UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF COATING TECHNOLOGY USING ROTARY PAN FOR PRODUCTION OF SLOW-RELEASE UREA

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By

FARAHNAZ EGHBALI BABADI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

May 2015

DEDICATION

To the soul of my Father, the first to teach me.

To my beloved Mother, for her prayers to me.

To my beloved sisters, for their care and support.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Professor Robiah Yunus, PhD
Faculty: Institute of Advanced Technology

Urea fertilizer has been used for many years to supplement nutrients in growing media. Urea has the advantages of low cost and easy availability, thus touts as the most popular nitrogenous fertilizer. However, the major disadvantage of urea is its high solubility in water and its susceptibility to nitrogen losses through various pathways like leaching, ammonia volatilization, nitrification and denitrification. This adds extra cost for fertilizers manufacturer and higher concentration of urea in the soil. Currently, the use of slow-release fertilizer is a trend to reduce fertilizer consumption and to minimize environmental pollution. Slow-release nitrogenous-based fertilizer is often linked to positive characteristics such as regular release of nitrogen over a long period, reductions in nitrate leaching and reduced volatilization. However, slow-release nitrogen sources tend to be more expensive compared to other products and may lead to nitrogen release mismatch.

The coating process of urea has been performed using different techniques and various materials to delay urea release. In this study, a low cost rotary pan coating technology running at room temperature was used as the coating process for urea. In the first experiment, a fractional factorial design of experiment was utilized to screen the operational parameters of rotary pan including urea particle size, proportion of coating, amount of spray water, rotation speed, pan inclination, pan loading and spray flow rate. In the second experiment; the most effective coating parameters were analyzed and optimized using a central composite design of experiments. The results of the optimized process correlated well with a second-order polynomial model with percentage of variation, R^2 at 95.12%.

In the next experiment, the effects of different coating formulations on the efficiency, crushing strength and morphology of the coated urea were examined. Urea fertilizer was coated using six different materials, namely, gypsum, sulfur, ground magnesium lime, kaolin clay, rice husk ash and zeolite based on the "optimal" parameters of rotary pan. A mixture of 25% of gypsum, 25% of sulfur and 50% zeolite gave the lowest rate of urea release with acceptable crushing strength. Six different models namely, zeroth order, first order, second order, Higuchi and Ritger & Peppas and Kopcha model were examined to understand better the relationship between coating layer and urea release mechanism. By comparing coefficient of determination (R^2) of models, the Ritger & Peppas model provided the highest R^2 value (≈ 0.93) for final coating formulation. The

efficiency of gypsum-sulfur-zeolite (25/25/50%) coated urea was improved further where microcrystalline wax and polyol was experimented as a sealant. The efficiency of gypsum-sulfur-zeolite coated urea sealed by 3% of microcrystalline wax improved to around 56% while the efficiency of commercial sulfur coated urea is about 65%. This indicates the potential of gypsum-sulfur-zeolite coated urea produced in a room temperature process to be commercialized and used as a slow released nitrogen fertilizer.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PERKEMBANGAN TEKNOLOGI SALUTAN MENGGUNAKAN PAN BERPUTAR BAGI PENGHASILAN PELEPASAN UREA SECARA PERLAHAN

Oleh

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Baja urea telah digunakan selama bertahun-tahun untuk membekalkan nutrien dalam media tumbuh. Urea mempunyai kelebihan, di antaranya adalah kos rendah dan ketersediaan mudah, sehingga menjadikannya baja bernitrogen yang paling popular. Walau bagaimanapun, kelemahan utama urea adalah kelarutan yang tinggi di dalam air dan kecenderungan untuk kehilangan nitrogen melalui pelbagai laluan seperti larut-lesap, pemeruapan ammonia, nitrifikasi dan proses pendenitritan. Hal ini menyebabkan penambahan kos pada penghasilan baja dan kepekatan urea yang tinggi dalam tanah. Kebelakangan ini, penggunaan baja dengan daya lepas perlahan adalah satu pendekatan baharu untuk mengurangkan penggunaan baja dan untuk mengurangkan pencemaran alam sekitar. Baja berasas nitrogen dengan pembebasan perlahan sering dikaitkan dengan ciri-ciri positif seperti pelepasan nitrogen dengan sekata dalam satu tempoh yang panjang, pengurangan larut lesap nitrat dan pemeruapan yang dikurangkan. Sebaliknya, sumber pelepasan nitrogen perlahan cenderung untuk menjadi lebih mahal berbanding dengan produk lain, dan boleh membawa kepada ketidaksepadanan pelepasan nitrogen, terutamanya jika pembolehubah alam sekitar memberi kesan kepada kadar pelepasan nitrogen.

Proses salutan baja telah dijalankan dengan teknik yang berbeza dan pelbagai bahan-bahan untuk melambatkan pelepasan urea. Dalam kajian ini, teknologi pan salutan putaran dengan berkos rendah telah dilakukan pada suhu bilik sebagai proses salutan untuk urea. Dalam percubaan pertama, reka bentuk eksperimen melalui pecahan faktorial telah digunakan untuk menyaring parameter operasi pan berputar termasuk saiz zarah urea, nisbah salutan, jumlah air semburan, kelajuan putaran, kemiringan pan, laju muat pan, dan kadar aliran semburan. Dalam kajian yang kedua; parameter lapisan paling berkesan telah dianalisis dan dioptimumkan menggunakan reka bentuk eksperimen komposit pusat. Hasil daripada proses pengoptimuman mempunyai kaitan yang baik dengan model polinomial susunan kedua dengan peratusan variasi yang menjelaskan, R^2 pada 95,12%.

Dalam eksperimen selanjutnya, kesan formulasi salutan yang berbeza pada keberkesanan, kekuatan terhadap penghancuran dan morfologi urea yang bersalut telah diperiksa. Baja urea disalut menggunakan enam bahan yang berbeza, iaitu, gipsum, sulfur, magnesium tanah kapur, tanah liat kaolin, abu sekam padi dan zeolite yang telah

dibuat menggunakan parameter pan berputar yang optimum. Campuran 50% gipsum-sulfur dan 50% zeolite memberikan kadar yang paling rendah dalam pelepasan urea dengan kekuatan terhadap penghancuran yang boleh diterima. Lima model yang berbeza iaitu, perintah sifar, perintah pertama, Higuchi dan Ritger & Peppas dan model Kopcha dikaji untuk memahami hubungan yang lebih baik diantara lapisan salutan dan mekanisme pelepasan urea. Dengan membandingkan pekali penentuan (R^2) model, model Ritger & Peppas memberikan nilai tertinggi R^2 (≈0.93). Keberkesanan urea bersalut gipsum-sulfur- zeolite (25/25/50%) telah ditingkatkan lagi dimana mikrohabluran lilin dan polyol dikaji sebagai tampalan. Keberkesanan gipsum-sulfur zeolite urea bersalut dengan menggunakan 3% daripada mikrohabluran lilin meningkat kepada kira-kira 56% manakala keberkesanan salutan untuk komersial urea bersalut sulfur adalah kira-kira 65%. Ini menunjukkan bahawa urea bersalut gipsum-sulfur zeolite yang dihasilkan pada suhu bilik berpotensi untuk dikomersialkan dan digunakan sebagai baja perlepasan nitrogen secara perlahan.

ACKNOWLEDGEMENTS

The presented research work has been conducted under the supervision of Prof. Dr. Robiah Yunus to whom I sincerely express my utmost gratitude and respect for her continuing support, assistance, guidance and inspiration. I would like to thank for encouraging my research. Your advice on both research as well as on my career have been of invaluable experiences. I would also be very much appreciative of my co-supervisors; Dr. Suraya bt. Abdul Rashid and Dr. Mohamad Amran b. Mohd Salleh for their valuable advices and help during this project. I would also like to thank members of the academic staff in the Institute of advanced technology for their advice and support.

I am extremely thankful and indebted to Mr. Khairul Ridzwan Mohd Ibrahim for sharing expertise, sincere and valuable guidance to me.

I would also be very much appreciative of the professional and enlightening support given by Dr. Soraya Hosseini throughout my PhD research whose generosity in the distribution of knowledge is beyond words.

I would like to specially thank Dr Azhari for his assistance in my research. I also would like to express my thanks to my friends Naghme Abbasi, Mahtab Samadi, Mohammad Rasool Malekbala, Nur Syamimi Rahman, Chang Teck Sin, Nurhidayat, Hadi Amirkhani, Ali Zamani, Nurliyana Abdul Rauf, Nur Atiqah Mohamad Aziz and Nagisa Darajeh for their advice, help, moral support and memorable days that we shared together.

Special thanks to my family. Words cannot express how grateful I am to my mother (Esmat Aref) and my sisters (Shahnaz, Sedigheh, Zohre and Azam Eghbali Babadi) for all the sacrifices that you have given to me. Thank you for supporting me and I cannot thank you enough for encouraging me throughout this experiences.

I certify that a Thesis Examination Committee has met on 28th May 2015 to conduct the final examination of Farahnaz Eghbali Babadi on her thesis entitled "Development of Coating Technology Using Rotary Pan for Production of Slow-Release Urea" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

AA	Acrylic Acid
AAPFCO	Association of American Plant Food Control Officials
AM	Acrylamide
ANOVA	Analysis of Variance
ASA	Alkenyl Succinic Anhydride
BMA	N-Butyl methacrylate
BPO	Benzoyl Peroxide
CCD	Central Composite Design
CCRD	Central Composite Rotatable Design
CMC	Carboxymethylcellulose
CRF	Controlled Release Fertilizer
DCD	Dicyandiamide
DCPD	Dicyclopentadiene
EC	Ethyl Cellulose
EDX	Energy Dispersed X-ray
EP	Epoxy resin
EVA	Ethylene Vinyl Acetate
FT-IR	Fourier Transform-Infrared
G	Gypsum
GML	Ground Magnesium limestone
HEC	Hydroxyethylcellulose
HPLC	High-Performance Liquid Chromatography
IBDU	Isobutyledene-Diurea
KC	Kaolin Clay
kC-SA	k-Carrageenan-Sodium Alginate
MBA	N,N′-Methylenebisacrylamide
MMA	Methyl Methacrylate
MPOB	Malaysian Palm Oil Branch
NAA	1-Naphthylacetic-Acid
NR	Natural Rubber
PE	Polyethylene
PHB	Polyhydroxybutyrate
PUF	Polyurethane Foams
RHA	Rice Husk Ash
RSM	Response Surface Methodology
SCU	Sulfur Coated Urea
SEM	Scanning Electron Microscopy
SRF	Slow-Release Fertilizer
TVA	Tennessee Valley Authority
UBC	University of British Columbia
UF	Urea-Formaldehyde

CHAPTER 1

INTRODUCTION

1.1 Background

There has been an exponential growth in the earth's population that has now reached approximately 7.0 billion and is expected to approach 9.5 billion by 2050 (Azeem et al., 2014). Global food requirements have also risen and the expected per capita food requirement is likely to double by 2050. Meanwhile, arable lands diminish due to industrialization, urbanization, desertification and land degradation from heavy flooding. These intimidating factors threaten global food security and demand a robust response. Multidimensional steps have already been taken worldwide to meet the challenge of food security with modifications to improve agricultural systems. To meet the increasing food demands, the agricultural sector is bound to employ enormous quantities of fertilizers that have thus far demonstrated undesirable environmental impacts. Hence, it is of paramount importance to develop systems that boost production and alleviate environmental problems. Controlled and slow release fertilizers may be one such solution as they are believed to enhance crop yield while reducing the environmental pollution caused by the hazardous emissions (NH_3, N_2O etc.) from the current fertilizer applications.

1.2 Problem statement

Plants need optimum quantities of the available nutrients for normal growing. These nutrients content may come from multiple sources, such as native soil minerals, soil organic matter, air (e.g., legumes), organic materials that are added to the soil (e.g., animal manures), and fertilizers. When the soil is not capable of providing sufficient nutrients to satisfy crop/plant requirements, fertilizers may be added to provide the required nutrients (Binford, 2006).

Among the three main essential nutrients applied to the plants, N, P and K, nitrogen is the one that is rapidly lost by leaching. Urea is the most widely used fertilizer globally because of its high nitrogen content (46%), low cost, easy application and availability. But the major disadvantages of urea are its high solubility in water and its susceptibility to nitrogen losses through various pathways like leaching, ammonia volatilization, nitrification and denitrification. This adds extra cost for materials and labor and causes inconvenience and a high solute concentration in the soil (Salman, 1989).

When the urea is applied to the soil, it undergoes a series of biological, chemical and physical transformations to produce plant available nutrients as follows (Azeem et al., 2014).

The need to control nitrogen losses initiated a wide range of research activities that fall under four development categories:
1. Slightly soluble materials such as urea formaldehyde (urea form);
2. Materials for deep placement such as urea super granules (USG);
3. Urease and nitrification inhibitors;
4. Fertilizers coated with semi-permeable or impermeable layer.

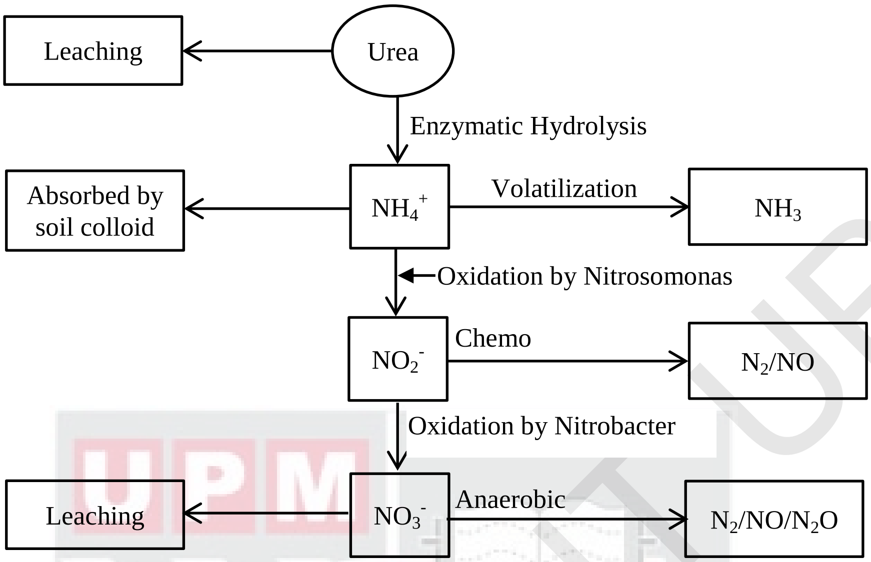

Figure 1.1. Nitrogen transformations of urea in the soil (Timilsena et al., 2014)

Figure 1.2 shows the problematic issues relates to the nitrogen losses from urea and the possible materials and methods solutions.

The use of slow or controlled release fertilizers is an effective way to solve the problems of resource waste and environmental pollution that would be caused by indiscriminate use of huge quantities of fertilizers (Lan et al., 2011). The physical intromission of urea granules in an appropriate coating material is one such technique that produces controlled release coated urea. The development of controlled release coated urea is a green technology that not only reduces nitrogen loss caused by volatilization and leaching, but also alters the kinetics of nitrogen release, which, in turn, provides nutrients to plants at a pace that is more compatible with their metabolic needs (Azeem et al., 2014).

The coating processes are quite complex and involve a number of chemicals. The overall process does not attract commercial attention. This not only increases costs due to solvents and their recovery, but also poses adverse environmental impacts in terms of hazardous emissions. Furthermore, many coatings materials are non-biodegradable after total nutrient release and present a new type of soil pollution that is undesirable. The coating process of fertilizer has been performed with different techniques (rotating drum, fluidized bed, spouted bed, rotating pan). To reduce operational cost, among different techniques, rotary pan can be chosen for producing slow release urea because of its flexibility, large throughputs and ability to handle a wide range of particles.

In case of coating materials, sulfur and polymer materials are common materials but have limitations. The sulfur increases the soil acidity and lowers the nitrogen content of the sulfur coated fertilizer. Although lime application can mitigate the acidifying effect and greater fertilizer dosage as well as can make up the necessary nitrogen requirement, both remedies add to the total cost. Therefore, it is important to reduce the sulfur content of SCU without significantly lowering the quality of SCU as a slow-release nitrogen fertilizer. Following the affair with sulfur, polymeric materials were widely used to coat urea since sulfur coatings were easily disrupted by microorganisms whereas polymer coatings were not. However, organic polymer coating materials involves organic solvents that not only inflict additional costs of the lean solvent and solvent recovery, but also cause hazardous environmental emissions (Azeem et al., 2014).

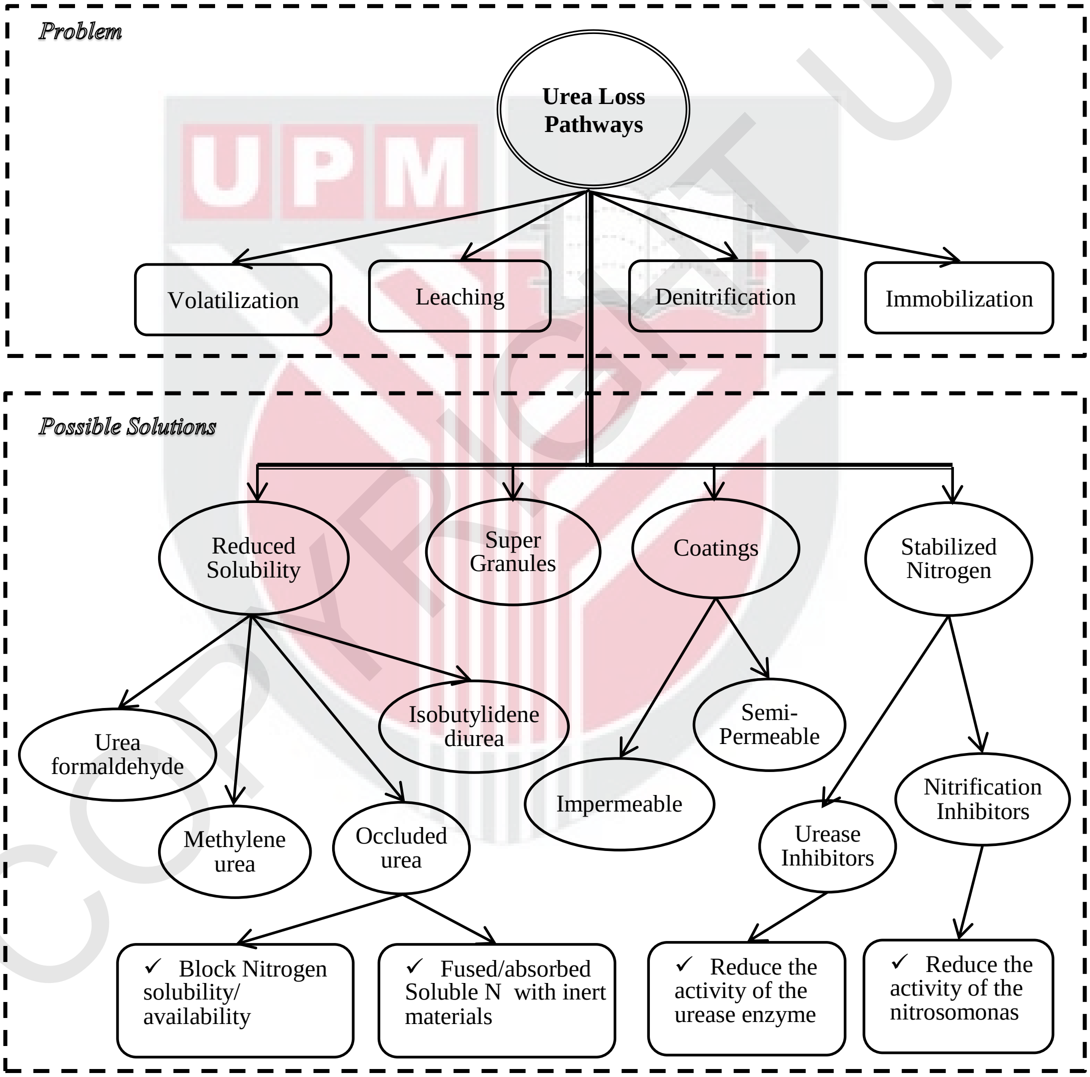

Figure 1.2. Development categories of control nitrogen losses from urea

Due to higher costs and process complexity along with issues of environmental pollution caused by sulfur and polymers, research frontiers shifted towards developing low cost, easily fabricable and environmentally friendly materials and technology.

1.3 Research objectives

The main aim of this thesis is to develop coating technology for urea in order to reduce the amount of urea released to the environment. This aim was achieved through improvement of coating formulation and optimization of coating process using a rotary pan. Overall, the objectives are divided into specific objectives as follows, which are the main contribution of the thesis to the body of knowledge:

i. To screen and optimize the most effective operational parameters of urea coating process in rotary pan by response surface methodology.
ii. To study suitable coating materials and kinetic models for different coating formulations.
iii. To optimize the operational parameters of rotary pan using new coating formulation by central composite design.
iv. To investigate the effect of applying sealants on coating efficiency of urea and suitable kinetics models for final coating.

1.4 Scope

1) In this research, rotary pan has been chosen for producing coated urea because of its versatility, flexibility, large throughputs and ability to handle a wide range of particles. Firstly, a mixture of gypsum-sulfur (ratio: 50/50%) was used as a coating materials and dry method applied to reduce cost of process. The Expert design software was employed for screening and optimization of operational parameters. To make a uniform solution and shorten the time of comparative study agitation factor in an incubator shaker was added in dissolution analysis.

2) To find suitable coating materials, inexpensive materials like gypsum, sulfur, kaolin clay, rice husk ash, ground magnesium lime and zeolite have been chosen based on their availability, price and potential of nutrient containing for plant. Based on these six materials, twenty two formulations were developed for screening coating formulations. The urea release mechanism was investigated using five kinetic models namely, zeroth order, first order, Higuchi, Ritger & Peppas and Kopcha. The 14 days dissolution analysis in the absence of agitation was used to evaluate urea release profile.

3) A central composite design was used to optimize operational parameters of coating formulation.

4) The biodegradable materials like microcrystalline wax and cellulose-based polyol provided the selection of sealants to study the effect of sealants on the efficiency of coating formulation.

1.5 Structure of thesis

This thesis is divided into five chapters. Chapter one covers introduction, problem statements, objectives, scope and thesis structure. Chapter two includes descriptions on the slow/controlled release fertilizers (SRFs/CRFs), their classification and advantages and disadvantages of SRFs. The different coating process, methods and materials are explained to demonstrate materials and design options available and to highlight the limitation of current materials and design deficiencies. Furthermore, this chapter consists of the mechanism of nutrient release and theory of multi-objective design optimization using response surface methodology. Chapter three presents the materials and method used for urea coating process. Chapter four consist an experimental design using fractional factorial on coating process to screen out most effective parameters of coating process. Then it continues to optimize operational parameters using response surface methodology. This chapter also covers the development of different coating formulate and choosing the best formulation by comparing results with commercial sample. In addition, the optimization of coating process conditions for new formulation is explained. Finally, the role of different sealant used as a top coating materials is also presented in chapter four. Conclusions and future works are presented in Chapter 5. Figure 1.3 is a short explanation of the chapters organized in this thesis.

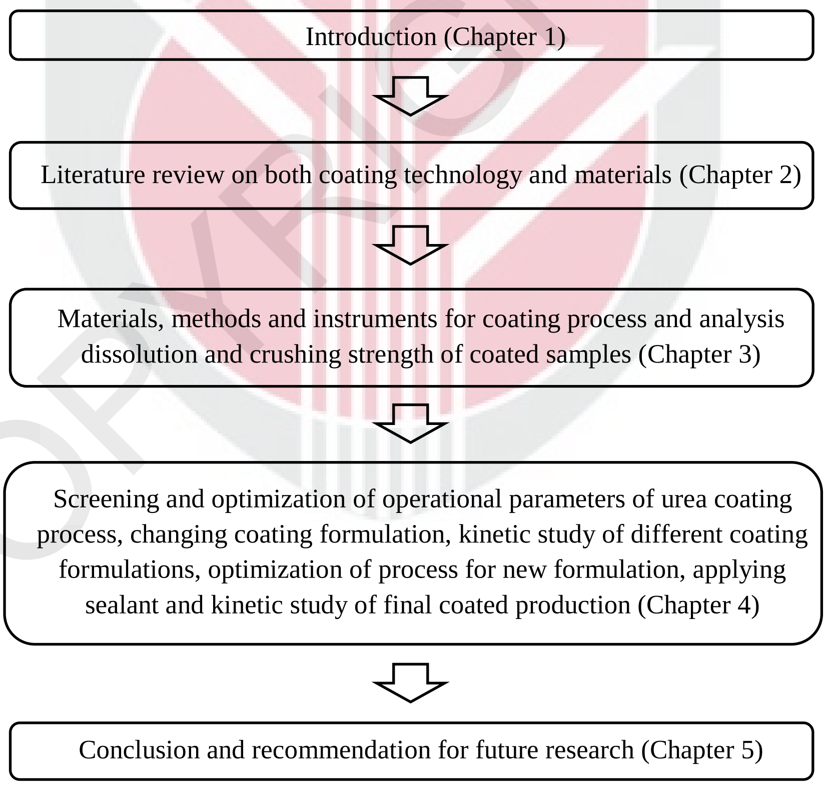

Figure 1.3. Structure of the thesis

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