

**EVALUATION OF PARAMETERS GOVERNING THE RELEASE RATE OF
PHOSPHATE IONS FROM CHITOSAN-COATED PHOSPHORUS
FERTILIZER PELLETS**

by

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	x
LIST OF SYMBOLS	xii
LIST OF APPENDICES	xvi
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER 1: INTRODUCTION	
1.1 Phosphorus Fertilizer	1
1.2 Global Issues on Phosphorus Fertilizers	2
1.3 Methods for Increasing the Efficiency of Fertilizers	4
1.3.1 Foliar Fertilizers	5
1.3.2 Slow and Controlled-Release Fertilizers	5
1.4 Problem Statement	7
1.5 Objectives	9
1.6 Scope of Study	9
1.7 Organization of Thesis	10
CHAPTER 2 : LITERATURE REVIEW	
2.1 Introduction to Fertilizers	12
2.2 Fertilizers and Soils	12
2.3 Overview on Slow and Controlled-Release Fertilizers	13
2.4 Fertilizer Coating	14
2.5 Coated Phosphorus Fertilizer	15
2.6 Nutrient Release Mechanisms and Pattern	16

2.7 Chitosan	
2.7.1 Introduction to Chitosan	18
2.7.2 Film-Firming Properties of Chitosan	19
2.7.3 Cross-linking of Chitosan Films	21
2.8 Chitosan in Controlled-Release Fertilizers	22
2.9 Theoretical Studies in Controlled-Release Systems	25
2.9.1 Emperical/Semi-empirical Model	26
2.9.2 Mechanistic Model	28
2.9.3 Parameters Involved in Controlled-Release Model	36

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials	40
3.2 Equipments	41
3.3 Experimental Procedures	41
3.3.1 Preparation of Phosphorus Fertilizer Pellets	44
3.3.2 Preparation of Chitosan-Coated Phosphorus Fertilizer Pellets	44
3.3.3 Characterization of Coating Films	45
3.3.4 Preparation of Aqueous Solution at Different pH Values	46
3.3.5 Phosphate Release Rate Experiments	46
3.3.6 Analysis of Phosphate Released	47
3.4 Application of Theoretical Model	48
3.4.1 Selection of Diffusion Model and Its Development	49
3.4.2 Extended Diffusion Model	54
3.4.3 Evaluation of the Parameters Based on the Diffusion Models	55

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Characterization of Chitosan Coating Films	57
4.1.1 Measurement of the Initial Thickness of Coating Films	57
4.1.2 Fourier Transform Infrared (FTIR) Analysis	58

4.1.3 Scanning Electron Microscope (SEM) Analysis	61
4.1.4 General Observations	68
4.2 Phosphate Release Rate	69
4.2.1 Variation of Phosphate Release Rate With Different pH Conditions	73
4.2.2 Variation of Phosphate Release Rate With Different Number of Coatings	77
4.3 Mechanisms of Nutrient Release	80
4.4 Evaluation of Parameters Based on Diffusion Model and Extended Diffusion Model	83
4.5 Analysis of Parameters From the Diffusion Models	85
4.5.1 Parameter $k_L C_o$	85
4.5.2 Parameter D	90
4.5.3 Parameter r	95
4.6 Validation of Diffusion Model	98
4.7 Summary	100

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions	101
5.2 Recommendations	103

REFERENCES	104
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APPENDICES

LIST OF PUBLICATIONS AND SEMINARS

LIST OF TABLES

		Page
Table 2.1	Classification of SRF and CRF	14
Table 2.2	Summary of chitosan film properties based on tensile strength (TS), water vapor permeability (WVP) and total soluble matter (TSM)	20
Table 2.3	Summary of the recent studies on chitosan-coated urea fertilizers	23
Table 2.4	Summary of the recent studies on chitosan-coated NPK fertilizers	24
Table 2.5	Values of exponent n of power law equation and release mechanism from polymeric controlled delivery systems of different geometry (Siepmann and Peppas, 2001)	27
Table 2.6	Description of diffusion models based on types of coated/reservoir formulation systems ^a (Baker, 1987)	32
Table 2.7	Diffusion based models with different geometries for drug release from non-constant and constant activity source ^a (Siepmann and Siepmann, 2012)	35
Table 3.1	List of chemicals	40
Table 3.2	Details of the equipments	41
Table 4.1	Initial thickness of different coating films, l_o	58
Table 4.2	Values of parameters of $k_L C_o$, r , D , m and correlation coefficient (R^2)	84
Table 4.3	The average values of k at different pH conditions	85

LIST OF FIGURES

		Page
Figure 2.1	Chemical structure (a) of chitin and (b) of chitosan from deacetylation process	19
Figure 2.2	Classification of reservoir systems based on source activity (Siepmann and Siepmann, 2008)	33
Figure 2.3	Illustration of concentration profiles across a dense membrane in a liquid phase (Seader and Henley, 1998)	38
Figure 3.1	Flowchart of research methodology	43
Figure 3.2	Illustration of concentration profile for nutrients transport through a coated pellet	51
Figure 4.1	FTIR spectra for (a) non-cross-linked chitosan and (b) cross-linked chitosan with citric acid	60
Figure 4.2	Formation of amide linkage via cross-linking reaction between amino groups of chitosan and carboxylic groups of citric acid	61
Figure 4.3	SEM image of coating films of (a) CTS1 (b) CTS2 (c) CTS3 before the release rate tests	63
Figure 4.4	Morphological surface of CTS2 coated film after (a) 10 hr and (b) 10 days of release test under pH (i) 5.7, (ii) 7.1, (iii) 8.5	65
Figure 4.5	Cross sectional view of CTS2 film of chitosan after 1 day of release test under pH 5.7 condition (Average thickness: 81 μm)	67
Figure 4.6	Cross sectional view of CTS2 film of chitosan after 5 days of release test under pH 5.7 condition (Average thickness: 45 μm)	67
Figure 4.7	Cross sectional view of CTS2 film of chitosan after 8 days of release test under pH 5.7 condition (Average thickness: 34 μm)	68
Figure 4.8	Decreasing trend of CTS2 coating film thickness during the release rate test at pH 5.7	68

Figure 4.9	Plots of phosphate concentration versus time for fertilizers with different number of coatings under pH (a) 5.7, (b) 7.1 and (c) 8.5 after 10 hr of release test	71
Figure 4.10	Plots of phosphate concentration versus time for fertilizers with different number of coatings under pH (a) 5.7, (b) 7.1 and (c) 8.5 after 10 days of release test	72
Figure 4.11	Plots of phosphate release rate versus time for fertilizers at different pH conditions for (a) CTS1, (b) CTS2 and (c) CTS3 coated pellets after 10 hr of release test	74
Figure 4.12	Plots of phosphate release rate versus time for fertilizers at different pH conditions for (a) CTS1, (b) CTS2 and (c) CTS3 coated pellets after 10 days of release test	76
Figure 4.13	Plots of phosphate release rate versus time for fertilizers with different number of coatings at pH (a) 5.7, (b) 7.1 and (c) 8.5 after 10 hr of release test	78
Figure 4.14	Plots of phosphate release rate versus time for fertilizers with different number of coatings at pH (a) 5.7, (b) 7.1 and (c) 8.5 after 10 days of release test	79
Figure 4.15	Scheme of nutrient release stage from a chitosan-coated fertilizer pellet	80
Figure 4.16	The trend of phosphate release rate through a chitosan-coated pellet.	82
Figure 4.17	Trend of $k_L C_o$ in different pH conditions of aqueous medium with variation of number of coatings for release test of 10 hr.	87
Figure 4.18	Trend of $k_L C_o$ for different period of release test in variation of pH conditions for (a) CTS1, (b) CTS2 and (c) CTS3 coated pellets	89
Figure 4.19	Trend of D in different pH condition of aqueous medium with variation of number of coatings for release test of 10 hr.	92
Figure 4.20	Trend of D for different periods of pellets exposure in the aqueous medium for (a) CTS1, (b) CTS2 and (c) CTS3 coated pellets.	94

Figure 4.21	Trend of r values in different pH condition of aqueous medium with variation of number of coatings for release test of 10 hr.	96
Figure 4.22	Trend of r for different periods of pellets exposure in the aqueous medium for (a) CTS1, (b) CTS2 and (c) CTS3 coated pellets	97
Figure 4.23	Plot of predicted phosphate release rate versus experimental release rate for condition at pH (a) 5.7, (b) 7.1 and (c) 8.5	99

LIST OF ABBREVIATIONS

Symbol	Description
N	Nitrogen
P	Phosphorus
K	Potassium
S	Sulphur
Mg	Magnesium
Ca	Calcium
Fe	Iron
Zn	Zinc
Mn	Manganese
Cu	Copper
B	Boron
Mo	Molybdenum
Cl	Chlorine
FAO	Food and Agriculture Organization of the United Nations
IFA	International Fertilizer Industry Association
Cd	Cadmium
SRF	Slow-release fertilizers
CRF	Controlled-release fertilizers
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscope
DD	Degree of deacetylation

TS	Tensile strength
WVP	Water vapor permeability
TSM	Total soluble matter
EDTA	Ethylenediamine tetraacetic acid
HPMC	Chitosan-hydroxy propyl methyl cellulose
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	Calcium dihydrogen phosphate
CaO	Calcium oxide
$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	Citric acid
Na_2CO_3	Sodium carbonate
$(\text{C}_6\text{H}_{11}\text{NO}_4)_n$	Chitosan
$\text{C}_2\text{H}_4\text{O}_2$	Glacial acetic acid
NaOH	Sodium hydroxide

LIST OF SYMBOLS

Symbol	Description	Unit
t	Time	min
c_{i0}	Solute concentration in the membrane just adjacent to the upstream membrane surface	g/m^3
c'_{i0}	Solute concentration in the feed side just adjacent to the upstream membrane surface	g/m^3
c_{iL}	Solute concentration in the membrane just adjacent to the downstream membrane surface	g/m^3
c'_{iL}	Solute concentration in the permeate side just adjacent to the downstream membrane surface	g/m^3
M_t	Absolute cumulative amount of solute released at time t	g
M_∞	Absolute cumulative amount of solute released at infinite time	g
n	Release exponent which represent the drug release mechanism	-
k_1	Constant incorporating structural and geometric characteristics of the release system	-
y	Percentage of nutrient released	%
a	Percentage of nutrient released in the first day	%
b	Order of Equation 2.2 with respect with time	-
m_r	m_n/M_o	-
m_n	Mass of nutrient diffusing out of granule	g
M_o	Initial or total mass of nutrient in the granule	g
S_p	Cross-sectional area of pore	cm^2

l	Coating thickness	cm
C_{sat}	Saturation concentration of nutrient in granule	g/cm ³
ρ	Density of fertilizer	g/cm ³
t_l	On-set of the period decaying rate of release	min
D_f	Diffusion coefficient of nutrient in water	m ² /min
t_z	Zero-order release time	min
V	Interior volume of coating	cm ³
C	Urea concentration	mol/cm ³
A_c	Coating area	cm ²
S	Solubility of urea	g/cm ³
D'	$D_u A_o / A$	cm ² /s
A_o	Cross-sectional area of orifice	cm ²
D_u	Diffusivity of urea	cm ² /s
d	Constant in Equation 2.5	-
π_s	Osmotic pressure at saturation	Pa
r_f	Radius of fertilizer granule	mm
\tilde{g}	Fractional release	-
A_g	Surface area of the device	cm ²
t'	Lag period	day
t^*	Time which all solid fertilizer dissolved	day
\tilde{P}_s	Specific solute permeability	cm ³ /day
r_{ex}	External radius of coated pellet	cm
r_{in}	Internal radius of coated pellet	cm

D	Diffusion coefficient of solute in the coating	m^2/min
k	Partition coefficient	-
P	Solute permeability across the coating	cm^2/s
Δc	Concentration difference over the membrane	g/m^3
c_t	Concentration of the drug in the release medium at time	g/m^3
V_r	Volume of drug reservoir	cm^3
c_s	Solubility of drug within reservoir	g/cm^3
Q	Amount of drug released at time t	g
Q_0	Total amount of the drug in the core tablet	g
A'	Lumped parameter in Equation 2.12	-
B	Lumped parameter in Equation 2.13	-
E	Lumped parameter in Equation 2.14	-
D_m	Diffusion coefficient of the drug in the medium of inner space of tablet	m^2/min
H_0	Radius of the coated tablet	m
R_c	Initial radius of the un-dissolved core tablet	m
m	Decreasing rate of the coated film thickness	m/min
C_0	Content of the drug in the core tablet	g
H	Length of cylinder	m
R_i	Inner radii of the sphere	m
R_0	Outer radii of the sphere	m
Z	Thickness of the pellet	m
A	Area of mass transfer	m^2
C_{av}	Average nutrient concentration in the release medium at time, t	g/m^3

R	Release rate of nutrient	g/min
k_L	Mass transfer coefficient for external surface of coat	m/min
C_2	Nutrient concentration at the outer surface of the coat at a time, t	g/m ³
C_a	Nutrient concentration outside the pellet at a distance ∞ from the inner boundary of the coat	g/m ³
$C_{III}(x,t)$	Concentrations of nutrient in the aqueous solution at a distance x from the external surface of the coat at a time t	g/m ³
C_o	Original concentration of nutrient within the pellet	g/m ³
r	$k(D/D_f)^{0.5}$	-
C_I	Solute concentrations within the pellet	g/m ³
C_m	Solute concentrations within the membrane	g/m ³
x	Transport region	-
l_o	Initial thickness of the coat	m
R^2	Correlation coefficient	-

Greek Symbols

α	Constant in Equation 2.6
\AA	Angstrom, 10^{-10}

LIST OF APPENDICES

- A.1 Values for experimental data of $Z \frac{dC_{av}}{dt}$ ($Z=0.004\text{m}$)
- A.2 MATLAB command for diffusion model in Equation 3.10
- A.3 MATLAB command for extended diffusion model in Equation 3.12
- A.4 Values of parameter P

PENILAIAN PARAMETER YANG MENGAWAL KADAR PEMBEBASAN ION FOSFAT DARI PELET BAJA FOSFORUS BERSALUT KITOSAN

ABSTRAK

Baja bersalut yang tergolong dalam kumpulan baja kawal bebas (CRF) telah digunakan secara meluas dalam bidang pertanian sebagai usaha untuk mengurangkan pencemaran air tanah dan pada masa yang sama meningkatkan kecekapan penggunaan nutrien oleh tanaman. Kitosan adalah salah satu daripada biopolimer yang boleh digunakan sebagai bahan salutan untuk mengawal kadar pembebasan nutrien daripada baja pelet disebabkan oleh sifat-sifatnya yang bagus. Kebanyakan kajian terdahulu yang berdasarkan salutan kitosan telah memberi tumpuan kepada baja urea dan baja sebatian nitrogen-fosforus-kalium (NPK). Kajian tentang baja fosforus bersalut kitosan masih belum dijalankan setakat ini. Tambahan pula, kajian sebelum ini juga mengabaikan penilaian parameter yang mengawal kadar pembebasan nutrien menggunakan model mekanistik. Pemahaman berkenaan parameter angkutan seperti pekali resapan nutrien melalui pelet yang bersalut adalah sangat penting dalam usaha untuk meningkatkan reka bentuk baja. Kajian ini tertumpu kepada mengkaji kadar pembebasan ion fosfat dari pelet baja fosforus bersalut kitosan dan penilaian parameter yang mengawal pembebasan nutrien menggunakan model mekanistik. Eksperimen yang bersesuaian telah dijalankan untuk menentukan kadar pembebasan ion fosfat daripada pelet dengan bilangan lapisan salutan kitosan yang berbeza (satu, dua dan tiga lapisan) di bawah variasi keadaan pH (pH 5.7, 7.1 dan 8.5). Ujian pembebasan juga telah dijalankan bagi tempoh jangka pendek dan panjang. Satu model resapan yang mempertimbangkan pembentukan lapisan sempadan pada permukaan luar pelet yang bersalut telah

digunakan dalam kajian ini dan model lanjutan yang mempertimbangkan perubahan ketebalan salutan telah dibangunkan. Penilaian parameter angkutan telah dilakukan dengan memadankan model dengan data eksperimen. Parameter angkutan telah dianalisis untuk memahami bagaimana mereka mempengaruhi kadar pembebasan fosfat di bawah perubahan bilangan salutan, pH dan pendedahan pada tempoh singkat/lama. Didapati bahawa kadar pembebasan fosfat dan parameter $k_L C_o$, D dan r menurun apabila bilangan salutan, nilai pH bagi media akueus dan tempoh pendedahan meningkat. Data eksperimen telah diperhatikan sepadan dengan model dan memberikan pekali korelasi yang memuaskan antara 0.932-0.953.

EVALUATION OF PARAMETERS GOVERNING THE RELEASE RATE OF PHOSPHATE IONS FROM CHITOSAN-COATED PHOSPHORUS FERTILIZER PELLETS

ABSTRACT

Coated fertilizers, which belong to the group of controlled-release fertilizer (CRF) have been widely used in agricultural field in order to reduce the ground water pollution and at the same time increase the nutrient use efficiency by crops. Chitosan is one of promising biopolymers that can be used as a coating material in order to control the release rate of nutrients from fertilizer pellets due to its excellent properties. Most of the previous studies based on the chitosan coating were focused on the urea and compound fertilizers of nitrogen-phosphorus-potassium (NPK). Studies regarding the chitosan-coated phosphorus fertilizers have not been addressed so far. Furthermore, previous studies also neglected the evaluation of parameters that govern the nutrient release rate using the mechanistic model. Understanding the transport parameters such as diffusion coefficient of nutrient through coated pellet is very important in order to improve the design of fertilizers. This study is mainly focused on investigating the release rate of phosphate ions from the chitosan-coated phosphorus fertilizer pellets and evaluation of parameters that controlled the nutrient release using mechanistic model. Appropriate experiments were carried out in order to determine the phosphate ions release rate from pellets with different number of chitosan coating layers (one, two and three layers) under variation of pH conditions (pH 5.7, 7.1 and 8.5). Experiments were also conducted for short and long period of release tests. A diffusion model considering the formation of boundary layer on the external surface of the coated

pellets was used in this study and the extended model, which considers the changes of coating thickness was developed. Evaluation of the transport parameters was carried out by fitting the model with the experimental data. The transport parameters were analyzed in order to understand how do they affect the release rate of phosphate under variation of number of coatings, pH and short/ long exposure. It was found that the phosphate release rate and parameters of $k_L C_o$, D and r decreased as the number of coatings, pH values of the aqueous medium and period of exposure increased. The experimental data was observed to fit the model and giving a satisfactory correlation coefficient ranging from 0.932 to 0.953.

CHAPTER 1

INTRODUCTION

For centuries, fertilizers have been widely used in agricultural activities in order to supply the essential nutrients for the growth of crops and to facilitate the increase of yields. These nutrients can be classified into two groups, which are macronutrient and micronutrient. Macronutrient is referred to the nutrient, which required by plants in large quantities and they can be further categorized as primary and secondary macronutrients. Nitrogen (N), phosphorus (P) and potassium (K) belong to the group of primary macronutrients since crops need them in large quantities. Secondary macronutrient, which consists of sulphur (S), magnesium (Mg) and calcium (Ca) is taken up by crops in lesser amounts compared to the primary macronutrients. Elements of iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), and chlorine (Cl) are classified as micronutrients and required by crops only in very small amounts (FAO and IFA, 2000). It is important for all of these nutrients to be supplied in a sufficient amount, since the deficiency of only a single nutrient is enough to limit the plant growth (IFA, 2007). Unfortunately, primary macronutrients of N, P and K are generally the most widely deficient elements in soils and they become major concern in agricultural field (Alley and Vanlauwe, 2009).

1.1 Phosphorus Fertilizer

Phosphorus is one of the macronutrients that play an important role for the growth of crops. The functions of phosphorus are mainly involved in the process of transferring energy, such as photosynthesis in plants (FAO and IFA, 2000).

Furthermore, the presence of phosphorus in soil can also promote the root development stage of crops (Windridge, 1998).

World production of phosphorus fertilizers is coming from the source of phosphate rock. The main producers for this type of fertilizer are USA, China, Africa and the Middle East (Isherwood, 2000). P is usually supplied to the crops either in the form of straight fertilizer or compound fertilizer. The term of “straight fertilizer” is generally used to express the fertilizer which contains only one primary nutrient (FAO and IFA, 2000). Examples of straight fertilizers for phosphorus are single superphosphate and triple superphosphate, while compound fertilizer types are ammonium phosphates, nitrophosphates, PK and NPK fertilizers. Superphosphate fertilizers are produced from the reaction between sulphuric acid and phosphate rock in order to obtain water soluble form of phosphorus, which is known as calcium dihydrogen phosphate. Single superphosphate fertilizers mostly have low content of phosphorus with a range between 7 to 9.5% P, while triple superphosphate could give higher phosphorus composition, around 17 to 23% P (Barak, 1999).

1.2 Global Issues on Phosphorus Fertilizers

The application of conventional fertilizers in agricultural field usually deals with problems of uncontrolled release of the nutrients. Excessive nutrients supplied to soil have a high possibility to be leached out and consequently create a number of problems in terms of environmental pollution and inefficient use of nutrients. For phosphorus fertilizers, the possibility of phosphate leaching is relatively small due to its fixation in soil, and phosphate losses are usually contributed by soil erosion and surface run-off (Isherwood, 2000). However, it is not impossible for phosphate to be

leached out if the maximum phosphate fixation capacity in soil is already reached, especially when phosphorus fertilizers are oversupplied.

The accumulation of phosphorus in lakes and rivers due to the leaching and surface run-off could increase the concentration in water. This condition might consequently promote an uncontrollable algae bloom. Algae bloom phenomenon or also known as eutrophication process would cause depletion of oxygen in water, preventing light from reaching the bottom of lakes and also releasing toxic chemicals upon decomposition (Johnston, 1995, Johnston, 2000). This condition is very harmful to the aquatic life and animals consuming the water.

Furthermore, the loss of nutrients into the soil is not efficient in terms of fertilizers utilization. The amount of nutrients available in soil for the plants uptake will be reduced through leaching and thus, will limit the plants growth process. This condition should definitely be avoided since any interruption in plants growth process would result in low crops yield. An increase in world's population and food demand have resulted in the increase of requirement in crops productivities. It is estimated that the global fertilizers demand and consumption will increase so as to produce more food to be supplied to the ever increasing growth population especially in the developing countries (Shaviv, 2000). According to the IFA (2009), the fertilizers demand in 2050 would be increased up to 50-80% above the current production, since the world population growth is averagely estimated to increase about 50 to 70 billion per year until mid 2030s (FAO, 2008). However, in contrast to the increasing food demand, the total area of land that available for agricultural activities will be lower in the future due to the rapid urbanization. This condition apparently implies the increase of nutrients load per unit area, which requires food

productivities to be more intensive and efficient than before (Shaviv, 2000, IFA, 2009).

An inefficient use of nutrients through the application of conventional phosphorus fertilizers has becoming a major concern in fertilizer industries since phosphate rock is a finite and non-renewable resource. Currently, about 83% of the world's phosphate rock mines are used to produce the phosphorus fertilizers (Johnston, 2000), which are needed for the increasing crops productivities. It was estimated by the International Fertilizer Industry Association (IFA) that the world's phosphate rock resources and reserves could only last between 105 and 470 years (Syers et al., 2008). Therefore, the current role of scientists in order to prolong the phosphate rock life span is mainly focused on the efforts of increasing phosphorus fertilizers efficiency in agricultural activities (Syers et al., 2008).

Another issues regarding phosphorus fertilizers is the presence of some trace elements originate from the phosphate rock source. Cadmium (Cd), which is one of these trace elements, is reported to be very harmful to humans (Johnston, 2000). High application rate of conventional phosphorus fertilizers would possibly increase the Cd content in soil in the future. Thus, any method that can reduce the application rate of phosphorus fertilizers can also reduce the buildup of this harmful trace element (Shaviv, 2000).

1.3 Methods for Increasing the Efficiency of Fertilizers

Currently, there are special types of fertilizers that can potentially reduce the losses of nutrients to the surrounding environment and result in an efficient release

rate. These fertilizers include; the foliar type and the slow/controlled-released fertilizers (Trenkel, 2010).

1.3.1 Foliar Fertilizers

Foliar fertilizers are substances in liquid forms containing primary nutrients or micronutrients applied to plants by spraying on their leaves. Absorption of nutrients also can be carried out through plants' leaves instead of using their roots pathways. The application of foliar fertilizers could provide high nutrients utilization, minimizing the nutrients losses due to leaching and hence, reducing the pollution of groundwater (Drach and Vosskamp, 2007, Trenkel, 2010). However, there are some disadvantages in using foliar fertilizers application since it is economically unfeasible to apply all necessary nutrients through plants' leaves (Trenkel, 2010). Furthermore, the drawbacks also include short action time of foliar fertilization and only small quantity of primary nutrients can be applied onto plants' leaves (Drach and Vosskamp, 2007).

1.3.2 Slow and Controlled-Release Fertilizers

The use of slow-release fertilizers (SRF) and controlled-release fertilizers (CRF) is one alternative that can be implemented in agricultural field in order to reduce the losses of nutrients and minimizing environmental hazards. Generally, the percentage of SRF and CRF application is still small compared to the total amount of common fertilizers used worldwide. However, the demand for the CRF in agricultural activities increases at an annual rate of about 10% (Shaviv, 2000). It was also reported that the world consumption of synthetic SRF and CRF in 2004/05 was increased about 45% compared to the period of 1995/96 (Trenkel, 2010).

SRF and CRF are fertilizers containing nutrients, which in the form that can delay the nutrients availability for the plant uptake and make the release period longer than the common fertilizers (Trenkel, 2010). One of the CRF, known as coated fertilizer which is encapsulated by a special material that can reduce the nutrients dissolution rate to the surrounding medium. Examples of commonly use coating materials are wax, sulfur, polymer (e.g. polyolefin, polysulfone, alkyd resin, polyurethane and polyethylene) and rubber (Tomaszewska and Jarosiewicz, 2002, Liang and Liu, 2006, Trenkel, 2010). However, there are some limitations in the application of these existing coating materials which mainly involves high production cost due to the expensive prices of coating materials (Trenkel, 2010). Furthermore, most of the polymer coatings are not degradable and will finally create another environmental problem due to the accumulation of the synthetic residues in soil. Following that, a number of studies have been carried out in order to investigate the applicability of biodegradable polymers as the coating materials for fertilizers. Chitosan is a promising biodegradable polymer which could be applied as a coating material that can reduce the dissolution rate of fertilizers. This renewable biopolymer becomes popular nowadays due to its biodegradability, bio-compatibility, non-toxicity and low cost (Dutta et al., 2004, Wu and Liu, 2008). It has been widely used in the field of biomedical, pharmaceutical, agricultural, food and cosmetic industries (Rinaudo, 2006, Wu and Liu, 2008). Recent studies report that the chitosan-coated fertilizers showed excellent properties of controlled-release NPK compound fertilizer (Wu and Lui, 2008, Wu et al., 2008).

1.4 Problem Statement

The nutrient losses to surrounding via leaching, soil erosion and surface runoff from the application of conventional fertilizers have contributed to the contamination of groundwater, which finally enters the lakes and river systems. In Malaysia, a comprehensive study conducted by Lomoljo et al. (2009) found that the concentrations of phosphorus in the surface intertidal waters of Kuala Gula Bird Sanctuary were the highest in the months coincided with the planting season of the nearby paddy fields. This proved that the excessive fertilizer application in the agricultural activities might contribute to the increasing nutrients concentration in the rivers and delta. Increasing the phosphorus concentration in the surface water will promote the eutrophication process, which is harmful to the aquatic life as well as land animals. Furthermore, phosphorus fertilizers may contain some trace elements such as cadmium which is very toxic to humans. Thus, excessive application rate of such fertilizers could possibly cause the accumulation of this trace element in soil and can also enter the water system via leaching. The efficiency of phosphorus-based fertilizers also needs to be increased more than before since the phosphate rock is a finite and non-renewable resource for the production of such fertilizers. Furthermore, an efficient use of phosphorus fertilizers is important in order to maintain the phosphorus availability in soils and promoting the crops growth and yields. Increasing food productivities is becoming one of global major concerns as the world's population is also arising.

The use of SRF or CRF in agricultural field is one method that can increase the efficiency of fertilizers. This special type of fertilizer could minimize the nutrients losses to environment, increase agronomic performance and economically effective since the frequency of fertilizers applied is reduced. For phosphorus

fertilizers, it was confirmed from research conducted by Garcia et al. (1997b) that the availability of P nutrient in soil could be increased by using CRF type of such fertilizers. Polymer-coated fertilizer is one of the CRF which has the potential for supplying the nutrients optimally during the crops growth period (Du et al., 2006). However, conventional polymers coatings are expensive and not degradable. Thus, there is a need in moving towards the use of low cost and biodegradable polymer coats in the production of fertilizers.

Chitosan is an abundant natural polysaccharide has become popular nowadays due to its biodegradability, bio-compatibility, non-toxicity and low cost material. However, there are still limited studies on the use of chitosan as coating material for fertilizers being reported. Previous studies regarding chitosan-coated fertilizers were mostly based on urea and NPK fertilizers and none of them reported specifically on the phosphorus fertilizers.

Understanding the mechanism and transport parameters such as diffusion coefficient, which governs the release rate of nutrient through chitosan-coated fertilizers is very important in order to design a better controlled-release fertilizer. Previous investigations did not extensively discussed on the kinetic release aspect and the evaluation of transport parameters was carried out only using a simple empirical model (Wu and Liu, 2008). Thus, in-depth investigation is required for the evaluation of nutrient release parameters using a mechanistic model, which then takes into account some important phenomena that can give better insight towards the nutrient release process. Furthermore, most of the previous studies also assumed that the transport parameter such as diffusion coefficient of nutrient through the coat is averagely constant throughout the release period of fertilizers application. However, in actual practice, the pellet composition and coating properties can vary

with time which consequently would affect the nutrient release rate from the coated fertilizers. Hence, the diffusion coefficient through coat is also expected to change with time and can vary from the short period to long period of fertilizers application.

1.5 Objectives

- i. To investigate the effect of various parameters on the phosphate release rate from chitosan-coated phosphorus fertilizer pellets.
- ii. To evaluate the parameters governing the release rate of phosphate through the chitosan coating using a suitable mechanistic model.

1.6 Scope of Study

For the first objective, the scope covers the preparation and characterization of the chitosan-coated phosphorus fertilizer pellets and to investigate the effect of pH conditions, number of coatings and period of release test to the phosphate release rate. In the first part of this work, chitosan solution was prepared by cross-linking with citric acid in order to improve the water barrier properties of the fertilizers coating. The non-cross-linked and cross-linked chitosan solutions were compared based on the characterization of the chemical bonding using Fourier Transform Infrared (FTIR) spectrometer. The prepared cross-linked chitosan solution was used to coat the phosphorus fertilizer pellets. The thickness of the coating films were measured using the micrometer screw gauge. The upper surface and cross sectional morphology changes of the coating before and after the phosphate release tests were observed using Scanning Electron Microscope (SEM). For the second part of this

work, the phosphate release tests were carried out by varying the number of coatings (one, two and three layers) and pH conditions (pH 5.7, 7.1 and 8.5) of the aqueous medium. The release tests were conducted in two set of experiments, which were set for short (10 hr) and long period of release (10 days). The results of the phosphate release rate were compared and analyzed.

For the second objective, the scope covers the evaluation of some parameters that govern the nutrients release such as diffusion coefficient using a mechanistic mathematical model. This mathematical model considers some important phenomena that might take place, such as the formation of boundary layer on the external surface of coating and also the changes of the coating thickness due to the chitosan erosion in acidic aqueous medium. The transport parameters were evaluated for each case under variation of number of coatings and pH conditions for respective short and long period of release tests. The model was validated using the experimental data obtained previously.

1.7 Organization of Thesis

This thesis is consists of five chapters. A general overview of each chapter is described as follow:

Chapter 1 gives a brief introduction on the phosphorus fertilizers and its related issues. This chapter also introduces chitosan as a promising material for coating the phosphorus fertilizers in order to control the nutrient release. The problem statement, objectives and scopes of study are also covered in this chapter.

Chapter 2 explains the detail about the slow and controlled-release fertilizers (SRF and CRF). It also discusses on polymer-coated fertilizers and the potential of chitosan as a promising biopolymer for controlled-release fertilizers application. The chitosan properties, chemical modification by cross-linking reaction, summary of the previous studies regarding the use of chitosan as coating material for fertilizers and theories of mathematical modeling are included in this chapter.

Chapter 3 covers the materials, equipments and experimental procedures carried out in this study. It also discuss on the development of mathematical model that was used to evaluate the experimental data.

Chapter 4 presents the results obtained from the experimental works. The analysis of the results is discussed in this chapter.

Chapter 5 gives the conclusion obtained from this research. The recommendations for future works also given for improvement and development of the present research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Fertilizers

Fertilizers are often needed to support the plant growth in soil which is lacking of nutrients. Usually, they can be obtained either in the form of organic or mineral fertilizers. Fertilizer from organic manure is good for improving the soil conditions but its nutrient contents usually is low (FAO and IFA, 2000). Thus, application of mineral fertilizers is required in order to supply the high nutrients demand for crops growth.

The term of “mineral fertilizers” is referred to the industrially manufactured fertilizers. These type of fertilizers can be produced either in the shape of granules or pellets. Granular fertilizers are fertilizers particles which in the range of 2 to 4mm diameter (Gowariker et al., 2009) and have advantageous in terms of less caking and less dustiness problems. Fertilizer pellets provide a more even and lasting supplement than granular fertilizers. This kind of fertilizers can last for three to six months (Petersen, 1999). Both granular and pelletized fertilizers are applied to the soil and dissolved over time, releasing the nutrients to the roots.

2.2 Fertilizers and Soils

When granular or pelletized fertilizers are applied to the soil, the nutrients will be released to the surrounding when they get in contact with the soil and the water. The nutrients released dissolved in the soil water, forming the soil solution, which becomes an important medium for the nutrients uptake by crops. According to

Syers et al. (2008), phosphorus nutrients in the soil solution are mainly transported to the roots by diffusion mechanism.

There are many factors affecting the nutrients uptake rate by the roots. These include; concentration of the nutrients in soil solution, soil acidity, soil texture (sand, clay content), bulk density and size of the root system (Syers et al., 2008, Alley and Vanlauwe, 2009). The plant roots usually showed greater growth in the soil zone containing higher concentration of nutrients and thus, resulted in higher nutrients uptake rate (Alley and Vanlauwe, 2009). Soil pH can be varied from acidic to basic range. Most of the soils in tropical regions are acidic while alkaline soil can be found in the dry sub-tropic, arid and semi-arid regions (Garcia et al., 1997a, FAO and IFA, 2000). The P availability in acidic soils usually is low due to its precipitation with soil elements of aluminum and irons. This condition consequently reduces the P uptake by roots and limits the plant growth in acidic soils. In alkaline soil, P nutrients can be fixed by the element of calcium but the P availability in these soils usually is high compared to that of acidic soils (Ludwick, 1998).

2.3 Overview on Slow and Controlled-Release Fertilizers

The use of conventional fertilizers in agricultural field often results in high dissolution rate in a short time and thus, potentially exposed the nutrients to the leaching and fixation process. As an alternative, slow and controlled-release fertilizers (SRF and CRF) can be applied in order to solve the aforementioned problems (Oertli, 1980, Shaviv, 2000). These fertilizers could prolong the nutrients availability in soil compared to the conventional fertilizers which often consumed faster. According to FAO and IFA (2000), there is no official differentiation stated

between the slow and controlled-release fertilizers. However, Shaviv (2000) has proposed the classification of the SRF and CRF which presented as in Table 2.1.

Table 2.1: Classification of SRF and CRF

Category	Types	Description	Examples
SRF	Organic-N low-solubility compounds	Biologically decomposing compounds	<ul style="list-style-type: none"> • urea-formaldehyde
	Inorganic low-solubility compounds	N/A	<ul style="list-style-type: none"> • metal ammonium phosphate • partially acidulated phosphate rock
CRF	Coated fertilizers	Fertilizers in which a physical barrier control the release Types of coating: <ul style="list-style-type: none"> • Organic polymer coating • Inorganic material coating 	<ul style="list-style-type: none"> • Thermoplastic, resin coated fertilizers • Sulphur or mineral based coated fertilizers
	Matrices fertilizers	Types of matrices: <ul style="list-style-type: none"> • Hydrophobic • Hydrophilic 	<ul style="list-style-type: none"> • Polyolefin, rubber • Gel-forming polymers(hydrogel)

According to the above classifications, coated fertilizers from the group of CRF are more common in practice (Shaviv, 2000) while the gel-based matrices of fertilizers are still under development (Trenkel, 2010).

2.4 Fertilizer Coating

Fertilizer coating is a technique which widely used in the CRF manufacturing industry. The advantages with the coated fertilizers include its ability to immobilize

the fertilizer pellets and control the nutrients release (Zou et al., 2009, Davidson and Gu, 2012). Furthermore, the frequency of fertilizers application can be reduced and consequently would save the spreading cost (Shaviv, 2000). For phosphorus fertilizers, it was found by Garcia et al. (1997a) that the application of coated triple superphosphate fertilizers would increase the P availability in soil compared to the use of uncoated fertilizers.

Various materials have been used as coating material to encapsulate the fertilizers. Commonly used coating materials include sulfur, wax, rubber and polymers (Jarosiewicz and Tomaszewska, 2003, Liang and Liu, 2006, Trenkel, 2010). Out of these, polymer coated fertilizers are currently the most popular CRF (Du et al., 2008). There are various types of polymer materials, which have been used to encapsulate the fertilizers for controlled-release purposes such as polyolefin, polyethylene, alkyd resin, polypropylene, polyurethane and polystyrene (Tian and Saigusa, 2002, Ge et al., 2002, Trenkel, 2010). However, the drawback for the application of conventional polymers is the accumulation of polymer residues in the soil (Golman, 2011).

2.5 Coated Phosphorus Fertilizer

Increasing the efficiency of phosphorus fertilizer is becoming one of the major concerns in agricultural field since this type of fertilizer is mainly produced from the finite source of phosphate rock. Thus, fertilizer coating has been employed as one of the technique in order to control the phosphate release to the soil and improve the nutrient use efficiency. This technique has been investigated since the 1960s and asphalt is one of the earliest coating materials that have been used to coat

the phosphorus fertilizers. However, Hall and Baker (1967) reported that asphalt coating was only effective on superphosphate fertilizers and not effective to coat the diammonium phosphate or magnesium ammonium phosphate due to the adhesion failure on the crystal surface. Allen and Mays (1971) studied on the sulphur-coated fertilizers. Their results showed that sulphur is not promising for the coating of phosphorus fertilizers since the P supply from the coated phosphorus fertilizer was lower than those of uncoated phosphorus fertilizer. Diez et al. (1992) investigated on the rosin-coated diammonium phosphate and found that the use of rosin coating can control the P fixation in calcareous soil.

2.6 Nutrient Release Mechanisms and Pattern

Generally, the mechanisms of nutrient release process consist of three stages as described by Shaviv (2000). In the first stage, water will penetrate into the fertilizer pellet or granule and dissolves some part of the fertilizer content. The second stage is a phase where nutrients are released. The release rate is constant if saturated solution exists inside the pellet or granule. Lastly, in the third stage, the release rate decreases as the nutrient concentration within the pellet or granule decreases. The third stage also known as the decay stage.

The nutrient release pattern or profile from a coated fertilizer usually depends on the properties of the fertilizers and its coating. At the initial part of the release profile, there are two types of release pattern that could be occurred known as lag phase and burst release.

(a) Lag Phase

A lag phase at the initial stage of release is a phase where almost no release is observed (Shaviv, 2000). Some of the coated fertilizers exhibit a lag phase on their release profile during the water penetration process which probably due to the properties of the voids formation inside the solid core and between the coating and the core. The higher the volume of the internal voids, the longer the time needed for water to fill the voids and prolong the duration of the lag phase (Shaviv, 2000).

(b) Burst Release

A burst release profile is indicated as high initial release rate at the beginning of the release stage. According to Huang and Brazel (2001), there are several factors that can lead to the burst release. For a coated formulation, the burst release could be due to the migration of the solute into the surface of membrane encapsulating the systems during the drying and storage process (Huang and Brazel, 2001, Siepmann and Siepmann, 2012). Thus, the solute will be released faster upon placing in the release medium.

Based on the previous study by Garcia et al. (1997b), the phosphate release behavior from the coated phosphorus fertilizers did not show the lag phase but exhibit rather a burst release at the beginning of the release profile. They were used lignin, a biopolymer as the coating material. A similar observation on the P release pattern was made by Wu and Liu (2008) who used the biopolymer to coat the NPK fertilizers. The high initial P release at the beginning of the release stage for phosphorus fertilizer coated with a biopolymer material could be due to the affinity of the phosphate to migrate to the swelling biopolymer surface during the coated fertilizer preparation process.

2.7 Chitosan

2.7.1 Introduction to Chitosan

Recently, hydrophilic and biodegradable polymers have attracted more attentions from researchers in the area of controlled-release fertilizers (Chen et al., 2008, Han et al., 2009, Ni et al., 2010, Ni et al., 2011). The application of hydrophilic polymers in controlled-release fertilizers was inspired by the successful application of these polymers in pharmaceutical field and also shown promise for minimizing fertilizer losses (Mikkelsen, 1994).

Chitosan is one of hydrophilic polymers which abundantly present in nature. This natural polysaccharide is derived from chitin which obtained from crustacean shells. Chitin was first discovered in 1811 by a French professor, Henry Braconnot, while derivation of chitosan from chitin was found 48 years later by C. Rouget (Primex, 1999).

The monomer of chitin is β -(1-4)-2-acetamido-2-deoxy- β -D-glucose (N-acetylglucosamine) and just differs from cellulose structure by containing acetamido groups (-NCOCH₃) at C-2 position (Dutta et al., 2004). Chitosan is N-deacetylated derivative of chitin, which is produced by treating chitin with alkali such as sodium hydroxide (Kumar, 2000). Chitosan can be characterized by the degree of deacetylation (DD), which indicates the relative number of amino groups to the total groups (acetamido and amino groups) (Aghdam, 2010). A biopolymer containing number of DD > 50% is considered as chitosan, showing the dominant amount of amino groups (Rinaudo, 2006, Pillai et al., 2009). The chemical structures of chitin and chitosan are shown in Figure 2.1.

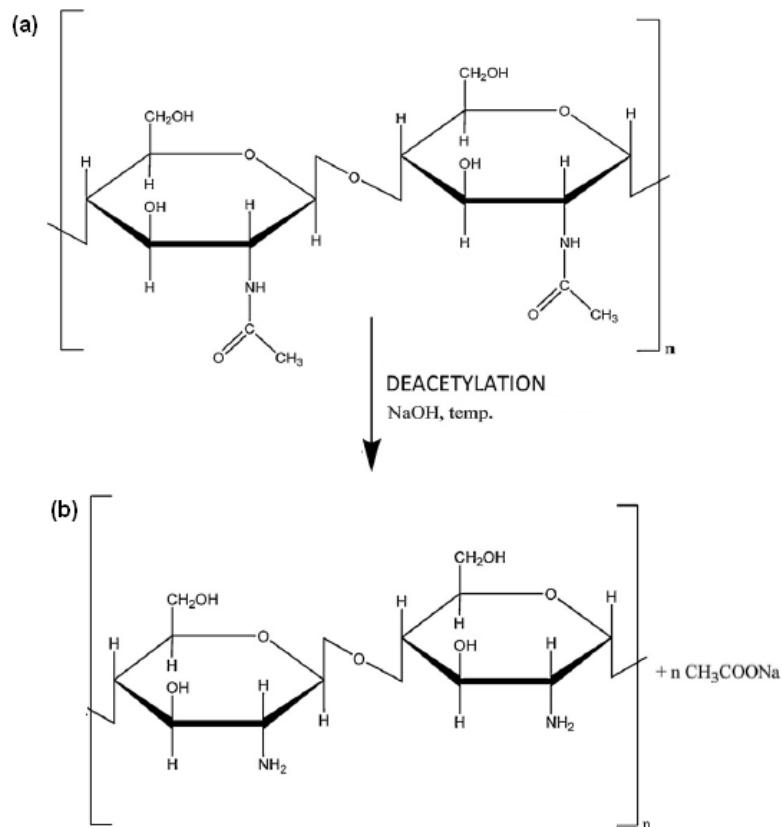


Figure 2.1: Chemical structure (a) of chitin and (b) of chitosan from deacetylation process

2.7.2 Film-forming Properties of Chitosan

Chitosan can be classified as highly basic polysaccharides. It is soluble in dilute acidic solutions below pH 6 and insoluble in aqueous, alkali and organic solvents (Ahonkhai et al., 2006). The amino groups of chitosan can be protonated at low pH and become a water-soluble cationic polyelectrolyte.

Chitosan film can be prepared by dissolving the chitosan powder in organic acid solvent such as acetic, formic and lactic acids (Kim et al., 2006). Among these solvents, acetic acid is the most commonly used in practice for preparing the chitosan film (Caner et al., 1998, Pillai et al., 2009). The summary of properties for chitosan

film based on acid solvent type used is shown in Table 2.2. It was reported that film prepared from acetic acid is the toughest followed by malic, lactic and citric acid (Park et al., 2002). Furthermore, chitosan film prepared based on acetic acid solvent has high water vapor barrier property and less hygroscopic. Kim et al. (2006) also found that acetic acid based chitosan film has the lowest total soluble matter (TSM) value which indicates good water resistance property compared to another types of acid based chitosan films. Lactic acid based chitosan film is the weakest film and can completely dissolve in water within 24 hours (Kim et al., 2006). From the literatures cited, acetic acid based chitosan film showed a high potential for film use in packaging and other applications due to the good water vapor barrier and mechanical properties.

Table 2.2: Summary of chitosan film properties based on tensile strength (TS), water vapor permeability (WVP) and total soluble matter (TSM)

Solvent type	Chitosan film properties			References
	TS	WVP	TSM	
Acetic acid	High	Low	Low	Caner et al., 1998, Park et al., 2002, Kim et al., 2006, Sobral et al., 2008
Formic acid	Low	High	High	Kim et al., 2006
Lactic acid	Low	High	High	Caner et al., 1998, Kim et al., 2006, Sobral et al., 2008
Malic acid	Low	Low	N/A	Park et al., 2002
Citric acid	Low	High	N/A	Park et al., 2002

2.7.3 Cross-linking of Chitosan Films

The hydrophilic nature of chitosan films and its solubility under acidic conditions are the limitations that should be solved for the broader application of chitosan films. This is important for the application of chitosan films to be in contact in aqueous solution such as pharmaceutical products.

Cross-linking is a method that can be used to improve the water vapor barrier properties of polymer films (Tsai and Wang, 2008, Bhattacharya et al., 2009). Examples of cross-linkers that have been used to modify the properties of chitosan are glutaraldehyde (Monteiro Jr and Airoidi, 1999, Krajewska, 2001a, Yang and Su, 2011), ethylenediamine tetraacetic acid (EDTA) (Shimizu et al., 2004), tripolyphosphate (Shen et al., 2008, Hu et al., 2010) and citric acid (Varshosaz and Alinagari, 2005, Yamaguchi et al., 2003). Glutaraldehyde is commonly used for cross-linking of polysaccharides but this cross-linking agent is reported to have toxic properties (Coma et al., 2003) and relatively expensive.

Citric acid is a type of polycarboxylic acid possessing one hydroxyl and three carboxyl groups, which can be used to cross-link the polymers. Its non-toxicity and low cost has attracted attentions as a cross-linker and being selected to modify the properties of polysaccharides such as cellulose and starch (Coma et al., 2003, Reddy and Yang, 2010). It was reported that citric acid cross-linking has successfully reduced nearly 40% of water solubility properties of chitosan-hydroxy propyl methyl cellulose (HPMC) (Moller et al., 2004). Previous studies found that the cross-linking agent should not be added more than 1.0% concentration to the chitosan solution since higher concentration of cross-linking agent would favor the film brittleness (Krajewska and Olech, 1996).

2.8 Chitosan in Controlled-Release Fertilizers

Chitosan has attracted many attentions from various fields of application due to its biodegradability, bio-compatibility, non-toxicity and a low cost material (Dutta et al., 2004, Hohne et al., 2007). It is widely used in biomedical, pharmaceutical, agricultural, food and cosmetic industries. In the agricultural applications, chitosan has been employed for seed and leaf coating and added as a part of fertilizers compound (Li et al., 1992, Zeng and Shi, 2008, Ziani et al., 2010). Studies on the potential of chitosan as a type of coating material for fertilizers are still limited in literature, since a lot of research mostly focused on utilizing this biopolymer as a nutrient source in organic or mineral fertilizers (Lubkowski and Grzmil, 2007).

Several studies have been reported regarding the application of chitosan in controlled-release fertilizers. These include the use of chitosan for matrix formulation of fertilizers (Corradini et al., 2010, Jamnongkan and Kaewpirom, 2010a, Jamnongkan and Kaewpirom, 2010b). The first study on chitosan-coated fertilizers was conducted by Teixeira et al. (1990) where they found that the encapsulation of urea beads by chitosan films could prolong the duration of the nutrient release by a factor of up to 180 compared to that of the uncoated urea beads. However, further studies on the chitosan-coated fertilizers only reported many years after that, with mainly focused on the urea and NPK compound fertilizer types. None of them reported on the applicability of encapsulating the phosphorus fertilizers with chitosan film. Table 2.3 and 2.4 show the summary on the studies of chitosan as coating material for urea and NPK fertilizers respectively.

Table 2.3: Summary of the recent studies on chitosan-coated urea fertilizers

Forms of chitosan coating	Parameters studied	Descriptions	References
Films	Effect of cross-linking agent types	<ul style="list-style-type: none"> • Urea release rate were much lower through N-propionylchitosan coating compared to N-acetylchitosan coating of urea beads 	(Teixeira et al.,1990)
N/A	N/A	<ul style="list-style-type: none"> • Nutrient release consists of two stages; steady and decay stage • Release rates coefficient was constant at steady stages but varied at decay stages • No lag stage observed 	(Chen et al., 2005)
Films	Effect of soil moisture, temperature, soil pH, water vapor pressure, ion concentration of liquid medium	<ul style="list-style-type: none"> • The release rate increased when: Soil moisture and temperature increased; ion concentration in liquid medium decreased • Soil pH does not have significance effect on nutrient release rate 	(Xia et al., 2009)

Table 2.4: Summary of the recent studies on chitosan-coated NPK fertilizers

Forms of chitosan coating	Parameters studied	Descriptions	References
Films	Chitosan concentration, degree of deacetylation of chitosan	<ul style="list-style-type: none"> • Low nutrients release rate observed for fertilizers coated with high concentration of chitosan and having low degree of deacetylation 	(Hanpichanchai, 2002)
Powder	Effect of parameters during superabsorbent polymer preparation	<ul style="list-style-type: none"> • NPK fertilizers were coated with two layers coating; inner coating was chitosan powder and outer coating was superabsorbent polymer. • Chitosan coating layer controlled the nutrient release and nutrients released did not exceed 75% on the 30th day 	(Wu and Liu, 2008) (Wu et al., 2008)