

# UTILIZATION OF SILK SERICIN AS COAGULANT AID AND

COAGULANT FOR TURBIDITY REMOVAL

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AN INDEPENDENT STUDY SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING MAJOR IN ENVIRONMENTAL ENGINEERING

# FACULTY OF ENGINEERING

**UBON RATCHATHANI UNIVERSITY** 

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# INDEPENDENT STUDY APPROVAL UBON RATCHATHANI UNIVERSITY

## MASTER OF ENGINEERING

# MAJOR IN ENVIRONMENTAL ENGINEERING FACULTY OF ENGINEERING

TITLE UTILIZATION OF SILK SERICIN AS COAGULANT AID AND COAGULANT FOR TURBIDITY REMOVAL

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Sma

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Sy	ymbol	Explain
	NTU	Nephelometric Turbidity Units
	°C	Celsius
	SF	Silk Fibroin
	%	Percentage
	mg/L	Milligram/Liter
	g	Gram
	mg	Milligram
	μm	Micrometer
	nm	Nanometer
	L	Liter
	min	Minute
	rpm	Revolutions per minute

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# บทคัดย่อ

ชื่อเรื่อง	<ol> <li>การใช้เซริซินจากไหมเป็นตัวช่วยโคแอกกูแลนด์และ โคแอกกูแลนด์</li> </ol>
	: ในการกำจัดความขุ่น
โดย	: สิทธิ์ชัย มากวิไล
ชื่อปริญญา	: วิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชา	: วิศวกรรมสิ่งแวคล้อม
ประชานกรรม	การที่ปรึกษา : ผู้ช่วยศาสตราจารย์ คร.วิภาคา สนองราษฎร์

ศัพท์สำคัญ : ความขุ่น เซริซิน โคแอกกูแลนท์

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการใช้เซริซินจากไหมเป็นโคแอกกูแลนท์และตัวช่วย ้โกแอกกูแลนท์ เพื่อกำจัดความขุ่นในน้ำขุ่นสังเคราะห์และน้ำผิวดิน โปรตีนเซริซินที่ใช้เป็นสารโก แอกกูแลนท์และตัวช่วยโคแอกกูแลนท์สกัดจากรังไหมโดยการด้มรังไหมด้วยสารละลายโซเดียม การ์บอเนต (0.50 wt % Na2CO3) ที่อุณหภูมิ 90 องศาเซลเซียส นาน 60 นาที การศึกษาประกอบด้วย 5 ชุคการทคลอง โดย 3 ชุคการทคลองแรกใช้น้ำขุ่นสังเคราะห์ที่มีความขุ่นเริ่มต้น 50 75 และ 100 NTU และชุดการทดลองที่ 4 ใช้น้ำผิวดินที่เก็บจากหนองอีเจมส์ มหาวิทยาลัยอุบลราชธานี สำหรับทั้ง 4 ชุดการทดลองนี้โปรตีนเซริซินถูกใช้เป็นสารตัวช่วยโดแอกกูแลนท์ ชุดการทดลอง ้สุดท้ายเป็นตัวอย่างน้ำงุ่นสังเคราะห์ที่ใช้โปรตีนเซริซินเป็นสารโคแอกกูแลนท์ ผลจากการทคลอง พบว่าสำหรับตัวอย่างน้ำขุ่นสังเคราะห์ที่มีความขุ่น 50 75 และ 100 NTU ประสิทธิภาพการกำจัด กวามขุ่นสูงสุด (93 ±1.41% 94 ±1.41% และ 93 ±0.70% ตามลำดับ)ได้จากการใช้สารส้มในปริมาณ 80 มิลลิกรับต่อลิตร โดยไม่มีการเติมโปรตินเซริซิน อย่างไรก็ตาม การเติมโปรตีนเซริซินลงไปใน ้ตัวอย่างน้ำที่ใช้สารส้มในปริมาณ 60 มิลลิกรัมต่อลิตร จะให้ค่าประสิทธิภาพการกำจัดความขุ่น สูงสุดที่ 95±0% 94±0.70% และ 93±2.12% ตามลำคับ สำหรับตัวอย่างน้ำผิวคิน ค่าประสิทธิภาพการ กำจัคสุดสุดที่ได้อยู่ที่ประมาณ 97±0% โดยการใช้สารส้มร่วมกับโปรตีนเซริซินและสารส้มอย่าง เคียว ผลงากการทคลองชุดสุดท้ายแสดงให้เห็นว่าโปรตีนเซริซินไม่สามารถนำมาใช้เป็นสาร โคแอก กูแลนท์ได้ จากการศึกษาแสดงให้เห็นว่าการเติมโปรตีนเซริซิน ซึ่งเป็นวัสดุธรรมชาติที่มีราคาถูก และหาได้ง่าย ไม่เพียงแต่ช่วยเพิ่มประสิทธิภาพการจำกัดความขุ่นของน้ำขุ่นสังเคราะห์ได้เล็กน้อย แต่ยังช่วยลคปริมาณการใช้สารส้มได้อีกด้วย นอกจากนึ่งานวิจัยนี้ยังได้ศึกษาจลนพลศาสตร์ของการ กำจัดกวามขุ่นของทุกชุดการทดลองด้วย

### ABSTRACT

TITLE

: UTILIZATION OF SILK SERICIN AS COAGULANT AID AND COAGULANT FOR TURBIDITY REMOVAL

BY	: SIDXAY MAKVILAY
DEGREE	: MASTER OF ENGINEERING
MAJOR	: ENVIRONMENTAL ENGINEERING

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## KEYWORDS : TURBIDITY / SILK SERICIN / COAGULANT AID

The main objective of this research was to investigate the use of silk sericin as a coagulant and coagulant aid in the removal of turbidity from synthetic turbid water and surface water. Silk sericin used as a coagulant and coagulant aid in this study was extracted from silk cocoons by boiling them with 0.5% (w/w) Na<sub>2</sub>CO<sub>3</sub> solution at 90°C for 60 minutes. The study included five sets of experiment, the first three set were synthetic turbid waters with initial turbidity of about 50, 75, and 100 NTU, and the fourth set was the surface water collected from Nong E James at Ubon Ratchathani University. For these four sets, silk sericin was used as coagulant aid. The last set was the synthetic turbid water using silk sericin as a coagulant. Results showed that for the samples of synthetic turbid water of 50, 75, and 100 NTU, the highest turbidity removal efficiencies of 93 ±1.41%, 94 ±1.41% and 93 ±0.70%, respectively were received at alum dosage of 80 mg/L without addition of silk sericin. However, the addition of silk sericin to an alum dosage of 60 mg/L resulted in the highest turbidity removal efficiencies of 95±0%, 94±0.70%, and 93±2.12%, respectively. For the surface water, the highest turbidity removal efficiency of about 97±0% was achieved by using alum with and without silk sericin. Results from the last set of experiment showed that silk sericin could not be applied as a coagulant. The study showed that the addition of silk sericin; an economic, easily accessible, and natural product, not only slightly improved the effectiveness of the turbidity removal efficiency of synthetic turbid water but also reduced the utilization of alum dosage. The kinetics of turbidity removal for all sets of experiment were also included in this study.

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# **CHAPTER I**

# INTRODUCTION

### 1.1 Statement of problem

A main feature of a water supply system is the provision of healthy water of a high quality for daily consumption. The improvement of water quality begins with the use of coagulants to destabilize colloids, followed by flocculation, and then the removal of turbidity by sedimentation.

Increased coagulation is necessary in the treatment of a water supply. This can be done by the use of chemical coagulants, such as inorganic coagulants and organic polymers. Inorganic coagulants include conventional metal salts [for example aluminum sulfate  $Al(SO_4)_3$ , ferric chloride (FeCl<sub>3</sub>), and lime (CaCO<sub>3</sub>)], and polymerized metal salts [such as polyaluminum chloride (p-AlCl<sub>3</sub>) and polyaluminum silicate sulfate (p-AlSiS)]. However, high doses of chemical coagulants present drawbacks. The benefits and proven efficacy of aluminum sulfate, the most widely-used coagulant in the treatment of water supply, is offset by the problem of residual metal contamination and by poor performance at low temperatures. High doses of metal salts generate large quantities of sludge and depress pH, leading to the need for additional amounts of pH adjustment chemicals. Use of synthetic organic polymer coagulants such as polyacrylamides and polyamines are also problematic as they may be toxic under certain circumstances (Sciban et al., 2009).

These problems have led to a ban on the use of many synthetic polymers. This study represents an attempt to find a more acceptable approach to overcoming the problems highlighted above by the use of silk sericin extracted from cocoons of the *Bombyx mori* silkworm by sodium carbonate ( $Na_2CO_3$ ) solution. In the silk cocoons include fibroin and sericin, all of them are having protein about 75% and 30%, respectively. The structure of protein use for synthetic polymers, so in this research is utilization of sericin extracted from cocoons for coagulant aid and coagulant.

## **1.2 Objectives**

This study aimed to investigate the use of silk sericin extracted from the silk cocoon as a cheaper and natural alternative to the use of synthetic polymer in the removal of turbidity in synthetic turbid water and natural water in 2 ways:

1.2.1 As a coagulant aid for the removal of turbidity

1.2.2 As a coagulant for the removal of turbidity

## 1.3 Scope of study

1.3.1 Turbid synthetic water used in this study was varied from 50, 75, and 100 NTU.

1.3.2 Natural surface water was collected from Nong E Jame, Ubon Ratchathani University.

1.3.3 Silk sericin was extracted from silk cocoons using sodium carbonate  $(Na_2CO_3)$  solution and distilled water.

1.3.4 Alum dosage was varied from 0, 20, 40, 60, 80, 100 mg/l.

1.3.5 Silk sericin dosage was fixed at 0.01ml in experimental steps 2 and 4. Whereas, it was varied from 0, 0.1, 0.2, 0.3, 0.4, and 0.5 ml in experimental step 3 (experimental step was described in chapter 3).

1.3.6 Initial pH was fixed at 7 by the use of sodium bicarbonate ( $Na_2HCO_3$ ) 5% solution.

## **1.4 Hypothesis**

1.4.1 Silk sericin extracted from silk cocoons acts as a coagulant aid in the removal of turbidity.

1.4.2 Silk sericin extracted from silk cocoons acts as a coagulant in the removal of turbidity.

# **1.5 Process operations**

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This research spend time about 12 month, I would like to show detail in the Table 1-1

1

Time	Operational plans	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.
1	Literature review										
2	Utilization of silk										
	sericin as										
	coagulant aid for										
	turbidity removal										
3	Utilization of silk							1			
	sericin as										
	coagulant for					-		ente a contra			
	turbidity removal										
								in the second se			
4	Conclusion,										
	writing and										
1	presentation										

# Table 1-1 Timetables

#### **CHAPTER II**

## **BACKGROUND AND LITERATURE REVIEWS**

#### 2.1 Coagulation and flocculation

The many unit processes and operations used in water treatment, coagulation and flocculation require an antique combination of chemical and physical phenomena for producing water acceptable for human consumption. These are essential pretreatment processes for the removal of finely divided particulate matter which, colloidal turbidity particles are too small (1-100 nm) to settle by gravity. They stay suspended and cause turbidity. Mostly, they are negatively charged. Their removal is accomplished by using substances that make them clump together to from large and heavy particles known as *floc* that will settle. These substances are known as coagulants. A coagulant is an electrolyte that provides cations (positively charged ions) to precipitate out the negatively charge on the cation, the more effective is the coagulant. Therefore, commonly used coagulants are aluminum and ferric compounds that provide Al<sup>+3</sup> and Fe<sup>+3</sup> cations, respectively. Some other substances are often used to facilitate the coagulants; those are known as coagulant aids. This treatment phase is the second barrier to remove turbidity, waterborne pathogens, and other contaminants. It consists of three parts: rapid mixing, coagulation, and flocculation. (Singh, 2006)

Stability of particulates, the principle characteristic of find particulate matter suspended in water is its relative stability, causing it to remain in suspension are thermodynamically unstable, and given sufficient time colloids and fine particles will settle. However this process is not economically feasible. Coagulation-flocculation facilities must eliminate particulate stability and thereby increase the rate of subsequent particulate removal by solid-liquid separation process. A review of the causes of particulate stability will provide an understanding of the techniques that can be used to destabilize particulates. (Montgomery, 1985)

Particulate characteristics, in water are broadly categorized into two major size groups: colloidal material, with an upper limit approximately 1 µm and a lower limit of approximately

5 nm, and suspended solids, consisting of particulates larger then approximately 0.5  $\mu$ m. Particles smaller then size spectrum covers roughly 6-7 orders of magnitude and encompasses a heterogeneous mixture of particulates with a wide range of physical, chemical, and biological properties.

In contrast, hydrophilic particulates are primarily of organic origin and include a wide diversity of biocolloids (humic and fulvic acids, viruses) and suspended living or dead microorganisms (bacteria, algae). Because biocolloids may absorb on the surface of inorganic particulates, particulates in natural water systems.

### 2.1.1 Origin of the Double Layer

Further insights into mechanism of stability can be obtained from a closer evaluation of particulate surface chemistry. When particulates are dispersed in water, ions of opposite change to the surface charges accumulate close to the particulate surface to satisfy electro neutrality. These two opposite forces, electrostatic attraction and diffusion, produce a diffuse cloud of ions surrounding the particulate which can extend up to 300 nm into the solution. This is known as the electrical double layer (Kruyt, 1952).



Figure 2-1 Schematic of electrical double layer at solid-liquid interfaces (Kawamura, 2000).

The structure of the double layer is show schematically in Figure 2-1. Bezause of the excess of cations in this case near the surface, an electrical potential difference arises, which decreases exponentially with distance from the surface a maximum value at the particle surface. A schematic of the shape of the electrical potential curves is shown in Figure 2-2.



Figure 2-2 Schematic of double layer. (a) Effect of increasing concentration of indifferent electrolyte. (b) Reversal of potential by specific adsorption. (Stumm and Morgan, 1981)

When a particle moves in an electric field, some portion of the water near the surface of the particle moves with it. This gives rise to the shear plane, shown in Figure 2-2. The electrical potential between the shear plane and the bulk solution can be determined by electrophoresis measurements (measurement of rate of movement of particulate in an eclectic field) and is called the *zero potential*.

	Zero Point of Charge pH zpc
INORGANIC (hydrophobic)	
"Al (OH) <sub>3</sub> " (amorph)	7.5-8.5
Al2O <sub>3</sub>	9.1
CuO <sub>3</sub>	9.5
"Fe(OH) <sub>3</sub> " (amorph)	8.5
MgO	12.4
MnO <sub>2</sub>	2-4.5
Sio <sub>2</sub>	2-3.5
Clays	
Kaolinite	3.3-4.6
Montmorillonite	2.5
Asbestos	
Chrysotile	10-12
Crocidolite	5-6
CaCO <sub>3</sub>	8-9
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	6-7
FePO <sub>4</sub>	3
Alpo <sub>4</sub>	4
ORGANIC (hydrophilic)	
Algae	3-5
Bacteria	3-4
Humic acid	3
Oil droplets	2-5

 Table 2-1 Surface characteristics of particulates commonly found in natural water and wastewater.

 (Parks (1967); Stumm and Morgan (1981))

## 2.1.2 Enmeshment (Sweep Floc)

The effective removal of the colloidal and suspended particulate from water depends on a reduction in particulates stability. Destabilization of particulates with sodium or calcium ions is not a viable strategy in water treatment. Some soluble cations, however, such as aluminum, ions, or magnesium, hydrolyze and form an insoluble precipitate, thereby minimizing the concentration of ions added to the water. This type of destabilization has been described as an enmeshment mechanism or sweep floc (Packham, 1965; Stuumm and O'Melia, 1968) in which finely divided particulate are entrapped in the amorphous particulate formed. The molecular events leading to sweep floc have not been clearly defined. It is likely that nucleation of the precipitate may occur on the surface of the particulates, leading to the growth of an amorphous structure. This mechanism where pH values are generally maintained between pH 6 and 8 and aluminum or ions salts are used at concentrations exceeding saturation with respect to the amorphous metal hydroxide solid that is formed. (For a thorough review of destabilization mechanisms see Stumm and O'Melia (1968)).



Figure 2-3 Effect of pH and alum dose on zeta potential of Kaolin (Packham, 1965).

A reduction of the surface charge by alteration of the pH or addition of specifically adsorbed ions can also lead to charge neutralization and destabilization of the particulates. In Figure 2-3, the effect of dissolved aluminum species on the electrophoretic mobility of kaolin solutions is depicted as a function of pH (Packham, 1962).

## 2.1.3 Charge Neutralization

Because most particulates in natural water are negative charged (clays, humic acids, bacteria) in the natural pH range (pH 6-8), cationic polymers find the widest use to achieve particulate destabilization through charge naturalization. Cationic polymers can be used in conjunction or in lieu of inorganic coagulant for this purpose. With hydrophobic particulates having a defined phase boundary, cationic polymers appear to adsorb on particulate surface in a patch like pattern (Kasper, 1971), reducing electrostatic repulsion such that particulates may attach to each other following induced collisions. Generally, the optimum dose occurs when particulate surface is only partially covered (less than 50 percent) with polymer. Overdosing will cause destabilization. The optimum dose appears to increase in proportion to the surface area concentration of the particulates.

For hydrophilic particulates, such as humic acids, a precipitation mechanism is postulated (Glaser and Edzwald, 1979) as evidenced by the stoichiometry observed between optimum dose and concentration of humic acid.

### 2.1.4 Polymer Bridging

Polymer bridging is complex and has not been adequately described analytically. Schematically, polymer chains adsorb on particulate surface at one or more sites, along the polymer chain. The remainder of the polymer may remain extended into the solution and absorb on available surface sites of the particulates, thus creating a "bridge" between the surfaces. If the extended polymer cannot find vacant sites on the surface of other particulates, no bridging will occur. Thus, there is an optimum degree of coverage or extent of polymer adsorption at which the rate of aggregation will be a maximum. In mineral slurries of high solids concentration (>1000 mg/L), an optimum coverage of 50 percent has been observed (LaMer and Healy, 1963).



Figure 2-4 Subprocesses controlling rate of particulate aggregation (Kawamura, 2000).

#### 2.2 Rapid mixing

Rapid mixing is fast and thorough mixing (*flash mixing*) of the various chemicals, such as coagulant and coagulant aid, with water for their proper chemicals reactions. It has  $30 \pm 15$  seconds detention time in a small tank. Rapid mixing disperses the chemicals immediately to reach their targets and start their precipitation it known as coagulation. It is the removal of colloidal particles. Rapid mixing is followed by coagulation (Singh, 2006).

### 2.3 Coagulation

Coagulation is defined as the destabilization of charge on the colloidal and suspended solids, including bacteria and viruses, by a coagulant.

# 2.3.1 Coagulant

Commonly used metal coagulants in water treatment are those based on aluminum, such as aluminum sulfate, sodium aluminates, potash alum, and ammonia alum; and those based on iron, such as ferric sulfate, ferrous sulfate, chlorinated ferrous sulfate, and ferric chloride. The description that follows gives some of the relevant properties and chemical reactions of these substances in the coagulation of water. The latter are presented in the form of hypothetical equations with the understanding that they do not represent exactly what happens in water. Studies have shown that the hydrolysis of iron and aluminum salts is far more complicated then these formulas would indicate; however, they are useful in approximating the reaction products and quantitative relationships (Singh, 2006).

Aluminum sulfate,  $Al_2 (SO_4)_3 \cdot 14.3H_2O$ , is by far the most widely used coagulant; the commercial product is commonly known as alum, filter alum, or alumina sulfate. Filter alum is a grayish-white crystallized solid containing approximately 17 percent water-soluble

 $Al_2O_3$  and is available in lump, ground, or powdered forms as well as concentrated solution. Ground alum is a solution tank from which it is transmitted to the point of application by pumping. Amber-colored liquid aluminum sulfate contains about 8 percent available  $Al_2O_3$ .

The hydrolysis of aluminum ion in solution is complex and is not fully defined. In pure water at low pH, the bulk of aluminum appears,  $Al^{+++}$ , while in alkaline solution complex species such as  $Al(OH)_4^{-}$  and  $Al(OH)_5^{-}$  have been shown to exist. In the hypothetical coagulation equations, aluminum *floc* is written as  $Al(OH)_3^{-}$ . This is the predominant form found in a dilute solution near neutral pH in the absence of completing anions other then hydroxide. The reaction between aluminum and natural alkalinity is given in equation (Singh, 2006).

Chemical reactions:

following:

$$Al_{2}(SO_{4})_{3} + 14.3H_{2}O + 3Ca(HCO_{3})_{2} \rightarrow 2Al(OH)_{3} + 3CaSO_{4} + 14.3H_{2}O + 6CO_{2}$$
 (2.1)

$$Al_{2}(SO_{4})_{3} \bullet 14.3H_{2}O + 3Ca(OH)_{2} \longrightarrow 2Al(OH)_{3} + 3CaSO_{4} + 14.3H_{2}O$$
 (2.2)

$$Al_{2}(SO_{4})_{3} + 14.3H_{2}O + 3Na_{2}CO_{3} + 3H_{2}O \longrightarrow 2Al(OH)_{3} + 3Na_{2}SO_{4} + 3CO_{2} + 14.3H_{2}O$$
 (2.3)

#### 2.3.1.1 Factors Affecting Coagulation

Different sources of water need different coagulants, such as the

## 1) Aluminum sulfate

Filer alum,  $Al_2 (SO_4)_3$  ·14 H2O (aluminum sulfate), a powder, is one of the most commonly used coagulants. It is a good coagulant for hard waters with high alkalinity and pH 5.5-8.0. It is also available as liquid alum ( $Al_2O_3$ ). Both provide  $Al^{+3}$  ions in the water. Normally, coagulation needs 1 mg/L of alum for every 5 NTU. Turbidity up to 30 NTU; and above that, 1mg/L for every 10 NTU.

Activated alum is alum with about 9 percent sodium silicate. It works as coagulant and coagulant aid.

Black alum is alum containing activated carbon. It is applied for certain water with carbon adsorption requirements.

#### 2) Ferric sulfate

Example 1 Ferric sulfate  $(Fe_2 (SO_4)_3)$  is the second most commonly used coagulant, which work for water with a pH range from 5 to 11.

3) Ferrous sulfate

Ferrous sulfate (FeSO<sub>4</sub>) is useful for water with high pH (8.5-11).

4) Chlorinated copperas

Chlorinated copperas, a mixture of ferric sulfate and ferric chloride (FeCl<sub>3</sub>), has also been used for water with a pH range from 5 to 11.

#### 5) Sodium aluminates

Sodium aluminates (NaAlO2) are useful for hard water as it works both as a softener and coagulant. Its solution is alkaline with pH 12.

6) Coagulant aids

These help the coagulation by creating better coagulation conditions, such as proper pH, alkalinity, and particulate nuclei. Some of them act as secondary coagulants. pH adjusting coagulant aids include lime, sodium carbonate, sodium bicarbonate, sodium hydroxide, hydrochloric acid, and sulfuric acid. The first four chemicals raise pH and the last two lower it.

Non-pH affecting coagulant aids are substances that provide particulate matter as nuclei for coagulation (e.g., clay, sodium silicate, and activate silica). They are also called *weighing substances*. These aids are useful when the turbidity is low and is hard to remove.

### 7) Polymers

Coagulating aids acting as secondary coagulants are polymers, mostly cationic. They attract negatively charged turbidity particles. Depending on the quality of water, anionic or nonionic polymers may work better for certain water.

8) pH

Effectiveness of a coagulant is generally pH dependent. Different water requires different coagulants based on its pH. Water with a color will coagulate better at the low pH (4.4-6) with alum.

## 9) Alkalinity

It is needs to provide anions, such as (OH) for forming insoluble compounds to precipitate them out. It could be naturally present in the water or needed to be added as hydroxides, carbonate, or bicarbonate, as coagulant aids. Generally, 1 part alum uses 0.5 parts alkalinity for proper coagulation.

10) Temperatures

The higher the temperature, the faster the reaction, and the more effective is the coagulation. Winter temperature will slow down the reaction rate, which can be helped by an extended detention time. Mostly, it is naturally provided due to lower demand in winter.

### 11) Times

Proper mixing and detention times are important

12) Velocities

The higher velocity causes the shearing or breaking of floc particles, and lower velocity will let them settle in the flocculation basins. Velocity around 1ft/sec in the flocculation basins should be maintained.

### 13) Zeta potential

It is charge at the boundary of the colloidal turbidity particle and the surrounding water. The higher the charge, the more is the repulsion between the turbidity particles, lass the coagulation, and vice versa. Higher zeta potential requires the higher coagulant dose. An effective coagulation is aimed at reducing zeta potential charge to almost 0 (Singh, 2006). Selection of a proper coagulant and a coagulant aid for a water supply is important. A jar test for water should be determine which coagulant and coagulant aid are economical and most effective.

Raw water characteristics the design of the coagulation process is determined by the raw water characteristics. The most common problem associated with the process of coagulation is clogging of the chemical diffuser orifices and feed lines. This is related directly to the haedness of the process water (metal hydroxides) and, in part, to dissolved and suspended solids. If the water hardness exceeds 30 mg/L, the metal and alkali chemical feed lines and the diffuser orifices will become clogged within several months or less. The design of



Figure 2-5 Solubility of common floc versus pH. (*a*,*b*) Equilibrium composition of solutions in contact with freshly precipitated Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>. (*c*) Effect of pH on solubility of alum floc.

#### 2.3.2 Coagulant aid

Difficulties with coagulation often occur because of slow-setting precipitate or fragile *flocs* are easily fragmented under hydraulic forces in basin by and improving settling and toughness of *floc*. The most widely used materials are polymers; others are adsorbent-weighting agents and oxidants.

Synthetic polymers are long-chain, high molecular-weight, organic chemicals commercially available under a wide variety of trade names. Polymers are classified according to the type of charge on the polymer chain. Those possessing negative charges are anionic, those carrying on electric charge are nonionic. Anionic or nonionic are often used with metal coagulant to provide bridging between colloids to develop and tougher *floc* growth. The dosage required as a flocculent aid is generally in the order of 0.1 to 1.0 mg/L. in the coagulation of some waters, polymers can promote satisfactory flocculation at significantly reduced alum dosages.

The potential advantages of polymer substitution are in reducing the quantity of waste sludge produced in alum coagulation and in changing the character of the sludge such that it can be more easily dewatered (Marsden, 2004).

Cationic polymers have been used successfully in some waters as primary coagulants for clarification. Although the unit cost of cationic polymers is about 10 to 15 times higher than the cost of alum, the reduced dosages required may nearly offset the increased cost of chemicals. Furthermore, unlike the gelatinous and voluminous aluminum hydroxide sludges, polymer sludges are relatively dense and easier to dewater for subsequent handling and disposal. Sometimes cationic and nonionic polymers may be used together to provide an adequate *floc*, the former being the primary coagulant and the latter a coagulant aid. Although significant strides have been made in the application of polymers in water treatment, their main application is still as an aid rather than as a primary coagulant. Many waters cannot be treated by using polymers alone but require aluminum or iron salte. Jar tests and actual plant operation must be used to determine polymers in flocculation of given water.

Bentonitic clays may be used in treating waters containing high color, low turbidity and low mineral content. Iron or aluminum *floc* produced under these conditions is frequently too light to settle readily. Addition of clay results in a weighting action that improves settle ability. Clay particles may also adsorb organic compounds, improving treatment. Although exact dosage must be determined by testing, 10 to 15 mg/L frequently results in formation of a good *floc*. Other weighting agents that have been used besides clay are powdered silica, limestone, and activated carbon; the latter possess the additional adventage of high adsorptive capacity.

Acids and alkalies can be added to adjust the pH for optimum coagulation. The common acid used to lower the pH is sulfuric acid. Increase in pH is done by the addition of lime, soda ash, or sodium hydroxide (Marsden, 2004).

#### **2.4 Flocculation**

Flocculation is the gentle is the mixing phase that follows the rapid dispersion of coagulant by the flash mixing unit. Its purpose is to accelerate the rate of particle collisions,

causing the agglomeration of electrolytic ally destabilized colloidal particles into settle able and filterable sizes.

The terms *coagulation* and *flocculation* are some time used in terchangeably in technical literature. However, the aggregation of particulate material is actually a two-step process. The initial step involved the addition of coagulant, to reduce or eliminate the interparticulate forces responsible for the stability of the particulates. This process is called *coagulation*. The subsequent particulate collisions and enmeshment of particulates into flocs occur as the result of molecular motion and the physical mixing of the liquid. This is *flocculation*. (Kawamura, 2000)

Flocculation is the clumping of micro floc particles to form large particles called *floc*. It is achieved by the gentle mixing of coagulate water in tanks known as *flocculation basins* to allow further clumping of coagulated matter and turbidity particles to from large particles. Flocculation basins have slow mixing mechanical paddles, known as *flocculators*, and baffles to provide adequate mixing and low velocity. These basins a velocity about  $1 \pm 0.25$  ft/sec and detention time of 15 to 45 minutes. The best floc is pinhead size and visible a few feet below the surface of coagulate water. Floc particles are heavy enough to settle to the bottom of basin by gravity. The flocculated water flows to the primary sedimentation basin for the next phase, the sedimentation.

The hardness removal is also achieved at this phase of treatment is use for predisinfection, and then chlorite removal can also be done here by using ferrous ions. For the proper chemical reactions, these chemicals should be applied in the following sequence: ferrous ions, alum, lime, and then soda ash. (Singh, 2006)

#### 2.5 Kaolinite properties

The most common mineral by far in the kaolin group of minerals is kaolinite. The physical and chemical properties of kaolin determine its use as an industrial mineral. These uses are governed by several factors including the geological conditions under which the kaolin formed the total mineralogical composition of the kaolin deposit, and the physical and chemical properties. Kaolin deposits can be sedimentary, residual, or hydrothermal and in almost every instance the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization.

As shown in Table 1, kaolin is usually white or near white in color. There is very little substitution in the structural lattice and thus it has a minimal layer charge and a low base exchange capacity. The kaolinite crystals, which make up most of the kaolin deposits, are pseudo-hexagonal along with plates, some larger books, and vermicular stacks (Fig. 2-7) Particle size and particle size distribution are also very important in determining the industrial uses of the kaolin. A coarse particle kaolin has very different physical and optical properties relative to a fine particle size kaolin. Other properties that are important are the relatively low surface area in comparison to smectite and palygorskite-sepiolite, and the low absorption capacity, which relates to the minimal layer charge and the low surface area.



Figure 2-6 SEM showing kaolin plates and stacks. Bars 1 µm (Murray, 1993)

One other area of use of kaolin that has grown rapidly in the last 10 years is as a raw material in the production of fiberglass. The kaolin supplies both silica and alumina, which are needed in the fiberglass formulation. The kaolins that are used must have a relatively low iron and titanium content. The reason for the increased use of fiberglass is because of the restricted use of asbestos due to health considerations.

Tailored or engineered kaolins to enhance specific properties such as opacity, gloss, ink, holdout, brightness, whiteness, and print quality can be produced by special processing. Several papers used kaolins mixing with water for preparation of synthetic water.

#### 2.6 Silkworm silk

## 2.6.1 Life cycle of silk worm

Silk is a valuable fabric that symbolizes wealth and prosperity. In earlier times, use of silk was reserved only for kings and monarchs. The Chinese, about two thousand years ago, had already mastered the art of deriving silk from silk worms while the rest of the world was still in the darkness. Now, it's a common knowledge that silk is a biological secretion of a moth named *Bombyx mor* (Jianhua, 2005).

This particular type of moth has become so domesticated, that now it has lost its ability to fend for itself in wild. The silkworm metamorphoses into a beautiful moth from its initial stage of an egg. The entire life cycle of silkworms does not last for more than a couple of months.

### 2.6.1.1 Egg

Egg is the first stage of a silkworm's life cycle. The female moth lays an egg about the size of an ink dot during summer or the early fall. The egg remains in dormant stage until spring arrives. The warmth of the spring stimulates the egg to hatch (Shiping, 2007).

After the first molt, the silkworm loses its hairy exterior and remains smooth and soft throughout this stage of its life.

#### 2.6.1.2 Larvae

The silk worm, upon hatching, is about 1/8th of an inch and extremely hairy. Young silkworms can only feed on tender mulberry leaves. However, during the growth phase they can eat tougher mulberry leaves as well. The larval stage lasts for about 27 days and the silkworm goes through five growth stages called instars, during this time. During the first molting, the silkworm sheds all its hair and gains a smooth skin.

### 2.6.1.3 Cocoon

Cocoon is the stage in which the larva spins silk threads around it, to protect itself from its predators. The larva traps itself inside the cocoon in order to pupate. The color of the cocoon varies, depending upon what the silkworm eats. It can range from white to golden yellow. The second molting occurs inside the cocoon, when the larva turns into a brown pupa. It takes about 2-3 weeks for the pupa to metamorphose into an adult moth.

#### 2.6.1.4 Adult moth

Once the adult moth comes out of its cocoon, it's only purpose is to find a member of the opposite sex, and mate. Males are larger than females and more active. They flap their wings rapidly to attract the females. Within 24 hours of mating, the male moth dies, while the female lays abundant eggs, after which it dies as well. There on, a new silkworm life cycle begins.

Normally, there is only one season in a year when silkworms reproduce to give one generation. However, in countries like India and China silkworms reproduce continuously, round the year. Also, when silkworms are bred for commercial purposes, they are made to reproduce round the year. Commercially, these insects have to be bred very systematically. They cannot eat or drink on their own. Thus, everything from their food to their habitat has to be organized artificially. Although, silkworms feed on mulberry leaves, it is not always possible to find them, especially during fall and winter. Commercial silkworm breeders feed larvae a substance called silkworm chow, which is a good alternative to mulberry leaves.

Silkworm life cycle is pretty short and simple. Yet, the various stages that it goes through during its short life span are simply mesmerizing.



# Life cycle of silkworms (Bombyx mori)

Figure 2-7 Life cycles of silk worms. (Florentyna K, 2010)

Silk is a natural biopolymer produced by silkworms during the formation of their cocoon. There are two main types of the silkworms, mulberry silk or *Bombyx mori* which is also called cultivated silk, and wild silk such as *Samia Cynthia ricini* or *A.pernyi*. Cultivated silk are find, almost white and soft filaments with luster. The world silk production consists of nearly

80-85% of cultivated silks. While wild silks are coarser, more irregular and brownish in appearance, they are never as white as the cultivated silk filament. Thai silk is one of the mulberry silkworms (*Bombyx mori*) silk but it differs somewhat in the appearance. It is yellower in color, the filaments are coarser, and it has more silk gum. The process of remove sericin is known as degumming. The silk fiber can be divided from silkworms into 2 types that are (Moy et al., 1991):

(1) Mulberry silk (*Bombyx mori*) is produced by cultivated silkworm. The cultivated silkworm is fed with mulberry leaves.

(2) Wild silk is produced by silkworm. The type often referred as Tussah silk. The wild silkworm is fed with oak leaves.

The wild silkworm is hard to culture and the silk fibers obtained from wild silkworm are coarser, irregular, and brownish in appearances. While the silk fiber obtained from cultivated silkworm are find, almost white (when degummed), and soft fiber with lusture. Moreover, wild silkworm' fiber has more silk gum (e.g. up to 38%) then *Bombyx mori (B. mori)* silkworm' fiber (20-25%). Form this characteristic, silk fiber by B. mori silkworm is well known and has been studied extensively in biomaterial application.

Silk manufacturing is one of the industrial sectors where intensive water consumption cannot avoided therefore resulting in large volume of wastewater. One of these is released form degumming process which is used for elimination external sericin prior to drying; generally, synthetic soap or sodium carbonate solution is used at 95°C for 1 hr (Fig. 2.8). Sericin is globular protein representing as a tube outside the silk fibroin with molecular weight distributed between 10,000 to 300,000 Da (Fabiani, et al., 1996). When subjecting to alkaline degumming process, sericin is degraded into sericin peptide or hydrolyzed sericin with molecular weight less than 20,000 Da (Zhang et al., 2004). This peptide and hydrolyzed of sericin have excellent moisture absorption property and a lot of biological activities such as antioxidation, tyrosinase activity inhibition and anticancer activity (Chang-Kee et al., 2002). As a result, they can be applied in many fields such as cosmetics, and biomaterial and textile (Zhang, 2002).






Figure 2-9 Processing of silk morphologies from aqueous silk fibroin solution into non-woven silk fibers; aqueous-and solvent-based porous sponges; hydro gels and films (Janjira, 2008).

**Fibroin** is one of the candidate materials for biomedical application because of its various characteristic such as good biocompatibility, good oxygen and water vapor permeability, and minimal inflammatory reaction. Additionally, fibroin has been used in cosmetic, material for human health, and food additive.

Sericin or silk gum is a natural protein that is mainly made of sericin and fibroin proteins. Sericin constitutes 25-30% of silk protein and it envelops the fibroin fiber with successive sticky layers that help in the formation of a cocoon. Sericin ensures the cohesion of the cocoon by gluing silk threads together. Removal of sericin from the silk fibroin is achieved by the process call degumming. If this sericin protein is recovered and recycled, it can represent a significant economic and social benefit.

Fibroin and sericin is a macromolecular protein. The sericin protein is made of 18 amino acids most of which have strongly polar side groups such as hydroxyl, carboxyl, and amino groups. In addition, the amino acids serine and aspartic acid constitute approximately 33.4% and 16.7% of sericin, respectively (Zhang, 2002).

#### 2.6.2 Bombyx mori silk fibroin structure

The amino acid composition of silk fibroin *B. mori* consist primarily of glycine non polar (Gly) (34%), hydrophobic alanine (Ala) (30%) and non ironical polar serine (Ser) (12%) (Kaplan, et al., 1998). The heavy chain consists of 12 domains that form the crystalline regions in silk fibers, which are interspersed with primary sequence that is non-repetitive and thus forms fewer organized domains in the fibers. The crystalline domains in the fibers consist of Gly-X reports, with X being Ala, Ser, Threonine (Thr) and Valine (Val). The crystalline forming domains consist of an average of 381 residues (596 in size in the seventh domain to 36 in the  $12^{th}$  domain). Each domain consists of subdomain hexapeptides incluing: GAGAGS, GAGAGY, GAGAGA, or GAGYGA where G is glycine, A is alanine, S is serine and Y is nonioning polar. These subdomains end with tetrapeptides such as GAAS or GAGS. The less crystalline forming regions of the fibroin heavy chain, also known as linkers, are between 42 amino acid residue (nonrepetitive sequence), which is composed of charged amino acids not found in the crystalline natural coblock polymer design. Efficient secretion of fibroin is believed to be due in part to the formation of a disulfide bond between the heavy and light fibroin chains. A naked pupa mutation in *B. mori* has been mapped to the same locus as of the light chain on the  $14^{th}$  chromosome. The resulting fibroin light chain does not have a disulfide bond with the fibroin heavy chain and cocoon has less than 0.3% fibroin protein content.

Silk fibroin (SF) is a core structural protein and is coated by sericin (silk gum), a family of glue-like proteins that hold the fibroin core together. The sericin is a minor component of fiber (i.e. 25% of the weight of raw silk) and also has some purities such as waxes, fat, and pigments. Silk is a fibrous protein unlike sericin which is a globular protein. The elemental compositions in SF are listed in the Table 2-2.

Element	Percentages of element
Carbon	48 <b>-49</b>
Hydrogen	6.40-6.51
Nitrogen	17.35-18.89
Oxygen	26.00-27.90

Table 2-2 The composition of elements in silk fibroin. (Vollrath and Knight, 2001)

The silk fibroin is a semi-crystalline protein polymer that consists of sheet crystals and non-crystalline amorphous regions (Gosline et al., 1987) (Fig. 2-8). silk fibroin as a linear polypeptide whose chemical composition comprised of few types of amino acid of alternating of Glycine (Gly) residue with two thirds Alanine (Ala) and one third Serine (Ser). Fibroin has a highly repetitive primary structure that contains of the motif –Gly-Ala-Gly-Ala-Gly-Ser-along its sequence. It is composed of the alpha consisting of crank shaft, pleated beta-sheet formation (Fibroin I) and the beta formation consisting of anti-parallel pleated beta-sheet formation (Fibroin II) (Magoshi et al., 1994). The polypeptide chains (Fig. 2-10) always form anti-parallel  $\beta$ -sheet because this structure has hydrogen bonds (H-bond) peptide groups on adjacent beta strands and these H-bonds can stabilize structure.

Sericin, on the other hand, is a mixture of proteins, which nonionic polar contains Ser, polar thr and polar Tyr. It is amorphous and soluble in water.



Silk Fibroin

Figure 2-10 Model of microstructure found in silk fibroin. Black rectangles represent beta-sheet crystallites and lines represent amorphous regions (Gosline et al., 1987)



Figure 2-11 a) and b) The polypeptide chain of silk fibroin consists of layers antiparallel β-sheets rich in Ala and Dly residues (Anthony, 2009)

Silk fibers after degumming are approximately 900-1,700 meters long and the diameter from 9 to 11 microns. Silk fibers are extremely strong. If silk fiber is heated at 140°C, it will remain unaffected for a long period of time but it is decomposed very quickly at temperature of 175°C or higher. As show in Fig.2.4, because the silk fibers have extensive hydrogen bonding, the abundant hydrophobic nature of their proteins, and the significant crystalline structure of the polypeptide chains in silk fibroin, so silk fibers are insoluble in most solvents, including water, dilute acid and alkali.

Туре	Side group (R-group)	Amino acid	Proportion (%)
	-н	Glycine	46.39
	-CH,	Alanine	44.55
Trend	-CH(CH <sub>3</sub> ) <sub>2</sub>	Valine	0.50
Inert	-CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Leucine	0.05
	-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	Isoleucine	0.08
	-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Phenylalanine	0.02
	-Сң2СООН	Aspartate	0.17
Acidic	-сн,сн,соон	Glutanmate	1.03
Desia	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	Lysine	0.07
Basic	-(CH <sub>2</sub> ) <sub>3</sub> NHC(NH)NH <sub>2</sub>	Arginíne	0.17
	-сң,он	Serine	7.17
Hydroxyl	-CH(OH)CH,	Threonine	0.15
	-CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	Tyrosine	0.14
Ring	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub>	Proline	0.02
Sulfur	-CH <sub>2</sub> -S-S-CH <sub>2</sub> -	<b>Cysteine</b>	0.02
	-CH2CH <sub>2</sub> -S-CH <sub>3</sub>	Methionine	0.04

Table 2-3 The composition of amino acid in silk fiber (%) (Zhou et al., 2001)

**Table 2-3** lists the composition of amino acid in silk fibers. These are different proportions of amino acid residues in fibroin and sericin. Fibroin has higher proportions of alanine, glycine, and serine than leading to antiparallel  $\beta$ -pleated sheet formation. The crystalline regions of dilk fibers are composed mainly of repeating unit of amino acid in silk fibroin chains. *Bombyx mori* and *A.pernyi* silk fibroin are composed mainly of -(alanine-alanine)<sub>n</sub> -sequences, while -(glycine-alanine)<sub>n</sub> -repetitions are characteristic to *Bombyx mori* silk fibroin. A small amount of cysteine and methioinine residues give a very small amount of sulfur in the fiber (Moy et al., 1991)

(1) A number of silk polymorphs have been reported, including the glandular state prior to crystallization (silk I), spun silk state which consists of the  $\beta$ -sheet secondary structure

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(silk II), and air/water assembled interfacial silk (silk III, with a helical structure). The silk I structure is the water-soluble atate and upon exposure to heat or physical spinning easily converts to a silk II structure. The silk I structure is observed in vitro in aqueous conditions and converts to a  $\beta$ -sheet structure when exposed to methanol or potassium chloride. The  $\beta$ -sheet structure are asymmetrical with one side occupied with hydrogen side chains from glycine and the other occupied with the methyl side chains from the alanines that populate the hydrophobic domains. The  $\beta$ -sheet are arranged so that methyl groups and hydrogen groups of opposing sheets interact to from the intersheet stacking in the crystals. Strong hydrogen bonds and van der Waals forces generate a structure that is thermodynamically stable. The inter- and intra chain hydrogen bonds from between amino acids perpendicular to the axis of the chains and the fiber. The silk II structure excludes water and is insoluble in several solvents including mild acid alkaline conditions, and several chaotropes (Kaplan et al., 1998).

(2) The silk II is identified by the <sup>13</sup>C chemical shifts that are indicative of anti-parallel  $\beta$ -sheet, while the silk I structure gives the chemical shifts that are related with a loose helix. The two structures can undergo a conformational transition form silk depending on any factors such as solvent, temperature, or shear and tensile stresses (Tanaka et al., 1999). The region of anti-parallel  $\beta$ -sheet is a crystal region which results in the stability and mechanical features of silk fibroin.

#### 2.6.3 Bombyx mori silk sericin

Silk derived from silkworm *Bombyx mori* is a natural protein that is mainly made of sericin and fibroin proteins. The sericin coating constitutes 25-30% of the weight of *B. mori*'s silk threads, and helps in the formation of silk cocoon by gluing the threads together. It is made of sericin, gum-like proteins that very in their molecular weight ranges widely between 10 to over 300 KDa, and are rich in the amino acid sericin. It is also thought to contain carotenoids, which are responsible for cocoon pigmentation. Sericins protein is useful because of its properties. The protein resists oxidation, is antibacterial, UV resistant, and can absorb and release moisture easily. These properties are valuable in the protection of silk from microbial degradation, animal digestion, and other degumming processes. Recent studies show some surprising properties of sericin; dietary sericin has been suggested to suppress the development of colon tumours by reducing call proliferation, and creating oxidative stress and nitric acid production. It has been found, under certain conditions, to induce bone-like apatite deposition (Solheim et al., 2000). However, sericin still considered an obstacle for *B. mori* silk biocompatibility, despite the coating being soluble in hot alkaline water and therefore removable. As discussed later in this review, insufficient sericin removal is still an issue in many biomedical applications.

### 2.6.4 Structure of silk threads

It is now clear that there is a strong connection between the structure of silk fibers and their physical (and mechanical) properties. Structural organization from protein sequence, through protein folding to the assembly of the fibrils appears to play a role in the toughness and elasticity of silk fibres (Zhou et al., 2001). Relating structural features and patterns to physical properties is valuable as it could contribute to the ability to control the properties of future man-made silk analogous (for example, anability to control mechanical properties by introducing a certain structural features to the thread during spinning could be beneficial). However, an understanding the structure of silk threads is still a challenge. Below is a review of the miin structural features of silkworm and spider silks, starting at the overall thread organization and going down to the protein makeup.

Most natural silk threads known to data are thought to consist of an inner silk core of polymer protein, a protein skin, and some type of coating. The core exhibits nanofibrils, with some assembled into bundles called microfibrils. Generally, the coating functions as glue, but there is some evidence that it may also act as a fungicidal or bactericidal agent. It may also have a role during the extrusion process. Micro-morphological studies show that the substructure of spider silks is very similar to that of mulberry silkworm silks. *B.mori* silk fiber has been shown to be composed of two protein-monofilaments (named brins) embedded in a gluelike sericin coating. A similar structure has been observed in other silkworms silk. The brins are fibroin filaments made up of bundles of nanafibrils, approx 5 nm in diameter, with a bundle diameter of around 100 nm. The nanofibrils are oriented parallel to the axis of the fibre, and are thought to interact strongly with each other (Meinel et al., 2004). A schematic representation of the structure of *B. mori* thread is shown in Fig. 2-12.



Figure 2-12 The structure of a raw silk filament (Meinel et al., 2004)

Fig. 2-12 present the structure of raw silk filament, which contains microfibrils that are packed together to form the fibril bundle. The several fibril bundles produce a single strand of fibroin. Sericin envelops two strand of fibroin together to form a raw silk filament. Both contain elongated tubular cavities or vacuoles called canaliculi. The role of these canaliculi may be to facilitate controlled crack formation in the fibres when it is stretched or loaded. Although thread diameter varies across silk types and species, the mean width of nanofibrils appears to be independent of the fibre size, ranging 90-170 nm (Putthanarat et al., 2000).

A comparison of mechanical properties (Table 2-4) suggests that *B.mori* silk provide a remarkable combination of strength and toughness. The distinguishing features of the silk fibroin filaments following extraction of sericin are the very high strength in combination with excellent elasticity in comparison with these other biomaterials. In additionally, these display resistance to failure in compression that distinguishes them from other high performance fiber such as Kevlar.

Matarial	Tensile Strength	Modulus	% Strain at
wateria	(MPa)	(GPa)	break
B. mori silk (w/ sericin) <sup>a</sup>	500	5-12	19
B. mori silk (w/o sericin) <sup>b</sup>	610-690	15-17	4-16
B. mori silk <sup>°</sup>	740	10	20
Spider silk <sup>d</sup>	875-972	11-13	17-18
Collagen <sup>°</sup>	0.9-7.4	0.0018-0.046	24-68
Collagen X-linked <sup>f</sup>	47-72	0.4-0.8	12-16
PLA <sup>g</sup>	28-50	1.2-3.0	2-6
Tendon (comprised of mainly	150	1.5	12
collagen)			
Bone	160	20	3
Kevlar (49 fiber)	3600	130	2.7
Synthetic Rubber	50	0.001	850

**Table 2-4** Compression of mechanical properties of common silk (silkworm and spider dragline)to several types of biomaterial fibers and tissues commonly used today.

\*Bombyx mori silkworm silk -determined from bave (multithread fibers naturally produced from the silkworm coated in sericin)

<sup>b</sup>Bombyx mori silkworm silk -determined from single brins (individual fibroin filaments following extraction of sericin)

<sup>c</sup>Bombyx mori silkworm silk -average calculated from single data in Ref. Cunniff et al., 1994

<sup>d</sup>Nephila clavipes silk produced naturally and through controlled silking

<sup>e</sup>Rat-tail collagen Type I extruded fibbers tested after stretching from 0% to 50%

Rat-tail collagen dehydrothermally cross-linked and tested after stretching from 0% to 50%

<sup>8</sup>Polylactic acid with molecular weights ranging from 50,000 to 300,000

Some synthetic fibers can be improved by coating with natural macromolecules such as chitin, chitosan, fibroin, and sericin. Synthetic polyester fibers have micropores of 0.001– 10 mm diameter. Sericin molecule can be introduced into these micropores and cross-linked.

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Yamada and Matsunaga, 1994 and Yamada et al., 1993. Reported a sericin-modified polyester fiber obtained by cross-linking with glyceryl polyglycidyl ether and diethylene triamine.

Sericin-coated fibers can prevent abrasive skin injuries and the development of rashes. In one study, synthetic and other fibers were coated by sericin by immersing in a 3% aqueous solution of sericin for a given time and drying at 100 \_C for 3 min. The fabrics woven from the sericin-coated fibers were tested in products such as diapers, diaper liners, and wound dressing. Also prepared a hydrophilic fiber by attaching 0.1–5% sericin on surfaces of a thermoplastic fiber (rayon) and a cellulose fiber (cotton), these sericin-coated fibers were absorbent and did not cause skin rash. There are reports of improving the synthetic fibers by treating with a combination of natural polymers such as chitosan and sericin (Nabeshima et al., 1997). Some useful animal and plant natural fibers have also been subjected to treatment with sericin (Nomura and Yamada, 1996)

## **CHAPTER III**

## **METHODOLOGY**

Five sets of experiment were conducted to investigate the potential utilization of silk sericin as coagulant aid and coagulant. Three sets were tested for turbidity removal of synthetic turbid water using silk serecin as a coagulant aid. The fourth set was tested for turbidity removal of natural surface water with and without a coagulant aid. The fifth experiment was conducted to investigate the ability of silk sericin as coagulant for removing of synthetic turbid water.

## 3.1 Materials

## 3.1.1 Chemicals

Aluminum sulfate  $(Al_2 (SO_4)_3 18H_2O)$ . The concentration of alum is having 5%, used was obtained from Ajax Finechem Pty Ltd (Australia).

Sodium bicarbonate ( $Na_2HCO_3$ ) and Sodium carbonate ( $Na_2CO_3$ ), used were obtained from VWR international ltd (England).

Kaolinite, used was obtained from Fluka chemie (Germany).

#### 3.1.2 Cocoons of the Bombyx mori silkworm

Cocoons of the Bombyx mori silkworm were collected from a local farm in Ubon Ratchathani province, Thailand. Life cycle of cocoons is 18 days.



Figure 3-1 Silk cocoons

## 3.2 Material preparation procedure

#### 3.2.1 Extraction of Silk Sericin

Silk sericin used as coagulant and coagulant aid in this study was extracted from silk cocoons. Cocoons were dried in sunlight and then cut into small pieces. Raw silk was extracted by boiling cocoons with 100 ml of 0.5% (w/w) Na<sub>2</sub>CO<sub>3</sub> solution at 90°C for 60 minutes. The sericin solution (light yellow color solution) was then separated from silk fibroin by using whatman filter paper 47mm, and the filtrate was kept in a refrigerator at 4 °C for future used.

#### 3.2.2 Preparation of synthetic turbid water

Three samples of synthetic turbid water with initial turbidities of about 50, 75, and 100 NTU. were prepared by adding kaolin at 0.830 g, 1.26 g, and 1.687 g into 12 liters of distilled water. The stock solution was then kept for coagulation tests

#### 3.3 Jar test procedure

One set of jar test is composed of six jars. Each jar contains 1 liter of water sample, different dosages of alum and fix silk sericin were added into each jar (as described in Figure 3-2), with mixing speeds of 100 rpm for 1 min and 30 rpm for 20 min.

As discussed previously, there were five sets of experiment to study the results of using silk cericin as coagulation and coagulaton aids for synthetic turbid water.

The first set of jar test was conducted to investigate the efficiency of turbidity removal using only alum (Figure 3-2).

The second set of jar test was to examine the turbidity removal of synthetic turbid water using alum and fix silk sericin (see Figure 3-3). Whereas, turbidity removal of natural surface water using only alum was done by the third set of jar test (see Figure 3-4).

The fourth set of jar test with different alum dosage and fix silk sericin at 0.01 mL assessed the effects on the turbidity of natural surface water (see Figure 3-5). The last set of jar test was performed to analyze the effects on the turbidity of the synthetic turbid water using only the extracted silk sericin (see Figure 3-6).



Figure 3-2 Jar test with different alum dosage of synthetic turbid water. (First set)

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Figure 3-3 Jar test with different alum dosage and fix silk sericin at 0.01 mL of the synthetic turbid water. (Second set)

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Figure 3-4 Jar test with different alum dosage of natural surface water. (Third set)

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Figure 3-5 Jar test with different alum dosage and fix silk sericin at 0.01 mL of natural water. (Four set)

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Figure 3-6 Jar test with silk sericin different dosage of synthetic turbid water. (Five set)

### 3.3 Analytical procedure

## 3.3.1 Total Organic Carbon Measurement

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Analysis of total organic carbon (TOC) in water content was performed before and after the addition of the silk sericin. A high temperature TOC analyzer (Shimadzu Corporation, TOC-VCPH, Japan) was used for the dissolved organic carbon determination of samples. The instrument utilized a high temperature catalytic combustion process using nondissolved infrared detector. Sample was put into the sample boat then automatic sampler collected a sample and injected into the TOC analyzer.

## 3.3.2 Calculation of turbidity removal efficiency

The following equation was used to estimate the efficiency of turbidity removal:

% Removal = 
$$\frac{C_i - C_e}{C_i} x_{100}$$
 (3-1)

In which % Removal = percent removal efficiency  $C_i$  = initial turbidity (NTU)

 $C_e$  = final turbidity (NTU)

#### 3.4 Kinetic study

Chemical kinetics is the study of the rate and mechanism by which one chemical species is converted to another. The rate is the mass, in moles, of a product produced or reactant consumed per unit time. The mechanism is the sequence of individual chemical events whose overall result produces the observed reaction.

Zero order reaction has a rate which is independent of the concentration of the reactant. Increasing the concentration of the reacting species will not speed up the rate of the reaction. Zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a catalyst, is saturated by the reactants. And k is the reaction rate coefficient with units of concentration/time.

A Products  

$$\frac{d [A]}{dt} = -k$$

$$\int_{[A]_0}^{[A]} d[A] = -k \int_{0}^{t} dt$$

$$[A] - [A]_{0} = -kt$$



Figure 3-7 Zero order reaction

First order reaction depends on the concentration of only one reactant (a unimolecular reaction). k is the first order rate constant, which has units of 1/time.

A Products  

$$\frac{d [A]}{dt} = -k [A]$$

$$\int_{[A]_0}^{[A]} \frac{d [A]}{[A]} = -k \int_0^t dt$$

$$\ln[A] = \ln[A]_0 - kt$$

$$[A] = [A]_0 e^{-kt}$$



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Second order reaction depends on the concentrations of one second-order reactant, or

two first-order reactants arun. k is the first order rate constant, which has units of concentrationtime.



Figure 3-9 Second order reaction.

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## CHAPTER 4

## **RESULTS AND DISCUSSION**

Five sets of experiment were conducted to investigate the potential utilization of silk sericin as coagulant aid and coagulant. Three sets were tested for turbidity removal of synthetic turbid water using silk serecin as a coagulant aid. The fourth set was tested for turbidity removal of natural surface water without and with a coagulant aid. The last one was conducted to investigate the ability of silk sericin as coagulant for removing of synthetic turbid water. Characteristics of extracted silk sericin were also examined. In addition, kinetics of turbidity removal are inclued in this study.

## 4.1 Characteristics of silk sericin

Silk sericin used as a coagulant aid in this study was extracted from silk cocoons. The sericin with a pH of 10.3 contains total organic carbon (TOC) in the amount of (2,334,811 mg/L) and has a light yellow color (see Figure 4-1).



Figure 4-1 Silk sericin was separated from silk fibroin

4.2 Turbidity removal of synthetic turbid water without and with a coagulant aid

4.2.1 Turbidity removal efficiency of synthetic turbid water without and with a coagulant aid

Tables 4-1 to 4-3 show the results of coagulation tests with and without a coagulant aid at synthetic turbidity of 50 NTU, 75 NTU, and 100 NTU, respectively. As seen from these tables, the turbidity removal efficiency increased with the increase of alum dosage. However, the optimum removal efficiency without the addition of a coagulant aid was at an alum dosage of 80 mg/L, while the optimum removal efficiency with the addition of silk sericin was obtained with an alum dosage of 60 mg/L. According to Tables 4-1-4-3, with 80 mg/L of alum the maximum removal efficiencies were obtained at around 94% without adding a coagulant aid. When silk sericin was added, a slight increase in the efficiency of the turbidity removal was observed particularly when alum concentration was less than or equal to 60 mg/L. The results indicated that silk sericin as a coagulant aid not only improved the efficiency of the turbidity removal but the amount of alum utilization could be reduced also. Furthermore, the different morphology of floc formation was observed, Figure 4-2 shows that the larger floc was formed and settled out of the solution with the addition of silk sericin. Therefore, it was concluded that silk sericin extracted from silk cocoon is an alternative material as a natural coagulant aid since it is easily prepared and less expensive than synthetic polymer.

According to the experiment, by increasing the amount of Alum dosage, it enhances the efficiency removal. Particularly when 80 mg/L of alum is used, high turbidity removal efficiency can be obtained. With the identical procedure but adding alum concentration at 100 mg/L, the efficiency of turbidity removal is reduced. Because of it's over dosage.

In experiments at the concentration of alum at 0 mg/L, the turbidity has decreased due to precipitation by themselves.

Sample No.	Alum	% Removal	Alum concentration	% Removal
	concentration	Efficiency	(mg/L) + 0.01 mL silk	Efficiency
	(mg/L)		sericin	
1	0	31 ±0.70	0	40 ±1.41
2	20	61 ±4.94	20	60 ±2.82
3	40	70 ±1.41	40	77 ±3.53
4	60	90 ±2.82	60	95 ±0
5	80	93 ±1.41	80	91 ±212
6	100	74 ±2.12	100	85 ±2.83

Table 4-1Turbidity removal efficiency of synthetic turbid water at 50 NTU using alum and alumwith 0.01 mL of silk sericin

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Table 4-2Turbidity removal efficiency of synthetic turbid water at 75 NTU using alum and alumwith 0.01 mL of silk sericin

Sample No.	Alum	% Removal	Alum concentration $(mg/I) + 0.01 mI cilk$	% Removal
	(mg/I)	Efficiency	(mg/L) + 0.01 mL sik	Enterency
	(mg/L)		30110111	
1	0	41 ±4.24	0	52 ±2.47
2	20	52±2.12	20	69 ±3.53
3	40	56 ±2.12	40	68 ±0.70
4	60	73 ±2.12	60	94 ±0.70
5	80	94 ±1.41	80	85 ±2.82
6	100	86 ±1.41	100	60 ±0.70

.....

Sample No.	Alum	% Removal	Alum concentration	% Removal
	concentration	Efficiency	(mg/L) + 0.01 mL silk	Efficiency
	(mg/L)		sericin	
1	0	51 ±0.70	0	57 ±4.94
2	20	61 ±1.41	20	74 ±1.41
3	40	73 ±0.70	40	77 ±2.82
4	60	90 ±1.41	60	93 ±2.12
5	80	93 ±0.70	80	82 ±2.12
6	100	74 ±2.82	100	68 ±2.12

 Table 4-3
 Turbidity removal efficiency of synthetic turbid water at 100 NTU using alum and alum with 0.01 mL of silk sericin

Results of turbidity removal in synthetic water (50, 75 and 100 NTU) using different Alum dosage (0, 20, 40, 60, 80 and 100 mg/L) shows the maximum turbidity removal at 80 mg/l all of three samples. Because the selected degrees of turbidity don't have a big gap, therefore, the maximum percent removal of all samples is reached at 80 mg/l of Alum dosage. This result corresponds to another experiment when adding Silk sericin. It shows that by using 60 mg/l with 0.01 ml/l of silk sericin, maximum turbidity removal is reported with all three samples of different degree of turbidity.

In conclusion, though applying Alum dosage with or without silk sericin addition to the different degree of turbidity (50, 75 and 100 NTU), the turbidity removal efficiency has no difference. It might be due to the selected degrees of turbidity are not significant enough to observe the behavior of turbidity removal when varying the degree of turbidity.

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a) with a coagulant aid b) without a coagulant aid Figure 4-2 Morphology of floc formation without and with a coagulant aid

4.2.2 Kinetics of turbidity removal of synthetic turbid water with and without a coagulant aid

Figure 4-3 to 4-8 show the results of coagulation tests with and without a coagulant aid at synthetic turbidity of 50 NTU, 75 NTU, and 100 NTU respectively. The samples were taken every 5 minutes (start collected sample from fast mixing). Turbidity removal efficiency decreases to 20 min. The process of slow mixing can encourage the particles to assemble lager and then settle by themselves.



Figure 4-3 Kinetic of turbidity removal of synthetic turbid water at 50 NTU using alum







Figure 4-5 Kinetic of turbidity removal of synthetic turbid water at 75 NTU using alum



Figure 4-6 Kinetic of turbidity removal of synthetic turbid water at 75 NTU using alum with 0.01 mL of silk sericin



Figure 4-7 Kinetic of turbidity removal of synthetic turbid water at 100 NTU using alum



Figure 4-8 Kinetic of turbidity removal of synthetic turbid water at 100 NTU using alum with 0.01 mL of silk sericin

The turbidity removal efficiency of synthetic turbid water at 50 NTU, 75 TU, and 100 NTU, when using alum 80 mg/L as a coagulant were 93±1.41%, 94±1.14%, and 93±0.70%. When using alum at 60 mg/L with silk sericin as a coagulant aid, the efficiency

reached 94%. Therefore, the silk sericin can be used as a coagulant aid to enhance turbidity removal.

This comparison of the use of synthetic turbid water at 50 NTU without silk sericin (Figure 4-9) and with silk sericin (Figure 4-10) showed that the reactions of two sets are zero order. Because these sets are low in turbidity, resulting in the low reaction rate but the experiment using alum with silk sericin K will have more value than without silk sericin. This aswell shows that the silk sericin is a wizard in the precipitation. By using alum 60mg/L as a coagulant with the 75 NTU and 100 NTU samples, the reactions were considered as first order and zero order respectively. In addition, under the same conditions but with the addition of silk sericin 0.01 mL, the reaction of two set were second order. As a result, the addition of silk sericin enhances the reaction rate with higher order in comparison to the sample without silk sericin.

Turbidity.	Without silk sericin		With silk	sericin
NTU	Order	k	Order	k
50	Zero order	0.8720	Zero order	1.1300
75	Zero order	1.2340	2 <sup>nd</sup> order	0.0004
100	1 <sup>st</sup> order	0.9730	2 <sup>nd</sup> order	0.0030

Table 4-4 Kinetic of turbidity removal of synthetic turbid water without and with silk sericin

#### 4.3 Turbidity removal of natural surface water with and without a coagulant aid

4.3.1 Turbidity removal efficiency of natural surface water without and with a coagulant aid

Sets of natural surface water experiments were conducted by varying the dosages of alum without and with addition of silk sericin as a coagulant aid. The results showed similar removal efficiencies for both cases as displayed in Table 4-4. Since most particle sizes in natural surface water are large and these particles are readily settled out of water sample using only a coagulant. Therefore, adding of coagulant aid did not improve turbidity removal efficiency and is not necessarily for this case.

Sample No.	Alum concentration (mg/L)	% Removal Efficiency	Alum concentration (mg/L) + 0.01 mL silk sericin	% Removal Efficiency
1	0	19 ±4.92	0	19 ±3.44
2	20	90 ±1.14	20	84 ±1.10
3	40	97 ±0	40	96 ±0.09
4	60	97 ±0	60	97 ±0
5	80	97 ±0	80	97 ±0
6	100	97 ±0	100	94 ±0.95

 Table 4-5 Turbidity removal efficiency of natural surface water using alum and alum with

 0.01 mL of silk sericin

4.3.2 Kinetics of turbidity removal of natural surface water without and with a coagulant aid

Figure 4-5 to 4-6 show the results of coagulation tests with and with out a coagulant aid of natural surface water. The kinetics of turbidity removal the results show that every 5 min the efficiency of the removal of turbidity decreases to respectively, until to 20 min. During 15 min to 20 min the floc separates and turbidity increases.

Table 4-6 Kinetic of turbidity removal of natural surface water without and with silk sericin

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Turbidity.	Without silk sericin		With sill	c sericin
NTU	Order	k	Order	<b>k</b> "
Natural surface	Zero order	1.642	Zero order	2.008
water				

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Figure 4-9 Kinetic of turbidity removal of natural surface water using alum dosage



Figure 4-10 Kinetic of turbidity removal of natural surface water using alum with 0.01 mL of silk sericin

The efficiency of turbidity removal of natural surface water with and without silk sericin can reach 97%±0. In addition, the reactions of the two sets are zero order due to the increased effect of the coagulant aid on the natural surface water.

### 4.4 Turbidity removal of synthetic turbid water using silk sericin as a coagulant

Silk sericin was used as a coagulant and was added in different dosages. The results showed that the addition of silk sericin as a coagulant did not remove turbidity (see Table 4-5) but the color of the water samples became darker.

 Table 4-7
 Turbidity removal efficiencies of synthetic turbid water at 50 NTU using silk sericin as coagulant

Sample	Silk sericin mL	% Removal Efficiency
1	0.0	33±4.24
2	0.1	37.5±4.94
3	0.2	12±2.82
4	0.3	1±2.82
5	0.4	0
6	0.5	0

## 4.5 Total organic carbon measurement (TOC) analysis

# 4.5.1 Total Organic Carbon (TOC) for synthetic turbid water

The values of TOC of water samples without and with silk sericin at turbilities of 50 NTU, 75 NTU, and 100 NTU are compared in Tables 4-6 – 4-8. As seen from the Tables, although silk sericin contains relatively high TOC value, most of water samples had no significant changes in the amount of TOC after adding 0.01 ml of silk sericin.

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Sample No.	Alum	TOC mg/L	Alum concentration	TÜC mg/L
	concentration		(mg/L) + 0.01 mL silk	
	(mg/L)		sericin	
1	0	4315	0	3994
2	20	2481	20	2613
3	40	2189	40	2325
4	60	1609	60	1970
5	80	1670	80	1571
6	100	1689	100	1749

Table 4-8 Total organic carbon (TOC) of synthetic turbid water at 50 NTU with and without silk sericin

 Table 4-9 Total organic carbon (TOC) for synthetic turbid water at 75 NTU with and without silk sericin

Sample No.	Alum	TOC mg/L	Alum concentration	TOC mg/L
	concentration		(mg/L) + 0.01 mL silk	
	(mg/L)		sericin	
1	0	4511	0	4491
2	20	2044	20	1934
3	40	1826	40	1855
4	60	1747	60	1787
5	80	1672	80	1750
6	100	1635	100	1638

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Sample No.	Alum	TOC mg/L	Alum concentration	TOC mg/L
	concentration		(mg/L) + 0.01 mL silk	
	(mg/L)		sericin	
1	0	4315	0	3994
2	20	2481	20	2613
3	40	2189	40	2325
4	60	1609	60	1970
5	80	1670	80	1571
6	100	1689	100	1749

 Table 4-8 Total organic carbon (TOC) of synthetic turbid water at 50 NTU with and without silk

 sericin

 Table 4-9 Total organic carbon (TOC) for synthetic turbid water at 75 NTU with and without silk sericin

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Sample No.	Alum	TOC mg/L	Alum concentration	TOC mg/L
	concentration		(mg/L) + 0.01 mL silk	
	(mg/L)		<b>seric</b> in	
1	0	4511	0	4491
2	20	2044	20	1934
3	40	1826	40	1855
4	60	1747	60	1787
5	80	1672	80	1750
6	100	1635	100	1638
### **CHAPTER 5**

#### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The study showed the feasibility of the use of silk sericin extracted from silk cocoons as a coagulant aid in the efficient removal of turbidity. The efficiencies of the removal of turbidity of pure Alum dosage and Alum dosage with silk sericin added were displayed. According to the study, the use of 80 mg/L of Alum in synthetic turbid water of 50, 75, 100 NTU resulted in efficiencies of the removal of turbidity of  $93\pm1.41\%$ ,  $94\pm1.14\%$ , and  $93\pm0.70\%$  respectively. At the same time, the addition of 0.01 ml of silk sericin in 60 mg/L of Alum gave better results in the efficiencies of the removal of similar degrees of turbidity –  $95\pm0\%$ ,  $94\pm0.70\%$ , and  $93\pm2.12\%$ efficiencies were reported for synthetic turbid water of 50, 75 and 100 NTU respectively.

In a parallel study of silk sericin, surface water of 80 NTU was tested using Alum with and without silk sericin. Regarding the efficiencies of the removal of turbidity of surface water with and without silk sericin as a coagulant aid, results showed that the higher removal efficiency is the same  $(97\%\pm0)$  as the coagulant aid cannot work well in the surface water because of the presence of many chemicals acting as inhibitors.

In addition, it was shown that the addition of silk sericin has no effect on the dissolved organic carbon (TOC) in water.

The results indicated that the use of silk sericin as a coagulant aid improved the efficiency of the removal of turbidity and the amount of alum used could be reduced. Furthermore, silk sericin as a natural coagulant aid extracted from silk cocoons can be used as a viable alternative material to enhance the efficiency of the removal of turbidity since it can be easily prepared, is readily available for collection from agricultural waste in Northeast and Central Thailand, and is cheaper compared to synthetic polymer.

### 5.2 Recommendations

It is recommended that further studies are completed using varying quantities of silk sericin and dry silk sericin as a coagulant aid in the removal of turbidity.

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APPENDICES

## APPENDIX A

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### Instrument for determine

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#### 1. Jar test (Phipps & Bird Stirrer Model 7790-402)

Jar testing is a useful tool to determine the practical optimum does of a chemical under the simulated plant conditions. It uses a range of increasing dose of a particular chemical in a series of six jars with a stirring and illumination mechanism. Most of the problems in the source water (particularly in the surface water) quality are due to seasonal variations or other unusual circumstances, such as drought, heavy rains, unexpected discharge of raw sewage, or runoffs from farm land. There problems can be solved by this test, which is important for coagulation, softening, sedimentation, removal of synthetic organics (such as atrazine), and for tastes and odor control. It makes the water treatment more effective, easy, and economical (Sarai, 2006).





#### 2. Turbidity meter

Turbidity is the murkiness in the water caused by colloidal and other suspended particles. Turbidity The Hach Model 2100P Portable Turbidimeter is measured as the amount of scattered light by the suspended particles in the sample. The turbidity unit, NTU, is based on the amount scattered by particles of formazine, a polymer, used as a reference standard due to the amount scattered by particles of formazine, a polymer, used as a reference standard due to the reproducibility of the results. Turbidity of the finished water should be equal to or less than 5 NTU (www.PCD.go.th).



Figure A-2 The HACH Model 2100P Portable Turbid meter.

#### 3. pH meter

pH is an important parameter in the water utility. It is used to determine the condition of water for proper coagulation, softening, and stabilization. pH meter method is a convenient and accurate method for this test. The meter measures the voltage difference developed between the electrodes due to hydronium ions in the solution. This differential is read as the pH of the sample. Testing procedure varies somewhat with different brands and models of the pH meter. Follow the instructions provided by the manufacturer. Proper calibration by using an appropriate buffer solution (solution with the stable pH), such as 6 or 9, is important. Rinse the electrode with the deionized (DI) water and wipe with a soft paper to remove the DI water.



Figure A-3 pH meter (WTW inoLab pH level 2, U.S.A.)

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# APPENDIX B

# Efficiency of the removal of turbidity in synthetic water

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				Alum		Turbidity	Turbidity		
	pН		temperature	concentration	Silk cericin	initial	final	% Removal	тос
Sample No.	initial	pH final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	7	6.92	26.3	0	0	50.1	34.9±1.79	31±0.70	4315
2	7	6.34	26.3	20	0	50.1	32.8±2.19	35±4.94	2481
3	7	6.19	26.3	40	0	50.1	21.1±0.77	58±1.41	2189
4	7	5.89	26.3	60	0	50.1	10.6±1.05	78±2.82	1609
5	7	5.63	26.3	80	0	50.1	3.21±0.70	94±1.41	1670
6	7	5.55	26.3	100	0	50.1	6.05±1.06	88±2.12	1689

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 Table B.1 Efficiency of the removal of turbidity of synthetic turbid water at 50 NTU using alum

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				Alum		Turbidity	Turbidity		
	pН	рН	temperature	concentration	Silk cericin	initial	final	% Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	7	6.93	26.4	0	0.01	54.3	35±1.13	40±1.41	3994
2	7	6.50	26.4	20	0.01	54.3	23.25±1.90	60±2.82	2613
3	7	6.09	26.4	40	0.01	54.3	13.8±1.76	77±3.53	2325
4	7	5.84	26.4	60	0.01	54.3	2.97±0.29	95±0	1970
5	7	5.63	26.4	80	0.01	54.3	5.53±1.23	91±2.12	1571
6	7	5.41	26.4	100	0.01	54.3	8.96±1.75	85±2.82	1749

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Table B.2 Efficiency of the removal of turbidity of synthetic turbid water at 50 NTU using alum with 0.01 mL of silk sericin

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						Turbidity	Turbidity		
	pН	pН	temperature	Alum concentration	Silk cericin	initial	final	% Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	7	7	24.9	0	0	78.7	51.9±3.18	37±3.18	4511
2	7	6.32	24.9	20	0	78.7	39.3±1.48	53±1.48	2044
3	7	6.91	24.9	40	0	78.7	36.0±2.19	57±2.19	1826
4	7	6	24.9	60	0	78.7	22.1±1.97	74±1.97	1747
5	7	5.65	24.9	80	0	78.7	6.05±0.42	94±0.42	1672
6	7	5.26	24.9	100	0	78.7	11.3±0.19	86±0.91	1635

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# Table B.3 Efficiency of the removal of turbidity of synthetic turbid water at 75 NTU using alum

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						Turbidity	Turbidity		тос
			temperature	Alum concentration	Silk cericin	initial	final	% Removal	mg/L
Sample No.	pH initial	pH final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	
1	7	7	21.6	0	0.01	76.1	41.5±1.48	42±2.47	4491
2	7	6.6	21.6	20	0.01	76.1	23.2±3.04	70±3.53	1934
3	7	6.25	21.6	40	0.01	76.1	24.1±0.28	69±0.70	1855
4	7	6.05	21.6	60	0.01	76.1	4.96±0.36	94±0.70	1787
5	7	5.76	21.6	80	0.01	76.1	11.1±2.24	85±2.82	1750
6	7	5.63	21.6	100	0.01	76.1	30.5±0.63	59 <del>±</del> 0.70	1638

# Table B.4 Efficiency of the removal of turbidity of synthetic turbid water at 75 NTU using alum with 0.01 mL of silk sericin

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				Alum		Turbidity	Turbidity		
	pН	pH	temperature	concentration	Silk cericin	initial	final	% Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	7	7	24.9	0	0	107	52.8±0.12	50±0.70	1929
2	7	6.31	24.9	20	0	107	41.5±1.83	61±1.41	1690
3	7	5.94	24.9	40	0	107	30.0±1.20	73±0.70	1699
4	7	5.76	24.9	60	0	107	10.6±1.59	90±1.41	1582
5	7	5.63	24.9	80	0	107	7.04±0.97	94±0.70	1682
6	7	5.43	24.9	100	0	107	27.7±2.96	74±2.82	1388

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# Table B.5 Efficiency of the removal of turbidity of synthetic turbid water at 100 NTU using alum

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				Alum		Turbidity	Turbidity	%	
	pН	pH	temperature	concentration	Silk cericin	initial	final	Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	7	6.98	23.3	0	0.01	105	48.5±5.92	57 <del>±</del> 4.94	2004
2	7	6.48	23.3	20	0.01	105	29±0.91	74±1.41	1798
3	7	6.22	23.3	40	0.01	105	25.7±2.96	77±2.82	1688
4	7	5.97	23.3	60	0.01	105	7.34±2.66	94±2.12	1603
5	7	5.89	23.3	80	0.01	105	19.6±3.04	83±2.12	1565
6	7	5.67	23.3	100	0.01	105	35.4±2.82	69±2.12	1441

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Table B.6 Efficiency of the removal of turbidity of synthetic turbid water at 100 NTU using alum with 0.01 mL of silk sericin

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# APPENDIX C

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Kinetics of turbidity removal efficiencies of synthetic turbid water

Time		Alum concentration. mg/L								
 min	0	20	40	60	80	100				
0	50.1±3.36	50.1±3.36	50.1±3.36	50.1±3.36	50.1±3.36	50.1±3.36				
5	50.4±2.89	46.2±0.84	45.5±0	44.2±0.63	43.2±0.49	42.5±0.56				
10	48.3±0.63	43.0±1.27	42.65±0.35	41.3±0.63	40.0±0.56	41.0±0.63				
15	43.0±0.77	36.4±1.69	37.3±1.13	36.4±0.21	35.3±0.91	37.9±0.35				
20	42.1±0.84	33.3±1.41	33.45±0.91	32.2±1.97	30.7±0.49	33.5±2.47				

 Table C-1 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at

 50 NTU using alum

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Table C-2 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at50 NTU using alum with 0.01 mL of silk sericin

Time		Alum concentration. mg/L									
min	0	20	40	60	80	100					
0	45.3±2.83	45.3±2.83	45.3±2.83	45.3±2.83	45.3±2.83	45.3±2.83					
5	51.0±1.97	44.5±1.62	44.0±1.69	43.2±0.91	42.9±0.42	42.3±0.84					
10	48.1±1.06	41.8±1.62	41.2±2.05	39.9±0.91	40.3±2.40	40.2±1.69					
15	44.2±0.63	35.2±0.77	33.6±1.55	31.9±0.63	31.8±0.14	33.5±0.77					
20	40.8±0.49	32.8±1.06	31.8±0.42	27.9±0.77	29.0 <b>±0.2</b> 1	30.3±0.28					

Time		Alum concentration. mg/L									
min	0 mg/L	20 mg/L	/L 40 mg/L 60 mg		<b>8</b> 0 mg/L	100 mg/L					
0	78.7±2.75	78.7±2.75	78.7±2.75	78.7±2.75	78.7±2.75	78.7±2.75					
5	73.6±1.06	65.8±0.42	68.0±0.49	64.6±1.20	64.4±1.55	63.5±1.41					
10	68.8±2.45	62.8±1.41	62.6±0.21	60.8±0.84	60.3±0.63	60.3±1.41					
15	66.9±1.90	58.3±0.49	55.9±2.61	55.2±2.40	51.7 <b>±0.6</b> 3	54.5±0.42					
20	62.5±1.69	55.8±0.63	49.7±0.49	50.3±0.84	48.1±0.70	51.6±0.28					

 Table C-3 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at

 75 NTU using alum

**Table C-4** Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at75 NTU using alum with 0.01 mL of silk sericin

Time	Alum concentration. mg/L								
min	0	20	40	60	80	100			
0	76.1±157	76.1±157	76.1±157	76.1±157	76.1 <b>±157</b>	76.1±157			
5	72.7±1.69	65.8±1.27	65.5±1.20	65.8±0.14	65. <b>5±0.42</b>	65.2±1.69			
10	68.1±0.35	57.8±2.26	56.8±2.47	55.8±3.39	56.8±4.10	56.8±2.89			
15	63.2±0.98	54.8±0.49	54.5±2.54	52.0±2.61	53.9±1.97	53.5±1.55			
20	60.1±2.40	51.9±0.21	49.6±1.69	46.5±0.91	47.6±0.35	49.9±2.75			

Time.		Alum concentration. mg/L									
min	0	20	40	60	80	100					
0	107±3.28	107±3.28	107±3.28	107±3.28	10 <b>7±3.28</b>	107±3.28					
5	94.5±1.90	88.2±1.97	86.8±0.28	86.5±1.55	85.4±0.70	84.4±0.63					
10	87.1±3.46	82.5±0.84	82.0±0.63	80.7±0.70	81. <b>2±2.05</b>	80.9±0.63					
15	81.5±3.18	77.7±4.31	76.3±3.60	73.5±3.04	74.1±4.24	73.7±4.31					
20	76.9±2.19	73.2±0.91	72.7±1.20	70.4±2.12	68.7±1.20	70.2±1.34					

 Table C-5 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at

 100 NTU using alum

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 Table C-6 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at

 100 NTU using alum with 0.01 mL of silk sericin

Time.	Alum concentration. mg/L								
min	0	20	40	60	80	100			
0	105±2.14	105±2.14	105±2.14	105±2.14	10 <b>5±2.14</b>	105±2.14			
5	97.5±1.55	91.1±2.82	86.2±1.90	85.0±0.28	86.1±1.55	81.8±0.70			
10	89.3±3.81	80.3±1.55	78.2±0.84	77.8±0.21	77.5±0.42	77.2±2.75			
15	85.1±4.87	74.8±3.04	77.2±1.76	71.0±0.49	73.4±1.34	76.6±1.69			
20	79.2±3.04	73.1±1.62	72.4±3.11	67.4±1.62	<b>7</b> 0. <b>0±0.98</b>	73.3±0.28			



Figure C-1 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 50 NTU using alum



Figure C-2 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 50 NTU using alum with 0.01 mL of silk sericin

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Figure C-3 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 75 NTU using alum



Figure C-4 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 75 NTU using alum with 0.01 mL of silk sericin



Figure C-5 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 100 NTU using alum



Figure C-6 Kinetic of the efficiency of the removal of turbidity of synthetic turbid water at 100 NTU using alum with 0.01 mL of silk sericin

### APPENDIX D

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# Efficiency of turbidity removal in surface water

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				Alum		Turbidity	Turbidity	%	
	рН	рН	Temperature	concentration	Silk cericin	initial	final	Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	6.85	6.8	25.3	0	0	72.5	59.9±1.97	19±4.92	3725
2	6.85	5.32	25.3	20	0	72.5	7.45±0.64	90±1.14	1731
3	6.85	5.22	25.3	40	0	72.5	2.27±0.03	97±0	1704
4	6.85	4.98	25.3	60	0	72.5	2.09±0.07	97±0	1776
5	6.85	4.76	25.3	80	0	72.5	1.86±0.06	97±0	1619
6	6.85	4.53	25.3	100	0	72.5	2.18±0.04	97±0	1587

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# Table D-1 Efficiency of the removal of turbidity of surface water using alum

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				Alum		Turbidity	Turbidity	%	
	pН	pH	temperature	concentration	Silk cericin	initial	final	Removal	тос
Sample No.	initial	final	°C	(mg/L)	mL	(NTU)	(NTU)	Efficiency	mg/L
1	6.85	6.79	25.2	0	0.01	76.5	63.60±0.84	1 <del>9±</del> 3.44	3704
2	6.85	5.88	25.2	20	0.01	76.5	12.65±0.41	84±1.10	1682
3	6.85	5.75	25.2	40	0.01	76.5	2.95±0.16	96±0.09	1753
4	6.85	5.61	25.2	60	0.01	76.5	3.19±0.09	96±0	1917
5	6.85	4.83	25.2	80	0.01	76.5	2.30±0.18	97±0	1442
6	6.85	4.67	25.2	100	0.01	76.5	4.99±0.89	94±0.95	1450

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### Table D-2 Efficiency of the removal of turbidity of surface water using alum with 0.01 mL of silk sericin

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## APPENDIX E

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# Kinetics of turbidity removal efficiencies of Surface Water

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Time.	Alum concentration. mg/L									
min	0	20	40	60	80	100				
0	72.5±1.27	72.5±1.27	72.5±1.27	72.5±1.27	72.5±1.27	72.5±1.27				
5	75.9±2.19	66.0±0.77	72.5±2.89	66.9±0.70	68.4±0.56	67.3±0.56				
10	76.2±2.22	61.0±1.41	60.5±1.55	63.4±0.70	62.9±0.21	63.2±1.13				
15	75.1±1.48	43.7±1.62	48.9±2.26	46.3±0.77	51.8±1.20	59.3±0.56				
20	75.9±0.98	58.2±1.83	66.2 <del>±</del> 0.91	66.7±0.56	66.3±2.05	66.9±1.41				

 Table E-1 Relation of time of the efficiency of the removal of turbidity of surface water using alum dosage

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 Table E-2 Relation of time of the efficiency of the removal of turbidity of surface water using alum with 0.01 mL of silk sericin

	Alum concentration. mg/L									
Time. min	0	20	40	60	80	100				
0	76.5±2.38	76.5±2.38	76.5±2.38	76.5±2.38	76.5±2.38	76.5±2.38				
5	80.1±0.77	67.2±1.90	66.0±0.35	66.5±1.62	66.8±0.77	64.9±0.07				
10	77.4±1.41	60.2±0.77	60.5±2.82	60.9±1.41	59.8±2.12	60.5±0.21				
15	76.9±2.33	43.1±0.49	44.7±0.56	44.9±3.18	50.8±4.24	59.6±4.24				
20	77.8±0.84	55.0±0.91	64.1±3.88	64.4±1.20	68.6±1.69	68.0±0.70				



Figure E-1 Kinetic of the efficiency of the removal of turbidity of surface water using alum



dosage

Figure E-2 Kinetic of the efficiency of the removal of turbidity of surface water using alum with 0.01 mL of silk sericin

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### APPENDIX F

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# Synthetic turbid water using silk sericin as coagulant

			temperature	Alum concentration	Silk cericin	Turbidity	Turbidity	% Removal
Sample No.	pH initial	pH final	°C	(mg/L)	mL	initial	final	Efficiency
1	7	6.95	24.6	0	0	53.6	35.8±2.25	33±4.24
2	7	7.07	24.6	0	0.1	53.6	33.7±2.68	37.5±4.94
3	7	7.22	24.6	0	0.2	53.6	47.1±1.55	12±2.82
4	7	7.35	24.6	0	0.3	53.6	53.15±1.48	1±2.82
5	7	7.33	24.6	0	0.4	53.6	56.05±1.06	0±0
6	7	7.37	24.6	0	0.5	53.6	59.0±0.28	0±0

 $\sim -iN_{\rm eff}$ 

# Table F-1 Turbidity removal efficiencies of synthetic turbid water at 50 NTU using silk sericin as coagulant

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Sidxay Makvilay, Wipada Sanongraj and Sompop Sanongraj. Potential study of silk sericin as coagulant aid for removal of synthetic turbid water. The Proceedings of 9<sup>th</sup> Asian-Pacific Regional Conference on practical Environmental Technologies, March 24-27, 2010, at UbonRatchathani University, Ubonratchathani, Thailand, Organized by the Environmental Engineering Association of Thailand