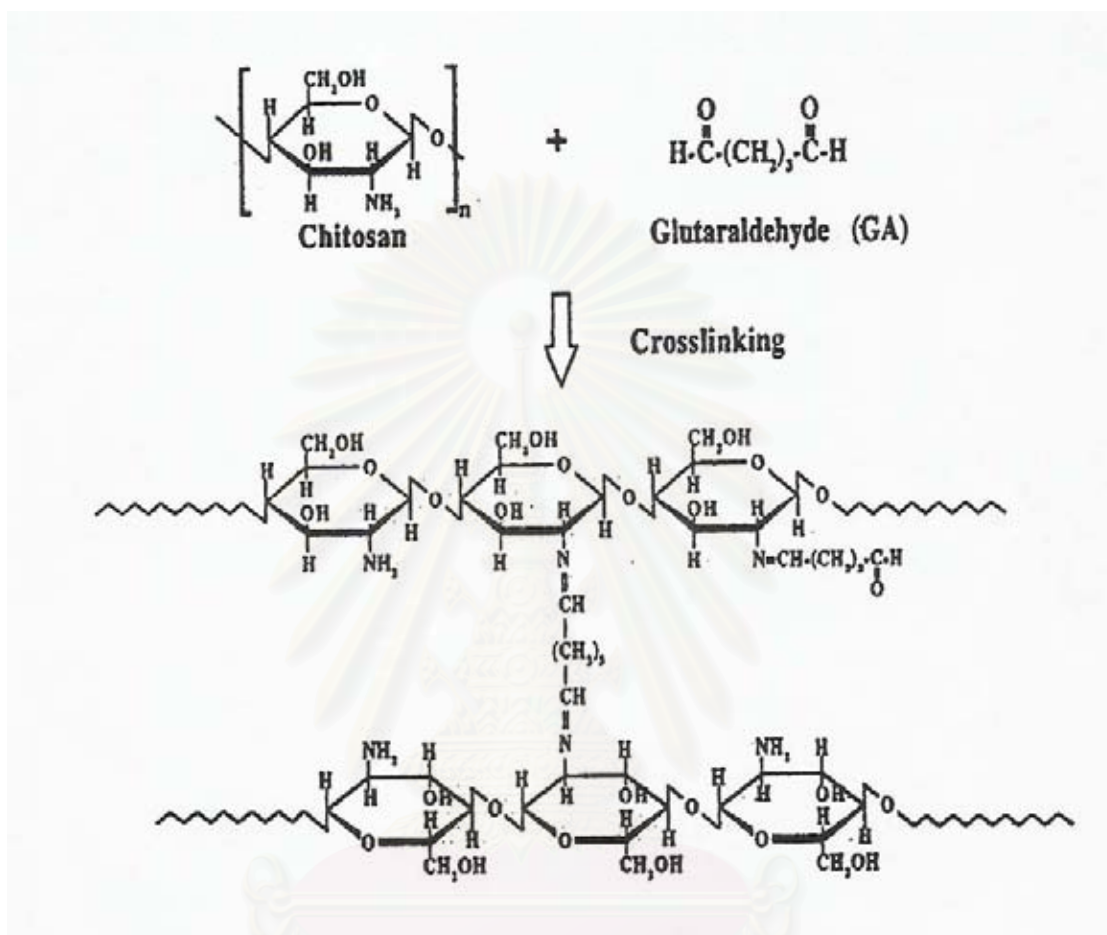
### 2.5.4 Crosslinked Chitosan

Since chitosan is very stable in neutral and alkaline solutions, there is no problem when chitosan is contacted with a solution of  $\text{pH} \geq 7$ . However, chitosan is soluble at low pH, especially in organic acids, and this precludes the use of this material as an adsorbent under acidic conditions (Yoshida et al., 1993). Some crosslinking agents such as epichlorohydrin or glutaraldehyde are used to stabilize chitosan in acid solutions (Ruiz et al., 2000; Chiou and Li, 2003).

Unlike other polysaccharides, chitosan possesses an amino group on each glucosamine residue, which can serve as a reaction site for two attractive chemical modifications. First, N-acetylation of chitosan can randomly add hydrocarbon side chains to a fraction of the amine groups. These hydrocarbon side chains can impart a hydrophobic substructure to the biopolymer and also disrupt the hydrogen-bonding network between chitosan chains to expose more amine sites. Second, interchain crosslinking of chitosan with bifunctional reagents such as glutaraldehyde can impart a three-dimensional network to the biopolymer (Hsien and Rorrer, 1995).

Glutaraldehyde crosslinking occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of chitosan to form imine functions as shown in **Figure 2.8** (Ruiz et al., 2000).

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**Figure 2.8:** The structure of glutaraldehyde crosslinked chitosan (Ruiz et al., 2000)



### **2.5.5 The Applications of Chitin and Chitosan**

The industrial production and use of chitin and chitosan has been steadily increasing since the 1970s. At that time, the major applications of chitosan were centered on sludge dewatering, food processing and metal ion chelation. The present trend, in industrial application, however, is toward producing high value products such as cosmetics, drug carriers, feed additives, semi-permeable membranes, and pharmaceuticals (Goosen, 1997; Kumar, 2000). **Table 2.4** lists some examples of the known and potential application for chitin, chitosan and their derivatives.

### **2.6 The Use of Chitosan for Color Removal**

The removal of dyes in an economic fashion remains an important problem. Considerable works have been carried out on the removal of color from textile dyeing industry wastewater through chemical coagulation, chemical oxidation, and by adsorption. Adsorption seems to offer the best prospects over all other treatment techniques. Activated carbon is the most popular adsorbent and has been used with great success, but it is expensive. Extensive investigations are being carried out to search for alternative cheap adsorbents capable of removing significant quantities of dyes such as sugar industry mud (Magdy and Daifullah, 1998), fruit peels (Annadurai et al., 2002), leaf (Bhattacharyya and Sarma, 2003), rice husk (Mckay et al., 1999; Robinson et al., 2002), fly ash (Albanis et al., 2000), clay (Ho and Chiang, 2001; Atun et al., 2003), coal (Mohan et al., 2002) and chitosan.

**Table 2.4:** Applications of chitin, chitosan and their derivatives

<b>Application area</b>	<b>Specific use</b>
Water treatment	Removal of metal ions Coagulating/flocculating agent
Membranes	Reverse osmosis Permeability control Solvent separation
Textile and paper	Fibers for textile and woven fabrics Paper and film
Agriculture	Fertilizer Seed coating Anti-microbial agents Plant elicitor
Food and health supplements	Hypocholesterolemic agent (slimming agents) Animal feed additives Filtration and clarification
Medical	Bandages, sponges Artificial blood vessels Burns and wounds dressings for humans and animals Dental/plaque inhibition Contact lens Controlled release of drugs
Cosmetics	Ingredients for hair and skin care
Biotechnology	Enzyme immobilization Cell immobilization Cell recovery Protein separation Chromatography

Chitosan is also known sorbent effective in the sorption of transition metal ions (Hsien and Rorrer, 1995; Aly et al., 1997; Kawamura et al., 1997; Gao et al., 2000; Schmuhl et al., 2001; Juang and Shao, 2002; Liu et al., 2002; Jeon and Holl, 2003). Due to its unique molecular structure, chitosan has an extremely high affinity for many classes of dyes (Kumar, 2000). Since the amino (-NH<sub>2</sub>) and hydroxy (-OH) groups on chitosan chains can serve as coordination and electrostatic interaction sites, respectively (Wu et al., 2000). And the previous studies have shown that chitosan has a high efficiency for color removal rather than activated carbon (Muzzarelli, 1983). From this regard, chitosan appears to be more economically attractive than activated carbon for adsorption removal of dyes from effluents because chitin is the second abundant polymer in nature next to cellulose.

Yoshida et al. (1993) developed the two different crosslinked chitosan fibers for use as adsorbents or ion exchangers for the recovery of dyestuffs. They found that the concentration of amino group in the adsorbent phase was 3 to 5 times larger than that of the commercial weak-base ion exchangers and decreased with increasing degree of crosslinking. The adsorption capacities of crosslinked chitosan fibers show higher value than activated carbon fiber. The amount of dye adsorbed increased with increase in initial concentration and decreased with increasing temperature. The presence of an inorganic salt also increased the amount of dye adsorbed.

Aly et al. (1997) investigated the chitin thiocarbonate-Fe (II)-H<sub>2</sub>O<sub>2</sub> redox system as the initiator for the graft copolymerization of acrylonitrile and acrylic acid monomers onto chitin powder to use in the wastewater treatments for adsorption and desorption of heavy metal ions as well as acid and basic dyes. All the prepared products have high adsorption amounts for metal ions and dyes; therefore, those products can be applied for the treatment of wastewater containing heavy metal ions and dyes.

Kim et al. (1997) studied the effect of deacetylation on sorption of dyes and chromium on chitin to determine an optimal degree of deacetylation (DD) which can effectively remove four dyes (Acid Blue 193, Acid Blue 40, Direct Yellow 44, and Direct Blue 78) and chromium ions from textile effluent. The results indicated that except for the chitin with a 67.2%DD, rate and capacity of the dyes and chromium sorption on the chitin increased with the increase of the DD for each pH, but decreased with the increase of pH.

Figueiredo et al. (2000) considered chitin which were prepared from squid and sepiia pens, and anodonta shells for color removal. The reactive and direct dyestuffs were selected for this study. In this study, chitin containing in natural materials showed promising adsorption capacities both batch and continuous studies.

Wu et al. (2000) compared the adsorption capacity of metal and dye on flake and bead types of chitosan. From their experiments, they found that the adsorption capacity on bead type was much larger than on flake type.

Juang et al. (2001) studied the chemically modified chitosan beads for sorption reactive dye RR222 and Cu as well as the enzyme immobilization. Chitosan was prepared from cuttlefish wastes and was crosslinked with different dosages of glutaraldehyde and glyoxal. The amounts of sorption of reactive dye and Cu, and the activities of immobilized enzymes, onto crosslinked chitosan beads were greatly affected by the degree of crosslinking.

Vachoud et al. (2001) reported the adsorption and desorption of acid dye, reactive dye and direct dye onto chitin gels. The network corresponding to a chitin gel can interact with dyes either by electrostatic or low energy interactions such as hydrophobic interactions.

Anjos et al. (2002) studied the interaction of indigo carmine dye with chitosan in aqueous medium. The adsorption experiments were carried out the batch mode from 35 to 50°C. The increase in the temperature decreased the adsorption of the dye.

Chiou and Li (2002) investigated the adsorption of reactive dye (RR 189) from aqueous solutions on crosslinked chitosan beads in a batch system. This study has shown that crosslinked chitosan beads have a high efficiency for removal of reactive dye. The initial dye concentration and the solution pH both significantly affect the adsorption capacity, but the temperature and crosslinking ratios are relatively minor factors.

Chiou and Li (2003) studied adsorption behavior of reactive dye in aqueous solution on chemical crosslinked chitosan beads. Epichlorohydrin (ECH), glutaraldehyde, and ethylene glycol diglycidyl ether was used as a cross-linking reagent. From the experiments, ECH showed a higher adsorption capacity. The adsorption capacity increased largely with decreasing solution pH or with increasing initial dye concentration.

Wong et al. (2004) studied the ability of chitosan from crab shell to remove acid dyes from effluent by adsorption technique. AG 25, AO 10, AO 12, AR 18 and AR 73 were used in their experiments. The different kinds of dyes showed the different adsorption capacities, this might be due to the difference in the molecular size of dye molecules and the number of sulphonate groups of each dye. Results demonstrated that monovalent and smaller dye particle had superior capacities due to increase in dye/chitosan ratio in the system, enabling a deeper penetration of dye molecules to the internal pore structure of chitosan.

A limited number of dye removal studies have been carried out on chitosan prepared from dried-crustacean shell. Several of these references related to the adsorption of dyes on chitin and chitosan in different forms such as powder, flake, fiber, bead and gel. All of these references used chitin and chitosan obtained from freshed-crustacean shell to treat dye-containing effluents. In addition, there is a lack of detail for the removal of dyes onto chitosan in a continuous experiment, even though high sorption capacities have been obtained from a batch experiment.

## CHAPTER III

### Materials and Methods

#### 3.1 Materials

##### 3.1.1 Chemicals

All the chemicals used in this study are analytical grade; ethanol ( $C_2H_5OH$ ) with 99.8% purity and sodium hydroxide (NaOH) with its purity of 99% were purchased from Merck, German. Reactive Red 120 and Sodium Tripolyphosphate ( $Na_5P_3O_{10}$ ) with 90-95% of purity were purchased from Sigma, German. The crosslinking agent glutaraldehyde (GA) with 50 wt% solution in water and Acid Blue 129 were purchased from Aldrich, USA. Acetic acid ( $CH_3COOH$ ) with 100% purity was purchased from BDH, England. Hydrochloric acid (HCl) with purity of 36.5-38% was purchased from J.T. baker, USA and potassium hydroxide (KOH) with 85% purity was purchased from Carlo Erba, Switzerland.

##### 3.1.2 Chitosan

**Figure 3.1** show the schematic diagram of the preparation of adsorbents. In this study, the chitosan was prepared from dried-shrimp shell. The shell was deproteinized with 5% by weight of NaOH for 3 h at 90 °C and then follow by demineralization with 10% by volume of HCl at room temperature for 18 h. After that it was deacetylated in 50% by weight of NaOH at 90 °C for 3 h. Finally flake type of chitosan was obtained.

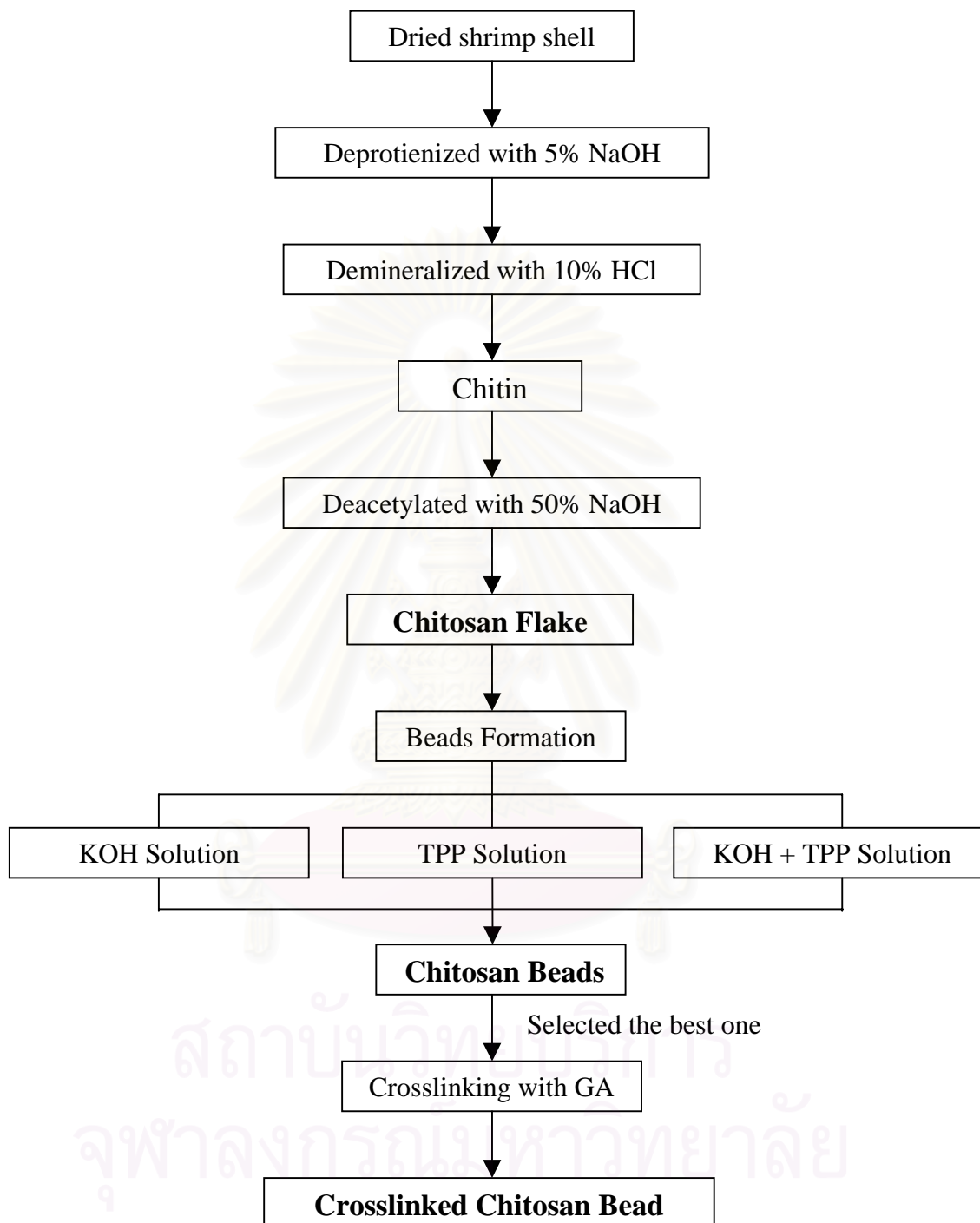
The degree of deacetylation and molecular weight of chitosan were determined. The surface area of chitosan in each form was also considered.

### **3.1.3 Chitosan Beads**

The preparation of chitosan beads involves two steps, chitosan dissolution and beads formation. The chitosan flake was dissolved in 2% by volume of acetic acid and then the chitosan solution was dropped into the solution. In this study, there are three types of solution, the first one contained 15 g of KOH and 25 ml of ethanol in 1 liter of solution. The second contained 1% TPP and the last one contained both KOH and TPP in ratio of 50:50 by volume. After beads were formed, they were left in the solutions for 16 hours, and then chitosan beads were filtered out and washed with distilled water.

### **3.1.4 Crosslinked Chitosan Bead**

Chitosan bead, which gave the highest performance of decolorization, was selected. The chitosan was crosslinked with glutaraldehyde. The ratio of glutaraldehyde to chitosan (crosslinking ratio) was 2.22 (standard level of crosslinking). Crosslinking reaction was carried out for 16 hours. The crosslinked chitosan bead was rinsed with distilled water.



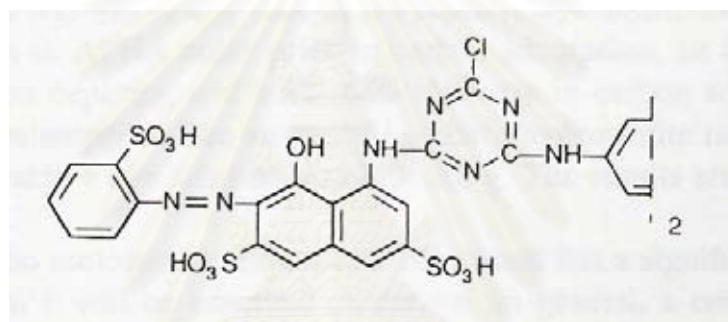
**Figure 3.1:** Preparation of adsorbents



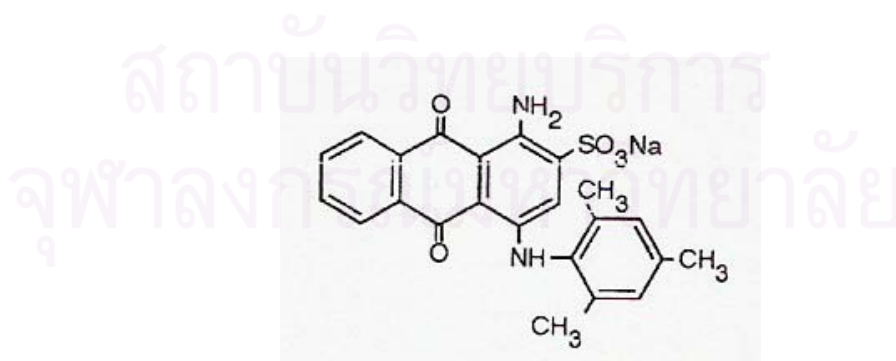
### 3.1.5 Preparation of synthetic dyeing wastewaters

Reactive Red 120 (RR 120) and Acid Blue 129 (AB 129) were chosen in this study. Reactive synthetic dyeing wastewater was prepared at concentration 30 and 100 mg/l. In case of acid dyeing wastewater, it was prepared at two levels of concentration as well. Distilled water was used throughout all experiments.

**Figure 3.2** and **3.3** display the structure of Reactive Red 120 and Acid Blue 129, respectively.



**Figure 3.2:** The structure of reactive red 120



**Figure 3.3:** The structure of acid blue 129

## 3.2 Methodology

The experiments are divided into two parts, a batch and continuous mode. An optimal condition obtained from a batch mode will be applied to a continuous mode. Then the performance each mode will be obtained. **Figure 3.4** show the schematic diagram of experiment.

### 3.2.1 Batch Mode Experiment

**a) To determine the equilibrium time and the appropriate amount of chitosan.**

At given pH 7 and 30 mg/l in concentration of 50 ml of either reactive or acid synthetic dyeing wastewaters, chitosan in each form were used to investigate a dye removal in a batch mode. The amount of chitosan in flake form was varied from 10-1000 mg. In case of bead and cross-linked form, the amount of chitosan were varied from 1-5 g. The wastewater was sampling every 30 minutes in the first 6 hours. After that it was sampling every 6 hours until reaching 48 hours. The remained dyeing concentration was measured by using UV/visible spectrophotometer (Thermo Electron Corporation model Helios Alpha) at wavelength corresponding to the maximum adsorbance, 536 nm for reactive red 120 and 629 nm for acid blue 129. In this stage, an appropriate amount of chitosan and equilibrium time were known.

**b) To studies the effect of pH and initial dye concentration.**

To determine a suitable pH for dyeing removal in a batch mode, pH of reactive and acid synthetic dyeing wastewaters were varied from 3 to 9 by using HCl and NaOH. Buffer solution was used as well. An appropriate amount of chitosan obtained from previous step was chosen. The concentrations of reactive and acid synthetic dyeing wastewaters were varied at 2 levels: 30 and 100 mg/l in order to study the effect of initial dye concentration.

**3.2.2 Continuous Mode Experiment**

To study the performance of dyestuff removal by chitosan when using different mode, an appropriate condition obtained from a batch mode was applied to a continuous mode.

A packed bed glass column with 20 cm of height and 2.5 cm diameter was used in a continuous mode. The bed height was varied by packing with a weighed amount of adsorbent, 10 g and 30 g; the reactive and acid dyestuff solution was pumped upflow with a peristaltic pump (Masterflex, model 77200-60) at flow rate 1 and 10 ml/min. The experiments were performed until saturation of the packed bed was observed.

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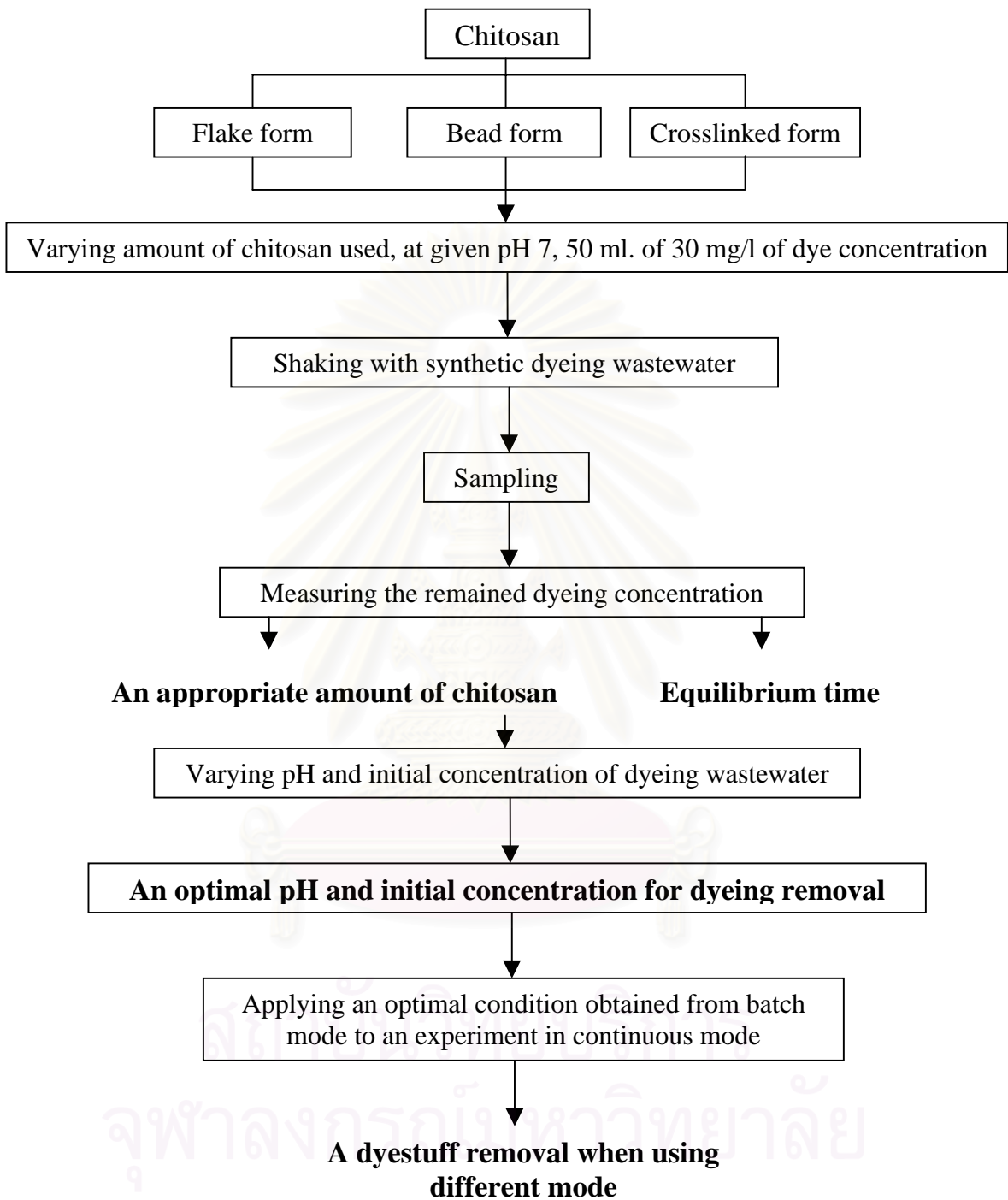


Figure 3.4: Diagram of experiment

# CHAPTER IV

## Results and Discussion

### 4.1 The Properties of Chitosan

#### 4.1.1 Chitosan Flake

Degree of deacetylation of chitosan prepared from dried-shrimp shell was 92.8 and the molecular weight was 265078. The ratio of chitosan to chitin is 0.75, which is slightly less than the theoretical value of 0.793 (Wu et al., 2000). Prior to further use, the flake was ground and sieved to particle size range of less than 2.2 mm.

#### 4.1.2 Chitosan Beads

The three types of chitosan beads treated in KOH or TPP or KOH/TPP had a spherical structure with diameter in the range of 2.3-2.5 mm. The BET surface areas were studied as shown in **Table 4.1**. Among these three types of chitosan beads, TPP-bead had the highest BET surface area, followed by KOH/TPP-bead and KOH-bead, respectively.

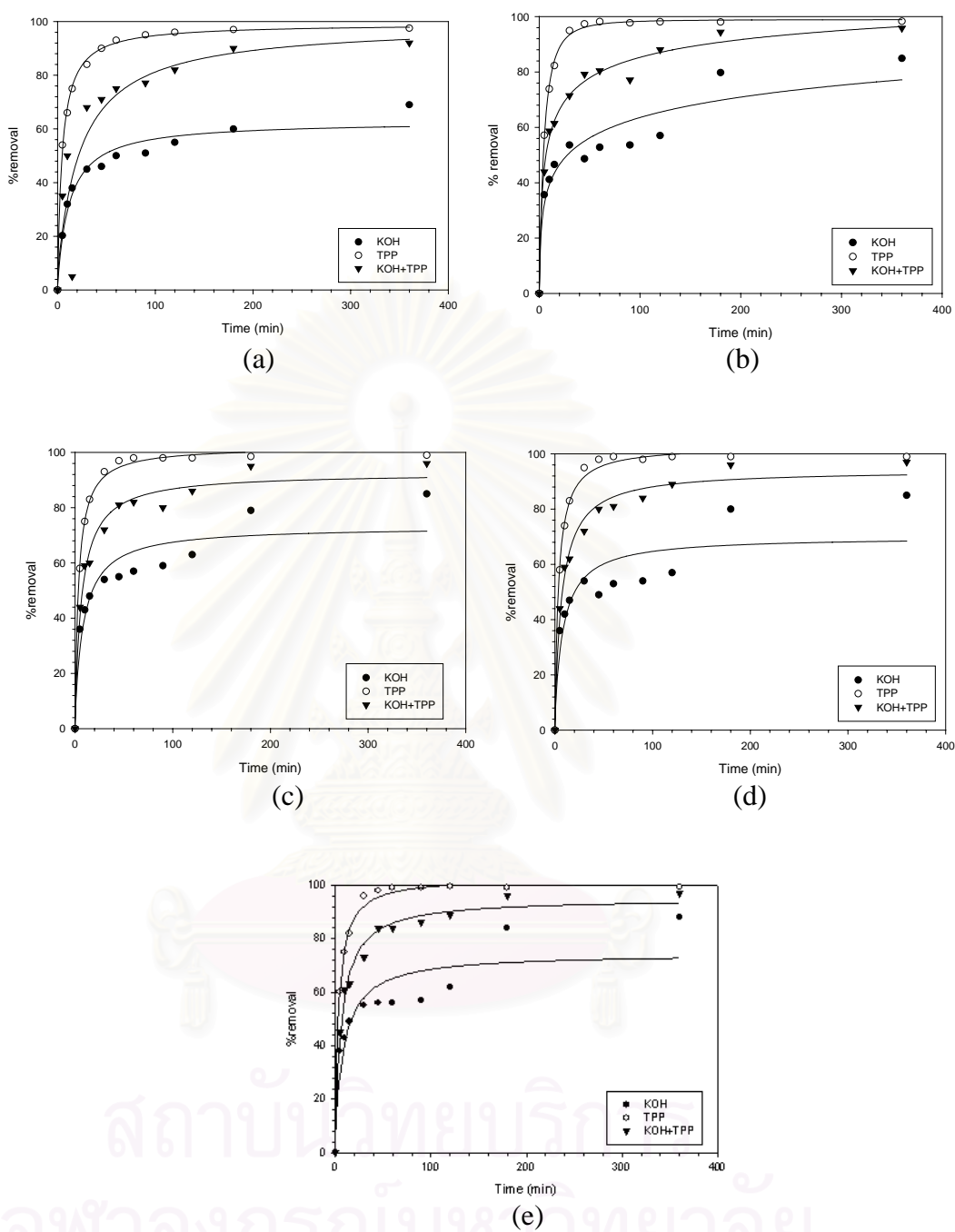
In order to find the chitosan bead, which gave a good performance for decolorization, only 30 mg/l of reactive dye wastewater were chosen. The adsorption capacities of the three types of chitosan beads are presented in **Figure 4.1**. Based on 1 to 5 g of chitosan beads, TPP-bead exhibited the highest efficiency for the removal of reactive dye and this bead was more rigid than KOH and KOH/TPP-beads, the TPP-

bead did not break after decolorization, unlike the KOH-bead and KOH/TPP-bead (**Figure 4.2**). Thus, the chitosan-TPP bead was used for crosslinking and all other studies in this work.

### 4.1.3 Crosslinked Chitosan Bead

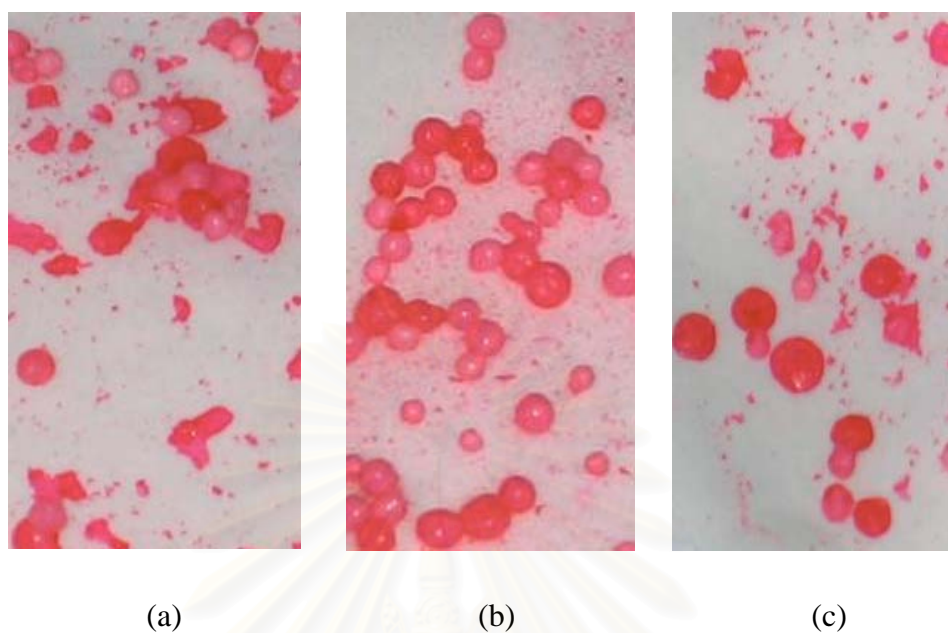
The crosslinked chitosan bead was almost spherical with a diameter about 2.3-2.5 mm, similar to non-crosslinked chitosan beads. However, it had a higher BET surface area than non-crosslinked chitosan beads (**Table 4.1**).

Crosslinking of chitosan bead due to the bonding of dialdehyde group (-CHO) on glutaraldehyde and amino group (-NH<sub>2</sub>) on chitosan may reduce the crushing strength of the bead. This can also be explained by the change from macropores to mesopores as the internal surface area increased. Crosslinking might have also rendered the chitosan itself less elastic to compression forces or making the chitosan more brittle (Hsien and Rorrer, 1995).



**Figure 4.1:** Comparison of adsorption capacities between KOH, TPP and

KOH/TPP chitosan beads at pH 7 and 30 mg/l of reactive dyeing wastewater (a) 1 g of chitosan beads (b) 2 g of chitosan beads (c) 3 g of chitosan beads (d) 4 g of chitosan beads and (e) 5 g of chitosan beads



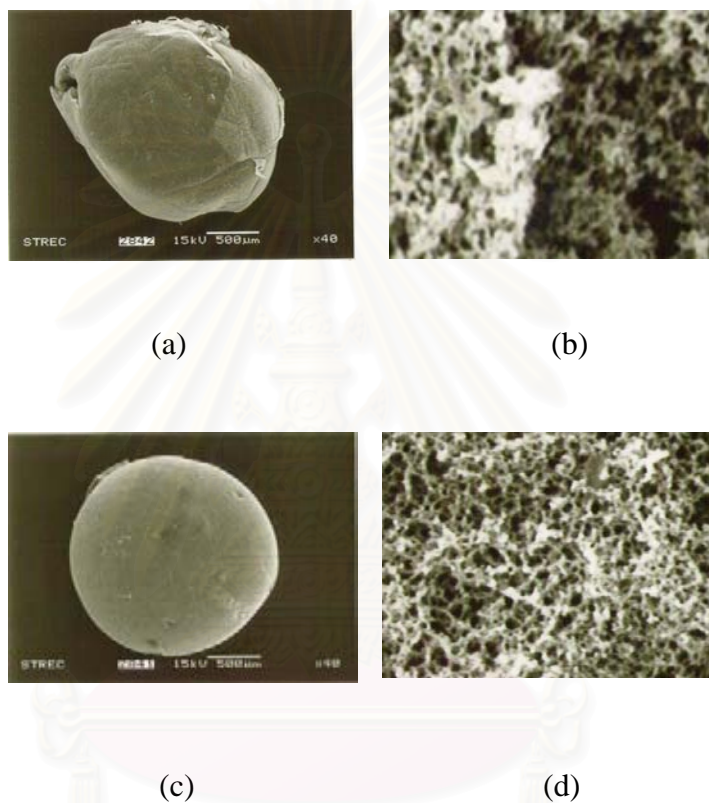
**Figure 4.2:** The chitosan beads after decolorization at 30 mg/l of reactive dyeing wastewater of pH 7, (a) KOH-bead (b) TPP-bead and (c) KOH/TPP bead.

**Table 4.1:** The BET surface of chitosan prepared from dried-shrimp shell

Chitosan	BET surface area (m <sup>2</sup> /g)
Flake	8.82
KOH-bead	31.26
KOH+TPP-bead	46.08
TPP-bead	51.06
Crosslinked bead	168.85



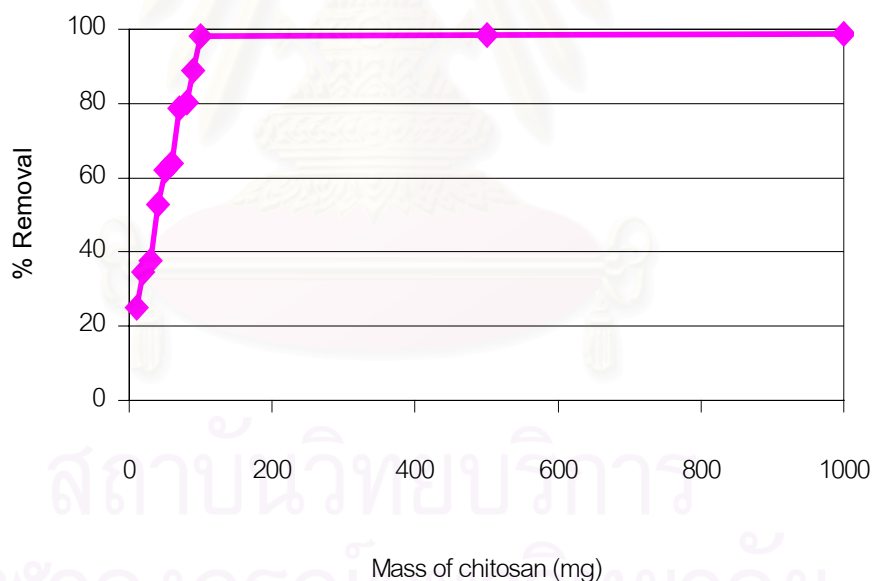
**Figure 4.3** shows the electron micrograph of the TPP chitosan bead and crosslinked chitosan bead. Both of them had a honeycomb structure with high porosity and these bead did not had the so-called skin-core structure.



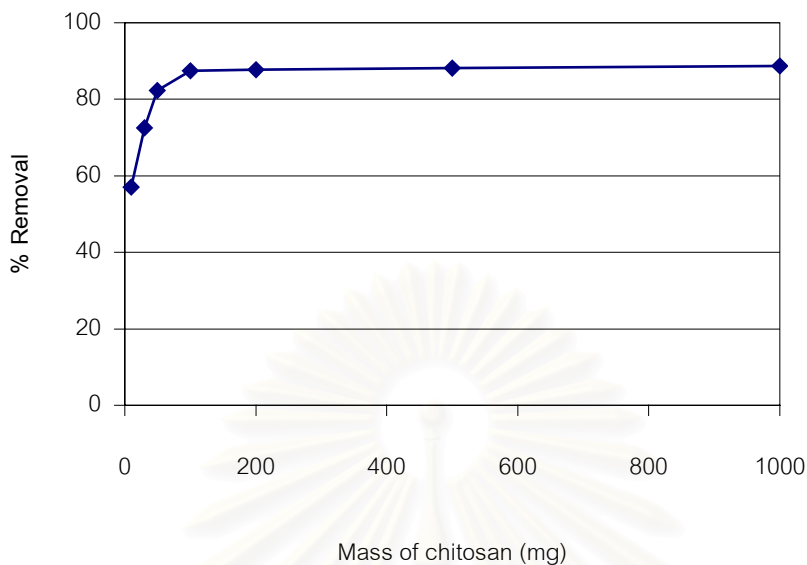
**Figure 4.3:** Scanning electron micrographs of chitosan bead and crosslinked chitosan bead. (a) whole view of the TPP-chitosan bead. (b) cross-section view of TPP-chitosan bead (c) whole view of the crosslinked chitosan bead. (d) cross-section view of crosslinked chitosan bead.

## 4.2 Effect of Adsorbent Dosage

In order to find an appropriate amount of chitosan, the amount of doses (10-1000 mg for flake and 1-5 g for bead and crosslinked form) were varied at constant pH 7 and the concentration of either reactive or acid dyeing wastewater was kept constant at 30 mg/l. **Figure 4.4** shows the percentage of reactive dyestuff removal at different dose of chitosan flake for 24 hours-contact time. The adsorption capacity increased significantly with the increase in chitosan dosage from 10-100 mg., after that the adsorption capacity remained unchanged. The removal of acid dye AB 129 showed the similar result as the reactive dye (**Figure 4.5**).

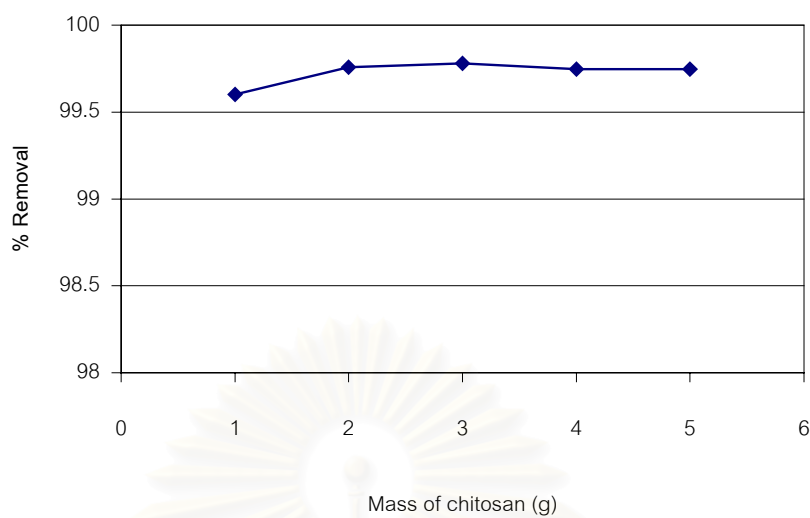


**Figure 4.4:** The dye removals of wastewater at pH 7 and initial reactive dye concentration of 30 mg/l for 24 h-contact time by using chitosan flake at various doses.

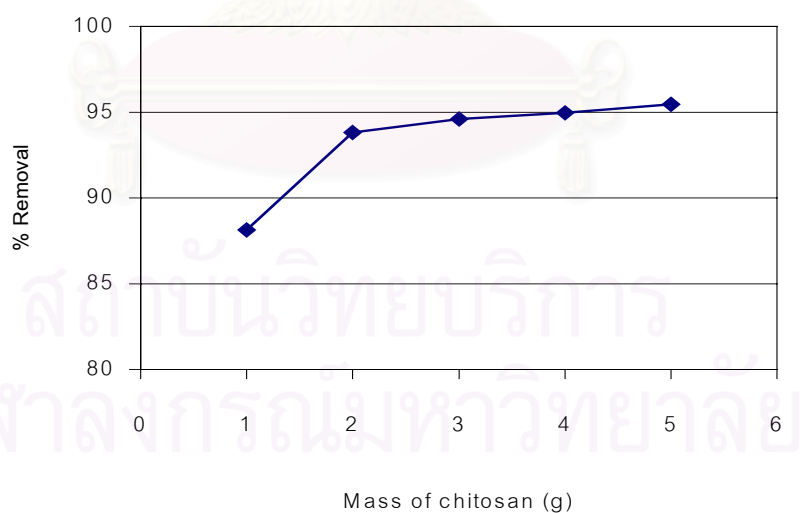


**Figure 4.5:** The dye removals of wastewater at pH 7 and initial acid dye concentration of 30 mg/l for 24 h-contact time by using chitosan flake at various doses.

**Figure 4.6** shows the removal of RR 120 by using chitosan bead for 24 h-contact time at dosage of 1-5 g. The adsorption capacity increased significantly with increasing chitosan dosage from 1 to 2 g, and slightly increased with increasing chitosan dosage from 2 to 5 g. The crosslinked chitosan bead showed the same result as non-crosslinked chitosan bead. The acid dye AB 129 also had the similar result in removing of dye for both chitosan bead and crosslinked chitosan bead as presented in **Figure 4.7**. Hence, from Figure 4.4 to 4.7 the appropriate amount of chitosan, 100 mg for flake and 2 g for bead and crosslinked bead were used in the following experiments.



**Figure 4.6:** The dye removals of wastewater at pH 7 and initial reactive dye concentration of 30 mg/l for 24 h-contact time by using TPP-chitosan bead at various doses.



**Figure 4.7:** The dye removals of wastewater at pH 7 and initial acid dye concentration of 30 mg/l for 24 h-contact time by using TPP-chitosan bead at various doses.

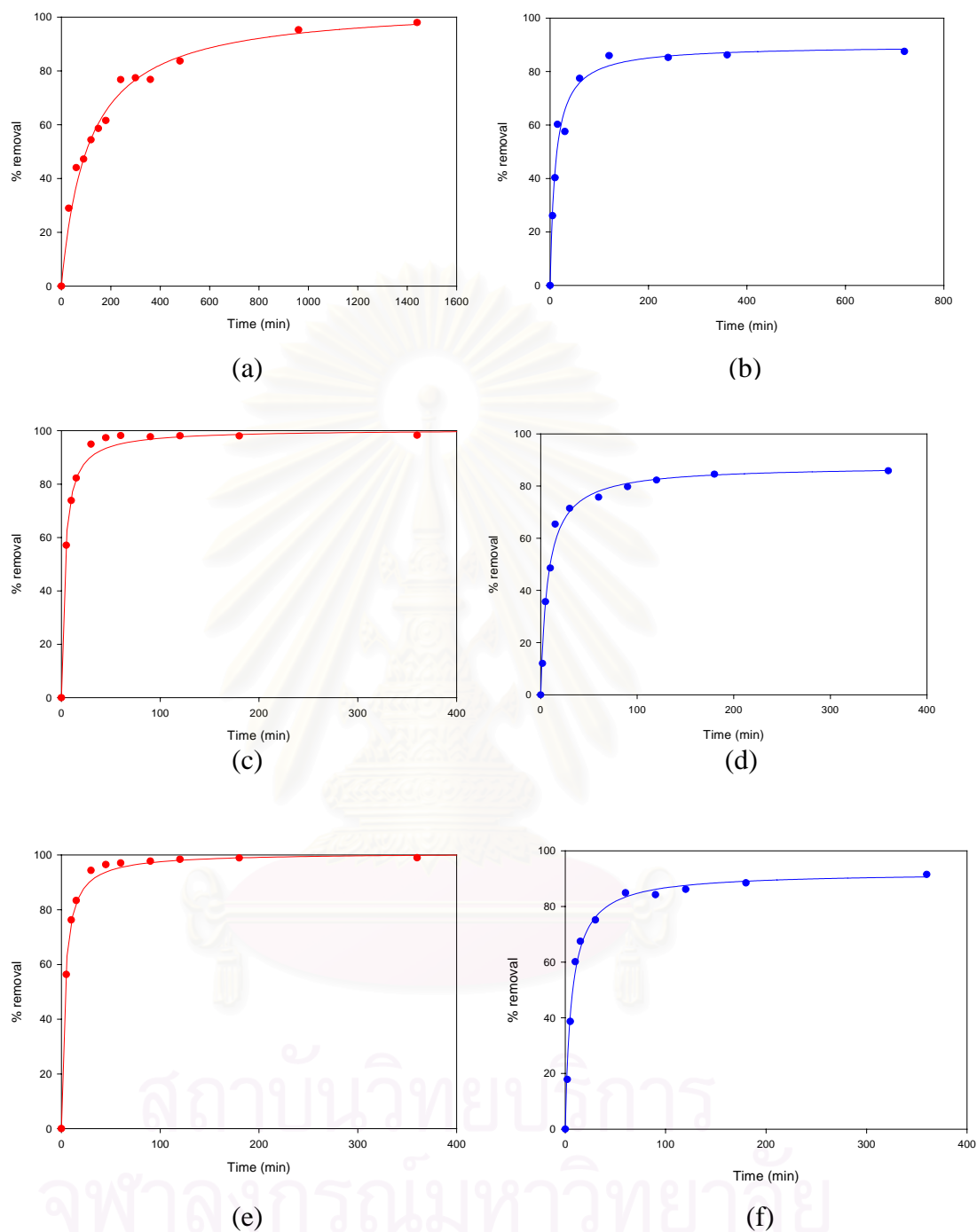
### 4.3 Equilibrium Time on Dyes Removal

**Figure 4.8** shows the sorption equilibrium of chitosan in different forms. All adsorbents showed their ability to adsorb the dye with various efficiencies. At pH 7 and the concentration of either reactive or acid dyeing wastewater was at 30 mg/l, chitosan in each form exhibited almost 100% of dye removal. The same result was observed when dye concentration was 100 mg/l, these chitosans also yielded the high efficiency in removal of dyes (**Figure 4.9**).

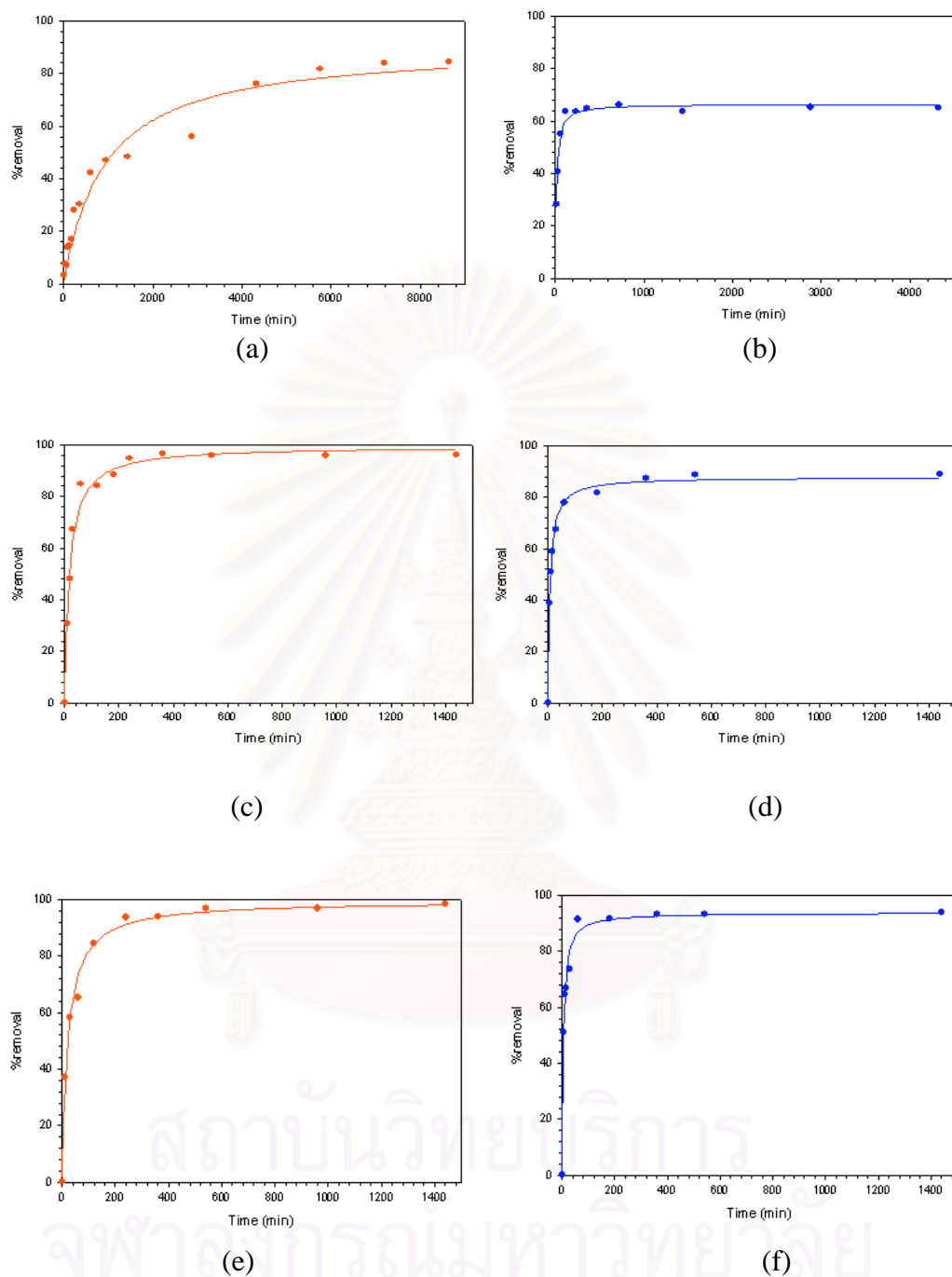
A steep sloped curve of chitosan-adsorbents indicates instantaneous sorption capacity. The plots present three distinct regions in which the first region (initial steep slope) indicates the immediate sorption of the dye molecules. This may be due to the interaction of dye molecules with the chitosan surface. The second region shows a gradual attainment of the equilibrium, it indicates the utilization of all active sites on chitosan surface. The last region of the plots shows the attainment of equilibrium of dye molecules with chitosan, in this region, the adsorption is relatively insignificant.

The sorption equilibrium of chitosan flake, chitosan bead and crosslinked chitosan bead was achieved in 6 hours, 60 minutes and 50 minutes, respectively for Reactive Red 120. For Acid Blue 129, the sorption equilibrium of chitosan flake, chitosan bead and crosslinked chitosan bead was achieved in 2 hours, 45 minutes and 30 minutes, respectively.

The adsorption of AB 129 dyeing wastewater reached equilibrium at shorter time than RR 120. This may be due to the dye's structures (**Figure 3.2** and **Figure 3.3**); AB 129 has a small dye molecule, while RR 120 has a large dye molecule. Therefore, AB 129 has higher ability to diffuse and adsorb on chitosan than RR 120.



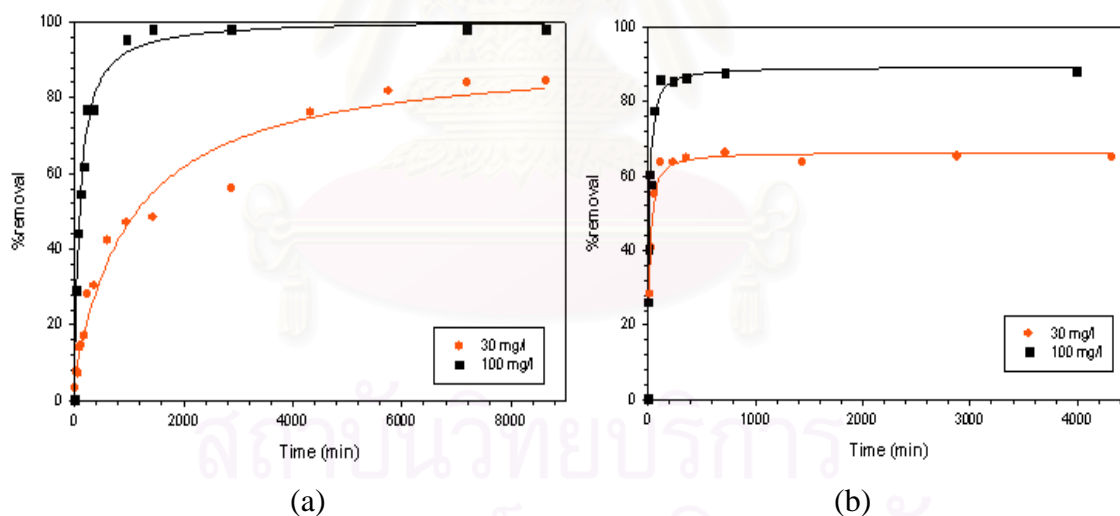
**Figure 4.8:** The adsorption equilibrium of chitosan in each form for 100 mg of chitosan flake, and 2 g chitosan bead and crosslinked forms at pH 7 and 30 mg/l dyeing wastewater (a) RR 120-flake (b) AB 129-flake (c) RR 120-bead (d) AB 129-bead (e) RR 120-crosslinked bead and (f) AB 129-crosslinked bead



**Figure 4.9:** The adsorption equilibrium of chitosan in each form for 100 mg of chitosan flake, and 2 g chitosan bead and crosslinked forms at pH 7 and 100 mg/l dyeing wastewater (a) RR 120-flake (b) AB 129-flake (c) RR 120-bead (d) AB 129-bead (e) RR 120-crosslinked bead and (f) AB 129-crosslinked bead

#### 4.4 Effect of Initial Dye Concentration

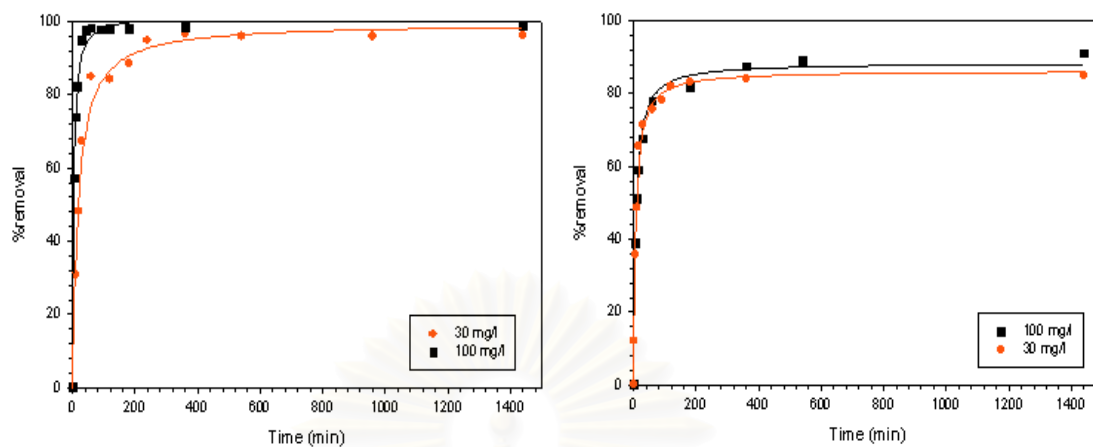
**Figure 4.10** shows the effect of initial dye concentration on the adsorption of 100-mg chitosan flake at pH 7 for the Reactive Red 120 and Acid Blue 129. An increase in the initial dye concentration leads to an increase in the adsorption capacity of dye on chitosan. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration. The same phenomenon was also observed in TPP-chitosan bead and crosslinked chitosan bead as shown in **Figure 4.11** and **Figure 4.12**, respectively. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dyes on chitosan.



**Figure 4.10:** The adsorption of Reactive Red 120 and Acid Blue 129 on 100 mg chitosan flake at pH 7 and various initial dye concentrations.

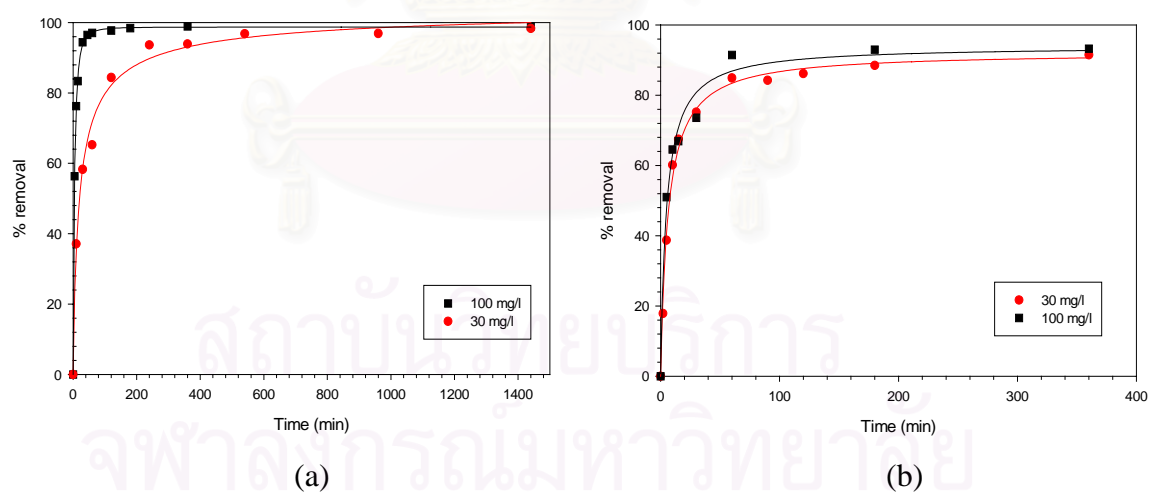
(a) Reactive Red 120 (b) Acid Blue 129





**Figure 4.11:** The adsorption of Reactive Red 120 and Acid Blue 129 on 2 g TPP-chitosan bead at pH 7 and various initial dye concentrations.

(a) Reactive Red 120 (b) Acid Blue 129

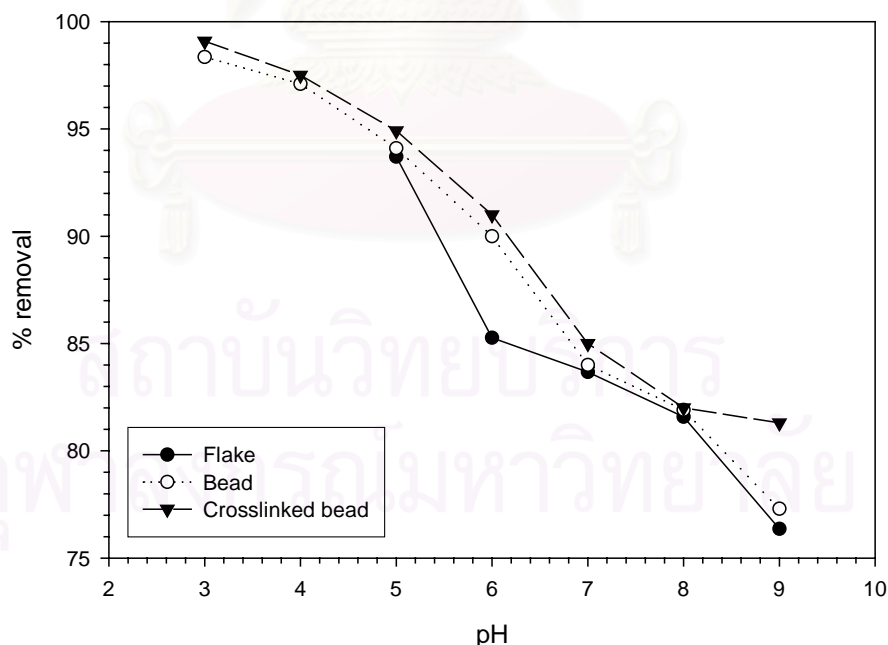


**Figure 4.12:** The adsorption of Reactive Red 120 and Acid Blue 129 on 2 g crosslinked chitosan bead at pH 7 and various different initial dye concentrations. (a) Reactive Red 120 (b) Acid Blue 129

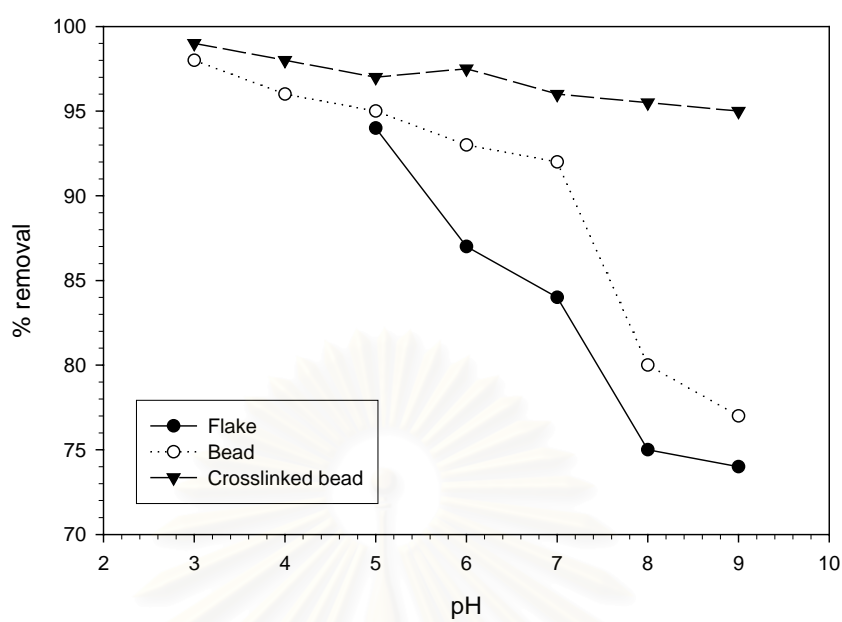
## 4.5 Influence of pH on Adsorption Capacity

The effect of solution pH on the dye removal by chitosan is shown in **Figure 4.13** to **Figure 4.16**. The adsorption capacity of chitosan increased significantly with decreasing pH. At low pH, the amino groups of chitosan ( $-NH_2$ ) are much easily protonated to form  $-NH_3^+$ . The high adsorption capacity was due to the strong electrostatic interaction between the  $-NH_3^+$  groups of chitosan and dye anions.

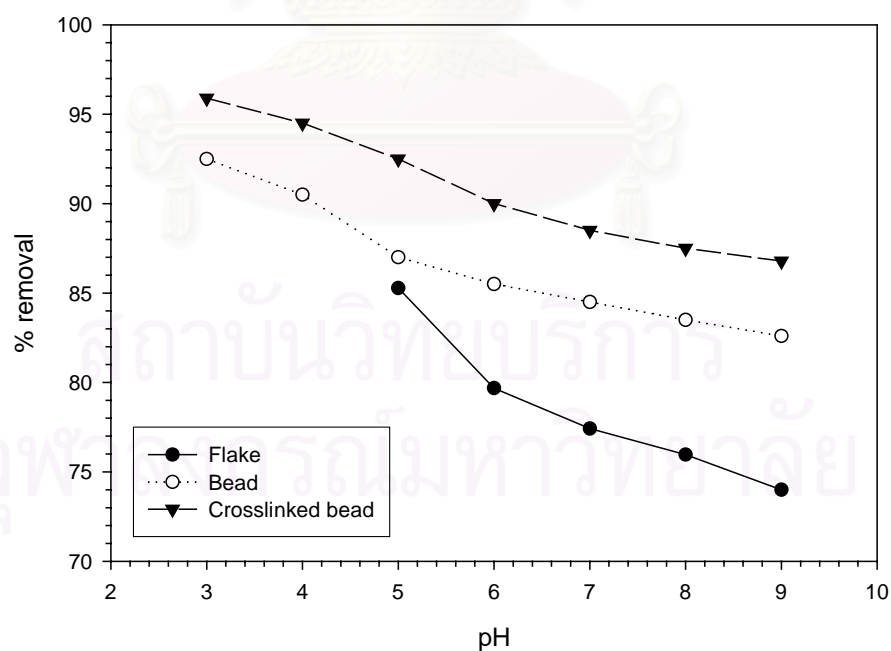
This result agrees with Yoshida et al. (1993) and Chiou and Li (2003). Furthermore, the time to achieve equilibrium decreased with decreasing solution pH as shown in **Figure 4.17**. At pH 3, the time to reach equilibrium of Acid Blue 129 was about 30 minutes, while at pH 9, the equilibrium time was about 90 minutes. The similar result was also observed for Reactive Red 120 (**Figure 4.18**). This indicates that pH of the wastewater is the important factor for the dye removal by chitosan.



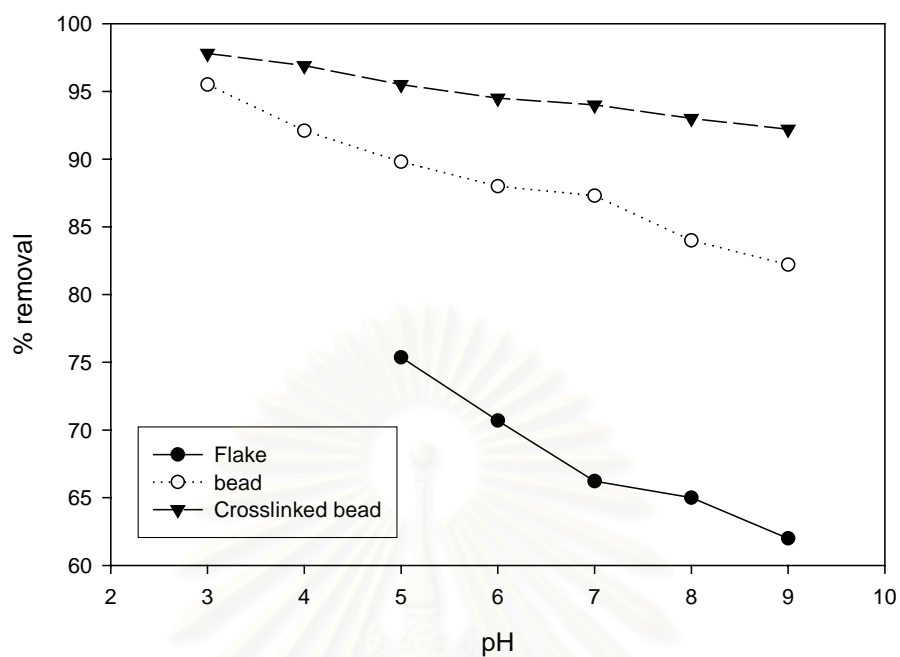
**Figure 4.13:** Effect of pH on the dye removal by chitosan in each form, initial RR 120 concentration is 30 mg/l



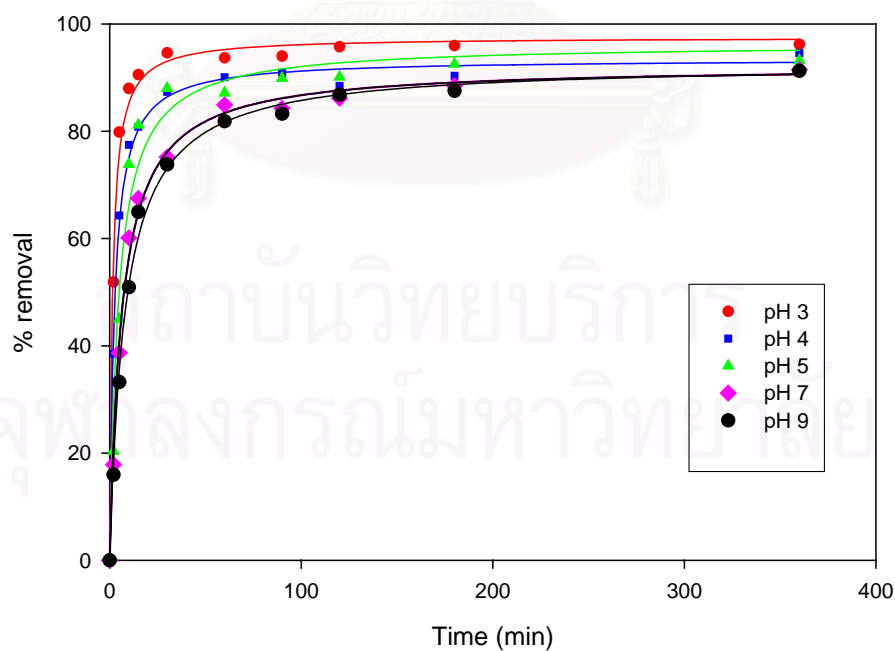
**Figure 4.14:** Effect of pH on the dye removal by chitosan in each form, initial RR 120 concentration is 100 mg/l



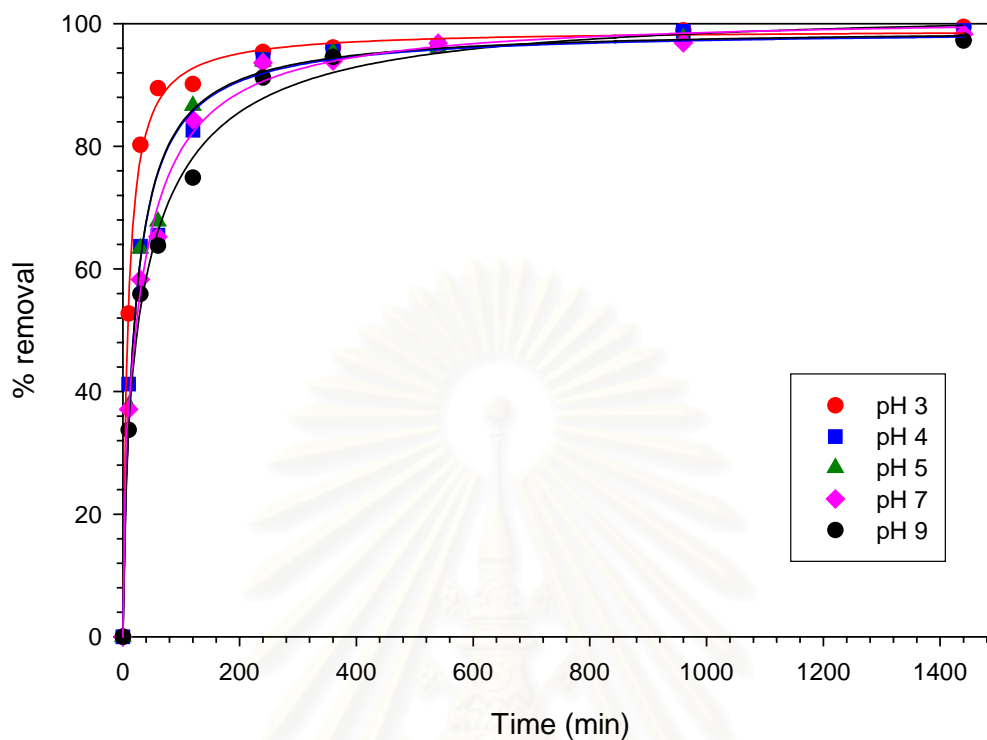
**Figure 4.15:** Effect of pH on the dye removal by chitosan in each form, initial AB 129 concentration is 30 mg/l



**Figure 4.16:** Effect of pH on the dye removal by chitosan in each form, initial AB 129 concentration is 100 mg/l



**Figure 4.17:** The adsorption of dye on crosslinked chitosan bead at various pH, initial AB 129 concentration is 100 mg/l



**Figure 4.18:** The adsorption of dye on crosslinked chitosan bead at various pH, initial RR 120 concentration is 100 mg/l

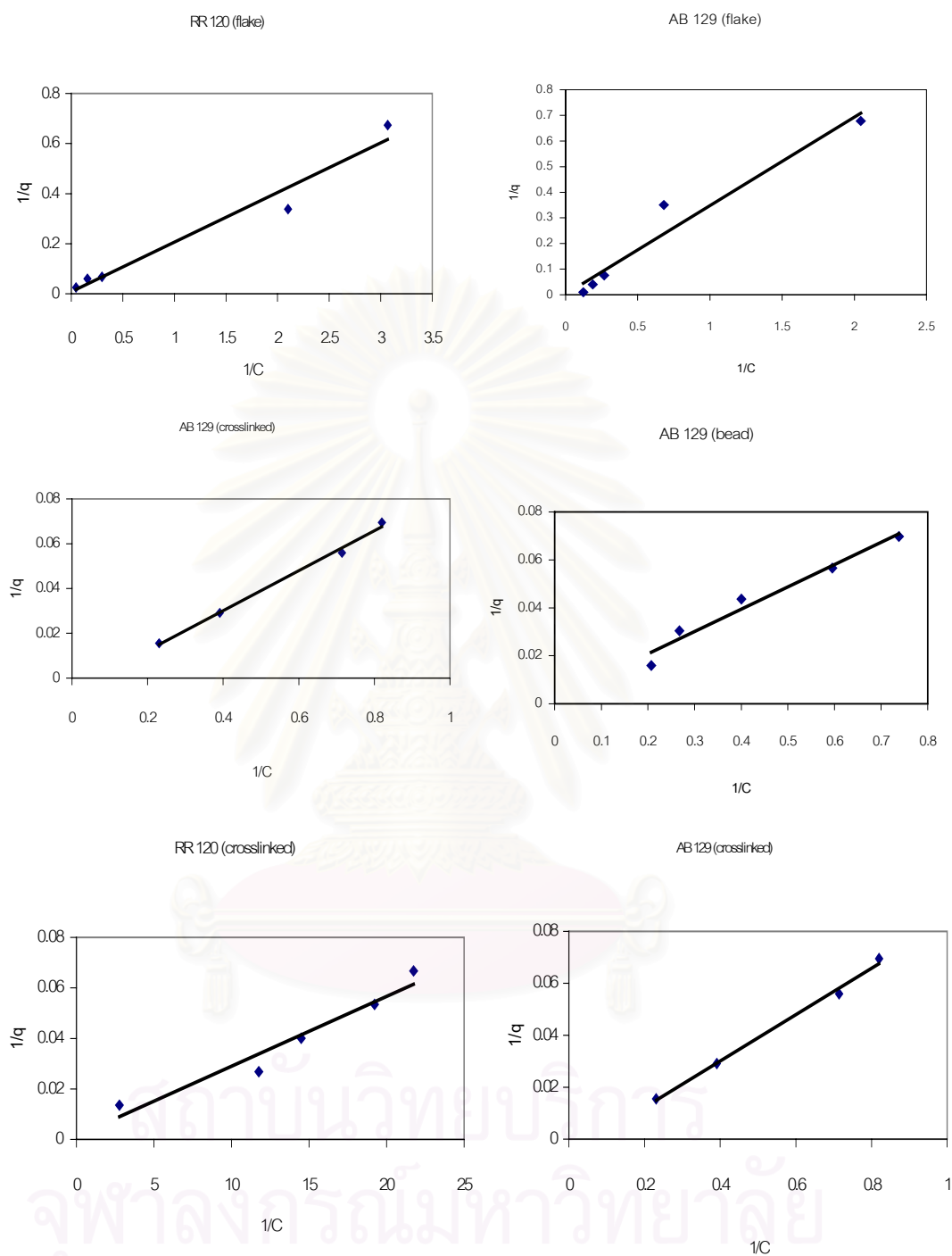
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## 4.6 Equilibrium Isotherms

By comparing the results listed in **Table 4.2**, it is shown that the Langmuir sorption isotherm can accurately describe the sorption of Reactive Red 120 and Acid Blue 129 on to chitosan in this study. The correlation coefficient ( $R^2$ ) obtained from Langmuir sorption isotherm is higher than that obtained from Freundlich sorption isotherm. The plots of linear transformation of Langmuir equation were shown in **Figure 4.19**. From Q value, it is noticed that the adsorption capacity of dye onto crosslinked chitosan bead is higher than TPP-bead and flake forms, respectively.

**Table 4.2:** Langmuir and Freundlich isotherm constants

Chitosan	Langmuir			Freundlich		
	Q (mg/g)	b(l/g)	$R^2$	$K_F$ (l/g)	n	$R^2$
Reactive Red 120						
Flake	333	0.448	0.99	5.9	1.96	0.73
Bead	500	0.003	0.98	143.5	1.51	0.90
Crosslinked bead	909	0.003	0.98	171	1.37	0.92
Acid Blue 129						
Flake	323	0.345	0.95	2.7	0.69	0.91
Bead	476	0.093	0.97	9.8	0.95	0.93
Crosslinked bead	833	0.082	0.99	11.4	0.92	0.89



**Figure 4.19:** Langmuir isotherm linear plots for the adsorption of RR 120 and AB 129 on chitosan at pH 7 and concentration at 30 mg/l.

The essential features of Langmuir adsorption isotherm can be expressed in terms of an dimensionless constant separation or equilibrium parameter ( $R_L$ ), which is expressed by the following equation

$$R_L = \frac{1}{1 + bC_0} \quad (4.1)$$

where  $C_0$  is the initial dye color concentration (mg/l) and  $b$  the Langmuir's adsorption constant (l/mg). By processing the above equation, the  $R_L$  values for investigated reactive dye-sorbents on chitosan flake, chitosan bead and crosslinked chitosan bead were 0.14, 0.93, and 0.92, respectively. And the  $R_L$  values for investigated acid dye-sorbents system on chitosan flake, chitosan bead and crosslinked chitosan bead were 0.09, 0.26 and 0.29, respectively. From the separation factor ( $R_L$ ) values, it is conformed that the dye-chitosan adsorption system was of 'favorable isotherm shape' indicating the favorable sorption of dye on chitosan sorbents (since  $R_L$  values fall in the range of 0 to 1).

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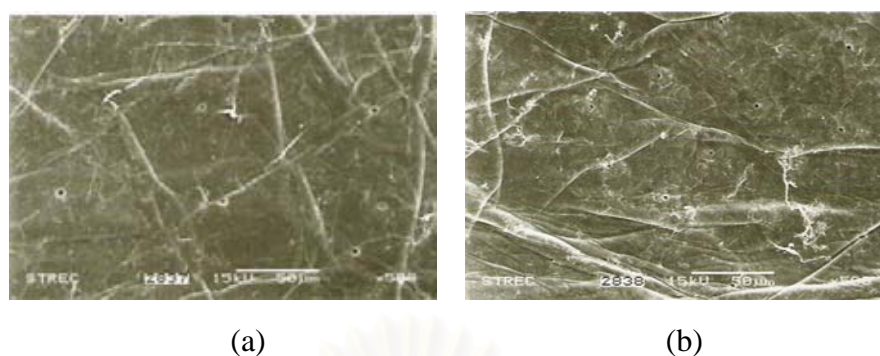
## 4.7 Comparison of the Adsorption Capacity of Chitosan

All adsorbents showed their ability to remove dye with various efficiencies. Among these, crosslinked chitosan bead had the highest efficiency to remove both reactive and acid dye from aqueous solution, followed by chitosan TPP-bead and chitosan flake, respectively.

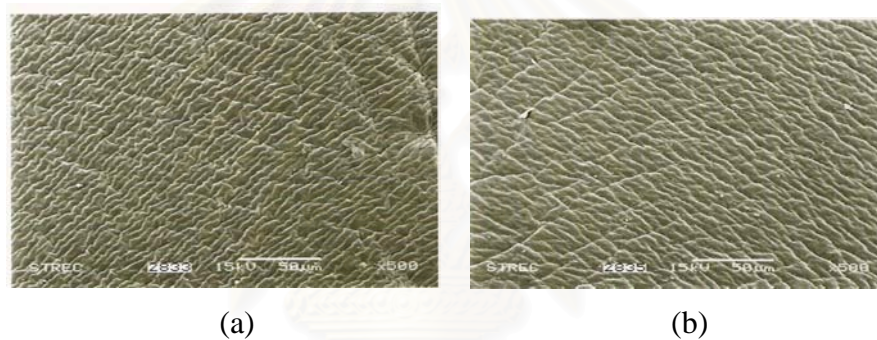
The adsorption capacity of crosslinked chitosan bead for reactive dye was 909 mg/g, while chitosan bead and chitosan flake was 500 and 333 mg/g, respectively. For acid dye, the adsorption capacity of crosslinked chitosan bead was 833 mg/g, while chitosan bead and chitosan flake was 476 and 323 mg/g, respectively.

Differential sorption capacities of chitosan in each form may perhaps due to their sorption area, i.e. more loose pore structure. From **Table 4.1**, crosslinked chitosan bead has higher BET surface area than the non-crosslinked chitosan bead and flake. The outer surfaces of each form of chitosan are shown in **Figure 4.20** to **Figure 4.22**. After dye adsorption, a significant change is observed in outer surface of crosslinked chitosan bead. The outer surface appears smoother than that before adsorption because it is partially covered by dye molecules. While there are no significant change observed in flake and bead forms. Thus, crosslinked chitosan bead and non-crosslinked chitosan bead were selected for the continuous mode experiment.

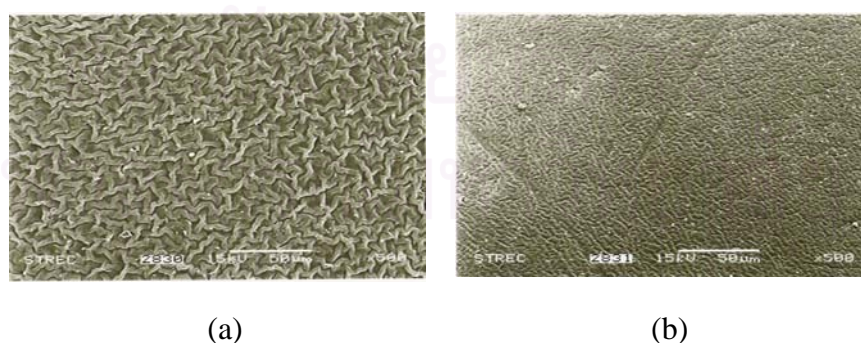
**Table 4.3** lists the comparison of adsorption capacity of dyes on various adsorbents. Compared with some data in literature, chitosan in this study have relatively high adsorption capacity for RR 120 and AB 129.



**Figure 4.20:** SEM images for chitosan flake, (a) chitosan flake before adsorption  
(b)chitosan flake after adsorption RR 120



**Figure 4.21:** SEM images for chitosan TPP-bead, (a) chitosan TPP-bead before  
adsorption (b)chitosan TPP-bead after adsorption RR 120



**Figure 4.22:** SEM images for crosslinked chitosan bead, (a) crosslinked chitosan bead  
before adsorption (b) crosslinked chitosan chitosan bead after adsorption  
RR120

**Table 4.3:** Comparison of the adsorption capacity of dye on various adsorbents

<b>Dyes</b>	<b>Adsorbents</b>	<b>Adsorption capacity (mg/g)</b>	<b>References</b>
RR 120	Chitosan flake	333	This work
RR 120	Chitosan bead (non-crosslinked)	500	This work
RR 120	Chitosan bead (crosslinked)	909	This work
AB 129	Chitosan flake	323	This work
AB 129	Chitosan bead (non-crosslinked)	476	This work
AB 129	Chitosan bead (crosslinked)	833	This work
RR 222	Chitosan flake	494	Wu et al. (2000)
RR 189	Chitosan bead (crosslinked)	1642	Chiou and Li (2002)
AG 25	Chitosan powder	645	Wong et al. (2004)
DY 44	Chitin	256	Kim et al. (1997)
Safranin	Cotton waste	875	McKay et al. (1999)
BY 28	Soil/fly ash	288	Albanis et al. (2000)
AB 9	Activated clay/carbon	54	Ho and Chiang (2001)
Direct Brown	Coal	7	Mohan et al. (2002)
Reactive dyes	Barley husks	19	Robinson et al. (2002)
Methyl Orange	Banana peel	21	Annadurai et al. (2002)
Brilliant Green	Neem leaves	216	Bhattacharyya and Sarma (2003)

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## 4.8 Column Studies

The optimal condition (pH 3 and 100 mg/l of dyestuff solution) obtained from the batch mode experiment was applied in the continuous experiment.

To study the effect of the bed depth on dye adsorption, the flow rate was constant at 1 ml/min, while the bed depth was varied at 2.5 and 6.5 cm. In the case of flow rate effect, the bed depth was 2.5 cm, while the flow rate was varied at 1 and 10 ml/min. The column apparatus is shown in **Figure 4.23**.



**Figure 4.23:** The column experiment

Experimental results were obtained by measuring the concentration of dye at various bed depths, flow rates and times. The experimental data were plotted as breakthrough curves in term of dimensionless concentration,  $C/C_0$  versus time,  $t$  (h), where  $C$  is the outlet concentration of dye at time  $t$  and  $C_0$  is the inlet concentration of dye. A typical set of adsorption results is presented in **Figure 4.24** and **Figure 4.25** for Reactive Red 120 and Acid Blue 129, respectively.

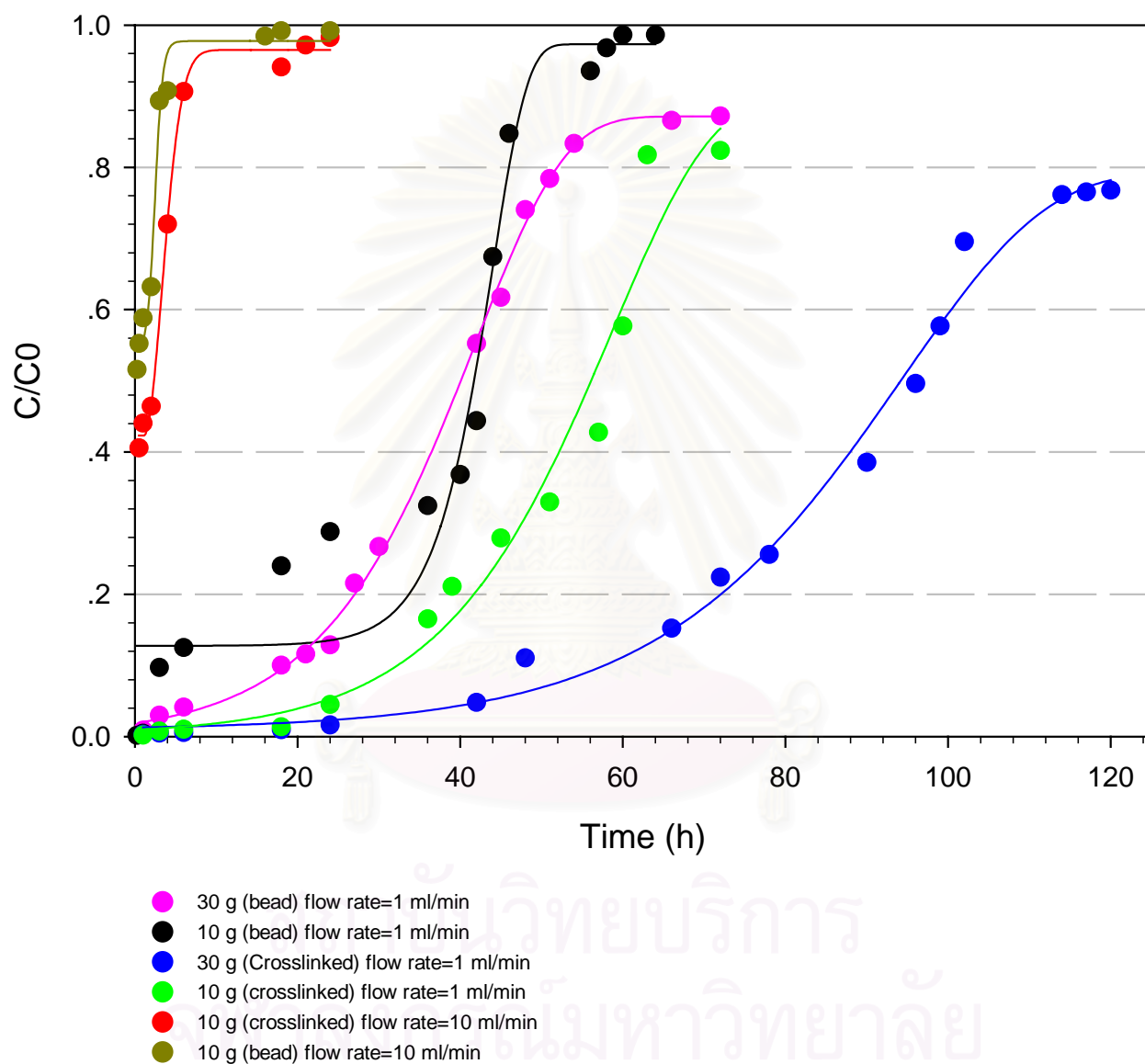
Initially, most dye was adsorbed, so the solute concentration in the effluent was low. As adsorption continued, the effluent concentration rised, slowly at first but then abruptly. The general behavior of the breakthrough curve depends on the capacity of the column with respect to the bed height and flow rate.

When the flow rate of feed dye solution keep constant at 1 ml/min., for chitosan in either bead or crosslinked form, breakthrough time increased with increasing chitosan from 10 to 30 g. When the amount of chitosan in each form was at 10 g, the short breakthrough time can be achieved when the flow rate of feed dye solution is high.

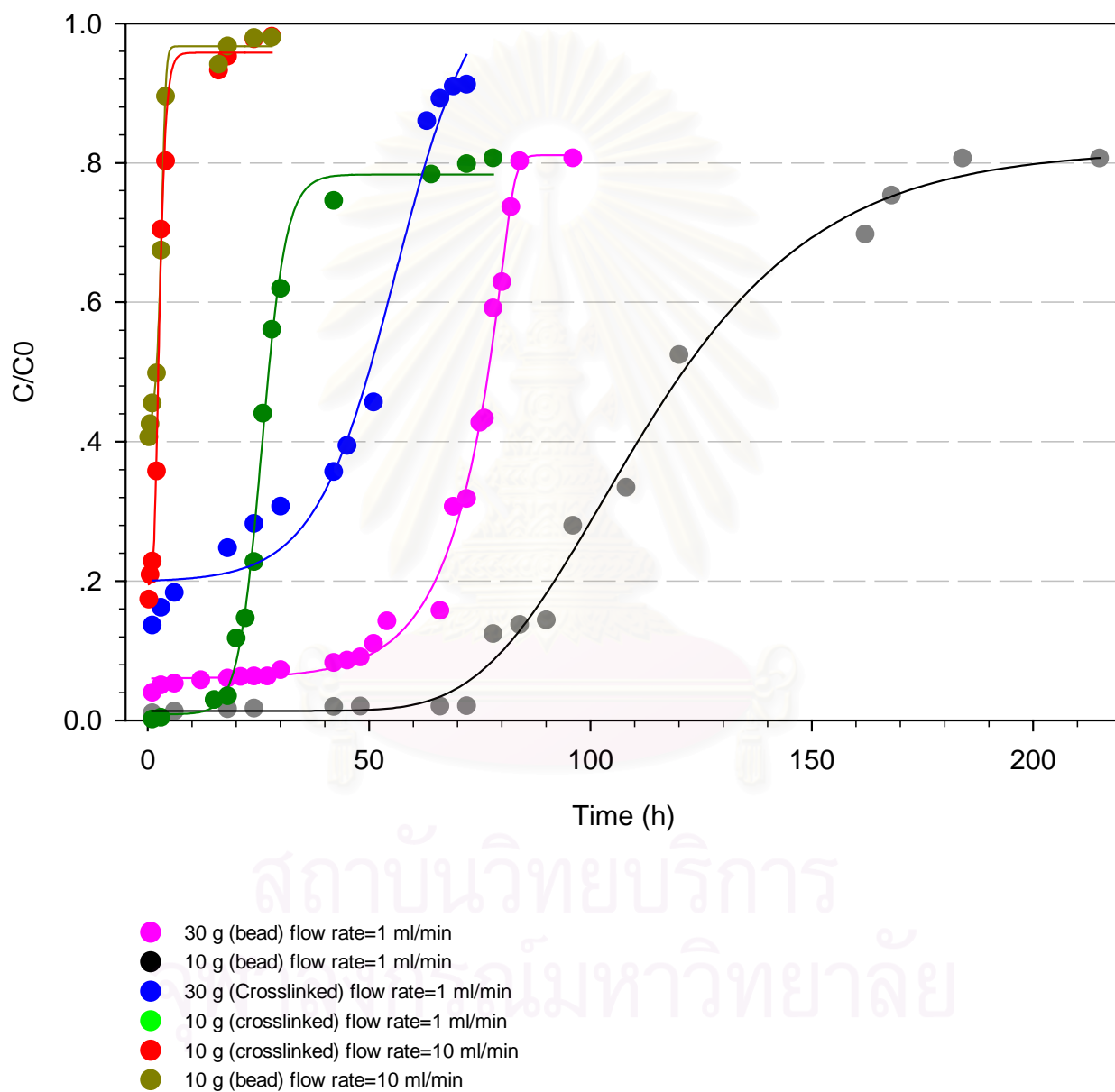
### 4.8.1 Effect of Bed Height

To study the effect of the bed height on dye removal, chitosan bead and crosslinked chitosan bead was varied at 6.5 and 2.5 cm bed height. The breakthrough curves for adsorption of Reactive Red 120 and Acid Blue 129 are shown in **Figure 4.26** and **Figure 4.27**, respectively. The 50% breakthrough was chosen as an indicator to characterize the performance of fixed bed adsorbers.

As can be seen from the results, an increase in the bed height from 2.5 to 6.5 cm, the breakthrough curves become s-shape and the breakthrough time was longer (**Table 4.3**). During the continuous mode operation, a chitosan bed consists of three zones. The main adsorption occurs in zone, called mass transfer zone (MTZ). After the mass transfer zone, the chitosan is saturated with dye. Above MTZ, the bed is essentially free of dye. Then the MTZ height is presented in **Table 4.4**. When feed concentration of RR 120 and AB 129 are 100 mg/l at flow rate of 1 ml/min., MTZ increased with the bed depth.

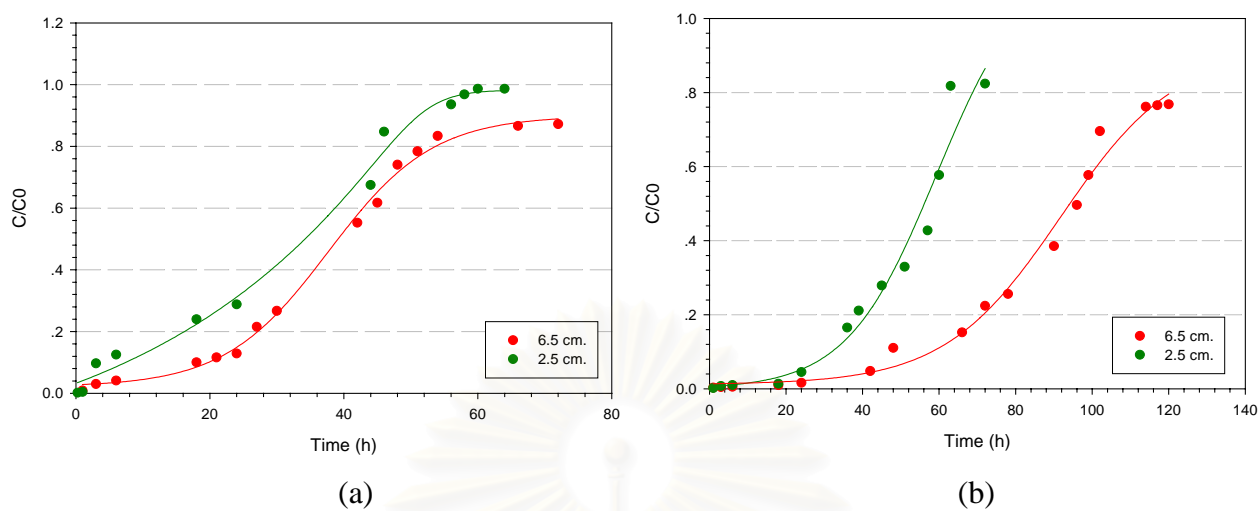


**Figure 4.24:** Breakthrough curves for adsorption of Reactive Red 120 at initial dye concentration of 100 mg/l and pH 3

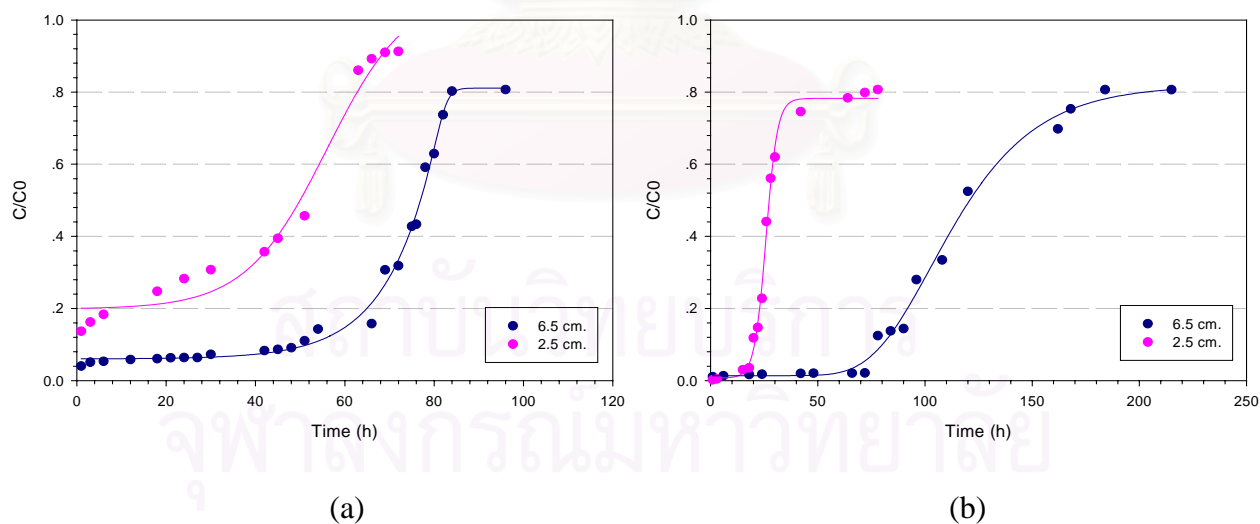


**Figure 4.25:** Breakthrough curves for adsorption of Acid Blue129 at initial dye concentration of 100 mg/l and pH 3





**Figure 4.26:** Breakthrough curves for adsorption of RR 120 at feed concentration of 100 mg/l flow rate of 1 ml/min and pH 3 at different bed height (a) chitosan TPP-bead (b) crosslinked chitosan bead.



**Figure 4.27:** Breakthrough curves for adsorption of AB 129 at feed concentration of 100 mg/l flow rate of 1 ml/min and pH 3 at different bed height (a) chitosan TPP-bead (b) crosslinked chitosan bead.

**Table 4.4:** Time for 50% breakthrough in column experiment.

Adsorbents/Bed height	Time at 50% breakthrough (h)	
	RR 120	AB 129
Chitosan bead		
6.5 cm	39	76
2.5 cm	34	50
Crosslinked chitosan bead		
6.5 cm	92	120
2.5 cm	50	25

**Table 4.5:** Mass transfer zone at 50% breakthrough in column experiment.

Adsorbents/Bed height	Mass transfer zone (cm)	
	RR 120	AB 129
Chitosan bead		
6.5 cm	2.659	1.354
2.5 cm	0.8	0.484
Crosslinked chitosan bead		
6.5 cm	1.345	1.300
2.5 cm	0.379	0.417

#### 4.8.2 Effect of flow rate

The effect of flow rate on the dye removal was investigated at 1 and 10 ml/min and the bed height was kept constant at 2.5 cm. **Figure 4.28** and **Figure 4.29** show the effect of flow rates on dyes removal, as the flow rate increased, the breakthrough curves became steeper. The 50% breakthrough time decreased (**Table 4.5**). At higher flow rate, the contact time of dye with chitosan is very short, resulted in a reduction in removal efficiency.

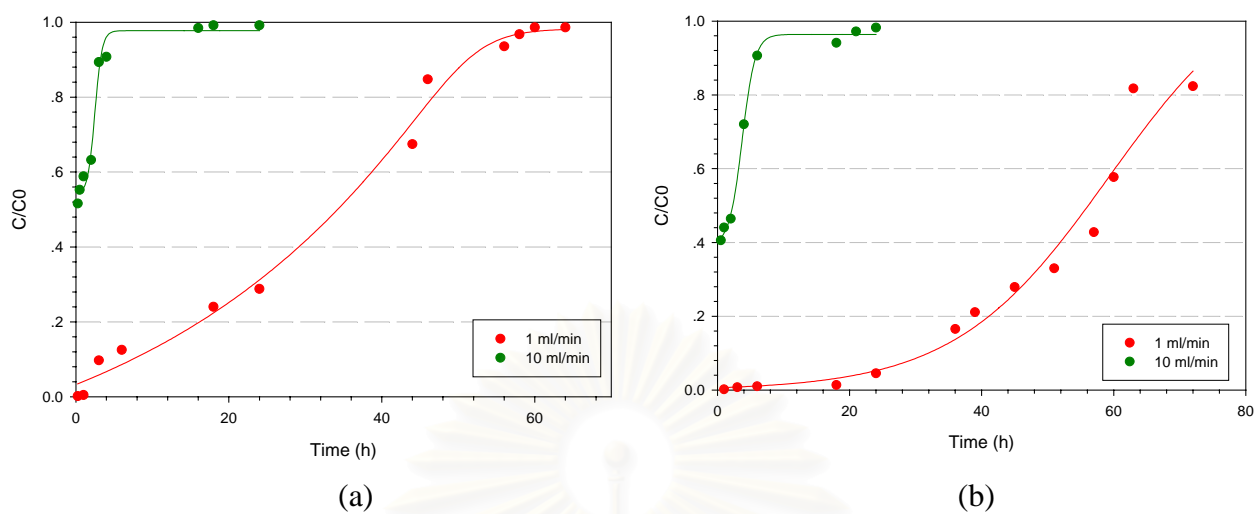
It is obvious that a larger MTZ is presented when a higher flow rate is operated as shown in **Table 4.6**. It resulted in the decreased chitosan bed life and can imply that the lower velocity gave a good adsorption capacity. Considering either RR 120 or AB 129 adsorption, crosslinked chitosan bead gave a smaller MTZ than chitosan bead. Thus, the crosslinked form has a higher performance of dye adsorption than bead form.

**Table 4.6:** Time for 50% breakthrough in column experiment.

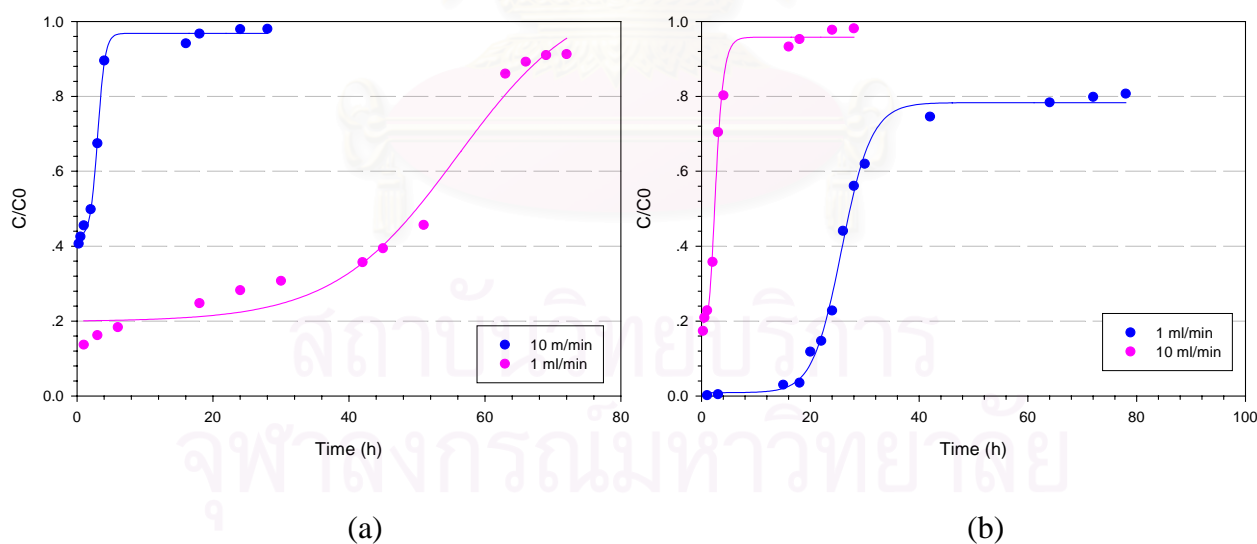
Adsorbents/Flow rate	Time at 50% breakthrough (h)	
	RR 120	AB 129
Chitosan bead		
1 ml/min	34	50
10 ml/min	1	2
Crosslinked chitosan bead		
1 ml/min	56	25
10 ml/min	2	2

**Table 4.7:** Mass transfer zone at 50% breakthrough in column experiment.

Adsorbents/Flow rate	Mass transfer zone (cm)	
	RR 120	AB 129
Chitosan bead		
1 ml/min	0.8	0.484
10 ml/min	1.875	0.833
Crosslinked chitosan bead		
1 ml/min	0.379	0.417
10 ml/min	1.25	0.833



**Figure 4.28:** Breakthrough curves for adsorption of RR 120 at feed concentration of 100 mg/l 2.5 cm bed height and pH 3 at different flow rate (a) chitosan TPP-bead (b) crosslinked chitosan bead.



**Figure 4.29:** Breakthrough curves for adsorption of AB 129 at feed concentration of 100 mg/l 2.5 cm bed height and pH 3 at different flow rate (a) chitosan TPP-bead (b) crosslinked chitosan bead.

## Chapter V

### Conclusions

In this study, the decolorization of Reactive Red 120 and Acid Blue 129 using chitosan prepared from dried-shrimp shell was investigated in both batch and continuous modes. The experiments could be divided into three parts, adsorbent preparation, batch experiments, and column study. The experiments started with preparation of chitosan from dried-shrimp shell followed by bead formation and crosslinking by glutaraldehyde. The efficiency of chitosan in each form was determined in the batch experiments, effect of solution's pH and dyeing concentration were also studied. Experimental data were then fitted to either Langmuir or Freundlich isotherm to determine which isotherm gave the best correlation fitted by experimental data. The optimal condition obtained from a batch mode was applied in a continuous mode. Lastly the continuous experiment was conducted in a glass column with 2.5-cm diameter and 20-cm height. The effect of bed depth and flow rate was investigated. From the experimental results obtained in this study, the conclusions are as follows:

1. The degree of deacetylation (DD) of chitosan prepared from dried-shrimp shell was 92.8 and the molecular weight was 265078. The BET surface area for chitosan flake, KOH-chitosan bead, TPP-chitosan bead, KOH+TPP-chitosan bead and crosslinked chitosan bead, were 8.82, 31.26, 51.06, 46.08 and 168.85 respectively.

2. Among three types of chitosan beads, the more rigid TPP-chitosan bead not only had a higher efficiency for removal of RR 120 and AB 129 than KOH and KOH+TPP-beads but also was more practical in the adsorption process and even in storage and transport due to their hardness.

3. From the batch equilibrium studies, the time to reach equilibrium obtained from flake is higher than bead and crosslinked form, respectively.

4. At pH 7 and the concentration of reactive and acid dyeing wastewater were equal to 30 mg/l, chitosan in each form showed almost 100% dye removal. When concentration was 100 mg/l, these chitosans also exhibited the high efficiency in dye removal, 94% for AB 129 and 95% for RR 120.

5. Both the initial dye concentration and the pH of aqueous solutions significantly affected the adsorption capacity of dye on chitosan. An increase in the initial dye concentration led to an increase in the adsorption capacity of dye on chitosan. While the decrease in the pH of solutions led to a large increase in the adsorption capacity.

6. The adsorption of both RR120 and AB 129 on chitosan were well fitted to Langmuir isotherm. The maximum monolayer adsorption capacity (Q) of RR 120 on chitosan were quite high, 333 mg/g for flake, 500 mg/g for TPP-bead and 909 mg/g for crosslinked bead. For adsorption of AB 129, the maximum monolayer adsorption capacities were 323 mg/g for flake, 476 mg/g for TPP-bead and 833 mg/g for crosslinked forms.

7. By comparing the adsorption efficiency, the crosslinked chitosan bead had the highest efficiency for dye removal both reactive and acid dyes.

8. The decolorization of dyeing wastewater in the column experiment showed the high efficiency, and the adsorption capacity was strongly depended on flow rate and bed height of column.

9. The removal of dye onto chitosan provided their potential possibility for industrial pollution control.

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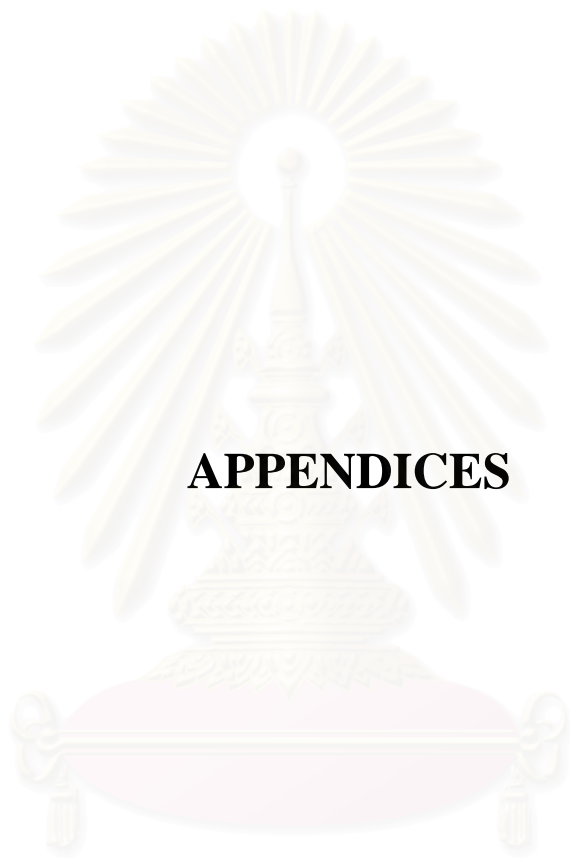


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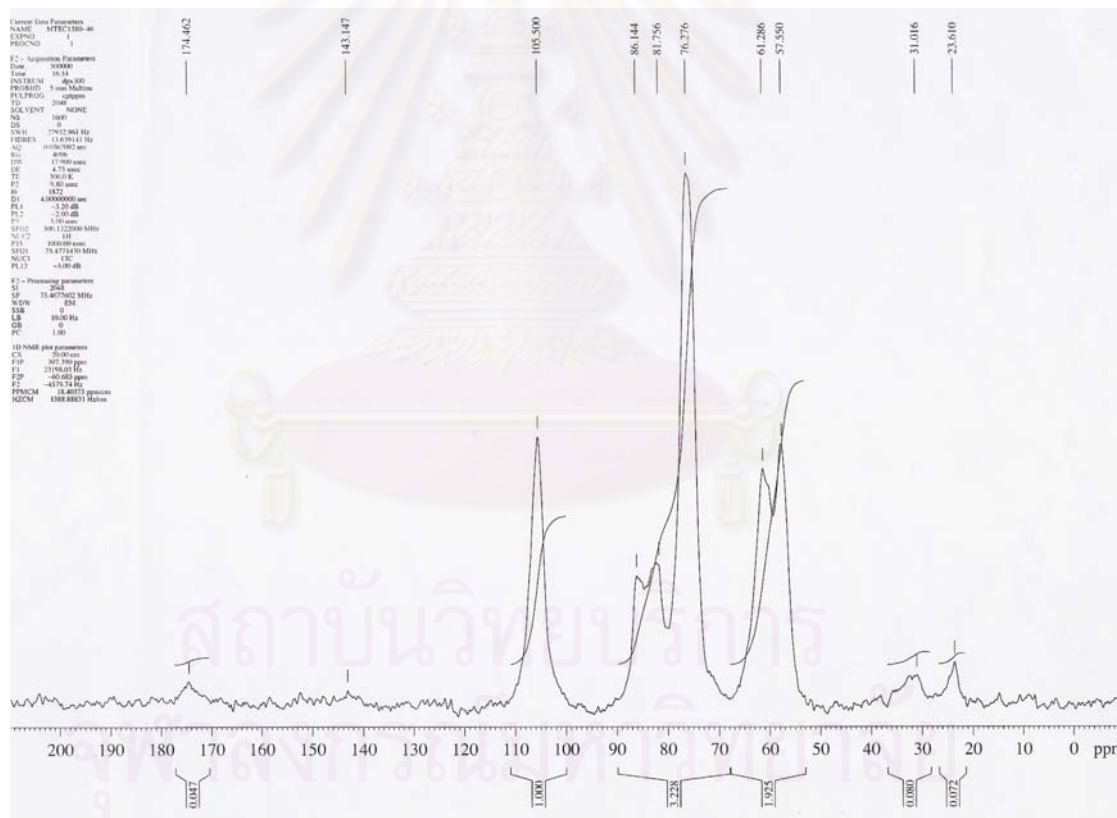
**APPENDICES**

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## Appendix A

### The determination of degree of deacetylation (DD)

The degree of deacetylation of chitosan in this work was determined by nuclear magnetic resonance (NMR) spectroscopy. **Figure A1** shows the NMR spectrum of chitosan. The degree of deacetylation of chitosan was 92.8.

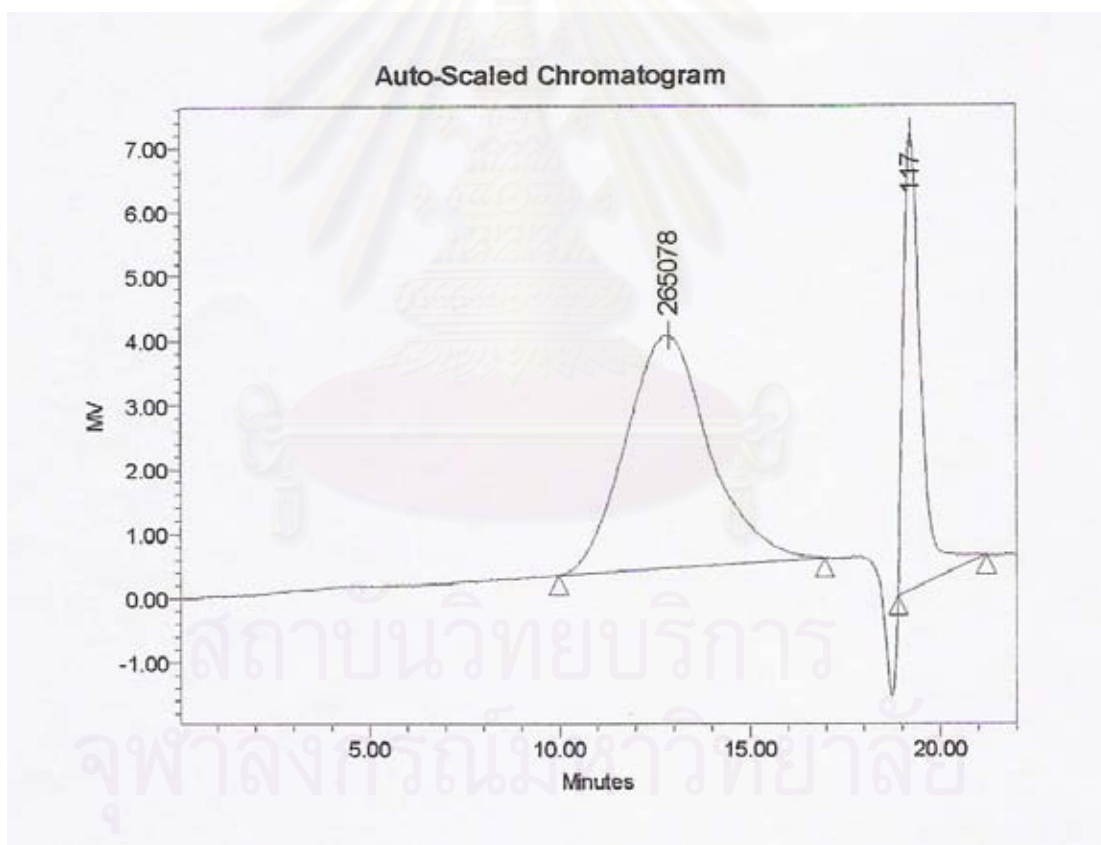


**Figure A1:** NMR spectrum of chitosan.

## Appendix B

### The determination of molecular weight

The molecular weight of chitosan in this work was determined by Gel Permeation Chromatography (GPC) method. **Figure B1** shows the GPC chromatogram of chitosan. The molecular weight of chitosan was 265078.



**Figure B1:** the GPC chromatogram of chitosan.

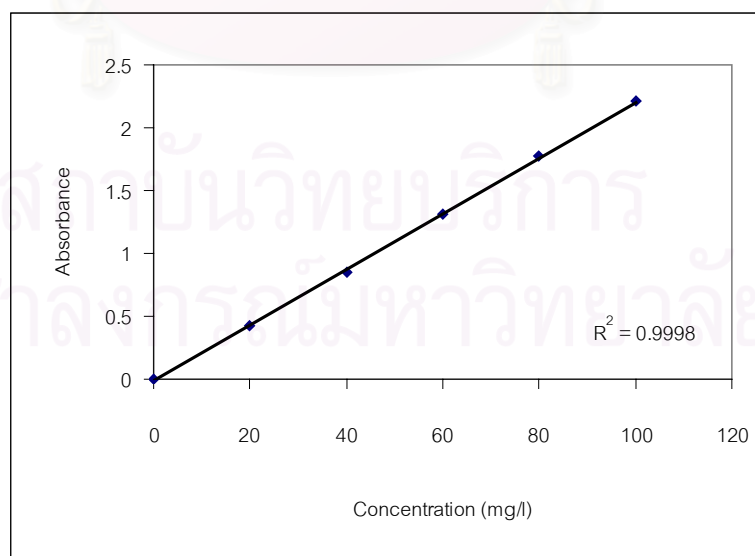
## Appendix C

### Calibration Curve of RR 120

**Table C1:** Relationship between concentration of RR 120 and absorbance at

$\lambda_{\max} = 536 \text{ nm}$ .

Concentration (mg/l)	Absorbance
0	0.000
20	0.426
40	0.854
60	1.309
80	1.771
100	2.209



**Figure C1:** Calibration Curve of RR 120

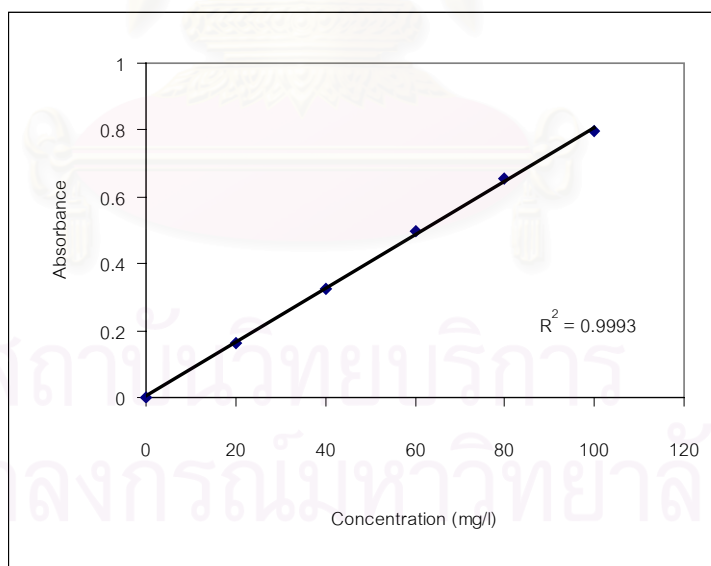


### Calibration Curve of AB 129

**Table C2:** Relationship between concentration of AB 129 and absorbance at

$$\lambda_{\max} = 629 \text{ nm.}$$

Concentration (mg/l)	Absorbance
0	0.000
20	0.162
40	0.327
60	0.495
80	0.653
100	0.795



**Figure C2:** Calibration Curve of AB 129

## Appendix D

### RR 120 Adsorption Calculation

$$\text{Dye adsorbed} = C_i - C_f$$

$$\% \text{ Removal} = (C_i - C_f) / C_i * 100$$

Where:  $C_i$  is initial concentration of dye solution (mg/l)

$C_f$  is final concentration of dye solution (mg/l)

#### Example:

At initial concentration of reactive red 120 is 30 mg/l, after adsorption the concentration of reactive red 120 is 15 mg/l

$$\begin{aligned} \text{Dye adsorbed} &= 30 - 15 \\ &= 15 \text{ mg/l} \end{aligned}$$

$$\begin{aligned} \% \text{ Removal} &= (30 - 15) / 30 * 100 \\ &= 50\% \end{aligned}$$

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**Table D1:** Equilibrium studies of RR 120 adsorption on chitosan flake

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
5	30	1.89	28.11	93.7
6	30	4.419	25.581	85.27
7	30	4.898	25.102	83.67
8	30	4.981	25.019	83.40
9	30	7.105	22.895	76.32
5	100	3.386	96.614	96.61
6	100	12.786	87.214	87.21
7	100	15.557	84.443	84.44
8	100	24.222	75.778	75.78
9	100	25.139	74.861	74.86

**Table D2:** Equilibrium studies of RR 120 adsorption on chitosan bead

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
3	30	0.493	29.507	98.36
4	30	0.594	29.406	98.02
5	30	0.693	29.307	97.69
7	30	0.789	29.211	97.37
9	30	0.895	29.105	97.02
3	100	1.83	98.17	98.17
4	100	2.593	97.407	97.41
5	100	3.464	96.536	96.54
7	100	4.074	95.926	95.93
9	100	12.763	87.237	87.24

**Table D3:** Equilibrium studies of RR 120 adsorption on crosslinked chitosan bead

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
3	30	0.273	29.727	99.09
4	30	0.555	29.445	98.15
5	30	0.668	29.332	97.77
7	30	0.89	29.11	97.03
9	30	1.007	28.993	96.64
3	100	0.518	99.482	99.48
4	100	1.21	98.79	98.79
5	100	2.298	97.702	97.70
7	100	3.125	96.875	96.86
9	100	4.176	95.824	95.82

Note: All data are presented in average form

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### **AB 129 Adsorption Calculation**

$$\text{Dye adsorbed} = C_i - C_f$$

$$\% \text{ Removal} = (C_i - C_f) / C_i * 100$$

Where:  $C_i$  is initial concentration of dye solution (mg/l)

$C_f$  is final concentration of dye solution (mg/l)

#### Example;

At initial concentration of acid blue 129 is 30 mg/l, after adsorption the concentration of reactive red 120 is 10 mg/l

$$\begin{aligned} \text{Dye adsorbed} &= 30 - 15 \\ &= 15 \text{ mg/l} \end{aligned}$$

$$\begin{aligned} \% \text{ Removal} &= (30 - 15) / 30 * 100 \\ &= 50\% \end{aligned}$$

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**Table D4:** Equilibrium studies of AB 129 adsorption on chitosan flake

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
5	30	2.237	27.763	92.54
6	30	2.989	27.011	90.04
7	30	3.755	26.245	87.48
8	30	4.029	25.971	86.57
9	30	4.819	25.181	83.94
5	100	23.422	76.578	76.58
6	100	27.86	72.14	72.14
7	100	35.013	64.987	94.99
8	100	36.151	63.849	63.85
9	100	37.101	62.899	62.90

**Table D5:** Equilibrium studies of AB 129 adsorption on chitosan bead

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
3	30	2.243	27.757	95.52
4	30	2.837	27.136	90.54
5	30	3.741	26.259	87.53
7	30	4.247	25.753	85.84
9	30	4.672	25.328	84.43
3	100	3.15	96.85	96.85
4	100	6.972	93.028	93.03
5	100	9.608	90.392	90.39
7	100	11.158	88.842	88.84
9	100	15.115	84.885	84.89

**Table D6:** Equilibrium studies of AB 129 adsorption on crosslinked chitosan bead

pH	C <sub>i</sub> (mg/l)	C <sub>f</sub> (mg/l)	Dye adsorbed (mg/l)	% Removal
3	30	1.146	28.854	96.18
4	30	1.637	28.363	94.54
5	30	2.046	27.954	93.18
7	30	2.557	27.443	91.48
9	30	2.631	27.369	91.23
3	100	2.198	97.802	97.80
4	100	3.062	96.938	96.94
5	100	4.456	95.544	95.54
7	100	6.003	93.997	94.00
9	100	7.825	92.175	92.18

Note: All data are presented in average form

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## Appendix E

### Mass Transfer Zone

The mass transfer zone (MTZ) is the part of the bed that displays a gradient in solid concentration from zero to equilibrium. This is the active part of the bed where adsorption actually takes place. The concentration of dyeing wastewater also changes continuously throughout this part of the bed, from a value close to zero at the beginning of the MTZ to the feed concentration at the end.

$$MTZ_L = H \cdot (t_S - t_B) / t_S$$

Where:  $MTZ_L$  is the length of mass transfer zone (cm.)

$H$  is the height of bed (cm.)

$t_S$  is saturated time (min)

$t_B$  is breakthrough time (min)

#### Example:

At the height of bed is 2.5 cm., saturated time is 300 min and breakthrough time is 120 min

$$\begin{aligned} MTZ_L &= 2.5 \cdot (300 - 120) / 300 \\ &= 1.5 \text{ cm.} \end{aligned}$$



## Appendix F

### Degree of Swelling

$$\text{Degree of swelling} = (W_{\text{wet bead}} - W_{\text{dry bead}}) / W_{\text{wet bead}} * 100$$

Where:  $W_{\text{wet bead}}$  is the weight of wet chitosan bead (g)

$W_{\text{dry bead}}$  is the weight of dry chitosan bead (g)

Example;

$$\begin{aligned} W_{\text{wet bead}} &= 1 \text{ g} \\ W_{\text{dry bead}} &= 0.002 \text{ g} \\ \text{Degree of swelling} &= (1-0.002)/0.002*100 \\ &= 99.8 \end{aligned}$$

### Crosslinking Ratio

Crosslinking ratio is the ratio of crosslinking agent to chitosan. In this study, glutaraldehyde (GA) was used as acrosslinking agent.

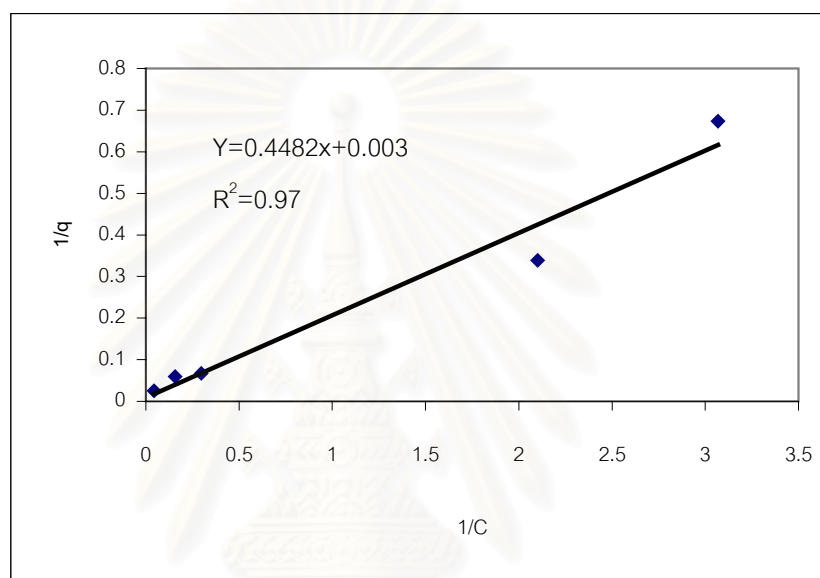
$$\text{Crosslinking ratio} = \text{molGA/mol chitosan}$$

Example;

$$\begin{aligned} \text{Mol GA} &= 8.37 \times 10^{16} \\ \text{Mol chitosan} &= 3.77 \times 10^{16} \\ \text{Crosslinking ratio} &= 2.22 \end{aligned}$$

## Appendix G

### Langmuir Isotherm



**Figure G1:** Langmuir isotherm of RR 120 adsorption onto chitosan flake at pH 7 and 30 mg/l of dye concentration

A plot of  $1/q_e$  versus  $1/C_e$  gives a straight line of slope  $b$  and intercept  $1/Q$ , a linear expression of Langmuir equation is:

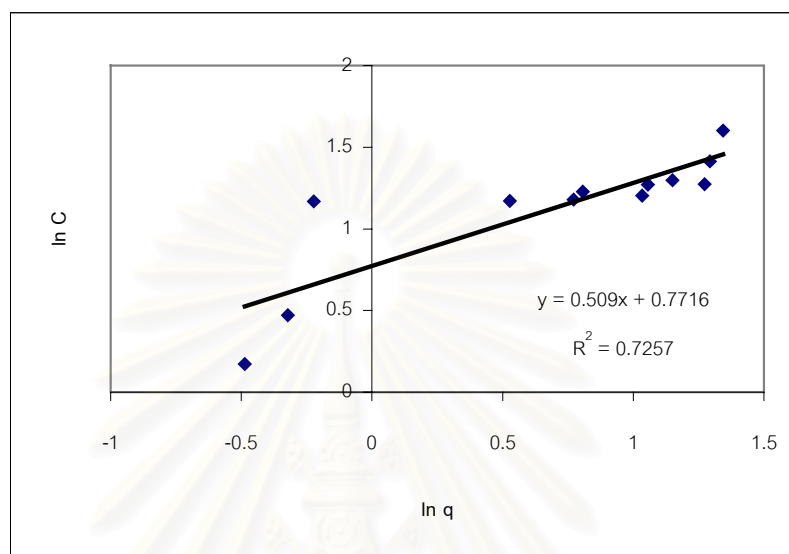
$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \left( \frac{1}{C} \right)$$

From graph,  $y = 0.4482x + 0.003$

Slope  $b = 0.4482$

Intercept  $1/Q = 0.003$  ;  $Q = 1/0.003 = 333.33$

### Freundlich Isotherm



**Figure G2:** Freundlich isotherm of RR 120 adsorption onto chitosan flake at pH 7 and 30 mg/l of dye concentration

A plot of  $\ln q_e$  versus  $\ln C_e$  enables the constant  $K_F$  and exponent  $1/n$  to be determined.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

From graph,  $y = 0.509x + 0.7716$

Slope  $1/n = 0.509$ ;  $n = 1/0.509 = 1.96$

Intercept  $\ln K_F = 0.7716$ ;  $K_F = 5.91$

## BIOGRAPHY

Kwanjai Satchatham was born on November 10, 1980 in Chanthaburi. She graduated from Faculty of Science, Chulalongkorn University in 2001 with B.Sc in General Science and major in Environmental Science. In May of 2002, she entered the National Research Center for Environmental and Hazardous Waste Management – Master of Science program in Environmental Management at Chulalongkorn University.



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