



## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

1.	Urea fertilizers 46-0-0	Rojpanakit Co., Ltd.
2.	Commercial cardanol	commercial grade
3.	Commercial tung oil	Bank of Thailand
4.	Commercial linseed oil	Union Chemical 1986 Co., Ltd.
5.	Cobalt napthenate	Fluka
6.	<i>tert</i> -butylhydroperoxide	Merck
7.	<i>p</i> - dimethylaminobenzaldehyde	analytical grade, Riedel
8.	Ethanol	Merck
9.	Hydrochloric acid	Merck
10.	Sodium hydroxide	Merck
11.	Salicylaldehyde	Merck
12.	Ethylenediamine	Merck
13.	Iron(III)chloride	Merck
14.	Dichloromethane	Merck
15.	Petroleumether	Merck
16.	Hydrogen Peroxide 30%	Merck
17.	Sulfuric acid	Merck

#### 3.2 Equipments

##### 3.2.1 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) model JSM-5410V, JEOL, Tokyo Japan, was used to measure the thickness of coatings and observe the morphology of surfaces.

### **3.2.2 UV-VIS Spectrophotometer**

The UV absorbance was read at 440 nm [4] on Microtiter plate reader, BioTek Synergy HT, for determining the contents of released urea.

### **3.2.3 Fourier Transform Infrared Spectrophotometer (FT-IR)**

The FT-IR spectra were recorded on a Perkin Elmer, Nicolet Impact 410 Fourier Transform Infrared Spectrophotometer. Solid sample were formally examined by incorporating the sample with potassium bromide (KBr) to form a pellet.

### **3.2.4 Nuclear Magnetic Resonance Spectrometer (NMR)**

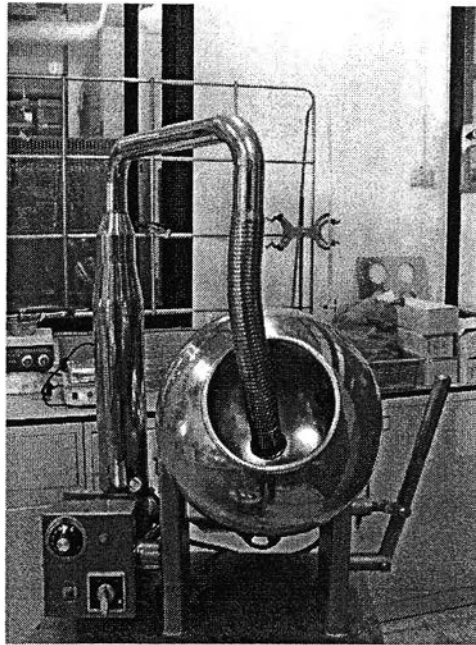
The  $^1\text{H}$  NMR spectra was recorded on a Varian, model Mercury+400 nuclear magnetic resonance spectrometer operating at 400 MHz. Chemical shifts are reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent signal as a reference.

### **3.2.5 Gel permeation Chromatography (GPC)**

The molecular weight and molecular weight distributions of polycardanol were determined by Gel Permeation Chromatography (GPC) using HPLC grade THF as eluent, Water E600 column connected to the refractive index detector. The flow rate was 1 mL/min. Narrow PS standards were used for the calibration curve.

### **3.2.6 Rotation drum (pan coater)**

A pan coating equipment, was used as lab-scale fertilizer coating. The pan coater combined with a rotatable pan for mixing and adjustable air blower for drying was used for fertilizer coating.



**Figure 3.1** Rotation drum

### **3.2.7 Scratch test**

The scratch test was usually defined as the resistance to deformation caused by attempted penetration of another body. This is represented by the force (g) which applied to the film.



**Figure 3.2** Scratch test

### 3.2.8 Specular glossmeter

The specular glossmeter was measured gloss which gloss directs a light at a specific angle to the test surface.

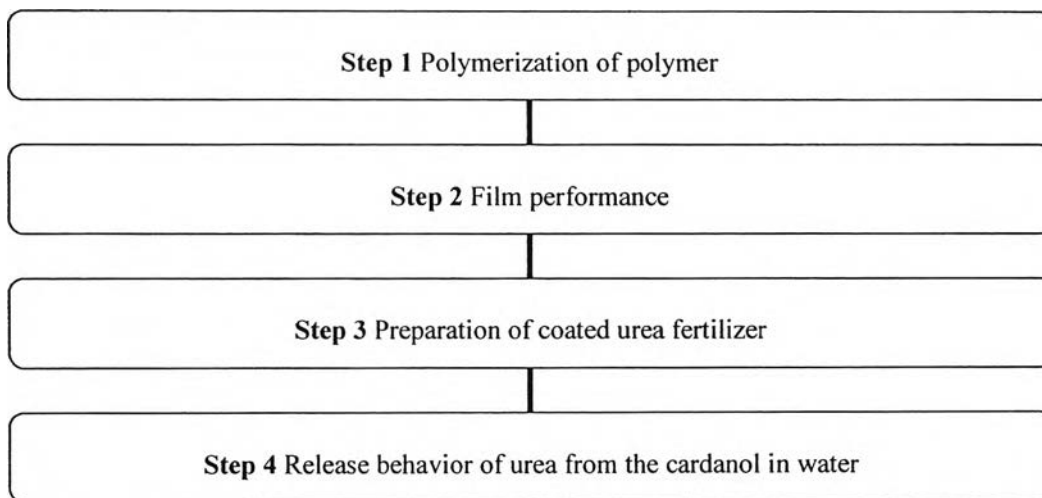


**Figure 3.3** Specular glossmeter

### 3.2.9 Viscometer

Viscometer model RION VISCOTESTER VT-04 was used to measure viscosity.

### 3.3 Experiments



**Figure 3.4** Step of experimental

Four types of cardanol desired coating including polycardanol, cardanol-tung oil, cardanol-linseed oil, and cardanol-formaldehyde were prepared. Polycardanol was synthesized by oxidative polymerization. The drying oil was heated before reacting with polycardanol to form cardanol-tung oil and cardanol-linseed oil, respectively. Cardanol-formaldehyde was synthesized by condensation reaction.

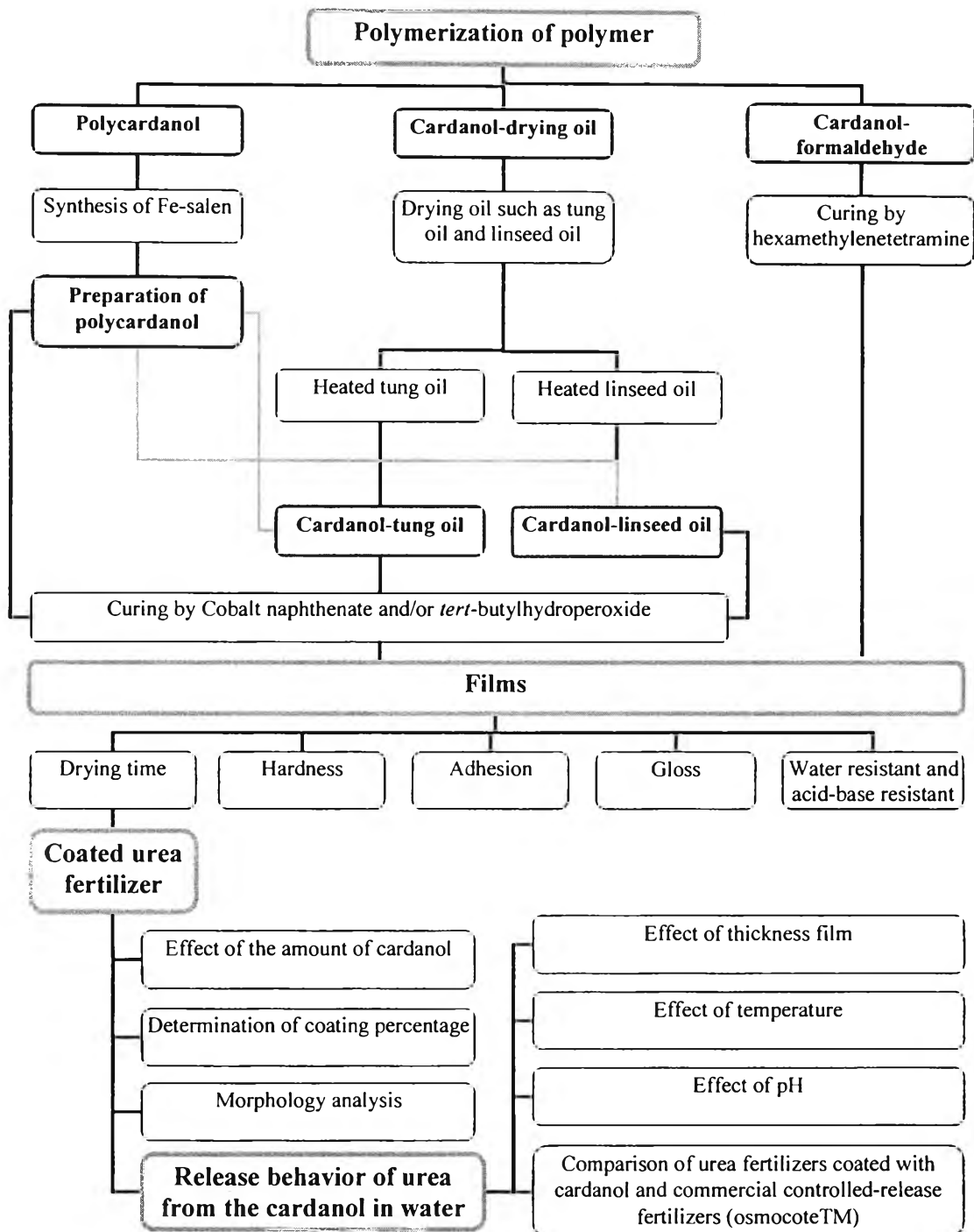


Figure 3.5 The experimental procedures

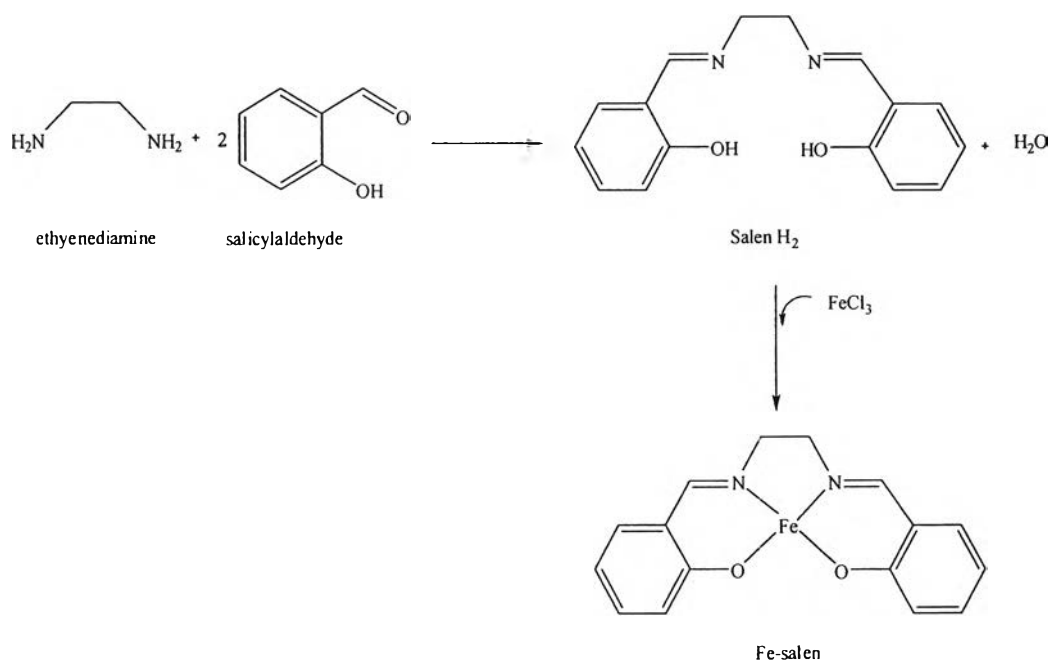
### 3.3.1 Polymerization of polymer

Cardanol was prepared by prepolymerization or applying a mixture of cardanol that was processed through polymerization with drying oil or condensation reaction of cardanol between cardanol and formaldehyde.

#### 3.3.1.1 Preparation of polycardanol

##### 3.3.1.1.1 Preparation of catalyst [31]

Fe-salen is used as a catalyst for polymerization of cardanol.



**Scheme 3.1** Synthesis of Fe-salen

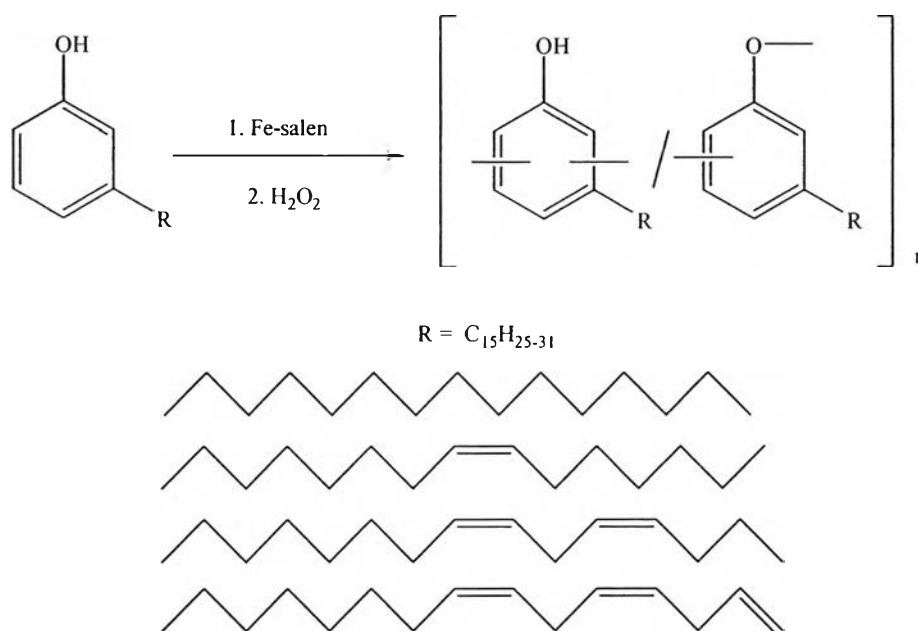
#### Procedure

Salen [N,N-ethylenebis(salicylidene-aminato)] was prepared by reaction of ethylenediamine and salicylaldehyde in ethanol. A 0.1 mol aliquot of ethylenediamine was first dissolved in 25 ml of ethanol, and then this mixture was added to the solution of 0.2 mol of salicylaldehyde in 150 ml of ethanol under stirring condition.

The obtained solution was refluxed for 1 h, and finally cooled-down and kept at ambient temperature for 3 h. The yellow solid product was filtered and recrystallized from ethanol.

Fe-salen complex was prepared using the following method: 0.01 mol of salen was dissolved in 50 ml of ethanol, and then the mixture was heated to boiling temperature. This was followed by the dropwise addition of a solution of 0.01 mol of iron(III)chloride in 125 ml of ethanol. The resultant solution was stirred and refluxed for 1 h. After the solution was cooled to room temperature, the product was separated by filtration and recrystallization from  $\text{CHCl}_3$ /petroleum ether.

### 3.3.1.1.2 Preparation of polycardanol [7]



**Scheme 3.2** Oxidative polymerization of polycardanol by Fe-salen and  $\text{H}_2\text{O}_2$

The following is a typical procedure for the polymerization. Under air, cardanol (6.0 g, 20 mmol) and Fe-salen (64 mg, 0.20 mmol) were placed in a dried glass flask. Hydrogen peroxide (30% aq. solution, 2.3 mL) was added under gentle stirring in air for 2 h. The residual monomer was removed by reprecipitation using methanol as non-solvent. A small portion of polycardanol was sampled for determination of molecular weight of the polymer by Gel Permeation



Chromatography (GPC) and determination of viscosity by viscometer. The structure of polycardanol was confirmed by Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infrared Spectroscopy (FT-IR).

### **3.3.1.2 Preparation of cardanol-drying oil**

**Preparation of polycardanol** such as 3.3.1.1.2

**Preparation of drying oil such as tung oil and linseed oil [30]**

The following is a typical procedure for the polymerization. The drying oil and 2% (w/w) Cobalt naphthenate were placed in a dried glass flask under gentle stirring in air at 150°C. The air was blown continuously through the oils. A small portion of drying oil was sampled for determination of viscosity by viscometer.

#### **3.3.1.2.1 Preparation of cardanol-tung oil**

The ratio of polycardanol: tung oil was varied from 9:1, 8:2, 7:3, 6:4 and 5:5, respectively.

#### **3.3.1.2.2 Preparation of cardanol-linseed oil**

The ratio of polycardanol: linseed oil was varied from 9:1, 8:2, 7:3, 6:4 and 5:5, respectively.

#### **3.3.1.3 Preparation of cardanol-formaldehyde resin [32]**

The cardanol-formaldehyde was prepared by the reaction of cardanol and formaldehyde with a molar ratio of 0.8:1 in 1% (w/w) concentrated sulfuric acid (pH 2.2). The reaction was kept at 100°C for 7 h, and the resulting viscous resin was added to toluene, washed with water, and then dried in vacuum at 70°C for 4 h. The structure of polycardanol was confirmed by Nuclear Magnetic Resonance Spectroscopy (NMR).

#### **3.3.1.4 Curing of polymer**

For curing test, the preparative production of polycardanol, cardanol-tung oil, and cardanol-linseed oil were performed. They were catalyzed Cobalt naphthenate and *tert*-butylhydroperoxide. The amount of catalyst was varied from 2, 4 and 6 percent by weight at 80 °C. While, the curing of cardanol-formaldehyde was carried out using 15% hexamethylenetetramine (HMTA) at 80°C.

### **3.4 Film performance**

The coating performance of the cured films was evaluated by determining drying time, hardness, gloss, adhesion, water resistance, and acid-base resistance using the standard method.

#### **3.4.1 Dry-hard Time Test [33]**

The end of the thumb resting on the test film and forefinger supporting on test panel, exert a minimum downward pressure of the thumb on the film. Lightly polish the contacted area with a soft cloth. The film was considered dry-hard when any mark left by the thumb was completely removed by the polishing operation.

#### **3.4.2 Hardness [34]**

Hardness property was usually defined as the resistance to deformation caused by attempted penetration of another body. Film hardness was tested by an automatic scratch test. This is represented by the force (g) which applied to the film.

#### **3.4.3 Adhesion [35]**

Adhesion test was determined by a very simple method which found widespread use in coating is the grid method. The method consist in making five to ten parallel cuts though the film to the substrates at distance of 1 mm apart, followed by repeating the cuts across those already made and at right angle to them. This gives a grid of squares of 1 mm<sup>2</sup>. The adhesion is judged to be good if the squares all sit fast and are not easily removed by stroking with the finger tip. In order to obtain a numerical result, a piece of pressure adhesive tape is applied to the grid and then

jerked away. The number of squares which are not removed from the substrate is a measure of the adhesion. (Appendix D1)

#### **3.4.4 Gloss [36]**

Gloss was measured by using a gloss meter which directs a light at a specific angle to the test surface. Gloss was measured by shining a known amount of light at a surface and quantifying the reflectance. The angle of the light and the method by which the reflectance is measured are determined by the surface. The measurement results in % reflection of the illuminated light.

#### **3.4.5 Water resistance and acid-base resistance**

Resistance test of the films toward distilled water, acid (23% sulfuric acid) and basic (1N NaOH) solutions was carried out. The samples were used for the evaluation. The film on the glass slide was immersed in the solution at room temperature. After 24 h (distilled water or NaOH) or 96 h (sulfuric acid), the film was washed with water and kept for 2 h for the observation of the film appearance.

### **3.5 Preparation of coated urea fertilizers**

#### **Pan coating process**

In this study, granular fertilizers are coated with cardanol and drier solution, which acts as a hydrophobic barrier. Procedure of fertilizer coating method was described below.

#### **3.5.1 Coated of urea fertilizer (urea 46-0-0) with cardanol**

Fertilizers were dried in an oven at 80°C for 24 h to remove moisture from granular fertilizers, and then kept in desiccator. The coated fertilizers were prepared by pan coating method. Approximately 100 g of granular fertilizers was placed into coating drum of pan coater followed by cardanol and catalyst. While fertilizer was coating, hot air was allowed to flow into coating drum in order to dry the granular fertilizers. The coatings fertilizer was placed in an oven at 80°C for 24 hours period to

allow the coated layer to dry. Multiple coatings were prepared by coated single-coated dried fertilizer granules several times with cardanol.

### 3.5.2 Effect of the amount of cardanol

The amount of cardanol was varied from 6, 10 and 15 part per hundred.

### 3.5.3 Determination of coating percentage [5]

Coated urea fertilizer (10 g) was ground with mortar and pestle and added into 250 mL deionized water. After 15 minute, the solution was filtered and the insoluble solid was washed with deionized water to ensure that no urea remained and dried in the oven at 100 °C for 4 hours or until its become constant.

### 3.5.4 Morphology analysis

The coating morphology was examined using a scanning electron microscopy (SEM). Before the measurement, the coated fertilizer granule was cut to obtain cross sections, and then coated with a gold layer for SEM observation. The thickness of each sample was averaged and calculated for the standard deviation (S.D.).

## 3.6 Release behavior of urea from the cardanol in water

The urea releasing from coated fertilizers was determined by using colorimetric method following the analytical protocol described by Potts [37]. *p*-Dimethylamino benzaldehyde (*p*-DMAB) reacts rapidly with many primary amines. According to Ehrlich reaction, *p*- dimethylamino benzaldehyde could react with urea to give lemon kelly color which absorbs visible light at 440 nm.

### 3.6.1 The method for determination of urea content

#### Reagent

*p*-Dimethylaminobenzaldehyde (DMAB) 8.00 g was dissolved in 500 ml 95% ethyl alcohol and 50 ml concentrated HCl. The solution was stable for 1 month.

### **Calibration curve**

The standard urea solutions were prepared by dissolving 5.000 g urea in water and diluted to 1000 ml. Then, pipetted 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ml into 250 ml volumetric flasks and diluted to volume with DI water. Before determining the urea released content, the absorbance of standard urea solution was determine and calibration curve was plotted.

### **Sample preparation**

Approximately 0.5 g of coated fertilizer was placed in 100 mL of deionized water maintained at room temperature. When reached the settle time, fertilizer was filtered from the urea solution. Urea content of the urea solution was determined by using UV-Vis spectroscopy.

### **Determination of urea concentration**

The sample solution was mixed with DMAB solution in ration 1:1 by volume. The mixture was allowed to react at room temperature for 10 minutes. Then the mixture was transferred into a 96-well microtiter plate and the absorbance of urea-DMAB complex was measured at 440 nm [4] and using a 1: 1 mixture of water and DMAB solution as blank (100% transmittance). The measuring of absorbance for each sample was duplicated.

## **3.6.2 Factors controlling urea release**

### **3.6.2.1 Effect of film thickness**

In this study, the effect of number layer of cardanol to release rate of nutrient was investigated. Fertilizer granules were coated with cardanol for one layer, three layers, five layers, seven layers, nine layers

Samples under temperature controlled, were collected 1, 2, 3, 4, 5, 6, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77, and 84 day. The solution was collected and analyzed for the amount of urea.

### **3.6.2.2 Effect of temperature**

The effect of temperature on the release rate of nutrients through the polymer coating was also determined. The test was performed at temperature of 25, 30, 35, and 40 °C in aqueous medium

Samples under temperature controlled, were collected every 2 day. The solution was collected and analyzed for the amount of urea.

### **3.6.2.3 Effect of pH**

The effect of pH on the release rate of nutrients through the polymer coating was also determined. The test was performed at pH 5, 6, 7, and 8 in aqueous medium.

Samples under temperature controlled, were collected every 2 day. The solution was collected and analyzed for the amount of urea.

### **3.6.2.4 Comparison of urea fertilizers (fertilizer 1 month for rice) coated with cardanol and commercial controlled-release fertilizers (osmocote™ 16-16-0; fertilizer 6 month for flower plant)**

Comparison on the release rate of nutrients of urea fertilizers coated with cardanol and commercial controlled-release fertilizers (osmocote™) was also determined. The test was performed at  $31 \pm 2^\circ\text{C}$  in aqueous medium

Samples under temperature controlled, were collected at 1, 2, 3, 4, 5, 6, 7, 14, 21, 28, and 35 day. The solution was collected and analyzed for the amount of urea.