

การควบคุมการละลายของเม็ดปุ๋ยโดยการเคลือบไคโตซาน



นาย พีรพงศ์ หาญพิชาญชัย

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2545

ISBN 974-17-2552-3

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CONTROLLED RELEASE OF GRANULAR FERTILIZER
USING CHITOSAN COATING



Mr. Peerapong Hanpichanchai

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2002

ISBN 974-17-2552-3

พีรพงศ์ หาญพิชาญชัย : การควบคุมการปลดปล่อยของเม็ดปุ๋ยโดยการเคลือบไคโตซาน.
(CONTROLLED RELEASE OF GRANULAR FERTILIZER USING CHITOSAN
COATING) อ. ที่ปรึกษา : อ.ดร. เจิดศักดิ์ ไชยคุนา, 82 หน้า. ISBN 974-17-2552-3

งานวิจัยนี้เป็นการศึกษาการควบคุมการปลดปล่อยของเม็ดปุ๋ยโดยวิธีเคลือบด้วยไคโตซาน ไคโตซานที่มีร้อยละของการกำจัดหมู่อะซิทิล ร้อยละ 79 และ ร้อยละ 95 จะถูกละลายในกรดอะซิติกเข้มข้น 1 โมลาร์ เพื่อให้ได้สารละลายไคโตซานที่มีความเข้มข้นร้อยละ 1 2 และ 3 โดยน้ำหนัก ศึกษาผลกระทบจากปริมาณของธาตุอาหารในปุ๋ยต่ออัตราการละลาย สารละลายไคโตซานจะถูกพ่นลงบนเม็ดปุ๋ยภายในถังเคลือบ และนำไปอบที่อุณหภูมิ 75 องศาเซลเซียสเป็นเวลาานาน 24 ชั่วโมง ปุ๋ยที่เคลือบด้วยไคโตซานจะนำไปศึกษาการละลายของธาตุอาหารในน้ำกลั่น และวัดปริมาณของธาตุอาหารซึ่งได้แก่ ไนโตรเจน ฟอสฟอรัส และ โพแทสเซียม ตามเวลาที่กำหนด

จากผลการทดลองพบว่า ไนโตรเจน ฟอสฟอรัส และ โพแทสเซียม ที่ปลดปล่อยออกมาจากปุ๋ยที่เคลือบด้วยไคโตซาน มีปริมาณน้อยกว่าปุ๋ยที่ไม่ได้เคลือบ อัตราการปลดปล่อยของธาตุอาหารจะขึ้นอยู่กับความเข้มข้นของสารละลายไคโตซาน และค่าร้อยละของการกำจัดหมู่อะซิทิลของไคโตซาน ปุ๋ยที่เคลือบด้วยสารละลายไคโตซานที่มีความเข้มข้นสูง และปุ๋ยที่เคลือบด้วยสารละลายไคโตซานที่มีค่าร้อยละของการลดหมู่อะซิทิลน้อย จะมีอัตราการปลดปล่อยธาตุอาหารช้าลง อัตราการปลดปล่อยธาตุอาหารจากปุ๋ยที่เคลือบด้วยไคโตซานจะขึ้นอยู่กับปริมาณของธาตุอาหารในปุ๋ยเคลือบ

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อ.....
สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา.....2545.....ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

437042722: MAJOR CHEMICAL ENGINEERING DEPARTMENT

KEY WORD: FERTILIZER/ CONTROLLED RELEASE/ CHITOSAN/ COATING

PEERAPONG HANPICHANCHAI : CONTROLLED RELEASE OF
GRANULAR FERTILIZER USING CHITOSAN COATING. THESIS

ADVISOR: JIRDSAK TSCHEIKUNA, Ph.D., 82 pp. ISBN 974-17-2552-3

Effects of concentration and degree deacetylation of chitosan solution on released rate of chitosan coated fertilizer was investigated in this study.

Concentrations of chitosan solution are 1%, 2%, 3% by weight dissolved in 1 M. acetic acid solution. Degrees of deacetylation of chitosan are 79% and 95%. The effect of different amount of nutrient elements on the release rate was also studied. The fertilizer was coated with chitosan solution in a coating drum and dried at 75°C for 24 hours. Coated fertilizer was put into deionized water and, at a specified period, water solution was analyzed for amounts of nitrogen, phosphorus, and potassium.

The results showed that amounts of nitrogen, phosphorus, and potassium released from coated fertilizer were less than the uncoated one. The release rate depends on concentration of chitosan solution and degree of deacetylation. The fertilizer coated with high concentration of chitosan solution has low release rate while fertilizer coated with chitosan having low degree of deacetylation also has low release rate. The release rate observed in this study depends on amounts of nutrient elements in the fertilizer.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Department...Chemical Engineering.....Student's signature.....

Field of study...Chemical Engineering.....Advisor's signature.....

Academic year..... 2002.....Co-advisor's signature.....

ACKNOWLEDGEMENT

The Author would like to express his gratitude and appreciation to his advisor, Dr. Jirdsak Tscheikuna for his guidance, valuable help and supervision during this study. In addition, he is also grateful to Assistant Professor Dr. Sasithorn Boon-Long, Assistant Professor Dr. Vichitra Chongvisal and Dr. Khemarath Osathaphan for serving as chairman and member of the thesis committee, respectively. In addition, he is very grateful to staffs at the Scientific and Technology Research Equipment Center, Chulalongkorn University. Finally, he would like to thank his parents and family, and his friends for their encouragement and financial support throughout this study.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT (IN ENGLISH).....	iv
ABSTRACT (IN THAI).....	v
ACKNOWLEDGEMENT.....	vi
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
CHAPTER	
1. INTRODUCTION.....	1
2. LITERATURE REVIEWS.....	3
2.1 Plant nutrients.....	3
2.1.1 Nutrient element form in soil.....	4
2.1.2 Nutrient losses from soil.....	4
2.2 Fertilizer.....	5
2.2.1 Nitrogen Fertilizer.....	6
2.2.2 Nitrogen losses from the system.....	6
2.2.3 Phosphorus fertilizer.....	7
2.2.4 Phosphorus losses from the system.....	7
2.2.5 Potassium fertilizer.....	7
2.2.6 Potassium losses from system.....	8
2.2.7 Fertilizer grade.....	8
2.3 Controlled release fertilizer.....	9
2.4 Type of element used the coated material.....	9
2.5 Chitosan.....	11
2.5.1 Characteristics of chitosan.....	13
2.5.2 Applications of chitosan.....	15
2.6 Linear least square fit method.....	18
3. EXPERIMENTAL AND ANALYSISMETHOD.....	20
3.1 Preparation of chitosan solution.....	20
3.2 Coating Fertilizer method.....	20

CONTENTS (Continued)

	Page
3.3 Experiment apparatus.....	21
3.4 Analytical method.....	23
3.4.1 Nitrogen analytical method.....	24
3.4.2 Phosphorus analytical method.....	25
3.4.3 Potassium analytical method.....	26
3.5 Experimental error.....	27
4. RESULTS AND DISCUSSIONS.....	30
4.1 Solubility of uncoated fertilizer.....	31
4.2 Appearance of chitosan coated fertilizer.....	39
4.3 Effects of concentration of chitosan solution.....	42
4.4 Effect of degree of deacetylation.....	47
4.5 Effect of different grade of fertilizer.....	50
4.6 Effect of number of chitosan layer.....	54
5. CONCLUSIONS AND RECOMMENDATIONS.....	59
5.1 Conclusions	59
5.2 Recommendation.....	60
REFERENCES.....	61
APPENDICES.....	65
Appendix A.....	66
Appendix B.....	75
VITA.....	82

LIST OF TALBES

Table	Page
2.1 Solubility of chitosan in various acids.....	14
3.1 Variable of the experiments.....	22
3.2 Amount of nitrogen dissolved in water solution repeatability study.....	28
3.3 Amount of potassium dissolved in water solution repeatability study.....	28
3.4 Amount of phosphorus dissolved in water solution repeatability study.....	29
4.1 Experimental conditions.....	30
4.2 Dissolve rate of each section and completely dissolved amount of uncoated fertilizer.....	36
4.3 Dissolve rate of each section and completely released amount of each concentration of chitosan coated fertilizer.....	44
4.4 Dissolve rate of each section and completely released amount of between 79%DD and 95%DD chitosan coated fertilizer.....	47
4.5 Dissolve rate of each section and completely released amount between the different fertilizer grade.....	51
4.6 Dissolve rate of each section and completely released amount between the different number layer of chitosan coated on fertilizer.....	56
1A Condition and results of controlled release experiments of uncoated fertilizer.....	63
2A Condition and results of controlled release experiments of 95%DD and 1% wt. chitosan solution coated fertilizer.....	64
3A Condition and results of controlled release experiments of 95%DD and 2% wt. Chitosan solution coated fertilizer.....	65
4A Condition and results of controlled release experiments of 95%DD and 3% wt. chitosan solution coated fertilizer.....	66

LIST OF TALBES (Continued)

Table	Page
5A Condition and results of controlled release experiments of 79%DD and 2% wt. Chitosan solution coated fertilizer.....	67
6A Condition and results of controlled release experiments of NPK 25:7:7 fertilizer coated with 95%DD and 2%wt chitosan solution.....	68
7A Condition and results of controlled release experiments of NPK 8:24:24 fertilizer coated with 95%DD and 2%wt chitosan solution.....	69
8A Condition and results of controlled release experiments of 5 layers fertilizer coated with 95%DD and 2%wt chitosan solution.....	70
9A Condition and results of controlled release experiments of 10 layers fertilizer coated with 95%DD and 2%wt chitosan solution.....	71
1B Properties of chitosan 79% degree of deacetylation.....	72
2B Properties of chitosan 95% degree of deacetylation.....	73
3B Properties of sulfuric acid.....	74
4B Properties of sodium chloride.....	75
5B Properties of caesium chloride.....	76
6B Properties of Boric acid.....	77
7B Properties of potassium nitrate.....	78

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figure	Page
2.1 Chemical structure of chitin, chitosan, and cellulose.....	12
2.2 The linear least square fit procedure.....	18
3.1 Schematic diagram of coating fertilizer granular.....	22
3.2 Schematic diagram of experimental apparatus.....	21
4.1 Uncoated fertilizer granular.....	32
4.2 The uncoated fertilizer in deionize water at zero minute.....	32
4.3 The uncoated fertilizer in deionize water at 15 seconds.....	33
4.4 The uncoated fertilizer in deionize water at 1 minute.....	33
4.5 The uncoated fertilizer in deionize water at 5 minutes.....	34
4.6 The uncoated fertilizer in deionize water at 15 minutes.....	34
4.7 Dissolution profiles of nitrogen from uncoated fertilizer.....	35
4.8 Dissolution profiles of potassium from uncoated fertilizer.....	35
4.9 Dissolution profiles of phosphorus from uncoated fertilizer.....	36
4.10 Comparison of uncoated fertilizer with chitosan coated fertilizer.....	38
4.11 Chitosan coated fertilizer in deionize water at zero minute.....	39
4.12 Chitosan coated fertilizer in deionize water at 15 second.....	39
4.13 Comparison of release rate of nitrogen between the different concentration of chitosan solution coated fertilizer.....	42
4.14 Comparison of release rate of potassium between the different concentration of chitosan solution coated fertilizer.....	42
4.15 Comparison of release rate of phosphorus between the different concentration of chitosan solution coated fertilizer.....	43
4.16 Comparison of release rate of nitrogen between 79%DD and 95%DD chitosan coated fertilizer.....	46
4.17 Comparison of release rate of potassium between 79%DD and 95%DD chitosan coated fertilizer.....	46
4.18 Comparison of release rate of phosphorus between 79%DD and 95%DD chitosan coated fertilizer.....	47

LIST OF FIGURES (Continued)

Figure	Page
4.19 Comparison of release rate of nitrogen between the different coated fertilizer grade	49
4.20 Comparison of release rate of potassium between the different coated fertilizer grade	49
4.21 Comparison of release rate of phosphorus between the different coated fertilizer grade	50
4.22 One layer coated fertilizer.....	52
4.23 Five layers coated fertilizer.....	53
4.24 Ten layers coated fertilizer.....	53
4.25 Comparison of release rate of nitrogen between the different number of chitosan layer coated on fertilizer.....	54
4.26 Comparison of release rate of potassium between the different number of chitosan layer coated on fertilizer.....	55
4.27 Comparison of release rate of phosphorus between the different number of chitosan layer coated on fertilizer.....	55

CHAPTER I

INTRODUCTION

Fertilizers are materials, which have been used extensively as nutrients for plant growth. At the present, fertilizers can be divided into two general types as natural fertilizer and chemical or synthesis fertilizer. The natural fertilizer is made from carcasses or remains that do not pollute environment, but the synthetic fertilizer is made from chemical materials. Large amounts of synthetic fertilizer are lost because of leaching or uncontrollable release, which increases the risk of surface or ground water pollution. In confronting these problems, controlled release technology is considered as a suitable method. Controlled release method can be used to decrease the lost amounts of nutrients while maintaining the benefits of their effectiveness in plants and reduce the risk of environmental damage (Jesus Novillo, 2001).

Controlled release fertilizers are commonly prepared by encapsulation (coating or matrix formation) of granular plant nutrients with low permeability hydrophobic membranes. Production of controlled release fertilizers uses high quality granular fertilizers which are regularly shaped and have as smooth as possible surfaces. Coating technologies of such fertilizers are complex. When fertilizers are coated with materials such as polyolephines, large quantities of organic solvents are used, where for in situ polymerization, multiple coating layers are required (Uri Shavit et.al, 1997).

Many investigators around the world are working on development of controlled release fertilizers. Many controlled release fertilizers such as urea formaldehyde or sulfur coated urea are commercialized. However, urea formaldehyde suffered from high production cost caused by chemical reaction (Lunt, 1971). Sulfur coated urea required supplementary application of a sealant compound over the sulfur coating to seal minute fissures and pinholes in the coating (Davis, 1976). Moreover, Sulfur has effect acidification of soil, which are serious problems afterward.

Chitosan is a natural polymer useful for medical and pharmaceutical applications (Muzzarelli, 1997). Among biocompatible and biodegradable natural polymers it displays interesting biological activities (Akbuga, 1995). Recent studies prove that chitosan has mucoadhesive properties (Lehr et al., 1992), and therefore it seems particularly useful to formulate bioadhesive dosage forms for mucosal administration. Furthermore, chitosan can be used as the wall material of the capsule. Chitosan capsules can be applied in food, drug, and biochemical areas (Rong Huei Chen, 1997). Controlled release by using chitosan method is often applied to drug controlled release studies. The release behaviors of drug that coated by chitosan-collagen matrices is pH dependent (Kwunchit Oungbho et.al, 1998). Chitosan microspheres cross-linked with glutaraldehyde were used as controlled release drug. Drug delivery was affected by the extent of cross-linking (Jameela S.R. and Jayakrishnas, 1995).

The objectives of this experiment are to study of release rate of chitosan coated fertilizer granular in deionize water, the effect of concentration of chitosan solution, degree of deacetylation, fertilizer grade, and number of coated layer.

In this study, chitosan is used as a coating media for controlled release of fertilizer. Chitosan solution was sprayed on granular fertilizers in a coating drum. After the fertilizers were coated with chitosan and dried, the fertilizer granules were placed in deionized water. At specific time, undissolved matter and water-fertilizer solution is separated by filter paper. The solution is analyzed for dissolved amount of nitrogen, phosphorus, and potassium. Nitrogen is determined to a Kjeldhal method. Phosphorus is determined by Inductively Coupled Plasmaspectrometer (ICP) Analysis. Potassium is determined by Atomic Absorption Spectrophotometer. The release rate of the nutrient element is calculated from the slope of graph that is plotted versus dissolved amount of element and time by least square fit method described in chapter II.

CHAPTER II

LITERATURE REVIEWS

2.1 Plant Nutrients.

Growth of plants needs suitable ratio and quantities element. There were only 16 essential elements of 90 elements, which can generally classify to two types, those are macronutrient elements and micronutrient elements.

Macronutrient elements are the elements that plants need larger amount than other elements for growth. Those are composed of 9 elements. From the air and water, plants utilize hydrogen (H^+ and HOH), oxygen (O_2 , OH^- , CO_3^{2-} , SO_4^{2-}) and carbon (CO_2). The other can classify to two types, primary essential elements and secondary essential elements. Primary essential elements are nitrogen (NH_4^+ and NO_3^-), phosphorus ($H_2PO_4^-$ and HPO_4^{2-}), and potassium (K^+). Secondary essential elements are calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulfur (SO_4^{2-}).

The elements that plant needs lesser amounts for growth are Micronutrient elements. There are 7 elements, which are composed of iron (Fe^{2+} and Fe^{3+}), manganese (Mn^{2+}), copper (Cu^{2+}), boron ($H_2BO_3^-$ and $B(OH)_4^{2-}$), molybdenum (MoO_4^{2-}), chlorine (Cl^-), and zinc (Zn^{2+}) (Raymond and Roy, 1990).

2.1.1 Nutrient Element Form in Soil

Normally, Elements form in soil can be described:

- ◆ Elements are dissolved in soil water. In this form, plants can take up the element
- ◆ Elements are on the soil particle surface. It can change to ion form and used by plants.
- ◆ Soil particle fixes or has chemical reaction with the elements to be in undissolve form or crystallize to solid. It is called Fixation. Plants can not take up this element.
- ◆ Fixation by bacteria is the element, which is temporary fixed by bacteria in soil. The element in this form can change to useable form later. (Yongyuth, 1985).

2.1.2 Nutrient Losses from Soil.

Loss of nutrient is the removal of nutrient elements from plant root area, or changing to unable take up form. The main causes of loss of fertilizer are:

- ◆ Erosion from water.
 - Reduction of the topsoil layer by water stream.
 - Infiltration of water dissolved nutrient element.

- ◆ Transformation of elements
 - Fixation, are the processes which chemical elements are converted from a soluble or exchangeable form to a much less soluble or to a nonexchangeable form (Raymond and Roy 1990).
 - Volatilization, are the processes which chemical elements are converted by denitrification or reduction and vaporize to atmosphere.
 - Burn, high temperature from burn on field destroys nutrient element and bacteria in soil.
 - Chemical reaction to be complex compound, such as phosphorus in high pH soil is transformed to insoluble complex compound.
- ◆ Erosion by wind
- ◆ Loss by human and animal.

2.2 Fertilizers

Fertilizers can generally classify to 2 types, which are:

- ◆ Organic fertilizer. Organic fertilizer is the fertilizer from organic materials, which decompose and convert to fertilizer compound.
- ◆ Inorganic fertilizer. Inorganic fertilizer, the element in fertilizer is synthesized by chemical process. In general it is call synthesis fertilizer or chemical fertilizer. Types of inorganic fertilizer can divide by amount of nutrient element in the fertilizer. Those are Single fertilizer or straight fertilizer, mixture fertilizer, and complex fertilizer.

The nutrient elements that often used with fertilizer compound are nitrogen, phosphorus, and potassium because they are required plants in large quantity (yongyuth, 1985).

2.2.1 Nitrogen Fertilizers.

Nitrogen is essential for all life processes in plants. Application of nitrogen fertilizer usually gives a rapid, visual increase in plant growth, and the use of nitrogen fertilizers has been essential to increase the productivity of agriculture. Generally, nitrogen is in nitrate (NO_3^-) and ammonium (NH_4^+) compound in chemical fertilizer. Examples of nitrogen compound in fertilizer are ammonium nitrate (NH_4NO_3), sodium nitrate (NaNO_3), ammonium phosphate ($(\text{NH}_4)_3\text{PO}_4$), and ammonium chloride (NH_4Cl).

2.2.2 Nitrogen Losses from the System.

- Leaching of soil nitrogen. Both ammonium (NH_4^+) and nitrate ion (NO_3^-) are very soluble in water. But the positively charged ammonium ion is held to cation exchange sites and resists leaching. Leaching losses of nitrates are increased as the quantities of percolating water increase.

- Denitrification, nitrate is changed to nitrogen gas by bacteria.

Denitrification usually occurs when poor aeration limits the amount of free oxygen in the soil. Soil Bacteria are forced to use the nitrogen in nitrate ion as an electron acceptor (normally O_2 is used), leaving the nitrogen gas and nitrous oxide. The gasses vaporize and move from soil to atmosphere.

- Ammonia volatilization, losses occur when ammonium is in a basic solution. The greatest losses occur from surface applications of any ammonium or urea fertilizer on calcareous (high carbonate content), higher temperatures, and low cation exchange capacities of soil.

2.2.3 Phosphorus Fertilizers.

Phosphorus is an essential part of nucleoproteins in the cell nuclei, which control cell division and growth, and of deoxyribonucleic acid (DNA) molecules, which carry the inheritance characteristics of living organisms. The phosphorus compounds that take up by plants are phosphate ion (H_2PO_4^- and HPO_4^{2-}). Phosphorus fertilizer is produced from phosphate rock. Because phosphate rock is undissolved compound, it should react with sulfuric acid or nitric acid transform to soluble compound. Phosphorus compounds that made fertilizer are monoammonium phosphates ($\text{NH}_4\text{H}_2\text{P}_2\text{O}_5$) and diammonium phosphates ($(\text{NH}_4)_2\text{HP}_2\text{O}_5$).

2.2.4 Phosphorus Losses from the System.

Phosphorus is mainly lost by surface runoff, which is the total P lost includes P dissolved in runoff water and P adsorbed to eroded particles. Hence heavy rainfall shortly after surface application of mineral fertilizer or manure can result in substantial losses. Mineralization of crop residues left on the ground gives particles rich in P those are at risk of erosion loss.

2.2.5 Potassium Fertilizers.

Fertilizer application is required in order to ensure and sustain an adequate supply of soluble K. Potassium chloride (KCl) is the major form of K fertilizer. Potassium sulfate (K_2SO_4) and potassium nitrate (KNO_3) are also available for application. They are mainly produced from potassium chloride, and are more expensive. They are preferred for crops that are sensitive to chloride or where there is potential for undesirable accumulation of salts in the soil.

2.2.6 Potassium Losses from System.

Because positively charged potassium ions (K^+) are held in an exchangeable and available form on negatively charged clay particles, potassium is not easily lost from the soil through leaching. Some leaching may take place on very sandy soils because they do not contain enough clay particles or humus to hold potassium. Organic soils (mucks and peats) do not hold potassium as strongly as other positively charged nutrients, such as calcium. Therefore, loss of potassium by leaching is one reason sandy and organic soils.

(Roy H. Follett et.al, 1981; M. Laegreid et.al, 1999; Raymond W. Miller, 1990).

2.2.7 Fertilizer Grade.

Fertilizer grade is the guaranteed minimum analysis in whole numbers, in percent, of the nitrogen, phosphorus, and potassium in a fertilizer material. For example, a fertilizer with a grade of 16:16:16 is guaranteed to contain 16 percent by weight of total nitrogen (N), 16 percent by weight of available phosphoric acid (P_2O_5), and 16 percent by weight of water-soluble potash (K_2O).

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.3 Controlled Release Fertilizer.

Loss of nutrient elements, which described in above parts, is large problem. It cause the insufficient of plant nutrients, increase process cost, and pollution to environment. Controlled release is one method that used to solve this problem.

Fertilizer controlled release method is mainly 3 types, these are:

- Fertilizer whose components have been turned to give difficulty soluble or difficulty decomposable properties through a chemical way.
- Fertilizers, which are turned into difficulty soluble form by some methods, for example incorporation of inorganic substances such as cements or organic substances such as wax.
- Fertilizers which are coated with a water-resisting substance.
(Toshio Fujita et al., 1977)

2.4 Type of Element Used the Coated Material.

- Semi-permeable membrane, the properties of this kind material is insoluble in water but it is permeable compound. The water slowly diffuse passes layer to make osmotic pressure. It breaks the coated layer and release fertilizer.
- Discontinuous or Perforated-impermeable membrane. This material is impermeable compound but it has small holes around surface, that water can diffuse into membrane and dissolve nutrient.
- Solid-impermeable membrane. This material is insoluble compound but it can decompose by bacteria to break the membrane.
(Siriporn, 2001)

Hepburn and Arizal (1988, 1989) prepared controlled release chemical fertilizer by coated sulfur compound on urea fertilizer. The fertilizer can be controlled release but it was not going well because there were a lot of porous on the coated surface. The coated fertilizer was brittle and breakable, there was the complicated production and high cost.

Hudson (1995) prepared the urea fertilizer, which was coated by sulfur, improved the coated surface to none porous and made the fertilizer to have abrasion resistant by sealant. The sealant was mixed from different waxes such as petroleum waxes, synthetic waxes, natural waxes, vegetable and mineral waxes with polymer that was soluble by wax. Then it added conditioner such as diatomaceous earth, calcium silicate, clay minerals, and perlite. Urea fertilizer that was coated by 13% sulfur and 1% sealant has a good moisture barrier. If it added sealant to 1.5%, the abrasion resistant of fertilizer increased and found conditioner improved release rate to slow down.

Robert (1994) found, when fertilizer was mixed with hydrophilic polymers, which classified to natural polymers from polysaccharides, semi-synthetic polymers from cellulose, and synthetic polymer, the release rate of added polymer fertilizer was slower than no added polymer fertilizer. It decreased the loss by leaching of nitrogen and potassium and increased amount of nutrient that was taken up by plant.

Chen and Geiger (1997) prepared urea fertilizer, which was coated by slow permeable polymer. Sulfonated terpolymer of ethylene, propylene and non-conjugated diene were coated to thin film, then repeated coating by sodium lignosulfonate solution from lignin of sulfate or sulfite in the paper pulp process. There was filler, talc or hydrous magnesium silicate that dispersed in the solution. They found the release rate of fertilizer, which coated the outer layer by lignosulfonate and filler was slower than the release rate of one polymer coated layer fertilizer. Because lignosulfonate and filler is moisture barrier and lignosulfonate held the nutrient in granular.

Valkanas (1992) prepared controlled release potassium fertilizer, which was coated by material mixed from paraffin waxes and wood rosin. It found the release rate of nutrient decreased. The release rate mechanism of potassium sulfate explained by square root of time release kinetics of diffusion controlled release mechanism. Release rate of potassium sulfate increased while amount of potassium sulfate increased.

Chang (1997) prepared controlled release urea fertilizer used zeolite, which adsorbed nutrient elements in porous. Then fertilizer was coated by gelatinous substance such as sodium acrylate, polyvinyl chloride, polyvinyl acetate, methyl cellulose, and carboxyl methyl cellulose, called zeolite urea. They found the plants that took up zeolite urea were more growth than the plants that took up regular urea.

Hon (1997) prepared controlled release fertilizer that mixed fertilizer with cellulosic material from newspaper's paper and thermoplastic resin such as polyethylene. They found nitrate was fast released in 24 hours because fertilizer from surface was early released, then concentration of nitrate decreased to constant and released with steady rate.

2.5 Chitosan

Chitosan [(1 → 4)-2-amino-2-deoxy-β-D-glucon] is a hydrophilic cationic polyelectrolyte prepared by N-deacetylation of chitin. Molecular structure of chitin and chitosan, similar to cellulose, are long linear chain molecules of (1-4) linked glycans as shown in Figure 2.1. Repeating unit in chitin is 2-acetamide-2-deoxy-D-glucose (N-acetylglucosamine), while for chitosan it is an inhomogeneous mixture with the deacetylated form (glucosamine).

The molecular weight of chitosan, for commercial product, varies within the range of 10,000-1,000,000 Dalton, depend on its processing conditions. The mole fraction of deacetylated units (glucosamine), define as the degree of deacetylation will usually range from 70%-90% (Waree, 1994).

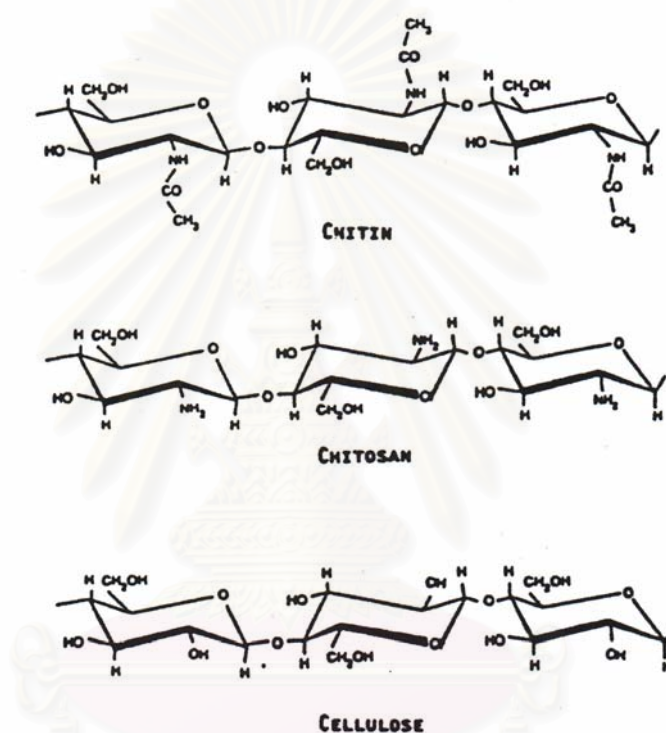


Figure 2.1 Chemical Structure of Chitin, Chitosan and Cellulose

2.5.1 Characteristics of Chitosan

Some important characteristics of chitosan can be briefly mentioned as the following:

Degree of Deacetylation

Chitosan does not refer to a specific compound but to two ranges of copolymers, containing the two monomer residue, anhydro-N-acetyl-Dglucosamine and anhydro-D-glucosamine. The former is the predominant component in chitin and the latter is the predominant component in chitosan. Usually, chitosan has degree of deacetylation between 70% and 90%. The molecular structure and properties of chitosan are affected by the degree of deacetylation.

Solubility

Chitosan is a cationic polymer having a pKa of about 6.3. Its solubility depends on the presence of the free amine groups capable of being protonated by the acid medium. It might be expected that would be a specific level of deacetylation above which solubility in acid solution would be exhibited. Certainly there would appear to be no need for the high level of deacetylation in order to induce solubility in acid solution. For example, chitosan having degree of deacetylation about 64% can be completely soluble (Robert, 1994).

The acid species that can solubilize and insolubilize the chitosan are listed in Table 2.1. Miscibility of chitosan solution with acetone, ethanol and methanol depends on a concentration of the organic solvent (Lower, 1984)

Table 2.1 Solubility of Chitosan in Various Acids.

Type	Soluble in	Insoluble in
Inorganic acid	HCl and HClO ₄	H ₂ SO ₄ and H ₃ PO ₄
Organic acid	Acetic, adipic, citric, formic, lactic, malic, malonic, oxalic, propionic, pyruvic succinic and tartaric acid	

Viscosity

The apparent viscosity of chitosan solution is dependent on the molecular weight, the concentration, the added salt concentration, and the temperature. The viscosity increases with an increase in molecular weight and concentration of chitosan, while it decreases the viscosity with an increase in temperature. The addition of salts will reduce the repelling effect of each positively charged deacetylated unit on neighboring glucosamine unit and will reduce in an extended conformation of the polymer in solution. This effect resulting in a more random coil like conformation of the molecule will decrease the viscosity of chitosan solution (Muzzarelli, 1977).

Crosslinking

Many multivalent anions can be reacted with the chitosan molecules giving the crosslinking products. Crosslinking can be done in acid, neutral or basic environment, depending on methods applied. Several gelling counter ions are available such as alginate, carboxymethyl cellulose, carrageenan, epichlorohydrin heparin, glutaraldehyde, molybdate, oxo acid and pectin (Lower, 1984; Skaugrud, 1989; Mireles et al., 1991).

2.5.2 Applications of Chitosan

Chitosan has been reported to have useful applications in the medical, cosmetic and pharmaceutical area, which are described below.

Medical Application

Chitosan has been used as blood coagulant, a wound healing accelerator, soft and hard contact lens and artificial kidney membrane.

Cosmetic Application

The main application areas in cosmetic are in hair care and skin care consumer products.

Pharmaceutical Application

Chitosan has many applications in pharmaceutical, examples of recent reports of its uses in this area are:

- ◆ As a direct compression diluent.
- ◆ As a vehicle for sustained release.
- ◆ Enhancement of dissolution rate of insoluble drug.
- ◆ As a tablet binder.
- ◆ As disintegrant in pharmaceutical tablet.

- ◆ Formulation of film dosage form.
- ◆ Gel preparation
- ◆ Microencapsulation for anticancer, cell culture and other drugs.
(Waree, 1994)

Rong Huei Chen et.al (1997) studied the effect of Preparation method and characteristics of chitosan on the mechanical and release properties of the prepared capsule. They found axial ratio and hemoglobin release percent of the capsule increased with the increase of the chain flexibility parameter, but decreased with the increased of the chitosan molecular weight or decreased degree deacetylation of chitosan.

Fwu-Long Mi et.al (1997) studied the effect of viscosity and swelling ability on the release rates of drugs, theophylline. Chitosan tablets containing theophylline were prepared by directly compressing the wet or dry blended polymer-drug powders. The results showed the release of theophylline increased with a decrease in the viscosity of the blending chitosan solution. On the other hand, the swelling ability of the polymer greatly influences the release kinetics of the theophylline tablets.

Ida Genta et.al (1998) studied the influence of glutaraldehyde on drug release and mucoadhesive properties of chitosan microspheres. The results had permitted to confirm the high affinity for mucin of uncross-linked chitosan microspheres and thus their bioadhesive properties. Moreover bioadhesive characteristics of the microparticulate drug delivery systems were depressed for glutaraldehyde cross-linked chitosan microspheres.

Thawatchai (1994) studied effect of variables in chitosan film formulations on propranolol hydrochloride tablets. The results showed that the plasticized coated tablets with the higher M.W. of chitosan H exhibited slower drug release than those coated with the plasticized lower M.W. of chitosan. For plasticized coated tablets with chitosan as the amount of propylene glycol increased, the drug release was faster.

Chirasak (1994) studied the feasibility to apply chitin and chitosanas film formers in entirely aqueous-based tablet coating was evaluated using pan-spray method. He found that the drug from coated tablet completely release within 24 hours. The drug release mechanism appeared to be concomitantly a combination of diffusion through the porous film structure and osmotically driven release. Increasing either the coating level or the proportion of water-insoluble film former in the coating formulations resulted in slower drug release characteristics.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

2.6 Linear Least Square fit Method

Linear least square fit is a mathematical procedure, which allows a calculation of the slope (m) and intercept (b) of a straight line that best fits the data. Assume there was data set comes in pairs (x, y) that can be labeled by an integer i . It is also assumed that x and y are functionally related. Each pair can be labeled as (x_i, y_i) . Then, the data pairs when plotted in an x - y diagram appears "correlated" and may be approximated by a straight line of the form.

$$Y_i = mx_i + b$$

Note that x_i are the input values and Y_i are the predicted values of assuming a line of unknown slope, m , and unknown intercept, b . Quantities Y_i and y_i are in general different.

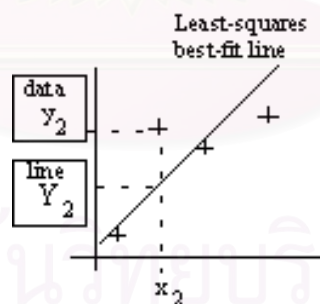


Figure 2.2 The Linear Least Square Fit Procedure.

Assuming such a line exists, the measured data can compare to the theoretical line point by point by computing the differences between the measured and predicted values:

$$(y_1 - Y_1), (y_2 - Y_2), (y_3 - Y_3), (y_4 - Y_4), \dots, \text{etc.}$$

If the assumed line is "balanced" among the data points, the sum of those numbers, $\Sigma(y_i - Y_i)$, approaches zero, since the positive and negative values would nearly cancel. Using the same reasons as in the definitions of variance and standard deviation, let's square the deviations, it end up with a positive number (M: recognize it as cumulative variance) for the sum of squares,

$$M = \Sigma (y_i - Y_i)^2$$

The criterion for a best fit will be to make the sum, M, of the squared deviations as small as possible.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

EXPERIMENTAL PROCEDURE AND ANALYSIS METHOD

3.1 Preparation of Chitosan Solution

In this study, concentrations of chitosan solution are 1%, 2%, and 3% by weight. Approximately 1, 2, and 3 grams of chitosan were dissolved in 1 M. acetic acid solution. The solution was kept for 5 days to allow chitosan to completely dissolve.

3.2 Coating of Fertilizer

In this study, fertilizer granular is coated with chitosan solution, which acts as a hydrophobic barrier. The apparatus used for coating of fertilizer is shown in Figure 3.1. Procedure of coating fertilizer method is described below.

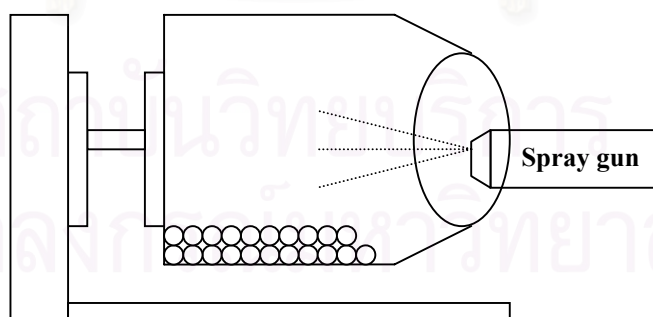


Figure 3.1 Schematic Diagram of Coating Fertilizer Granular

1. Fertilizers were dried in the oven at 75°C for 24 hours to remove moisture from fertilizer granular, and then kept in desiccator.
2. Approximately 100 grams of fertilizer granular was placed into the coating drum, which was rotated at 15 rpm.
3. Approximately 15 ml. of chitosan solution was placed in spray gun and was sprayed on the fertilizer granular.
4. While chitosan solution was spraying, hot air was allowed to flow into coating drum in order to dry the granular.
5. The coated fertilizer was placed in the oven at 75°C for 24 hours period to allow the coated layer to dry.

3.3 Experiment Apparatus

The apparatus was comprised of a 750 ml. polyethylene bottle. Approximately 500 ml. of deionized water was added into the bottle. Then 2 grams of the coated fertilizer having average size of 3-5 mm. were placed into each bottle and kept at room temperature. Table 3.1 shows the variables for this experiment and Figure 3.2 shows the schematic diagram of experimental apparatus. The method for keeping the sample of water-fertilizers solution is described below.

Table 3.1 Variables of the Experiment.

Grade of fertilizer	NPK grade 16:16:16 NPK grade 8:24:24 NPK grade 25:7:7
Chitosan concentration (% wt.)	1 2 3
Degree of deacetylation	79 95

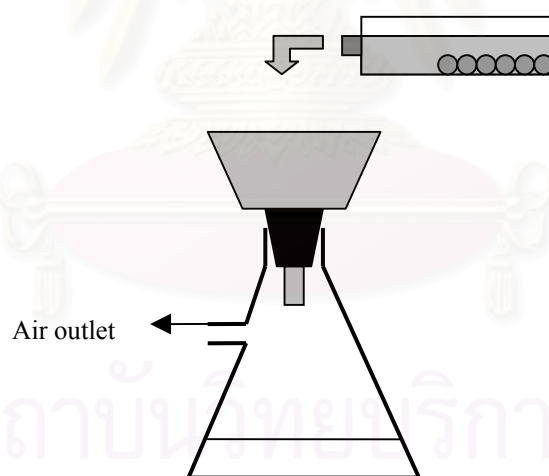


Figure 3.2 Schematic Diagram of Experimental Apparatus

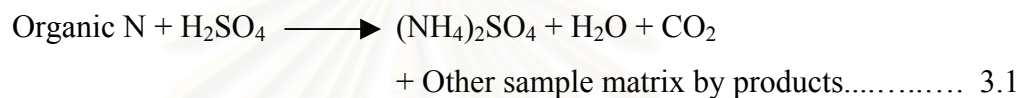
1. The coating fertilizer granular was weighed out approximately 2 grams and put into 500 ml. of deionized water in bottle.
2. Samples, which were water-fertilizer solution, were collected at specific times.
3. The solution was filtered with filter paper to separate insoluble compounds from the water-fertilizer solution.
4. The solution was passed through filter paper into the suction flask, which connected with vacuum pump to remove air in the flask to increase flow rate of solution passing a filter paper.
5. The insoluble compound was placed in the drier for remove moisture and was weighed.
6. The solution in the suction flask was collected in bottle and analyzed for dissolved amount of nitrogen, phosphorus, and potassium.

3.4 Analytical Method

This section described analytical techniques of the experiment. In each experiment, water solution samples were analyzed for dissolved amount of nutrient element such as nitrogen, phosphorus, and potassium. Analytical procedures are described below. Analytical results were shown in chapter IV.

3.4.1 Nitrogen Analytical Method

Kjeldahl method was used in this study to find total nitrogen in the solution. Sample solution was digested before the analysis. The procedure of digestion used concentrated acids, sulfuric acid, to decompose nitrogen in organic samples. After the procedure, nitrogen was exchanged to ammonium sulfate solution as shown in equation 3.1. The solution was analyzed by Kjeldahl method with nitrogen analysis instrument.



Nitrogen Digestion

1. Approximately 10 ml of water solution was introduced into flask.
2. Approximately 1 ml. of concentrated sulfuric acid and catalysts were added into the sample.
3. The solution in the flask was boiled at approximate temperature 390°C for 60 minutes.
4. The flask was removed from the hot plated and cooled to room temperature and then the sample was analyzed.

The results of Kjeldahl analytical method are %nitrogen by volume. It was calculated back to grams of nitrogen by using equation 3.2 and equation 3.3.

$$\text{Grams of nitrogen in water solution} = \frac{C \times V \times MW}{1000} \dots\dots\dots 3.2$$

Where

$$C = \frac{10 \times \%v \times \rho}{MW} \dots\dots\dots 3.3$$

- %v = % nitrogen by volume from Kjeldahl analytical method
- V = Volume of water solution (ml.), 500 ml in this study
- ρ = Nitrogen density = 1.03 kg/m³
- MW = Molecular weight of nitrogen
- C = Concentration of nitrogen solution.

3.4.2 Phosphorus Analytical Method

Amount of phosphorus that dissolved in a sample was determined by Inductively Coupled Plasmaspectrometer (ICP) Analysis. Approximately 20 ml of sample solution was analyzed. In this study, the dissolved amount of phosphorus was determined with Inductively Coupled Plasma spectrometer instrument (Perkin-Elmer Plasma 1000). The results of ICP analytical method gave ppm. Level of phosphorus, which were calculated to gram of phosphorus using equation 3.4.

$$\text{Grams of nutrient} = \frac{m \times M_s}{10^6} \dots\dots\dots 3.4$$

Where m = ppm. of nutrient.

M_s = grams of water solution.

In this study, M_s equaled to 502 grams.

3.4.3 Potassium analytical method

In this study, the dissolved amount of potassium in solution was determined by Atomic Adsorption Spectrophotometer. Atomic Adsorption Spectrophotometer instrument Varian SpectrAA 300 is an instrument to measure amount of the dissolved potassium. The result of this analytical method was at the ppm level of potassium, which were calculated back to gram of potassium by using equation 3.4.

Sample Preparation for Potassium Analysis

1. Approximately 20 ml. of sample solution was put in 120 ml. flask.
2. Approximately 1 ml. of 5% wt. cesium was added into the solution.
3. The solution was diluted to 100 ml. with deionized water and analyzed later.

3.5 Experimental Error

In this section, experiments are conducted to verify the repeatability, and an average and a standard deviation value of the experiment. The experiment was repeated for 5 times at the same condition. Equation 3.2 and Equation 3.3 define an average value and percent deviation.

$$\text{Average value } \bar{X} = \frac{\sum x_i}{n} \dots\dots\dots 3.2$$

$$\text{Percent deviation from average value} = \frac{\sqrt{(x_i - \bar{x})^2}}{\bar{x}} \times 100 \dots\dots\dots 3.3$$

After each experiment, the sample solution was analyzed for the dissolved amount of nitrogen, phosphorus, and potassium. The experiment was repeatedly released at the same condition for 5 times, then the samples was digested and analyzed. Average dissolved amount of each nutrient element and the maximum percent deviation value were calculated and shown in tables 3.2 to 3.4.

From the experiment result, it is certain that the amount of dissolved nutrient in experiment is at 95 % confidence level.

Table 3.2 Amount of the Dissolved Nitrogen in Water-Solution Repeatability Study.

Grade of fertilizer	1 (grams)	2 (grams)	3 (grams)	4 (grams)	5 (grams)	Average amount (grams)	Percent of deviation
16:16:16	0.2189	0.2060	0.2112	0.2060	0.2060	0.2096	4.4226
25:7:7	0.3320	0.3279	0.3250	0.3294	0.3347	0.3298	1.4830
8:24::24	0.1302	0.1306	0.1309	0.1306	0.1307	0.1306	0.3071

Table 3.3 Amount of the Dissolved Potassium in Water-Solution Repeatability Study.

Grade of fertilizer	1 (grams)	2 (grams)	3 (grams)	4 (grams)	5 (grams)	Average amount (grams)	Percent of deviation
16:16:16	0.2598	0.2583	0.2615	0.2610	0.2560	0.2593	1.2727
25:7:7	0.1073	0.1143	0.1078	0.1150	0.1133	0.1115	3.8117
8:24::24	0.3610	0.3568	0.3603	0.3893	0.3900	0.3715	4.9939

Table 3.4 Amount of the Dissolved Phosphorus in Water-Solution
Repeatability Study.

Grade of fertilizer	1 (grams)	2 (grams)	3 (grams)	4 (grams)	5 (grams)	Average amount (grams)	Percent of deviation
16:16:16	0.1151	0.1184	0.1123	0.1122	0.1116	0.1139	3.9546
25:7:7	0.0473	0.0487	0.0500	0.0505	0.0508	0.0495	4.2766
8:24::24	0.1783	0.1796	0.1803	0.1819	0.1879	0.1816	3.4779



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV

RESULTS AND DISCUSSIONS

This Chapter covers all experimental results and discussions for this study. Each experiment was conducted in a batch system. Coated fertilizer was put into deionized water. At specific time, water-fertilizer solution was taken for analysis of nitrogen, phosphorus, and potassium. Table 4.1 shows experimental conditions used in this study.

Table 4.1 Experimental Conditions.

Temperature	30 degree of Celsius
Fertilizers	Grade NPK 16:16:16, Grade NPK 8:24:24, Grade NPK 25:7:7
Concentration of chitosan solution	1% , 2%, 3% by weight dissolved in 1 M acetic acid
Degree of deacetylation of chitosan	79%, 95%
Deionized water	500 ml.
Sampling	At 1, 5, 15, 30, 60, 120, 180, 240 minutes.
Diameter of fertilizer	3-5 mm.

4.1 Solubility of Uncoated Fertilizer

The fertilizer used in this study was uncoated fertilizer available in market. Figure 4.1 shows the photograph of uncoated fertilizer. Figures 4.2 to 4.6 show the photographs of uncoated fertilizer grade 16:16:16 in deionized water at different times. When the fertilizer granular was added into deionized water, the green thin layer, believed to be external layer of fertilizer, started to break up. Then the fertilizer disintegrated into small gray pieces and particles within 15 seconds and completely disintegrated within 15 minutes. Water solution with fertilizer was filtered to remove insoluble matters from water solution. The liquid part was analyzed for nitrogen, phosphorus, and potassium.

Figures 4.7 to 4.9 show amount of each nutrient in fertilizer grade 16:16:16 that dissolved in the water solution plotted as a function of time. It was observed that dissolve rate of fertilizer could be divided into three sections. Initial dissolving of fertilizer occurred during the first minute after it was added into water. It was described as a very fast dissolve rate. The second section occurred between the time of 1 to 15 minutes in which the dissolve rate is slower than the initial section. The third section occurred within the period of 15 to 60 minutes in which the dissolve rate was gradually slow down until complete dissolving. Maximum dissolved amount of nitrogen, phosphorus and potassium was determined as the amount of each nutrient after 60 minutes. Table 4.2 showed the dissolve rate of nitrogen, potassium, and potassium of each section and maximum dissolved amount of each nutrient.



Figure 4.1 Uncoated Fertilizer Granular.

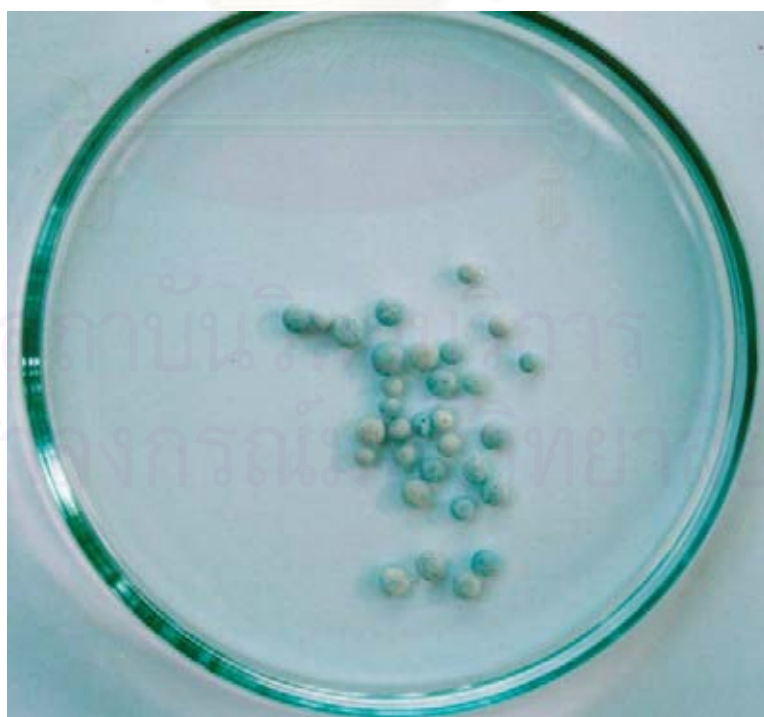


Figure 4.2 The Uncoated Fertilizer in Deionized Water at Zero Minute.

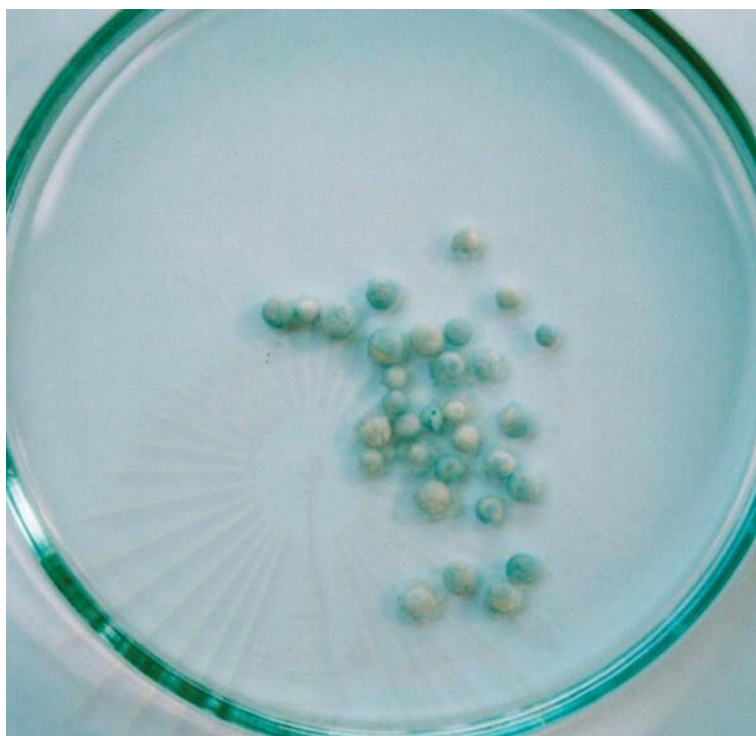


Figure 4.3 The Uncoated Fertilizer in Deionized Water at 15 Second.

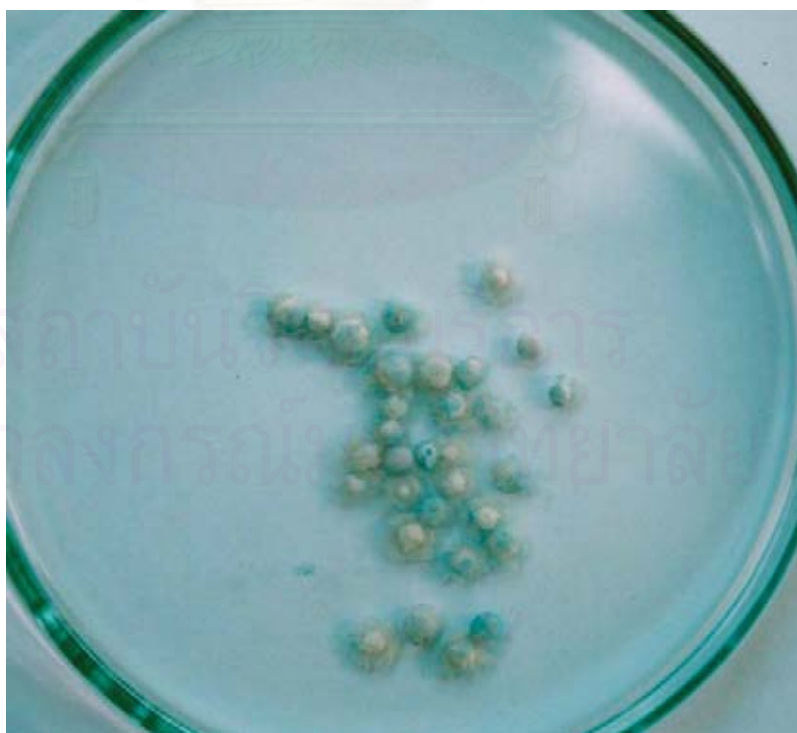


Figure 4.4 The Uncoated Fertilizer in Deionized Water at 1 Minute.

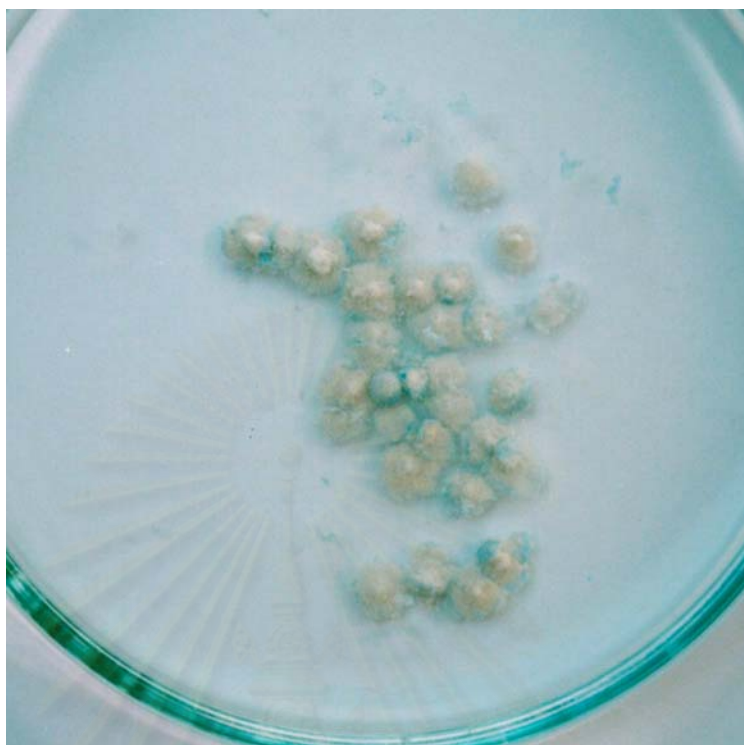


Figure 4.5 The Uncoated Fertilizer in Deionized Water at 5 Minutes.



Figure 4.6 The Uncoated Fertilizer in Deionized Water at 15 Minutes.

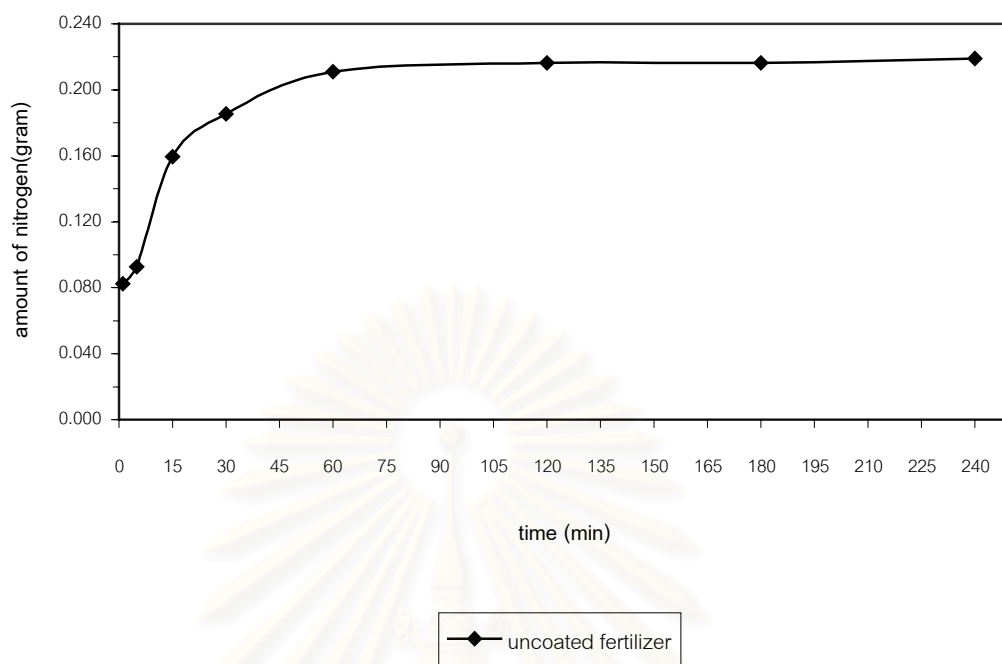


Figure 4.7 Dissolution Profiles of Nitrogen from Uncoated Fertilizer.

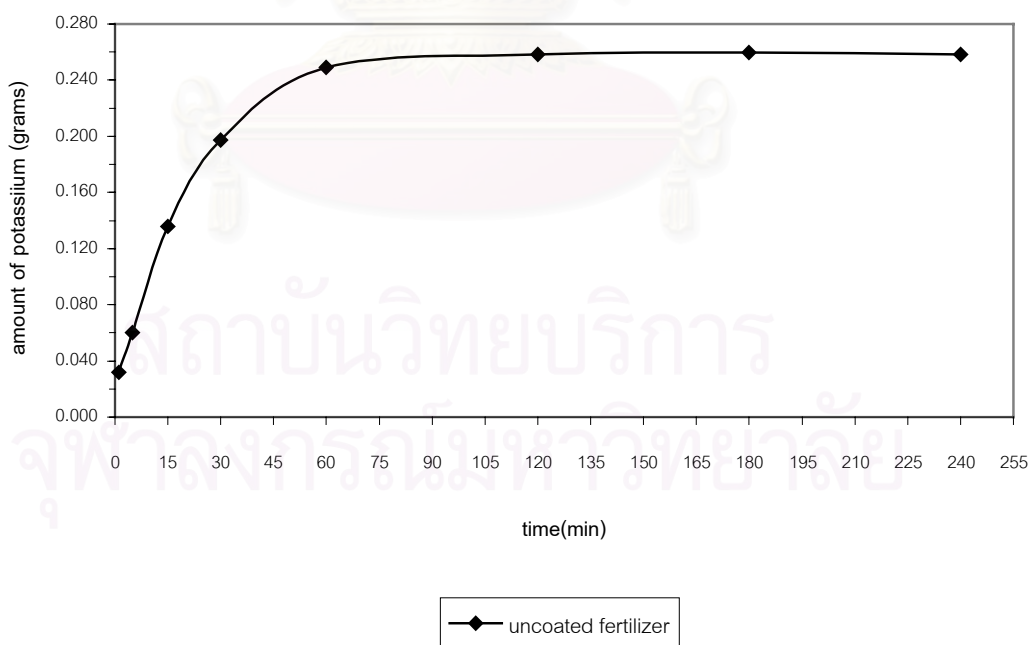


Figure 4.8 Dissolution Profile of Potassium from Uncoated Fertilizer

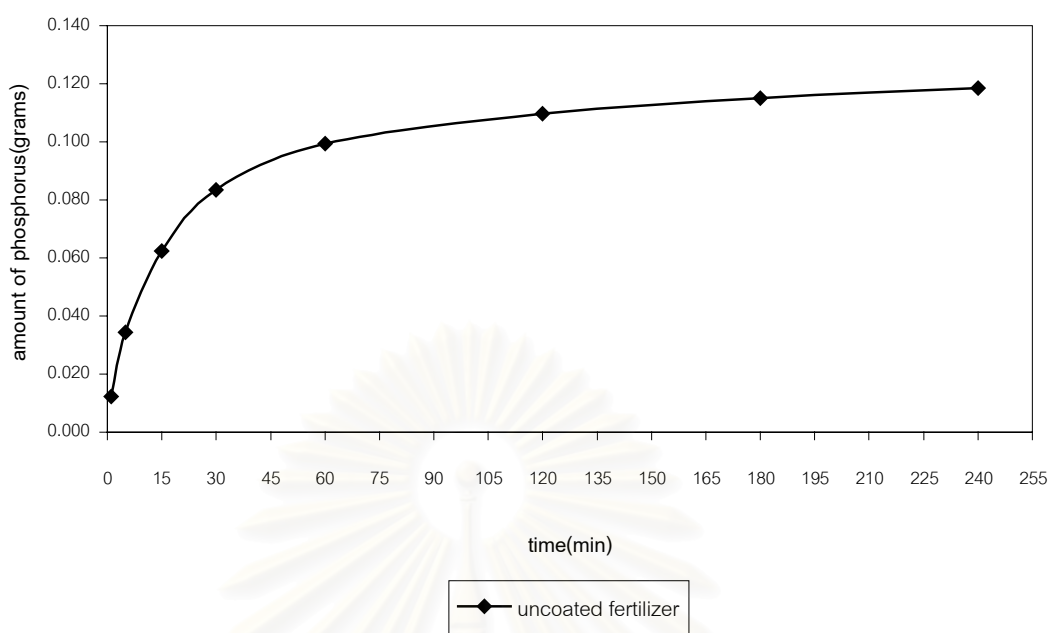


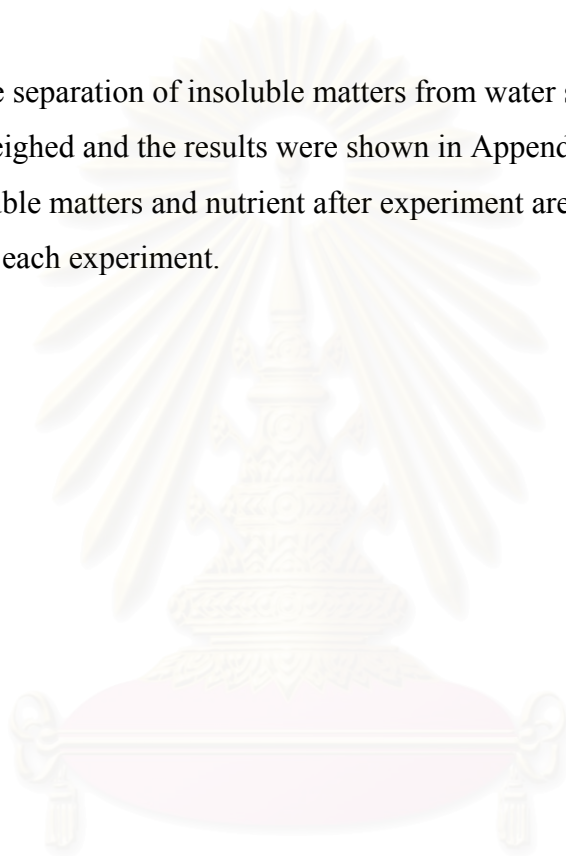
Figure 4.9 Dissolution Profile of Phosphorus from Uncoated Fertilizer

Table 4.2 Dissolve rate of Each Section and Maximum Dissolved amount of Uncoated Fertilizer grade 16:16:16.

Fertilizer nutrient	Dissolve rate (grams per minute)			Maximum dissolved amount (grams)
	First section	Second section	Third section	
Nitrogen	0.0824	0.0057	0.0011	0.2172
Potassium	0.0320	0.0075	0.0024	0.2588
Phosphorus	0.0123	0.0034	0.0008	0.1144

Table 4.3 shows analysis of each nutrient component, total nitrogen, phosphoric acid, and potassium dioxide, in each type of fertilizer, 16:16:16, 25:7:7, and 8:24:24. The numbers indicated for each type of the fertilizer and the amount of each nutrient component in percent. It was clearly seen from our analysis that the amount of each nutrient component indicated by the manufacture was not equal to the actual amount in it

After the separation of insoluble matters from water solution, the insoluble matters were weighed and the results were shown in Appendix A. It is found that the weight of insoluble matters and nutrient after experiment are not equal with weight of fertilizer before each experiment.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.3 Amount and Percentage of the Nutrient Specified from Label and determined from the Experiment.

Uncoated Fertilizer	Amount of nutrient specified from label (grams)			Amount of nutrient determined from experiment (grams)			Percentage of nutrient specified from label			Percentage of nutrient determined from experiment		
	Nitrogen	Phosphorus	Potassium	Nitrogen	Phosphorus	Potassium	Total Nitrogen	Phosphoric	Potassium oxide	Total Nitrogen	Phosphoric	Potassium oxide
Grade 16:16:16	0.3200	0.1396	0.2656	0.2172	0.1144	0.2588	16	16	16	10.86	13.11	15.59
Grade 25:7:7	0.5000	0.0611	0.1162	0.3320	0.0506	0.1166	25	7	7	16.60	5.80	7.02
Grade 8:24:24	0.1600	0.2095	0.3985	0.1319	0.1849	0.3896	8	24	24	6.60	21.19	23.47

4.2 Appearance of Chitosan Coated Fertilizer.

In coating procedure, fertilizer was placed in coating drum rotating at a speed of 15 rpm. Chitosan solution prepared by dissolving chitosan in acetic acid solution was sprayed on fertilizer granular while the fertilizer was rolling in the drum. It was observed during the coating process that the external green layer of the fertilizer was dissolved in chitosan solution. Some parts of the dissolved external layer adhered on inner surface of the drum. After the coated fertilizer was dried, the external surface color of coated fertilizer was yellow instead of green, which was the original color of the fertilizer. Figure 4.10 shows comparison of uncoated fertilizer with chitosan coated fertilizer.

4.3 Solubility of Chitosan Coated Fertilizer

In this study, chitosan was used as a coating material on fertilizer. In this experiment, coated fertilizer granules were added into deionized water to allow the fertilizer to be dissolved in water. It was observed that coated fertilizer granules in water did not disintegrate or break up to small pieces as the uncoated granules did. When water solution and coated fertilizer was filtered to remove insoluble matters, it was observed that the yellow thin layer contained insoluble matters. Figures 4.11 and 4.12 show the coated fertilizer granules in deionized water at zero minute and 15 minutes. The solution was analyzed for the amount of nitrogen, potassium, and phosphorus at specific time, and summarized in Appendix A and presented in the following sections.

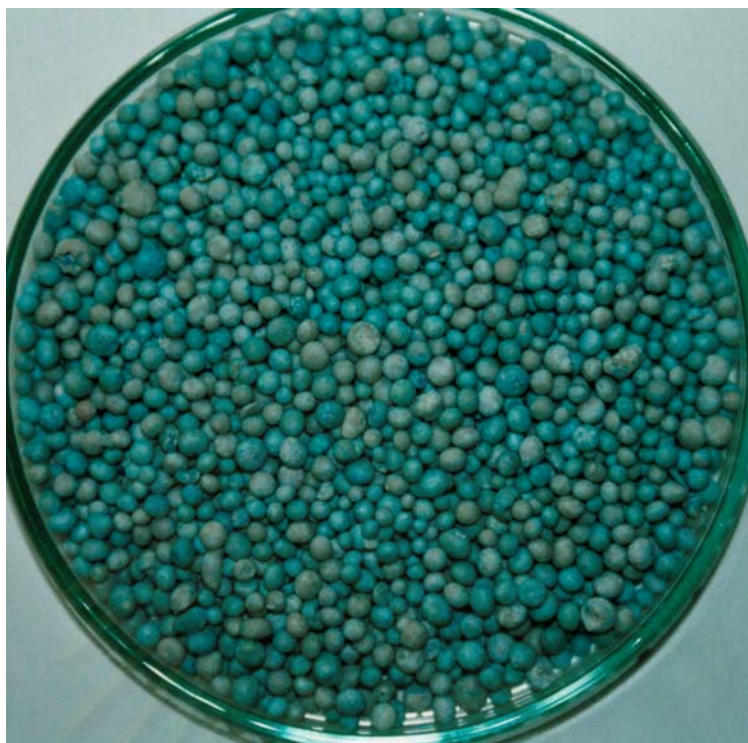
**A****B**

Figure 4.10 Comparison of Uncoated Fertilizer (A) with Chitosan Coated Fertilizer (B)



Figure 4.11 Chitosan Coated Fertilizer in Deionized Water at Zero Minute.



Figure 4.12 Chitosan Coated Fertilizer in Deionized Water at 15 Minutes.

4.3 Effects of Concentration of Chitosan Solution.

The experiment was designed to study the effects of concentration of chitosan solution coated on the fertilizer on release rate of nutrient. Dissolved amount of nitrogen, phosphorus, and potassium was plotted as a function of time shown in Figures 4.13 to 4.15. Dissolve rate of coated fertilizer was divided into three sections as described in section 4.1. Table 4.4 shows the release rates of nitrogen, phosphorus, and potassium of each section and the maximum release amount of each element.

The experimental results indicated that, in the first section, the release rate of nitrogen, potassium and phosphorus of uncoated fertilizer were slower than the release rate of chitosan coated fertilizer. From an observation of the uncoated fertilizer, there was a green layer coated on the fertilizer. This layer was dissolved in chitosan solution during preparation procedure, and water was diffused through chitosan layer, which directly dissolved fertilizer nutrient. The faster release rate of nutrient of coated fertilizer was possibly due to the high degree of deacetylation of chitosan, 95%, used in this experiment. Rong Huei Chen and Min Larng Tsaih (1997) studied the effect of chitosan characteristics on the release properties of the prepared capsule and found that the high degree of deacetylation chitosan had large pore sizes or high permeability

Table 4.4 indicated that in the first section, an increase in concentration of chitosan solution led to a decrease in the release rate of nutrient. High concentration of chitosan solution has higher of density and viscosity. Higher density of chitosan solution resulted in a decrease in the diffusion rate of nutrient. The release fertilizer mechanism appeared to be concomitantly a combination of the diffusion through the porous structure and osmotically driven release (Chirasak, 1994).

The release rates of second section of the coated fertilizer were slower than the first section because the osmotic pressure in granular gradually dropped. The release rate between the coated and uncoated fertilizer were similar, because the green layer that believed to be the external layer of uncoated fertilizer in water was disintegrated, which caused the release rate of uncoated fertilizer increased. During fertilizer release experiment, chitosan layer swelled, pore size could be enlarged resulted in higher permeability, which was the effect of the osmotic pressure (Chirasak, 1994). It caused the similar of release rate of each concentration.

The release rates of the third section of each nutrient indicated that it had reversed relationship with the release rates of the first section. Because the release rate of the second section for each concentration of chitosan solution were similar, so the amount of each nutrient in the granule after the second section was inversely proportional to the release rate of first section. The lower amount of nutrient in granule after the second section resulted in lower osmotic pressure, which caused the decrease of release rate of nutrient.

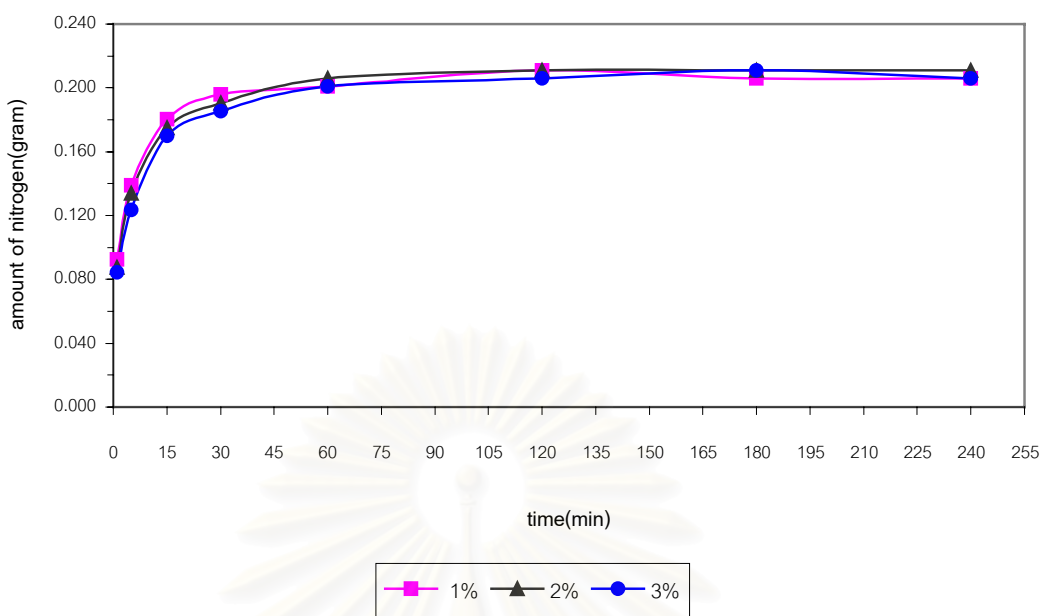


Figure 4.13 Comparison of Release Rate of Nitrogen between Different Concentration of Chitosan Solution Coated fertilizer.

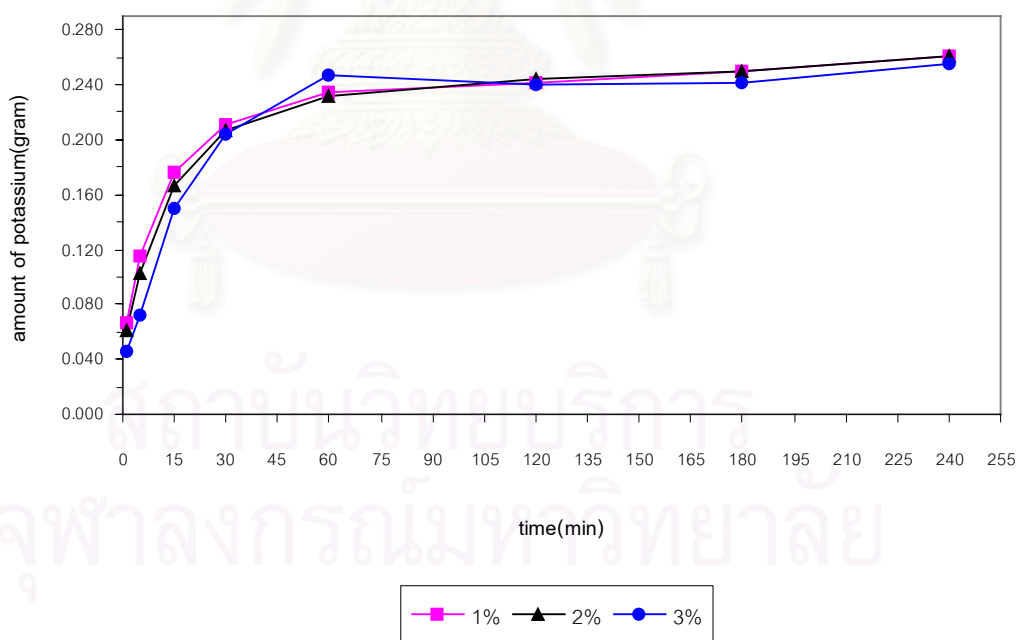


Figure 4.14 Comparison of Release Rate of Potassium between Different Concentration of Chitosan Solution Coated Fertilizer.

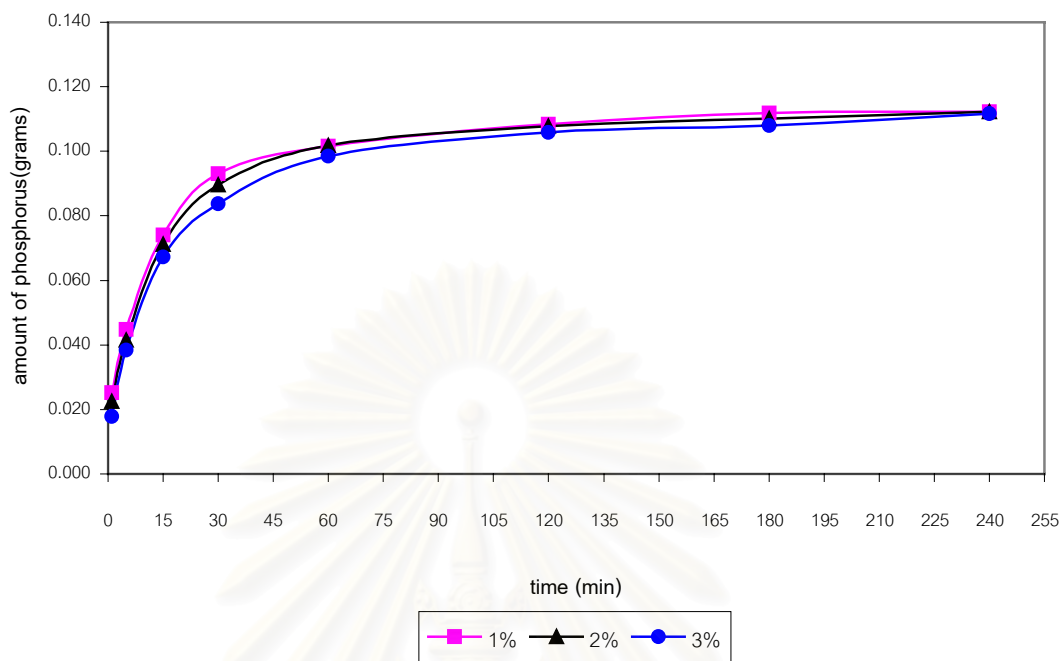


Figure 4.15 Comparison of Release Rate of Phosphorus between Different Concentration of Chitosan Solution Coated Fertilizer.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.4 Dissolve Rate of Each Section and Maximum Dissolve Amount of Different Concentration of Chitosan Solution Coated on Fertilizer.

Fertilizer compound	Dissolve rate (grams per minute)												Maximum dissolve amount (grams)			
	First section				Second section				Third section							
	uncoated	1%	2%	3%	uncoated	1%	2%	3%	uncoated	1%	2%	3%	uncoated	1%	2%	3%
Nitrogen	0.0824	0.0927	0.0876	0.0845	0.0057	0.0058	0.0058	0.0059	0.0011	0.0005	0.0007	0.0007	0.2172	0.2077	0.2112	0.2077
Potassium	0.0320	0.0670	0.0610	0.0460	0.0075	0.0074	0.0074	0.0074	0.0024	0.0012	0.0014	0.0021	0.2588	0.2508	0.2516	0.2460
Phosphorus	0.0123	0.0252	0.0226	0.0178	0.0034	0.0034	0.0034	0.0034	0.0008	0.0006	0.0006	0.0007	0.1144	0.1109	0.1100	0.1085

4.4 Effect of Degree of Deacetylation

The effect of degree of deacetylation (DD) of chitosan on the release rate of the coated fertilizer was compared using the chitosan of 79% and 95 % DD. Dissolved amount of nitrogen, potassium, and phosphorus were plotted as a function of time in Figures 4.16 to 4.18. The release rate of each section of coated fertilizer and maximum dissolved amount of nutrients were determined and presented in Table 4.5.

The release rates shown in Table 4.5 indicated that the release rate in the first and second section decreased when degree of deacetylation increased. Rong Huei Chen and Min Larng Tsaih (1997) proposed that the chitosan layer prepared from higher degree of deacetylation chitosan had larger pore sizes or higher permeability than the one prepared from lower degree of deacetylation chitosan, which caused the increase of release rate of high degree of deacetylation chitosan coated fertilizer. The third section release rate of lower degree of deacetylation was higher than the release rate of higher degree of deacetylation. Because the release rate of the first and second section of 79% DD was lower than the release rate of 95% DD, thus the amount of each nutrient of 79% DD after the second section was also more than the amount of each nutrient of 95% DD, which caused the release rate of 79% DD chitosan coated fertilizer to be higher than the release rate of 95% DD.

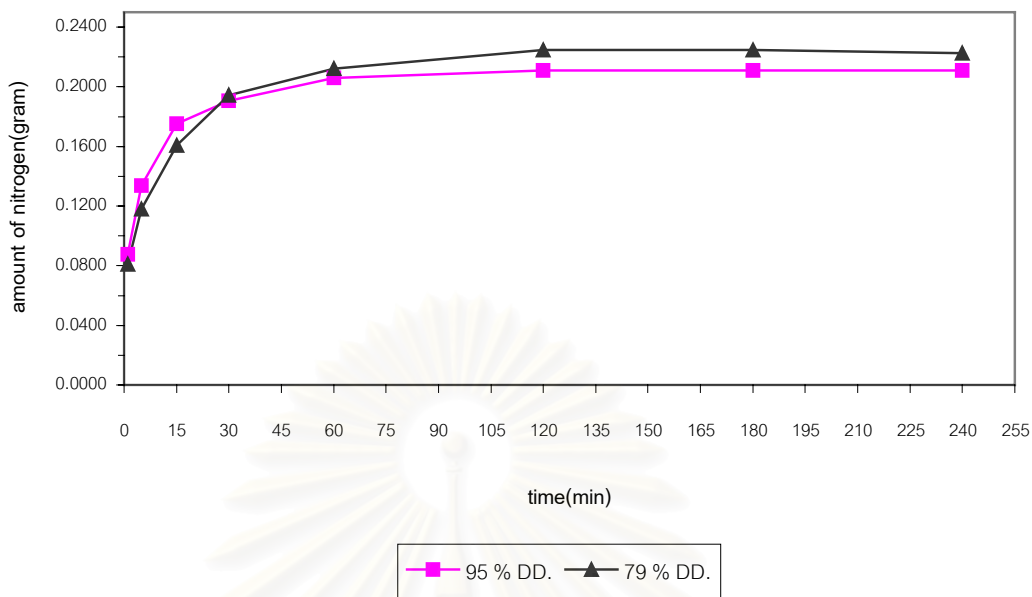


Figure 4.16 Comparison of release Rate of Nitrogen between 79% DD and 95% DD Chitosan Coated Fertilizer.

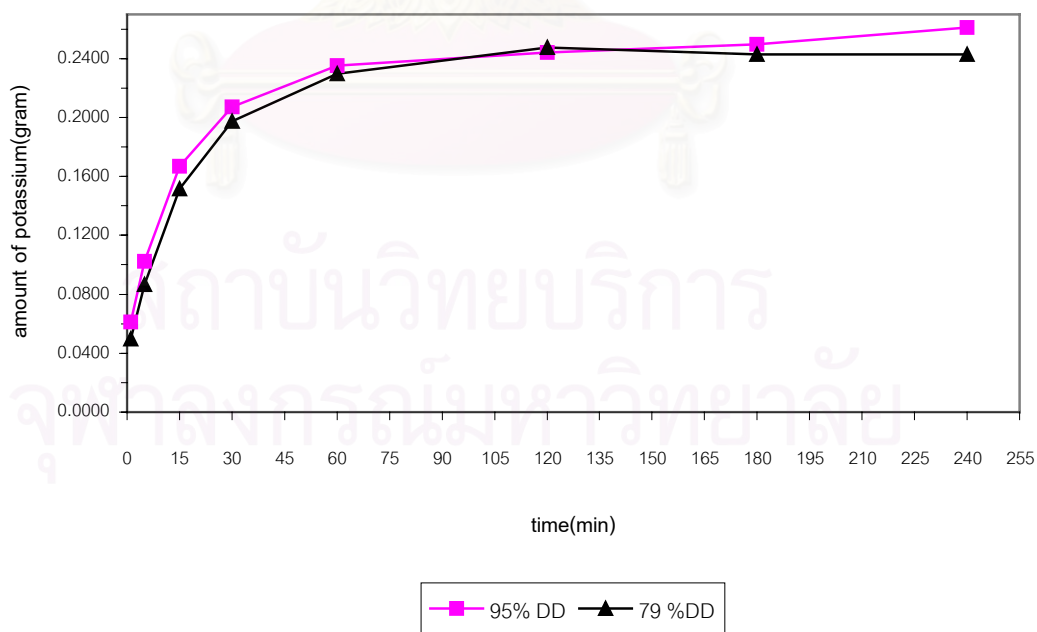


Figure 4.17 Comparison of Release Rate of Potassium between 79% DD and 95% DD Chitosan Coated Fertilizer.

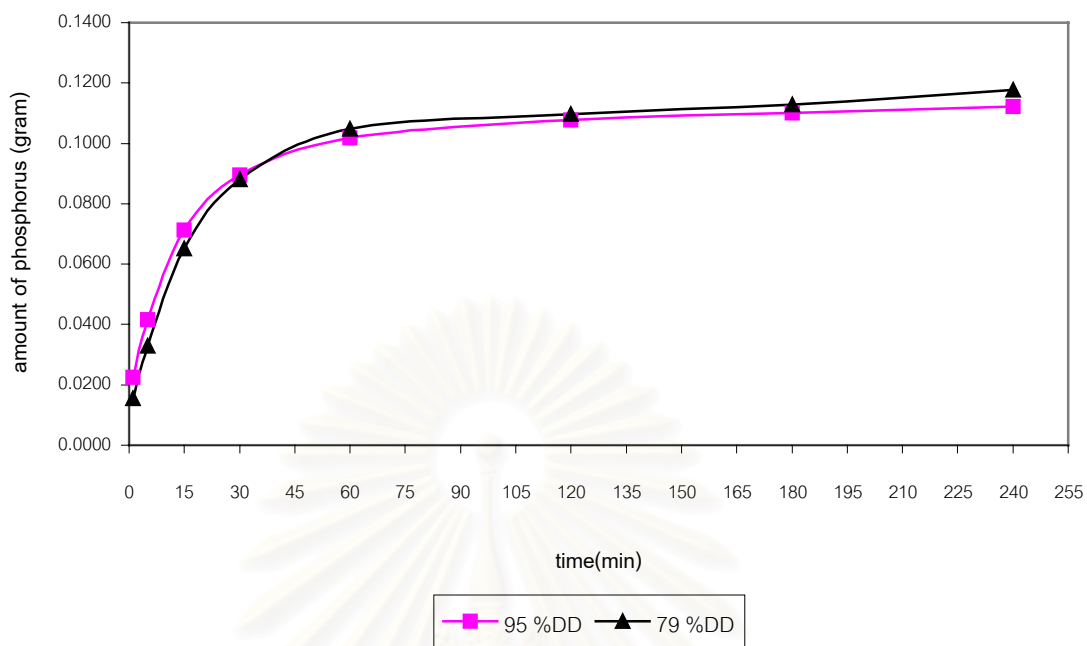


Figure 4.18 Comparison of Release Rate of Phosphorus between 79% DD and 95% DD Chitosan Coated Fertilizer.

Table 4.5 Dissolve rate of Each Section and Maximum Dissolved Amount of between 79% DD and 95% DD Chitosan Coated Fertilizer.

Fertilizer nutrient	Dissolve rate (grams per minute)						Maximum dissolved amount (grams)	
	First section		Second section		Third section		79%	95%
	79%	95%	79%	95%	79%	95%		
Nitrogen	0.0808	0.0876	0.0054	0.0058	0.0011	0.0007	0.2239	0.2112
Potassium	0.0498	0.0610	0.0071	0.0074	0.0016	0.0014	0.2445	0.2516
Phosphorus	0.0156	0.0226	0.0033	0.0034	0.0008	0.0006	0.1134	0.1100

4.5 Effect of Different Grade of Fertilizer

There are many grades of fertilizer in the market. Each grade has different amount of each nutrient element. This experiment was designed to study the effect of different grade of fertilizer grade (NPK 16:16:16, NPK 25:7:7, and NPK 8:24:24) on the release rate of coated fertilizer. Figures 4.19 to 4.21 showed the effect of different grade of fertilizer. The release rate of each section of coated fertilizer and maximum dissolved amount of nutrient were presented in Table 4.6

The results indicated that release rate of nitrogen of coated fertilizer grade NPK 25:7:7 was fastest while the release rate of nitrogen of coated fertilizer grade NPK 8:24:24 was slowest in all three sections. The release rate of phosphorus and potassium of coated fertilizer grade 8:24:24 was fastest while the release rate of coated fertilizer grade NPK 25:7:7 was slowest. The effect of fertilizer grade on the release rate of nutrient was obviously exhibited. The release rate of each element increased while amount of nutrient in fertilizer grade increased. The release rate of nutrient depended on the osmotic pressure in fertilizer granular. Amount of element in granular affected the osmotic pressure. If amount of nutrient increased, the osmotic pressure certainly increased, it caused an increase in release rate.

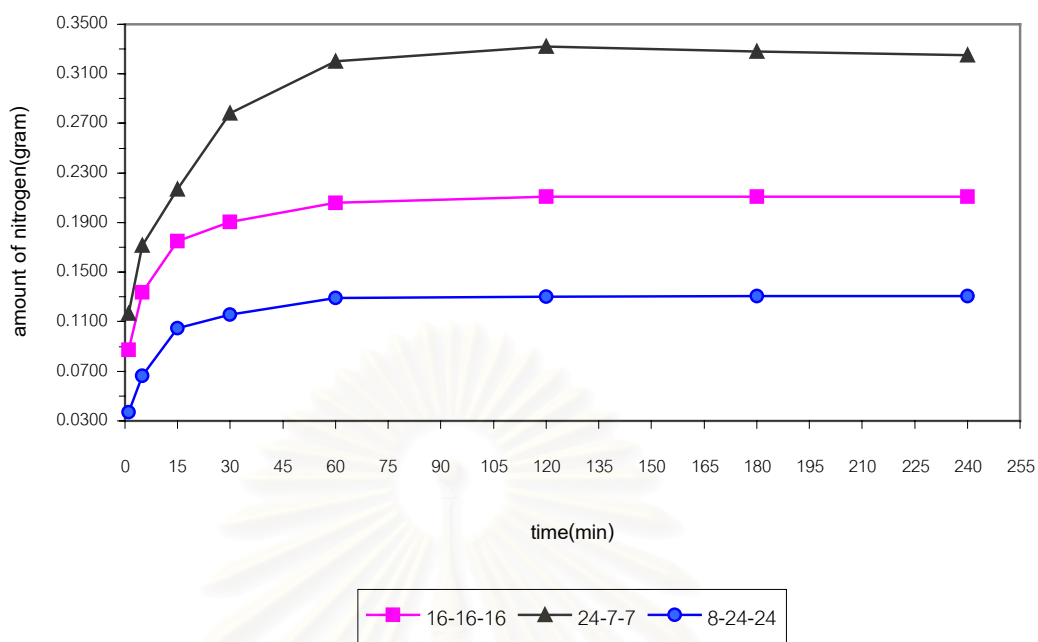


Figure 4.19 Comparison of Release Rate of Nitrogen between Different Coated Fertilizer Grade.

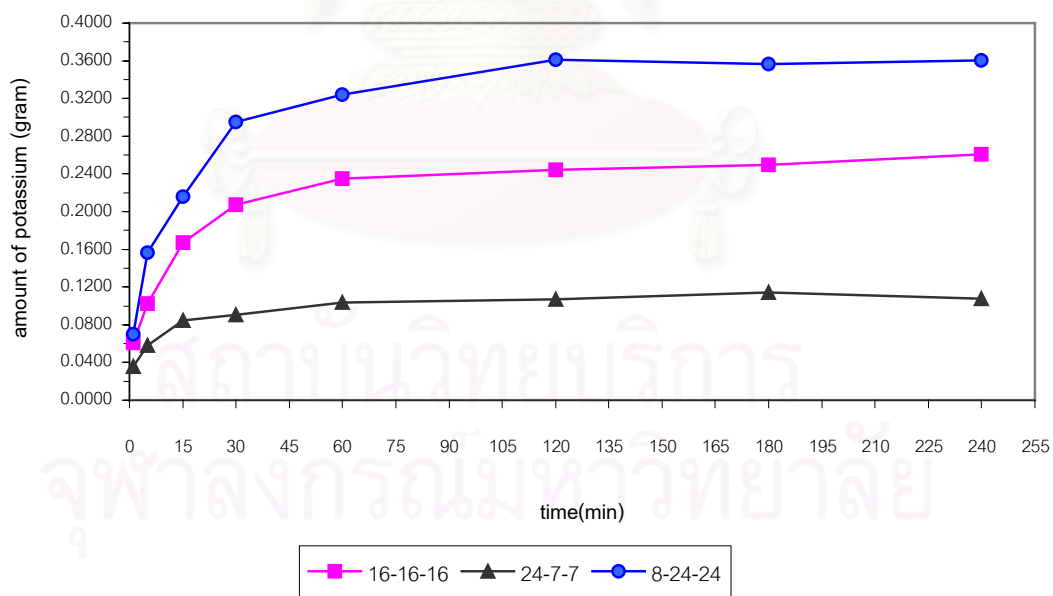


Figure 4.20 Comparison of Release rate of Potassium between Different Coated Fertilizer Grade.

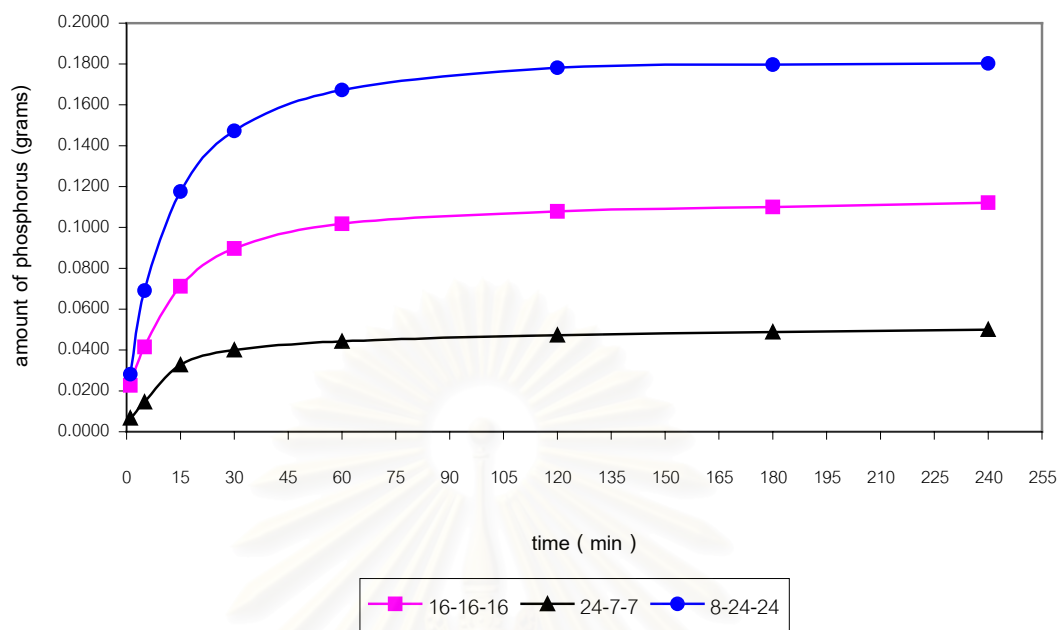


Figure 4.21 Comparison of Release Rate of Phosphorus between Different Coated Fertilizer Grade.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.6 Dissolve Rate of Each Section and Maximum Dissolve amount of Different Grade of Fertilizer.

Fertilizer compound	Dissolve rate (grams per minute)									Maximum dissolve amount (grams)		
	First section			Second section			Third section					
	16:16:16	25:07:07	8:24:24	16:16:16	25:07:07	8:24:24	16:16:16	25:07:07	8:24:24	16:16:16	25:07:07	8:24:24
Nitrogen	0.0876	0.1169	0.0372	0.0058	0.0066	0.0046	0.0007	0.0022	0.0005	0.2112	0.3283	0.1306
Potassium	0.0610	0.0355	0.0703	0.0074	0.0033	0.0095	0.0014	0.0004	0.0022	0.2516	0.1098	0.3593
Phosphorus	0.0226	0.0068	0.0282	0.0034	0.0018	0.0061	0.0006	0.0002	0.0010	0.1100	0.0487	0.1794

4.6 Effect of Number of Chitosan Layer

In this experiment, it was assumed that a single coated layer of chitosan occurred when fertilizer was sprayed coated and dried for at least 24 hours. Next coating layer was later applied to the coated fertilizer. In this study, there were different number of layers, one layer, five layers, and ten layers, coated on fertilizer. Their release rates of the nutrient were compared. It was observed that the yellow colour of chitosan film was darker when number of chitosan layers increased. Figures 4.22 to 4.24 show the fertilizer granular that coated with one, five, and ten layers.



Figure 4.22 One Layer Coated Fertilizer.

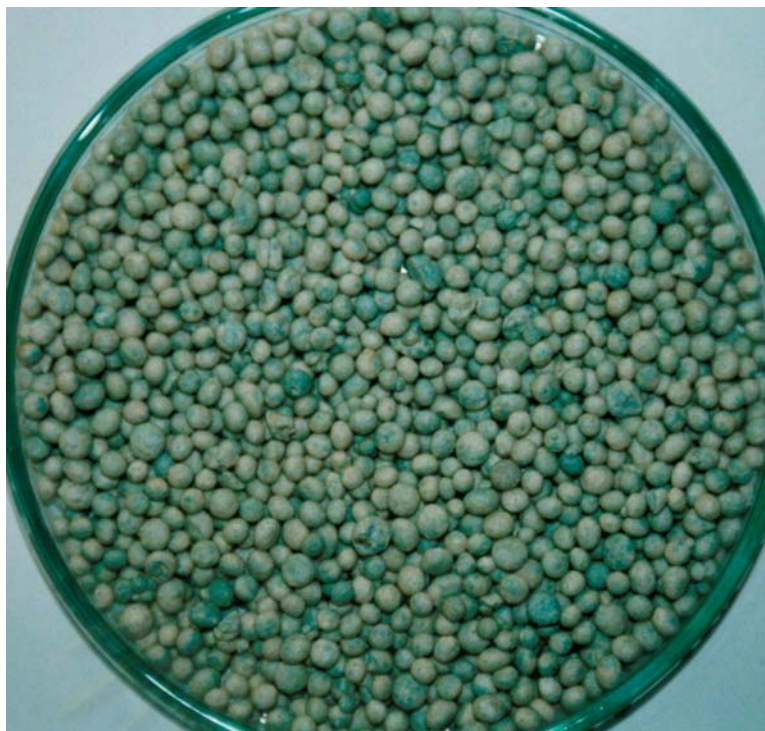


Figure 4.23 Five Layers Coated Fertilizer.



Figure 4.24 Ten Layers Coated Fertilizer.

The effect of number of layer was shown in Figures 4.25 to 4.27. The dissolve rates of each element in three sections and maximum dissolved amount of one, five, and ten layers coated fertilizer were determined and were shown in Table 4.7. From the results, the release rate of coated fertilizer in the first section was higher than uncoated fertilizer and the increase of number of chitosan layer slightly decreased the release rate of nutrient. This effect could be described that the increase number of chitosan layer increased the thickness of chitosan film on the granule surface, which resulted in the less chance of water to penetrate into the fertilizer granular. In the second section, the swelling of chitosan layers affected the similar release rate of nutrient between the different number of chitosan layers coated fertilizer. In the third section, the release rate of nutrient of each number of chitosan layers depended on the release rate in the first section, as discussed in Section 4.3.

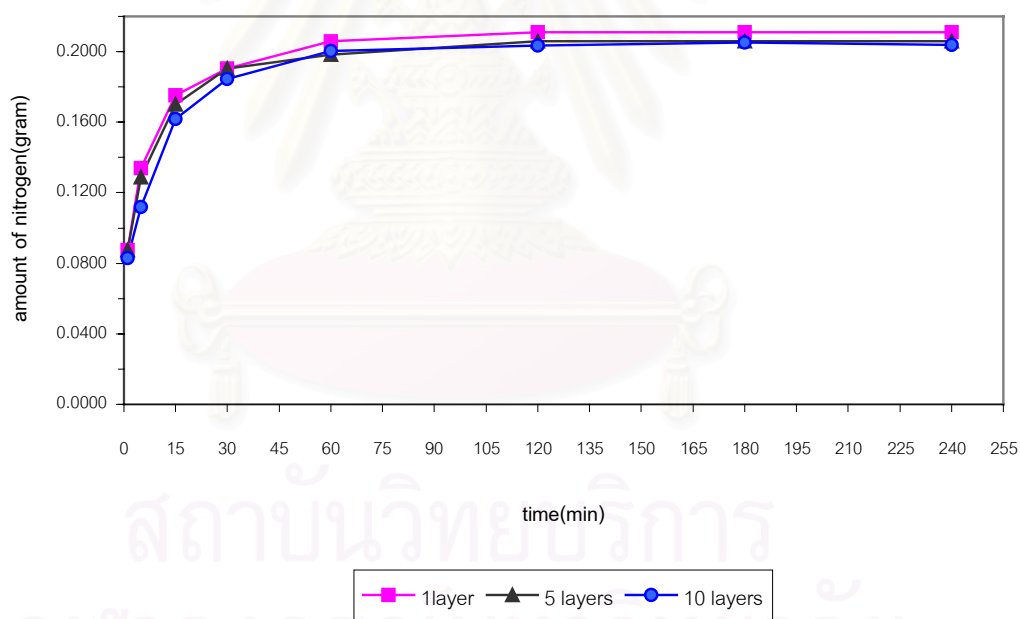


Figure 4.25 Comparison of Release Rate of Nitrogen between Different Number of Chitosan Layer Coated on Fertilizer.

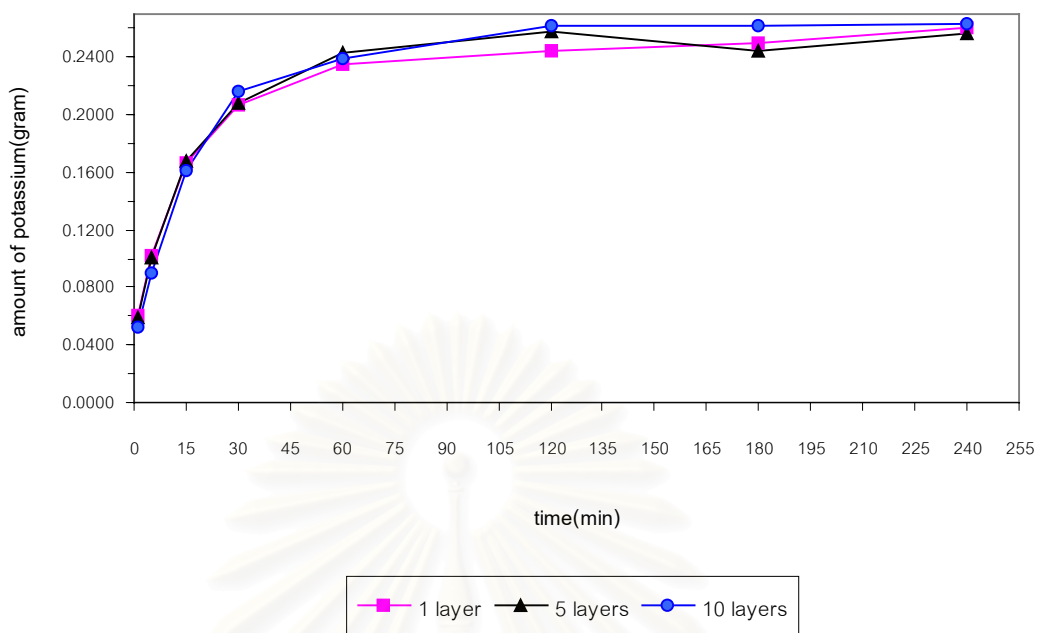


Figure 4.26 Comparison of Release Rate of Potassium between Different Number of Chitosan Layer Coated on Fertilizer.

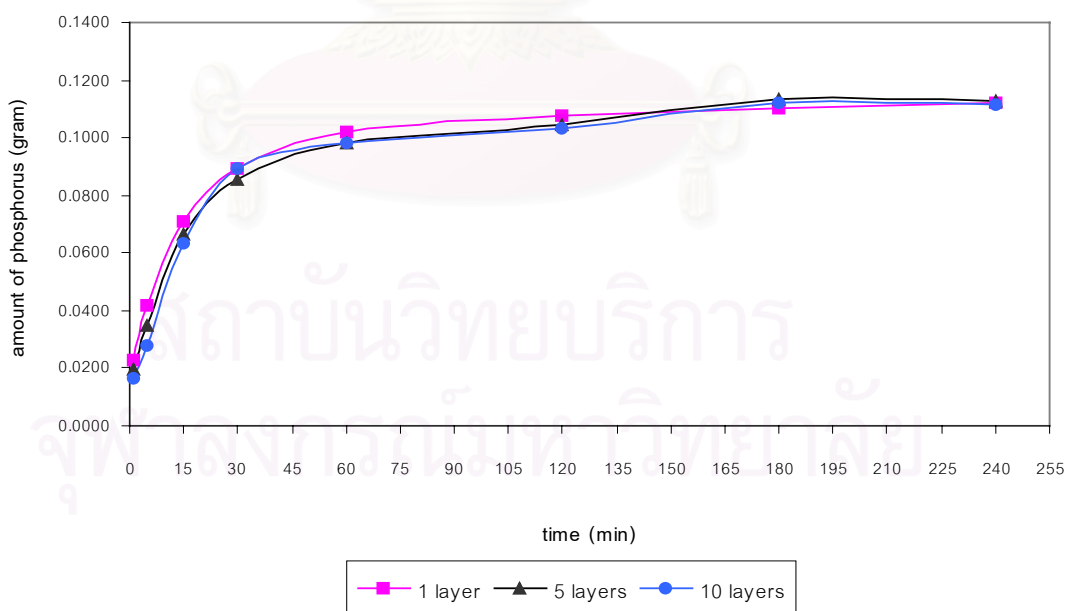


Figure 4.27 Comparison of Release Rate of Phosphorus between Different Number of Chitosan Layer Coated on Fertilizer.

Table 4.7 Dissolve Rate of Each Section and Maximum Dissolve amount between the Different Number of Chitosan Layer Coated on Fertilizer.

Fertilizer compound	Dissolve rate (grams per minute)												Maximum dissolve amount (grams)			
	First section				Second section				Third section							
	uncoated	1 layer	5 layers	10 layers	uncoated	1 layer	5 layers	10 layers	uncoated	1 layer	5 layers	10 layers	uncoated	1 layer	5 layers	10 layers
Nitrogen	0.0824	0.0876	0.0876	0.0829	0.0057	0.0058	0.0055	0.0055	0.0011	0.0007	0.0006	0.0008	0.2172	0.2112	0.2060	0.2042
Potassium	0.032	0.0610	0.0588	0.0520	0.0075	0.0074	0.0076	0.0077	0.0024	0.0014	0.0016	0.0016	0.2588	0.2516	0.2529	0.2623
Phosphorus	0.0123	0.0226	0.0199	0.0163	0.0034	0.0034	0.0033	0.0034	0.0008	0.0006	0.0007	0.0007	0.1144	0.1100	0.1103	0.1090

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from this study:

1. The release rate of nutrient of chitosan coated fertilizer was higher than the one of uncoated commercial fertilizer.
2. Comparison of concentration of chitosan solution showed that the release rate of chitosan coated fertilizer decreased while the concentration of chitosan solution increased.
3. Comparison of degree deacetylation of chitosan solution showed that the release rate of fertilizer decreased while the degree deacetylation of chitosan solution decreased.
4. Comparison of coated fertilizer grade (NPK 16:16:16, NPK 24:7:7, NPK 8:24:24) showed that the release rate of nitrogen, phosphorus, and potassium increases while the amount of nitrogen, phosphorus, and potassium compound in fertilizer increased.
5. Comparison of amount of chitosan layer showed that the increasing number of chitosan layer coated on fertilizer granular slightly decreased the release rate of nutrient.

5.2 Recommendations

1. Nowadays, crosslinking agent, such as glutaraldehyde, and plasticizer are used to apply in chitosan coating on drug tablet research for modification chitosan film structure. The same set of experiment should be preformed to investigate the effect of other crosslinking agents and plasticizers, using in the coating procedure, on the released rate of chitosan coated fertilizer.

2. The same set of experiment should be studied with other coating fertilizer methods or granulation fertilizer methods, such as adding chitosan solution in granulation procedure.

3. The chitosan coated fertilizers should be added in soil and study the influence of coated fertilizers on plant growth. The same set of experiment should be varied conditions of experiment, such as type of soil and pH of water, in order to study the effect of those conditions on the release rate of fertilizer.

4. The same set of experiment should be studied mass transfer and diffusion of nutrient elements pass chitosan film coated on fertilizer surface.

REFERENCES

- Akbuga, J. A biopolymer: Chitosan, Int. J. Pharm Adv. 1(1995): 2-18
- Bassi, R. et al. Removal of selected metal ions from aqueous solution using chitosan flakes. Separation Science and Technology 35, 4 (2000): 547-560.
- Chang, H.J. Method of preparing a slow release fertilizer. United States Patent 56955142. 1997.
- Chirasak Kusonwiriawong. Application of chitin and chitosan as film formers in propranolol hydrachloride sustained release film coated tablets compared with celluloses. Major manufacturing pharmacy. Chulalongkorn University, 1994.
- Davis, C.II., Ed. Controlled Release Fertilizers, TVA Bulletin. 107(1976): 21-31.
- Fwu-Long Mi, et al. Chitosan Tablets for Controlled Release of Theophylline: Effect of Polymer-Drug Wet or Dry Blending and Anionic-Cationic Interpolymer Complex, Journal of Applied Polymer Science. 66(1997): 2495-2505.
- Guibal, E. et al. Influence of polymer structural parameters and experimental conditions on metal anion sorption by chitosan. Polymer International 48 (1999): 671-680.
- Hepburn, c., and Arizal, R. Slow-release fertilizers based on natural ruber. British Polymer Journal. 20 (1988): 487-491.
- Hon, D.N.S., Encapsulated fertilizers and pesticides and process. United States Patent 5679129, 1997.

- Hudson, A.P. Abrasion resistant coatings for fertilizers. United States Patent 5466274. 1995.
- Ida, G. et al. Influence of glutaraldehyde on drug release and mucoadhesive properties of chitosan microspheres, Carbohydrate Polymers. 36(1998): 81-88.
- Jesus, N., Rico, M.I., and Alvarez J.M. Controlled Release of Manganese into Water from Coated Experimental Fertilizers. Laboratory Characterization, J. Agric. Food Chem. 49(2001): 1298-1303.
- Laegreid, M., Bockman, O.C., and Kaarstad, O. Agriculture fertilizers and the environment. Norway: CABI publishing in association with Norsk Hydro ASA, 1999.
- Lehr, C.M., Bouwstra, J.A., Schacht, E.H., and Junginger, H.E. In vitro evaluation of mucoadhesive properties of chitosan and some other natural polymers, Int. J. Pharm. 78(1992): 43-48
- Li, Q. et al. Application and properties of chitosan. Journal of bioactive and compatible polymers. 7(1992): 370-395.
- Lower, E.S. Polymers from the sea chitin&chitosan, Manuf. Chem. 10(1984): 47,49,52.
- Lunt, O.R. Controlled Release Fertilizers: Achievements and potential, J. Agric. Food Chem. 19(1971): 797-800.
- Muzzarelli, R.A.A. Chitin. Oxford: Pergamon Press, 1977.
- Onsoyen, E. and Skaugrud O. Metal recovery using chitosan. Journal of Chemical Technology Biotechnology 49 (1990): 395-404.

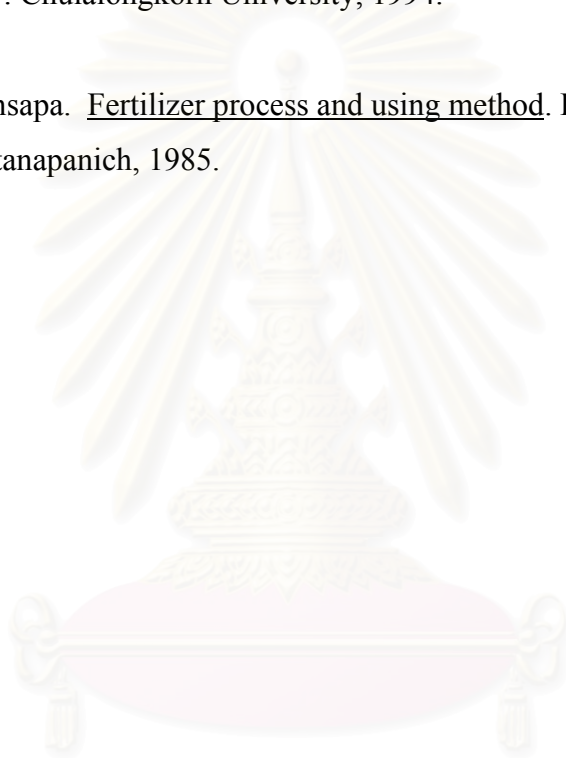
- Raegreid, M., Bockman, O.C., and Kaarstad, O. Agriculture Fertilizers and the Environment. Norway: CABI Publishing in association with Norsk Hydro ASA, 1999.
- Raymond, W.M., and Roy, L.D.. SOILS an Introduction to Soils and Plant Growth. 6th ed. Prentice-Hall International, 1990.
- Robert, L.M., Using hydrophilic polymers to control nutrient release. Fertilizer Research. 38(1994): 53-59.
- Rong Huei Chen, and Min Larng Tsaih. Effect of Preparaton Method and Charcteristics of Chitosan on the Mechanical and Release Properties of the Prepared Capsule, Journal of Applied Polymer Science. 66(1997):161-169
- Roy, H.F., Larry, S.M., and Roy, L.D. Fertilizers and Soil Amendments. New Jersey: Prentice-Hall, Englewood Cliffs, 1981.
- Siriporn Chaometeewut. Preparation of controlled release nitrogen fertilizer from biodegradable agricultural waste. Inter department of environmental science. Chulalongkorn university, 2001.
- Skaugrud, O. Chitosan makes the grade, Manuf. Chem. 9(1989): 31-35
- Thawatchai Phaechamud. Effect of variables in chitosan film formulations on propranolol hydrochloride tablets. Major manufacturing pharmacy Chulalongkorn University, 2001.
- Toshito Fujita, et al. Coated granular fertilizer capable of controlling the effect of temperature upon dissolution out rate. United state patent 4,369,055. 1983.

Uri, S. et al. Release Characteristics of a new controlled release fertilizer, Journal of Controlled Release. 43(1997): 131-138.

Valkanas, G.N., Controlled release fertilizer. United States Patent 5137563. 1992.

Waree Tiyafoonchai, Preparation and evaluation of chitosan carbosymethyl cellulose sustained microcapsules containing indomethacin. Major manufacturing pharmacy. Chulalongkorn University, 1994.

Yongyuth Osothsapa. Fertilizer process and using method. Bangkok: Thaiwattanapanich, 1985.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Appendix A.

Table 1A. Condition and Results of Controlled Release Experiments of Uncoated Fertilizer.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0196	0.6800	0.0824	0.0123	0.0320
2	5	2.0065	0.3862	0.0927	0.0343	0.0600
3	15	2.0305	0.1768	0.1597	0.0623	0.1360
4	30	2.0133	0.1624	0.1854	0.0834	0.1975
5	60	2.0184	0.1550	0.2112	0.0993	0.2493
6	120	2.0125	0.1638	0.2163	0.1098	0.2585
7	180	2.0335	0.1608	0.2163	0.1151	0.2598
8	240	2.0137	0.1773	0.2189	0.1184	0.2583

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 2A. Condition and Results of Controlled Release Experiments of 95% Degree Deacetylation and 1% wt. Chitosan Solution Coated Fertilizer.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0039	0.5213	0.0927	0.0252	0.0670
2	5	2.0200	0.2647	0.1391	0.0448	0.1158
3	15	2.0176	0.1872	0.1803	0.0740	0.1760
4	30	2.0089	0.1827	0.1957	0.0931	0.2108
5	60	2.0160	0.1802	0.2009	0.1016	0.2345
6	120	2.0197	0.1886	0.2112	0.1084	0.2408
7	180	2.0096	0.1739	0.2060	0.1119	0.2503
8	240	2.0141	0.1620	0.2060	0.1123	0.2615

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 3A. Condition and Results of Controlled Release Experiments of 95% Degree Deacetylation and 2% wt. Chitosan Solution Coated Fertilizer.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0218	0.6237	0.0876	0.0226	0.0610
2	5	2.0272	0.3595	0.1339	0.0415	0.1025
3	15	2.0274	0.1822	0.1751	0.0712	0.1670
4	30	2.0189	0.1856	0.1906	0.0896	0.2070
5	60	2.0246	0.1723	0.2060	0.1019	0.2315
6	120	2.0012	0.1744	0.2112	0.1078	0.2440
7	180	2.0422	0.1792	0.2112	0.1101	0.2498
8	240	2.0228	0.1714	0.2112	0.1122	0.2610

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 4A. Condition and Results of Controlled Release Experiments of 95% Degree Deacetylation and 3% wt. Chitosan Solution Coated Fertilizer.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0352	0.6363	0.0845	0.0178	0.0460
2	5	2.0132	0.3321	0.1236	0.0383	0.0718
3	15	2.0021	0.2011	0.1700	0.0673	0.1493
4	30	2.0177	0.1866	0.1854	0.0837	0.2045
5	60	2.0394	0.1795	0.2009	0.0986	0.2468
6	120	2.0192	0.1774	0.2060	0.1058	0.2403
7	180	2.0167	0.1751	0.2112	0.1080	0.2418
8	240	2.0307	0.1787	0.2060	0.1116	0.2560

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 5A. Condition and Results of Controlled Release Experiments of 79% Degree Deacetylation and 2%wt Chitosan Solution Coated Fertilizer.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0030	0.5929	0.0808	0.0156	0.0460
2	5	2.0216	0.1902	0.1179	0.0328	0.0865
3	15	2.0196	0.1868	0.1607	0.0651	0.1518
4	30	2.0191	0.1784	0.1943	0.0879	0.1975
5	60	2.0150	0.1778	0.2121	0.1047	0.2298
6	120	2.0189	0.1770	0.2246	0.1096	0.2475
7	180	2.0200	0.1737	0.2245	0.1128	0.2430
8	240	2.0054	0.1737	0.2227	0.1178	0.2430

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 6A. Condition and Results of Controlled Release Experiments of NPK 25:7:7 Fertilizer Coated with 95% Degree Deacetylation and 2%wt Chitosan Solution.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0113	0.4695	0.1169	0.0068	0.0355
2	5	2.0255	0.2619	0.1714	0.0145	0.0583
3	15	2.0205	0.1361	0.2167	0.0326	0.0845
4	30	2.0248	0.1170	0.2781	0.0401	0.0908
5	60	2.0132	0.1097	0.3199	0.0444	0.1035
6	120	2.0094	0.1028	0.3320	0.0473	0.1073
7	180	2.0164	0.1093	0.3279	0.0487	0.1143
8	240	2.0125	0.0985	0.3250	0.0500	0.1078

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 7A. Condition and Results of Controlled Release Experiments of NPK 8:24:24 Fertilizer Coated with 95% Degree Deacetylation and 2%wt Chitosan Solution.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0118	1.3405	0.0372	0.0282	0.0703
2	5	2.0020	1.0034	0.0661	0.0692	0.1563
3	15	2.0074	0.7340	0.1049	0.1176	0.2158
4	30	2.0116	0.4913	0.1158	0.1472	0.2953
5	60	2.0058	0.2888	0.1294	0.1673	0.3243
6	120	2.0148	0.2707	0.1302	0.1783	0.3610
7	180	2.0098	0.2718	0.1306	0.1796	0.3568
8	240	2.0136	0.2584	0.1309	0.1803	0.3603

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 8A. Condition and Results of Controlled Release Experiments of 5 layers Fertilizer Coated with 95% Degree Deacetylation and 2%wt Chitosan Solution.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0054	0.6139	0.0876	0.0199	0.0588
2	5	2.0182	0.3310	0.1288	0.0350	0.1003
3	15	2.0090	0.1719	0.1700	0.0668	0.1678
4	30	2.0230	0.1730	0.1906	0.0852	0.2078
5	60	2.0262	0.1821	0.1983	0.0982	0.2488
6	120	2.0178	0.1755	0.2060	0.1043	0.2578
7	180	2.0227	0.1742	0.2060	0.1136	0.2445
8	240	2.0062	0.1825	0.2060	0.1130	0.2565

* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table 9A. Condition and Results of Controlled Release Experiments of 10 layers Fertilizer Coated with 95% Degree Deacetylation and 2%wt Chitosan Solution.

Sample	Times (minutes)	Weight. Before* (grams)	Weight. After** (grams)	Amount of Nutrient (grams)		
				Nitrogen	Phosphorus	Potassium
1	1	2.0056	0.6264	0.0829	0.0163	0.0520
2	5	2.0094	0.3538	0.1119	0.0278	0.0900
3	15	2.0070	0.2075	0.1619	0.0635	0.1610
4	30	2.0221	0.1642	0.1845	0.0895	0.2165
5	60	2.0167	0.1794	0.2004	0.0984	0.2385
6	120	2.0212	0.1750	0.2036	0.1031	0.2620
7	180	2.0391	0.1817	0.2050	0.1121	0.2615
8	240	2.0289	0.1896	0.2039	0.1117	0.2633

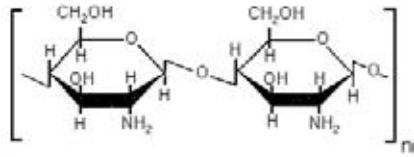
* Weight of Fertilizer before Experiment

** Weight of Filtered Fertilizer after Experiment

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Appendix B.

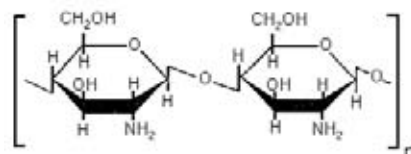
Table 1B Properties of Chitosan 79 % Degree of Deacetylation *

Structure	
Chemical Name	poly (1→ 4)-2-amino-2-deoxy-β-D-glucan
Appearance	Yellowish
Particle Size	Mesh No.18
Ash Content	0.55%
Moisture Content	9.0%
Deacetylation	79%
Solution (1% in 1% acetic acid)	
Insoluble	0.93%
Viscosity	696 cps
Heavy Metal	0 ppm
Microbial Content	
Total Plate Count	50 cfu/g
Yeast & Mold	10 cfu/g
E.coli & Salmonella	Null

* From Seafresh Chitosan (Lab) Co., Ltd.

Table 2B Properties of Chitosan 95 % Degree of Deacetylation *

Structure



Chemical Name poly (1→4)-2-amino-2-deoxy-β-D-glucan

Appearance Yellowish

Particle Size Mesh No.18

Ash Content 0.15%

Moisture Content 9.0%

Deacetylation 95%

Solution (1% in 1% acetic acid)

Insoluble 0.4%

Viscosity 648 cps

Heavy Metal 0 ppm

Microbial Content

Total Plate Count 10 cfu/g

Yeast & Mold 10 cfu/g

E.coli & Salmonella Nill

* From Seafresh Chitosan (Lab) Co., Ltd.

Table 3B Properties of Sulfuric Acid *

Formula	H ₂ SO ₄
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	98.09
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	~ 290
Melting Point (°C)	10
Specific Gravity	1.84
Solubility	Soluble in Water
Purity	> 99%
Supplier	Merck

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

* From Merck Index.

Table 4B Properties of Sodium Chloride *

Formula	NaCl
Chemical Name	Sodium Chloride
Physical Properties	
Molecular Weight	58.54
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	804
Melting Point (°C)	-
Specific Gravity	2.17
Solubility	Soluble in Water
Purity	> 99%
Supplier	Carlo Erba

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

* From Merck Index.

Table 5B Properties of Cesium Chloride *

Formula	CsCl
Chemical Name	Cesium Chloride
Physical Properties	
Molecular Weight	168.36
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	-
Melting Point (°C)	-
Specific Gravity	-
Solubility	Soluble in Water
Purity	> 99.5%
Supplier	Carlo Erba

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

* From Merck Index.

Table 6B Properties of Boric Acid *

Formula	H ₃ BO ₃
Chemical Name	Boric Acid
Physical Properties	
Molecular Weight	61.83
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	-
Melting Point (°C)	-
Specific Gravity	-
Solubility	Soluble in Water
Purity	> 99%
Supplier	Carlo Erba

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

* From Merck Index.

Table 7B Properties of Potassium Nitrate *

Formula	KNO ₃
Chemical Name	Potassium Nitrate
Physical Properties	
Molecular Weight	101.10
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	-
Melting Point (°C)	-
Specific Gravity	-
Solubility	Soluble in Water
Purity	> 99%
Supplier	Carlo Erba

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

* From Merck Index.

VITA

Mr.Peerapong Hanpichanchai was born on November 21, 1979 in Bangkok, Thailand. He received the Bachelor degree of Chemical Engineering from Faculty of Engineering, Srinakharinwirot University in April 2000. He continued his Master's study at Chulalongkorn University in June 2000.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย