การดูดซับเคอร์คูมินและสีสกัดจากหัวขมิ้น (*Curcuma longa* Linn.) บนเส้นใยไหม

นางสาวศรีวัย กัณหาไชสง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ปีการศึกษา 2553

ADSORPTION OF CURCUMIN AND EXTRACTED DYE FROM TURMERIC RHIZOME (*Curcuma longa* Linn.) ONTO SILK FIBERS

Sriwai Kanhathaisong

A Thesis Submitted in Partial Fulfillment of the Requirements for the

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ADSORPTION OF CURCUMIN AND EXTRACTED DYE FROM TURMERIC RHIZOME (*Curcuma longa* Linn.) ONTO SILK FIBERS

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

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ศรีวัย กัณหาไธสง : การดูดซับเคอร์คูมินและสีสกัดจากหัวขมิ้น (*Curcuma longa* Linn.)
บนเส้นใยไหม (ADSORPTION OF CURCUMIN AND EXTRACTED DYE FROM
TURMERIC RHIZOME (*Curcuma longa* Linn.) ONTO SILK FIBERS)
อาจารย์ที่ปรึกษา : รองศาสตราจารย์ ดร.เสาวณีย์ รัตนพานี, 195 หน้า.

งานวิจัยนี้เป็นการศึกษาจลนพลศาสตร์และอุณหพลศาสตร์ของการดูดซับเคอร์คูมิน สารเชิงซ้อนคอปเปอร์(II)-เคอร์คูมิน สีสกัดจากหัวขมิ้น (*Curcuma longa* Linn.) และสารเชิงซ้อนคอปเปอร์(II)-สีสกัดจากหัวขมิ้นบนเส้นใยไหม พบว่าความเข้มข้นเริ่มต้นของสีย้อมและสารเชิงซ้อนของสีย้อม เวลาในการดูดซับ ค่าพีเอชของสารละลายสีย้อมและสารเชิงซ้อนของสีย้อม อัตราส่วนของเส้นใยไหมต่อปริมาตรของสารละลายสี และอุณหภูมิมีผลต่อปริมาณการดูดซับสีอย่างมีนัยสำคัญ

สภาวะที่เหมาะสมสำหรับการดูดซับเคอร์คูมินและสีสกัดจากหัวขมิ้นบนเส้นใยไหมคือ ความเข้มข้นเริ่มต้นของสีย้อมเท่ากับ 16.58 มิลลิกรัมต่อลิตร เวลาในการดูดซับเท่ากับ 60 นาที สำหรับเคอร์คูมิน และ 120 นาทีสำหรับสีสกัดจากหัวขมิ้น ค่าพีเอชของสารละลายสีเท่ากับ 5.5 อัตราส่วนของเส้นใยไหมต่อปริมาตรของสารละลายสีเท่ากับ 1:100 กรัมต่อมิลลิลิตร และอุณหภูมิเท่ากับ 30 องศาเซลเซียส การดูดซับนี้เกิดขึ้นได้เองและเป็นกระบวนการคายความร้อนมีค่า ΔH° เท่ากับ -124.47 และ -209.50 กิโลจูลต่อโมลสำหรับเคอร์คูมินและสีสกัดตามลำดับ นอกจากนี้การดูดซับนี้เป็นกระบวนการอันดับสองเสมือนมีค่า E_a เท่ากับ 43.32 และ 87.99 กิโลจูลต่อโมล สำหรับเคอร์คูมินและสีสกัดตามลำดับ

สำหรับการศึกษาสารเชิงซ้อน พบว่า ไอออนคอปเปอร์(II) เกิดสารเชิงซ้อนกับเคอร์คูมินในสารละลายน้ำด้วยอัตราส่วน 1:2 โดยโมล สภาวะที่เหมาะสมสำหรับการดูดซับสารเชิงซ้อนคอปเปอร์(II)-เคอร์คูมิน และสารเชิงซ้อนคอปเปอร์(II)-สีสกัดบนเส้นใยไหมคือ ความเข้มข้นเริ่มต้นของสีย้อมเท่ากับ 16.58 และ 20.26 มิลลิกรัมต่อลิตร สำหรับสารเชิงซ้อนคอปเปอร์(II)-เคอร์คูมิน และสารเชิงซ้อนคอปเปอร์(II)-สีสกัดตามลำดับ เวลาในการดูดซับเท่ากับ 120 นาที ค่าพีเอชของสารละลายของสารเชิงซ้อนเท่ากับ 5.0 อัตราส่วนของเส้นใยไหมต่อปริมาตรของสารละลายของสารเชิงซ้อนเท่ากับ 1:100 กรัมต่อมิลลิลิตร และอุณหภูมิเท่ากับ 30 องศาเซลเซียส การดูดซับนี้เกิดขึ้นได้เองและเป็นกระบวนการคายความร้อนมีค่า ΔH° เท่ากับ -20.55 และ -4.95 กิโลจูลต่อโมล สำหรับสารเชิงซ้อนคอปเปอร์(II)-เคอร์คูมิน และสารเชิงซ้อนคอปเปอร์(II)-สีสกัดตามลำดับ โดยการดูดซับนี้เป็นกระบวนการอันดับสองเสมือนมีค่า E_a เท่ากับ 16.24 และ 27.38 กิโลจูลต่อโมล สำหรับสารเชิงซ้อนคอปเปอร์(II)-เคอร์คูมินและสารเชิงซ้อนคอปเปอร์(II)-สีสกัดตามลำดับ

นอกจากนี้ได้ศึกษาการใช้เศษใยไหมและรังไหมเป็นตัวดูดซับในการกำจัดไอออนคอปเปอร์(II) และสีที่เหลือจากการย้อม พบว่า เศษใยไหมมีปริมาณการดูดซับสูงกว่ารังไหม และกระบวนการดูดซับโดยเศษใยไหมมีลักษณะเช่นเดียวกันกับกระบวนการดูดซับโดยเส้นใยไหม โดยมีค่า E_a เท่ากับ 46.75 กิโลจูลต่อโมล และค่า $\Delta H°$ เท่ากับ -3.72 กิโลจูลต่อโมล

สาขาวิชาเคมี ลายมือชื่อนักศึกษา____________

ปีการศึกษา 2553 ลายมือชื่ออาจารย์ที่ปรึกษา____________

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม____________

SRIWAI KANHATHAISONG : ADSORPTION OF CURCUMIN AND EXTRACTED DYE FROM TURMERIC RHIZOME (*Curcuma longa* Linn.) ONTO SILK FIBERS. THESIS ADVISOR : ASSOC. PROF. SAOWANEE RATTANAPHANI, Ph.D. 195 PP.

ADSORPTION/ KINETICS/ THERMODYNAMICS/ CURCUMIN/ CURCUMINOIDS/ COPPER/RESIDUAL SILK FIBERS/ COCOON

The adsorption kinetics and thermodynamics of curcumin, Cu(II)-curcumin complex, extracted dye from *Curcuma longa* Linn., and Cu(II)-extracted dye complex for dyeing onto silk fibers were investigated in this research. It was found that the adsorption capacities were significantly affected by the initial dye and dye complex concentration, contact time, pH of dye and dye complex solution, Material to Liquor Ratio (MLR), and temperature.

The optimal condition for adsorption of curcumin and extracted dye onto silk was found to be 16.58 mg/L for the initial dye concentration, 60 minutes and 120 minutes for the contact time for curcumin and extracted dye, respectively, 5.5 for pH of the dye solution, 1:100 g/mL for MLR, and 30 °C for the temperature. The adsorption was spontaneous and exothermic with $\Delta H°$ value of -124.47 and -209.50 kJ/mol for curcumin and extracted dye, respectively. Furthermore, the adsorption was a pseudo second-order process and of the chemisorption type with E_a values of 43.32 and 87.99 kJ/mol for curcumin and extracted dye, respectively.

For the dye complex study, it was found that Cu(II) ion formed a complex with curcumin in aqueous solution with the mole ratio of Cu(II) ion to curcumin as

1:2. The optimal condition for adsorption of the Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk was found to be 16.58 mg/L and 20.26 mg/L for the initial dye concentration of Cu(II)-curcumin complex and Cu(II)-extracted dye complex, respectively, 120 minutes for the contact time, 5.0 for the pH of the dye complex solution, 1:100 g/mL for MLR, and 30 °C for the temperature. The adsorption was spontaneous and exothermic with $\Delta H°$ values of -20.55 and -4.95 kJ/mol for the Cu(II)-curcumin complex and Cu(II)-extracted dye complex, respectively. Moreover, the adsorption was a pseudo second-order process of the chemisorption type with E_a values of 16.24 and 27.38 kJ/mol for the Cu(II)-curcumin complex and Cu(II)-extracted dye complex, respectively.

In addition, the use of residual silk fibers and cocoons as adsorbents for the removal of copper(II) ion and unfixed dyes from the waste dye solution was studied. It was found that residual silk fibers had higher adsorption capacities than cocoons, and the adsorption process for residual silk fibers followed the same manner as that of silk fibers with an E_a value of 46.75 kJ/mol and $\Delta H°$ value of -3.72 kJ/mol.

School of Chemistry Student's Signature____________________

Academic Year 2010 Advisor's Signature S. Rattaphi____________________

Co-advisor's Signature T. Luyen____________________

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Sriwai Kanhathaisong

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CHAPTER I

GENERAL INTRODUCTION

From earliest time, colours have played an important role in human culture. Tens of thousands of years ago, body painting was already part of the ritual connected with waging war and funerals. In southern Europe, coloured drawing of hunting scenes have been found in caves and shelters used by people in the Stone Age. Coloured cloths and utensils have been found in ancient Egyptian and Indian tombs (Freeman and Peters, 2000). In the beginning, plant material and minerals were used to prepare dyes.

Natural dyes were well known and used in ancient times. More than 2000 years ago, plants such as woad (*Isatis tinctoria* L.), *Rubia* species, and indigo (*Indigofera* species) were known to be substances that could be used for colouring cloths, implements, and utensils. The rind of the pomegranate (*Punica granatum* L.) may have been the source of a yellow dye and madder root (*Rubia tinctorum* L.) of a red dye. The 19th century was the peak for the use of many natural dyes. At the end of that century, the natural dyes were largely replaced by synthetic ones, starting with mauveine, a basic violet dye. This was the first synthetic aniline dye in common use. It was used mostly for dyeing silk and cotton (Christie, 2001).

At the present day, the batik dyeing processes still employ natural dyes obtained from several plant species. The batik process is often associated with the artisans of Java, Indonesia. They usually use cotton cloth, which is mainly produced locally from domestically grown cotton of coarser grades. Finer grade imported from the Americas is also used. Silk clothing today is not in common use, but most of the dyes used with silk are natural. Silk fabrics were popular before the Second World War. The invention of synthetic fibers led to a decrease in the use of silk. Recently, silk has seen a renaissance with the fashion industry more focused on Asian designs.

The natural dyes are enormously important to textile industry today. Interestingly, the same natural dyes, madder and indigo have been used since the 19th century (Freeman and Peters, 2000). There are many problems with the use of natural dyes, such as, poor solubility in water, issues with adsorption onto fibers and fading when washed or exposed to air and sunlight. Although plants exhibit a wide range of colours, not all of these pigments can be used as dyes. It remains a mystery, why plants reward us with such vibrant colours. Humans developed colour vision to improve their food gathering skill and to judge the ripeness of fruits and vegetables.

The demand for natural products is increasing dramatically as the synthetic dyes are found to be linked to health risks. This growth in demand is part of the negative reaction to a world based on synthetic materials, and a growing movement devoted to artisan crafts and natural products.

1.1 Natural dyes

Natural dyes are classified based on their structures, sources, methods of application, and colour. The following section briefly describes three types of dye classification.

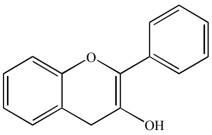
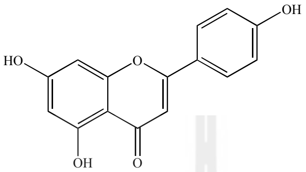
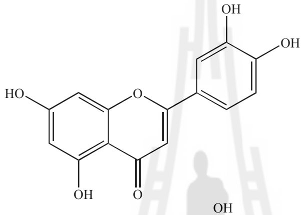
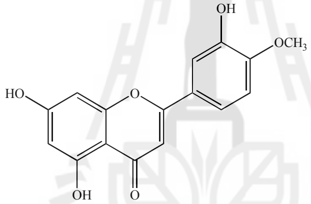
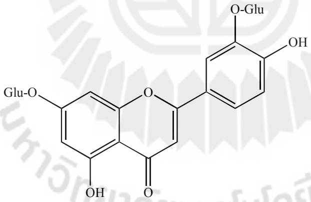
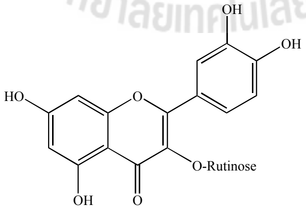
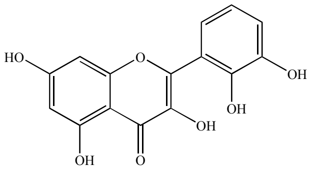
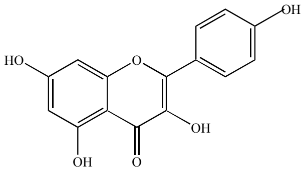
1.1.1 Flavonoids

Flavonoids, a subclass of polyphenols, are hydroxy and methoxy derivatives of benzene; their pigments are extensively present in plants. The term flavonoid has been derived from the Latin word *flavus* meaning yellow, indicating the widespread yellow colour of flavonoids found in many plants. The basic flavonoid structure consists of the flavan core, which has 15 carbon atoms arranged in three rings (C6-C3-C6), labeled A, B, and C, i.e., a condensed benzodihydropyran skeleton bonded to benzene (Kaur and Arora, 2010).

Flavonoids are large group of about 4000 naturally occurring polyphenolic compounds, found exclusively in foods of plant origin (Harborne, 1986). These are primarily recognized as the pigments responsible for the colours of leaves, especially in autumn. Flavonoids are widely distributed in fruits, vegetables, nuts, seeds, herbs, spices, stems, and flowers as well as tea and red wine. They are usually subdivided according to their substituent into flavonols (kaempferol, quercetin), anthocyanins, flavones, flavonones, and chalcones. The colours and application of flavonoids are shown in Table 1.1.

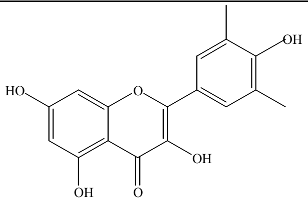
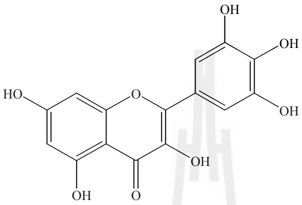
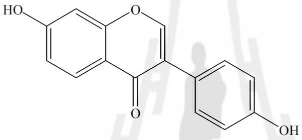
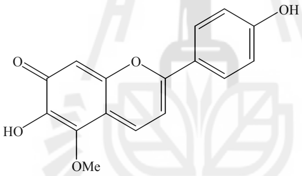
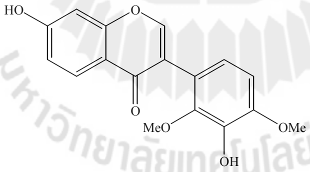
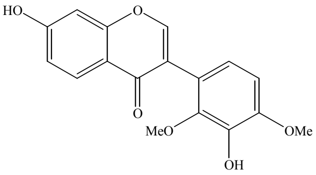
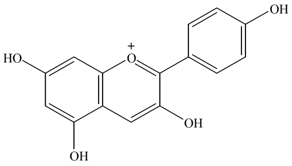
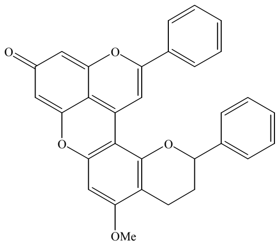
Homoisoflavonoids exhibit a flavonoid-like structure and can be classified as a subgroup of flavonoids. The homoisoflavonoids are pink-yellow in colour, for examples: brazilein and brazilin (Figure 1.1).

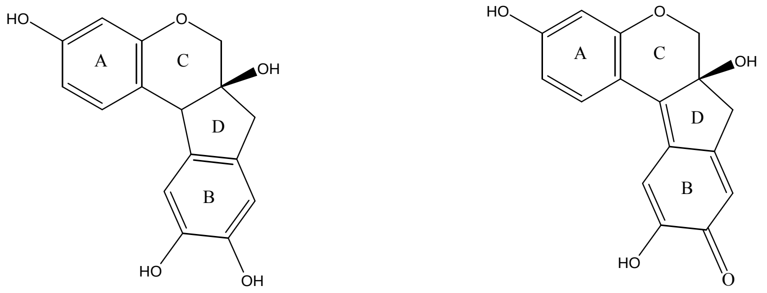
Table 1.1 Colours and application of flavonoids.

Natural dyes **Compound/class** **Colour**	**Structure**	**Source/Part/Application**
Catechin Flavone Brown, olive		*Acacia catechu (Linn.F) Willd.* Heartwood Silk, wool, and hair dyeing
Apigenin Flavone Yellow		*Reseda luteola L* Leaves and seeds Silk, wool, and textile dyeing
Luteolin Flavone Yellow		*Reseda luteola* Leaves and seeds Silk, wool, and textile dyeing
Diosmetin Flavone Yellow		*Reseda luteola* Leaves and seeds Silk, wool, and textile dyeing
Butrin Flavanone Yellow-orange		*Butea monospherma* Flowers Silk and cotton dyeing
Rutin Flavonol Yellow		*Sophora japonica* Flower buds threads, silk dyeing, and embroidery
Quercetin Flavonol Yellow		*Melastoma malabathricum* Fruits Cotton dyeing
Kaempferol Flavonol Yellow		*Crocus sativus L.,(Iridaceae)* Cotton dyeing

From: Ferreira, Hulme, McNab, and Quye (2004); Bhat, Nagasampagi, and Sivakumar (2005); Kaur and Arora (2010); Vankar (2000).

Table 1.1 Colours and application of flavonoids (Continued).

Natural dyes **Compound/class** **Colour**	**Structure**	**Source/Part/Application**
Hesperedin Flavonone Yellow		*Citrus reticulata* Penggan peel Cotton dyeing and embroidery
Myricetin Dihydroflavonol Yellow		*Cotinus coggyria L.* Wood Tanning
Daidzein Isoflavone Yellow		*Glyciene max* Berries Food supplement
Carajurin Anhydro base Red		*Bignonia chika* – Textile dyeing
Santal Isoflavone Red		*Pterocarpus santalinus* Wood Cotton, wool, leather, and wood dyeing
Santal Isoflavone Red		*Pterocarpus santalinus* Wood Cotton, wool, leather, and wood dyeing
Pelargoidin Anthocyanidin Purple		*Crocus sativus L.* (*Iridaceae*) – Cotton dyeing
Dracorubin Anhydro base Red		*Dracaena draco* – Textile dyeing



Brazilein Brazilin

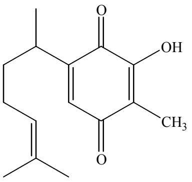
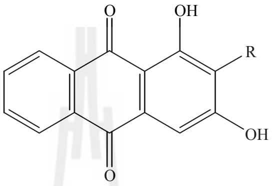
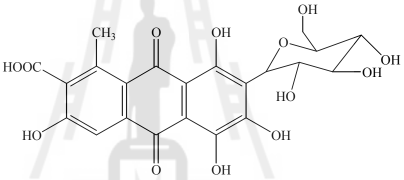
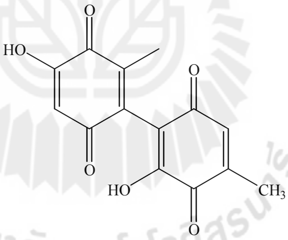
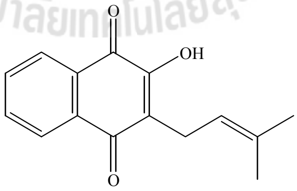
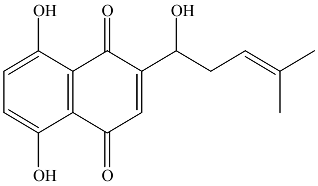
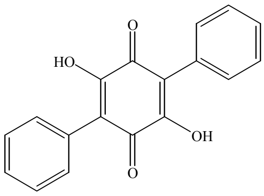
Figure 1.1 Chemical structure of brazilein and brazilin.

From: Wongsooksin, Rattanaphani, S., Tangsathitkulchai, Rattanaphani, V., and Bremner (2008).

1.1.2 Quinones

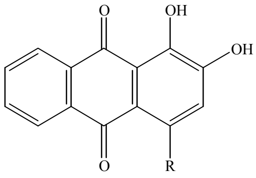
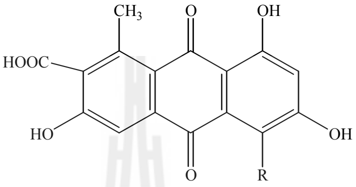
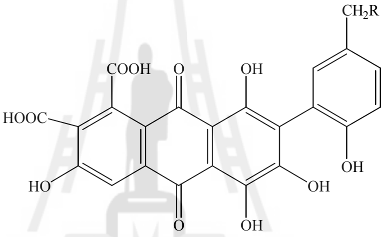
Quinones, a subclass of quinonoids, are a class of organic compounds that are formally derived from aromatic compounds such as benzene or naphthalene structures. The class includes derivatives of heterocyclic aromatic compounds. Four classes of quinone dyes including benzoquinones, naphthoquinones, anthraquinones, and extensive quinones are well known. Quinonoids are important naturally occurring pigments that are widely distributed in nature. Quinonoids, anthraquinones, and their precursors, anthrones, are natural products found in insects, higher plants, and lichens (Ferreira et al., 2004; Tang, Wang, Fu, He, Wu, and Huang, 2008). The colours and application of quinones are shown in Table 1.2.

Table 1.2 Colours and application of quinones.

Natural dyes **Compound/class** **Colour**	**Structure**	**Source/Part/Application**
Perezone Benzoquinone Orange		*Trixis pipitzahue* Roots Textile dyeing
Xanthopurpurin (R=H) Rubiadin (R=CH_3) Lucidin (R=CH_2OH) Munjistin (R=COOH) Anthraquinone Red		*Rubiaceae galium* and *Rubiaceae relbunium* Roots Cloth dyeing
Carminic acid Anthraquinone Red		*Porphyrophora hamelii* Insect Wood dyeing
Phoenicin Di-benzoquinone Yellow		*Pencillium phoeniceum* Bacteria Textile dyeing
Lapachol Naphthoquinone Yellow		*Tabebuia serratifolia* and *Avicennia tomentosa* Wood
Alkannin Naphthoquinone Red		*Anchusa tinctori* Roots Red dye, cosmetic, and food
Polyporic acid Benzoquinone Bronze		*Polyporus fries* Fungus -

From: Ferreira et al. (2004); Tang et al. (2008).

Table 1.2 Colours and application of quinones (Continued).

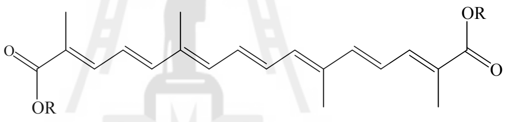
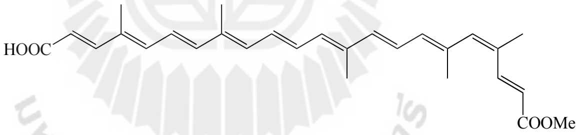
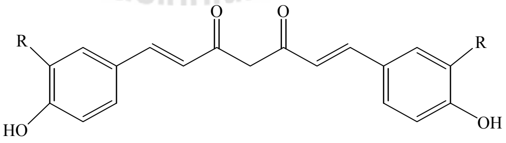
Natural dyes **Compound/class** **Colour**	**Structure**	**Source/Part/Application**
Alizarin (R=H) Purpurin (R=OH) Anthraquinone Red		*Rubiaceae galium* and *Rubiaceae relbunium* Roots Cloth dyeing
Kermesic acid (R=OH) Flavokermesic acid (R=H) Anthraquinone Red		*Kermes vermilio* Planchon Insect Textile dyeing
Laccaic acid A ($R=CH_2NHCOMe$) Laccaic acid B ($R=CH_2OH$) Anthraquinone Red		*Coccus laccae* Insect Wood dyeing

1.1.3 Saffron, annatto, and turmeric

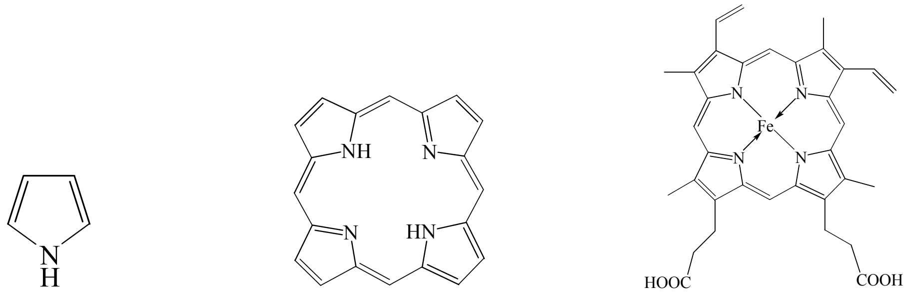
Saffron is obtained from the stigma of the flowers of *Crocus sativus* L. and has a long and well documented history of use as a direct dye. The colour derived from saffron is a beautiful orange yellow colour that is frequently used with alum mordant. It was later replaced by less expensive synthetic dyes, with better fastness properties. Another dye of similar chemical characteristics is annatto or orellana, extracted from the fruit of *Bixa orellana* L., a shrub indigenous to central America (Popoola, 2000). The colouring principle bixin is a polyunsaturated di-acid which is used as a direct dye for cotton, wool, or silk. Turmeric or curcuma, also known as Indian saffron, is obtained from the ground roots of *Curcuma domestica* Valet. or

Curcuma longa Linn., a plant growing abundantly in the South and Southeast Asia and China. It was used as a direct dye on cotton, wool, or silk, mainly in combination with other dyes. The main colouring matter is a mixture of curcuminoids. The main chromophores of saffron, annatto, and turmeric and their application are shown in Table 1.3.

Table 1.3 Colours and application of the main chromophores of saffron, annatto, and turmeric.

Natural dyes **Compound/class** **Colour**	**Structure**	**Source/Part/ Application**
Crocintin (R=H) Crocin (R = gentobiose) Apocarotinoid Golden yellow		*Crocus sativus* Pistil Food
Bixin Apocarotenoid Golden yellow		*Bixus Orellena* Seedcoat Food dyeing
Curcumin (R = OMe) Demethoxycurcumin (R = OMe, H) Bisdemethoxycurcumin (R = H) Curcuminoid Orange red		*Curcumin langa* L. Roots Food dyeing

From: Ferreira et al. (2004); Fan, Peng, Hamann, and Hu (2002).



Pyrrol Porphyrin Heme

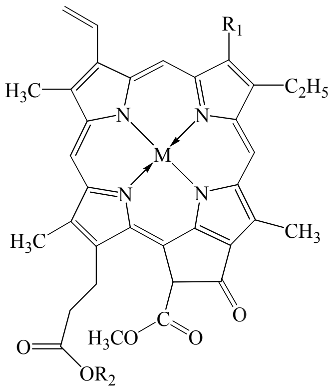
Figure 1.2 Chemical structures of pyrrole, porphyrin, and heme.

From: Fan et al. (2002); Wikipedia (2011).

1.1.4 Organic nitrogenous dye

Pyrrole, a heterocyclic aromatic organic compound (Figure 1.2) with five-membered ring (Fan et al., 2002) is a colourless volatile liquid that darkens readily upon exposure to air. Substituted derivatives are also called pyrroles, e.g., *N*-methylpyrrole, $C_4H_4NCH_3$. Porphobilinogen, a trisubstituted pyrrole, is the biosynthetic precursor to many natural products such as heme. Heme contains a heterocyclic ring known as porphyrin with a complexed iron (Fe) ion which confers a red colour. This porphyrin ring consists of four pyrrole molecules cyclically linked together (by methene bridges) with the iron ion bound in the center (Wikipedia, 2011).

Chlorophyll is a green pigment found in leaves and green stems of all plants, algae, and cyanobacteria. Chlorophyll derivatives include a broad spectrum of green-grey-brown pigments of very different polarities. Figure 1.3 shows the structures and names of the different compounds considered. Pheophytins and chlorophyllides are Mg-free (replaced by 2 H's) and phytyl-free derivatives, respectively, of the parent chlorophylls, whereas the pheophorbides are free of both Mg and phytol (Fraser and Frankl, 1985). Consequently, chlorophyllides and pheophorbides are considered as acidic pigments, while chlorophylls and pheophytins present low polarity.



Pigment	M	R_1	R_2
Chlorophyll a	Mg	CH_3	$C_{20}H_{39}$
Chlorophyll b	Mg	CHO	$C_{20}H_{39}$
Chlorophyllide a	Mg	CH_3	H
Chlorophyllide b	Mg	CHO	H

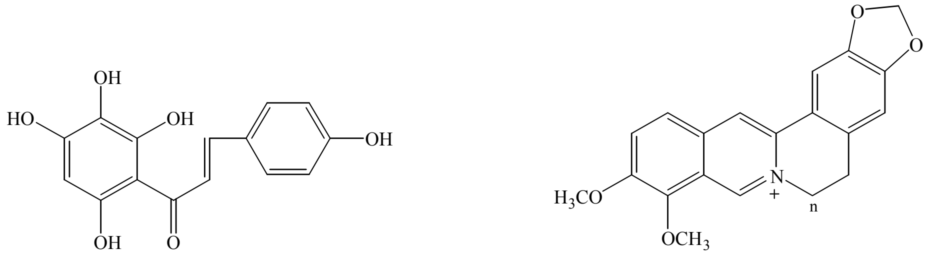
Figure 1.3 Chemical structures of chlorophyll derivatives.

From: Fraser and Frankl (1985); Wikipedia (2011).

1.2 Natural dyes for protein fibers

1.2.1 Direct dyes

Direct dyes or substantive dyes are a class of hot water dyes for use on cellulose fibers, such as cotton and protein fibers. Their high substantivity for cellulose enables direct dyeing by simple adsorption processes, due to the total strength of their intermolecular interactions with this substrate (Zollinger, 2003). Animal fibers like wool and silk contain acidic and basic positions in their protein molecules. Thus, dyes with basic or acidic surrounds (so-called cationic and anionic dyes, a subgroup of direct dyes) undergo salt formation with the acidic and basic positions, respectively, in the textile. An example of direct dyes is carthamin (Figure 1.4(a)) which is also applied as mordant dye and that of natural basic dyes is berberine (Figure 1.4(b)).



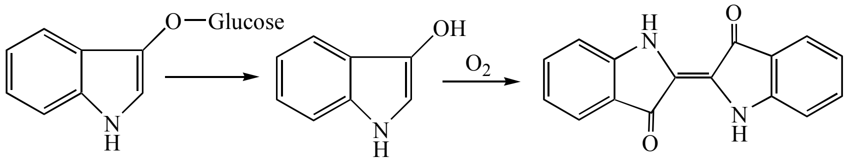
(a) Carthamin (b) Berberine

Figure 1.4 Chemical structures of (a) carthamin and (b) berberine.

From: Christie (2001).

1.2.2 Vat dyes

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye. Oxidation of the dye on the fiber creates the desired water-insoluble colorant. In the case of indigo, the classic blue dye from *Indigofera tinctoria*, the treatment with urine transfers the glycoside indican into the water-soluble indoxyl (Figure 1.5). The action of sunlight on the fiber causes oxidation of indoxyl to the insoluble dye (Christie, 2001).



Indicant Indoxyl Indigo

Figure 1.5 Chemical structures of indicant, indoxyl, and indigo dyes.

From: Christie (2001).

Natural dyes with an alkaloid structure are indigo and tyrian purple (Figure 1.6). Alkaloids are compounds that contain nitrogen, usually from higher plants. Tyrian from shellfish of the genera *Murex* and *Purpura*, and berberine, the yellow dye from berberries (*Berberis valgaris*) are classified as alkaloids.

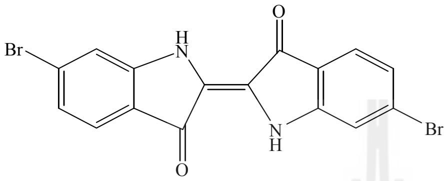


Figure 1.6 Chemical structure of tyrian purple.

From: Christie (2001).

1.2.3 Mordant dyes

In case of natural dyes that are not substantive, they require a mordant to fix them to the fabric and prevent the colour from either fading with exposure to light or washing out. Mordant is the chemical that fixes the dye to a substrate (fabric) by combining with the dye compound to form an insoluble compound. The choice of mordant is very important as different mordants can change the final colour significantly. Most natural dyes including flavonoids, tannins, terpenoids, napthoquinones, anthraquinones, and alkaloids are mordant dyes. The literature on them is large, describing dyeing and mordant techniques.

Mordants can be classified into three types (Vankar, 2000).

Natural mordants (tannins): Tannins are the common mordants in dyeing textile fibers with myrobalan and sumach.

Inorganic mordants: Most of the inorganic mordants are metal salts such as potassium dichromate and salts of aluminium, copper, iron, and tin; they are applied as pre-mordants, post-mordants, and simultaneous mordants. It is important to note that many mordants, particularly those of the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

Oil mordants: Most of oil mordants are used for dyeing with madder. The main function of the oil mordant is to form a complex with alum used as the main mordant. The sulfonated oils, which possess better metal binding capacity than the natural oils due to the presence of sulfonic acid groups, bind to metal ions forming a complex with the dye to give superior fastness.

Table 1.4 shows sources of mordant dyes with various colours and mordants used.

The majority of natural dyes need a mordant to fix the colour and increase fastness. When using mordants, there are four possible ways to carry out the dyeing process (Bechtold, Turcanu, Ganglberger, and Geissler, 2003; Moeyes, 1993) as follows: (i) mordanting before dyeing, called pre-mordanting; (ii) mordanting and dyeing at the same time, called “stuffing”; (iii) mordanting after dyeing, called after-mordanting or post-mordanting; and (iv) a combination of pre-mordanting and after-mordanting.

Table 1.4 Sources of dyes with different colours and mordants.

Mordant dyes	Botanical name	Parts used	Mordants used
Yellow dye			
Golden rod	*Solidago grandis* DC.	Flower	Alum
Teak	*Tectona grandis* L. f.	Leaf	Alum
Marigold	*Tagetes* sp.	Flower	Chrome
Saffron	*Crocus sativus* L.	Flower	Alum
Flame of the forest	*Butea monosperma* (Lam) Taubert.	Flower	Alum
Red dye			
Caesalpinia	*Caesalpinia sappan* L.	Wood	Alum
Madder	*Rubia tinctorium* L.	Wood	Alum
Khat palak	*Rumex dentatus* L.	Wood	Alum
Indian mulberry	*Morinda tinctoria* L.	Wood	Alum
Kamala	*Mallotus philippinensis* Muell.	Flower	Alum
Lac	*Coccus lacca* Kerr.	Insect	Stannic chloride
Orange dye			
Annota	*Annota*	Seed	Alum
Dhalia	*Dhalia sp.*	Flower	Alum
Lily	*Convallaria majalis* L.	Leaf	Ferrous sulphate
Nettles	*Urtica dioica* L.	Leaf	Alum
Black dye			
Alder	*Alnus glutinosa* (L.) Gaertn.	Bark	Ferrous sulphate
Rofblamala	*Loranthus pentapetalus* Roxb.	Leaf	Ferrous sulphate
Harda	*Terminalia chebula* Retz.	Fruit	Ferrous sulphate
Blue dye			
Indigo	*Indigofera tinctoria* L.	Leaf	Alum
Pivet	*Ligustrum vulgare* L.	Fruit	Alum and iron
Water lily	*Nymphaea alba* L.	Rhizome	Iron and acid

From: Vankar (2000).

1.3 Synthetic dyes

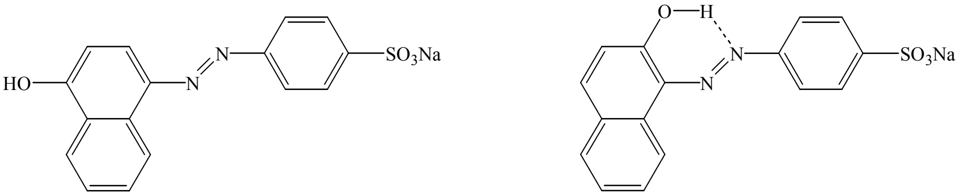
Most of the colours seen today are synthetic dyes. They are widely used for dyeing and painting in a broad range of industry. The synthetic dyes can be named according to the chemical structure of their particular chromophoric group, e.g., diphenylmethane derivatives, triphenylmethane compounds, oxazine compounds, xanthene compounds, and azo dyes. Synthetic dyes for textile fibers may be classified according to other chemical structure features, or according to the method of application (Lillie, 1977; Christie, 2001). The classification of synthetic dyes according to chemical structure can be grouped into four classes as listed below.

1.3.1 Acid dyes

Acid dyes comprise wide varieties of colours. They are fairly fast to light and to washing. They are water-soluble and contain acidic anionic groups (sulfonic acid, carboxylic acid, or phenolic groups). Their application proceeds in an acid bath to increase the protonated cationic groups on the textile. They are mainly used on fibers such as nylon, wool, silk, and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Examples of acid dyes are shown in Figure 1.7 (Christie, 2001; Xu, Jingli Wang, Wu, Jide Wang, and Li, 2006).

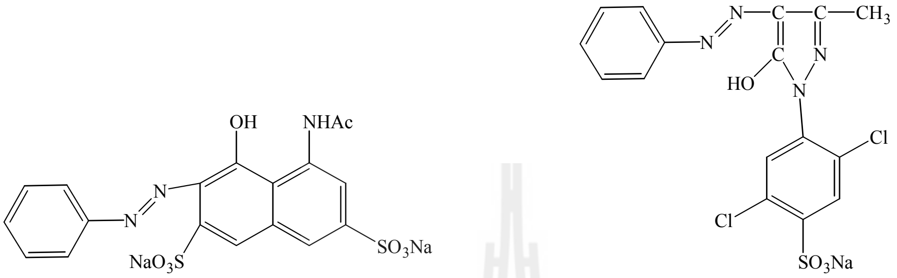
1.3.2 Basic dyes

They are water-soluble cationic substances with functional groups like $–NR_3^+$ or $=NR_2^+$, are fairly fastness when it comes to both light and washing, and can create a brilliant colour. As basic dyes are stained with cationic or positive charges, they react well with anionic or negative charges of materials. This is the reason that they are not only mainly used on natural and acrylic fibers, but also on wool and silk. Basic dyes are also used in the colouration of paper. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Examples of basic dyes are shown in Figure 1.8 (Xu et al., 2006).



C. I. Acid Orange 20

C. I. Acid Orange 7

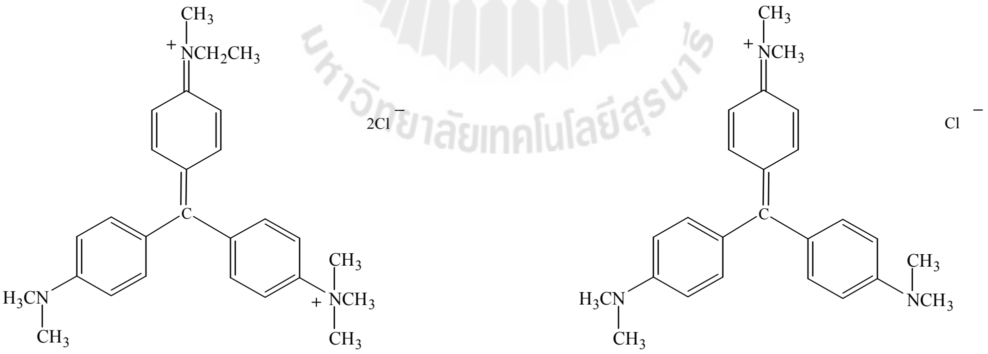


Acid red G

Acid light yellow 2G

Figure 1.7 Examples of acid dyes.

From: Christie (2001); Xu et al. (2006).



Methyl Green

Methyl Violet

Figure 1.8 Examples of basic dyes.

From: Xu et al. (2006).

1.3.3 Azoic (or naphthol) dyes or substantive dyes

Azoic (or naphthol) dyes or substantive dyes are water-insoluble azo dyes. They are produced on the fiber by applying and combining naphthol and a diazotized base or salt at a low temperature to form the insoluble dye molecule with the fiber. Naphthols are phenols that are soluble in alkaline solution and substantive by fiber such as cotton. The naphthol ions are coplanar and preferably have elongated molecular structure. An example of a dye coupling component, aniline of 3-hydroxy-2-naphtholic acid, is shown in Figure 1.9 (Christie, 2001). It is colourless and has a low molecular mass. Bases for naphthol dyes are available as the free amine bases and their hydrochloride salts.

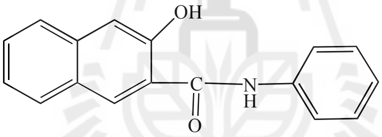
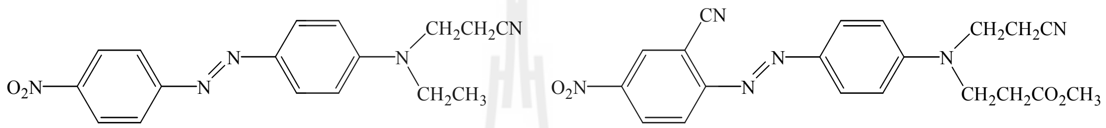


Figure 1.9 The chemical structure of 3-hydroxy-2-naphtholic acid.

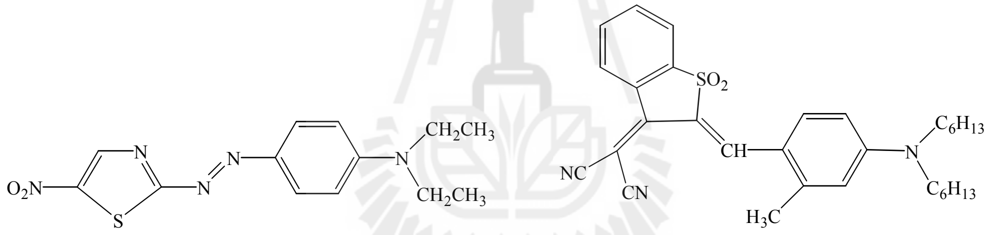
From: Christie (2001).

1.3.4 Disperse dyes

Disperse dyes were originally developed for the dyeing of synthetic fibers such as cellulose acetate, polyester, and polyamine which are water insoluble fibers. The dyes are finely ground in the presence of a dispersing agent in the water. It can react as well with hydrophobic synthetic fiber. Disperse dyes are non ionic molecules that effectively dissolve in polyester. The dye-fiber affinity in solid solution form is generally considered to involve a combination of van der Waals and dipolar forces and hydrogen bonding. The polar groups consisting in these dyes include the nitro (NO_2), cyano (CN), hydroxyl, amino, ester, amido (NHCO), and sulfone (SO_2) groups. The very fine particle size or the polarity of dye molecule gives a large surface area that aids dissolution to allow uptake by the fibers and enhances fastness to sublimation. In some cases, a dyeing temperature of 130 °C is required, and a press erased dye bath is used. Some examples of typical disperse dyes are illustrated in Figure 1.10 (Christie, 2001).



C. I. Disperse Orange 25　　　　C. I. Disperse Red 90



C. I. Disperse Blue 339　　　　C. I. Disperse Blue 354

Figure 1.10 The chemical structures of several disperse dyes.

From: Christie (2001).

1.4 Textile fibers

1.4.1 Protein fibers

Silk, a natural polymer produced by *Lepidopteron* insects of the family *Bombycidae* and *Saturniidae*, has been widely used in textile industries due to its luster and mechanical properties. The silk fibers are composed of a fibrous protein core with sericin surrounding it. The amino acid composition (in mol%) of the fibrous protein of *B. mori* shows a predominance of four amino acids: Gly (42.9%), Ala (30.0%), Ser (12.2%), and Tyr (4.8%) (Yao, Ohgo, Sugino, Kishore, and Asakura, 2004). The molecular mass of sericin ranges from 24 to 400 kDa with predominant amino acids serine (40%), glycine (16%), glutamic acid, aspartic acid, threonine, and tyrosine (Takasu, Yamada, and Tsubouchi, 2002). Thus it contains polar side chains with hydroxyl, carboxyl, and amino groups that enable easy cross-linking, copolymerization, and blending with other polymers to form improved biodegradable materials (Dash, Mandal, and Kundu, 2009). Fibroin, the protein core, is hydrophobic in nature while sericin is hydrophilic. Basic unit of structure of fibroin is illustrated in Figure 1.11 (Christie, 2001).

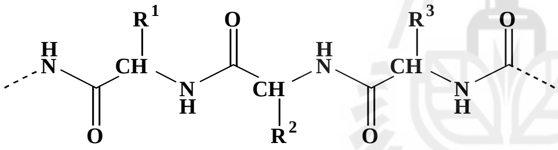


Figure 1.11 Basic unit of structure of fibroin.

From: Christie (2001).

1.4.2 Cellulose fibers

Cellulosic fibers are natural fibers derived from plant sources. The most important cellulose fibers are cotton, viscose, linen, jute, hemp, and flex. The principal component of the cotton fibers is cellulose, the structure of which is shown in Figure 1.12.

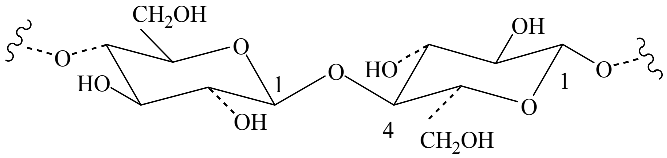


Figure 1.12 Structure of cellulose.

From: Christie (2001).

Cotton is in fact almost pure cellulose (up to 95%). Cellulose is a polysaccharide. It is a high molecular mass polymer consisting of long chains of repeating glucose units, with up to around 1300 such units in each molecule. Cellulose has a fairly open structure, which allows large dye molecules to penetrate relatively easily into the fiber. Each glucose unit contains three hydroxyl groups, two of which are secondary and one primary, and these give the cellulose molecule a considerable degree of polar character. The presence of the hydroxyl group is of considerable importance in the dyeing of cotton. For example, the ability of the hydroxyl groups to form intermolecular hydrogen bonds is thought to be of some importance in direct dyeing, while reactive dyeing involves a chemical reaction of the hydroxyl group with the dye to form dye-fiber covalent bonds. The tendency of the hydroxyl groups to ionize to a certain extent (to $–O^-$) means that the fibers can carry a small negative charge. There is a larger number of applications of classes of dyes for cellulosic fibers such as cotton than that for any other fiber (Christie, 2001).

1.4.3 Synthetic fibers

The only significant semi-synthetic fibers used today are derived from cellulose as the starting material, the two most important of these being viscose rayon and cellulose acetate. Viscose rayon is a regenerated cellulosic fiber. It is manufactured by reacting cellulose, e.g. from wood pulp, with carbon disulfide in alkali solution to give its water-soluble xanthate derivative. This is followed by regeneration of the cellulose in fibrous form using sulfuric acid. Cellulose acetate is a chemically modified cellulose derivative, manufactured by acetylation and partial hydrolysis of cotton. The most important completely synthetic fibers are polyester, polyamides (nylon), and acrylic fibers (Christie, 2001).

1.5 Cocoon

Cocoon shells produced by silkworm caterpillars are one kind of materials which possess excellent mechanical properties. A silkworm caterpillar spins a light weight and compact cocoon around itself by continuously moving its head in the shape of either a figure 8 or an S and by cyclically bending and stretching its body. A cocoon is a natural polymeric composite shell made of a single continuous silk strand with a length in the range of 1,000-1,500 meters and conglutinated by sericin (Kerkam, Viney, Kaplan, and Lombardi, 1991). The cocoon produces a pigment in sericin layer, which forms a solid sheath or cocoon. The texture of silk thread is shown in Figure 1.13.

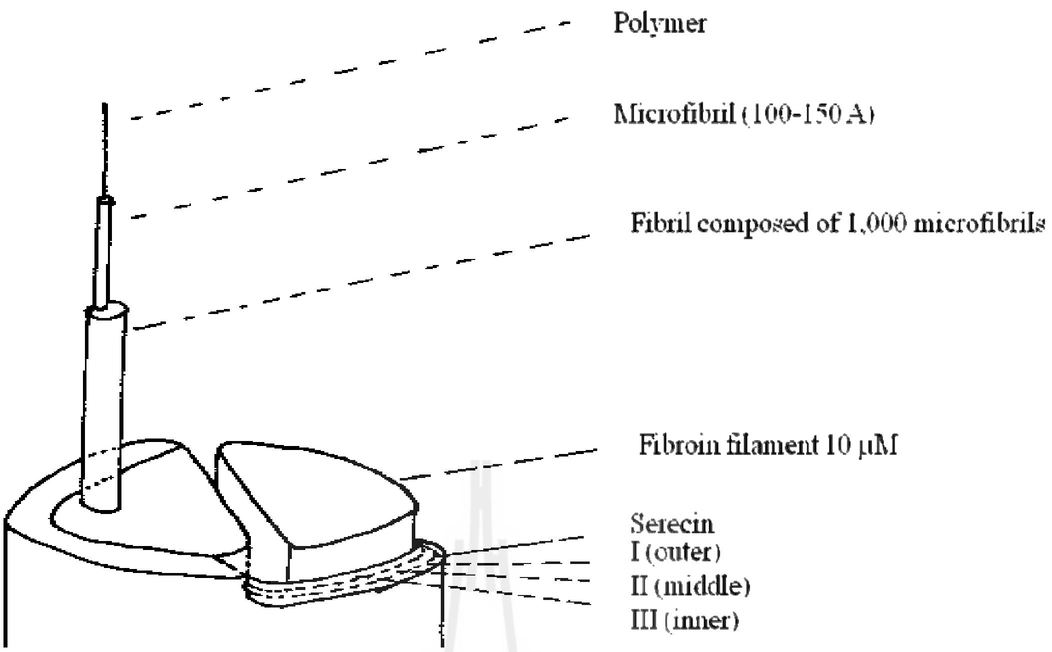


Figure 1.13 Texture of the silk thread.

From: Lee and Choung (2011).

The silk fibroin of cocoon, protein keratin, is composed of stacked antiparallel β-sheets. The β-sheet is composed of the repeating sequence [Gly-Ala-Gly-Ala-Gly-Ser-Gly...]. This sequence allows the sheets to stack on each other with the Ser or Ala residues opposite to a Gly residue (Fossey, Nemethy, Gibson, and Scheraga, 1991; Putthanarat, Stribeck, Fossey, and Adams, 2000). Wool fibroins contain carboxyl and protonated amino groups which result in its amphoteric characteristics (Corr, 1995). The secondary structures of fibroin are illustrated in Figure 1.14 (Christie, 2001; Fossey et al., 1991). As a functional material, fibroin has excellent properties in terms of stability, fixing ability for enzymes, permeability for water and oxygen, and favorable fitness for biological tissues.

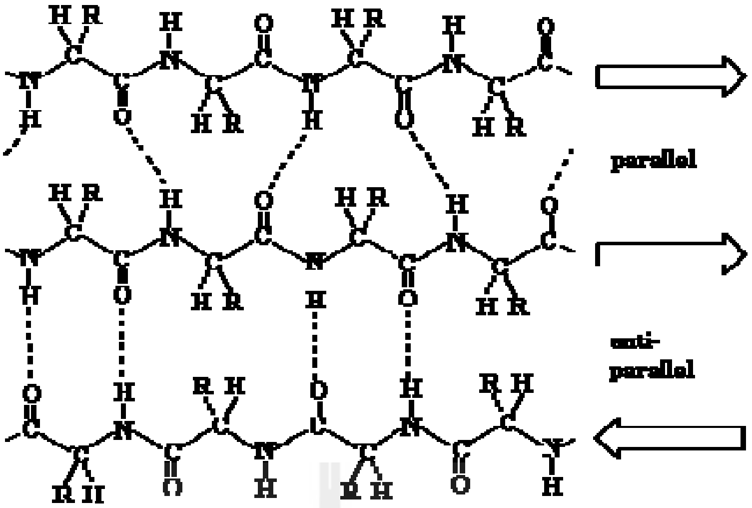


Figure 1.14 Parallel and antiparallel β-sheet structure of fibroin.

From: Christie (2001); Fossey et al. (1991).

1.6 Treatment of dye effluents

The process of using copper(II)-curcumin complex dye for dyeing onto silk fiber will be assessed for suitability. Unfixed dyes and some ions, metal ions and anions, found in the waste solution from a dyeing process will be removed by using the degumming residual silk fiber of cocoon and the residual silk fiber after the reeling process. After dyeing with waste solution, the resulting cocoons can be used for new processes such as the producing of artificial flowers while the resulting residual silk fiber can be used for making rough paper. In addition, They can be used to produce silk powder which consists of traits of copper(II) ion, curcumin, and Cu(II)-curcumin complex which are useful for cosmetics.

1.7 Adsorption

Adsorption is defined as the accumulation of a substance on the surface of a solid resulting from the interaction between the substance present in the fluid phase (gas or liquid phase) and the solid surface. This interaction gives rise to higher molecular density near the solid surface than in the bulk. The solid is called the adsorbent while adsorbate is the substance which is adsorbed (Ruthven, 1997).

There are two types of adsorption depending on the strength (energy) of the sorptive binding, i.e. physical adsorption (physisorption) and chemical adsorption (chemisorption).

1.7.1 Physical adsorption

In physical adsorption, the interactions between the adsorbate molecule and adsorbent surface result from the formation of relatively weak intermolecular forces, such as London dispersion forces or van der Waals forces. There is no direct bonding and hence, physical adsorption is reversible and an exothermic process.

1.7.2 Chemical adsorption

Chemical adsorption is a stronger adsorption force than physical adsorption due to chemical interaction between adsorbate molecule and adsorbent surface. Chemical adsorption is less common than physical adsorption and, due to chemical bonds being formed, the regeneration of the adsorbent for subsequent re-use is often difficult. The general characteristics of physical adsorption and chemical adsorption are summarized in Table 1.5.

Table 1.5 General characteristics of physical and chemical adsorption.

Parameter	Physical adsorption	Chemical adsorption
Heat of adsorption (kJ mol^{-1})	20-40	> 80
Specificity	Non-specific	Very specific
Nature of adsorbed phase	Monolayer or multilayer dependent on conditions	Monolayer only
Temperature range	Only significant at relative low temperatures	Possible over a wide range of temperatures
Temperature dependence of uptake (with increasing temperature)	Decrease	Increase
Forces of adsorption	No electron transfer although polarization of adsorbate may occur	Electron transfer leading to bond formation between adsorbate and adsorbent
Rate of adsorption (at 273 K)	Fast	Slow
Desorption	Easy by reduced pressure or increased temperature	Difficult (high temperature required to break bonds)
Desorbed species	Adsorbate unchanged	May be different from original adsorbate
Reversibility	Rapid, non activated, reversible	May be slow, activated, irreversible

From: Ruthven (1997).

1.8 Research objectives

1.8.1 To study the interactions of curcumin and extracted dye from turmeric rhizome of *Curcuma longa* Linn. with some metal ions.

1.8.2 To study the optimum conditions as well as thermodynamics and kinetics of adsorption of curcumin, extracted dye from turmeric rhizome of *Curcuma longa* Linn., curcumin-metal complexes, and extracted dye-metal complexes on dyeing onto silk fibers.

1.8.3 To study the optimum conditions as well as thermodynamics and kinetics of adsorption of metal ions and curcumin-metal complexes onto residual silk fibers and waste silk cocoons.

1.9 Scope and limitations of the study

Turmeric rhizome of *Curcuma longa* Linn. was collected from Noontapoo, Nongbuadeang, Chaiyaphum, Thailand. The interactions of curcumin and extracted dye from turmeric rhizome of *Curcuma longa* Linn. with some metal ions were investigated by spectroscopic techniques. The optimum conditions as well as the thermodynamics and kinetics of adsorption on dyeing onto silk fibers were determined by UV-Visible spectroscopy and those onto residual silk fibers and silk cocoons were determined by atomic adsorption spectrometry.

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CHAPTER II

ADSORPTION OF CURCUMIN AND EXTRACTED DYE FROM *Curcuma Longa* Linn. ONTO SILK

2.1 Abstract

The adsorption kinetics and thermodynamics of dyeing silk fibers with curcumin and turmeric extracted dye from *Curcuma longa* Linn. indicated that the adsorption capacity was significantly affected by the initial dye concentration, contact time, pH of the dye solution, material to liquor ratio (MLR), and temperature. The initial dye adsorption rate of curcumin on silk yarn was faster than that of the extracted dye. The adsorption rate of dyes on silk before equilibrium time increased with increasing temperature. The pseudo-second-order kinetic model indicated that the two dyes, curcumin and extracted dye, dyed on silk at pH 5.5 with an activation energy (E_a) of 43.32 and 87.99 kJ/mol, respectively. The values of the enthalpy of activation ($\Delta H^{\#}$) of the dyes at pH 5.5 were 40.67 and 85.53 kJ/mol, respectively. The activation energy for the adsorption of higher than 40.0 kJ/mol usually suggests that the adsorption is chemisorption. The free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) terms for dyeing curcumin and extracted dye onto silk were also determined. The negative values of $\Delta G°$ and $\Delta H°$ obtained indicated that adsorption process of both dyes was a spontaneous and an exothermic process.

2.2 Introduction

2.2.1 Turmeric extracted dye

Natural plant and animal sources have traditionally been important sources of textile dyes since the prehistoric times. Among these dyes, the rhizome of turmeric, *Curcuma longa* Linn. (Figure 2.1), contains chemicals giving a yellow, natural pigment which is used in the dyeing of textiles in much of Southeast Asia, where the plant is native. The rhizome of turmeric is a food additive namely “curry.” This pigment is largely used as a food colourant, which is called C. I. Natural Yellow 3. WHO and FAO committees have approved it as a food additive (Han and Yang, 2005). It has been used as a natural dye for centuries (Moeyes, 1993). The compounds responsible for the yellow pigment are curcumin, 1,7-bis(4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione, and two other curcuminoids, demethoxy-curcumin and bisdemethoxycurcumin (Jayaprakasha, Jagan, Mohan Rao, and Sakariah, 2002; 2005; He, Lin, Lian, and Lindenmaier, 1998; Jiang, Timmermann, and Gang, 2006). As previous experiments have established that all three curcuminoids have essentially equivalent absorbency and chelating ability, they were treated together.

In selecting this particular dye, we considered various attributes which might affect its feasibility as a study subject. Importance, then, is that using the colourful properties of turmeric presents a problem: though it’s insoluble in water and bonds well to fabric, its solubility in alkaline solutions, such as detergent, and its sensitivity to sunlight cause washing and wearing treated fabric to degrade the strength of the intramolecular bonds. In the history of Thailand, as over a century ago, monks turned to turmeric for colouring their robes and found little time to meditate, having to constantly re-dye their clothing (Moeyes, 1993). The ability of detergent to dissolve the turmeric combined with the ability of sun to degrade the molecules cause a lack of colour fastness, and turmeric was eventually abandoned in favour of longer-lasting dyes (Wang, Pan, Cheng, Lin, Ho, Hsieh, and Linet, 1997). One advantage of the bright yellow dye, curcuminoid, is that it is referred to as friendly to nature. Besides being used as a spice, it is also known for its antibacterial activity, wherein the curcumin surprisingly benefits from the same oxidation which causes problems for its dyes (Han and Yang, 2005; Tønnesen, Másson, and Loftsson, 1997).

Figure 2.1 Morphological illustration of *Curcuma longa* Linn., its turmeric rhizome (lower left hand side) and its turmeric rhizome powder (lower right hand side).

From: Find Me A Cure (2009).

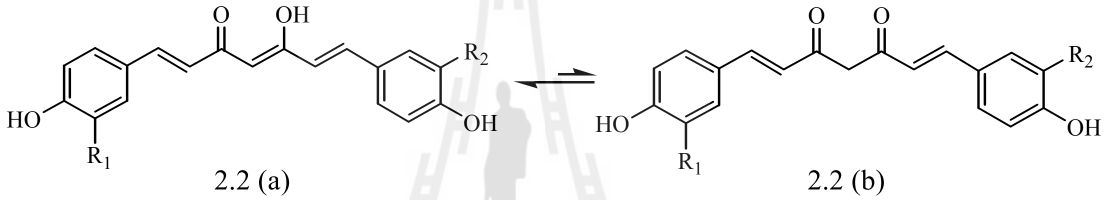
Curcumin is able to confer protection to light sensitive drugs in formulations for soft gelatin capsules (Jayaprakasha et al., 2005), and has also been used in cosmetic compositions as a natural sunscreen (Jayaprakasha et al., 2002). Many uses of turmeric as medicine, spice, and even sunscreen have been well studied within the scientific community. However, its use as a dye has not been studied. Perhaps with the use of a mordant to act as a barrier against degradation by sun and wash, the light-sensitive molecules of the curcuminoids can give wash and color fastness. In fact, use of curcumin as a dye is well documented. Villagers within the growth range of turmeric are already well aware by now that the addition of some metal ions to the dyeing process can achieve this.

Use of turmeric as a dye, though not used on the scale of synthetic dyes, is still fairly common in Asian tropical (especially rural) zones, from India to China, and interest in natural sources of dye and other consumables increases with ecological concerns worldwide. Large clothing production companies do not use turmeric because of its expense over synthetic dyes. As stated, many people know to add a reagent to fix the otherwise weak curcumin molecule to sun and wash, but no one knows the optimum conditions for the fixing. This causes over-use of reagents, inferior colour fastness, ineffective dye adsorption, or toxicity from excess metal ions, which are the typical mordants. Previous experiments have well established the structures of curcuminoids (Jayaprakasha et al., 2002, 2005; He et al., 1998; Jiang et al., 2006) both individually and as a compound, as well as its physical and chemical properties, biological interactions for medicinal purposes, etc. Thus, a great deal of research is spared us in approaching a model of effective application of turmeric to fabric. What conditions of initial dye and reagent concentrations, temperature, and pH will allow maximum absorbancy of colour and a molecular structure capable of withstanding the rigors associated with the life of the average garment?

The use of natural yellow dyes is related to “poor fastness” properties which have problems both in light fastness and wash fastness (Moeyes, 1993). Curcuminoids are especially problematic when dyeing onto silk fibroin, cotton, and wool (Popoola, 2000; Tsatsaroni, Liakopoulou-Kyriakides, and Eleftheriadis, 1998). This problem is usually solved by using metal ions as mordants (Tsatsaroni et al., 1998). In the northeast of Thailand, villagers usually use some mordants for silk dyeing by trial and error (Moeyes, 1993), for example, alum salt, iron oxide, and copper(II) sulphate. In the north and the northeast of Thailand, extracted dye from *M. cochinchinensis* is used as a natural yellow dyestuff for silk dyeing but the fastness properties and reproducibility to give consistency in production are still problems to be solved. As part of the approach to tackle these problems, fundamental physical studies on the dyeing process are important.

Curcuminoid is a yellow-orange crystalline powder which is insoluble in water, poorly soluble in hydrocarbon solvents, soluble in alcohol, and sensitive to light, but moderately stable to heat (Sowbhagya, Smitha, Sampathu, Krishnamurthy, and Bhattacharya, 2005; Wang et al., 1997). The dried rhizome of *Curcuma longa* Linn. was reported to contain 2-7% of essential oils and 3-5% of aromatic yellow curcuminoids (He et al., 1998). Its two tautomeric forms, 2.2 (a) and 2.2 (b), are shown in Figure 2.2.

As mentioned above, curcumin is a major component of the turmeric rhizome of the plant *Curcuma longa* Linn. and alkaline extracts of the rhizome of this plant are used for the dyeing of silk. However, the use of this natural dye mixture is often linked to poor fastness properties and thus metal-based mordants are used to increase fastness (e.g. wash fastness) properties. Some metal ions and curcumin complexes have been investigated (Chapter III). The scientific results from this study will hopefully give a better understanding of the adsorption mechanism in this dyeing process. Since demethoxycurcumin and bisdemethoxycurcumin are minor components in this plant, the study of these two curcuminoids will not be followed in this section.



2.2 (a) 2.2 (b)

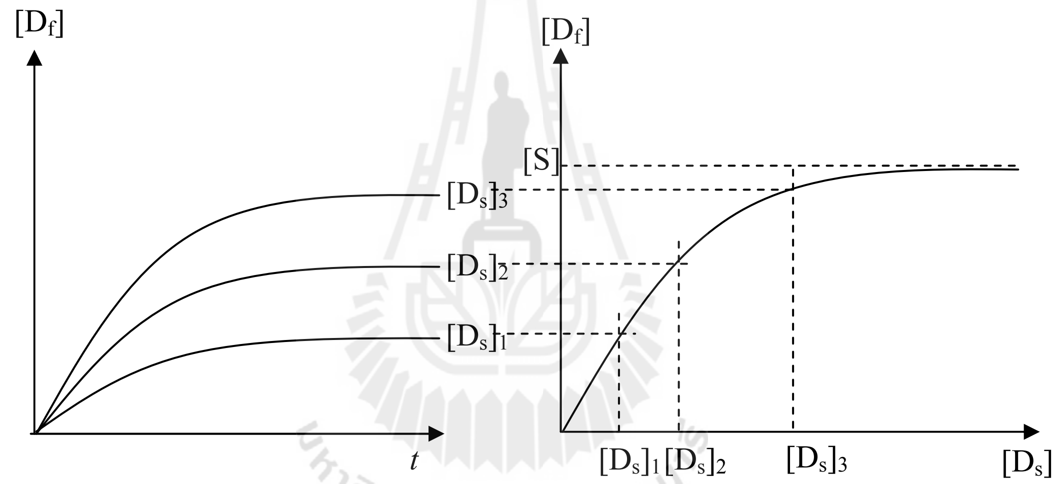
Compound	R_1	R_2	MW
Curcumin	$-OCH_3$	$-OCH_3$	368.38
Demethoxycurcumin	$-OCH_3$	–H	338.38
Bisdemethoxycurcumin	–H	–H	308.38

Figure 2.2 Chemical structures and molecular weight of curcuminoids.

From: He et al. (1998).

2.2.2 Physical chemistry of dyeing process

The scientific investigation of the dyeing processes involves two experimental methods which can be described by dyeing kinetics and dyeing equilibria (Zollinger, 2003). The dyeing process involves the distribution of a dye between at least two phases, namely dye bath and substrate. The distribution process is called adsorption if the substance to be distributed is retained by a surface (e.g. gas on a solid). If the substance does not stay at the surface but enters the interior of a body (e.g. gas in liquid), the process is termed sorption. Dyeing processes of water soluble dyes in aqueous dye baths with any substrate always require a distribution process between two phases (dye bath and substrate) (Perkins, 1996). The kinetics of dyeing are represented by dye uptake curves which give the rate of transfer of dye in solution from the dye bath into the substrate. The position of sorption versus desorption after infinite time is represented by the dyeing equilibrium of the dyeing process. Graphical representations of a dyeing process are shown in Figure 2.3.



$[D_f]$: concentration of dye in substrate, $[D_s]$: concentration of dye in solution, [S]: saturation value, and *t*: time

Figure 2.3 Graphical representations of a dyeing process: kinetics (left) and equilibrium (right).

From: Zollinger (1993).

If the dyeing process is done under different isothermal conditions, a series of curves (Perkins, 1996) are given as shown in Figure 2.4. The initial adsorption rate increases with an increase in dyeing temperature. This can be explained by the fact that the dye adsorption by fibers at higher temperature is faster than that at lower temperature and hence leads to an increase in the initial rate. The slope of curve varies depending on the temperature, type of fiber, type of dye, amount of agitation of the dye bath, amount and type of dyeing auxiliaries used, and other factors. As the amount of dye on the fibers increases and the sites are covered, the dye must leave the surface and diffuse toward the interior of the fiber before additional dye molecules can be adsorbed from the dye bath.

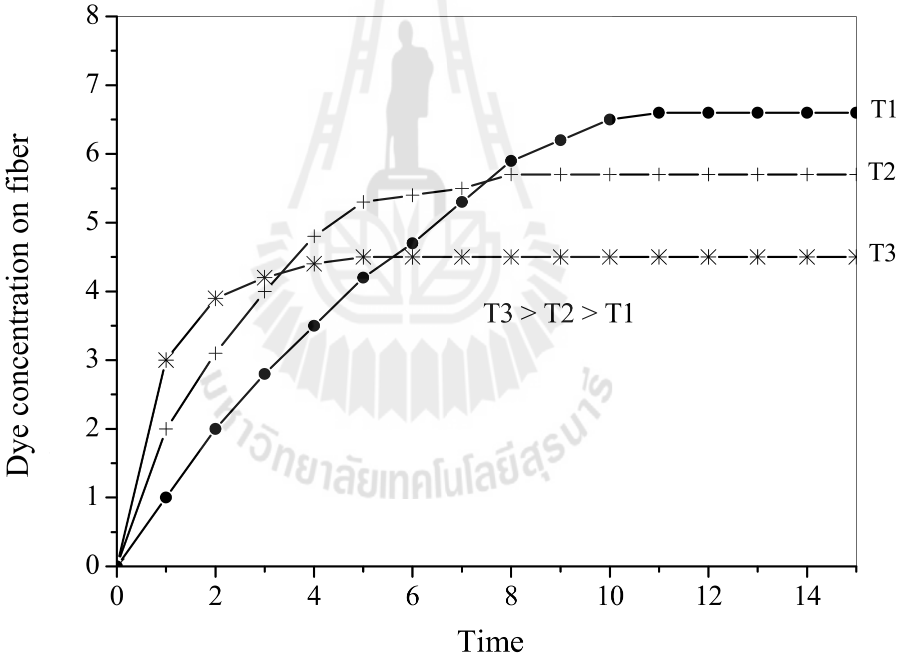


Figure 2.4 Rate of dyeing isotherms.

From: Perkins (1996).

The kinetic behaviour of a dye in the dyeing of a textile material comprises at least four stages (Zollinger, 2003):

(a) convectional diffusion to the fiber surface, occurring in the dye bath;

(b) molecular diffusion through the hydrodynamic boundary layer;

(c) adsorption at the outer surface; and

(d) molecular diffusion into the fiber (sorption).

The stages (a), (c), and (d) are important for the kinetics of the overall dyeing process. After some period of time, the slope of the isotherm becomes flat indicating that the system has reached equilibrium. The time required to reach equilibrium is always shorter at higher dyeing temperature. It is mainly due to the fibers containing more dye at higher temperatures in the early stages but less dye in the latter stages of dyeing. Therefore, an increase in the temperature leads to an increase in the dyeing rate but a decrease in the ultimate exhaustion after the equilibrium time, as shown in Figure 2.4. This shows that dye molecules can be adsorbed to a greater degree at a lower temperature because the dyeing reaction is exothermic.

$$\text{Dye} + \text{Fiber} \rightleftharpoons \text{Dye—Fiber} + \text{heat}$$

Desorption of dye molecules from fibers to dye bath takes place at higher dyeing temperatures because of more heat in the dyeing process. Thus, the equilibrium position of this process is shifted to the left hand side.

There are several different intermolecular and intramolecular interactions that are essential for understanding the chemistry of textile dyeing. The five main types of interactions are covalent forces, ionic forces, van der Waals forces, hydrogen bonds and dipole-dipole forces (Christie, 2001; Zollinger, 2003) and are described below:

Covalent forces

Covalent forces result from the sharing of a pair of electrons by two atoms. An especially important use of covalent bonding in colour application technology is the application of reactive dyes to cellulosic and protein textile fibers (Christie, 2001). After dyeing fibers with reactive dyes, the dyes interact chemically with the fibers to form a covalent bond.

Ionic forces

An ionic bond is formed by electron transfer from one atom to another atom or atoms. The atom that loses electrons becomes a positively charged species or cation. The atom that gains electrons becomes a negatively charged species or anion. Ionic bonds are the resulting electrostatic attraction between these oppositely charged ions. In the dyeing of wool, silk, and polyamides with anionic dyes, these fibers contain amino and carboxyl groups. Depending on the pH value in dyeing process, under lower pH these fibers have an overall positive charge (NH_3^+) because the carboxyl groups in the side chains are hardly ionized under acid condition. Therefore, anionic dyes are attracted towards the positively charged amino acid by ionic forces (Chairat, Rattanaphani, S., Bremner, and Rattanaphani, V., 2005).

Van der Waals forces

Van der Waals forces or dispersion forces are the forces of attraction involved between non-polar molecules (Christie, 2001). The distances between molecules have an important effect on the strength of van der Waals forces. They are the weakest intermolecular forces. Although in a non-polar molecule there is no overall charge distribution, the electrons are in constant motion so that at any instant, small dipoles will be present. These instantaneous dipoles in turn induce oppositely-oriented dipoles in neighboring molecules and a weak attraction between the molecules results. Van der Waals forces are therefore only effective for sorption of dyes to fiber molecules if the distance between the dye and the fiber molecules is small. The influence of van der Waals forces is particularly important in dyeing of cellulose fibers.

Hydrogen bonds

Hydrogen bonds are an especially strong type of dipole-dipole interactions. This interaction occurs between molecules containing a hydrogen atom which can interact with a nitrogen, oxygen, or fluorine atom (Christie, 2001). A partially positive hydrogen atom of one molecule is attracted to the unshared pair of electrons of the electronegative atom of another molecule. Intermolecular and intramolecular hydrogen bonds between functional groups on dye molecules and fiber molecules play an important role in many interactions in dye-fiber systems.

Dipole-dipole forces

Dipole-dipole interactions may make a contribution to the forces of attraction between dye and fiber molecules (Christie, 2001). Dipolar intermolecular forces involve the attraction of the positive centers in one polar molecule for the negative centers in another. As a result of these forces, polar molecules are generally attracted to each other more strongly than non-polar molecules of comparable molecular size. However, as the charges are only partial, dipole-dipole interactions are weaker than ionic forces.

2.2.3 Kinetic models of adsorption

In order to investigate the controlling mechanism of adsorption processes such as mass transfer, diffusion control, and chemical reaction, several methods have been used to test the experimental data. A simple kinetic analysis of adsorption is the Lagergren equation. The Lagergren equation, a pseudo-first-order equation, describes the kinetics of the adsorption process as follows (Ho and McKay, 1998; Wu, Tseng, and Juang, 2001; Chiou and Li, 2002, 2003; Doğan and Alkan, 2003; Chairat et al., 2005; Uzun, 2006):

$$\frac{dq_\mathrm{t}}{dt} = k_1(q_\mathrm{e} - q_\mathrm{t}) \qquad (2.1)$$

where k_1 is the rate constant of pseudo-first-order adsorption (s^{-1}), and q_e and q_t are the amount of dye adsorbed per gram of silk (mg/g silk) at equilibrium and time t, respectively. After definite integration by applying the initial conditions $q_\mathrm{t} = 0$ at $t = 0$ and $q_\mathrm{t} = q_\mathrm{t}$ at $t = t$, equation (2.1) becomes:

$$\ln(q_\mathrm{e} - q_\mathrm{t}) = \ln q_\mathrm{e} - k_1 t \qquad (2.2)$$

A straight line of $\ln(q_\mathrm{e} - q_\mathrm{t})$ versus t suggests the applicability of this kinetic model to fit the experimental data. The first-order rate constant k_1 and equilibrium adsorption density q_e are calculated from the slope and intercept of this line, respectively.

In addition, the pseudo second order kinetic model (Ho and McKay, 1998, 1999; Wu et al., 2001; Chairat, Rattanaphani, S., Bremner, and Rattanaphani, V., 2008) is based on adsorption equilibrium capacity and can be expressed as:

$$\frac{dq_\mathrm{t}}{dt} = k_2 (q_\mathrm{e} - q_\mathrm{t})^2 \tag{2.3}$$

where k_2 (g silk/mg min) is the rate constant for pseudo-second-order adsorption. Integrating equation (2.3) and applying the initial conditions gives:

$$\frac{1}{(q_\mathrm{e} - q_\mathrm{t})} = \frac{1}{q_\mathrm{t}} + k_2 t \tag{2.4}$$

or equivalently,

$$\frac{t}{q_\mathrm{t}} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}} t \tag{2.5}$$

And

$$h_\mathrm{i} = k_2 q_\mathrm{e}^2 \tag{2.6}$$

where h_i (Chiou and Li, 2003; Chairat et al., 2005, 2008) is the initial dye adsorption rate (mg/g silk min). If the pseudo-second-order kinetics are applicable, the plot of t/q_t versus t shows a linear relationship. The slope and intercept of the plot are used to calculate q_e and the pseudo second-order rate constant k_2, respectively. It is likely that the behaviour over the whole range of adsorption is in agreement with the chemisorption mechanism being the rate-controlling step (Chiou and Li, 2003).

In general, the rates of chemical reactions increase with an increase in the temperature. In the rate law, temperature dependence appears in the rate constant. The dependence of rate constants on temperature over a limited range can usually be represented by an empirical equation proposed by van't Hoff and Arrhenius in 1884 (Laidler, Meiser, and Sanctuary, 2003):

$$k = Ae^{-E_a/RT} \tag{2.7}$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant equal to 8.3145 J $K^{-1}mol^{-1}$. The pre-exponential factor A has the same unit as the rate constant. An alternative form is obtained by taking the logarithm of each side.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{2.8}$$

A straight line is obtained by plotting the logarithm of the rate constant against the reciprocal of the absolute temperature. Such a graph is often referred to as an Arrhenius plot. The magnitude of activation energy may give an idea about the type of adsorption. In physical adsorption the reaction is easily reversible, equilibrium is rapidly attained, and its energy requirements are small. The activation energy for physical adsorption is usually not more than 4.2 kJ/mol because the forces involved in physical adsorption are usually weak. So the activation energy is of the same magnitude as the heat of chemical reactions. This type of adsorption is usually referred to as physisorption. However, chemical adsorption is specific and involves forces much stronger than in physical adsorption. It is usually referred to as chemisorption (Aksu, 2002).

The enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and free energy ($\Delta G^{\#}$) of activation can also be calculated using the Eyring equation (House, 1997; Laidler et al., 2003) as follows:

$$\ln\left[\frac{k}{T}\right] = \ln\left[\frac{k_b}{h}\right] + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \tag{2.9}$$

where k_b and h refer to the Boltzmann's constant and the Planck's constant respectively. The enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation are calculated from the slope and intercept of a plot of ln(k/T) versus $1/T$, respectively. Gibbs energy of activation ($\Delta G^{\#}$) can be written in terms of enthalpy and entropy of activation (House, 1997; Laidler et al., 2003) as follows:

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{2.10}$$

Based on fundamental thermodynamics concept, it is assumed that in an isolated system, energy cannot be gained or lost and entropy change is the only driving force. The Gibbs free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The thermodynamic parameters for the adsorption process, namely Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) of adsorption are evaluated using the following equations (Chiou and Li, 2003):

$$K_c = \frac{C_{ad,\,e}}{C_e} \tag{2.11}$$

$$\Delta G^\circ = -\,RT\ln K_c \tag{2.12}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{2.13}$$

In the above equations, K_c is the equilibrium constant, and $C_{ad,e}$ and C_e are the dye concentration adsorbed at equilibrium (mg/L) and the concentration of dye left in the dye bath at equilibrium (mg/L), respectively. T is the solution temperature (K) and R is the gas constant. The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption are calculated from the slope and intercept of van't Hoff plots of $\ln K_c$ versus $1/T$, respectively.

2.3 Experimental

2.3.1 Chemicals

(a) Silk yarn from Chul Thai Dyeing Co., Ltd, Phetchabun, Thailand

(b) 98% Curcumin [458-37-7] from Across Organics

(c) Sodium hydroxide, NaOH, from Aldrich

(d) Ammonium acetate, NH_4OOCCH_3, from Merck

(e) Ammonium hydroxide, NH_4OH, 25% m/v, commercial grade, from Merck

(f) Hydrochloric acid, HCl, 37% m/v, from Merck

(g) Ethanol, C_2H_5OH, analytical grade, from Merck

(h) Copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, from Merck

2.3.2 Instruments

(a) A UV-Vis spectrophotometer (Agilent 8453) employed for absorbance measurements using quartz cells with path length of 1 cm

(b) A pH meter (Jenway/4330) used to measure the pH values of dye solutions

(c) A shaker bath (Type TW20 P Selecta, UK), operated at 45 strokes/min and used to study the adsorption kinetics and thermodynamics of silk dyeing

2.3.3 Experimental methods

2.3.3.1 Silk yarn preparation

The degummed silk yarn (1.00 kg) was added to 0.5 M HCl (3 L) at room temperature. It was soaked for 30 minutes, then the HCl was removed and the silk was washed with deionized water until the rinsed water was neutral. The silk yarn was then squeezed to remove excess liquor and dried at room temperature (Chairat, 2004; Septhum, 2006; Wongsooksin, 2008).

2.3.3.2 Preparation of curcumin stock solutions

A fresh curcumin stock solution (1.842 g/L) was prepared by dissolving 0.1842 g of curcumin in a small amount of 95% ethanol in a 100-mL amber volumetric flask and adding more ethanol to obtain the final volume of 100.00 mL. Lower concentrations of curcumin solutions were made by dilution of this stock solution with deionized water and all solutions were kept in amber bottles during use.

2.3.3.3 Plant material and dye extraction

The turmeric rhizome of *Curcuma longa* Linn. was collected from Chaiyaphum Province, Thailand. Fleshy parts of turmeric rhizome were peeled and chopped into small pieces. A weighed amount of turmeric rhizome pieces was extracted with 0.1 M sodium hydroxide solution using blender operated at 1,200 rpm for one minute. The standard procedure ratio was 100 g of material to 1 L of liquid. The extracted dye solution was filtered and, from the red filtrate, the dye was precipitated by drop-wise addition of 0.1 M acetic acid solution until a yellow suspension was formed. The suspension was then centrifuged and the liquid was decanted. The crude extract was then air dried in a dark room to give a crude extracted dye with a yield of 9.4%. This yellow powder was then used without further purification.

2.3.3.4 Determination of the amount of curcumin in the crude extracted dye

Solutions of crude dye extract and curcumin were prepared separately by dissolving 0.1842 g of each in a 100-mL amber volumetric flask with 95% ethanol (using small amount first and adding more to make the final volume to 100.00 mL). The resulting solutions (50.0 μL for curcumin and 100.0 μL for extracted dye) were then diluted separately with deionized water in a 10-mL amber volumetric flak and the diluted solutions were analyzed using UV-Vis spectrophotometer to determine λ_{max} values.

2.3.3.5 Turmeric extracted dye stock solutions

A fresh extracted dye stock solution (12.28 g/L of extracted dye) was prepared by dissolving 1.228 g of crude extracted dye in a 100-mL amber volumetric flask with 95% ethanol (using small amount first and adding more to make the final volume to 100.00 mL). Lower concentrations of the extracted dye solutions were made by dilution of this stock solution with deionized water and all solutions were kept in amber bottles during use.

2.3.3.6 Effects of initial concentrations of curcumin and extracted dye and contact time on the adsorption onto silk

Curcumin solutions with concentration of 12.9, 16.6, and 20.3 mg/L at pH approximately of 6.1 without any adjustment were prepared from the stock solution by pipetting 0.175, 0.225, and 0.275 mL of the stock solution, respectively and diluting each with deionized water to obtain the final volume of 25.00 mL in a 25-mL amber volumetric flask. The adsorption experiments were carried out by pre-warming each dye solution (25.00 mL) without shaking in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, and 60 minutes for each concentration. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 427 nm versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t which were calculated by the following mass balance relationship:

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{2.14}$$

where C_0 is the initial concentration and C_t represents the concentration at time t of the dye (mg/L), V is the volume of the solution (L), and W is the mass of the silk used (g).

The study of the effects of the initial concentration of extracted dye and contact time on the adsorption onto silk was carried out in a similar manner as that of curcumin using the dye solutions with concentration of 86.0, 111, and 135 mg/L of extracted dye at pH approximately of 6.1 without any adjustment. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 419 nm versus dye concentration.

2.3.3.7 Effect of pH on the adsorption of curcumin and extracted dye onto silk

Curcumin solutions with concentration of 16.6 mg/L containing 10.00% v/v buffer solutions of ammonium acetate/acetic acid of various pH were prepared in 25-mL amber volumetric flasks using curcumin stock solution (0.225 mL), 2.0 M ammonium acetate solution (2.50 mL), glacial acetic acid (drop-wise adding until the desired pH was obtained), and deionized water. The pH values of the prepared curcumin solutions were 4.19, 4.69, 5.47, 5.87, 6.28, 6.57, and 7.09. Adsorption experiments were carried out by pre-warming each dye solution (25.00 mL) without shaking in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after 60 minutes. Dye concentrations at each pH were determined at time zero and at 60 minutes using calibration curves of each pH based on absorbance at λ_{max} of each pH versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t which were calculated by equation (2.14).

The study of the effect of pH on extracted dye dyeing onto silk was carried out in a similar manner as that on curcumin using the dye solutions containing 111 mg/L of extracted dye and the dyeing time of 120 minutes. The pH values of the prepared dye solutions before dyeing were 4.00, 4.53, 5.11, 5.58, 6.09, 6.39, and 7.01. Dye concentrations were determined at time zero and at 120 minutes using calibration curves of each pH based on absorbance at λ_{max} of each pH versus dye concentration.

2.3.3.8 Effect of material to liquor ratio (MLR) on the adsorption of curcumin and extracted dye onto silk

The optimum MLR of silk yarn (g) and 16.6 mg/L curcumin solutions (mL), prepared at pH 5.5 in a similar manner as noted in section 2.3.3.7, for the adsorption was studied using the ratios of 1:50, 1:100, and 1:150 g/mL. The adsorption experiments were carried out by pre-warming each dye solution (12.50, 25.00, and 37.50 mL) without shaking in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, and 60 minutes. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 427 nm versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t which were calculated by equation (2.14).

The study of the effect of material to liquor ratio on the adsorption of extracted dye onto silk was carried out in a similar manner as that of curcumin using 12.50, 25.00, and 37.50 mL of dye solution containing 111 mg/L of extracted dye prepared at pH 5.5. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 419 nm versus dye concentration.

2.3.3.9 Effect of temperatures on the adsorption of curcumin and extracted dye onto silk

The adsorption experiments were carried out by pre-warming each 16.6 mg/L curcumin solution (25.00 mL), prepared at pH 5.5 in a similar manner as noted in section 2.3.3.7, without shaking in a 100-mL amber reagent bottle in a shaker bath at 30, 45, and 60 °C, separately. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in each dye solution. The silk yarn samples were then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, and 60 minutes. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 427 nm versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t which were calculated by equation (2.14).

The study of the effect of temperatures on the adsorption of extracted dye onto silk was carried out in a similar manner as that of curcumin using dye solution containing 111 mg/L of extracted dye prepared at pH 5.5. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 419 nm versus dye concentration.

2.3.3.10 Equilibrium experiments of the adsorption of curcumin and extracted dye onto silk at optimum condition

An experiment on the equilibrium adsorption isotherm was carried out by pre-warming 16.6 mg/L curcumin solution (25.00 mL), prepared at pH 5.5 in a similar manner as noted in section 2.3.3.7, without shaking in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after 60 minutes. The initial and equilibrium dye concentrations were estimated using a calibration curve based on absorbance at 427 nm. The experiment was repeated three times to obtain the average amount of dye adsorbed onto silk at equilibrium, q_e (mg/g silk) which was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{2.15}$$

where C_0 and C_e are the initial and equilibrium concentrations of dye (mg/L), respectively, V is the volume of the solution (L), and W is the mass of silk used (g).

The equilibrium study of the adsorption of extracted dye onto silk was carried out in a similar manner as that of curcumin using the dye solution containing 111 mg/L of extracted dye prepared at pH 5.5 and the contact time of 120 minutes.

The initial and equilibrium dye concentrations were estimated using a calibration curve based on absorbance at 419 nm.

2.3.3.11 Adsorption and desorption studies of curcumin and extracted dye on dyeing onto silk

Adsorption experiments on dyeing curcumin and extracted dye onto silk were carried out in a similar manner as the equilibrium experiments but the contact times were varied at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, 120, 150, 180, 240, 300, and 360 minutes for both curcumin and extracted dye. All experiments were repeated twice to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t which were calculated by equation (2.14).

After the adsorption experiments, the silk yarn samples were removed from the dye solutions, squeezed, and air dried at room temperature. The dried silk yarn samples dyed for 60, 90, 120, 150, 180, 240, 300, and 360 minutes in the curcumin case and those dyed for 120, 150, 180, 240, 300, and 360 minutes in the extracted dye case were selected for the desorption experiments. Each selected silk yarn sample was then soaked in deionized water (25.00 mL) at 30 °C with the desorption time according to its adsorption time, e.g. the silk yarn dyed for 60 minutes was soaked in deionized water for 60 minutes. The desorbed dye concentrations (q_{de}) were determined using a calibration curve based on absorbance at 427 nm for curcumin and 419 nm for extracted dye versus dye concentration. All experiments were repeated twice to obtain the average remaining amounts of dye adsorbed onto silk after desorption which were calculated by subtraction.

2.4 Results and discussion

2.4.1 Determination of the amount of curcumin in crude extracted dye

It was found that the λ_{max} of 9.21 mg/L curcumin in aqueous solution appeared at 427 nm with an absorbance of 0.82549 and that of extracted dye at 419 nm with an absorbance of 0.24758. The absorbance of extracted dye solution at 427 nm was 0.24632, indicating that 14.9% of curcumin was present in the extracted dye, when assuming that Beer's Law holds and no other interfering absorbing species at this wavelength were present. The adsorption behaviour of curcumin and the extracted dye onto silk as well as the adsorption kinetics and thermodynamics were further investigated without purification.

2.4.2 Optimum condition of silk dyeing with curcumin and extracted dye

In the course of the investigation of the adsorption of curcumin and extracted dye onto silk, experimental parameters including initial dye concentration, contact time, pH of dye solution, MLR, and temperature were varied in order to find the optimum condition for adsorption. The mechanisms of adsorption of curcumin and extracted dye onto silk were investigated by using the pseudo-first-order and pseudo-second-order models. Moreover, the activation parameters and thermodynamic parameters of adsorption were calculated.

2.4.2.1 The effects of initial concentrations of curcumin and extracted dye and contact time on the adsorption onto silk

The effects of initial dye concentrations of curcumin and extracted dye and contact time on the adsorption onto silk are presented in Figure 2.5 and 2.6, respectively.

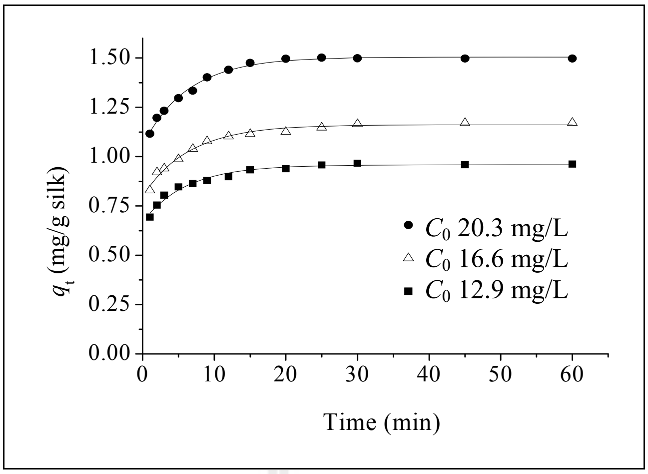


Figure 2.5 The effects of initial concentrations of curcumin and contact time on the adsorption onto silk at 30 °C and pH 6.1 with an MLR of 1:100 g/mL.

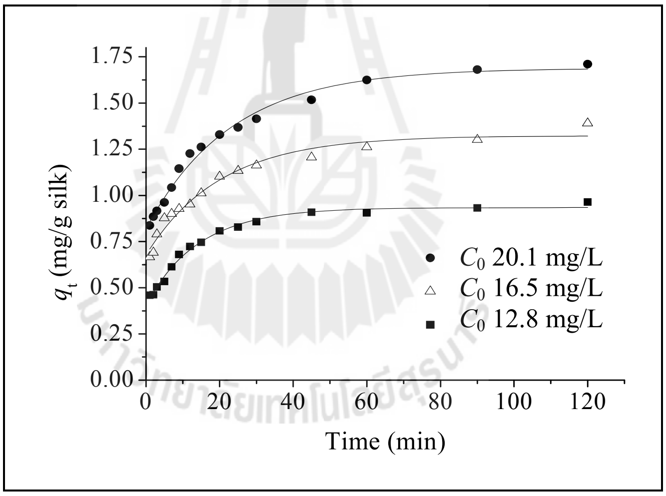


Figure 2.6 The effects of initial concentrations of extracted dye and contact time on the adsorption onto silk at 30 °C and pH 6.1 with an MLR of 1:100 g/mL.

The adsorption of curcumin and extracted dye onto silk was found to reach equilibrium after 60 and 120 minutes, respectively. The equilibrium times were independent of initial dye concentrations but, in the first 12 minutes for curcumin and 60 minutes for extracted dye, rates of adsorption were larger for higher initial dye concentrations at the same shaking speed. This was because an increase in the initial dye concentration accelerated the diffusion of dyes from the dye solution into silk due to an increase in the driving force of the concentration gradient (Chiou and Li, 2002; Chairat et al., 2005).

The average adsorption capacities at equilibrium, q_e, at 30 °C and pH 6.1 in curcumin case were found to increase from 0.9626 to 1.1712 and to 1.4970 mg/g silk with an initial dye concentration of 12.9, 16.6, and 20.3 mg/L, respectively and an MLR of 1:100 g/mL. In extracted dye case, the average adsorption capacities at equilibrium, q_e, at 30 °C and pH 6.1 increased from 0.9582 to 1.1617 and to 1.5049 mg curcumin/g silk with an initial concentration of 86.0, 111, and 135 mg/L of extracted dye (containing approximately 12.8, 16.5, 20.1 mg/L of curcumin, respectively), respectively and an MLR of 1:100 g/mL. However, since both curcumin and extracted dye started to precipitate upon standing during pre-warming step at higher rate for higher initial dye concentration and the apparent colours of dyed silk in each case were not different by naked eyes, the optimum initial dye concentration was chosen to be 16.6 mg/L for convenience.

2.4.2.2 The effect of pH on the adsorption of curcumin and extracted dye onto silk

One of the most important parameters controlling the adsorption capacity of dye onto silk is the pH of the dye solution (Christie, 2001; Chairat et al., 2005). To study the influence of pH on the adsorption capacity of curcumin and extracted dye onto silk, experiments were carried out with different initial dye solution pH values with no silk present. The obtained results are presented in Figure 2.7 and 2.8.

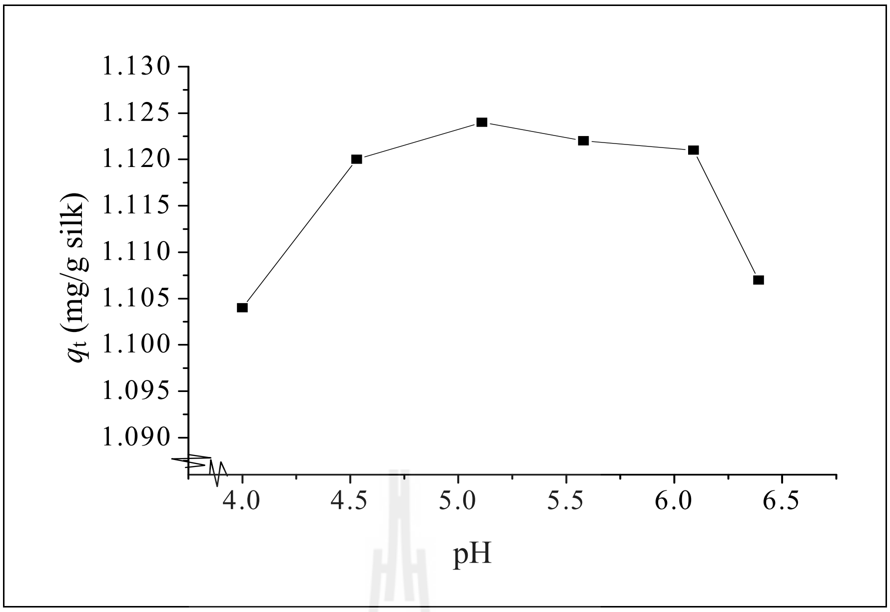


Figure 2.7 The effect of curcumin solution pH on the adsorption onto silk at 30 °C with dye concentration of 16.6 mg/L, contact time of 60 minutes and an MLR of 1:100 g/mL.

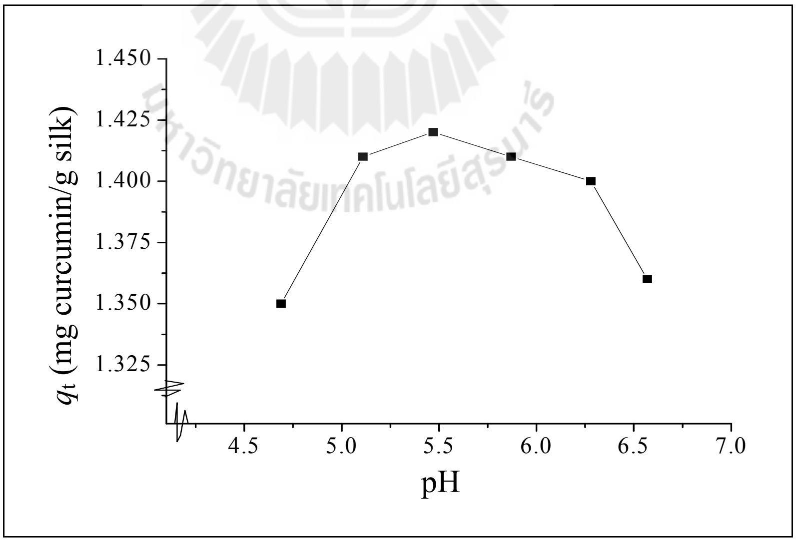


Figure 2.8 The effect of extracted dye solution pH on the adsorption onto silk at 30 °C with dye concentration of 16.5 mg curcumin/L, contact time of 120 minutes and an MLR of 1:100 g/mL.

In both curcumin and extracted dye cases, the dye adsorption capacities onto silk were maximized over the pH range of 5.0-6.0. The pKa_1 value of 6.1 for curcumin and values close to 6.1 for its derivatives are based on ketone-enol tautomery whereas the *N*-terminal and *C*-terminal of silk would bear a positive and negative charge, respectively at pH 6.1 (Corr, 1995). After dyeing silk fibers in the pH range of 5.0-6.0, the dyes might interact chemically with the fibers to form covalent bonds, which were ester bond type, between the carbonyl carbons (C=O) at *C*-terminal of the fibers and the phenolic oxygens of the dyes, enhancing the dye uptake into the silk fibers.

From the experiments, curcumin started to precipitate from the solution at pH 4.0 while the extracted dye at pH 3.5. This could be explained by the fact that curcumin and its derivatives were protonated at the carbonyl oxygens destroying the hydrogen bonds between water molecules and the carbonyl oxygens, making curcumin less soluble in water. At pH above 6.1, the solubility of curcumin in aqueous solution was reported to increase with increasing pH due to the deprotonation of the phenol groups to form a di-anion and, at the same time, curcumin decomposed more easily (Wang et al., 1997). Therefore, the optimum pH value of initial dye solution was chosen to be 5.5.

2.4.2.3 The effect of material to liquor ratios (MLR) on the adsorption of curcumin and extracted dye onto silk

The results of the MLR experiments carried out using initial dye concentration of 16.6 mg/L of curcumin and of extracted dye at pH 5.5 and dyeing temperature of 30 °C are shown in Figures 2.9-2.12.

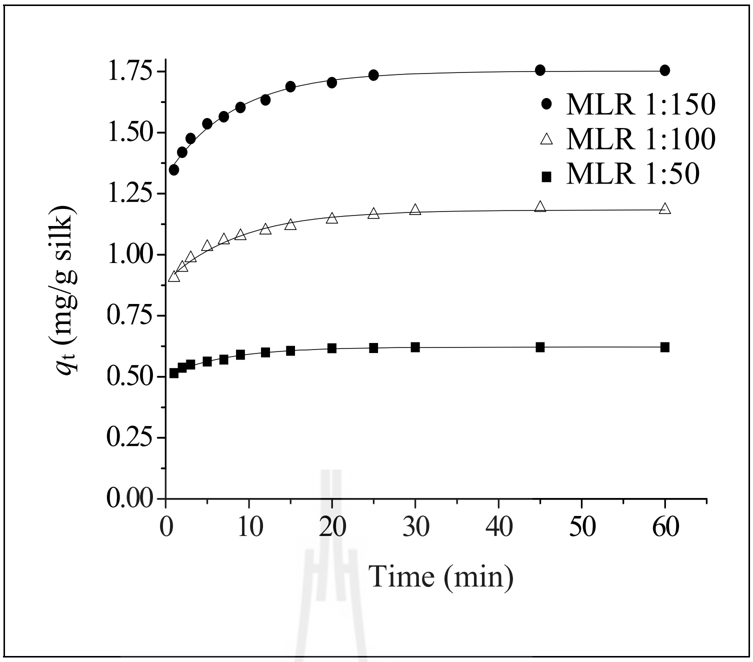


Figure 2.9 The effect of MLR on the adsorption of curcumin onto silk at 30 °C with dye concentration of 16.6 mg/L and dye solution pH of 5.5.

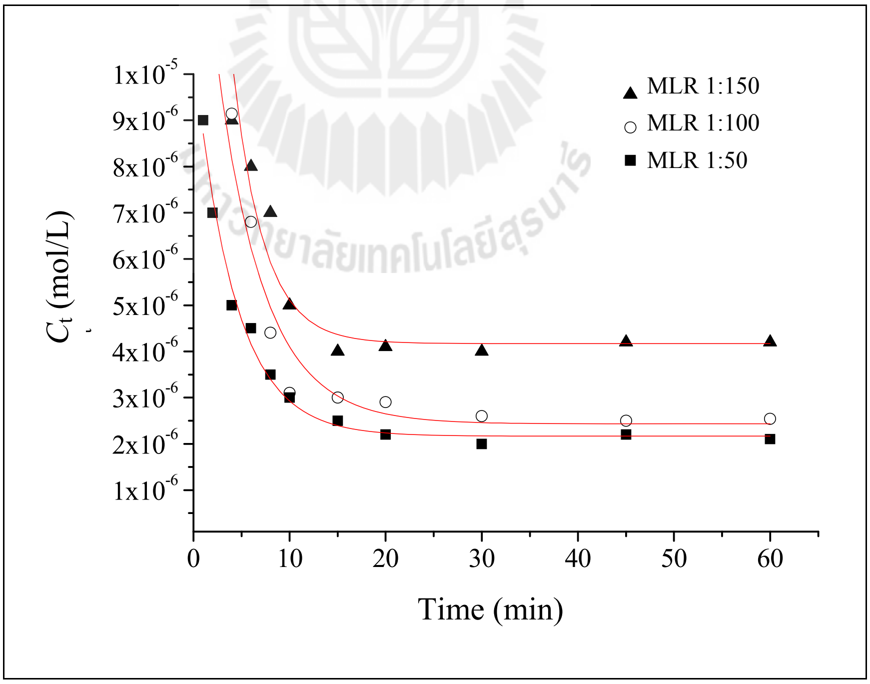


Figure 2.10 The effect of MLR on the remaining concentration of curcumin in solution at 30 °C with initial dye concentration of 16.6 mg/L and dye solution pH of 5.5.

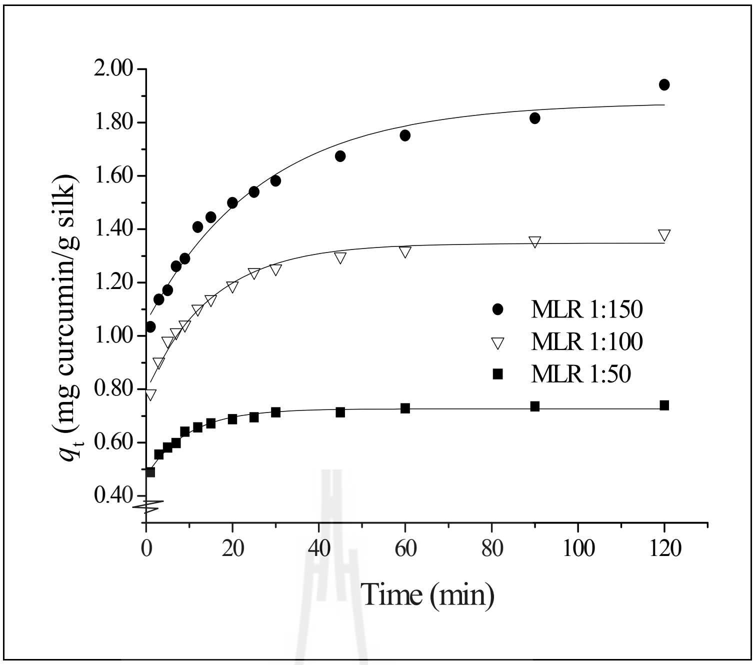


Figure 2.11 The effect of MLR on the adsorption of extracted dye onto silk at 30 °C with initial dye concentration of 16.5 mg curcumin/L and dye solution pH of 5.5.

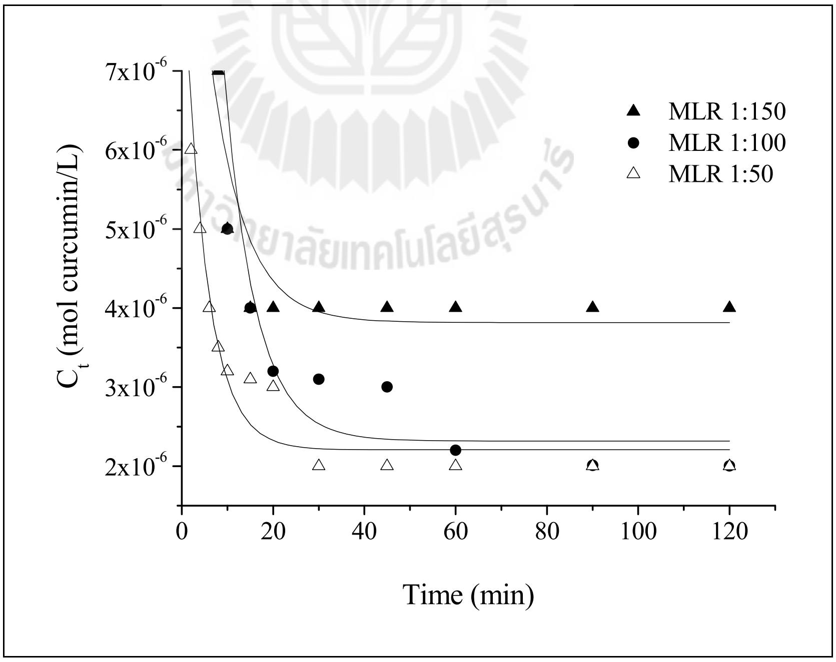


Figure 2.12 The effect of MLR on the remaining concentration of extracted dye in solution at 30 °C with initial dye concentration of 16.5 mg curcumin/L and dye solution pH of 5.5.

It was found that an increase in volume of the dye solution resulted in an increase in the amount of dye adsorbed onto silk (as shown in Figure 2.9 and 2.11). This indicated that the higher the amount of dye existing in the solution, the higher the adsorption onto silk. However, as shown in Figure 2.10 and 2.12, with an MLR of 1:150 g/mL, the amount of dye left in the solution was higher than that with an MLR of 1:100 g/mL significantly. Therefore the optimum MLR was chosen to be 1:100 g/mL.

2.4.2.4 The effect of temperatures on the adsorption of curcumin and extracted dye onto silk

The study of the temperature dependence of the adsorption gives more valuable information on the enthalpy change of adsorption. The effect of temperature on the adsorption rate was studied by carrying out a series of experiments at 30, 45, and 60 °C. It was found that an increase in the temperature led to an increase in initial adsorption rate. Figure 2.13 and 2.14 show different trends in the adsorption capacities at different temperatures before and after equilibrium. Before equilibrium was established, an increase in the temperature led to an increase in the dye adsorption rate indicative of a kinetically controlled process. The maximum uptake of curcumin after equilibrium was dependent on the temperature of the dyeing bath. Higher temperature caused a decrease in the maximum amount of adsorbed curcumin, suggesting an exothermic process. The extracted dye also showed the same trends but with less dependence on the temperature.

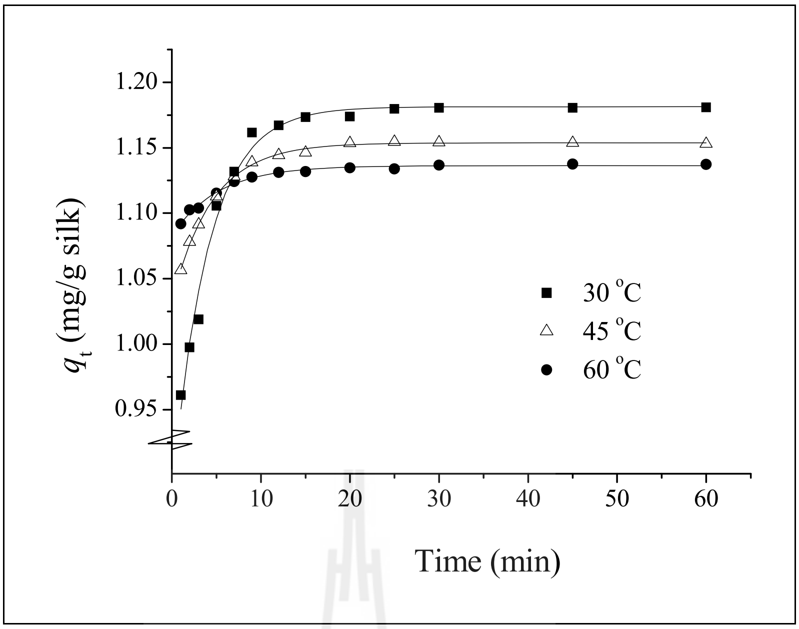


Figure 2.13 The effect of temperatures on the adsorption of curcumin onto silk with initial dye concentration of 16.6 mg/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

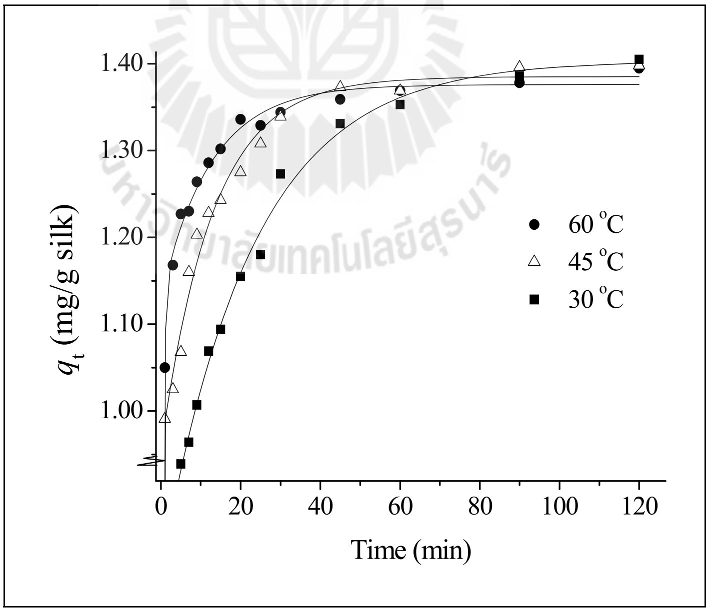


Figure 2.14 The effect of temperatures on the adsorption of extracted dye onto silk with initial dye concentration of 16.5 mg curcumin/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

2.4.3 Kinetic study on the adsorption of curcumin and extracted dye onto silk

Linear plots of pseudo-first-order and pseudo-second-order equations on the adsorption of curcumin and extracted dye onto silk under optimum condition are shown in Figures 2.15-2.18.

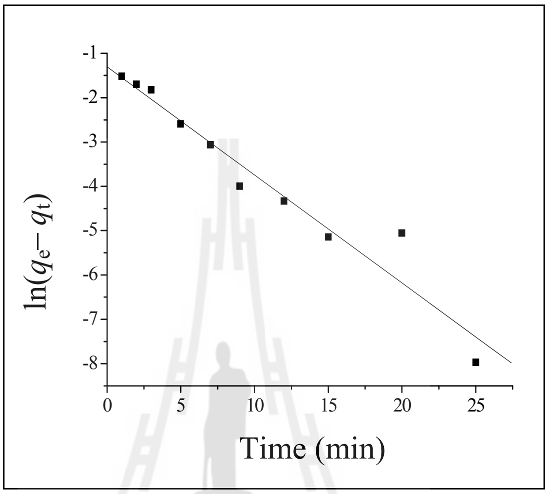


Figure 2.15 A plot of $\ln(q_e - q_t)$ versus time (pseudo-first-order equation) on the adsorption of curcumin onto silk at 30 °C with initial concentration of 16.6 mg/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

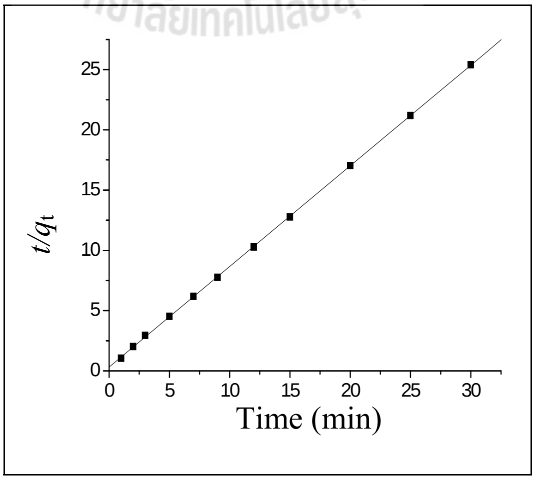


Figure 2.16 A plot of t/q_t versus time (pseudo-second-order equation) on the adsorption of curcumin onto silk at 30 °C with initial concentration of 16.6 mg/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

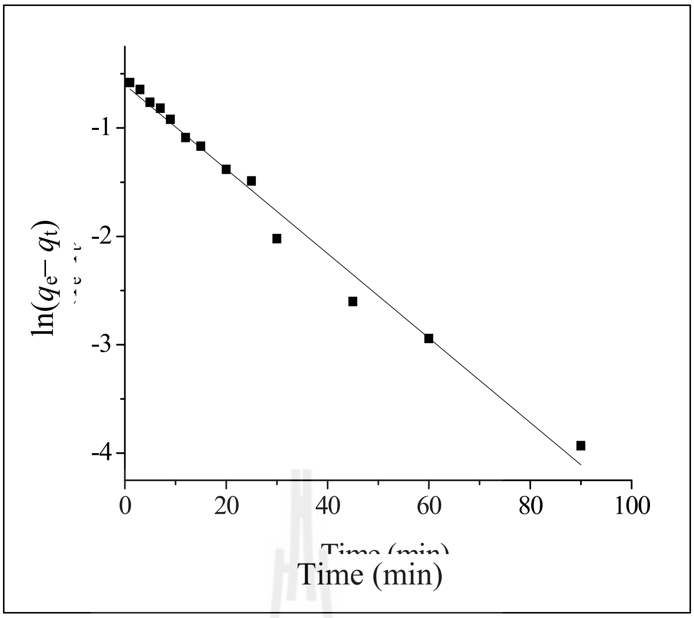


Figure 2.17 A plot of $\ln(q_e - q_t)$ versus time (pseudo-first-order equation) on the adsorption of extracted dye onto silk at 30 °C with initial concentration of 16.5 mg curcumin/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

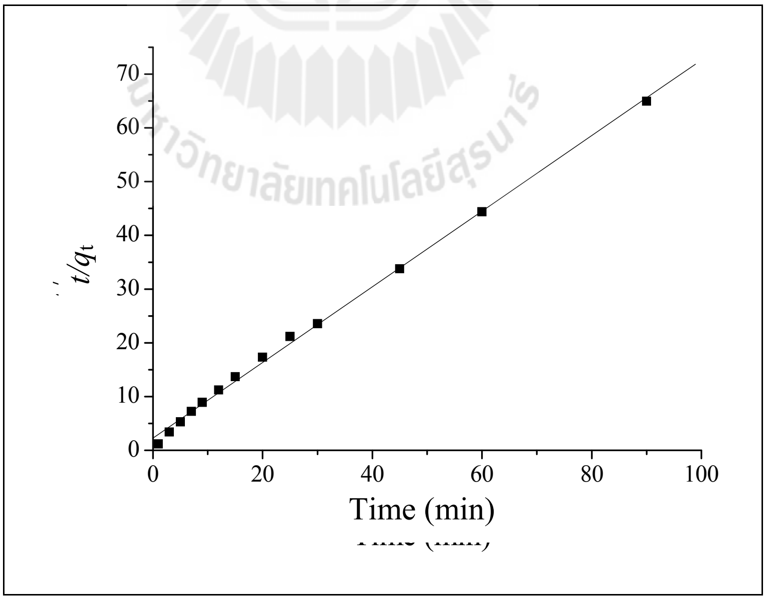


Figure 2.18 A plot of t/q_t versus time (pseudo-second-order equation) on the adsorption of extracted dye onto silk at 30 °C with initial concentration of 16.5 mg curcumin/L, dye solution pH of 5.5, and an MLR of 1:100 g/mL.

Regression coefficients of linear plots (R^2) and kinetic parameters of pseudo-first-order equation (k_1), and pseudo-second-order equation (k_2 and h_i) on the adsorption of curcumin and extracted dye onto silk under optimum condition are tabulated in Table 2.1. It was found that the regression coefficients of the fitted pseudo-second-order equation were high (> 0.99) for both curcumin and extracted dye and were higher than those of the pseudo-first-order one. Furthermore, the calculated equilibrium adsorption capacities ($q_{e,cal}$) in the pseudo-second-order model fitted well to the experimental ones ($q_{e,exp}$). This suggests that the adsorption of both curcumin and extracted dye onto silk was a pseudo-second-order process in which the overall adsorption was likely controlled by the chemical process involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Özacar and Şengil, 2005).

Table 2.1 Regression coefficients of linear plots and kinetic parameters of pseudo-first-order and pseudo-second-order models on the adsorption of curcumin and extracted dye onto silk under optimum condition.

Parameters	Curcumin	Extracted dye
Pseudo-first-order model:		
R^2	0.9730	0.9942
$q_{e,exp}$ (mg curcumin/g silk)	1.1805	1.4330
k_1	0.2436	0.0429
$q_{e,cal}$ (mg curcumin/g silk)	0.2706	0.5855
Pseudo-second-order model:		
R^2	0.9999	0.9977
$q_{e,exp}$ (mg curcumin/g silk)	1.1805	1.4330
k_2	2.2932	0.2167
h_i	3.2835	0.4377
$q_{e,cal}$ (mg curcumin/g silk)	1.1966	1.4213

The effects of MLR, initial dye concentration, and temperature on the adsorption rate constant, k_2, and the initial dye adsorption rate, h_i, were also studied. Linear plots of pseudo-second-order equation on the adsorption of curcumin and extracted dye onto silk at different MLR's, initial dye concentrations, and temperatures are shown in Figures 2.19-2.24.

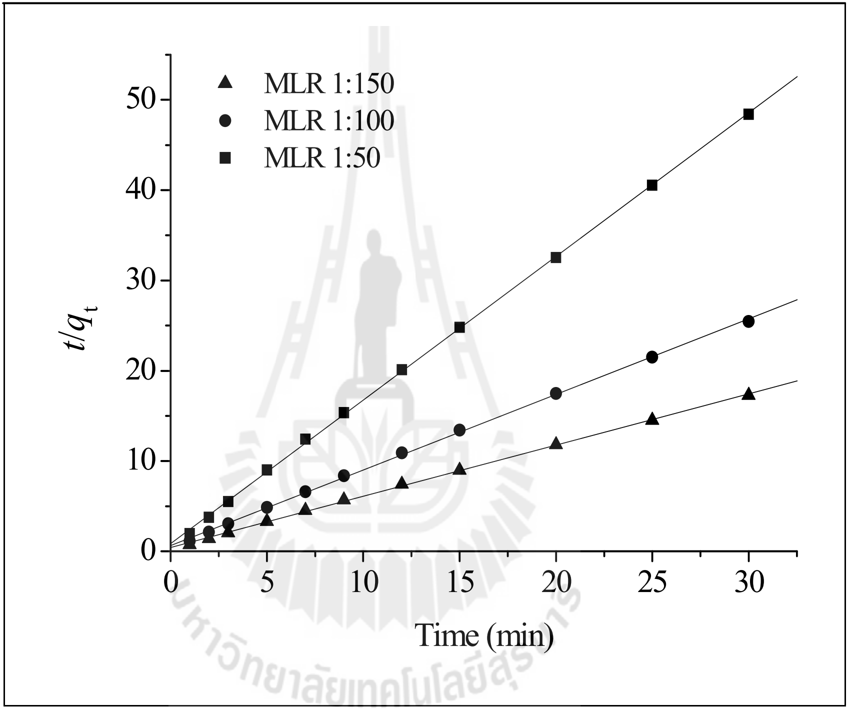


Figure 2.19 The plots of pseudo-second-order equation on the adsorption of curcumin onto silk at different MLR's, with initial dye concentration of 16.6 mg/L, dye solution pH of 5.5, and dyeing temperature of 30 °C.

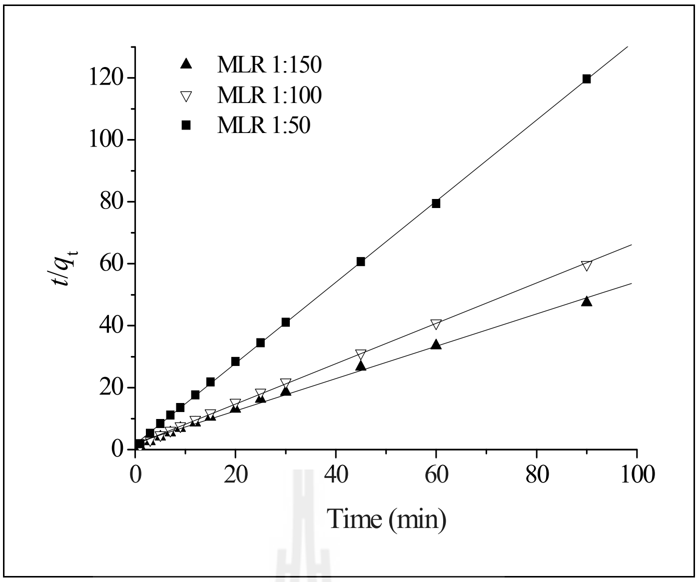


Figure 2.20 The plots of pseudo-second-order equation on the adsorption of extracted dye onto silk at different MLR's, with initial dye concentration of 16.5 mg curcumin/L, dye solution pH of 5.5, and dyeing temperature of 30 °C.

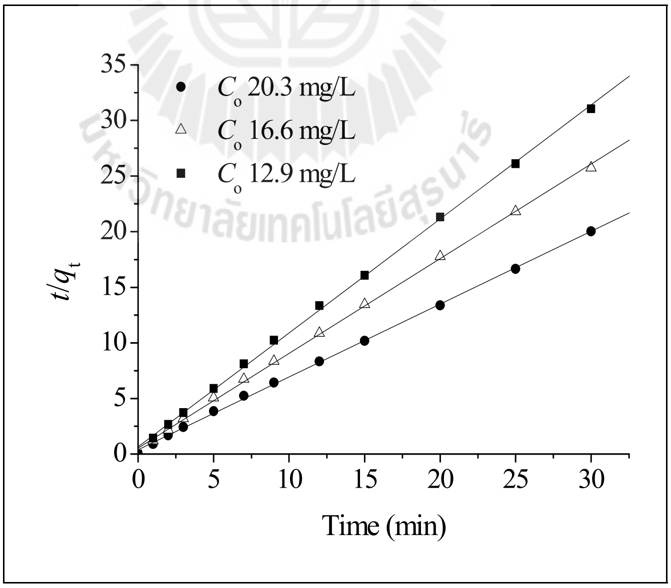


Figure 2.21 The plots of pseudo-second-order equation on the adsorption of curcumin onto silk at different initial dye concentrations with an MLR of 1:100 g/mL, dye solution pH of 5.5, and dyeing temperature of 30 °C.

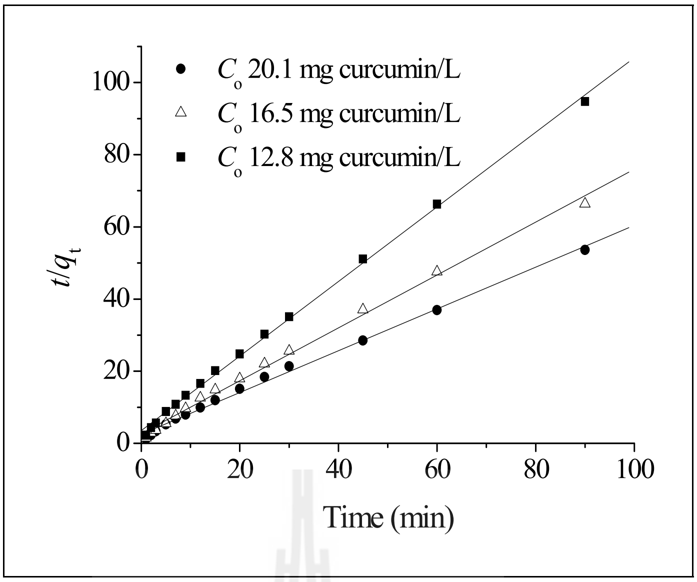


Figure 2.22 The plots of pseudo-second-order equation on the adsorption of extracted dye onto silk at different initial dye concentrations with an MLR of 1:100 g/mL, dye solution pH of 5.5, and dyeing temperature of 30 °C.

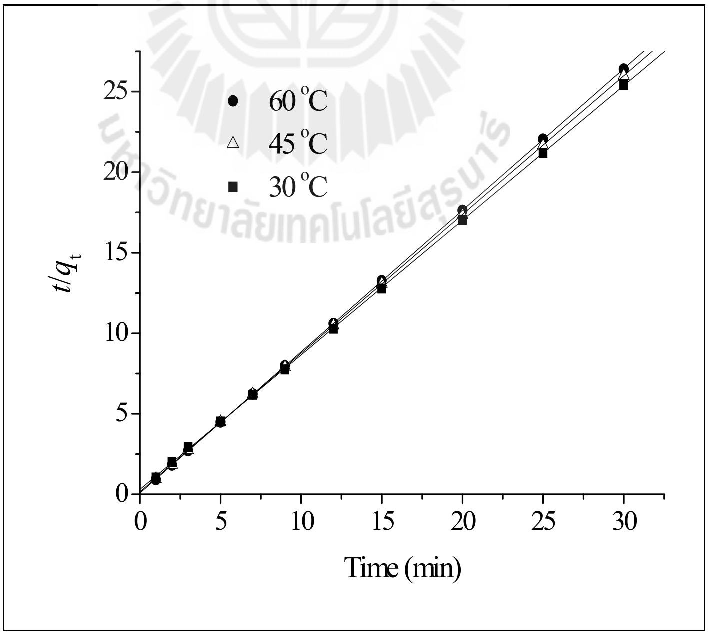


Figure 2.23 The plots of pseudo-second-order equation on the adsorption of curcumin onto silk at different temperatures with initial dye concentration of 16.6 mg/L, an MLR of 1:100 g/mL, and dye solution pH of 5.5.

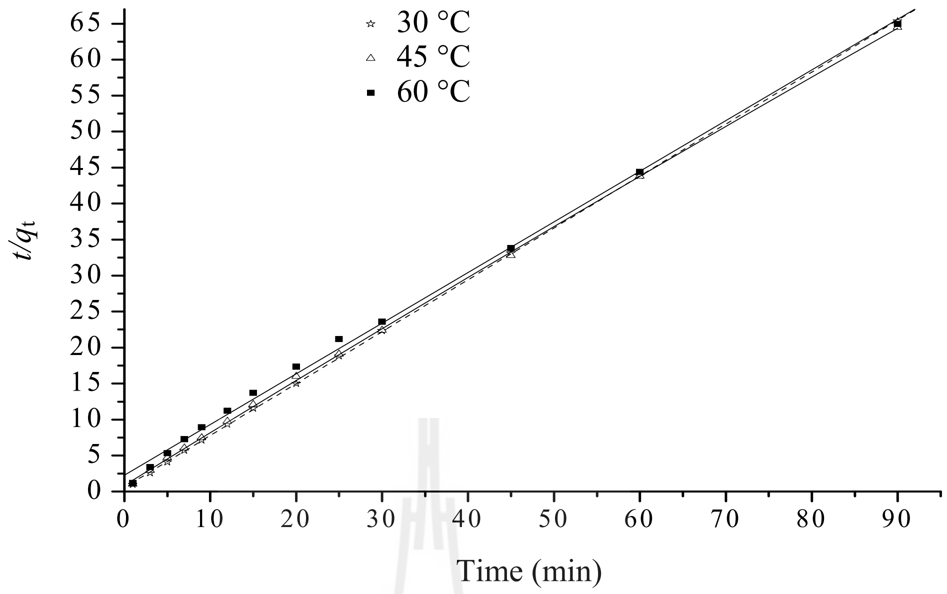


Figure 2.24 The plots of pseudo-second-order equation on the adsorption of extracted dye onto silk at different temperatures with initial dye concentration of 16.5 mg curcumin/L, an MLR of 1:100 g/mL, and dye solution pH of 5.5.

Regression coefficients of linear plots and kinetic parameters of pseudo-second-order equation (k_2 and h_i) on the adsorption of curcumin and extracted dye onto silk under different conditions are tabulated in Tables 2.2 and 2.3, respectively. It was found that the regression coefficients were all high (> 0.99) and the calculated equilibrium adsorption capacities were in good agreement with the experimental data. In addition, the k_2 and h_i values were found to be significantly affected by MLR, initial dye concentration, and temperature in the case of curcumin. The k_2 value on the adsorption of curcumin onto silk increased with increasing MLR, decreasing initial dye concentration, and increasing temperature while the h_i value increased with decreasing MLR, increasing initial dye concentration, and increasing temperature. The k_2 value on the adsorption of extracted dye onto silk followed the same trends as that of curcumin, but the trend of h_i value was fluctuated due to the nature of mixture.

Table 2.2 Pseudo-second-order adsorption rate constants, experimental q_e. calculated q_e, and regression coefficients of linear plots on the adsorption of curcumin onto silk under various conditions.

Parameters	$q_{e,exp}$ **(mg/g silk)**	**Second-order kinetic model**			
		k_2	h_i	$q_{e,cal}$ **(mg/g silk)**	R^2
MLR (g/mL): *initial dye concentration* (C_0) *16.6 mg/L, pH 5.5, temp. 30 °C*					
1:50	0.6208	0.7667	2.3822	0.6286	0.9997
1:100	1.1920	1.1234	1.6014	1.1940	0.9997
1:150	1.7555	3.0339	1.199	1.7627	0.9999
Initial dye concentration (mg/L): *MLR 1:100 g/mL, pH 5.5, temp. 30 °C*					
12.9	0.9587	1.6288	1.5494	0.9753	0.9995
16.6	1.1711	1.3465	1.8550	1.1737	0.9996
20.3	1.4974	1.1145	2.5967	1.5264	0.9996
Temperature (°C): *initial dye concentration* (C_0) *16.6 mg/L, MLR 1:100 g/mL, pH 5.5*					
30.0	1.1805	2.2932	3.2835	1.1966	0.9999
45.0	1.1537	5.0210	6.7696	1.1611	0.9999
60.0	1.1375	10.7868	13.9880	1.1388	0.9999

Table 2.3 Pseudo-second-order adsorption rate constants, experimental q_e. calculated q_e, and regression coefficients of linear plots on the adsorption of extracted dye onto silk under various conditions.

Parameters	**$q_{e,exp}$ (mg/g silk)**	**Second-order kinetic model**			
		k_2	**h_i**	**$q_{e,cal}$ (mg/g silk)**	**R^2**
MLR (g/mL): *initial dye concentration (C_0) 16.5 mg* curcumin*/L, pH 5.5, temp. 30 °C*					
1:50	0.7394	1.0200	0.5953	0.7640	0.9999
1:100	1.3830	0.2585	0.6082	1.3538	0.9995
1:150	1.9416	0.1312	0.4825	1.9179	0.9977
Initial dye concentration (mg/L): *MLR 1:100 g/mL, pH 5.5, temp. 30 °C*					
12.9	0.9634	0.3044	0.2846	0.9671	0.9991
16.5	1.3898	0.1995	0.3715	1.3647	0.9978
20.2	1.7105	0.1332	0.3972	1.7270	0.9977
Temperature (°C): *initial dye concentration (C_0) 16.5 mg* curcumin*/L, MLR 1:100 g/mL, pH 5.5*					
30.0	1.4330	0.7307	1.0331	1.4213	0.9977
45.0	1.4153	1.1236	1.7865	1.4144	0.9995
60.0	1.4035	1.4121	2.5913	1.4130	0.9999

2.4.4 Activation parameters for the adsorption of curcumin and extracted dye onto silk

The rate constants, k_2, for pseudo-second-order reaction at different temperatures listed in Table 2.2 were used to estimate the activation parameters of the adsorption of curcumin onto silk. The slope of the plot of lnk_2 versus $1/T$ (Figure 2.25) was used to evaluate E_a, while the slope and intercept of the plot of lnk_2/T versus $1/T$ (Figure 2.26) were used to evaluate $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively, as listed in Table 2.4.

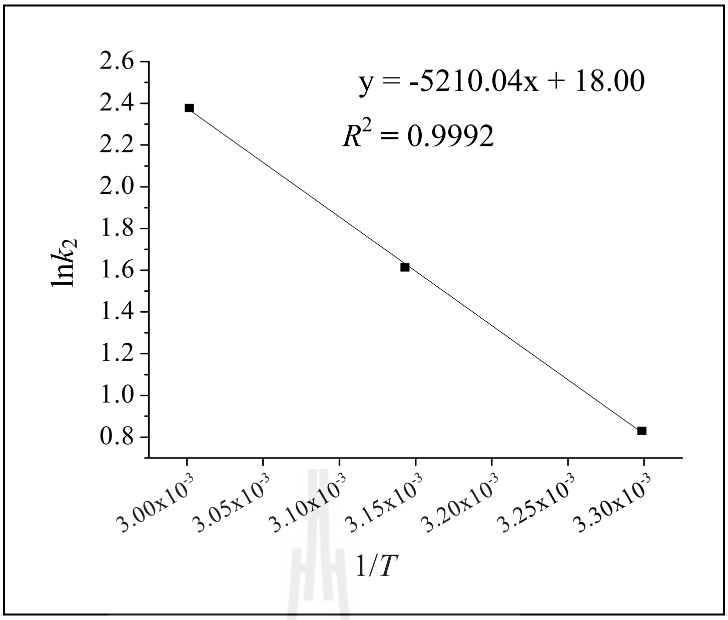


Figure 2.25 An Arrhenius plot for the adsorption of curcumin onto silk.

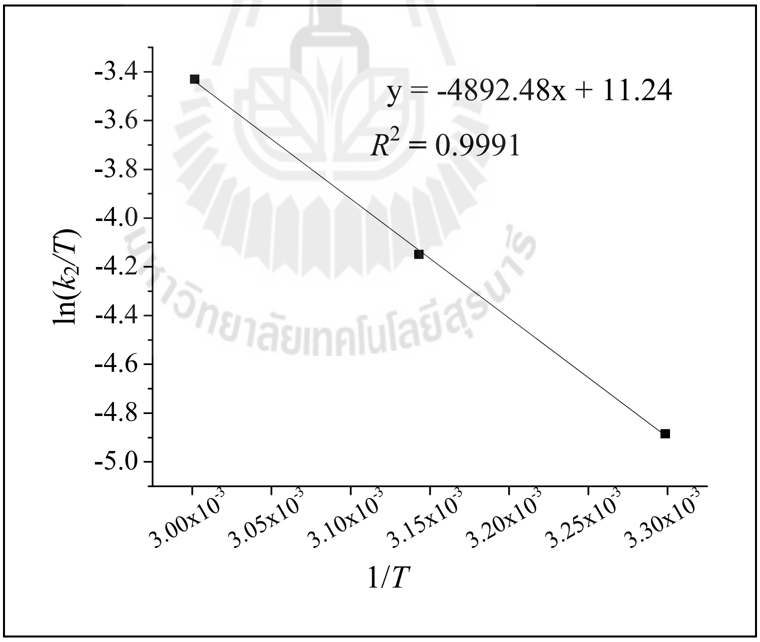


Figure 2.26 A plot of $\ln(k_2/T)$ versus $1/T$ for the adsorption of curcumin onto silk.

Table 2.4 The activation parameters for the adsorption of curcumin onto silk with initial dye concentration of 16.6 mg/L.

Temp (^{o}C)	***k*$_2$ (g silk/mg s)**	***E*$_a$ (kJ/mol)**	**Δ*H*$^{\#}$ (kJ/mol)**	**Δ*S*$^{\#}$ (kJ/mol K)**	**Δ*G*$^{\#}$ (kJ/mol K)**
30	2.29	43.32	40.68	-104.05	72.22
45	5.02				73.78
60	10.79				75.34

Nollet and coworkers reported that physisorption processes usually have low activation energies (5-40 kJ/mol), while higher activation energies (40-800 kJ/mol) suggest chemisorption (Nollet et al., 2003). From the E_a value of 43.32 kJ/mol observed for curcumin, we could infer that the adsorption of curcumin onto silk was likely a chemisorption process.

The value of $\Delta G^{\#}$ was calculated at 303, 318, and 333 K by equation (2.10) using $\Delta H^{\#}$ and $\Delta S^{\#}$ and these values are listed in Table 2.4. The negative value of entropy ($\Delta S^{\#}$) reflected more aggregation and greater interaction between curcumin and the silk fiber.

The rate constants, k_2, for pseudo-second-order reaction at different temperatures listed in Table 2.3 were used to estimate the activation parameters of the adsorption of extracted dye onto silk. The slope of the plot of $\ln k_2$ versus $1/T$ (Figure 2.27) was used to evaluate E_a, while the slope and intercept of the plot of $\ln k_2/T$ versus $1/T$ (Figure 2.28) were used to evaluate $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively, as listed in Table 2.5.

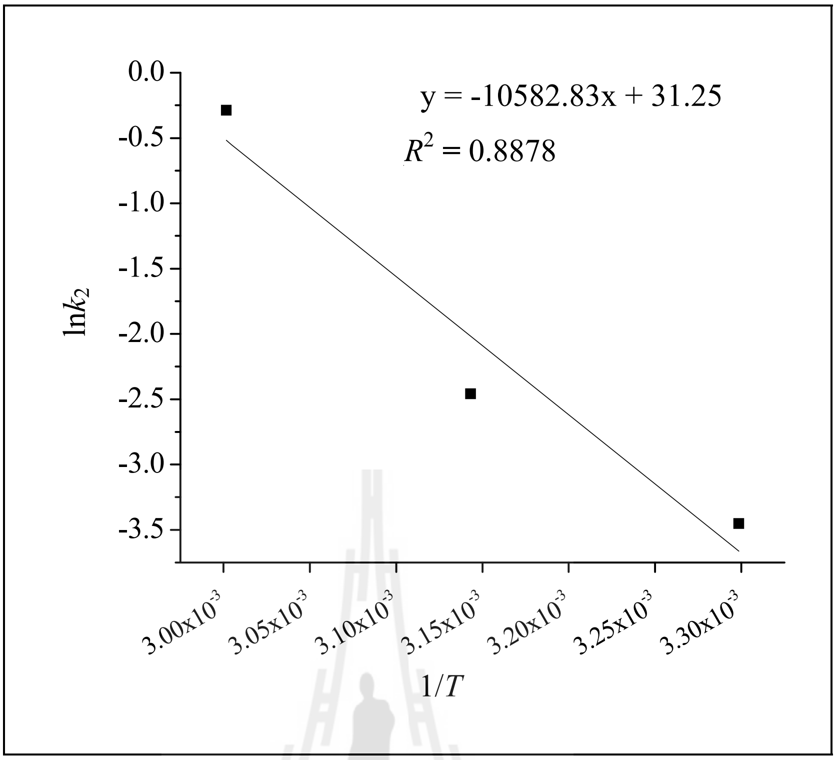


Figure 2.27 An Arrhenius plot for the adsorption of extracted dye onto silk.

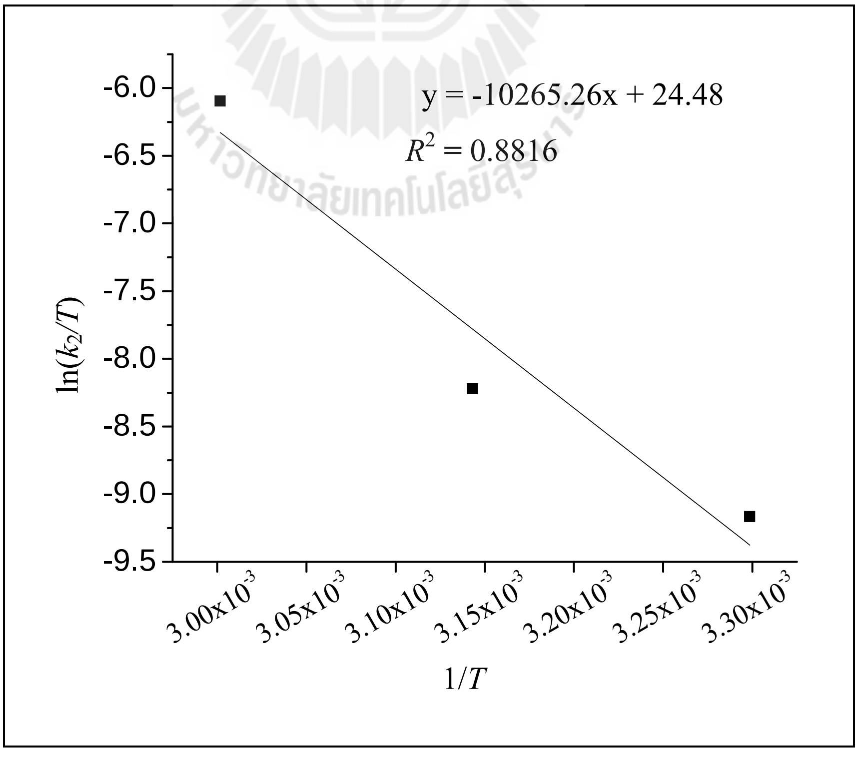


Figure 2.28 A plot of ln(k_2/*T*) versus 1/*T* for the adsorption of extracted dye onto silk.

Table 2.5 The activation parameters for the adsorption of turmeric extracted dye onto silk with initial dye concentration of 16.5 mg curcumin/L.

Temp (^{o}C)	***k*$_2$ (g silk/mg s)**	***E*$_a$ (kJ/mol)**	**$\Delta H^{\#}$ (kJ/mol)**	**$\Delta S^{\#}$ (kJ/mol K)**	**$\Delta G^{\#}$ (kJ/mol K)**
30	0.7307	87.99	85.35	6.03	83.52
45	1.1236				83.43
60	1.4121				83.34

From the E_a value of 87.99 kJ/mol observed for turmeric extracted dye, we could also infer that the adsorption of extracted dye onto silk was likely a chemisorption process. The values of $\Delta G^{\#}$ at 303, 318, and 333 K were calculated using the same equation as that for curcumin and these values are listed in Table 2.5.

2.4.5 Thermodynamic parameters on the adsorption of curcumin and extracted dye onto silk

As mentioned earlier, the adsorption of curcumin and extracted dye onto silk was exothermic process. In order to confirm the exothermic behaviour quantitatively, the thermodynamic parameters of adsorption, $\Delta G°$, $\Delta H°$, and $\Delta S°$, of both dyes after reaching equilibrium were calculated using the equations (2.11)-(2.13). The results are listed in Table 2.6.

The negative values of $\Delta G°$ indicated that the adsorption of dyes onto silk was spontaneous. The negative value of $\Delta H°$ confirmed that the adsorption process was exothermic. Furthermore, the entropy change ($\Delta S°$) in dyeing which represents the entropy difference of the dye molecules within the fiber (Kim, Son, and Lim, 2005) was negative in value. This indicated that adsorbed dyes became more restrained within the silk fiber than in the dyeing solution.

Table 2.6 Thermodynamic parameters for the adsorption of both dyes with initial dye concentration 16.6 mg/L of curcumin dye and 16.5 mg curcumin/L of extracted dye.

Dyes	**Temperature (°C)**	**lnK_c**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol K)**	R^2
Curcumin	30	3.72	-134.68	-124.47	0.85	0.9923
	45	3.80	-147.50			
	60	4.03	-160.33			
Extracted dye	30	2.71	-35.73	-14.48	0.70	0.9836
	45	2.90	-36.78			
	60	3.23	-37.83			

2.4.6 Adsorption-desorption of curcumin and turmeric extracted dye on dyeing onto silk

After the adsorption of curcumin and turmeric extracted dye onto silk was equilibrated, desorption was carried out in deionized water. Plots of the amount of dye adsorbed onto silk, q_t, versus t after adsorption and desorption experiments (Figure 2.29) showed little loss of both curcumin and turmeric extracted dye uptake after desorption.

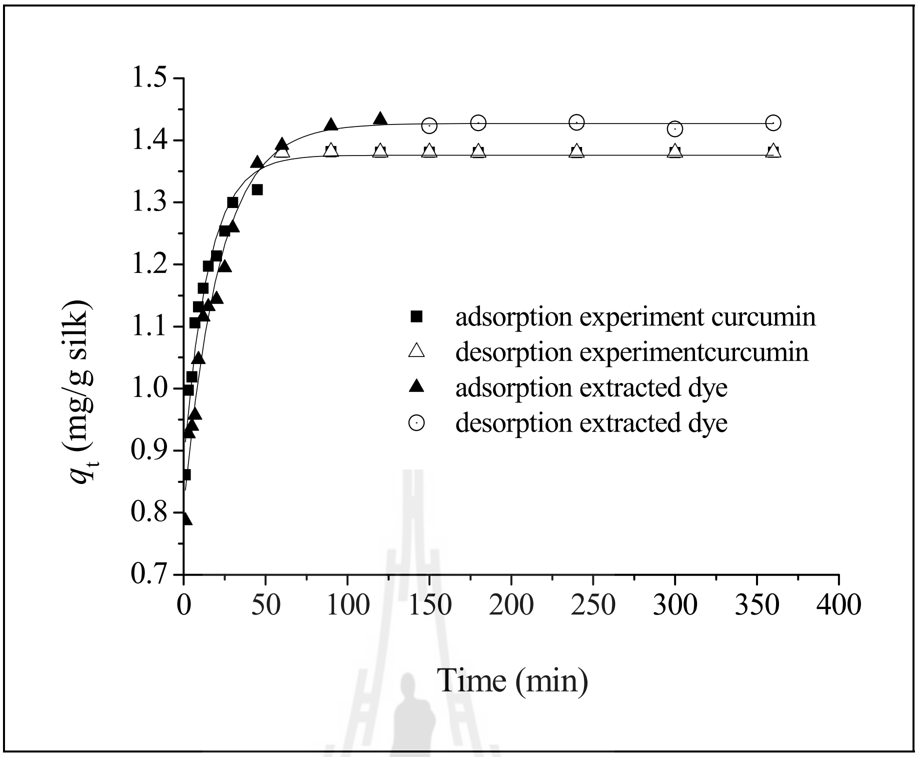


Figure 2.29 Adsorption-desorption studies of curcumin and turmeric extracted dye on dyeing onto silk at 30 °C with initial dye concentration of 16.6 mg/L of curcumin dye and 16.5 mg curcumin/L of extracted dye, dye solution pH of 5.5, and an MLR of 1:100.

2.5 Conclusion

The adsorption kinetics and thermodynamics of curcumin and turmeric extracted dye on dyeing onto silk were investigated in this chapter. The initial dye concentration, contact time, pH of dye solution, MLR, and temperature were found to influence the dyeing process. To avoid precipitating of both dyes in aqueous solution during the pre-warming step, the initial dye concentration was optimized at 16.58 mg/L. The adsorption of dye onto silk was found to reach equilibrium after 60 minutes for curcumin and 120 minutes for extracted dye with adsorption capacities maximized over the pH range of 5.0-6.0. When taking into account the amount of dye adsorbed and the amount of dye left in the solution, the MLR value in both cases was optimized at 1:100 g/mL. Since higher temperature caused a decrease in the maximum amount of dye adsorbed, the optimum dyeing temperature was chosen to be 30 °C which was close to room temperature.

The adsorption of curcumin onto silk was found to follow a pseudo-second-order kinetic model with an activation energy of 43.32 kJ/mol. This suggested that the overall rate of curcumin adsorption was likely controlled by a chemical process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 40.67 kJ/mol and -104.05 J/mol K, respectively, and the free energy of activation ($\Delta G^{\#}$) at 30 °C was 72.22 kJ/mol. In addition, the adsorption of curcumin onto silk was a spontaneous and an exothermic process with the free energy change ($\Delta G°$) value at 30 °C of -134.68 kJ/mol and the enthalpy change ($\Delta H°$) value of -124.47 kJ/mol.

The adsorption of turmeric extracted dye was also found to follow a pseudo-second-order kinetic model with an activation energy of 87.99 kJ/mol. This also suggested that the overall rate of extracted dye adsorption was likely controlled by a chemical process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 85.35 kJ/mol and 6.03 J/mol K, respectively, and the free energy of activation ($\Delta G^{\#}$) at 30 °C was 83.32 kJ/mol. Furthermore, the adsorption of extracted dye onto silk was also a spontaneous and an exothermic process with the free energy change ($\Delta G°$) value at 30 °C of -97.86 kJ/mol and enthalpy change ($\Delta H°$) value of -209.50 kJ/mol.

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CHAPTER III

A SPECTROSCOPIC INVESTIGATION OF THE COMPLEX OF TURMERIC DYE WITH COPPER(II) IN AQUEOUS SOLUTION

3.1 Abstract

The structure of the complex formed between Cu(II) and curcumin in aqueous solution was investigated using UV-visible spectroscopy. The molar ratio method was applied to ascertain the stoichiometric composition of the complex in aqueous solution. The resulting stoichiometry for Cu(II) to curcumin was 1:2. A structure for $Cu(Cur)_2$ was proposed. Curcumin uses the β-diketone moiety as the binding site with copper(II) ion. In addition, IR spectra, diffuse reflectance UV-Vis spectra, and MS spectra were performed to support the experimental observations.

3.2 Introduction

The rhizome of turmeric is source of a natural yellow pigment. The compounds answerable for the yellow colour pigment are curcumin, demethoxycurcumin, and bisdemethoxycurcumin, which are shown in Figure 2.2. The yellow-orange curcuminoids are sensitive to light to become colourless, but are moderately stable to heat (Wang et al., 1997). The chemical structures of products obtained from the degradation of curcumin are shown in Figure 3.1.

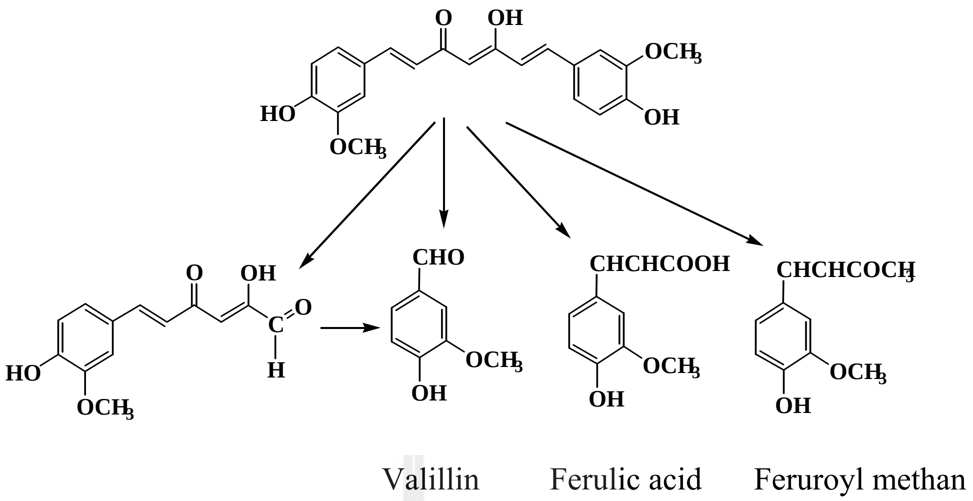


Figure 3.1 The chemical structures of products obtained from the degradation of curcumin.

From: Wang et al. (1997).

Wang and coworkers found that more than 90% of curcumin decomposed rapidly in phosphate buffer systems at neutral-basic pH conditions. The increased stability of curcumin in acidic pH condition may be contributed by the conjugated diene structure. However, when the pH is adjusted to neutral-basic conditions, proton is removed from the phenolic group, leading to the destruction of this structure.

The solubility of curcumin in aqueous media is improved when the systems in which it is present are at high pH values (Bernabé-Prineda, Ramírez-Silva, Romero-Romo, González-Vergara, and Rojas-Hernández, 2004; Tønnesen, Másson, and Loftsson, 2002). There are three pKa's measured for curcumin as follows: 10.51 and 9.88 corresponding to the hydrogen of phenol parts of the curcumin, and 8.38 attributed to the acetylacetone type group (Bernabé-Prineda et al., 2004; Jovanovic, Steenken, Boone, and Simic, 1999; Dietze, Arrieta, and Zimmer, 1997). Curcumin is a diferuloyl methane having two *o*-methoxy phenolic groups attached to the *α,β*-

unsaturated *β*-diketone (heptadiene-dione) moiety, which could form chelates of the type 1:1 and 1:2 with boron, copper, iron and other transition metals (Uppström, 1968; Barik et al., 2005, 2007; Shen, Zhang, and Ji, 2005; Borsari, Ferrari, Grandi, and Saladini, 2002; Bernabé-Prineda et al., 2004), such as vanadyl curcumin ($VO(Cur)_2$), manganese curcumin ($Mn(Cur)_2$), while gallium and indium were recently synthesized as complexes with curcumin in a ratio of 1 to 3 (Mohammadi et al., 2005). Cu(II) curcumin complex ($Cu(Cur)_2$) is liable to dissociate in solution. Because of the steric repulsion between the methoxyl groups in both curcumins of the complex, the structure of the Cu(II) curcumin complex molecule is nearly planar (Barik et al., 2007) so that it will easily interact with the amino group of protein fibroin.

Curcuminnoid dye is not favored in comparison with the yellow dye from other plants such as flavonoid dyes. It has poor fastness, especially light fastness on keratin protein fiber and cotton fiber. To improve the fastness of the native dye-bearing plants, metal ions such as copper(II) sulphate, potassium dichromate, stannous chloride and alum were usually used as mordants (Bhuyan and Saikia, 2005). The researches on the structure, properties of curcuminoids extracted from *Curcuma longa* Linn., and the metal curcuminoid complexes are reported as follows:

Because of its high sensitivity, curcumin can be used for the determination of very small amounts of metal ion such as boron. Two methods for the determination of boron with curcumin and a simplified water elimination procedure have been developed, one using the rubrocurcumin complex and the other using rosocyanin complex (Uppström, 1968). The structures of these two complexes correlate to Roth and Miller (1964) are shown in Figure 3.2. The rubrocurcumin complex is formed in a reaction between boric acid, oxalic acid, and curcumin in acetic acid. It is not very stable against hydrolysis, which causes lack of reproducibility in its use for the determination of boron. Rosocyanin complex is formed in a strongly acidic and almost water-free solution, which is very stable, and which has a high extinction coefficient and is suitable for boron analysis.

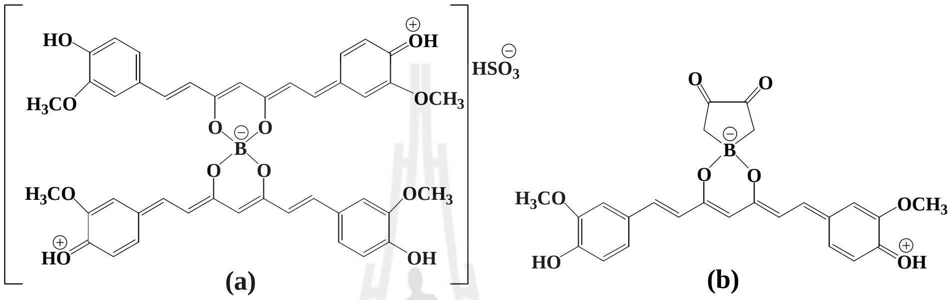
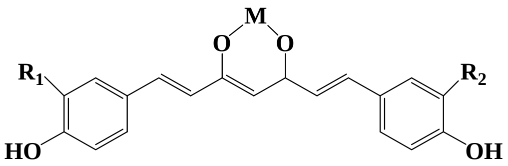


Figure 3.2 Chemical structures of rubrocurcumin (a) and rosocyanin (b).

From: Roth and Miller (1964) and Uppström (1968).

Synthesis and characterization of vanadyl, gallium, and indium curcumin complexes for medicinal applications have been studied (Mohammadi et al., 2005). Curcumin and its derivative, bisdemethoxycurcumin (BDC), were used for synthesis of acetylated analogs in the methanol or acetone media, diacetylcurcumin (DAC) and diacetylbisdemethoxycurcumin (DABC). A series of novel oxovanadium(IV) curcuminoid complexes (VO(DMC)$_2$, VO(BDC)$_2$, VO(DAC)$_2$ and VO(DABC)$_2$) were synthesized and characterized, as well as two new Ga(III) complexes, Ga(Cur)$_3$ and Ga(DAC)$_3$, and their In(III) analogs, In(Cur)$_3$ and In(DAC)$_3$. Spectroscopic characterization of the ligands and their complexes confirmed the proposed structures are shown in Figure 3.3.



VO(Cur)$_2$, VO(DAC)$_2$	M = VO, R_1 = H, Ac; R_2 = OCH_3
VO(BDC)$_2$, VO(DABC)$_2$	M = VO, R_1 = H, Ac; R_2 = H
Ga(Cur)$_3$, Ga(DAC)$_3$	M = Ga, R_1 = H, Ac; R_2 = OCH_3
In(Cur)$_3$, In(DAC)$_3$	M = In, R_1 = H, Ac; R_2 = OCH_3

Figure 3.3 The structures of the metal complexes.

From: Mohammadi et al. (2005).

The ratio of Ga(III)-curcumin complex was presented in a 1:3 molar ratio which differs from other complexes (Borsari et al., 2002). Ga(III)-curcumin complex in water/methanol 1:1 media shows 1:1 molar ratio. Moreover, The pKa values of curcumin and diacetylcurcumin are determined by means of spectroscopic and potentiometric measurements, and the enolic proton is more acidic. The interaction of Fe^{3+} with curcumin and diacetylcurcumin, in water/methanol 1:1 solution, leads to the formation of the complex species 1:1 which prevails near pH 7. ^{1}H-NMR data indicated that the dissociated β-diketo moiety of the ligands is involved in metal chelation.

A mononuclear (1:1) copper complex of curcumin, was synthesized in methanol and characterized (Barik et al., 2005; Baum and Ng, 2004). The complex was characterized by elemental analysis, IR, NMR, UV-VIS, EPR, mass spectroscopic methods, and TG-DTA, from which it was found that a copper atom is coordinated through the keto-enol group of curcumin along with one acetate group and one water molecule. Cyclic voltammetric studies of the complex showed a reversible Cu^{2+}/Cu^{+} couple with a potential of 0.402 V vs NHE, normal hydrogen electrode. The Cu(II)-curcumin complex is soluble in lipids and DMSO. Unluckily, it is insoluble in water which is colourant for textile dyeing. The structure of the Cu(II)-curcumin complex is shown in Figure 3.4.

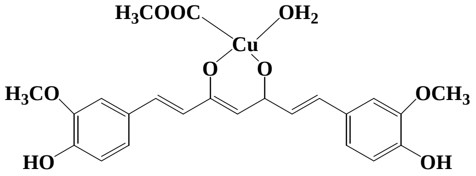


Figure 3.4 Structure of the Cu(II)-curcumin complex.

From: Barik et al. (2005) and Baum and Ng (2004).

In addition, the Cu(II)-chelating properties of curcumin (Shen et al., 2005) was calculated. The findings were that each Cu(II) binds at least two curcumin molecules and the enolic proton of curcumin is ready to dissociate in solution. The theoretical study showed calculated four Cu(II)-O bond lengths of the complexes, in line with the four equivalent coordinated oxygen atoms. In addition, both curcumin molecules are nearly planar, which probably results from the steric repulsion between the methoxyl groups in both curcumins. The structure of the complex is shown in Figure 3.5.

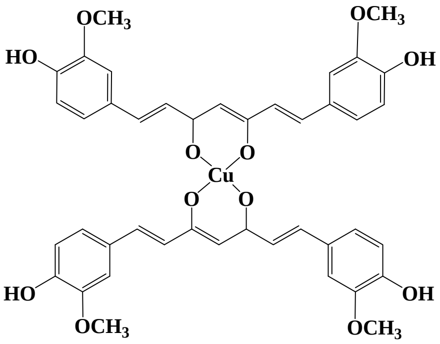


Figure 3.5 Structure of the Cu(II)-curcumin complex from calculation.

From: Shen et al. (2005).

However, the complex formation of copper(II) with curcumin which is a major composition of curcuminoid dyes in aqueous solution has not yet been reported. The aim of this present work is to determine the stoichiometric composition of the curcumin - Cu(II) complex formed between curcumin and the Cu(II) ion in an aqueous solution. The complex formation between curcumin dye and the Cu(II) ion was investigated by using the UV-Vis spectrophotometry method. These complexes can be directly applied to dyeing silk.

3.3 Experimental

3.3.1 Chemicals

(a) 98% Curcumin [458-37-7] in amber wide mouthed reagent bottle from Across Organics

(b) Copper(II) nitrate trihydrate, Cu $(NO_3)_2 \cdot 3H_2O$, from Merck

(c) Copper(II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), from Merck

(d) Sodium hydroxide, NaOH, from Aldrich

(e) Ammonium acetate, NH_4OOCCH_3, from Merck

(f) Ammonium hydroxide, NH_4OH, 25% m/v, commercial grade, from Merck

(g) Glacial acetic acid, CH_3COOH, from Merck

(h) Ethanol, C_2H_5OH, analytical grade, from Merck

3.3.2 Instrumental

(a) An Agilent 8453 UV-Vis spectrophotometer employed for absorbance measurements using quartz cells with path length of 1 cm.

(b) A pH meter (Jenway/4330) was used to measure the pH values of dye solutions.

(c) A Perkin-Elmer Lambda 2S spectrophotometer equipped with an integrating sphere attachment was used to recorded diffuse reflectance spectrum of polycrystalline complex in the rang of 9,090 to 20,000 cm^{-1}.

(d) A Bio-Rad FTS 175C FTIR spectrophotometer was used to observe the stretching frequencies of the carbonyl group of the β-diketone moiety in curcumin and the Cu(II)-curcumin complex.

(e) An Agilent 1100 Liquid chromatography mass spectrometer was used to determined the accurate mass of the complex performed on Thermo Finnigan LTQ quadrupole ion trap (QIT) and an electrospray ionization (ESI) source was used. The flow-rate of the solution was set at 10 μL min^{-1}. The heated capillary temperature was kept at 275 °C. The ESI spray voltage was set at +4.5 kV. The injection time was set at 50 ms. All spectra were obtained in the positive mode. The scan mode was positive and the isolation width for MS^n was 1.0-6.0 Da.

3.3.3 Experimental methods

3.3.3.1 Determination of the mole ratio for the Cu(II)-curcumin complex

The molar ratio method was used to determine the composition of this complex in aqueous solution employing spectrophotometric spectra. For this method, fresh 5.0×10^{-3} M curcumin stock solution was prepared by dissolving 0.1842 g of curcumin in 100 mL 95% ethanol in the volumetric flask and kept in an amber reagent bottle. A 5.0×10^{-3} M copper(II) nitrate stock solution was prepared in deionized water. A 2.5×10^{-5} M curcumin in aqueous solution was prepared by pipetting 50 μL of

5.0×10^{-3} M curcumin stock solution into a 10 mL volumetric flask, and adjusted using deionized water. A concentration of 2.5×10^{-5} M of curcumin in aqueous solution was used kept constant whereas that of the copper(II) nitrate stock solution was varied from 0 to 7.5×10^{-5} M. The pH was controlled using a buffer system consisting of 4% of 1.0 M ammonium acetate-acetic acid buffer pH 5.5 which was added to a mixture of copper(II) and curcumin dye. In order to reach the complexation equilibrium, the absorption spectra of the solution in the rang of 200 to 800 nm were recorded after standing for 20 minutes.

3.3.3.2 Preparation of Cu(II)-curcumin solid complex

The synthesis of the solid 1:2 complex between copper(II) ion and curcumin was carried out by the addition of 10 mL MeOH to 0.25 mmol curcumin, after which 240 mL deionized water was added, followed by the drop-wise addition of 0.125 mmol copper(II) nitrate in aqueous solution. The resulting mixture was stirred for 2 h at room temperature. After standing overnight, a yellow green solution and a gelatinous product appeared. The product was then isolated by vacuum filtration, washed with cold MeOH, and dried overnight in a desiccator. The crude solid was then recrystallized in MeOH-acetic acid solution. The crystals were separated and washed with cold MeOH-water solution. The resulting polycrystalline complex were recorded using a diffuse reflectance spectrum of UV-Vis spectrophotometry and was used to characterize the solid complex. The Bio-Rad FTS 175C FTIR spectrophotometry was used to observe the stretching frequency of the carbonyl group of the *β*-diketone moiety in curcumin and the Cu(II)-curcumin complex.

3.3.3.3 Sample preparation for LC-MS

Fresh 5.0×10^{-3} M curcumin stock solution was prepared by dissolving 0.1842 g of curcumin in 100 mL 95% ethanol in an amber volumetric flask and kept in an amber reagent bottle. A 5.0×10^{-3} M copper(II) nitrate stock solution was prepared in deionized water. A concentration of 2.5×10^{-5} M of curcumin in aqueous solution was prepared by pipetting 100 µL of 5.0×10^{-3} M curcumin stock solution into a 10 mL amber volumetric flask, and diluting with deionized water. A solution of 5.0×10^{-5} M of curcumin was mixed with 2.5×10^{-5} M copper(II) nitrate by pipetting 50 µL of 5.0×10^{-3} M copper(II) nitrate stock solution, and adjusted using deionized water to give 1:2 mole ratio. In order to reach the complexation equilibrium, determination of the accurate masses of the complexes was after kept standing for 45 minutes.

3.4 Results and discussion

3.4.1 UV-visible spectra of curcumin in aqueous solution at pH 5.5

It was found that increasing the Cu(II) concentration decreased the absorption band at 427 nm of curcumin and also resulted in the appearance of a new band at 361 nm of a new compound. The effect of the Cu(II) concentration on λ_{max} of the visible spectra of Cu(II) curcumins with pH controlled at 5.5 is shown in Figure 2 and indicates a large hypsochromic shift of 66 nm in band 427 nm. The results of a large hypsochromic shift will be explained below.

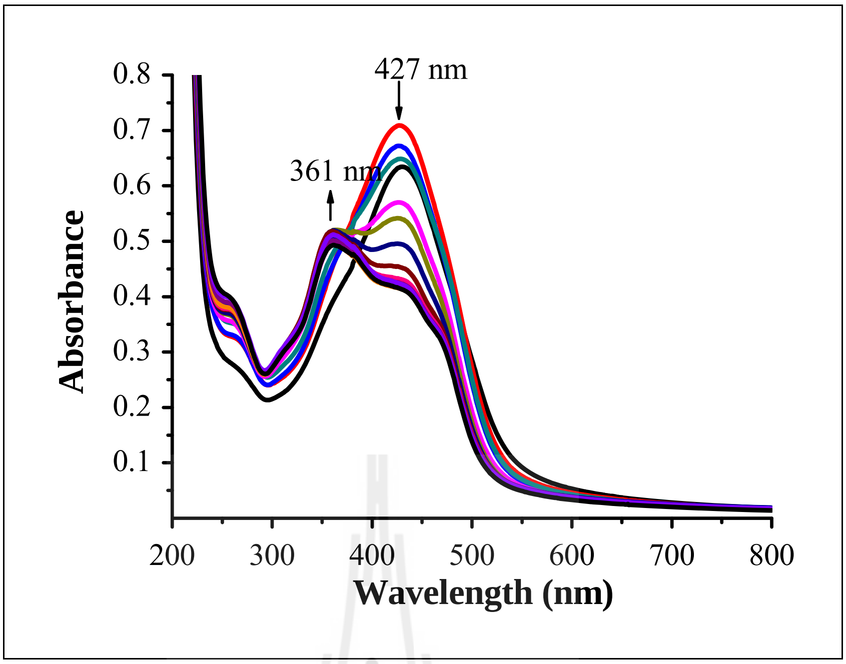


Figure 3.6 Electronic absorption spectra of curcumin (2.5×10^{-5} M) in aqueous solution in the absence and presence of copper(II) from 0 to 2.5×10^{-5} M at pH 5.5.

Barik reported that the UV-Vis region showed two absorption bands of curcumin ligands: an $n\rightarrow\pi^*$ transition at ~360-430 nm and $\pi\rightarrow\pi^*$ transition at ~240-290 nm (Barik et al., 2007). The absorption band showed decay of the parent Cu(II)-curcumins band at 427 nm after being mixed with copper(II) ions. The UV-Vis spectrum of curcumin in aqueous solution at pH 5.5 exhibited a maximum adsorption band at 427 nm with an extinction coefficient of 31,528 $cm^{-1}M^{-1}$. A new band which increases with the amount of added copper(II) appeared at 361 nm with an extinction coefficient of 18,772 $cm^{-1}M^{-1}$.

The 427 nm peak due to curcumin in aqueous solution is attributed to the $n\rightarrow\pi^*$ transition of curcumin. A 361 nm band (Figure 3.6) is attributed to the curcumin →Cu(II) charge transfer band (Tønnesen and Karlsen, 1992). This study corresponds to Barik et al. (2007) in which the *β*–diketone of curcumin chelated with copper in DMSO and Zhao et al. (2005) showing a large blue shift of the *β*–diketone of *trans*-ASTX with copper from 480 nm to 373 nm in ethanol (Zhao, Chen, Zhao, Wang, Liao, and Hu, 2005).

3.4.2 Complex stoichiometry of curcumin and copper(II) in aqueous solution at pH 5.5

In this study, the stoichiometry of the complex was determined by using the molar ratio method. Increasing the copper(II) ion resulted in a decrease of absorbance at 427 nm (Figure 3.7), which showed inflection at [Cu]/[curcumin] = 0.45, and indicates stoichiometric of Cu(II) to curcumin of 1:2 for the complex.

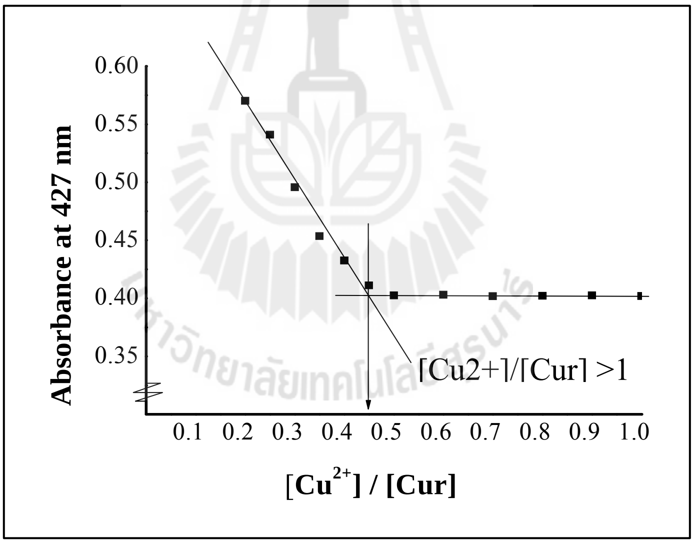


Figure 3.7 Absorbance versus [Cu]/[curcumin] molar ratio plots at 427 nm at pH 5.5.

The diffuse reflectance UV-Vis spectrum of the solid crystal of Cu(II)-curcumin (Figure 3.8) showed three major absorption bands with wavelength maxima at 316 nm (band I), 472 nm (band II), and 701 nm (band III), respectively. An intense band I which occurred in the UV region was considered to be associated with the absorption due to the $\pi\rightarrow\pi^*$ transition of curcumin, and band II at 400-550 nm was due to the $n\rightarrow\pi^*$ transition of curcumin ligand (Annaraj, Ponvel, and Athappan, 2004; Barik et al., 2007). A broad band III centered on 700 nm is usually assigned to a *d-d* transition band (Welch and Chapman, 1993), indicating that the solid was a compound of copper(II) with curcumin. Cu(II) was present in the complex and coordinated to the curcumin ligand (Figure 3.8).

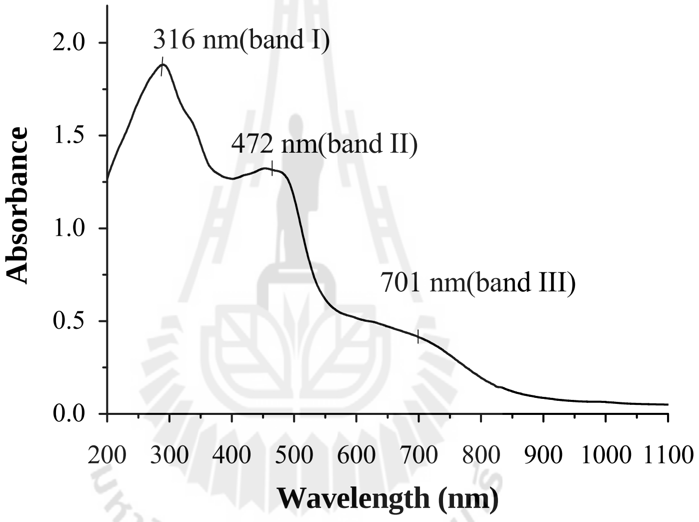


Figure 3.8 The diffuse reflectance UV-Vis spectrum of solid crystal of Cu-curcumin complex.

The IR spectra of the curcumin copper(II) complex showed the υ (C=O) a large intense band at 1,509 cm^{-1} which shifted from 2 bands at 1,513 cm^{-1} and 1,588 cm^{-1} of free curcumin. The copper(II) curcumin complex showed a symmetrically large broad band at 3,448 cm^{-1} of O-H stretching which is a symmetrical structure of complex compound. The υ (C-O-Cu) band of the complex at 478 cm^{-1} suggested that curcumin forms a complex with copper(II) and uses the *β*-

diketone part as the binding site (Barik et al., 2007). Figures 3.9 and 3.10 showed the proposed structure of the Cu(Cur)$_2$ complex in aqueous solution and in solid state corresponded to Karlsen et al. (1988).

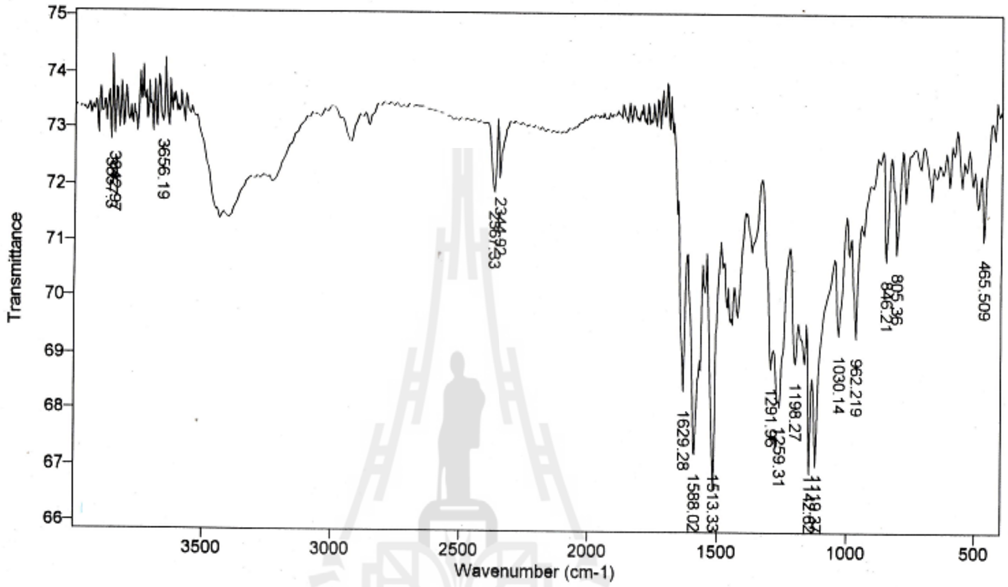


Figure 3.9 FT-IR spectrum of curcumin alone.

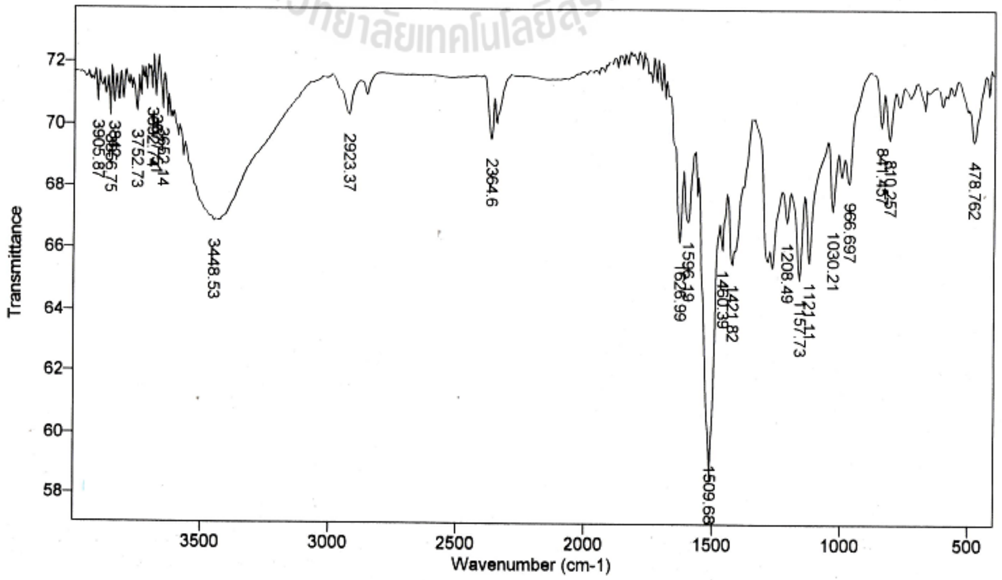


Figure 3.10 FT-IR spectrum of the Cu(curcumin)$_2$ complex.

The Cu(II) curcumin complex was identified based on UV-Vis spectra, IR spectra and mass spectra in comparison with data of curcumin, listed in Table 3.1.

Curcumin showed a intense protonated molecules $[M+H]^+$ at *m/z* 369 and sodiated adduct ion $[M+Na]^+$ at *m/z* 391, and less intense fragment ions at *m/z* 288 corresponding to double demethoxylation and removal of 1 water, 244 corresponding to $C_{14}H_{12}O_4^+$ which is the fragment after removal of one complete phenolic group of mass 123 and one H, 131 ($C_8H_2O_3^+$ or $C_9OH_7^+$), 101 probably C_7OH^+ from the heptane skeleton and 87 ($C_7H_3^+$), strong intense fragment ions at *m/z* 117 (probably $C_7O_2H^+$), 88 ($C_7H_4^+$), 83 ($C_6H_{11}^+$ or $C_5OH_7^+$ or $C_4O_2H_3^+$), and 74 (probably $C_6H_2^+$ from the phenyl ring). The most intensive fragment appears at *m/z* 100 attributed to $[C_5H_8O_2]^+$. The mass spectrum of curcumin is shown in Figure 3.11.

The Cu(II)-curcumin complex showed very intense protonated molecules of curcumin $[M+H]^+$ at *m/z* 369, less intense adducts and fragments at *m/z* 391, $[M+Na]^+$, 289 (fragment of mass 288 + H), 209 ($C_{14}H_9O_2^+$ corresponding to fragment of mass 244 + H – 2 H_2O), 131 ($C_8O_2H_3^+$ or $C_7O_2H_{15}^+$), 119 ($C_7H_2O_3^+$), and 83 (C_5Na^+ or $C_5H_7O^+$ or $C_6H_9^+$). All showed strong intense fragments attributed to the complex at *m/z* 770 (probably the complex of mass 799/797 after demethoxylation or double demethylation and adduct formation with hydrogen), 692 (probably fragment of mass 770 after double demethoxylation and extraction of one O), 558 (maybe the complex after removal of two phenolic side groups, each of mass 123, and adduct formation with hydrogen) and 416 (may be the Cu-complex with demethylated and dehydrogenated curcumin). Their mass spectra of Cu(II)-curcumin complex are shown in Figure 3.11-3.14.

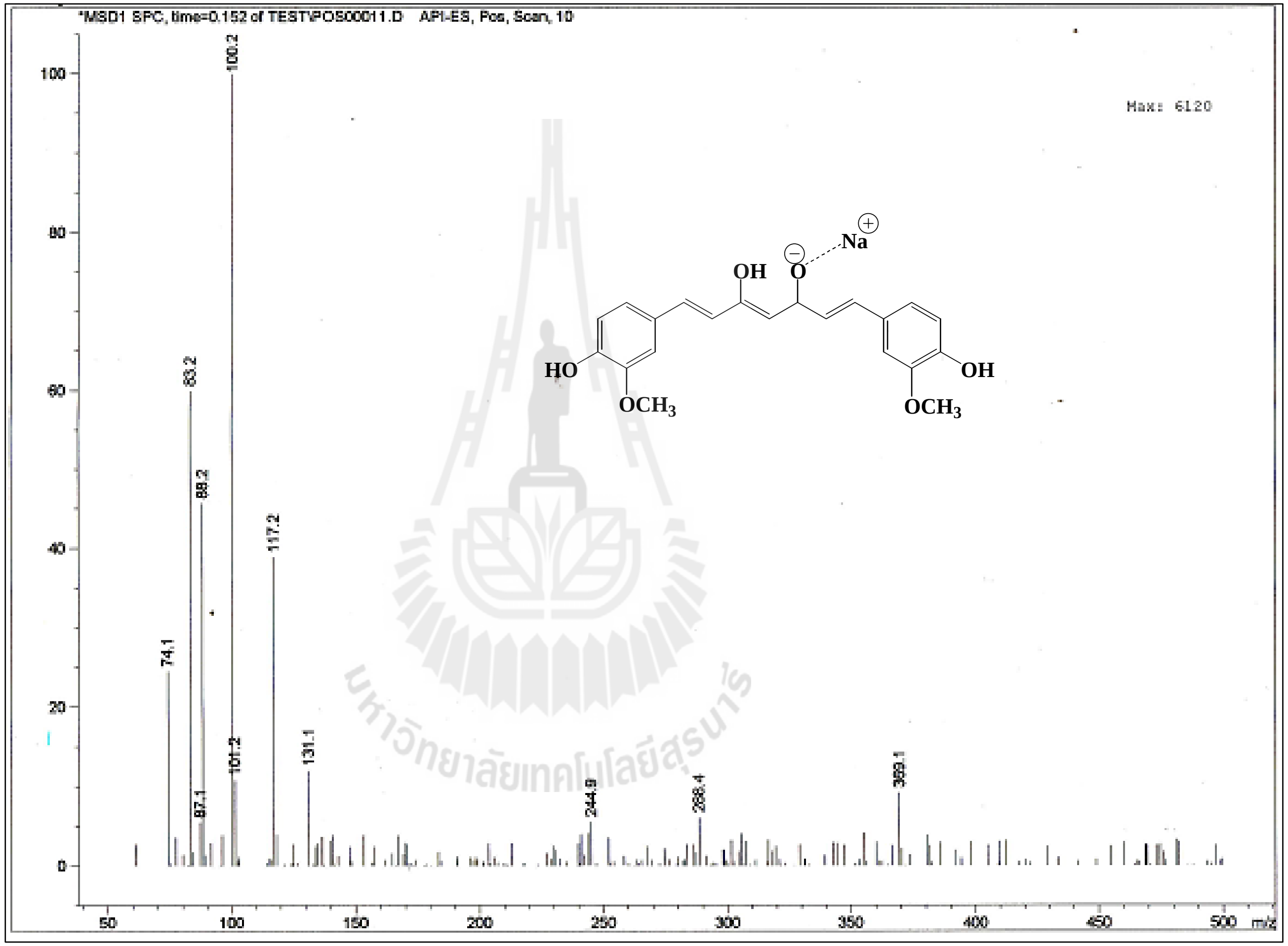


Figure 3.11 Full scan mass spectrum of the curcumin compound.

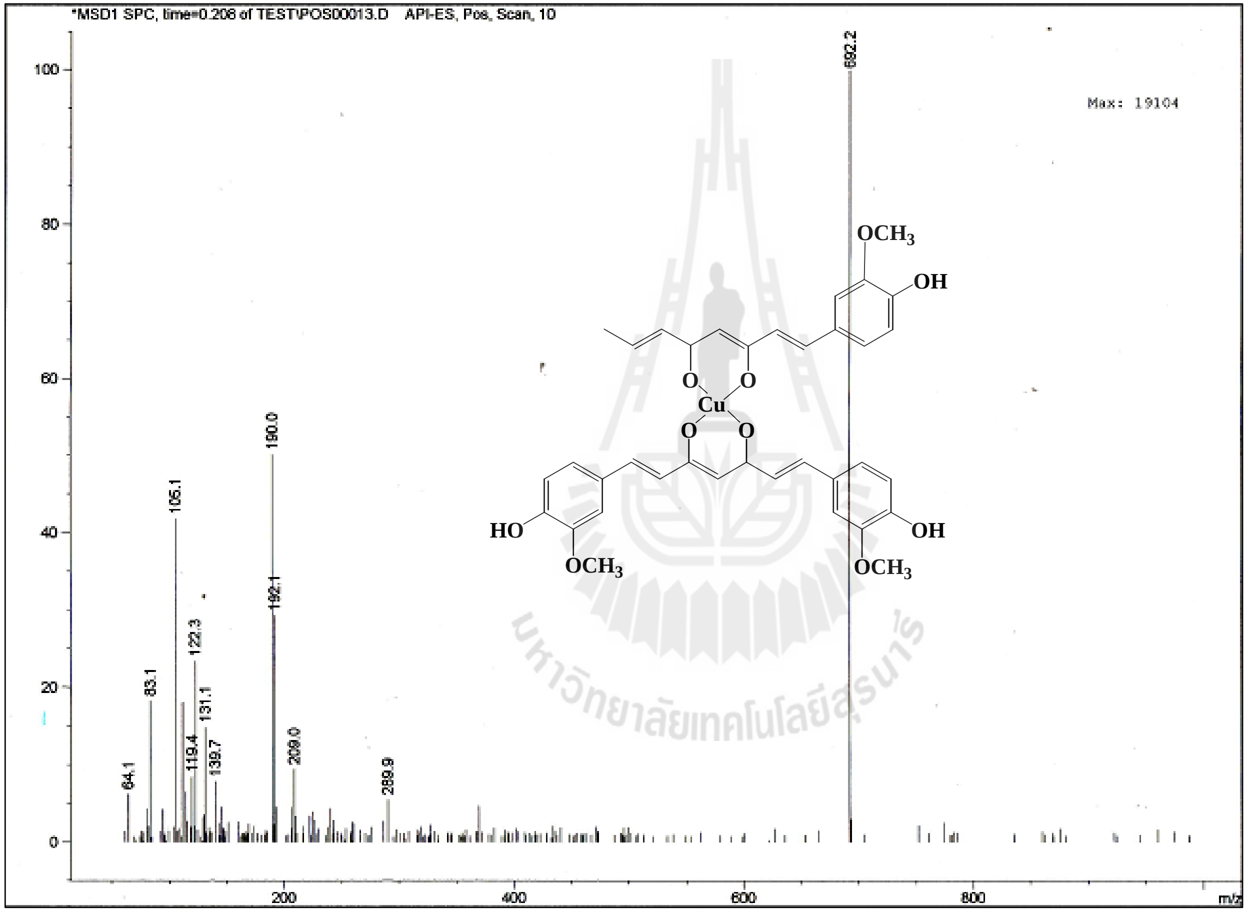


Figure 3.12 Full scan mass spectrum of the Cu(curcumin)$_2$ complex.

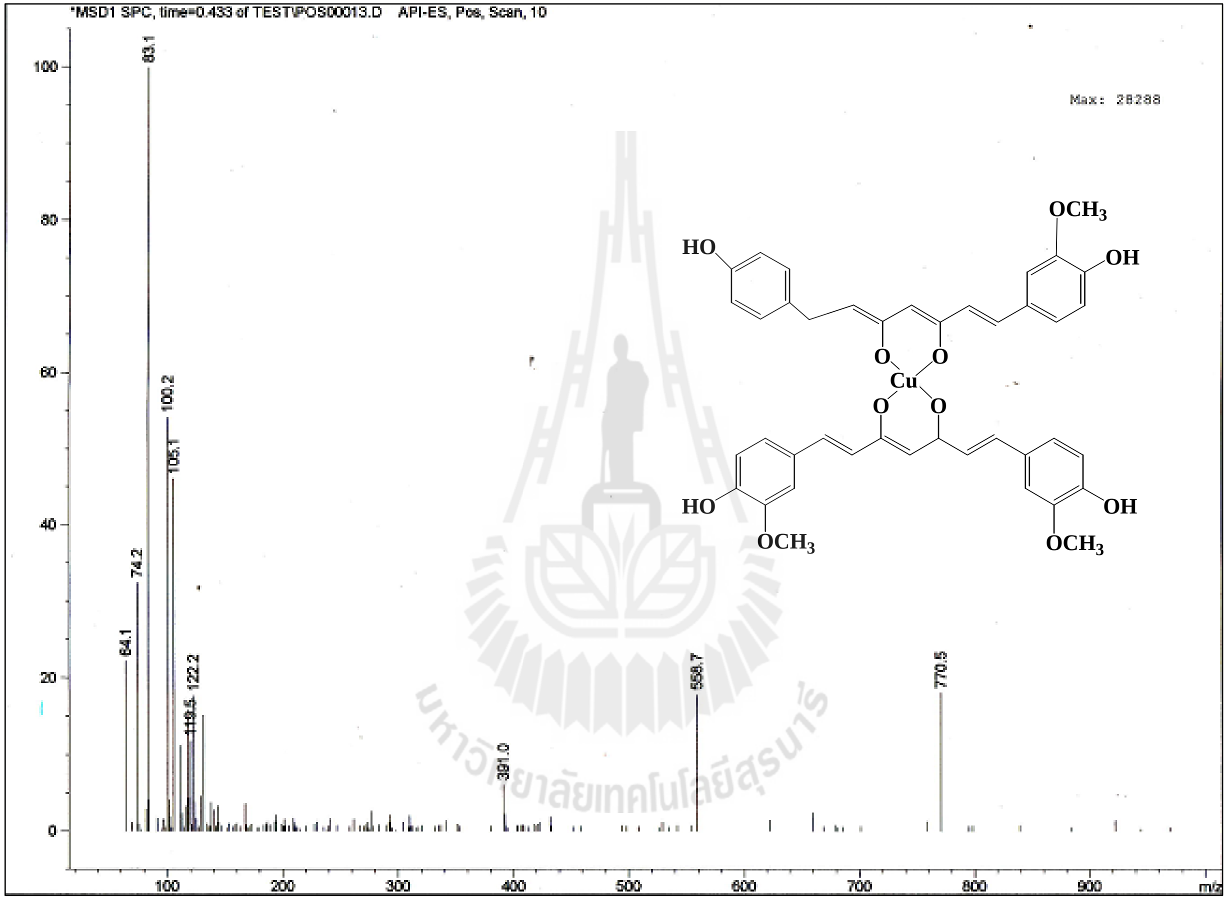


Figure 3.13 Full scan mass spectrum of the Cu(curcumin)$_2$ complex.

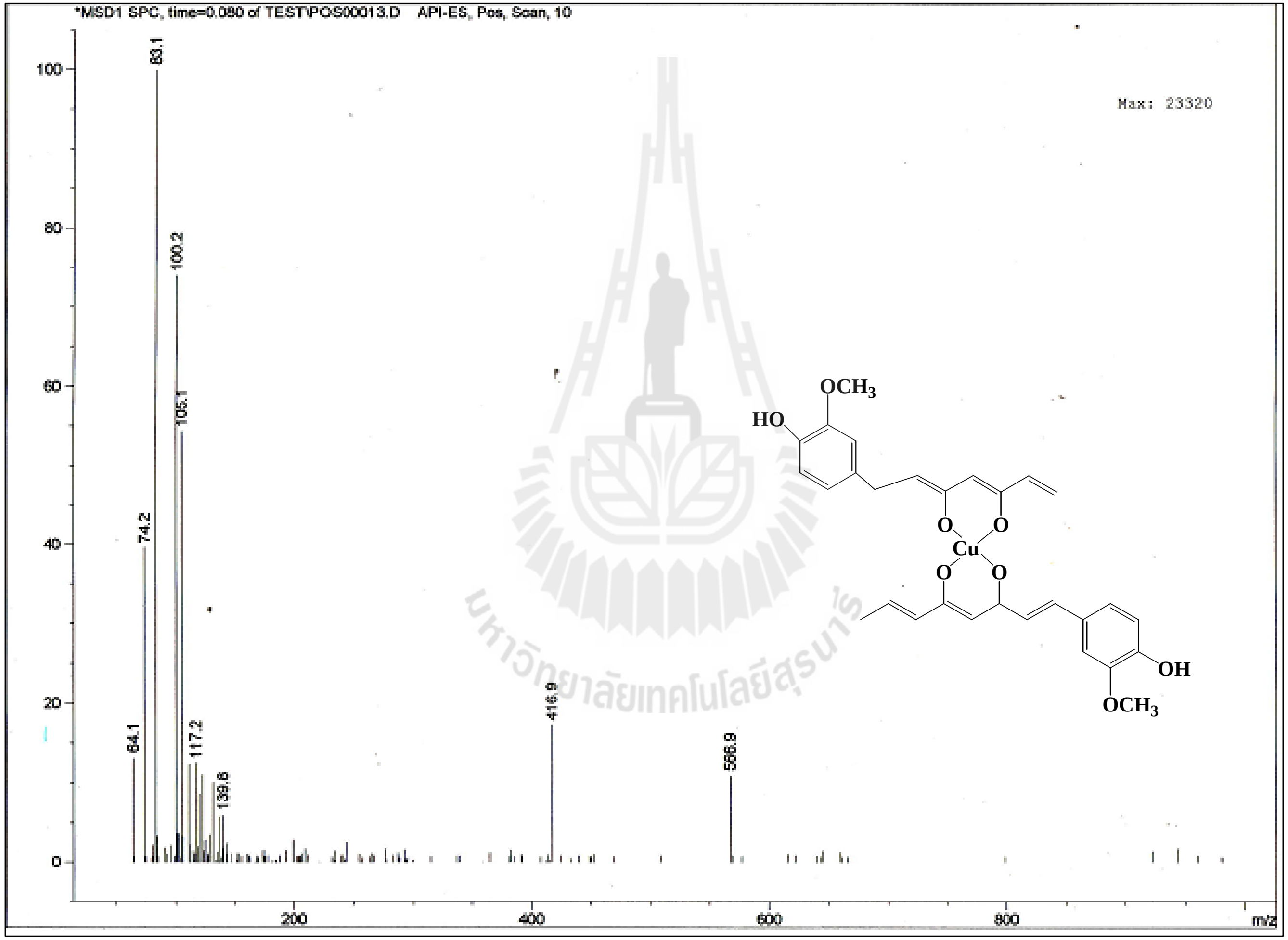


Figure 3.14 Full scan mass spectrum of the Cu(curcumin)$_2$ complex.

Table 3.1 Exact mass measuments and elemental composition for ions derivative from curcumin.

Identification compounds	**$[M+H]^+$ *m/z***	**$[M+Na]^+$ *m/z***	**$[2M+Na]^+$ *m/z***	**Other ions *m/z***
Curcumin	369	391	-	288, 244, 224, 208, 188, 131, 122, 117, 111, 105, 100, 88, 83, 74, 60

Table 3.2 Exact mass measuments and elemental composition for ions derivative from Cu(curcumin)$_2$ complexes.

Identification compounds	**$[M+H]^+$ *m/z***	**$[M+Na]^+$ *m/z***	**$[2M+Cu]^+$ *m/z***	**Other ions *m/z***
Cu(II) curcumin complex	64	391	770, 692, 558	289, 209, 192, 190, 139, 131, 122, 105, 100, 83, 74

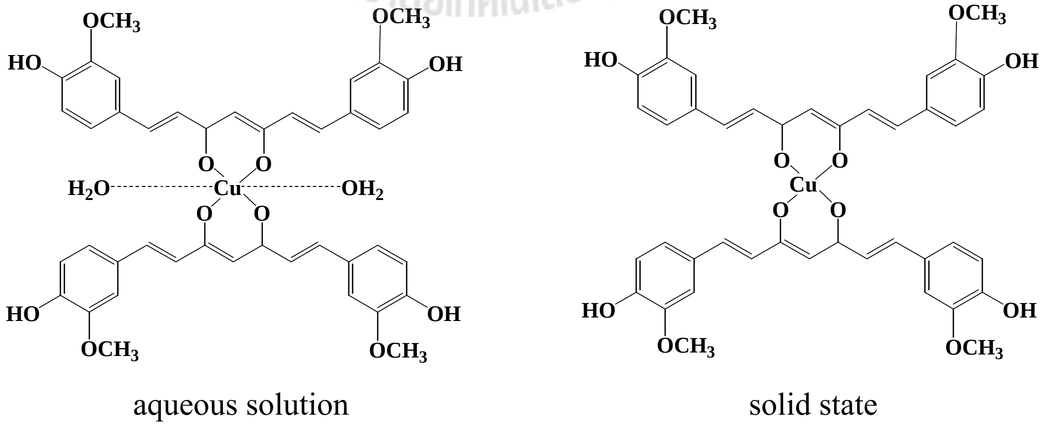


Figure 3.15 Suggestion the structure of Cu(curcumin)$_2$ complex.

3.5 Conclusion

The interaction of curcumin and Cu(II) was studied by UV-Vis spectroscopy and a significant large hypsochromic shift was observed for the absorption band of the Cu(II)-curcumin complex. Using the molar ratio method, it was found that the stoichiometric composition of the complex in aqueous solution was Cu(curcumin)$_2$. The diffuse reflectance UV-Vis spectra, IR spectra, and mass spectrum indicated it was likely to be reasonably stable in both aqueous solution and solid state.

3.6 References

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CHAPTER IV

ADSORPTION OF METAL CURCUMIN COMPLEXES AND EXTRACTED DYE COMPLEXES FROM *Curcuma Longa* (Linn.) DYEING ONTO SILK

4.1 Abstract

The adsorption kinetics and thermodynamics of Cu(II)-curcumin complex and Cu(II)-extracted dye complex from *Curcuma longa* Linn. dyeing onto silk fibers indicated that the adsorption capacity is significantly affected by the initial dye concentration, contact time, pH of dye solution, Material to Liquor Ratio (MLR), and temperature. The adsorption rates of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk before equilibrium time increased with an increase in temperature. The pseudo second-order kinetic model was indicated in the Cu(II)-curcumin complex and Cu(II)-extracted dye complex dyeing onto silk at pH 5.0, with activation energies (E_a) of 16.24 and 27.38 kJ/mol, respectively. The values of the enthalpy ($\Delta H^{\#}$) of both dyes at pH 5.0 were 13.60 and 24.73 kJ/mol, respectively. Activation energies for the adsorption of lower than 40.0 kJ/mol usually suggest that the adsorption is physisorption. The free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) terms for Cu(II)-curcumin complex and Cu(II)-extracted dye complex dyeing onto silk were also determined, and the negative values of $\Delta G°$ and $\Delta H°$ obtained indicated that both dyes' adsorption processes are spontaneous and exothermic.

4.2 Introduction

Dyeing is an ancient art which predates written records. Primitive dyeing techniques included sticking plants to fabric or rubbing crushed pigments into cloth. The methods became more sophisticated with time and techniques using natural dyes from crushed fruits, berries and other plants, which were boiled into the fabric and gave light and water fastness (resistance), were developed. Nowadays, dyeing is a complex, specialized science. The most dyestuffs are now produced from synthetic compounds. This means that applications have been quite certain, costs have been greatly reduced and wear characteristics have been greatly enhanced. But many handcraft of natural dying, i.e. using naturally occurring sources of dye, maintain that natural dyes have a far superior aesthetic quality which is much more pleasing to the eye. On the other hand, many people feel that natural dyes are non-viable on grounds of both quality and economics. In the Thailand, natural dyeing is now practiced only as a handcraft, synthetic dyes being used in all commercial applications. Some craft spinners, weavers, and knitters use natural dyes as a particular feature of their work.

Turmeric rhizome, natural plant is sources have traditionally been an important yellow source of textile dyes since prehistoric times. Among these dyes, *Curcuma longa* Linn., contains of three curcuminoids giving natural yellow pigment which is used in the dyeing of textiles in much of Southeast Asia, where the plants are native (Christie, 2000). As previous experiments have established that all curcuminoids have essentially equivalent absorbency and chelating ability to bond to other metal ions such as copper(II) ions, iron ion, and alum as mordanting agents.

The use of natural yellow dyes, curcuminoids dye, turmeric rhizome extracted dye, is related to “poor fastness” properties which have problems both in light fastness and wash fastness. Curcuminnoids are especially problematic when dyeing onto silk fibroin, cotton and wool (Popoola, 2000; Tsatsaroni, Liakopoulou-Kyriakides, and Eleftheriadis, 1998; Yoshizumin and Crews, 2003). This problem is usually solved by using metal ions as mordants (Tsatsaroni et al., 1998). People favour the use of synthetic dyes with fastness for dyeing textiles (Christie, 2000). In the north and the northeast of Thailand people still use some yellow dyes from plants, and improve the fastness properties of the textiles by adding some metal ions, alum and copper sulphate, to the dye solution as mordanting agents (Moeyes, 1993). The metal ions as mordants in solution are adsorbed by the fiber allowing the metal ions to become complexes to appropriate functional groups in the structure of the fibroin.

During the dyeing process, the dye interacts with the mordant-fiber complex to form an insoluble brightly colored species. The mordant ensures the brightness and wash fastness of the dye and also has great influence on the final color obtained. A number of naturally occurring polyphenolics have been used for a long time to dye wool. The two natural pigments, curcumin and crocin, can be fixed to wool fibers by a metal ion mordant with the polyhydroxyl groups present in wool protein to provide the necessary metal ion binding sites (Tsatsaroni et al., 1998). Wool undergoes a variety of chemical reactions induced by exposure to UV radiation (Yoshizumin and Crews, 2003) which eventually manifest themselves as changes in the tensile strength and elasticity of the fiber (phototendering). It is expected that UV-absorbing dyes applied to wool fibers will provide some photoprotection to the fibers by partially screening them from this damaging radiation. Several metal ions used as mordants such as ferric, zinc, cupric, stannic and aluminium have different effects on the rates of this phototendering of dyed wool fabric.

In order to investigate the kinetic and thermodynamic models of adsorption of complex dye such as Cu(II)-curcumin complex and Cu(II)-extracted dye complex these were carried out in a similar manner to those referred to in Chapter II (section 2.2.3). Therefore the dyes, curcumin and turmeric extracted dye, were changed to Cu(II)-curcumin complex and Cu(II)-extracted dye complex. Cu(II)-curcumin complex and Cu(II)-extracted dye complex were easily prepared in aqueous solution as mentioned in Chapter III (section 3.3.3).

Natural dye in the North and the North-east of Thailand are developing, however, natural dyes can offer not only a rich and varied source of dyestuff, but also the possibility of an income through sustainable harvest and sale of these dye plants. Many dyes are available from tree waste or can be easily grown in market gardens. In areas where synthetic dyes, mordants (fixatives) and other additives are imported and therefore relatively expensive, natural dyes can offer an attractive alternative. Consequently, studying the thermodynamics and kinetics of dyeing using extracted dye from turmeric rhizome of *Curcumin longa* Linn. onto silk would be one way to help the villagers solve the problem of poor fastness. When further studies on improvements in the chemistry of dyeing are carried out, the problems of the dyeing process using natural dyes will eventually be solved. This will also improve the economic situation and well-being of the poorest villagers in the North and the Northeast of Thailand (Moeyes, 1993).

4.3 Materials and methods

4.3.1 Chemicals

(a) Silk yarn from Chul Thai Dyeing Co., Ltd, Phetchabun, Thailand

(b) 98% Curcumin [458-37-7] from Across Organics

(c) Sodium hydroxide, NaOH, form Aldrich

(d) Ammonium acetate, NH4OOCCH3, from Merck

(e) Ammonium hydroxide, NH4OH, 25% m/v, commercial grade, from Merck

(f) Hydrochloric acid, HCl, 37% m/v, from Merck

(g) Ethanol, C2H5OH, analytical grade, from Merck

(h) Copper(II) nitrate trihydrate, Cu(NO3)2·3H2O, from Merck

4.3.2 Instruments

(a) A UV-Vis spectrophotometer (Agilent 8453) employed for absorbance measurements using quartz cells with path length of 1 cm

(b) A pH meter (Jenway/4330) used to measure the pH values of dye solutions

(c) A shaker bath (Type TW20 P Selecta, UK), operated at 45 strokes/min and used to study the adsorption kinetics and thermodynamics of silk dyeing

4.3.3 Experimental methods

4.3.3.1 Preparation of silk yarn and dye stock solutions

Silk yarn preparation experiment was carried out in a similar manner as mention of the section 2.3.3.1. Preparation of curcumin stock solution and turmeric extracted dye stock solution were prepared in a similar manner as that in section 2.3.3.2 to obtain concentration of 5×10^{-5} M of curcumin stock solution and section 2.3.3.5 to obtain 5×10^{-5} M of curcumin in extracted dye stock solution.

4.3.3.2 Preparation of 100 mg/L Cu(II) ions stock solution

The 1,000 mg/L Cu(II) stock solution was prepared by dissolving 3.8020 g of copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) in a small amount of deionized water in a 1,000-mL volumetric flask and adding more deionized water to obtain the final volume of 1,000.00 mL. This solution was then diluted to 100 mg/L Cu(II) stock solution and kept in a polyethylene bottle.

4.3.3.3 Effects of initial concentration of Cu(II)-curcumin complex and Cu(II)-extracted dye complex and contact time on the adsorption onto silk

Cu(II)-curcumin complex solutions with different concentrations were prepared by keeping fix the ratio 1:2 of Cu(II) ions with curcumin. Those complex solutions were obtained by pipetting into a 25-mL amber volumetric flasks, 1.61, 2.07, and 2.54 mL of the Cu(II) ions stock solutions. Then, by pipetting, 0.175, 0.227, and 0.275 mL of a 5.0×10^{-3} M curcumin stock solution were added in the above solutions, respectively. The mixture solutions were kept at room temperature for 45 minutes to obtain Cu-curcumin complex with concentrations of 12.9, 16.6, and 20.3 mg/L of curcumin complexes. Finally, more deionized water was added to reach the desired 25.00 mL volume.

The adsorption experiments were conducted by pre-warming and shaking each complex solution (25.00 mL) in a 100-mL amber reagent bottle by keeping in a shaker bath at 30 °C. After 30 minutes of pre-warming in the same shaker bath, the silk yarn samples (0.25 g) were immersed into the complex solutions, then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 360 nm versus dye concentration. Experiments were perform for each of the three concentrations listed above and repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t was calculated by equation (2.14).

The study of the effect of the contact time and initial concentration of Cu(II)-extracted dye complex on the adsorption onto silk was carried out in a similar manner as that of Cu(II)-curcumin complex using the dye solutions with concentration of 12.8, 16.5, and 20.1 mg curcumin/L of extracted dye at pH approximately of 5.0 without any adjustment. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 360 nm versus dye concentration.

4.3.3.4 Effect of pH on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

Cu(II)-curcumin complex solutions with concentration of 16.6 mg/L of curcumin, containing 10.00% v/v buffer solutions of ammonium acetate/acetic acid of various pH were prepared in 25-mL amber volumetric flasks using 1:2 of copper(II) stock solution to curcumin stock solution, 2.0 M ammonium acetate solution, glacial acetic acid, and deionized water. The pH values of the prepared Cu(II)-curcumin complex solutions were 5.05, 5.50, 5.57, 6.10, and 6.38. Adsorption experiments were carried out by shaking each dye solution (25.00 mL) in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after 120 minutes. Dye concentrations at each pH were determined at time zero and at 120 minutes using calibration curves of each pH based on absorbance at λ_{max} of each pH versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t was calculated by equation (2.14).

The study of the effect of pH on Cu(II)-extracted dye complex dyeing onto silk was carried out in a similar manner as that on Cu(II)-curcumin complex using the dye solutions containing 16.5 mg curcumin/L of extracted dye and the dyeing time of 120 minutes. The pH values of the prepared dye solutions before dyeing were 5.05, 5.50, 5.57, 6.10, and 6.38. Dye concentrations were determined at time zero and at 120 minutes using calibration curves for each pH based on absorbance at λ_{max} of each pH versus dye concentration.

4.3.3.5 Effect of material to liquor ratio (MLR) on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

The optimum material to liquor ratio of silk yarn (g) and 16.6 mg/L Cu(II)-curcumin complex (mL), containing 10.00% v/v buffer solutions of ammonium acetate/acetic acid at pH 5.0 prepared in a similar manner as noted in section 4.3.3.4, was studied using the ratios of 1:50, 1:100, and 1:150 g/mL. The adsorption experiments were carried out by shaking each dye solution (12.50, 25.00, and 37.50 mL) in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 360 nm versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t was calculated by equation (2.14).

The study of the effect of material to liquor ratio on the adsorption of Cu(II)-extracted dye complex onto silk was carried out in a similar manner as that of Cu(II)-curcumin complex using 12.50, 25.00, and 37.50 mL of dye solution containing 16.5 mg curcumin/L of extracted dye prepared at pH 5.0. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 419 nm versus dye concentration.

4.3.3.6 Effect of temperature on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

The adsorption experiments were carried out by shaking each 16.6 mg/L Cu(II)-curcumin complex solution (25.00 mL) prepared from 1:2 of copper(II) stock solution to curcumin stock solution, at pH 5.0 using 10.00% v/v ammonium acetate/acetic acid buffer in a 100-mL amber reagent bottle in a shaker bath at 30, 45, and 60 °C, separately. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in each dye solution. The silk yarn samples were then rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at 360 nm versus dye concentration. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t was calculated by equation (2.14).

The study of the effect of temperature on the adsorption of Cu(II)-extracted dye complex onto silk was carried out in a similar manner as that of Cu(II)-curcumin complex using a dye solution containing 16.5 mg curcumin/L of extracted dye prepared at pH 5.0. Dye concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes using a calibration curve based on absorbance at 360 nm versus dye concentration.

4.3.3.7 Equilibrium experiments of the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk at optimal condition

An experiment on the equilibrium adsorption isotherm was carried out by shaking 16.6 mg/L Cu(II)-curcumin complex solution (25.00 mL) prepared from 1:2 of copper(II) stock solution to curcumin stock solution, at pH 5.0 using 10.00% v/v ammonium acetate/acetic acid buffer in a 100-mL amber reagent bottle in a shaker bath at 30 °C. After 30 minutes, the silk yarn (0.25 g), which had been pre-warmed in the shaker bath for 30 minutes, was immersed in the dye solution. The silk yarn samples were then rapidly withdrawn after 120 minutes. The initial and equilibrium dye concentrations were estimated using a calibration curve based on absorbance at 360 nm. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk at equilibrium, q_e (mg/g silk) was calculated by the mass balance relationship:

$$q_e = \left(C_0 - C_e\right)\frac{V}{W} \tag{2.15}$$

where C_0 and C_e are the initial and equilibrium concentrations of dye, respectively (mg/L), V is the volume of the solution (L), and W is the mass of silk used (g).

The equilibrium study of the adsorption of Cu(II)-extracted dye complex onto silk was carried out in a similar manner as that of Cu(II)-curcumin complex using the dye solution containing 16.5 mg curcumin/L of extracted dye prepared at pH 5.0 and the contact time of 120 minutes. The initial and equilibrium dye concentrations were estimated using a calibration curve based on absorbance at 360 nm.

4.3.3.8 Adsorption and desorption studies of Cu(II)-curcumin complex and Cu(II)-extracted dye complex dyeing onto silk

Adsorption experiments on dyeing Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk were carried out in a similar manner as the equilibrium experiments as the mention in the section 4.3.3.7 but the contact times were varied at 1 to 360 minutes for both Cu(II)-curcumin complex and Cu(II)-extracted dye complex. All experiments were repeated three times to obtain the average amounts of dye adsorbed onto silk, q_t (mg/g silk), at time t was calculated by equation (2.14).

After the adsorption experiments, the silk yarn samples were removed from the dye solutions, squeezed, and air dried at room temperature. The dried silk yarn samples of both dyed for 120, 150, 180, 240, 300, and 360 minutes were selected for the desorption experiments. Each selected silk yarn samples were then soaked in deionized water (25.00 mL) at 30 °C with the desorption time according to its adsorption time. All experiments were repeated three times to obtain the average amounts of desorbed dye concentrations (q_{de}) were determined using a calibration curve based on absorbance at 360 nm for both dyes versus dye concentration. The remaining amount of dye adsorbed onto silk after desorption was then calculated by subtraction.

4.4 Results and discussion

4.4.1 Optimal condition of silk dyeing with Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

In the course of the investigation of the absorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk, the experiment parameters included initial dye concentration and contact time, pH of dye solution, material to liquor ratio (MLR), and temperature were manipulated to determine the optimal conditions for absorption. The mechanisms of adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex dyeing onto silk were investigated by using the pseudo first-order and pseudo second-order models. Moreover, the activation parameters and thermodynamics parameters of adsorption were calculated.

4.4.1.1 The effects of initial concentration of Cu(II)-curcumin complex and Cu(II)-extracted dye complex and contact time on the adsorption onto silk

The effects of initial dye concentration of Cu(II)-curcumin complex and Cu(II)-extracted dye complex and contact time on the adsorption onto silk are presented in Figures 4.1 and 4.2, respectively.

The adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk was found to reach equilibrium after 120 minutes. The equilibrium times were independent of initial dye concentrations but, in the first 60 minutes for Cu(II)-curcumin complex and 45 minutes for Cu(II)-extracted dye complex, rates of adsorption were larger for higher initial dye concentrations at the same shaking speed. This was because an increase in the initial dye concentration accelerated the diffusion of dyes from the dye solution into silk due to an increase in the driving force of the concentration gradient (Chiou and Li, 2002; Chairat et al., 2005).

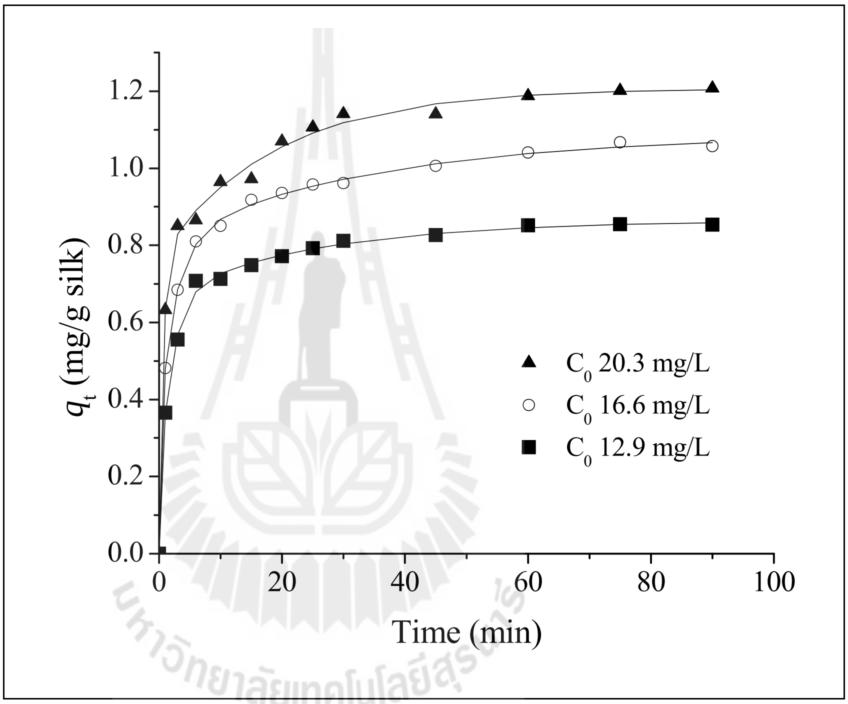

Figure 4.1 The effects of initial concentration of Cu(II)-curcumin and contact time on the adsorption onto silk at 30 °C and pH approximated 5.0 with an MLR of 1:100 g/mL.

The average adsorption capacities at equilibrium, q_e, at 30 °C and approximated pH 5.0 in Cu(II)-curcumin complex case were found to increase from 0.8586 to 1.0662 and to 1.2038 mg/g silk with an initial dye concentration of 12.9, 16.6, and 20.3 mg/L, respectively and an MLR of 1:100 g/mL. In Cu(II)-extracted dye complex case, the average adsorption capacities at equilibrium, q_e, at 30 °C and approximated pH 5.0 increased from 1.7428 to 1.1859 and to 2.5619 mg Cu(II)-curcumin/g silk with an initial concentration of 86.0, 111, and 135 mg/L of Cu(II)-extracted dye complex (containing approximately 12.8, 16.5, 20.1 mg/L of curcumin, respectively), respectively and an MLR of 1:100 g/mL. However, since both Cu(II)-curcumin complex and Cu(II)-extracted dye complex started to precipitate upon standing during pre-warming step at higher rate for higher initial dye concentration and the apparent colours of dyed silk in each case were not different by naked eyes, the optimum initial dye concentration were chosen to be16.6 mg/L of Cu(II)-curcumin and 16.5 mg curcumin/L of Cu(II)-extracted dye complex for convenience.

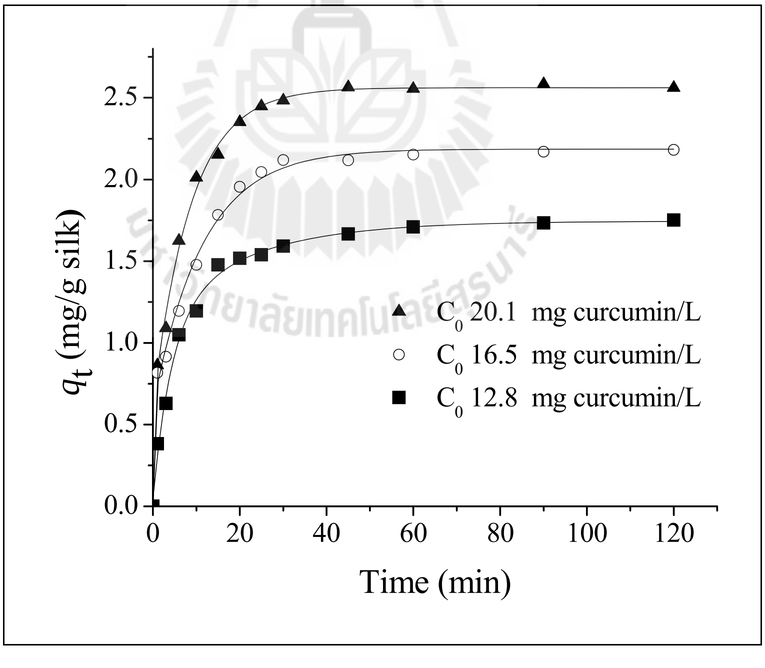

Figure 4.2 The effects of initial concentration of Cu(II)-extracted dye complex and contact time on the adsorption onto silk at 30 °C and pH approximated 5.0 with an MLR of 1:100 g/mL.

4.4.1.2 The effect of pH on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

One of the most important parameters controlling the adsorption capacity of dye onto silk is the pH of the dye solution (Christie, 2001; Chairat et al., 2005). To study the influence of pH on the adsorption capacity of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk, experiments were carried out with different initial dye solution pH values with no silk present. The obtained results are presented in Figure 4.3 and 4.4.

In both Cu(II)-curcumin complex and Cu(II)-extracted dye complex cases, the dye adsorption capacities onto silk were maximized lower than the pH range of 4.5-5.5. After dyeing silk fibers in the pH range of 4.5-5.5, the dyes might interact chemically with the fibers to form coordinate bonds, which were six-coordinate with N-terminal and C-terminal of silk, between the carbonyl carbons (C=O) at C-terminal of the fibers and the phenolic oxygens of the dyes, enhancing the dye uptake into the silk fibers. Cheng and coworkers reported studies on binuclear complexes of copper(II) with the binucleating ligand 2,6-diformyl-4-methylphenol di(benzoylhydrazone) where it was found that copper is six-coordinate with octahedral coordination geometry, besides copper with a square-pyramidal geometry with five-fold coordination (Cheng, 1996). Thus, it seems somehow clear that copper may exist in octahedral geometry with six-fold coordination as it is assumed with the copper(II)-curcumin complex bound to the silk fiber.

From the experiments, Cu(II)-curcumin complex started to precipitate from the solution at pH 3.5 while the Cu(II)-extracted dye complex at pH 3.0 which its lower the pH of curcumin and extracted dyes. This could be explained by the fact that

Cu(II)-curcumin complex and its derivatives were suggested in square planar geometry, Cu-O, with four coordination bonds. This could be assumed that may exist with polar composition of complex compounds which it were dissolved in water, they spread out and become surrounded by water molecules. In mind acidic condition solution, however, hydroxyl groups of phenolics curcumin ligand could be protonated with free H^+ ion to form hydronium ion groups that were solvated by water molecules, complex compounds could be service in mind acidic condition. At pH above 7.0 from experiments, an orange-red dye solution was form that could be explained that complex compound were hydrolysis to form copper ions, free curcumin and it derivatives. Belonging to Cheng and coworker, they reported that increase decomposed curcumin with increasing pH (Cheng, Liao, Yan, Jiang, Wang, Yao, and Wang, 1996). Therefore, the optimum pH value of initial dye solution was chosen to be 5.0.

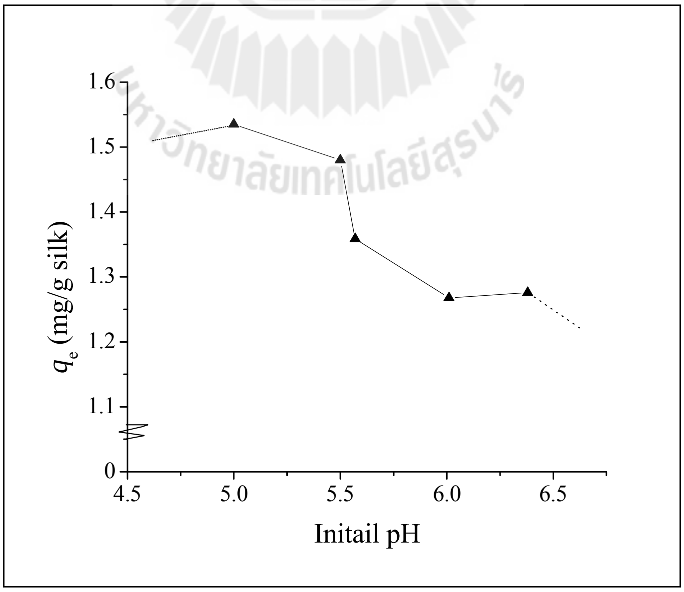

Figure 4.3 The effect of Cu(II)-curcumin complex solution pH on the adsorption onto silk at 30 °C with dye concentration of 16.6 mg/L, contact time of 120 minutes and an MLR of 1:100 g/mL.

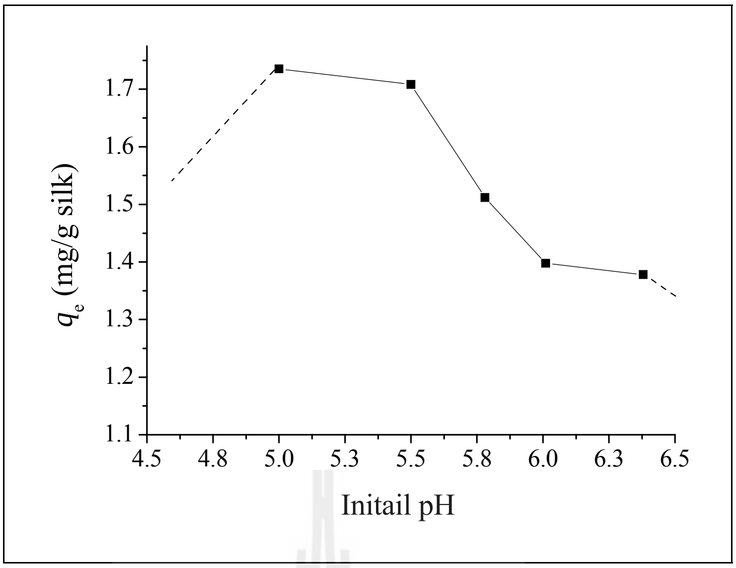

Figure 4.4 The effect of Cu(II)-extracted dye complex solution pH on the adsorption onto silk at 30 °C with dye concentration of 16.5 mg curcumin/L, contact time of 120 minutes and an MLR of 1:100 g/mL.

4.4.1.3 The effect of the MLR on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

The results of the MLR experiments carried out using an initial dye concentration of 16.6 mg/L of Cu(II)-curcumin complex and 16.5 mg curcumin/L of Cu(II)-extracted dye complex at pH 5.0 and at a dyeing temperature of 30 °C are shown in Figures 4.5-4.8. The results were found to be similar for both, curcumin and extracted dye, in a way that an increase in the volume of the dye solution resulted in an increase of the amount of dye adsorbed onto silk (as shown in Figures 4.5 and 4.7). This indicated that the higher is the amount of dye existing in the solution, the higher is the adsorption onto silk. However, as shown in Figures 4.6 and 4.8, with an MLR of 1:150 g/mL, the amount of dye left in the solution was significantly higher than that with an MLR of 1:100 g/mL. Therefore, the optimum MLR was chosen to be 1:100 g/mL.

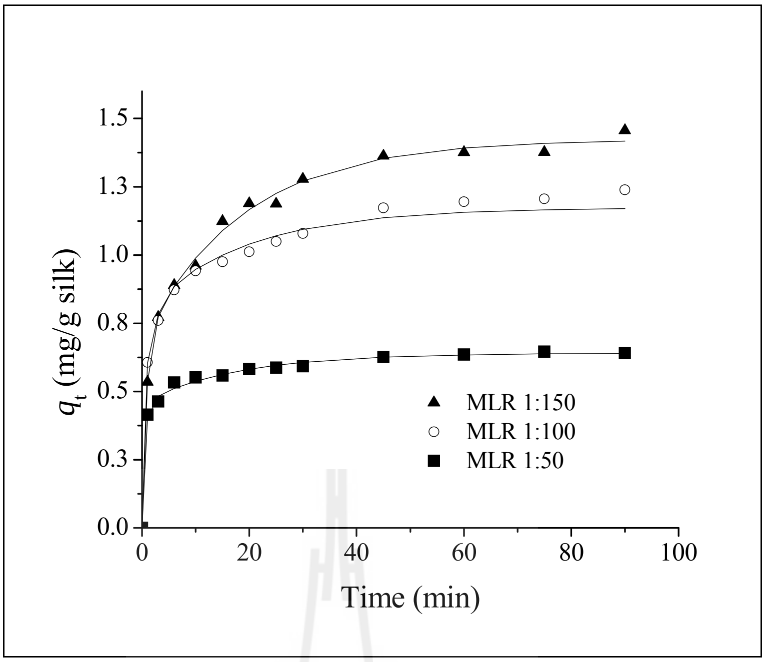

Figure 4.5 The effect of MLR on the adsorption of Cu(II)-curcumin complex onto silk at 30 °C with dye concentration of 16.6 mg/L and dye solution pH of 5.0.

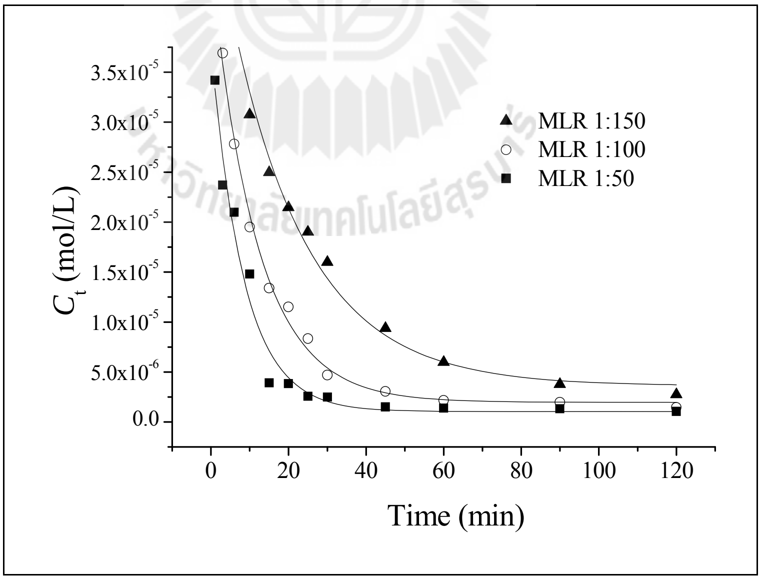

Figure 4.6 The effect of MLR on the concentration of Cu(II)-curcumin complex remaining in solution at 30 °C with initial dye concentration of 16.6 mg/L and dye solution pH of 5.0.

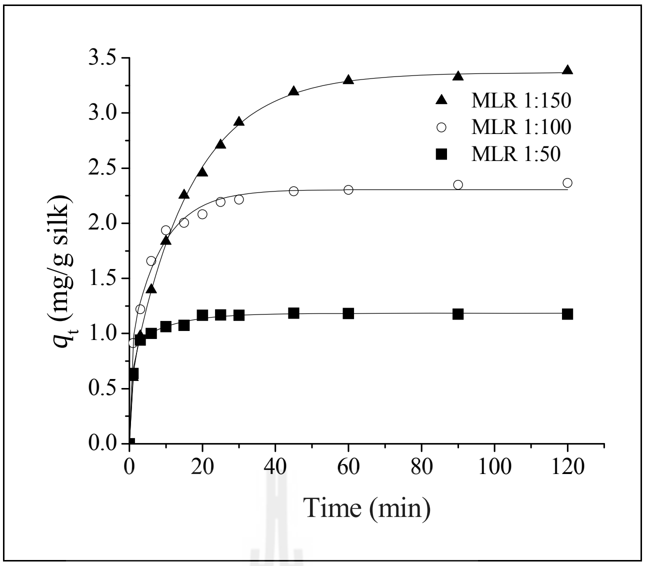

Figure 4.7 The effect of MLR on the adsorption of Cu(II)-extracted dye complex onto silk at 30 °C with dye concentration of 16.5 mg curcumin/L and dye solution pH of 5.0.

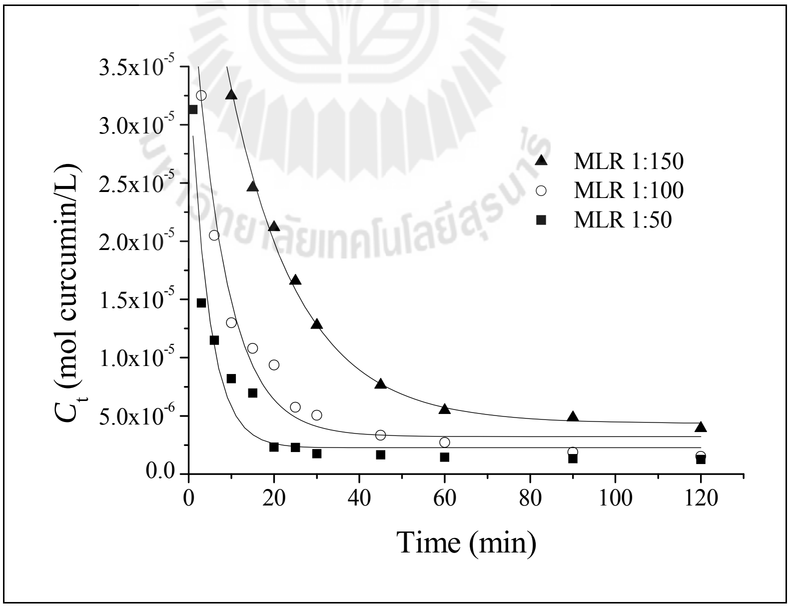

Figure 4.8 The effect of MLR on the concentration of Cu(II)-extracted dye complex remaining in solution at 30 °C with initial dye concentration of 16.5 mg curcumin/L and dye solution pH of 5.0.

4.4.1.4 The effect of temperature on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

As the mention in section 2.4.2.4, the study on the effect of temperature dependence on the dye adsorption onto silk gives more valuable information on the enthalpy change. The studied on the effect of temperature on the adsorption rate was carrying out a series of experiments at 30, 45, and 60 °C. It was found that an increase in the temperature led to an increase in initial adsorption rate. Figures 4.9 and 4.10 show different trends in the adsorption capacities at different temperatures before and after equilibrium. Before equilibrium was established, an increase in the temperature led to an increase in the dye adsorption rate indicative of a kinetically controlled process. The maximum uptake of Cu(II)-curcumin complex after equilibrium was dependent on the temperature of the dyeing bath. Higher temperature caused a decrease in the maximum amount of adsorbed Cu(II)-curcumin complex dye, suggesting an exothermic process. The Cu(II)-extracted dye complex also showed the similar trends but with less dependence on the temperature.

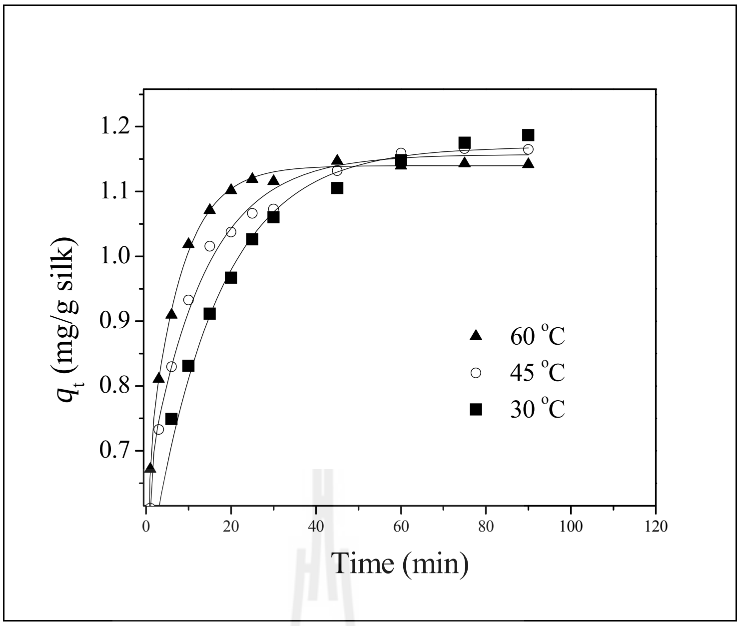

Figure 4.9 The effect of temperature on the adsorption of Cu(II)-curcumin complex onto silk with initial dye concentration of 16.6 mg/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

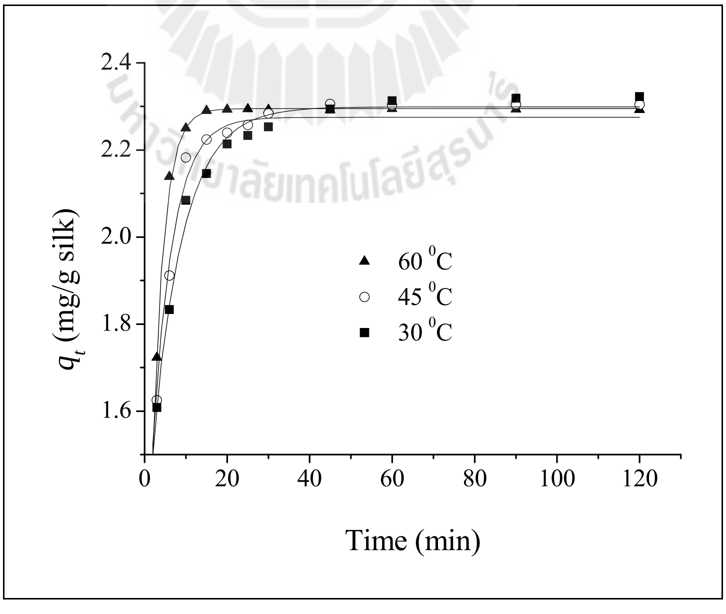

Figure 4.10 The effect of temperature on the adsorption of Cu(II)-extracted dye complex onto silk with initial dye concentration of 16.5 mg curcumin/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

4.4.2 Kinetic study on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

Linear plots of pseudo-first-order and pseudo-second-order equations on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk under optimum condition are shown in Figures 4.11-4.12.

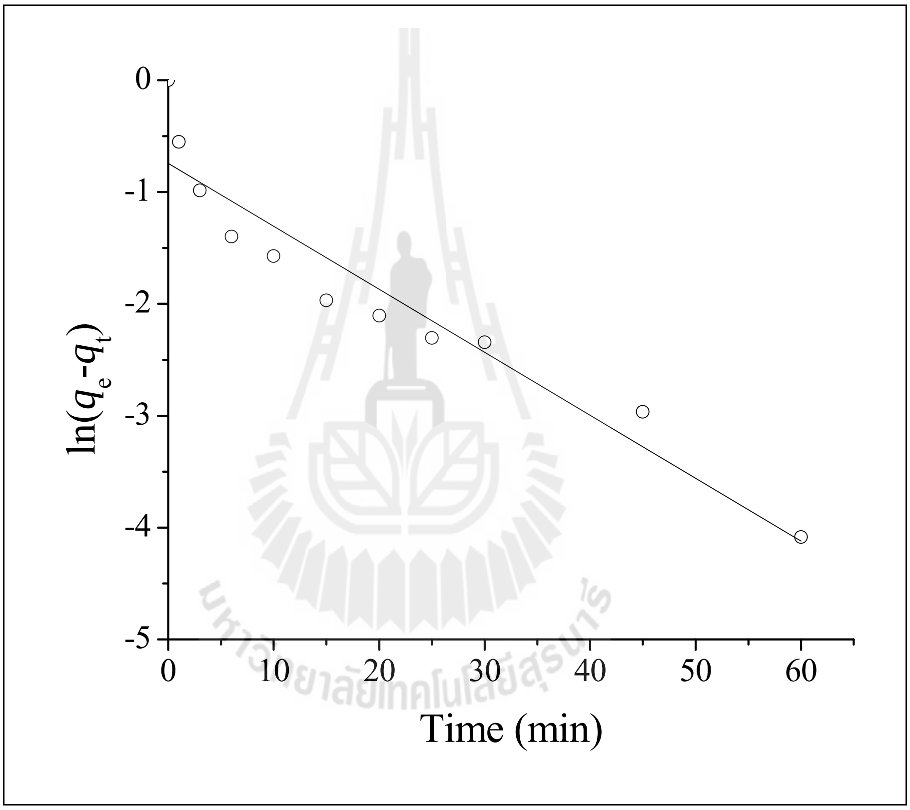

Figure 4.11 A plot of $\ln(q_e - q_t)$ versus time (pseudo-first-order equation) on the adsorption of Cu(II)-curcumin complex onto silk at 30 °C with initial concentration of 16.6 mg/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

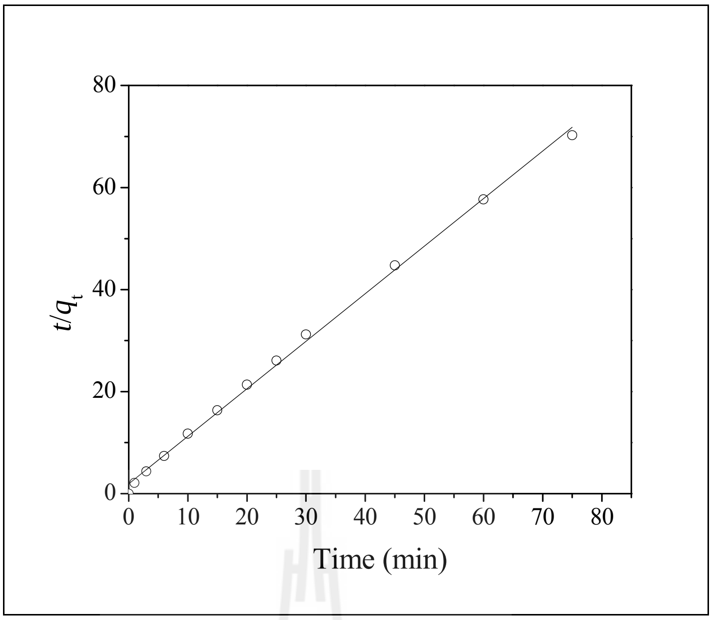

Figure 4.12 A plot of t/q_t versus time (pseudo-second-order equation) on the adsorption of Cu(II)-curcumin complex onto silk at 30 °C with initial concentration of 16.6 mg/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

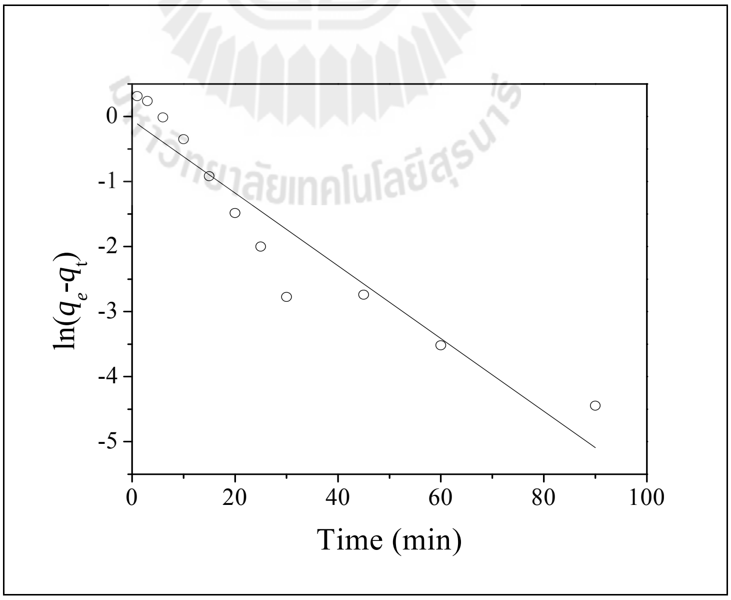

Figure 4.13 A plot of $\ln(q_e - q_t)$ versus time (pseudo-first-order equation) on the adsorption of Cu(II)-extracted dye complex onto silk at 30 °C with initial concentration of 16.5 mg curcumin/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

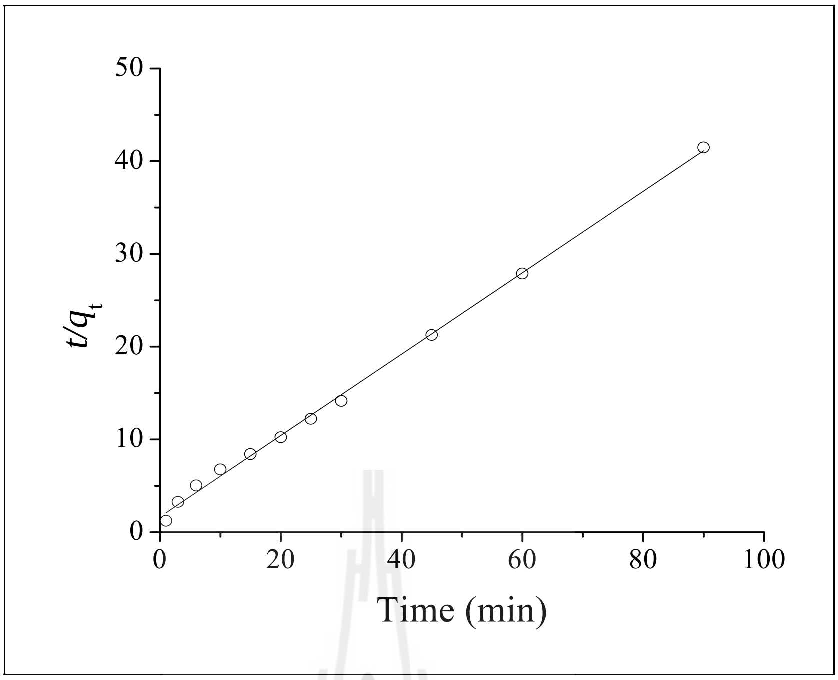

Figure 4.14 A plot of t/q_t versus time (pseudo-second-order equation) on the adsorption of Cu(II)-extracted dye complex onto silk at 30 °C with initial concentration of 16.5 mg curcumin/L, dye solution pH of 5.0, and an MLR of 1:100 g/mL.

Linear regression coefficients plots (R^2) and kinetic parameters of pseudo-first-order equation (k_1), and pseudo-second-order equation (k_2 and h_i) on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk under optimum condition are tabulated in Table 4.1. Resulting was found similar to trend that the regression coefficients of the fitted pseudo-second-order equation were high (> 0.99) for both Cu(II)-curcumin complex and Cu(II)-extracted dye complex and were higher than those of the pseudo-first-order one.

Table 4.1 Regression coefficients of linear plots and kinetic parameters of pseudo-first-order and pseudo-second-order models on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk under optimum condition.

Parameters	Cu(II)-curcumin	Cu(II)-extracted
Pseudo-first-order model:		
R^2	0.9766	0.8245
$q_{e,exp}$ (mg curcumin/g silk)	1.1869	2.3225
k_1	0.0500	0.0414
$q_{e,cal}$ (mg curcumin/g silk)	0.6977	0.4894
Pseudo-second-order model:		
R^2	0.9896	0.9999
$q_{e,exp}$ (mg curcumin/g silk)	1.1869	2.3225
k_2	0.5570	0.3155
h_i	0.6171	1.7129
$q_{e,cal}$ (mg curcumin/g silk)	1.0526	2.3299

Furthermore, the calculated equilibrium adsorption capacities ($q_{e,cal}$) in the pseudo-second-order model fitted well to the experimental ones ($q_{e,exp}$). This suggests that the adsorption of both Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk was a pseudo-second-order process in which the overall adsorption was likely controlled by the chemical process involving valence forces through sharing and coordinated covalent bonds between adsorbent and adsorbate.

The effects of MLR, initial dye concentration, and temperature on the adsorption rate constant, k_2, and the initial dye adsorption rate, h_i, were also studied. Linear plots of pseudo-second-order equation on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk at different MLR’s, initial dye concentrations, and temperatures are shown in Figures 4.15-4.20.

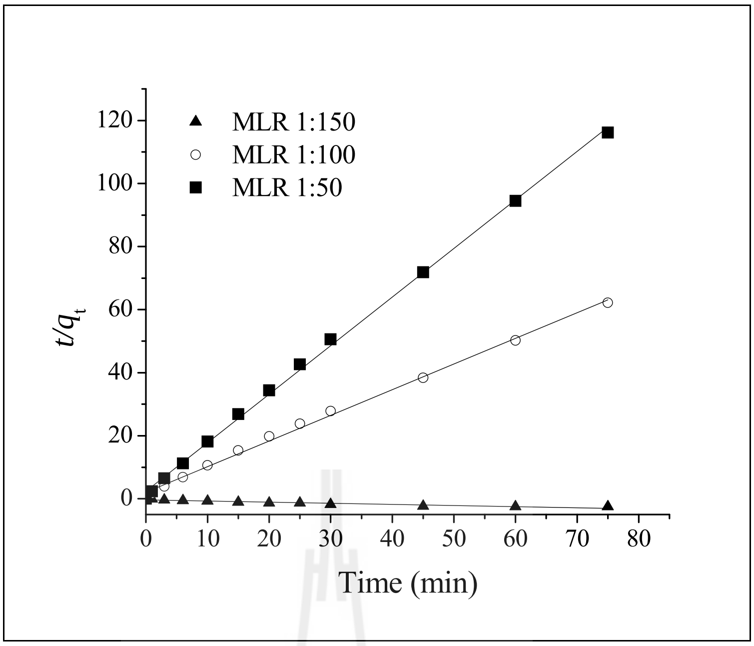

Figure 4.15 The plots of pseudo-second-order equation on the adsorption of Cu(II)-curcumin complex onto silk at different MLR’s, with initial dye concentration of 16.6 mg/L, dye solution pH of 5.0, and dyeing temperature of 30 °C.

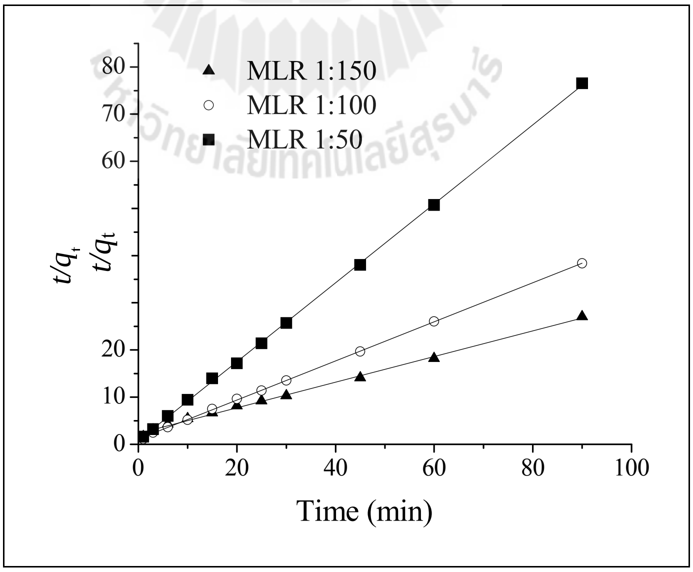

Figure 4.16 The plots of pseudo-second-order equation on the adsorption of Cu(II)-extracted dye complex onto silk at different MLR’s, with initial dye concentration of 16.5 mg curcumin/L, dye solution pH of 5.0, and dyeing temperature of 30 °C.

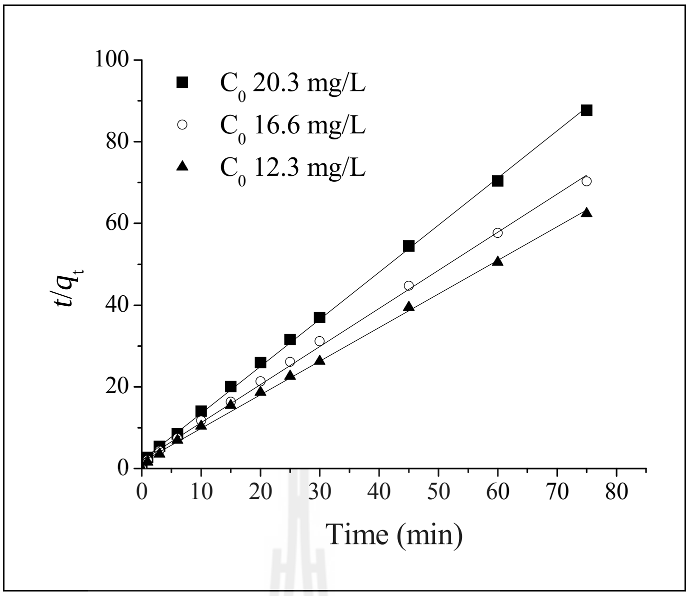

Figure 4.17 The plots of pseudo-second-order equation on the adsorption of Cu(II)-curcumin complex onto silk at different initial dye concentrations with an MLR of 1:100 g/mL, dye solution pH of 5.0, and dyeing temperature of 30 °C.

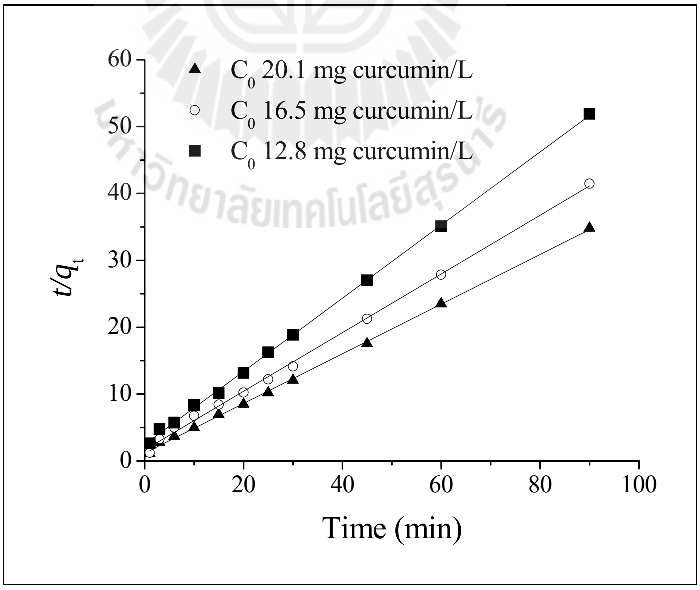

Figure 4.18 The plots of pseudo-second-order equation on the adsorption of Cu(II)-extracted dye complex onto silk at different initial dye concentrations with an MLR of 1:100 g/mL, dye solution pH of 5.0, and dyeing temperature of 30 °C.

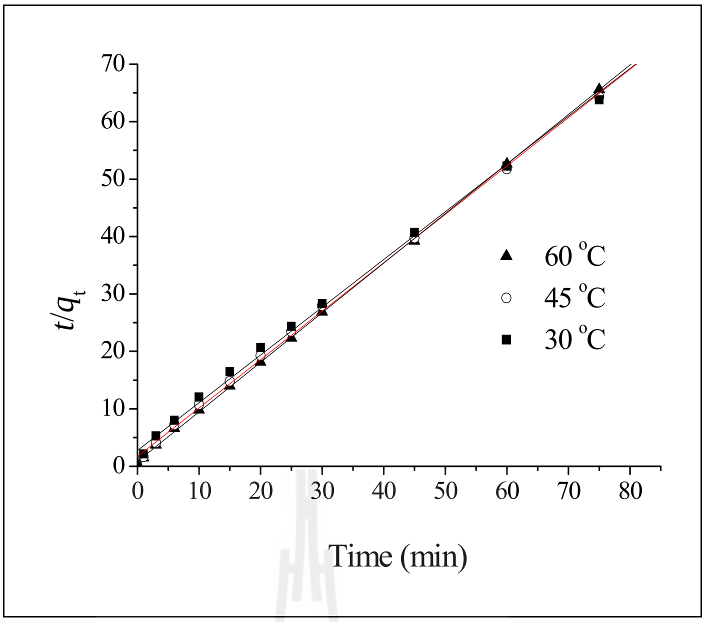

Figure 4.19 The plots of pseudo-second-order equation on the adsorption of Cu(II)-curcumin complex onto silk at different temperatures with initial dye concentration of 16.6 mg/L, an MLR of 1:100 g/mL, and dye solution pH of 5.0.

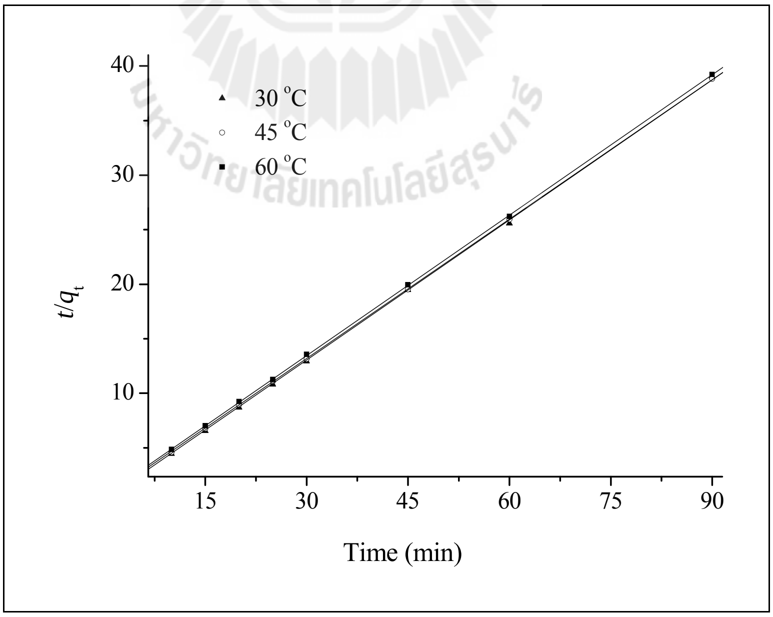

Figure 4.20 The plots of pseudo-second-order equation on the adsorption of Cu(II)-extracted dye complex onto silk at different temperatures with initial dye concentration of 16.5 mg curcumin/L, an MLR of 1:100 g/mL, and dye solution pH of 5.0.

Regression coefficients of linear plots and kinetic parameters of pseudo-second-order equation (k_2 and h_i) on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk under different conditions are tabulated in Table 4.2 and 4.3, respectively. It was found that the linear regression coefficients were all high (> 0.99) and the calculated equilibrium adsorption capacities were in good agreement with the experimental data. In addition, the k_2 and h_i values were found to be significantly affected by MLR, initial dye concentration, and temperature in the case of Cu(II)-curcumin complex. The k_2 value on the adsorption of Cu(II)-curcumin complex onto silk decreased with increasing MLR, decreasing initial dye concentration, and decreasing temperature while the h_i value increased with increasing MLR, increasing initial dye concentration, and increasing temperature

Table 4.2 Pseudo-second-order adsorption rate constants, experimental q_e. calculated q_e, and regression coefficients of linear plots on the adsorption of Cu(II)-curcumin complex onto silk under various conditions.

Parameters	**$q_{e,exp}$ (mg/g silk)**	**Second-order kinetic model**			
		k_2	**h_i**	**$q_{e,cal}$ (mg/g silk)**	**R^2**
MLR (g/mL): initial dye concentration (C_0) 16.6 mg/L, pH 5.0, temp. 30 °C					
1:50	0.6403	1.0040	0.4230	0.6491	0.9984
1:100	1.2388	0.3234	0.4882	1.2287	0.9963
1:150	1.4568	0.0036	2.2825	1.4162	0.8989
Initial dye concentration (mg/L): MLR 1:100 g/mL, pH 5.0, temp. 30 °C					
12.9	0.8538	0.6811	0.5216	0.8675	0.9990
16.6	1.0575	0.4523	0.5208	1.0731	0.9978
20.3	1.2077	0.4184	0.6189	1.2163	0.9979
Temperature (°C): initial dye concentration (C_0) 16.6 mg/L, MLR 1:100 g/mL, pH 5.0					
30.0	1.1869	0.5570	0.6171	1.0526	0.9896
45.0	1.1651	0.8513	1.0144	1.0916	0.9947
60.0	1.1422	0.9911	1.2971	1.1440	0.9968

In the case of Cu(II)-extracted dye complex the k_2 value on the adsorption of Cu(II)-extracted dye onto silk decreased with increasing MLR, decreasing initial dye concentration, and increasing temperature while the h_i value decreased with increasing MLR, increasing initial dye concentration, and increasing temperature. The k_2 value and the trend of h_i value on the adsorption of Cu(II)-extracted dye complex onto silk were fluctuated due to the nature of mixture.

Table 4.3 Pseudo-second-order adsorption rate constants, experimental q_e. calculated q_e, and regression coefficients of linear plots on the adsorption of Cu(II)-extracted dye complex onto silk under various conditions.

Parameters	$q_{e,exp}$ **(mg/g silk)**	**Second-order kinetic model**			
		k_2	h_i	$q_{e,cal}$ **(mg/g silk)**	R^2
MLR (g/mL): *initial dye concentration (C_0) 16.5 mg/L, pH 5.0, temp. 30 °C*					
1:50	1.1751	0.9254	1.3200	1.1943	0.9997
1:100	2.3656	0.1589	0.9233	2.4102	0.9997
1:150	3.9102	0.0323	0.4362	3.6765	0.9963
Initial dye concentration (mg/L): *MLR 1:100 g/mL, pH 5.0, temp. 30 °C*					
12.8	1.7507	0.1218	0.4068	1.8278	0.9994
16.5	2.2815	0.1172	0.6086	2.2789	0.9979
20.1	2.5606	0.1168	0.8480	2.6940	0.9991
Temperature (°C): *initial dye concentration (C_0) 16.5 mg/L, MLR 1:100 g/mL, pH 5.0*					
30.0	2.3225	0.3155	1.7129	2.3229	0.9999
45.0	2.3040	0.4374	2.4114	2.3480	0.9999
60.0	2.3023	0.8442	4.4608	2.3364	0.9997

4.4.3 Activation parameters for the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

The rate constants, k_2, for pseudo-second-order reaction at different temperatures listed in Table 4.2 were used to estimate the activation parameters of the adsorption of Cu(II)-curcumin complex onto silk. The slope of the plot of lnk_2 versus $1/T$ (Figure 4.21) was used to evaluate E_a, while the slope and intercept of the plot of lnk_2/T versus $1/T$ (Figure 4.22) were used to evaluate $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively, as listed in Table 4.4.

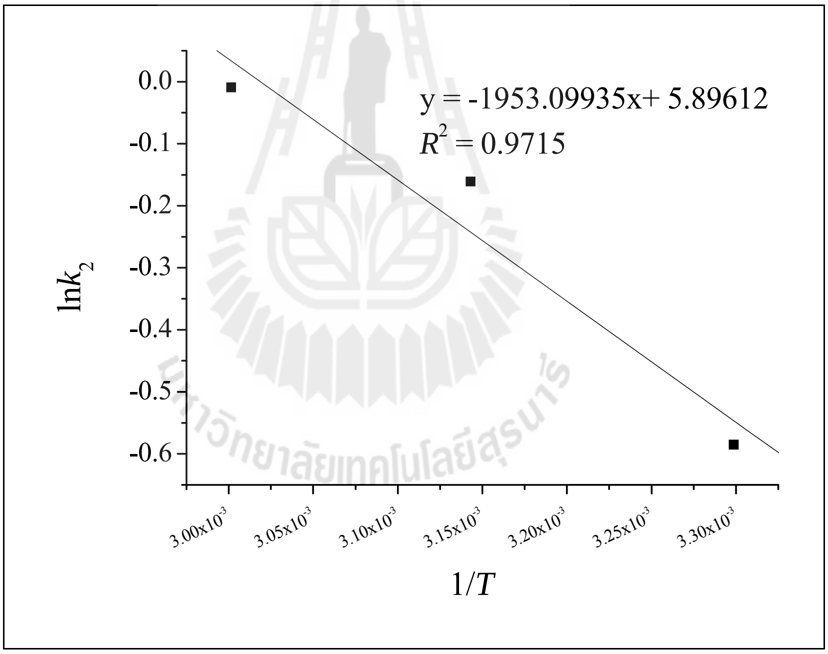

Figure 4.21 An Arrhenius plot for the adsorption of Cu(II)-curcumin complex onto silk.

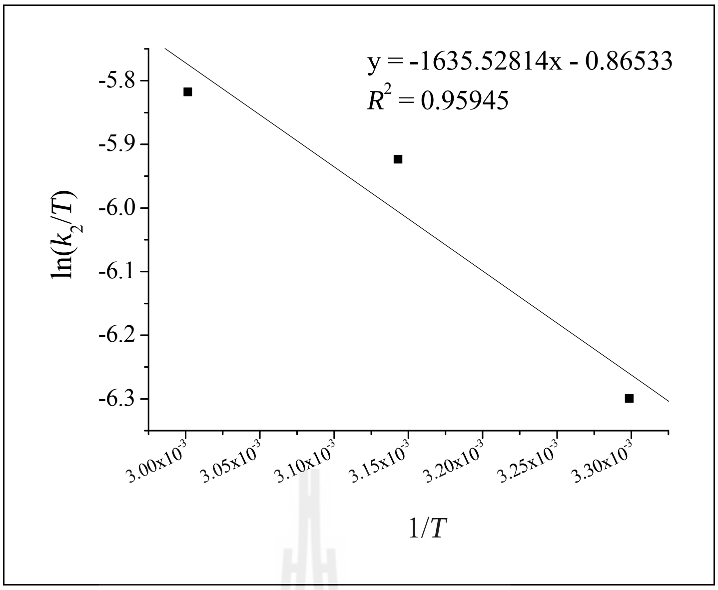

Figure 4.22 A plot of $\ln(k_2/T)$ versus $1/T$ for the adsorption of Cu(II)-curcumin complex onto silk.

Table 4.4 The activation parameters for the adsorption of Cu(II)-curcumin complex onto silk with initial dye concentration of 16.6 mg/L.

Temp (^{o}C)	**k_2 (g silk/mg s)**	**E_a (kJ/mol)**	**$\Delta H^{\#}$ (kJ/mol)**	**$\Delta S^{\#}$ (J/mol K)**	**$\Delta G^{\#}$ (kJ/mol K)**
30	0.5570	16.24	13.60	-204.75	75.67
45	0.8513				78.74
60	0.9911				81.81

Nakamura et al. studied physisorption process using formal HF-based and B3LYP based charge densities for the frame works $[Zn(1,4\text{-bdc})]_n$ and $[Cu_3(1,3,5\text{-btc})_2]_n$ 1,3,5-btc^{3-} =1,3,5-benzenetricarboxylate) complexes, the isosteric heats of adsorption for N_2, Ar, and H_2 are small and lie in the range of values for physisorption (<10 kcal/ mol) (Nakamura, Negishi, Kutsuna, Ihara, Sugihara, and Takeuchi, 2000). From the E_a value of 16.24 kJ/mol observed for Cu(II)-curcumin complex, we could infer that the adsorption of Cu(II)-curcumin complex onto silk was likely a physisorption process.

The value of $\Delta G^{\#}$ was calculated at 303, 318, and 333 K by equation (2.10) using $\Delta H^{\#}$ and $\Delta S^{\#}$ and these values are listed in Table 4.4. The negative value of entropy ($\Delta S^{\#}$) reflected more aggregation and greater interaction between Cu(II)-curcumin complex and the silk fiber.

The rate constants, k_2, for pseudo-second-order reaction at different temperatures listed in Table 4.5 were used to estimate the activation parameters of the adsorption of Cu(II)-extracted dye complex onto silk. The slope of the plot of $\ln k_2$ versus $1/T$ (Figure 4.23) was used to evaluate E_a, while the slope and intercept of the plot of $\ln k_2/T$ versus $1/T$ (Figure 4.24) were used to evaluate $\Delta H^{\#}$ and $\Delta S^{\#}$, respectively, as listed in Table 4.5.

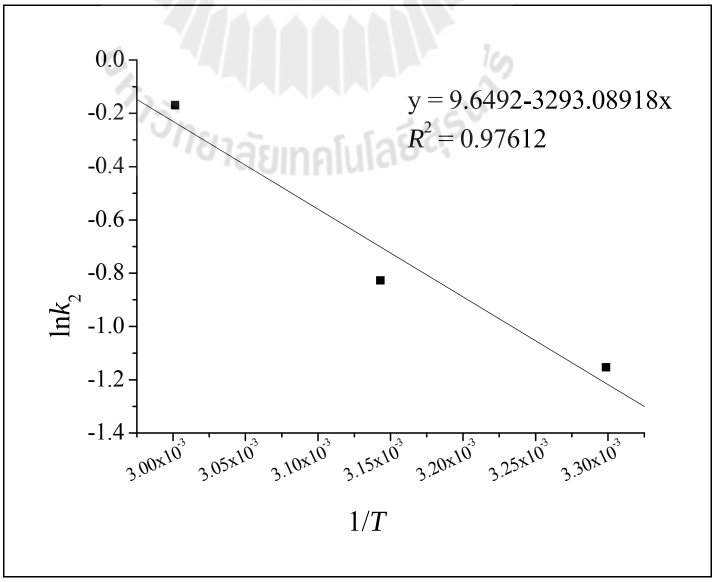

Figure 4.23 An Arrhenius plot for the adsorption of Cu(II)-extracted dye complex onto silk.

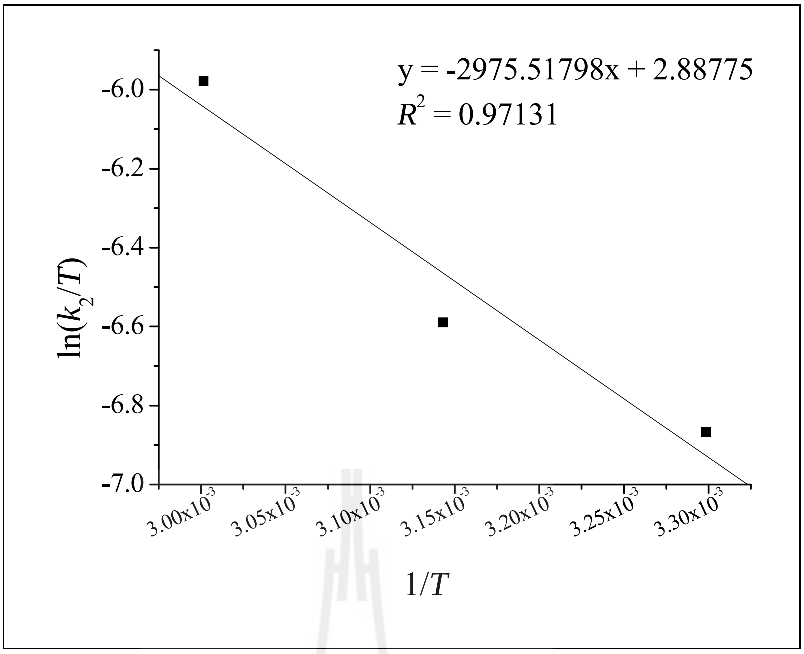

Figure 4.24 A plot of ln(k_2/T) versus 1/T for the adsorption of Cu(II)-extracted dye complex onto silk.

Table 4.5 The activation parameters for the adsorption of Cu(II)-extracted dye complex onto silk with initial curcumin dye concentration of 16.6 mg/L.

Temp (°C)	**k_2 (g silk/mg s)**	**E_a (kJ/mol)**	**$\Delta H^{\#}$ (kJ/mol)**	**$\Delta S^{\#}$ (J/mol K)**	**$\Delta G^{\#}$ (kJ/mol K)**
30	0.3155	27.38	24.73	-173.54	77.35
45	0.4374				79.54
60	0.8442				82.56

Sagara et al., reported that Physisorption of H_2 in $[Zn_4O(1,4\text{-bdc})_3]_n$ have been examined using second-order Møller–Plesset perturbation theory. The results calculated using this theory indicate that binding at the $Zn_4O(CO_2)_6$ clusters at 300 K is perhaps 1.5 kJ/mol, the highest observed for a micro porous coordination polymer (Sagara, Klassen, and Ganz, 2004). From the E_a value of 27.38 kJ/mol observed for Cu(II)-extracted dye complex, we could also infer that the adsorption of Cu(II)-extracted dye complex onto silk was likely a physisorption process. The values of $\Delta G^{\#}$ at 303, 318, and 333 K were calculated using the same equation as that for curcumin and these values are listed in Table 4.5.

4.4.4 Thermodynamic parameters on the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk

As mentioned earlier, the adsorption of Cu(II)-curcumin complex and Cu(II)-extracted dye complex onto silk was exothermic process. In order to confirm the exothermic behaviour quantitatively, the thermodynamic parameters of adsorption, $\Delta G°$, $\Delta H°$, and $\Delta S°$, of both dyes after reaching equilibrium were calculated using the equations (2.11)-(2.13). The results are listed in Table 4.6.

The negative values of $\Delta G°$ indicated that the adsorption of dyes onto silk was spontaneous. The negative value of $\Delta H°$ confirmed that the adsorption process was exothermic. Furthermore, the entropy change ($\Delta S°$) in dyeing which represents the entropy difference of the dye molecules within the fiber (Kim, Son, and Lim, 2005) was positive in value. This indicated that adsorbed dyes became more restrained within the silk fiber than in the dyeing solution.

Table 4.6 Thermodynamic parameters for the adsorption of both dyes with initial dye concentration 16.6 mg/L of Cu(II)-curcumin complex and 16.5 mg curcumin/L of Cu(II)-extracted dye complex.

Dyes	**Temperature (°C)**	**lnK_c**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol K)**	**R^2**
Cu(II)-	30	3.30	-8.31			
curcumin	45	3.84	-10.15	-20.55	95.62	0.9709
complex	60	4.03	-11.15			
Cu(II)-	30	3.53	-8.89			
extracted dye	45	3.67	-9.71	-4.95	45.80	0.9537
complex	60	3.71	-10.26			

4.4.5 Adsorption-desorption of Cu(II)-curcumin complex and Cu(II)-turmeric extracted dye on dyeing onto silk

After the adsorption of Cu(II)-curcumin complex and Cu(II)-turmeric extracted dye onto silk was equilibrated, desorption was carried out in deionized water. Plots of the amount of dye adsorbed onto silk, q_t, versus t after adsorption and desorption experiments (Figure 4.25) showed little loss of both Cu(II)-curcumin complex and Cu(II)-turmeric extracted dye uptake after desorption.

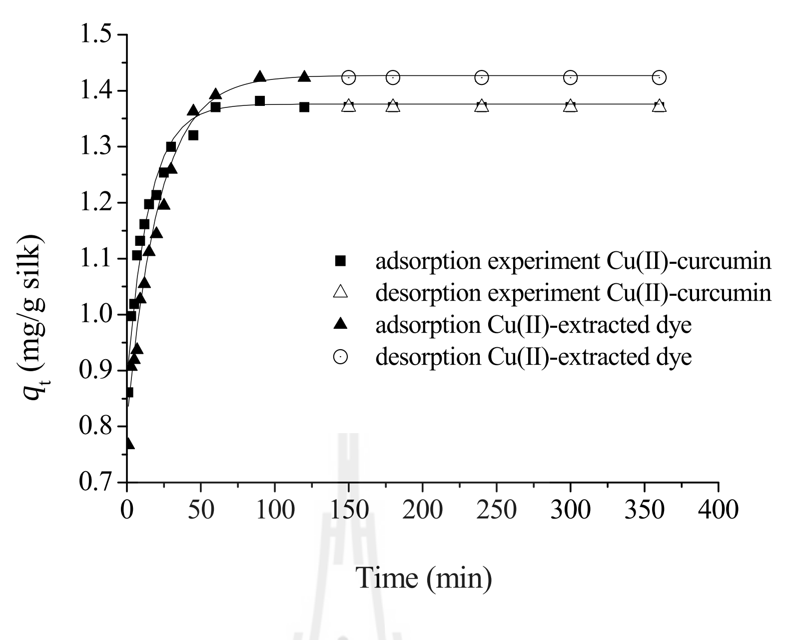

Figure 4.25 Adsorption-desorption studies of both dyes with initial dye concentrations of 16.6 mg/L of Cu(II)-curcumin complex and 16.5 mg curcumin/L of Cu(II)-turmeric extracted dye on dyeing onto silk at 30 °C, dye solution pH of 5.0, and an MLR of 1:100.

4.5 Conclusion

The adsorption kinetics and thermodynamics of the Cu(II)-curcumin complex and Cu(II)-turmeric extracted dye on dyeing onto silk were investigated. The parameters, including initial dye concentration, contact time, pH of the dye solution, MLR, and temperature were found to influence the dyeing process. To avoid precipitating of both dyes in aqueous solution during the pre-warming step, the initial dye concentrations were optimized at 16.6 mg/L of Cu(II)-curcumin complex dye and at 16.5 mg curcumin/L of Cu(II)-extracted dye complex. The adsorption of dye onto silk was found to reach equilibrium after 120 minutes for both dyes, with adsorption capacities maximized over the pH range of 5.0-6.0. When taking into account the amount of dye adsorbed and the amount of dye left in the solution, the MLR value in both cases was optimized at 1:100 g/mL. Since higher temperature caused a decrease in the maximum amount of dye adsorbed, the optimum dyeing temperature was chosen to be 30 °C, which was close to room temperature.

The adsorption of Cu(II)-curcumin complex onto silk was found to follow a pseudo-second-order kinetic model with an activation energy of 16.24 kJ/mol. This suggested that the overall rate of Cu(II)-curcumin complex adsorption was likely controlled by a physical sorption process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 13.60 kJ/mol and -204.75 J/mol K, respectively, and the free energy of activation ($\Delta G^{\#}$) at 30 °C was 75.76 kJ/mol. In addition, the adsorption of curcumin onto silk was a spontaneous and an exothermic process with the free energy change ($\Delta G°$) value at 30 °C of -8.31 kJ/mol and the enthalpy change ($\Delta H°$) value of -20.55 kJ/mol.

The adsorption of Cu(II)-turmeric extracted dye was also found to follow a pseudo-second-order kinetic model with an activation energy of 27.38 kJ/mol. This also suggested that the overall rate of extracted dye adsorption was likely controlled by a physical sorption process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 24.73 kJ/mol and -173.54 J/mol K, respectively, and the free energy of activation ($\Delta G^{\#}$) at 30 °C was -8.89 kJ/mol. Furthermore, the adsorption of Cu(II)-extracted dye complex onto silk was also a spontaneous and an exothermic process based on the free energy change.

4.6 References

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CHAPTER V

ADSORPTION OF COPPER(II) IONS ON RESIDUAL SILK FIBERS AND COCOONS

5.1 Abstract

The adsorption of Cu(II) ions from mixture solutions of Cu(II) ions and curcumin onto residual silk fibers and cocoons was investigated. The kinetics of adsorption as function of initial concentration of Cu(II) ions, contact time, pH, Material to Liquor Ratio (MLR), and temperature were studied. Two simplified kinetic models, based on pseudo first-order and pseudo second-order equations, were computed to describe the adsorption mechanism. The pseudo second-order kinetic model fitted properly with the behaviour of the adsorption of Cu(II) ions onto silk residual fiber, and supported the hypothesis of chemical adsorption. The activation energy (E_a) for the adsorption of Cu(II) ions onto silk residual fiber and cocoon were 46.75 kJ/mol and 25.35 kJ/mol, respectively. For the adsorption of Cu(II) ions from mixture solutions onto silk residual fiber, the enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and free energy of activation ($\Delta G^{\#}$) at 30 °C were 44.10 kJ/mol, -102.50 J/mol K, and 75.18 kJ/mol, respectively. For the adsorption of Cu(II) ions from mixture solutions onto cocoon, the enthalpy, entropy and free energy of activation at 30 °C were 22.71 kJ/mol, -164.23 J/mol K, and 25.34 kJ/mol, respectively. At the equilibrium, negative values of ΔG° show that the adsorption of Cu(II) ions onto silk residual fiber is

spontaneous. The negative value of $\Delta H°$ confirms that the adsorption process is an exothermic one. The negative value of $\Delta S°$, equal to -0.07 J/mol K, indicates that the adsorbed Cu(II) ions have a reduced level of disorder within the silk residual fiber in comparison with that in the dyeing solution. It could be observed that the quantity of copper adsorbed on cocoon was 8 times less than that adsorbed on silk residual fiber. Therefore, the process was not investigated further and the thermodynamic values were not computed.

5.2 Introduction

The presence of dyes in effluents is a major concern due to their adverse effects on many forms of life. Metivier-Pignon, Faur-Bresquet, and Cloirec (2003) reported that the discharge of dyes into the environment is a matter of concern for both toxicological and aesthetic reasons. Industries such as textile, leather, paper, plastics, etc., consume substantial volumes of water in their use of dyes to colour their products. As a result, they generate an extensive amount of coloured waste water (Ravi, Deebika, and Balu, 2005).

Although the driving force of environmental protection on industrial development promotes the development of eco friendly technologies (Desphande, 2001) that reduce the consumption of fresh water and lower the output of waste water, the release of large amounts of synthetic dyes into the environment causes extensive environmental pollution, resulting in health-risks, legislation issues, and serious concerning on the part of both the public and the scientific community. While superior amounts of dyes are toxic for aquatic organisms, small concentrations of them in effluent water are highly visible. Consequently, the removal of colour from effluents containing various kinds of synthetic dyes becomes important. Methodologies have been developed for the removal of synthetic dyes from water and waste water to decrease their impact on the environment. The technologies involve adsorption on inorganic or organic matrices, decolourization by photocatalysis and/or by oxidation processes, microbiological or enzymatic decomposition, etc. (Hao, Kim, and Chiang, 2000).

Past research has concentrated on measuring adsorption isotherms of pollutants from aqueous solutions on naturally occurring materials to evaluate the adsorption efficiency by varying experiment parameters. Colour is the clearest indicator of water pollution. The discharge of coloured waste water into receiving streams greatly affects the aesthetic nature and also interferes with transmission of sunlight into streams and therefore reduces photo synthetic activity (Namasivayam, Radhika, and Suba, 2001). Dyes and pigments represent one of the problem; they are discharged into water from various industrial branches, generally from the dye manufacturing and textile finishing of the consumers and villagers. The chemical classes of dyes can be classified as the azo, anthraquinone, sulfur, indigoid, triphenylmethyl (trityl) and phthalocyanine derivatives (Moeyes, 1993; Mishra and Tripathy, 1993).

Copper(II) sulphate, is widely used as a mordant-fixative for natural fibers with natural dyes (Moeyes, 1993). It is released into ground or river water without treatment, especially from domestic dyeing. In the case of the American textile industry, contamination from metal such as copper is believed to result mainly from the use of metallic dyes (Baughman, 2001). Briefly, any process or container using copper material may contaminate products such as food or water (Nuhoglu and Oguz, 2003). An excessive intake of copper results in an accumulation in the liver and kidney which may lead to serious kidney failure and liver diseases. It is also toxic to aquatic organisms even at very small concentrations in natural water. Although copper is an essential metal for human life, it is potentially toxic as well like all other heavy metals (Nuhoglu and Oguz, 2003).

To remove copper from waste water, traditional technology uses the principle of adjusting the pH of the waste water, followed by precipitation and solid–liquid separation. Removal of toxic-heavy metals or decreasing their concentrations to the permitted discharge levels is made more important by an increase in industrial activities (Nuhoglu and Oguz, 2003). There are different methods used for removal of heavy metals from waste water such as chemical precipitation, membrane filtration, ion exchange, reverse osmosis, evaporation, electrolysis, and adsorption (Kandah, 2004; Fourest and Roux, 1992; Bayhan, Keskinler, Cakici, Levent, and Akay, 2001). Biosorption is the removal of the heavy metals from solutions such as waste biomass, natural materials, chitosan, fly ash etc by organic substances rich in functional groups such as carboxylic acids, alcohols, ketones, and phenolic hydroxides (Fourest and Roux, 1992; Bayhan et al., 2001).

Silk is a continuous strand of two filaments cemented together forming the cocoon of silkworm, *Bombyx mori*. Silk filament is a double strand of fibroin, which is held together by a gummy substance called silk sericin or silk gum. Silk fibroin is the protein that forms the filament of silkworm and gives its unique physical and chemical properties. Silk adapts various secondary structures, including α-helix, β-sheet, and crossed β-sheet (Padamwar and Pawar, 2004). Fibroin filament is made of both crystalline and amorphous domains. The amorphous domains are known to have amino acid groups with bulkier side chains, whereas more is known about the composition of crystalline domains, which have alanine 12%, glycine 30%, and serine 40%. Silk cocoon and silk residual fiber are biomass from silk process. They are organic substances rich in functional groups those can be used in the removal of heavy metals from solutions (Daithankar, Padamwar, Pisal, Paradkar, and Mahadik, 2005).

However, there has been no study regarding the adsorption of Cu(II) ions onto cocoon and silk residual fiber. The main aim of this work is to study the efficiency of silk residual fiber and cocoon in removing Cu(II) ions from mixture solutions of Cu(II) ions and curcumin and to establish the probable mechanism of copper adsorption. The influence of operating variables such as pH, initial concentration, contact time, material to liquor ratio, and temperature were experimentally tested and the reaction conditions of the two adsorbent wastes were optimized for maximum adsorption capacity. The equilibrium and kinetic data of the adsorption processes were then analyzed in order to evaluate the ability of these adsorbents to adsorb copper(II) ions and to study their adsorption models.

5.3 Materials and methods

5.3.1 Chemicals

(a) Standard Cu(II) nitrate solution (1,000 mg/L) from Merck

(b) Copper(II) nitrate trihydrate, $Cu(NO_3)_2{\cdot}3H_2O$, from Merck

(c) 98% Curcumin [458-37-7] from Across Organics

(d) Sodium hydroxide, NaOH, from Aldrich

(e) Ammonium acetate, NH_4OOCCH_3, from Merck

(f) Ammonium hydroxide, NH_4OH, 25% m/v, commercial grade, from Merck

(g) Ethanol, C_2H_5OH, analytical grade, from Merck

(h) Silk residue fiber, Nongbuadaeng, Chaiyaphum, Thailand

(i) Cocoon, Nongbuadaeng, Chaiyaphum, Thailand

5.3.2 Instruments

(a) An atomic absorption spectrometer, AAS. (Varian SpectrAA 250 Plus), equipped with a hollow cathode lamp for Cu at a wavelength of 324.8 nm, the slit width of 0.7 nm, and the integration time of 5 seconds using evaluation via the peak area. The oxidant gas was nitrous oxide and the fuel gas was acetylene.

(b) A pH meter (Jenway/4330) used to measure the pH values of the mixture of Cu(II) ions and curcumin solutions

(c) A shaker bath (Type TW20 P Selecta, UK), operated at 45 strokes/min and used to study the adsorption kinetics and thermodynamics

5.3.3 Experimental methods

5.3.3.1 Preparation of 100 mg/L Cu(II) stock solution

The 1,000 mg/L Cu(II) stock solution was prepared by dissolving 3.8020 g of copper(II) nitrate trihydrate in a small amount of deionized water in a 1,000-mL volumetric flask and adding more deionized water to obtain the final volume of 1,000.00 mL. This solution was then diluted to 100 mg/L Cu(II) stock solution and kept in a polyethylene bottle.

5.3.3.2 Preparation of 5.0×10^{-3} M curcumin stock solution

A fresh curcumin stock solution was prepared by dissolving 0.1842 g of curcumin in a small amount of 95% ethanol in a 100-mL amber volumetric flask and adding more ethanol to obtain the final volume of 100.00 mL. Lower concentrations of curcumin solutions were made by dilution of this stock solution with deionized water. All solutions were kept in amber bottles during use.

5.3.3.3 Preparation of a calibration curve

The 1,000 mg/L Cu(II) ion standard solution was diluted to 100 mg/L with deionized water. Solutions of 2, 4, 6, 8, and 10 mg/L Cu(II) ions were then prepared by diluting an appropriate aliquot of the 100 mg/L Cu(II) ion standard solution. The atomic absorption spectrometer was used to measure the absorbance of Cu(II) ion at wavelength of 324.8 nm and the calibration curve was obtained by plotting the absorbance against concentrations.

5.3.3.4 Effects of initial concentrations of the mixture solution of Cu(II) ions and curcumin and contact time on the adsorption onto residual silk fibers and silk cocoons

The 10 mg/L Cu(II) ion solution mixed with 0.40 mg/L curcumin was prepared in a 25-mLvolumetric flask by mixing 2.50 mL of the 100 mg/L Cu(II) stock solution (5.3.3.1) with 5.43 µL of the 5.0×10^{-3} M curcumin stock solution (5.3.3.2) and adding deionized water to obtain the final volume of 25.00 mL. The 25 mg/L Cu(II) ion solution mixed with 1.0 mg/L curcumin and the 40 mg/L Cu(II) ion solution mixed with 1.6 mg/L curcumin were prepared in the similar manner by using 6.25 and 10.00 mL of the Cu(II) stock solution and 13.57 and 21.71 µL of the curcumin stock solution, respectively. The pH of all the mixtures were varied from 4.0 to 5.0 and were not adjusted.

The 14 adsorption experiments were conducted for each of the three concentrations listed above by pre-warming each mixture solution (25.00 mL) in a 125-mL Erlenmeyer flask in a shaker bath at 45 strokes/min and 30 °C for 30 minutes.

Residual silk fibers (0.25 g), which had been pre-warmed in the same shaker bath, were then immersed in the mixture solution and rapidly withdrawn from the mixture solution after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes for each concentration. The Cu(II) ion concentrations left in the flask were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes by using the AAS calibration curve relating absorbance at 324.8 nm versus concentration (5.3.3.3). Each experiment was repeated three times in order to compute the average amounts of Cu(II) ions adsorbed onto residual silk fibers at time *t*, q_t (mg/g), by applying the equation (2.14).

The study of the effects of the initial concentrations of mixture of Cu(II) ions with curcumin and contact time for the adsorption onto silk cocoons, was carried out in a similar manner as that for residual silk fibers ; mixture solutions with concentration of 2, 3, and 4 mg/L of Cu(II) ions and 0.08, 0.12, and 0.16 mg/L of curcumin, respectively, with pH of approximately 5.0, without any adjustments, were used. Cu(II) ion concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes by using AAS. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto silk cocoons at time *t*, q_t (mg/g), by applying the equation (2.14).

5.3.3.5 Effect of pH of mixtures of Cu(II) ions and curcumin on the adsorption onto residual silk fibers and silk cocoons

Mixtures of Cu(II) ions and curcumin with concentration of 25 mg/L Cu(II) ions and 10.00% v/v buffer solutions of ammonium acetate/acetic acid of various pH were prepared by pipetting 6.25 mL from the 100 mg/L Cu(II) stock solution, 13.57 μL of the 5.0×10^{-3} M curcumin stock solution, and 2.50 mL from 2.0

M ammonium acetate solution. Glacial acetic acid was then added dropwise until the desired pH was obtained; finally deionized water was dropped to fill the 25.00 mL volume. The pH values for the prepared mixture solutions were 3.37, 4.11, 5.06, 6.03, 6.98, and 8.03. Adsorption experiments were carried out by pre-warming and shaking 25.00 mL of each mixture in a 125-mL Erlenmeyer flask, using a shaker bath at 45 strokes/min and 30 °C. After 30 minutes, the residual silk fibers (0.25 g), which had been pre-warmed in the same shaker bath, were immersed in the mixture solution. After 120 minutes the silk residual fiber samples were rapidly withdrawn from the mixture solution. Cu(II) ion concentrations left in the mixture solution of different pH were determined at time zero and at 120 minutes by using the calibration curve based on absorbance at 324.8 nm. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto residual silk fibers at time t, q_t (mg/g), by applying the equation (2.14).

The study of effect of pH of mixtures of Cu(II) ions and curcumin on the adsorption onto silk cocoons was carried out in a similar manner as that for residual silk fibers ; mixture solutions with concentration of 3 mg/L of Cu(II) ions and 0.12 mg/L of curcumin at pH 3.37, 4.11, 5.06, 6.03, and 6.98 using the ammonium acetate acetic buffer solution were prepared. Cu(II) ion concentrations were determined at time zero and 120 minutes by using AAS. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto silk cocoons at time t, q_t (mg/g), by applying the equation (2.14).

5.3.3.6 Effect of material to liquor ratios (MLR) on the adsorption of mixtures of Cu(II) ions and curcumin onto residual silk fibers and silk cocoons

The optimum MLR of residual silk fibers (g) and mixture of 25 mg/L of Cu(II) ions and 1.0 mg/L of curcumin, prepared at pH 6.0 in a similar manner as noted in section 5.3.3.5, for the adsorption was determined from the ratios of 1:50, 1:100, and 1:150 g/mL. Adsorption experiments were carried out by pre-warming and shaking 25.00 mL of each mixture solution in a 125-mL Erlenmeyer flask, using a shaker bath at 45 strokes/min and 30 °C. After 30 minutes the residual silk fibers (0.25 g), which had been pre-warmed in the same shaker bath, were immersed in the mixture solution and were rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes. The Cu(II) ion concentrations left in the Erlenmeyer flasks were then determined by using AAS calibration curve relating absorbance at 324.8 nm versus concentration. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto residual silk fibers at time t, q_t (mg/g), by applying the equation (2.14).

The study of optimum MLR of silk cocoon (g) and mixture of Cu(II) ions and curcumin was carried out in a similar manner as that for residual silk fibers ; mixture solution with concentration of 3 mg/L of Cu(II) ions and 0.12 mg/L of curcumin at pH equal to 6.0 obtained by using ammonium acetate acetic buffer was prepared. Cu(II) ion concentrations were determined at time zero and at 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes by using AAS. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto silk cocoons at time t, q_t (mg/g), by applying the equation (2.14).

5.3.3.7 Effect of temperatures on the adsorption of mixture of Cu(II) ions and curcumin onto residual silk fibers and silk cocoons

The optimum temperature of residual silk fibers (g) and mixture of 25 mg/L of Cu(II) ions and 1.0 mg/L of curcumin, prepared at pH 6.0 in a similar manner as noted in section 5.3.3.5, for the adsorption was determined from the temperatures of 30, 45, and 60 °C. Adsorption experiments were carried out by pre-warming and shaking 25.00 mL of each mixture solution in a 125-mL Erlenmeyer flask, using a shaker bath at 45 strokes/min and 30 °C. After 30 minutes the residual silk fibers (0.25 g), which had been pre-warmed in the same shaker bath, were immersed in the mixture solution and were rapidly withdrawn after different immersion times of 1, 3, 5, 9, 12, 15, 20, 25, 30, 45, 60, 90, and 120 minutes. The Cu(II) ion concentrations left in the Erlenmeyer flasks were then determined by using AAS calibration curve relating absorbance at 324.8 nm versus concentration. All experiments were repeated three times in order to obtain the average amounts of Cu(II) ions adsorbed onto residual silk fibers at time t, q_t (mg/g), by applying the equation (2.14).

The study of the effect of temperatures for the adsorption onto silk cocoons, was carried out in a similar manner as that for residual silk fibers; mixture solution with concentration of 3 mg/L of Cu(II) ions and 0.12 mg/L of curcumin at pH of 6.0 using ammonium acetate acetic buffer was prepared. Concentration of Cu(II) ions determined by the same procedure as that for residual silk fibers in order to compute q_t (mg/g).

5.3.3.8 Equilibrium experiments of the adsorption of mixture of Cu(II) ions and curcumin onto residual silk fibers and silk cocoons at optimum condition

An isothermal experiment on the equilibrium adsorption was carried out by pre-warming and shaking mixture of 25 mg/L of Cu(II) ions and 1.0 mg/L of curcumin prepared at pH 6.0 (25.00 mL), in a 125-mL Erlenmeyer flask using a shaker bath at 45 strokes/min and 30 °C. After 30 minutes, the residual silk fibers (0.25 g), were immersed in the mixture solution. After 120 minutes the samples were rapidly withdrawn. The initial and equilibrium Cu(II) ion concentrations were estimated using the calibration curve based on absorbance at 324.8 nm. The experiment was repeated three times in order to obtain the average amount of Cu(II) ions adsorbed onto residual silk fibers at equilibrium, q_e (mg/g), which was calculated by the equation (2.15).

5.4 Results and discussion

5.4.1 Adsorption of copper(II) ions on residual silk fibers

5.4.1.1 Optimum condition

- Effects of initial concentrations of mixture solution of Cu(II) ions and curcumin and contact time

Effects of initial concentrations of mixture of Cu(II) ions and curcumin in aqueous solution and contact time on the adsorption onto residual silk fibers are shown in Figure 5.1. It is a plot of milligrams of Cu(II) ions adsorbed per gram of residual silk fibers (q_t) at various times (t). Different initial Cu(II) ion and curcumin concentrations of 10:0.4, 25:1.0, and 40:1.6 by mg/L per mg/L with the same ratio of 25:1 were tested at 30 °C. It was found that, in all cases, the equilibrium was obtained after 20 minutes while the adsorption capacity depended on the initial Cu(II) ion and curcumin concentrations and rates of adsorption were larger for higher initial concentrations. However, there was no adsorption when the initial concentration of Cu(II) ions was 25 mg/L with no curcumin added. Since Cu(II) ions in the mixture solutions existed in two forms, hydrated ions and Cu-curcumin complexes, and at pH around 4.0 to 5.0, amino groups of silk fibers were in the protonated forms which were unable to form attractive forces with hydrated Cu(II) ions, they were not adsorbed on the residual silk fibers. However, Cu(II)-curcumin complexes contained phenolic groups which was able to form ester bond with carboxyl group. As a result, Cu(II) ions in the form of complexes with curcumin were adsorbed on the residual silk fibers. As the initial concentration of the complex increased, its diffusion onto residual silk fibers increased due to an increase in the driving force of the concentration gradient.

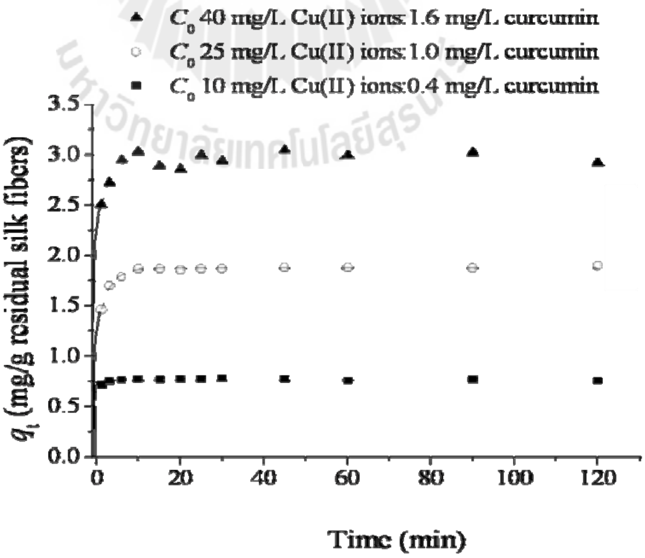

Figure 5.1 Effects of initial concentrations of Cu(II) ions and curcumin in the mixture solution and contact time on the adsorption onto residual silk fibers at 30 °C with an MLR of 1:100 g/mL.

The average adsorption capacities at equilibrium, q_e, at 30 °C with an MLR of 1:100 g/mL were found to increase from 0.7580 to 1.8988 and to 2.9172 mg Cu(II) per g residual silk fibers with the initial Cu(II) ion and curcumin concentrations of 10:0.4, 25:1.0, and 40:1.6 by mg/L per mg/L, respectively. However, as shown in Figure 5.2, with Cu(II) initial concentration of 40 mg/L, the amount of Cu(II) ions left in the mixture solution was much higher than that with the initial concentration of 25 mg/L. Hence the concentration of 25 mg/L Cu(II) ions and 1.0 mg/L curcumin was chosen as the optimum initial concentration of the mixture solution for all adsorption experiments.

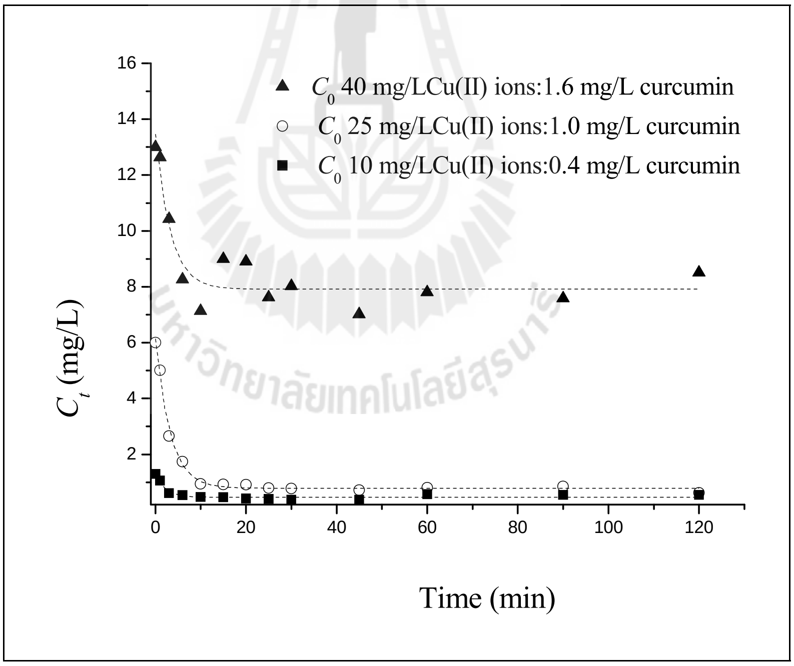

Figure 5.2 The effect of initial concentrations on the remaining concentration of Cu(II) ions in the mixture solution at 30 °C with an MLR of 1:100 g/mL.

- Effect of pH

To study the influence of pH on the adsorption capacity of Cu(II) ions in mixture solution onto residual silk fibers, experiments were carried out with different initial mixture solution pH values with no residual silk fibers present. Effect of pH on the adsorption of Cu(II) ions in the mixture solution with initial concentration of 25 mg/L of Cu(II) ions and 1.0 mg/L curcumin onto 0.25 g residual silk fibers were investigated at pH values of 3.37, 4.11, 5.06, 6.03, 6.98, and 8.03. The results are shown in Figure 5.3.

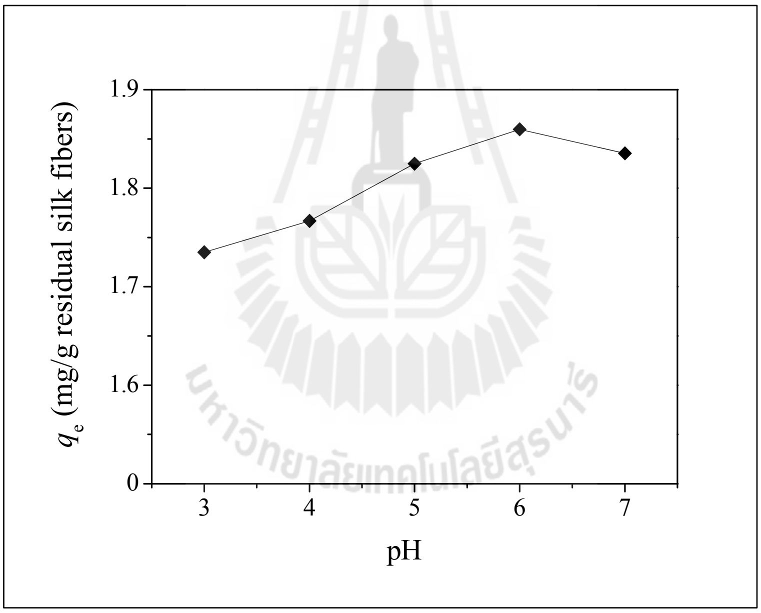

Figure 5.3 Effect of pH of mixture solution of 25 mg/L Cu(II) ions and 1.0 mg/L curcumin on the adsorption onto residual silk fibers at 30 °C with contact time of 120 minutes and an MLR of 1:100 g/mL.

The relationship between the amount of Cu(II) ions uptake onto residual silk fibers. It clearly showed that the adsorption was highly dependent on the pH since it altered the surface charge of the residual silk fibers.

A maximum adsorption capacity was observed at pH 6.0 and a slightly decline at pH below and above 6.0. At pH around 6 the N-terminal and C-terminal of silk fibers (Corr, 1995)

In the former the adsorption capacity decreases due to the protonation of amine group present in the silk protein fibers; in fact it reduces the number of binding sites necessary for the adsorption of Cu(II) ions, hence its adsorption is governed by the charge exchange only. However, the competition exerted by H^+ retards Cu^{2+} exchange. The adsorption studies at pH values higher than 7.0 could not be carried out caused by the precipitation of $Cu(OH)_2$ as explained by Volanti and co-worker (Volanti, Orlandi, Andrés, and Longo, 2010).

The highest uptake value was recorded in the pH range from 5.0 to 7.0. This is attributed to the presence of free lone pair of electrons at the *N*-terminal and deprotonated oxygen atoms at the *C*-terminal of silk protein fibers. They are suitable ligands for coordinated bonds with *d*-orbitals such that present in copper ions. As the residual silk fibers possess higher adsorption capacity at pH range between 5.0-7.0, further studies were limited at pH 6.0.

- Effect of material to liquor ratios (MLR)

Result of the material liquor ratios from experiments conducted by using mixture solution, with concentration of 25:1.0 by mg/L of Cu(II) ions and curcumin at pH 6.0 and adsorbing temperature of 30 °C are shown in Figure 5.4.

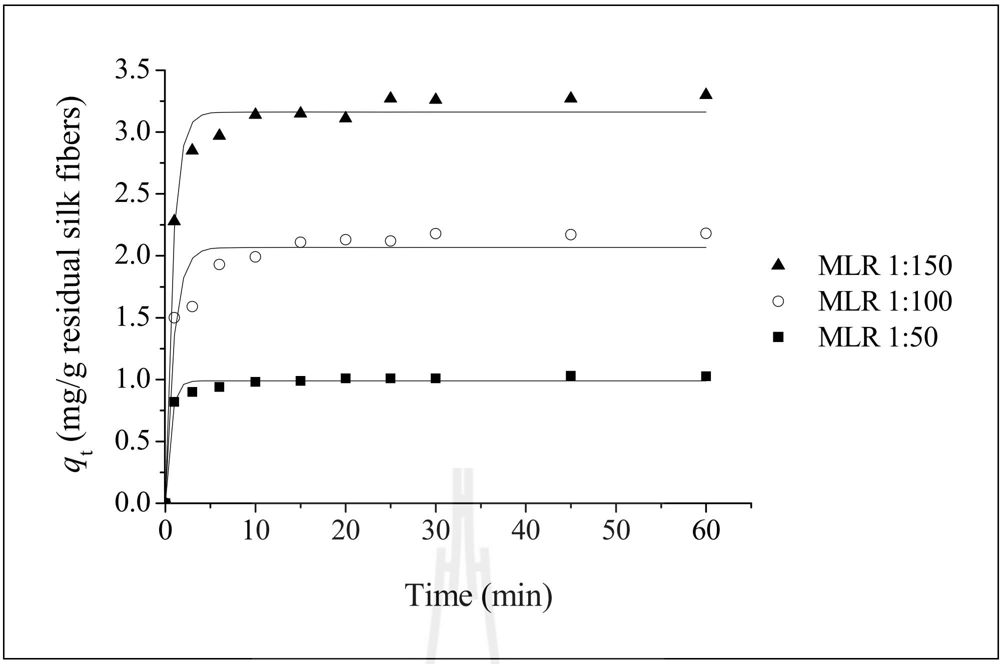

Figure 5.4 Effects of MLR on the adsorption of Cu(II) ions and curcumin in mixture solution onto residual silk fibers with initial concentrations of 25:1.0 by mg/L, at pH 6.0, and adsorbing temperature of 30 °C.

As shown in Figure 5.4, an increase in volume of mixture solution resulted in increases the amount of Cu(II) ions and curcumin adsorbed onto silk residual fiber. This indicates that an higher amount of Cu(II) ions and curcumin containing in the mixture solution, the higher adsorption onto the residual silk fibers . Nevertheless, as shown in Figure 5.3, with an MLR of 1:150 g/mL, the amount of Cu(II) ions left in the mixture solution bath was higher than that with an MLR of 1:100 g/mL significantly. Hence, in order to minimize the waste of process, the 1:100 g/mL MLR was chosen and used for all the kinetic experiments.

- Effect of temperatures

As the mentioned in section 2.4.2.4 the study of the temperature on the adsorption gives valuable information on the enthalpy change for the adsorption process. The effect of temperature on the adsorption rate of Cu(II) ions and curcumin in the mixture solution onto residual silk fibers was studied by performing a series of experiments at 30, 50, and 70 °C.

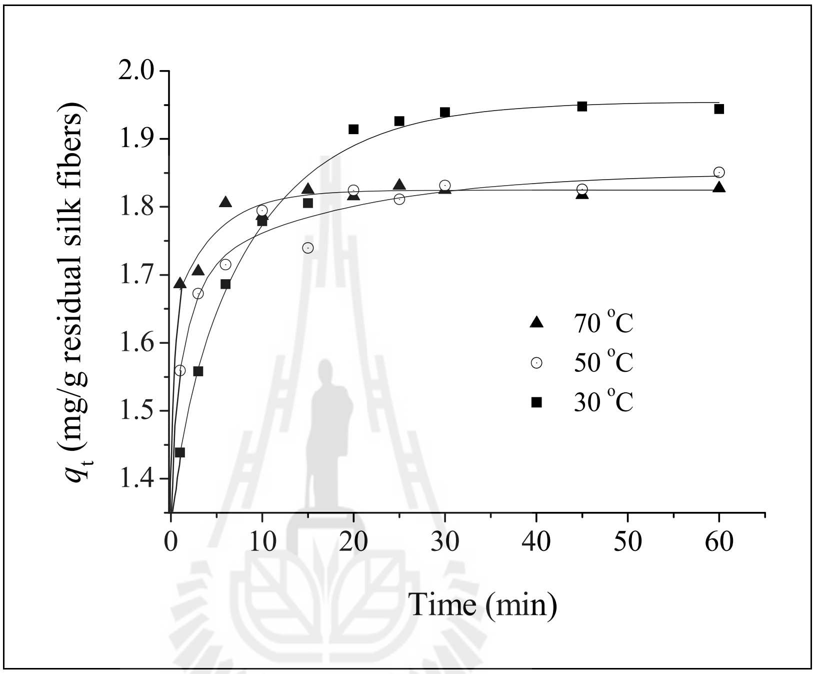

Figure 5.5 Effect of temperatures on the adsorption of Cu(II) ions from the mixture of 25 mg/L of Cu(II) ions and 1.0 mg/L curcumin onto residual silk fibers at pH of 6.0 and an MLR of 1:100 g/mL.

It was found that an increase in temperature led to an increase in initial adsorption rate. The similarity of the three trends of Figure 5.5 shows that the adsorption capacities are different before and after equilibrium. Before equilibrium was established, an increase in the temperatures led to an increase in the Cu(II) ions, in the forms of complexes adsorption rate indicative of a kinetically controlled process while rich to the equilibrium higher temperatures slow down the adsorption process.

Temperature has been shown to have a similar effect on the adsorption of alum-morin onto silk (Septhum et al., 2009) as well as on the adsorption of reactive dye on cross-linked chitosan beads (Chiou and Li, 2002).

5.4.2 Adsorption of copper(II) ions on silk cocoons

5.4.2.1 Optimum condition

Effects of initial concentrations of mixture solution of Cu(II) ions and curcumin and contact time

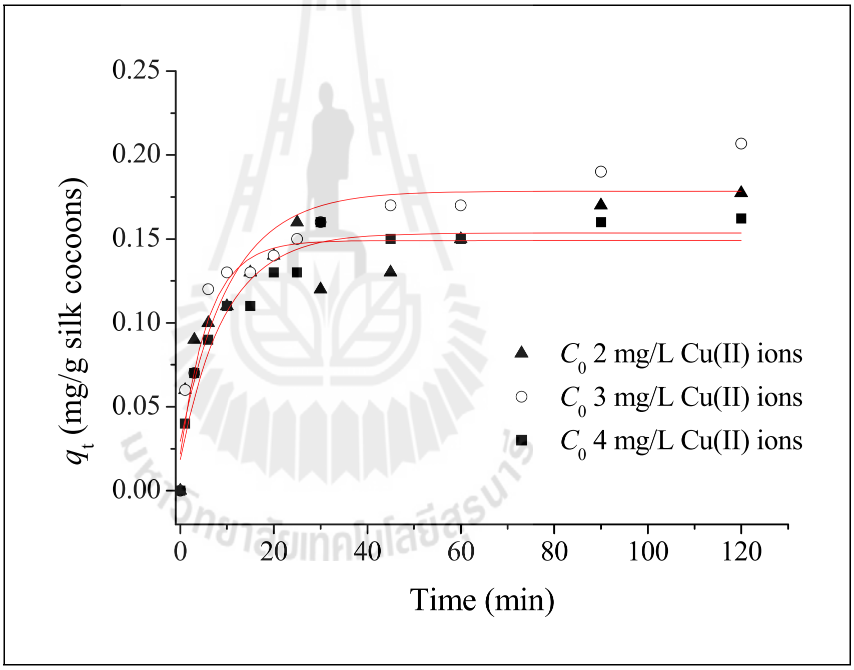

Figure 5.6 Effects of initial concentrations of Cu(II) ions and curcumin in the mixture solution and contact time on the adsorption onto silk cocoons at 30 °C with an MLR of 1:100 g/mL.

It can be observed that the quantity of copper adsorbed by cocoons is less then 8 times as that as adsorbed on residual silk fibers, therefore the process is not worth to be employed and the thermodynamic values will not be computed.

5.4.3 Kinetic study

Linear plots, under optimum condition, of pseudo-fist-order and pseudo-second-order equations about the adsorption of Cu(II) ions from the mixture of 25 mg/L Cu(II) ions and 1.0 mg/L curcumin onto silk residual fiber are shown in Figure 5.7-5.8.

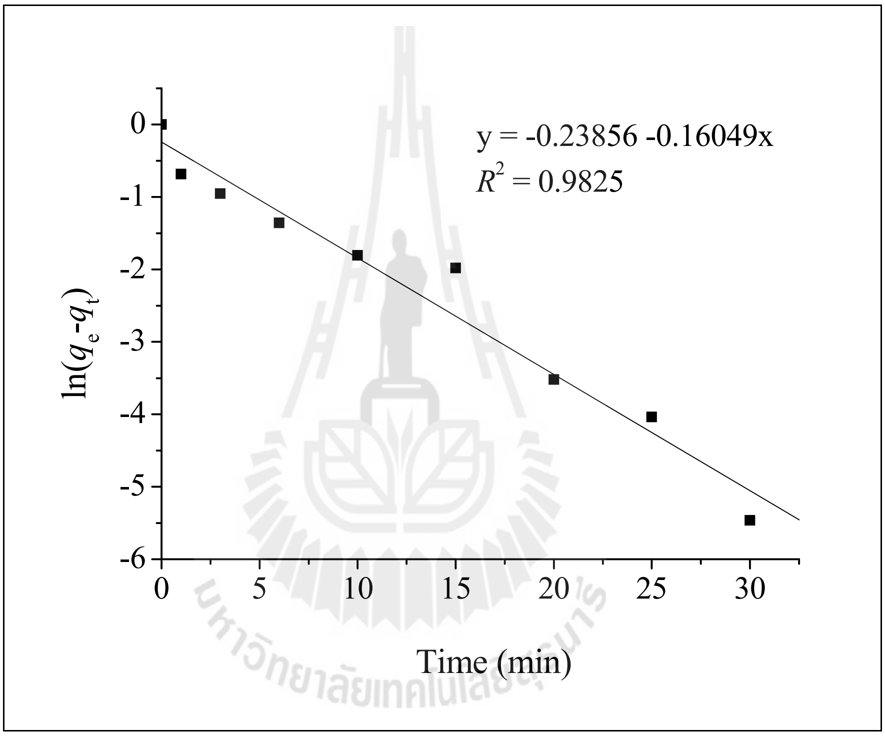

Figure 5.7 The pseudo-first-order equation about the adsorption of Cu(II) ions from the mixture with initial concentration of 25 mg/L Cu(II) ions and 1.0 mg/L curcumin onto residual silk fibers at pH 6.0 and MLR of 1:100 g/mL.

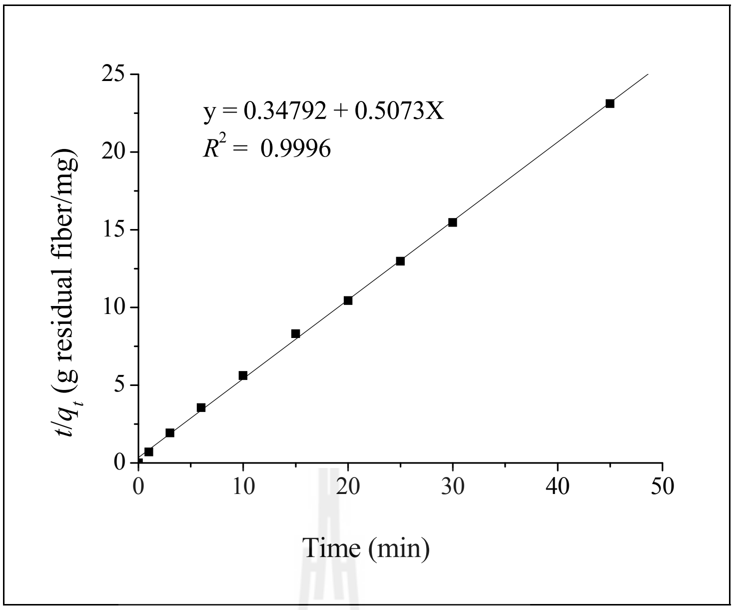

Figure 5.8 The pseudo-second-order equation about the adsorption of Cu(II) ions from the mixture with initial concentration of 25 mg/L Cu(II) ions and 1.0 mg/L curcumin onto residual silk fibers at pH 6.0 and MLR of 1:100 g/mL.

Regression coefficients of linear plots (R^2), kinetic parameters of pseudo-first-order equation (k_1) and pseudo-second-order equation (k_2 and h_i) about the adsorption process, under optimum condition, are tabulated in Table 5.1. It was found that the linear regression coefficients of the pseudo-second-order equation, was higher (> 0.99) than that of the pseudo-first-order equation.

Furthermore, the calculated equilibrium adsorption capacities ($q_{e,cal}$) derived from the pseudo-second-order model fit well to the experimental ones ($q_{e,exp}$). This suggests that the adsorption of Cu(II) ions from mixture solutions onto residual silk fibers is a pseudo-second-order process in which the overall adsorption is likely controlled by the chemical process involving valence forces through sharing or exchanging electrons between functional group of residual silk fibers as adsorbent and Cu(II) ions from mixture of Cu(II) ions and curcumin as adsorbate.

Table 5.1 Regression coefficients determined from the linear plots and kinetic parameters of pseudo-first-order and pseudo-second-order models about the adsorption under optimum condition.

Parameters	***Pseudo-first-order model:***	***Pseudo-second-order model:***
R^2	0.9825	0.9996
$q_{e,exp}$ (mg Cu^{2+}/g silk residual fiber)	1.9447	1.9447
k	-0.1605	0.7397
h_i	-	2.8742
$q_{e,cal}$ (mg Cu^{2+}/g silk residual fiber)	0.7878	1.9712

Kinetic parameters from linear plots of pseudo first-order (Figure 5.5) and pseudo second-order (Figure 5.6) models are tabulated in Table 5.1. The data show a good agreement with the pseudo second-order equation and the regression coefficients, R^2, for the linear plot is high (>0.99). The calculated equilibrium sorption capacity, $q_{e,cal}$, for the second-order process is more reasonable than that for the first-order process, in fact the latter when compared with experimental data is much lower.

The effects of the initial mixture concentration, MLR, and temperature on the adsorption rate constant, k_2, and the initial Cu(II) ions from mixture solutions adsorption rate, h_i, were also studied. Linear plots of pseudo-second-order equation concerning the adsorption of Cu(II) ions from mixture solutions onto residual silk fibers at different initial concentrations of Cu(II) ions, MLR's, and temperatures are shown in Figures 5.9, 5.10, and 5.11, respectively.

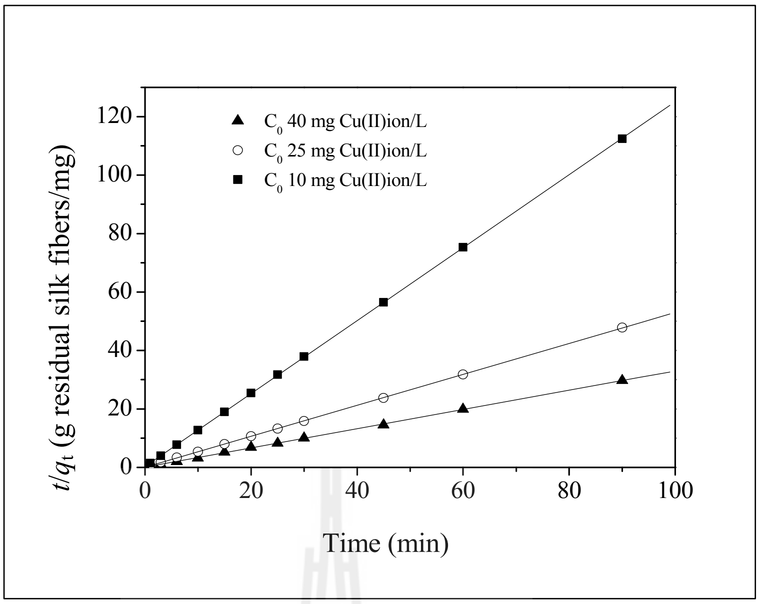

Figure 5.9 Plots of the pseudo-second-order equation about the adsorption of Cu(II) ions from mixture solution onto residual silk fibers at different initial concentrations with an MLR of 1:100 g/mL, at pH 6.0, and 30 °C.

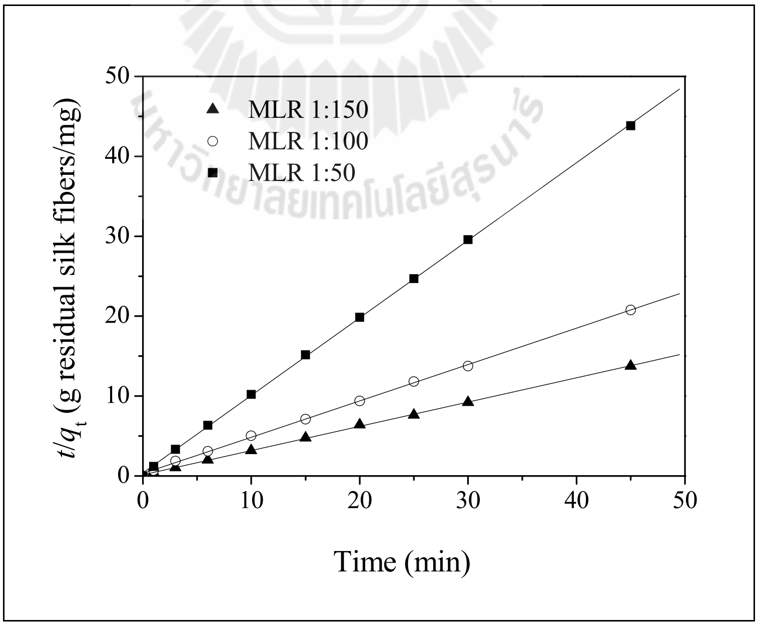

Figure 5.10 Plots of the pseudo-second-order equation about the adsorption of Cu(II) ions from mixture solution onto silk residual fiber at with different MLR's, initial concentrations of 25 mg/L, at pH 6.0, and 30 °C.

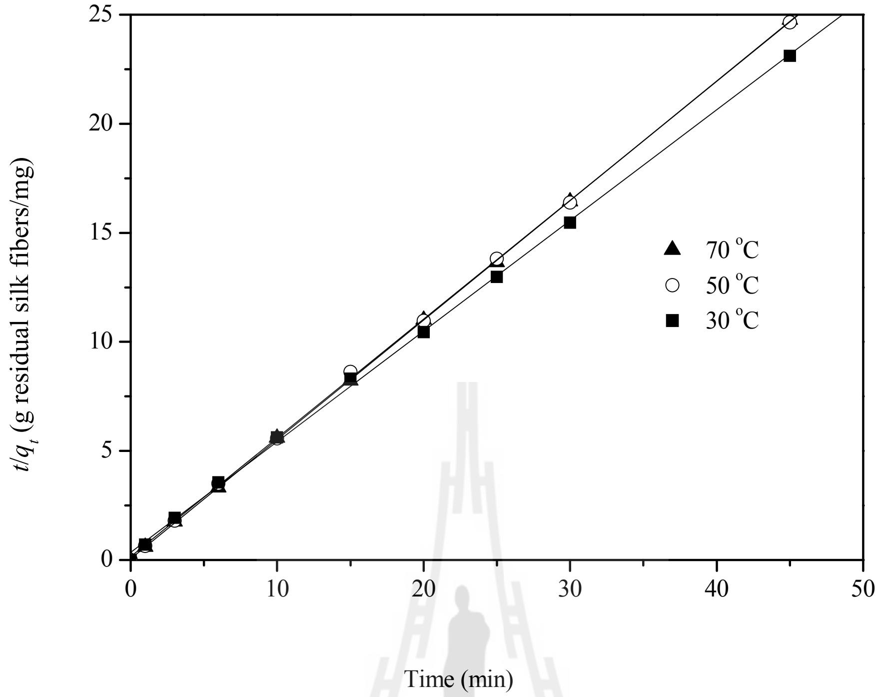

Figure 5.11 Plots of the pseudo-second-order equation about the adsorption of Cu(II) ions from mixture solution onto silk residual fiber at different temperatures, MLR of 1:100 g/mL, initial concentrations of 25 mg/L, and pH 6.0.

Regression coefficients of linear plots and kinetic parameters of pseudo-second-order equation (k_2 and h_i) concerning the adsorption of Cu(II) ions from mixture solution onto silk residual fiber under different conditions are tabulated in Table 5.2. It was found that the regression coefficients were all high (> 0.99) and the calculated equilibrium adsorption capacities were in good agreement with the experimental data. In addition, the k_2 and h_i values were found to be significantly affected by initial concentration, MLR, and temperature. The k_2 and h_i values on the adsorption of Cu(II) ions from mixture solution onto silk residual fiber both increased with increasing MLR, and increasing temperature.

Table 5.2 Pseudo-second-order adsorption rate constants, experimental $q_{e,exp}$, calculated $q_{e,cal}$, and regression coefficients of linear plots about the adsorption of Cu(II) ions from mixture solution onto silk residual fiber under various conditions.

Parameters	$q_{e,exp}$ **(mg/g silk)**	**Second-order kinetic model**			
		k_2	h_i	$q_{e,cal}$ **(mg/g silk)**	R^2
Initial dye concentration; *(mg/L)*: *MLR 1:100, pH 6.0, temp. 30 °C*					
10	0.7580	0.5716	3.6688	0.7710	0.9999
25	1.8988	0.6812	3.3220	2.2083	0.9999
40	2.9172	0.9618	8.8028	3.0253	0.9999
MLR: *initial dye concentration* (C_0) *25 mg/L, pH 6.0, temp. 30 °C*					
1:50	1.0253	2.4951	2.6475	1.0301	0.9999
1:100	2.1818	0.6873	3.3220	2.1986	0.9997
1:150	3.2988	0.6374	6.9166	3.2940	0.9998
Temperature (°C) : *initial dye concentration* (C_0) *25mg/L, MLR 1:100, pH 6.0*					
30	1.9437	0.7397	2.8742	1.9712	0.9996
50	1.8507	2.0007	6.7413	1.8356	0.9999
70	1.8273	6.6923	22.3015	1.8255	0.9999

5.4.4 Activation parameters about the adsorption of Cu(II) ions from mixture solution onto silk residual fiber

Activation energy of the Cu(II) ions from mixture solution, can be calculated using Equation 2.8 proposed by van’t Hoff and well known as the Arrhenius equation. This parameter describes the apparent activation energy defined as the energy value that allows the activated Cu(II) ions to overcome the fiber resistance as studied by Riva and co-worker (Riva, Algaba, and Prieto, 2002).

The linear plot between ln*k* and 1/*T*, shown in Figure 5.11, yields the activation energy of the diffusion that can be obtained from the slope. The calculated activation energy is presented in Table 5.2.

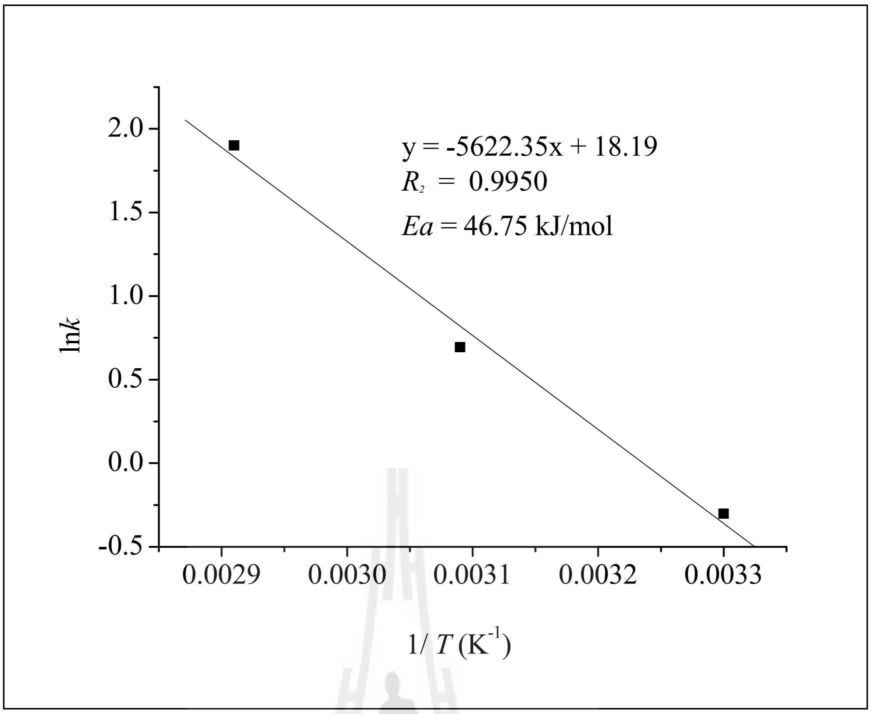

Figure 5.11 Relationship between ln*k* and 1/*T* about activation energy of Cu(II) ions from mixture solution onto silk residual fiber.

From the Eyring equation, enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation were calculated from the slope and the intercept of the plot of ln(*k/T*) versus 1/*T*, (Figure 5.12). The value of $\Delta G^{\#}$ was calculated at 303, 313, and 333 K by using equation (2.10), and these values are listed in Table 5.3. The negative entropy value ($\Delta S^{\#}$) in the neighborhood of the zero reflects more aggregation and higher interaction between Cu(II) ions from the mixture solution and silk residual fiber as adsorbent.

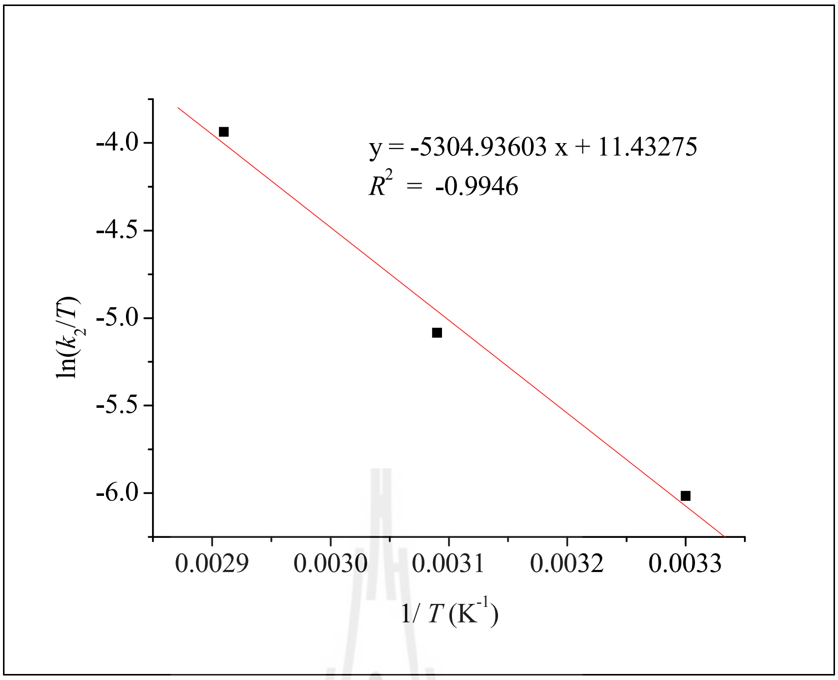

Figure 5.12 Plot for $\ln(k_2/T)$ versus $1/T$ for the adsorption of Cu(II) ions from mixture solution onto silk residual fiber.

Table 5.3 The activation parameters for the adsorption of Cu(II) ions from mixture solution onto silk residual fiber with the optimal condition.

Temp (°C)	**k_2 (g silk /mg second)**	**Ea (kJ/mol)**	**R^2**	**$\Delta H^{\#}$ (kJ/mol)**	**$\Delta S^{\#}$ (J/mol K)**	**$\Delta G^{\#}$ (kJ/mol K)**	**R^2**
30	0.74	46.75	0.9950	44.11	-102.50	75.18	0.9946
50	2.00					77.23	
70	6.69					79.28	

The observed activation energy (E_a) and enthalpy of activation ($\Delta H^{\#}$) for Cu(II) ions from mixture solution onto silk residual fiber, shown in Table 5.3, match evenly with those calculated from the theory of reaction ($E_a = \Delta H^{\#} + T\Delta S^{\#}$). As stated by Scheckel and Sparks in their article an E_a below 42 kJ mol−1 generally indicate diffusion-controlled processes and higher values represent chemical reaction processes (Scheckel and Sparks, 2001), so it might be concluded that the observed activation energy ($E_a > 42$ kJ/mol) indicates a chemically controlled process (Scheckel and Sparks, 2001).

The $\Delta G^{\#}$ value of 75.18, 77.23, and 79.28 kJ/mol were calculated at 303, 318, and 333 K, with initial concentration of 25 mg/L by using the equation (2.10); these values are listed in Table 5.3. The negative $\Delta S^{\#}$ reflects the expected structural interaction in the activated state between Cu(II) ions from mixture solution and silk residual fiber. A similar $\Delta S^{\#}$ value was obtained from the kinetics of adsorption for methyl violet onto perlite (Doğan and Alkan, 2003).

5.4.5 Thermodynamic parameters for the adsorption of Cu(II) ions from mixture solution onto silk residual fiber

As mentioned earlier, the Cu(II) ions from mixture solution adsorption onto silk residual fiber is an exothermic reaction process. In order to confirm this behaviour quantitatively, the thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the adsorption at the equilibrium, were calculated using the Equations (2.11), (2.12), and (2.13). The results are listed in Table 5.4. Negative values of $\Delta G°$ show that the adsorption of Cu(II) ions from mixture solution onto silk residual fiber is spontaneous. The negative value of $\Delta H°$ confirms that the adsorption process is an exothermic one. Furthermore, the entropy change ($\Delta S°$), equal to -0.07 J/mol K, in dyeing shows that the reaction becomes steadier within the silk residual fiber than in the dyeing solution.

Table 5.4 Thermodynamic parameters for the adsorption of Cu(II) ions from mixture solution at the optimal concentration.

Temperature (°C)	**ln K_c**	**$\Delta G°$ (kJ/mol)**	**$\Delta H°$ (kJ/mol)**	**$\Delta S°$ (J/mol K)**	**R^2**
30	3.82	-9.22	-3.72	-0.07	0.9229
50	2.55	-7.78			
70	2.41	-6.35			

5.4.6 Activation parameters about the adsorption of Cu(II) ions from mixture solution onto cocoon

The activation energy for the adsorption of Cu(II) ions from mixture solution can be calculated using Equation (2.10) in a similar manner to section 5.4.3. The activation energy of the adsorption can be obtained from the slope in the linear relationship between ln*k* and 1/*T*, shown in Figure 5.13. The calculated activation energy is presented in Table 5.4.

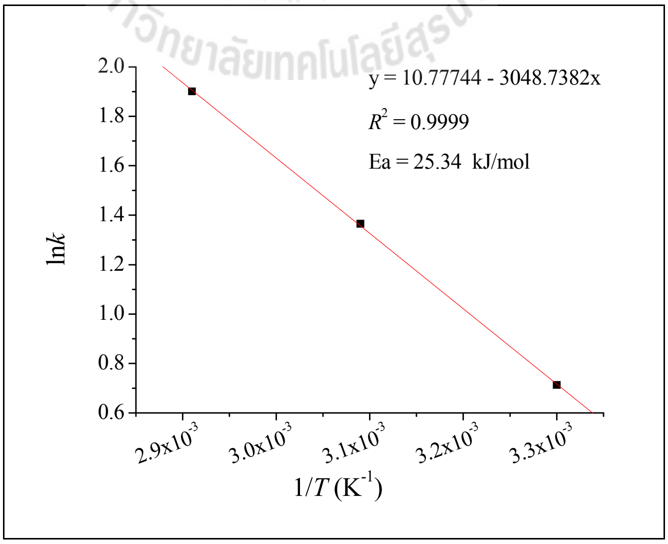

Figure 5.13 Plot for the relationship between ln*k* and 1/*T* about the activation energy of Cu(II) ions solution onto cocoon.

The enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation were calculated from the slope and intercept of a plot of ln(*k/T*) versus 1/*T* (Figure 5.13). The value of $\Delta G^{\#}$ was calculated at 303, 323, and 343 K by using equation (2.10), and used to compute the Eyring equation. All these values are listed in Table 5.5. The negative value of entropy ($\Delta S^{\#}$) reflects more aggregation between Cu(II) ions from mixture solutions and adsorbent such as silk residual.

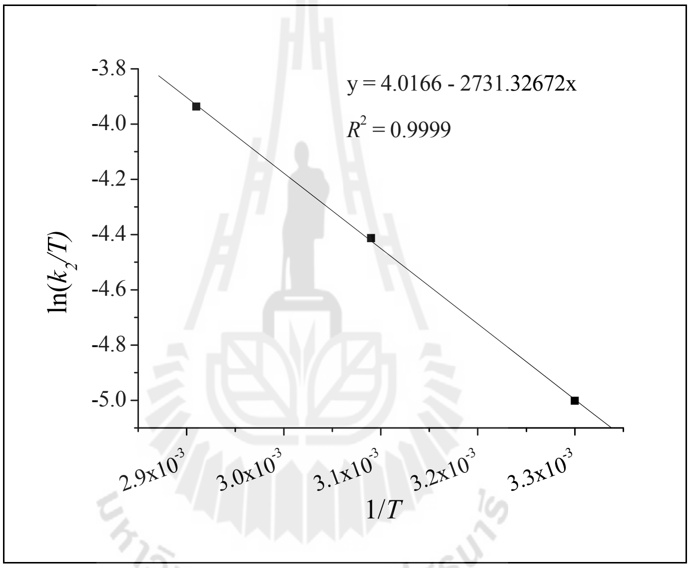

Figure 5.14 Plot of ln(*k*/*T*) versus 1/*T* about the adsorption of Cu(II) ions from mixture solution onto cocoon.

Table 5.5 Activation parameters concerning the adsorption of Cu(II) ions from mixture solution onto cocoon under the optimal condition.

Temp (°C)	**k_2 (g silk/mg second)**	***E*a (kJ/mol)**	**R^2**	**$\Delta H^{\#}$ (kJ/mol)**	**$\Delta S^{\#}$ (J/mol K)**	**$\Delta G^{\#}$ (kJ/mol K)**	**R^2**
30	2.04	25.35	0.9999	22.71	-164.23	72.48	0.9999
50	3.92					75.76	
70	6.69					79.04	

The value of $\Delta G^{\#}$ was calculated at 303, 323, and 343 K, with an initial concentration of 3 mg/L, by using equation (2.10). The negative $\Delta S^{\#}$ reflects the expected structural interaction in the activated state between the Cu(II) ions from mixture solution and the cocoon. The value of E_a is 25.34 kJ/mol (Table 5.5), it is lower than 42 kJ/mol as mention as many researchers studied on the removal some metal ions by adsorption onto surfaces. They found that E_a ranged from 0.0 to 27.7 kJ/mol, indicating diffusion-controlled biosorption (Scheckel and Sparks, 2001). However, the adsorption of Cu(II) ions from solution onto cocoon shows a similar trend to that of Cu(II) ions from mixture solution onto silk residual fiber. It may be that the cocoon contains more polar sericin components, gum protein that cover the fiber, which can react with Cu(II) ions from the mixture solution and after the equilibrium the sericin-Cu(II) components can be dissolve to a higher degree into water. It can be observed that the quantity of copper absorbed by cocoon is as less as 8 times that absorbed on silk residual fiber, therefore, the process is not worth to employed and the thermodynamic will not be considered

5.4.7 Comparison of activation parameters between the adsorption of Cu(II) ions from mixture solution onto silk residual fiber and cocoon

The activation parameters of the adsorption of Cu(II) ions from mixture solutions onto silk residual fiber and cocoon are shown in Table 5.6. It was found that the activation energy for silk residual fiber was higher than that for cocoon, indicating that the former may contain less polar sirecines. The reaction between the cocoon and Cu(II) ions from the mixture is easier than that between the silk residual fiber and Cu(II) ions from the mixture solution. However, since the Cu(II) ions from the mixture solution bond with the water-soluble sericine present in the cocoon, they form a component that is polar, hence easily dissolved and the dyeing is less effective. The entropy values in activation state obtained during these investigations over residual silk fibers and cocoons are negative, suggesting for both an increase in the order of the system.

The value of the activation energy for Cu(II) ions from mixture solution adsorbed onto silk residual fiber is 46.75 kJ/mol and it is thus concluded that the kinetic of adsorption involves a chemical reaction. The activation energy for cocoons was lower but positive and this could be explain as a reaction with other components that cause the binding with the free Cu(II) ions in the mixture onto sericine dissociated into water.

Table 5.6 Activation parameters for the adsorption of Cu(II) ions from mixture solution onto silk residual fiber and cocoon.

Adsorbents	**Temp (°C)**	**k_2 (g silk/mg second)**	**E_a (kJ/mol)**	**R^2**	**$\Delta H^\#$ (kJ/mol)**	**$\Delta S^\#$ (J/mol K)**	**$\Delta G^\#$ (kJ/mol)**	**R^2**
Silk residual	30	0.73	46.75	0.9950	44.11	-102.50	75.18	0.9946
	50	2.00					77.23	
	70	6.69					79.28	
Cocoon	30	2.04	25.34	0.9999	22.71	-164.23	72.50	0.9999
	50	3.92					75.70	
	70	6.68					79.03	

5.5 Conclusion

The kinetics of adsorption of Cu(II) ions from mixture solutions onto silk residual fiber was investigated and the following results obtained:

1. The pH studies indicate that acidity affect the adsorption capacity of Cu(II) ions from the mixture solution onto silk residual fiber.
2. Before equilibrium an increase in temperature led to an increase in the adsorption rate, which indicates an exothermic and kinetically controlled process.
3. A pseudo second-order kinetic model fits accordingly with the absorption onto silk residual fiber and cocoon, and supports the hypothesis of a chemical adsorption reaction.
4. The negative values of the Gibb's free energy ($\Delta G°$), the low negative values of the entropy ($\Delta S°$) and negative values for the enthalpy ($\Delta H°$) suggest that the adsorption is a spontaneous and exothermic process.

5.6 References

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APPENDIX

APPENDIX

Calibration of curcumin dye solution

In order to determine the calibration curve of curcumin dye solution, the various concentrations of curcumin dye solution were prepared in aqueous solution. The absorbances of dye solution were measured using UV-VIS spectrophotometer at 427 nm. Then the relationship between curcumin concentration and its absorbance are plotted as shown in Figure A.1.

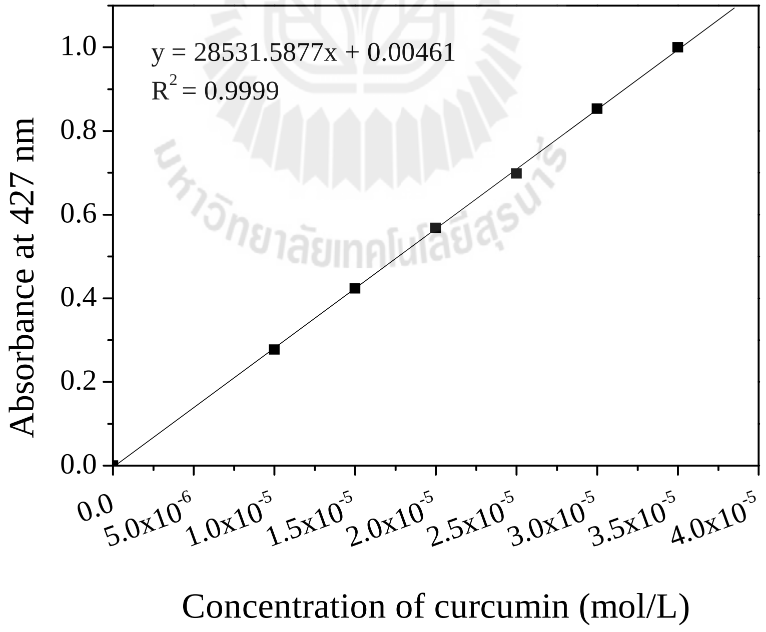

Figure A.1 Calibration curve extracted dye solution.

Calculation of dye concentration from calibration curve

Equation of calibration curve: $y = 28531.5877x + 0.00461$

When y = absorbance and x = extracted dye concentration (mol/L)

$$\text{Diluted dye concentration} = \frac{\mathit{Absorbance} - 0.00461}{28531.5877}$$

Calibration of extracted dye solution

In order to determine the calibration curve of extracted dye solution, the various concentrations of extracted dye solution were prepared in aqueous solution. The absorbances of dye solution were measured using UV-VIS spectrophotometer at 425 nm. Then the relationship between curcumin concentration and its absorbance are plotted as shown in Figure A.2.

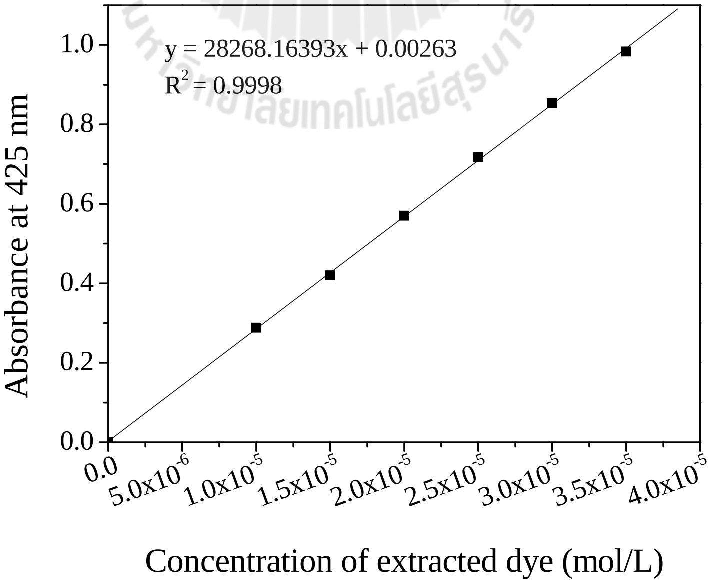

Figure A.2 Calibration curve extracted dye solution.

Calculation of dye concentration from calibration curve

Equation of calibration curve: $y = 28268.16393x + 0.00263$

When y = absorbance and x = extracted dye concentration (mol/L)

$$\text{Diluted dye concentration} = \frac{Absorbance - 0.00263}{28268.16393}$$

Calibration of Cu(II)-curcumin complex dye solution

In order to determine the calibration curve of Cu(II)-curcumin complex dye solution, the various concentrations of Cu(II)-curcumin complex dye solution were prepared in aqueous solution. The absorbances of dye solution were measured using UV-VIS spectrophotometer at 360 nm. Then the relationship between Cu(II)-curcumin complex dye concentration and its absorbance are plotted as shown in Figure A.3.

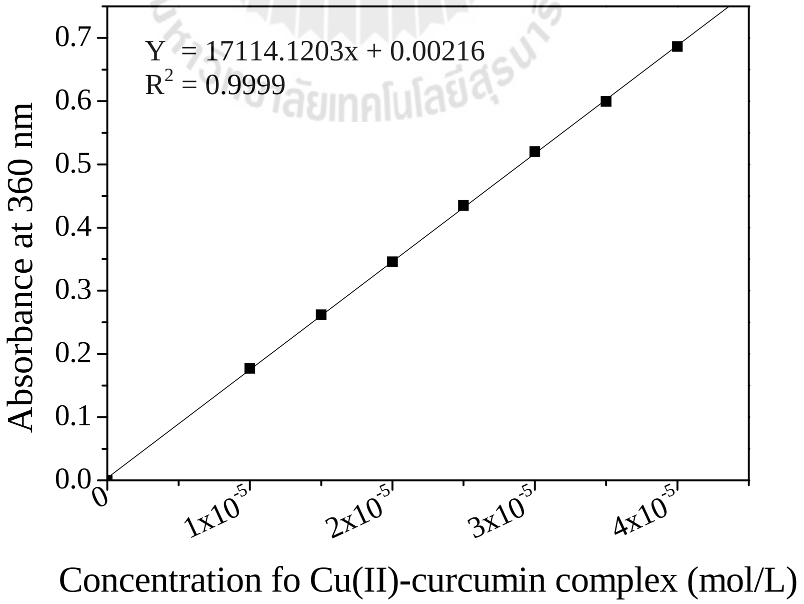

Figure A.3 Calibration curve of Cu(II)-curcumin complex dye solution.

Calculation of dye concentration from calibration curve

Equation of calibration curve: $y = 17115.1203x + 0.00216$

When y = absorbance and x = Cu(II)-curcumin complex dye concentration (mol/L)

$$\text{Diluted dye concentration} = \frac{\mathit{Absorbance} - 0.00216}{17115.1203}$$

Calibration of Cu(II)-extracted dye complex solution

In order to determine the calibration curve of Cu(II)-extracted dye complex solution, the various concentrations of Cu(II)-extracted dye complex dye solution were prepared in aqueous solution. The absorbances of dye solution were measured using UV-VIS spectrophotometer at 410 nm. Then the relationship between Cu(II)- extracted dye complex concentration and its absorbance are plotted as shown in Figure A.4.

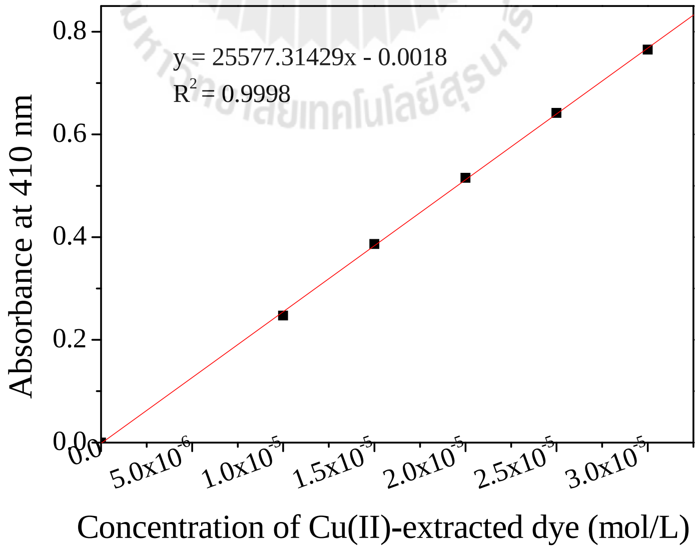

Figure A.4 Calibration curve of Cu(II)-extracted dye complex solution.

Calculation of dye concentration from calibration curve

Equation of calibration curve: $y = 25577.31429x - 0.0018$

When y = absorbance and x = Cu(II)-extracted dye complex concentration (mol/L)

$$\text{Diluted dye concentration } = \frac{Absorbance + 0.0018}{25577.31429}$$

Calibration of Cu(II)-curcumin dye solution

In order to determine the calibration curve of Cu(II)-curcumin dye solution, the various concentrations of Cu(II)-curcumin dye solution were prepared in aqueous solution. The absorbances of dye solution were measured using Atomic Absorption spectrophotometer at 324.8 nm. Then the relationship between Cu(II)-curcumin dye concentration and its absorbance are plotted as shown in Figure A.5.

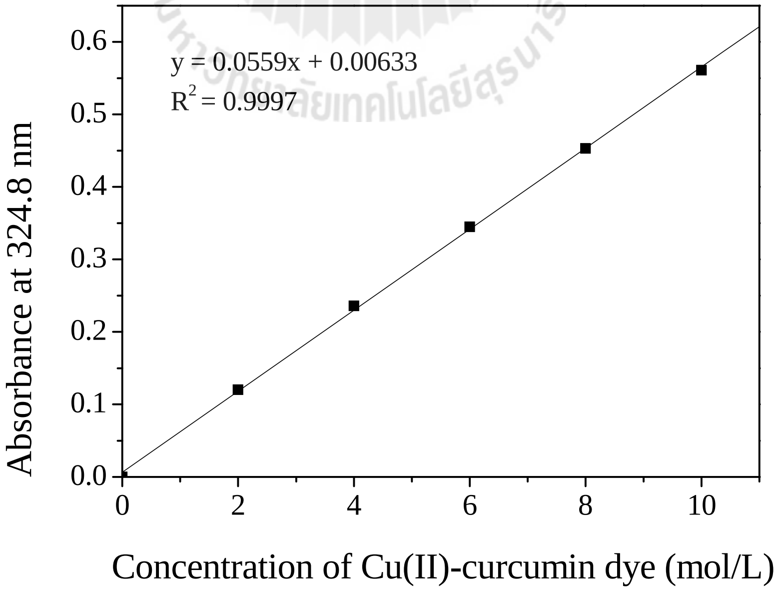

Figure A.5 Calibration curve of Cu(II)-extracted dye complex solution.

Calculation of dye concentration from calibration curve

Equation of calibration curve: $y = 0.0559x - 0.00633$

When y = absorbance and x = Cu(II)-extracted dye complex concentration (mol/L)

$$\text{Diluted dye concentration} = \frac{Absorbance + 0.00633}{0.0559}$$

Optimum conditions of Cu(II)-curcumin dye removing with cocoon

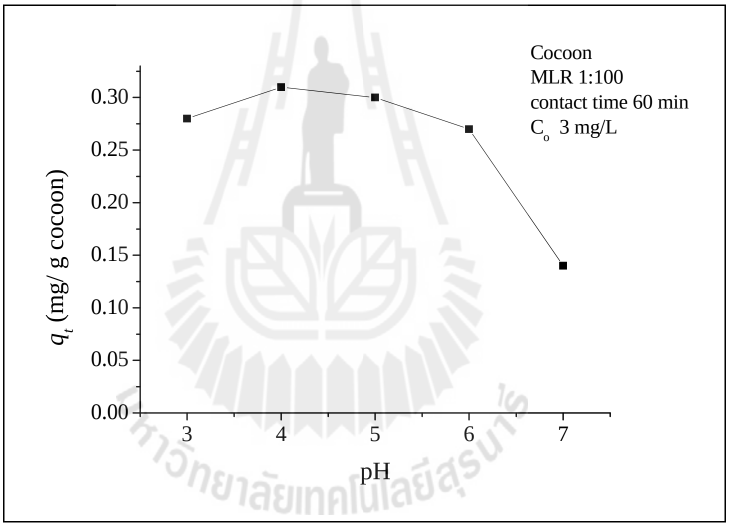

Figure A.6 Comparison the relationship between removal Cu (II) ions at different initial solution pH with sorption capacities cocoon.

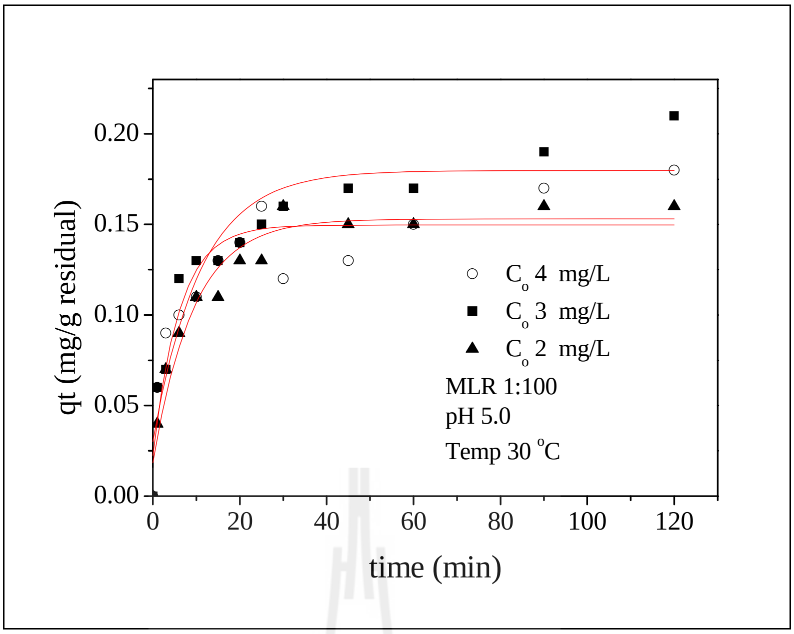

Figure A.7 Adsorption kinetics for Cu(II)-curcumin dye solution onto silk residual fibre at different initial Cu(II)-curcumin dye concentrations (*W*, 0.25 g; *V*, 25 mL; temperature 30 °C; pH 5.0).

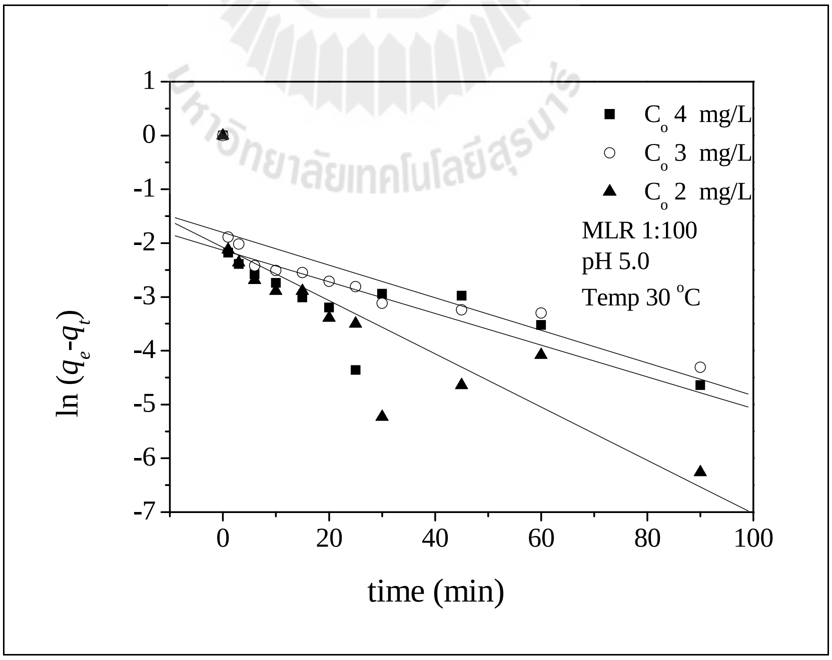

Figure A.8 The pseudo first-order equation at different initial Cu(II)-curcumin dye concentration and the adsorption of Cu(II)-curcumin dye onto cocoon.

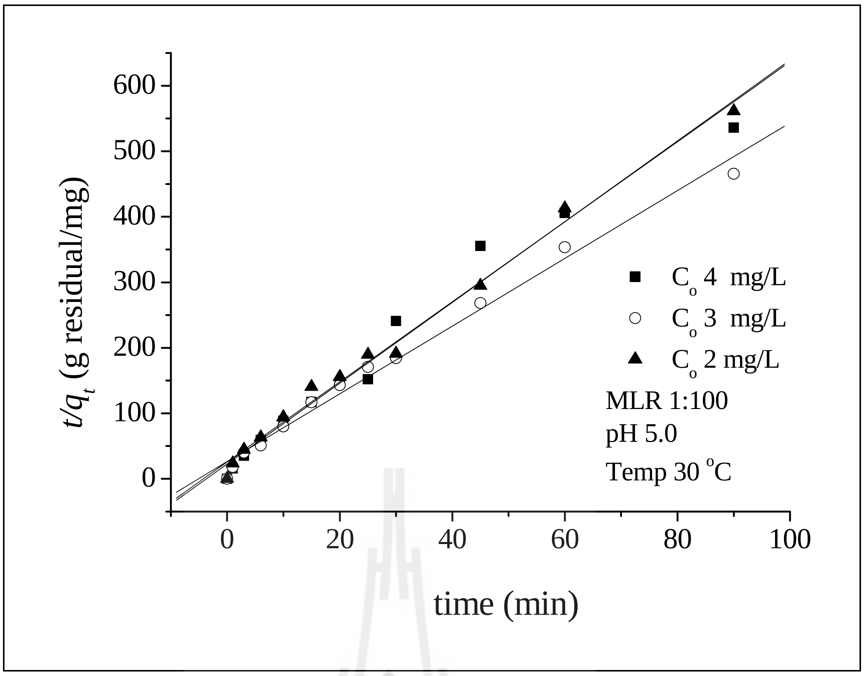

Figure A.9 The pseudo second-order equation at different initial Cu(II)-curcumin dye concentration and the adsorption of Cu(II)-curcumin dye onto cocoon.

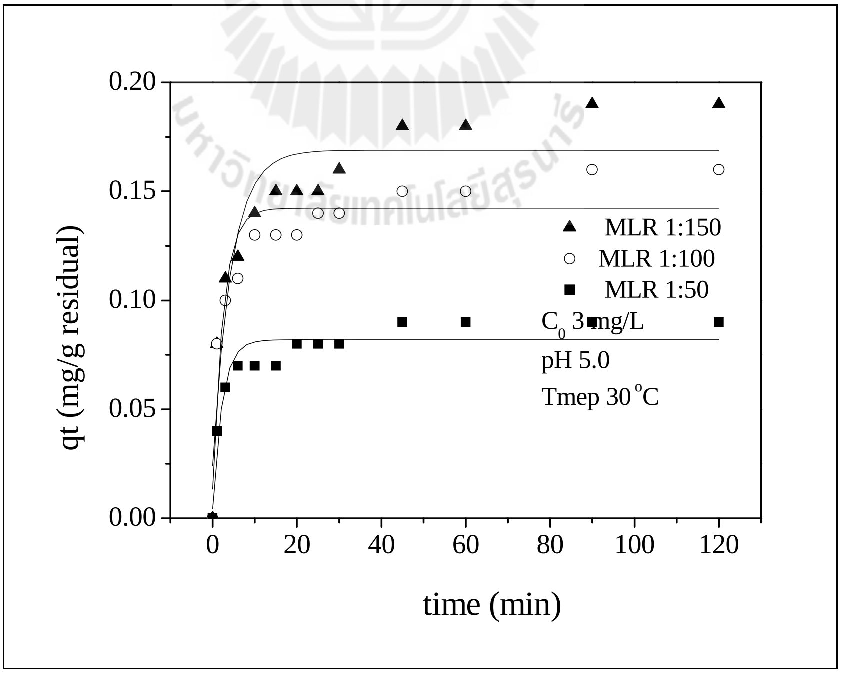

Figure A.10 The effect of material to liquor ratio on the adsorption of Cu(II) dye onto cocoon.

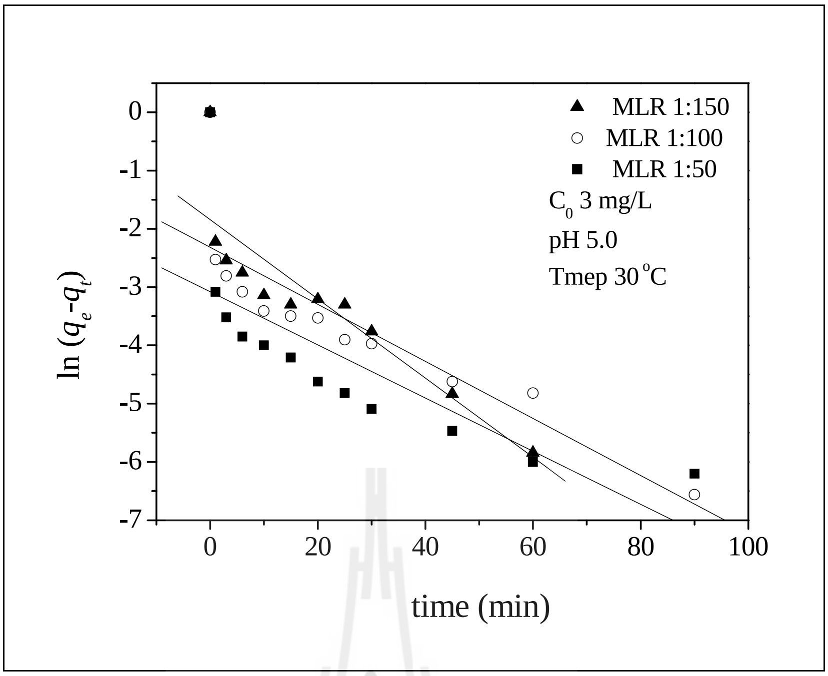

Figure A.11 Application of the pseudo first-order equation at different material to liquor ratios on the adsorption of Cu(II)-curcumin dye onto cocoon.

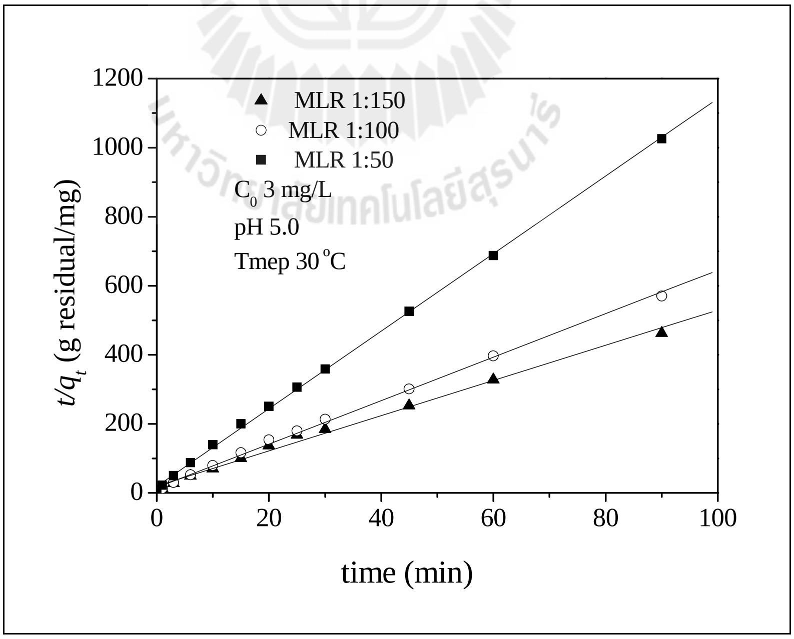

Figure A.12 Application of the pseudo second-order equation at different material to liquor ratios on the adsorption of Cu(II)-curcumin dye onto cocoon.

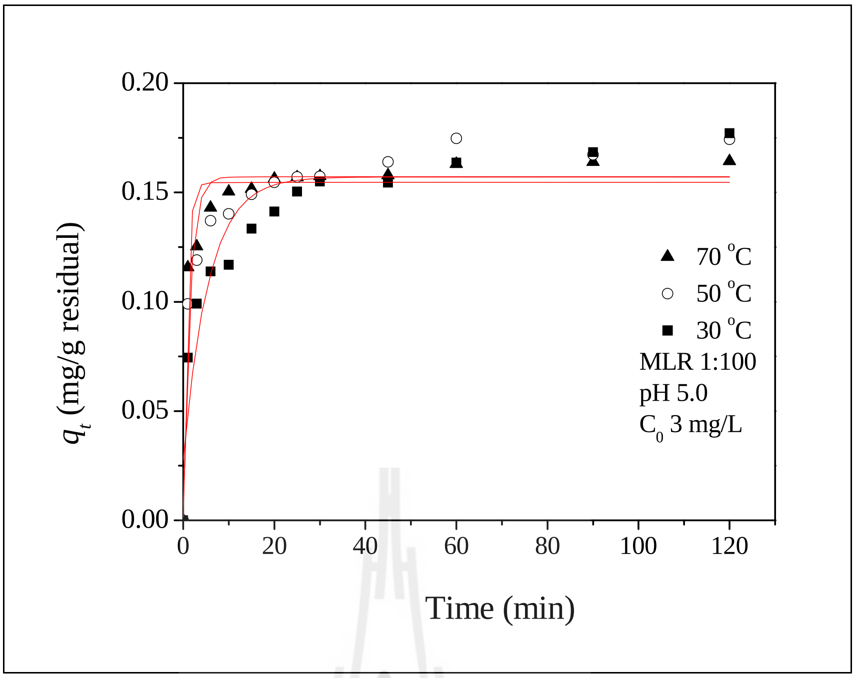

Figure A.13 The effect of temperature on the adsorption of Cu(II) dye onto cocoon.

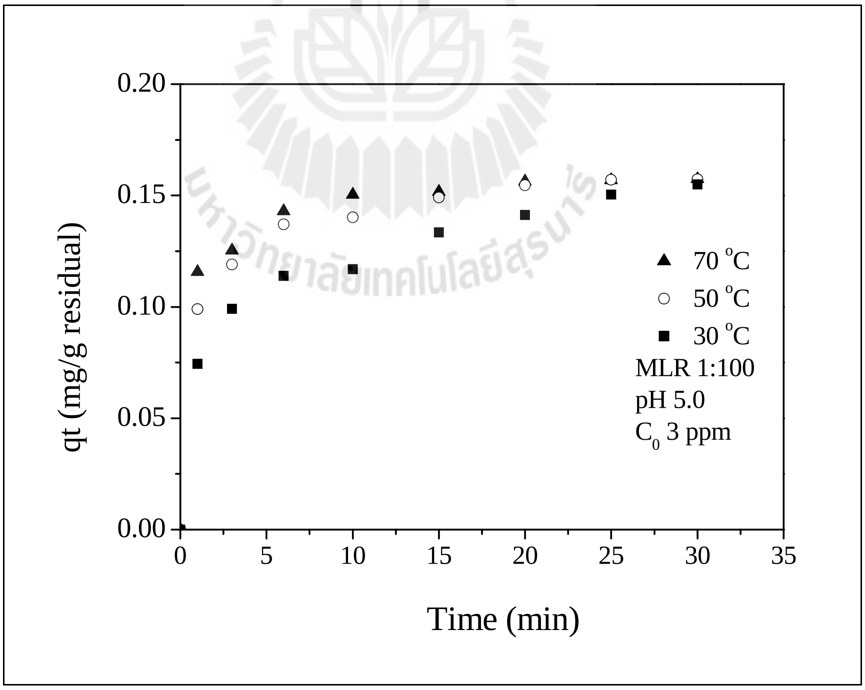

Figure A.14 The effect of temperature on the adsorption of Cu(II) dye onto cocoon.

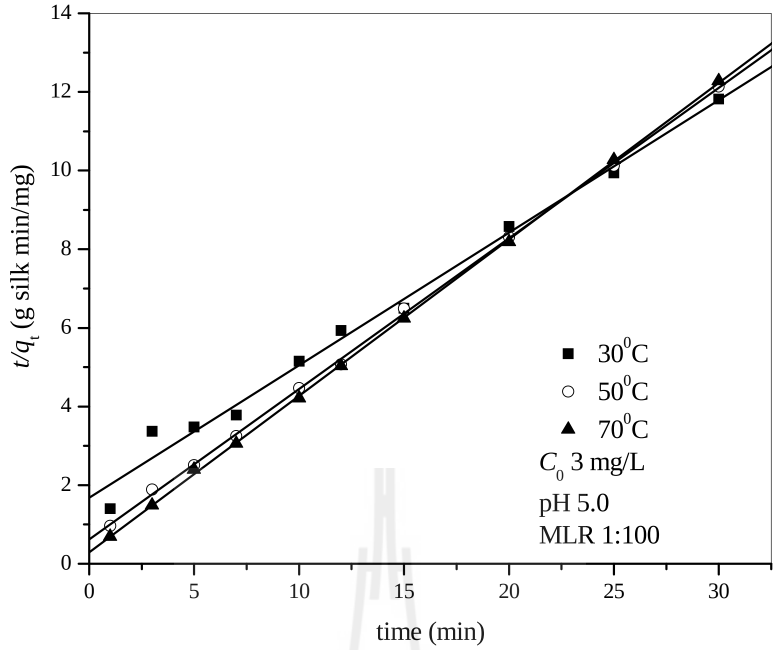

Figure A.15 The pseudo first-order equation at different temperatures on adsorption of Cu(II) dye onto cocoon.

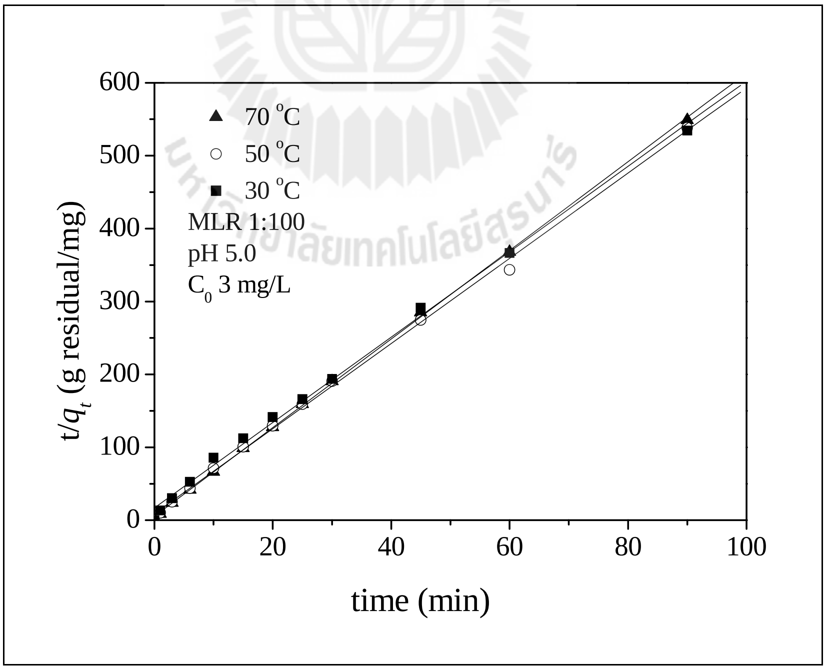

Figure A.16 The pseudo second-order equation at different temperatures on adsorption of Cu(II) dye onto cocoon.

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