Experimental and Machine Learning Hybrid Strategy for Optimizing Nitrogen Release from Chitosan-Functionalized Biogenic Silica Nanoparticle-Coated Urea Fertilizer

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Chemical Engineering

Supervisor: Dr. Muhammad Bilal Khan Niazi

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S/No:	Code:	Title:	Core/Elective:	CH:	Grade:
1.	CHE-843	Separation Processes In Che	Compulsory	3.0	A
2.	CHE-847	Chemical Kinetics& Reactor Design	Compulsory	3.0	A
3.	RM-898	Research Methodology	Additional	2.0	Q
4.	CHE-848	Gasification Processes	Elective	3.0	B+
5.	CHE-873	Membrane Technology	Elective	3.0	A
6.	CHE-814	Product Technology	Elective	3.0	A
7.	EME-921	Momentum Heat & Mass Transfer In CHE	Compulsory	3.0	A
8.	CHE-815	Nano Catalysis	Elective	3.0	B+
9.	ESE-911	Carbon Capture And Utilization	Elective	3.0	A

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Presented on: **24 Oct 2024** at: **1500 hrs in SCME Seminar Hall**

Be accepted in partial fulfillment of the requirements for the award of Master of Science degree in **Chemical Engineering**.

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I Mahzeb Saleem hereby state that my MS thesis titled "**Experimental and Machine Learning Hybrid Strategy for Optimizing Nitrogen Release from Chitosan-Functionalized Biogenic Silica Nanoparticle-Coated Urea Fertilizer"** is my own work and has not been submitted previously by me for taking any degree from National University of Sciences and Technology, Islamabad or anywhere else in the country/ world.

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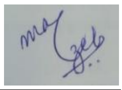

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"This thesis is dedicated to my beloved parents and siblings for their unwavering love, support, and encouragement. And to my teachers and mentors for their invaluable guidance."

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Mahzeb Saleem

ABSTRACT

The current world's population increased three times than it was in the mid of the 20th century. The dramatic rise in population has imposed a tremendous load on agricultural industry to meet rising demand for food. The application of conventional fertilizers is one of the most common and effective strategies for raising crop yields. These fertilizers release essential plant nutrients, both organic and inorganic, into soil to promote the growth of crops. Nitrogenous fertilizers are utilized to address nitrogen deficiencies.

Urea is one of the most commonly used nitrogenous fertilizers that contains 46% nitrogen. However, it has been observed that on average, more than 70% of this urea fertilizer is wasted in the localized region of crop fields, which is related to environmental contamination and long-term economic losses. Slow-release urea fertilizer was created in such a manner that fulfills plant needs according to the requirement for growth. Coating urea fertilizer with appropriate materials decreases its water solubility and slows its release in the soil.

This research study will focus on the usage of chitosan functionalized silica nanoparticles for coating of urea granules. Urea granules were coated using fluidized bed coater. Different formulations were made, and their release rates were calculated in water using UV-Visible Spectroscopy. Scanning Electron Microscopy (SEM) was used to check the surface structure of synthesized nanoparticles and coated granules. Fourier Transform Infrared Spectroscopy, X-ray diffraction and crushing strength were employed to identify the nature of chemical bonds, the structural parameters and shelf life of the prepared samples.

The nitrogen release from coated urea is a complex phenomenon. In the present study, machine learning models were employed to optimize the release of nitrogen from coated urea fertilizers. Data gathered from the literature was used to train four machine learning models i.e. Decision Trees, Gaussian Process Regression, Ensembled Learning Trees and Support Vector Machines. Particle Swarm Optimization and Genetic Algorithms were also combined with the machine learning models. The results suggest that Gaussian Process Regression combined with GPR is favored for optimizing the nitrogen release ($R^2 \sim 0.9766$ and RMSE ~ 0.1215). In addition, a Graphical User Interface had been developed using the optimized GPR to facilitate the calculation of Release Time.

Key words: Slow release Urea Fertilizer, chitosan functionalized silica nanoparticles, Nitrogen release, Machine learning, Optimization, Genetic Algorithm, Particle Swarm Optimization.

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ABBREVIATIONS

bSNPs	Biogenic Silica Nanoparticles
Cs-bSNPs	Chitosan Functionalized Biogenic Silica Nanoparticles
UC	Uncoated Urea
CU	Chitosan Coated Urea
SU	bSNPs Coated Urea
CSU	Cs-bSNPs Coated Urea
CRUF	Control release urea fertilizer
SEM	Surface Electron Microscope
FTIR	Fourier Transform Infra-Red
XRD	X-ray diffraction
MATLAB	MATrix LABoratory
ML	Machine Learning
GA	Genetic Algorithm
PSO	Particle Swarm Optimization
GPR	Gaussian Process Regression
DT	Decision Tree
ELT	Ensembled Learning Tree
SVM	Support Vector Machine
PDP	Partial Dependengt Plot
GUI	Graphical User Interface

CHAPTER 1: INTRODUCTION

The current world's population increased three times than it was in the mid of the 20th century. By the end of 2024, the global population will have reached 8.2 billion. The global population will reach roughly 8.5 billion, by 2023, with an additional 1.2 billion expected to be added during the next two decades, resulting in a total of 9.7 billion by 2050 [1]. The present model of a rapidly expanding population is clearly unsustainable, and it increases the risk of food shortages, emphasizing the significance of achieving "resource efficiency" within a "circular economy" to ensure sufficient and consistent food supply [2]. The dramatic rise in population has imposed a tremendous load on agricultural industry to meet rising demand for food [3], [4], [5], [6], [7]. To resolve food shortage, significant initiatives in the Agricultural sector had been required to increase crop productivity while making efficient use of total arable land [8]. The use of synthetic fertilizers is one of the most common and effective strategies for raising crop yields around the world [9], [10]. The contribution of chemical fertilizer is an essential mean to boost crop productivity. Farmers kept on adding fertilizer to get increased crop yield. These fertilizers release essential plant nutrients, both organic and inorganic, into soil to promote the growth of crops [11].

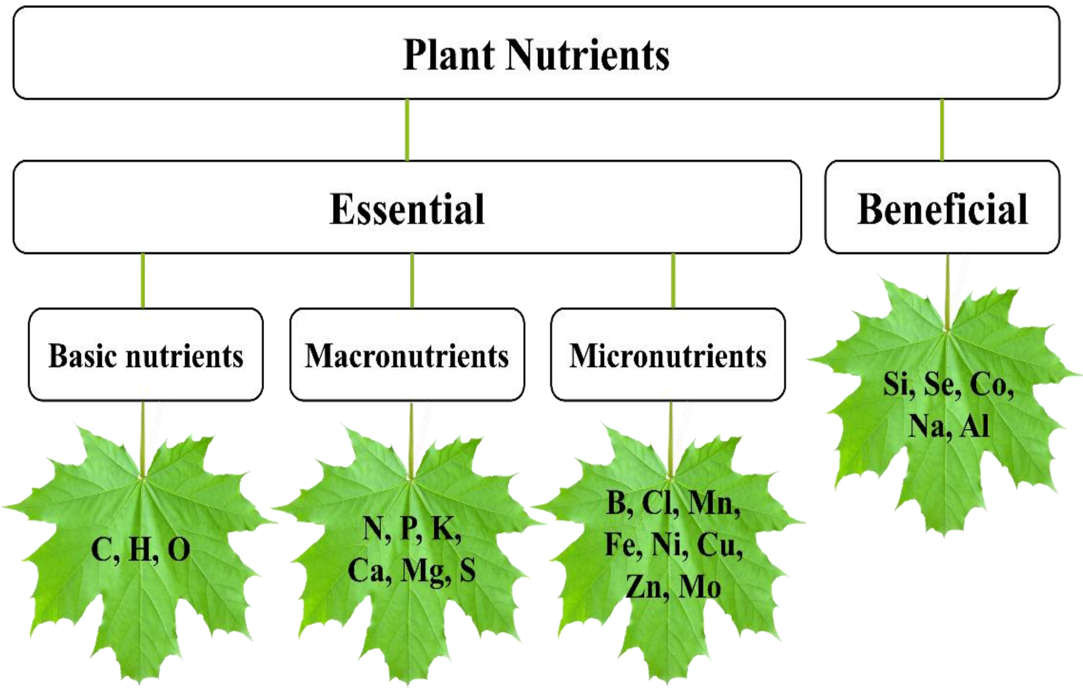


Figure 1-1: Different Categories of Plant Nutrients

There are twenty-two essential and beneficial plant nutrients. Seventeen essential nutrients are necessary for the normal growth of plants. These plant nutrients are categorized into three groups: basic nutrients, macronutrients, and micronutrients. The basic plant nutrients consist of three elements Hydrogen, Carbon and Oxygen [12]. Their basic source is air and water normally. The macronutrients contain six elements and micronutrients contain eight elements. There are five beneficial elements which stimulate plant growth but are either non-essential or only essential for specific species [13]. These twenty-two plant nutrients are depicted in **Figure 1-1** above.

Plant components such as roots, shoots, branches, and leaves assimilate nutrients from the soil using various methods. The soil contains a large amount of these nutrients, but only a small amount is available for plant growth. The efficiency with which plants absorb these mineral nutrients is determined by how they are available and in exactly what forms [14]. Other factors that influence the uptake mechanism include pH, colloids interaction, and soil physical properties. The humidity of the soil and its acidic or basic nature are the most essential factors. In soil, these essential plant nutrients exist in three forms: solid, liquid, and gaseous [15]. **Table 1-1** below depicts important nutrients and their different forms.

Fertilizers are used to deliver these essential nutrients to plants. However, a substantial dosage and inadequate application rate of conventional fertilizers have caused a wide range of adverse consequences, such as greenhouse effect, water pollution, resource waste, and more [16]. According to the figures, fertilizer usage has increased by a factor of 100 during the last 50 years [17], [18]. Several studies have found that many nutrients from synthetic fertilizers are wasted into the environment, lowering the overall fertilizer efficiency [19], [20].

Nitrogen is an essential nutrient that plants are highly dependent on. Low nitrogen level in plants can lead to decreased yield as it is an essential nutrient for crop development. Nitrogen is essential to produce chlorophyll, proteins, and protein-carrying compounds [20]. Amino acids (AA) are the fundamental units of proteins, formed by the biological combination of nitrogen with carbon, hydrogen, oxygen, and sulfur. Plants rely on AA to make protoplasm, which is responsible for cell division and growth. Nitrogen enhances the quality and amount of dry matter in green vegetables. Nitrogen deficiency symptoms include stunted growth, chlorosis on older leaves, low protein levels in seeds and vegetative organs, and early maturity in certain crops, leading to lower productivity and quality. Severe cases may lead to mortality or dropping of mature leaves [21], [22].

Table 1-1: Important Plant Nutrients and their accessible states in Soil

Essential Element	Chemical Symbol	Available States
Non-Mineral Elements		
Carbon	C	CO_2 (g)
Hydrogen	H	H_2O (l) & H^+
Oxygen	O	H_2O (l) & O_2
Mineral Elements		
Major Nutrients		
Nitrogen	N	NH_4^+& NO_3^-
Phosphorus	P	HPO_4^- & $H_2PO_4^-$
Potassium	K	K^+
Secondary Nutrients		
Calcium	Ca	Ca^{2+}
Magnesium	Mg	Mg^{2+}
Sulphur	S	SO_4^{2-}
Micro-Nutrients		
Iron	Fe	Fe^{2+} & Fe^{3+}
Manganese	Mn	Mn^{2+}
Zinc	Zn	Zn^{2+}
Copper	Cu	Cu^{2+}
Boron	B	$B(OH)_3$ (Boric Acid)
Molybdenum	Mo	MoO_4^{2-}
Chlorine	Cl	Cl^{-1}

1.1 Urea Fertilizer:

Nitrogenous fertilizers are utilized to address nitrogen deficiencies. Urea is the most commonly used nitrogenous fertilizer. It is the only synthetic fertilizer that contains the highest nitrogen content, which is 46 % in dry form with the lowest manufacturing expenditure along with ease of usage [23]. However, it has been observed that on average, more than 70% of this urea fertilizer is wasted in the localized region of crop fields, which is related to environmental contamination and long-term economic losses. These unfavorable side effects are mostly caused by urea losses from leaching, decomposition, and ammonia volatilization losses. The remaining losses include damage when transferring during supply, bagging, and shipping [24].

Harm to crop occurred due to over fertilization as fertilizer losses enhance the localized concentration levels. This results in negative effects rather than positive plant growth [25].

1.2 Soil Nitrogen Interaction:

Around 70 percent of nitrogen from urea fertilizer is lost due to rapid chemical conversion caused by leaching, volatilization, and runoff, resulting in low nitrogen utilization efficiency [22].

1.2.1 Hydrolysis:

When added into the soil, urea undergoes a reaction with soil enzyme urease and water, resulting in the conversion of urea into ammonium ions. The process consist of three fundamental steps in which firstly urea is converted into ammonia and cyanate ions. In the next step, cyanate is converted into carbon dioxide and ammonia. In the last step, ammonia reacts with carbon dioxide in the presence of water, producing ammonium and bicarbonate [26].

$$NH_2 - CO - NH_2 \rightarrow NH_3 + H^+ + CNO^- \tag{1-1}$$

$$CNO^- + H^+ + H_2O \rightarrow NH_3 + CO_2 \tag{1-2}$$

$$NH_3 + CO_2 + H_2O \rightarrow NH_4^+ + HCO_3^- \tag{1-3}$$

1.2.2 Nitrification:

The process consists of two steps, wherein Nitrosomonas bacteria initially convert ammonium ions into nitrite salts. The subsequent stage involves the conversion of nitrite ions into nitrate ions by Nitrobacter bacteria [27].

$$2NH_4^+ + 4O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{1-4}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{1-5}$$

1.2.3 Denitrification:

This process involves the conversion of nitrite into nitric oxide in the presence of nitrite reductase, followed by the conversion of nitric oxide into nitrous oxide by nitric oxide reductase. At last, nitrous oxide by enzyme nitrous oxide reductase is converted into nitrogen (N_2) [28].

$$NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (1\text{-}6)$$

This overall process of soil nitrogen interaction is exhibited in the following **Figure 1-2**.

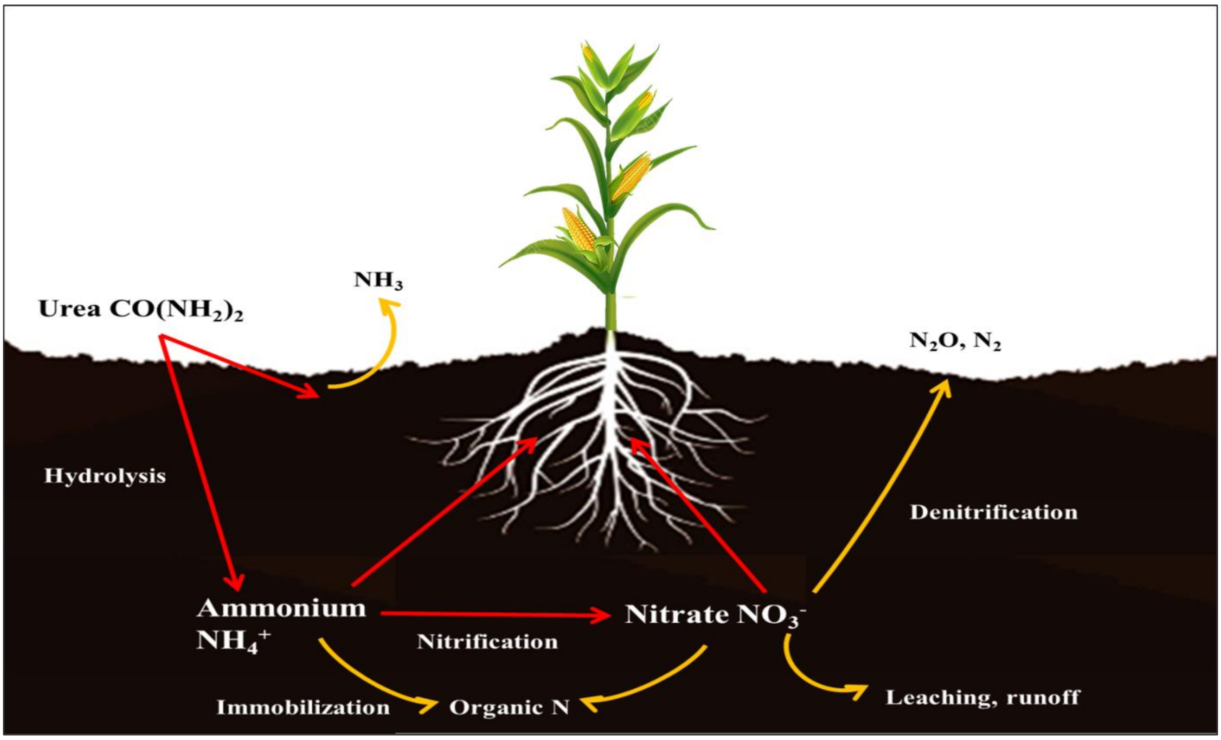


Figure 1-2: Soil Nitrogen Interactions leading to Nitrogen losses

The use of conventional urea fertilizer is directly associated with numerous constraints, including combined environmental issues. This is the most frequently discussed issue around the world. This urea discrepancy can be reduced by delaying its solubility, which can be achieved by employing several approaches and methodologies [29]. A potential solution is to synthesize a new slow-release urea fertilizer that improves efficiency and reduces environmental contamination compared to traditional fertilizers [30].

1.3 Slow-Release Urea Fertilizers:

Slow-release urea fertilizer was created in such a manner that fulfills plant needs according to the requirement for growth [31]. Coating urea fertilizer with appropriate materials reduces its solubility in water and slows nitrogen release in the soil. The materials used to encapsulate urea fertilizer provide a physical barrier that influences the rate at which it dissolves in water when applied to soil [20], [30].

1.3.1 Mechanism of Slow-Release Urea Fertilizer (SRUF):

The mechanism governing the release of SRUF is a highly complex phenomenon. The release of nutrients from SRFs must be sigmoidal in order to mimic the general pattern of plant nitrogen uptake. The nutrient's release from coated urea is governed by diffusion [32]. Many physical parameters influence the entire process, including moisture content, soil type, coating materials, and ambient weather conditions. Mostly used is an approach in the literature known as multi-stage diffusion model [33].

1.3.2 Multi-stage Diffusion Mechanism:

This mechanism consists of the following steps.

- Water molecules permeate the covering barrier and enters the fertilizer core.
- Fertilizer core swelling and increased internal osmotic pressure.
- Burst release of nutrients through the coating from the fertilizer core.

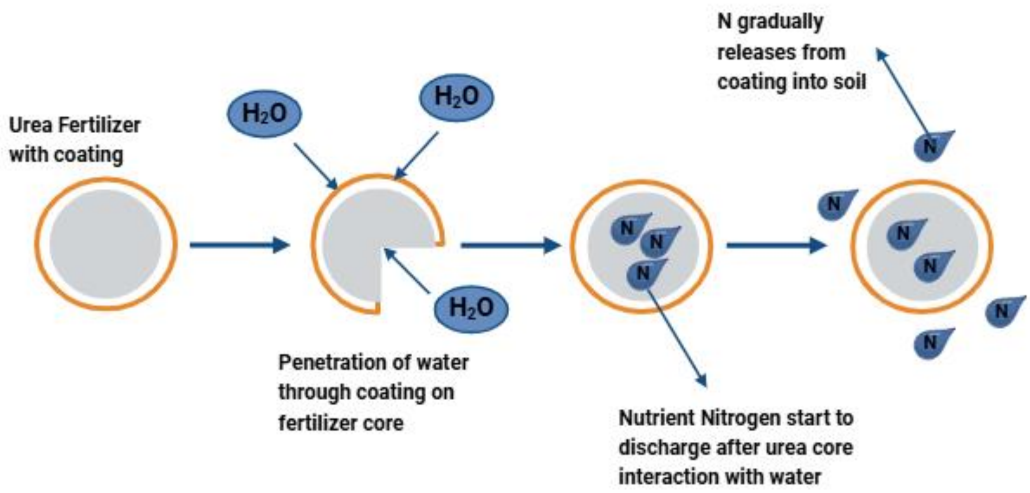


Figure 1-3: Multi-stage diffusion model

According to the above-mentioned model, the initial stage involves the penetration of water via coating after the coated fertilizer is applied to crops in soil. In the following stage, water swells the fertilizer core, increasing osmotic pressure within it. Finally, nutrients began to be released from the swollen core, which acted like a membrane film structure and served as a controlling parameter for nutrient nitrogen release. The entire phenomenon is depicted in **Figure 1-3**.

1.4 Machine learning for optimization of release rate:

Mathematical models based on the multi-diffusion mechanism are used to study the release of nitrogen from slow-release urea fertilizers. The model exhibited nitrogen release behavior(s) and mechanisms, resulting in inconsistencies between previous simulations and experimental data. However, limitations to the model's future improvement, include the effect of urea content on effective diffusivity, in addition to the influence of particle shape and size [34]. These mechanistic models have disadvantages such as overparameterization, oversensitivity to changes in the operating circumstances, and require a significant amount of effort for calibration and validation [35]. This model is limited in its ability to incorporate data from various data and time scales, as well [36]. In order to solve these constraints Machine Learning (ML) models might be employed. In contrast, ML is a data analysis tool that can acquire knowledge from incoming data and make decisions autonomously [37], [38]. These algorithms detect a well-defined pattern using data input data during the training phase, resulting in a more precise output [39].

1.5 Benefits of Slow-Release Urea Fertilizers (SRUF's):

The improved efficiency of coated fertilizer saves labor costs and the number of times fertilizer is applied to soil. Slow-release urea fertilizer is the most cost-effective and fair option. Many negative effects, such as over-fertilization, can be reduced by applying the coating on urea particles, as well as seed damage. The plant's nutrient utilization is also boosted by the nitrogen's slow release from coated urea. The coating also helps to prevent environmental contamination through NH_3 volatilization losses. This coating improves handling capability, reducing losses during bagging and supply chain [40]. This efficiency boost can be achieved by applying the coating and decreasing its release rate in the soil. This can be done by using suitable coating components including polymeric polymers, organic and inorganic compounds on urea fertilizer particles. [30].

1.6 Disadvantages of Slow-Release Urea Fertilizers (SRUFs):

The synthesis of slow-release urea fertilizer is currently a popular issue. Slow-release urea fertilizer is not commercially accepted for a variety of reasons, including its non-biodegradability, which contributes to soil erosion and water contamination. Few slow-release urea fertilizers change soil pH, which is detrimental to many food-producing crops. Particle abrasion produces nutrient discharge before the crop's needed time [41]. Slow-release urea fertilizer is determined by its release kinetics when in contact with soil and water. This event occurred because to a shift in soil composition, pH, microbes, and moisture conte

CHAPTER 2: LITERATURE REVIEW

Slow-release urea fertilizers have been extensively studied since 1960. Researchers have investigated a variety of materials and strategies to optimize the nitrogen release rate from slow-release urea fertilizers. These materials not only serve as slow-releasing agents but also provide plant nutrients.

2.1 Categorization of Slow-Release Urea Fertilizers:

Hydrophobic materials are utilized for coating of urea that serves to limit its release rate in the soil. Coating materials are typically classified as either organic polymeric substances or inorganic materials. Polymer based resins and thermoplastics are organic chemicals, whereas inorganic coatings include bentonite, sulfur, gypsum, silica, and other inorganic materials [20], [43].

2.1.1 Polymer-Based Coatings:

Polymeric materials effectively manage nutrients by providing a long-lasting physical barrier. These materials are generally placed to the surface of urea to form a matrix layer that controls nitrogen release. These coatings will behave hydrophobically, similar to polyolefin and rubber. Hydrogel materials can also fall within this category [44]. Yang et al. [45] used a combination of polystyrene, polyurethane (PU) and wax additive to coat urea. The study demonstrates that PU is superior to wax in lowering rate of release with a similar percentage of coating, as wax is unable to prevent water from permeating the coating layer during the initial phases of release. Enlarging the size of tablet lowers the rate and the necessary coating material, cutting manufacturing costs. Azeem et al. [46] investigated the effectiveness of Ploy vinyl alcohol enhanced waterborne starch-based biopolymer as a coating ingredient for producing controlled release urea fertilizer (CRUF). The study looks into the impact of coating thickness on the release of nutrients in CRUF. The findings reveal that release time increases with thickness, but not for coating defects or porous films. The decrease in thickness decreases the diffusion coefficient while it increases for defective samples and porous coatings. Achieving both the optimal thickness and film integrity is essential. Yu et al. [47] synthesized a nitrogenous fertilizer with a slow-release mechanism to enhance urea efficiency, retrieve phosphogypsum, and mitigate soil contamination. In order to enhance adhesion, the phosphogypsum-granulated urea was coated with SpanTM 80 rubber and paraffin wax. The findings indicated that the release in water over a period of 28 days was below 35%, and the release distribution was determined using a logistic model.

Qingshan et al. [48] investigated polyurethane-coated urea fertilizer comprising polyols, isocyanate, and paraffin. Upon reaction with polyols, isocyanate forms a polyurethane exterior layer on the surfaces of urea granules. This exterior layer has outstanding thermal stability. After 40 days of ambient conditions, no isocyanate was discovered in the layer. The polyurethane coated urea has a release period of 40-50 days in soil. Paraffin inhibits water penetration into polyurethane skin layers. In their study, Dai et al. [49] employed gradient hydrophobic films to synthesize coated urea fertilizer. The production of this film involved the sequential coating of a copolymer consisting of polyurethane and hydroxypropyl-terminated polydimethylsiloxane at varying proportions. The implementation of the coating led to a reduction in the rates at which urea diffuses and an increase in the duration of UEA release by over 60 days when compared to uniform films. A novel approach was devised by Ye et al. [50] to manufacture environmentally sustainable slow-release urea fertilizers by utilizing integrated circuits (ICs) derived from degradable polyesters. These fertilizers have a lower, adjustable release rate compared to neat urea. Factors like granular size, compactness, and polymer species are crucial for optimizing release performance. The weaker crystallizability of polyester chains helps achieve a slower release rate. The granules exhibited a 14-day release time and measured 3 mm in size.

Li et al. [51] developed an epoxy using liquefied bagasse as a coating material for CRUF. Their findings demonstrated that the varying ratios of liquefied bagasse (LB) and bisphenol-A diglycidyl ether (BDE) had an effect on the structure and properties of the coating substance. Optimizing the amount of BED improves the compactness and hydrophobicity thus slowing the rate of release. Chen et al. [52] synthesized a slow-release fertilizer utilizing biochar and a waterborne based copolymer of polyvinylpyrrolidone and polyvinyl alcohol as coating ingredients to improve the nitrogen release rate. They investigated the impact of sources and concentrations of the coating ingredients on the characteristics of biochar-copolymers. Biochar enhanced degradability and reduced the water absorption, improving the slow-release characteristic of the coated fertilizer. The biochar based copolymer proved significant release behavior with a release rate of 65.28%. Santos et al. [53] studied the coatings of polyurethane (PU) derived from soybean and castor oil. It was found that castor oil-based polyurethane exhibits superior adhesion properties, resulting in extended-release times. 5% castor and 7.5% soybean based PU coating released nitrogen within fourty days, exhibiting that similar results may be attained with castor oil derived PU of reduced coating thickness.

Uzoh et al. [54] synthesized a CRUF by coating urea granules with starch-based bio-composites. The bio-composites were derived from cassava starch, rubber and castor seed oils. The optimal nitrogen release was determined based on the release time, pH and coating thickness. They observed that castor oil can offer enhanced controlled release characteristics with reduced cost. Liu et al. [55] synthesized a variety of eco-friendly poly (eugenol sulfone) using eugenol and SO_2 as raw materials. These materials were used to coat urea fertilizer. They observed that high molecular weight poly (eugenol sulfone) exhibited a smoother shell, which showed superior slow-release performance and gradual degradability. Rychter et al. [56] developed a CRUF using starch, with urea functioning as a plasticizer. They discovered that urea decreases the moisture content, therefore improving the mechanical properties of the matrix. Higher urea content reduces the release; however, they observed that it was insufficient i.e. 75% nutritional release in approximate 12 hours and that additional adjustment is required to improve hydrophobicity for prolonged use.

In their study, Giroto et al. [57] found that the release of a starch/melamine/urea Control release fertilizer is hindered by higher melamine content. This inhibition is attributed to the interaction among the amine group of urea with both melamine and starch. Within a span of 120 hours, it liberates 40% of urea. Xie et al. [58] produced a new class of macromolecular fertilizers known as poly dimethylurea phosphate, which has a reduced solubility compared to urea. Experimental evidence has confirmed that PDPU functions as a physical obstruction, effectively decelerating the flow rate. Employing a superabsorbent covering made from wheat straw enhances performance by allowing it to gradually expand into a hydrogel and release 67.6% of the nutrients within a 30-day period. Li et al. [59] conducted analogous studies; however, the release was documented at 85% within 8 days, perhaps attributable to the more rapid breakdown of urea compared to PDPU. Araújo et al. [60] produced a coating material by incorporating humic components (peat, humic acid, and humin) with chitosan. Their findings indicate that the rate of release differs based on the specific humic compounds and the pH of the watery solution, owing to the functional groups and possible interactions of urea with each component.

Niu et al. [61], used starch chemically bounded with vinyl acetate to enhance its hydrophobic properties. This reduces susceptibility to swelling, enhances the effectiveness of encapsulation, and restricts the cumulative release of nutrients to 50% during a 30-hour timeframe, which is slower compared to previous investigations. Versino et al. [62] produced a coating material predominantly composed of starch, with urea serving as the plasticizer and bagasse as a strengthening component. This improves the mechanical properties, and, consistent with other studies, raising the urea content and reinforcing agent promotes interactions that postpone the release. Prior studies have shown that this composite material exhibits superior performance in terms of progressive release, releasing 95% of the urea over a period of 15 days.

2.1.2 Inorganic Material-Based Coatings:

Ibrahim et al. [63] employed a combination of 4 distinct materials, specifically gypsum, cement, sulfur, and zeolite, for the purpose of designing coating materials. A urea coating containing same amount of gypsum and sulfur demonstrated superior crushing strength and reduced release rate. Nevertheless, the efficiency was enhaced by that of putting liquefied paraffin wax onto the heated urea surface. Integrating gypsum-sulfur (20% total coating), 3% paraffin wax, and sifting the coating components prior to application led to a 26% enhancement in the efficiency of the urea coating. Babadi et al. [64] investigated the use of gypsum, sulfur, and crushed magnesium lime as economical formulations for coatings. The results of their study suggest that urea, when coated with an equivalent proportion of gypsum-ground magnesium lime (GML), exhibited a decreased urea release and a notable fracture strength. Employing polyols as a sealer on the outer layer of the urea coating led to enhanced performance. A 34.2% enhancement in the effectiveness of the urea coating was seen when gypsum–GML (1:1 ratio) containing 1.1% polyols was utilized.

Yu and Li [65] developed a phosphogypsum/paraffin controlled release formulation (CRF). It demonstrated better controlled release characteristics of urea compared to earlier research and meets the controlled release requirements set by the CEN. The enhanced adherence of the brittle paraffin coating can be attributed to the incorporation of the emulsifier, Span− 80. Moreover, the rate at which it is released decreases considerably with the increase in thickness of the paraffin covering. Dubey et al. [66] developed a zeolite coated urea fertilizer by incorporating various binders (corn and potato starch, bentonite, white cement, acrylic polymer) using a pan granulator under dynamic operating circumstances. The zeolite-coated urea with acrylic polymer exhibited excellent structural stability and demonstrated robust crushing strength. This regulated the nitrogen release by 54.7% more effectively than other CRUFs.

2.1.2.1 Nanoparticle-Based Coatings:

Nanoparticles have amazing qualities, including a high surface area-to-volume ratio and improved optoelectronic, thermal, and physicochemical capabilities as compared to their bulk counterpart [67]. In agriculture, nanotechnology shows potential for increasing production efficiency through the use of nano fertilizers (NFs) [68], [69], [70]. NFs are synthesized from nanoparticles (NPs). NFs improve nitrogen use efficiency (NUE), water retention capacity, nutrient uptake, crop yield, and overall production efficiency. Furthermore, NFs aid to reduce fertilizer demands, production costs, and negative environmental impacts [71]. NFs can be divided into three categories: (1) nano-nutrients, in which essential nutrients are converted into nanoparticles; (2) nano-additives, in which nanoscale additives are incorporated into chemical fertilizers; and (3) nano-coating, in which nanoparticles are applied as a coating or loaded onto traditional fertilizers. Fertilizer encapsulation employing nanoparticles coating has proven to be more efficient and adaptable than other types of NFs. The notable nanoparticles explored in literature include Zn, Fe, Si, Cu, Mn, S, N, P, and K [72], [73].

Beig et al. [74] developed a CRUF by coating urea with zinc oxide nanoparticles. They found that these coatings increase the release time of urea. The coated formulation releases 100% of urea in 160 minutes, improving nutrient availability. The coating materials chosen by Shakeel et al. [75] for urea fertilizer include micronutrients (B, Fe, Zn, and Cu). In order to coat urea prills, a total of thirty combinations of these coating ingredients were prepared, using either half or full prescribed values. Applications of (B) full and (Fe+Zn) full coated urea can decrease the volatilization of Ammonia and extend the duration of urea exposure in soil, thereby promoting efficient plant absorption.

Li et al. [76] synthesized and characterized mesoporous silica exhibiting three distinct morphologies, namely fiber, nano-rod, and sphere. In-situ reactive-layer spray method was employed to fabricate polyurethane (PU)/silica composites using urea granules. The release characteristics of PU were greatly enhanced by rod-like silica nanoparticles at the same filler loading, whereas other fillers did not contribute to this improvement. The nitrogen release period of the coating extended to 80 days when the weight of the coating accounted for 3.5 percent of the coated urea solution.

2.1.2.2 Chitosan functionalized Silica nanoparticles:

Silica nanoparticles (SiNPs) have been proven to exert a beneficial influence on the growth and development of plants. In addition to their growth-stimulating properties, SiNPs are documented to enhance the level of stress tolerance in plants. Silica nanoparticles (SiNPs) are known to alleviate the adverse effects of drought and salinity stress by enhancing the absorption of nutrients and optimize water use efficiency [77]. Silicon is absorbed by the plant roots via aquaporins and subsequently transported to the aboveground sections by xylem loading and unloading mechanism [78], [79], [80], [81]. Silica promotes the salicylic acid biosynthesis genes (EDS1 and PAD4) to activate the defense-related genes, therefore triggering the activation of pathogen-related defense genes [82].

Recently, silica derived from natural resources has attracted significant attention due to its abundant availability, affordable price, and environmentally friendly nature. A variety of living organisms, including higher plants, have developed the ability to synthesize biogenic silica [23]. As an agricultural byproduct, rice husk (RH) produces more than 600 million tons annually worldwide [24]. Nevertheless, the use of rice husk is very limited because of its low nutritional value, resistance to degradation, and high ash content [25]. Furthermore, RH consists of 15 - 20% SiO_2 [26]. A variety of techniques, such as sol-gel processes [27], microwave hydrothermal processes [28], flame synthesis [29], and combustion synthesis [30], have been employed to produce biogenic silica nanoparticles from RH. Nevertheless, the majority of silica manufacturing techniques are laborious and yield silica of compromised purity.

Surface functionalization of silicon nanoparticles (SiNPs) provides an added benefit compared to the unmodified SiNPs in terms of their capacity to accurately transport molecules or chemicals that can enhance the plants' capabilities to counteract the negative impacts of stressors more effectively [83]. To avoid unwanted interactions of SiNPs and improve the efficient absorption of SiNPs, the surface has been modified using several polymeric stabilizers. Surface functionalization encompasses both physical and chemical alterations that enhance its versatility, biocompatibility, and suitability for various applications [84], [85], [86]. Functionalization of silica nanoparticles with chitosan improves its bioavailability and biodegradability. Chitosan is renowned for its exceptional biocompatible and biodegradable characteristics, making it a highly favored biopolymer [87].

2.1.3 Machine learning for optimizing nitrogen release:

Irfan et al. [88] developed a ML model built on Gaussian process regression (GPR) to forecast the nutrient's release from a biopolymer coated fertilizer that experiences simultaneous enzymatic and microbiological degradation. Furthermore, this work introduces the concept of kernel optimization for the GPR. By taking into account the inputs of coating thickness, temperature, granule radius, and nutrient's concentration, the optimized model has excellent predictability with a $R2$ value of 1 and RMSE value of 0.003. The model findings are scrutinized against the experimental results, and the projected outcomes demonstrate a significant degree of agreement with the experimental results.

Swain et al. [89] employed three different types of coatings to USG: bentonite clay and neem oil without heat, bentonite clay and neem oil with heat, and sulfur and acacia oil respectively. A variety of methods, including artificial neural networks, SVM, random forests, reduced error pruning trees, and Response surface methodology, were used to evaluate the acquired data for predicting nitrate leaching of USG. The response surface approach consistently demonstrated superior prediction capabilities for all coating types. SVM and Random forest algorithms are applicable for modeling nitrate leaching in USG.

According to Shen et al. [90], the nutrient release profiles from a CRF population were directly influenced by the characteristics of the core fertilizer, coating material, coating %, distribution of granule radii, and coating thickness. The LS-SVM model, which included the variability within a CRF population, demonstrated high effectiveness and accuracy in simulating nutrient release from the population. The Relative Percentage Demand was 6.98, Relative Predictive Value was 0.994, and Relative Mean Squared Error was 1.48%. Both inverse 'L' ($R2 = 0.999$ and RMSE = 0.54%) and 'S' ($R2 = 0.998$ and RMSE = 1.15%) display a significant level of similarity.

2.2 Research Gap

Prior research has not investigated the application of chitosan-functionalized biogenic silica nanoparticles for coating urea in slow-release fertilizers. And, although machine learning models have been used to enhance the efficiency of fertilizers, there is currently no study that has integrated machine learning with genetic algorithms (GA) and Particle Swarm Optimization (PSO) to optimize the rate at which nitrogen is released from these coatings. These research gaps indicate the need for additional research on the development of innovative coating materials and the implementation of optimization techniques to enhance the efficiency of fertilizers.

CHAPTER 3: RESEARCH OBJECTIVES

Fertilizers have been applied to fields to improve agricultural productivity and soil fertility. Urea is the most commonly used artificial fertilizer due to its high nitrogen content. Because of its greater solubility, urea releases most of its nitrogen content into the atmosphere via ammonia volatilization and leaching mechanisms. The usage of conventional urea fertilizer is directly related to several restrictions, including compounded environmental concerns. The aim of this project is to develop chitosan functionalized silica nanoparticles coated urea fertilizer.

The main objectives of this research study are:

- Synthesis of Chitosan functionalized biogenic SiO_2 nanoparticles coated Urea Fertilizer.
- Characterization of the Chitosan functionalized biogenic SiO_2 nanoparticles coated Urea Fertilizer.
- Analysis of nitrogen release rate from the formulated fertilizers.
- Development of a Machine Learning model to optimize the nitrogen release from formulated fertilizer.
- Comparison of experimental results with model predictions to assess the accuracy and effectiveness of the machine learning model.

CHAPTER 4: MATERIALS AND METHODS

This chapter outlines the methodology employed in both experimental and computational aspects of this study. The experimental part focuses on the synthesis, functionalization and coating of biogenic silica nanoparticles, followed by characterizations. Simultaneously the machine learning part focuses on optimizing the process of coating and predicting nitrogen release behavior of the coated urea fertilizer. The integration of machine learning models allowed for the refinement of coating parameters to enhance the fertilizers efficiency. In both methodologies each step is described to ensure clarity.

4.1 Experimental Methodology

4.1.1 Materials

All the chemical reagents utilized in the present research study are of laboratory grade with highest purity. The Pyrex glassware was used during the experimentation and analysis. The chemicals include hydrochloric acid, acetic acid, chitosan, p-methyl amino Benz aldehyde, ethanol, and deionized water. Urea fertilizer was purchased from local vendor with 46% N content. Rice husk was purchased from the local market.

4.1.2 Synthesis of Biogenic Silica nanoparticles (bSNPs)

An aqueous solution of 1 N hydrochloric acid (HCl) was made using deionized water. Further, 5 grammes of rice husk were combined with 25 millilitres of this solution using magnetic stirring. The solution was moved to an autoclave and subjected to a temperature of 120 ºC for a duration of 2 hours while being sealed under pressure. Following acid treatment, the rice husks were rinsed with deionized water to eliminate hydrochloric acid [91]. The acid-treated rice husks were subsequently dried in an oven at 80 ºC for 3 hours, followed by incinerating the dried pretreated rice husks at 700 ºC for 3 hours in a muffle furnace. The production of silica nanoparticles was indicated by the acquisition of a white residue at completion.

4.1.3 Surface Functionalization of Biogenic Silica nanoparticles (bSNPs):

A 20 mL chitosan solution was prepared by dissolving 1% (w/v) chitosan in 10% acetic acid. 100 mg of bSNPs were introduced in this solution. After that, the solution was ultra-probe sonicated for 2 hours, followed by additional stirring for 3 hours to get the bSNPs functionalized with chitosan (Cs-bSNPs). After washing the solution with deionized water, the purified Cs-bSNPs were collected and dried in an oven [92].

4.1.4 Coating solution Preparation:

The solutions used in the coating process were prepared in deionized water. The prescribed amount of bSNPs, Chitosan and Cs-bSNPs were added in the beaker filled with water to form a suspension. The suspension was heated at 80°C with sonication using an ultra-probe sonicator for 2 h. All the formulations were prepared using similar methodology.

Table 4-1: Coating Formulation used in Experiment

Coating Formulation	Wt. % /100 g urea		
	Chitosan	**bSNPs**	**Cs-bSNPs**
UC	-	-	-
CU	2	-	-
SU	-	1	-
CSU	-	-	1

4.1.5 Fluidized Bed Coating:

The coating process was initiated with the sieving of urea granules. The coating was carried out using a fluidized bed coater YC-1000 manufactured by Shanghai Pilotech Instrument & Equipment Company Limited. The chamber was initially dried using hot air at 80 ºC for 5 minutes in order to remove any moisture. The granules were loaded into a fluidized bed, which was set at 80 oC. The air blower was operated at a frequency of 40 Hz. The inbuilt peristaltic pump was installed to facilitate the flow of hot solution. It was maintained at 15 rpm for pumping the solution. Before being sprayed over fluidized granules in the bed, the heated coating solution was atomized using pressured air supplied through a compressor. To prevent the agglomeration of nanoparticles, the coating solution must be continuously stirred while being heated. After the coating, the drying process started for 15 minutes with hot air. Upon drying, the granules were then taken out from the fluidized bed and analyzed using different characterization techniques.

The **Figure 4-1** below summarizes the experimental workflow for silica nanoparticles synthesis, functionalization and coating on urea granules.

4.1.6 Characterization Techniques:

The bSNPs and Cs-bSNPs were characterized with SEM, XRD and FTIR. The uncoated urea prills and coated prills were examined using UV-VIS Spectrophotometer, SEM, FTIR, XRD and Crushing Strength. The surface structure and morphology were studied by utilizing a scanning electron microscope. The IR spectra were got in the wave number ranging from 400-4000cm^{-1} using a Fourier transforms IR spectrophotometer. Uncoated and coated prills were examined using scan angle ranging from 0^{o} to 90^{o} on X- ray diffraction apparatus.

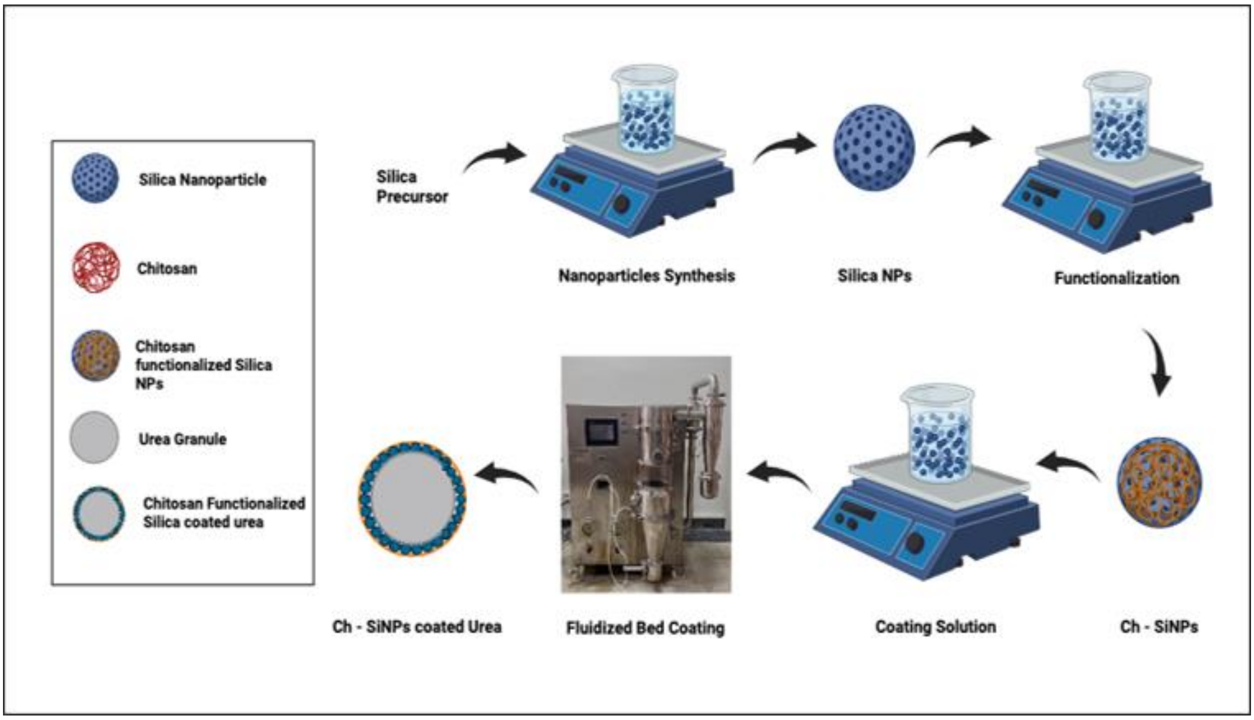


Figure 4-1: Experimental plan for silica nanoparticles synthesis, chitosan functionalization and urea coating

4.1.6.1 Nitrogen Release Rate in water:

The nitrogen release from all the coated treatments along with uncoated granules was performed using the p-methyl amino Benz aldehyde method. Initially, analytical grade urea was used to draw the calibration curve (99.9% Pure) by utilizing GENESYS^{TM} 20 UV-Visible spectrophotometer. Normalized solutions of lab grade urea (20ppm, 40ppm, 60ppm, 80ppm, and 100 ppm) were prearranged to get the slope from the drawn calibration curve as shown in **Figure 4-2**. The absorbance of the standardized solutions were noted using UV-Visible Spectrophotometer shown in **Table 4-2**. The following mentioned test protocol was implemented to calculate the release nitrogen from urea.

p-methyl amino Benzaldehyde method:

10 g of the coated urea sample was added in a beaker containing 5 liters of distilled water. 10 mL sample solution was collected at different intervals 3, 6, 9, 12, 15, 30, 60 and 120 minutes. 1 mL of HCl solution and 5 mL of coloring agent (p-methyl amino benzaldehyde) were added

along with deionized water to the markup level of measuring flask. This final solution was then well shake and applied in spectrophotometer to check its absorbance at 418 nm [93]. This absorbance was then converted into concentration with the help of **Equation** (4-1) and efficiency with help of **Equation (4-2)**.

$$urea\ (ppm) = \frac{Absorbance - Y\ intercept}{Slope} \tag{4-1}$$

$$Efficiency\ (\%) = \frac{C_U - C_{CU}}{C_U} * 100 \tag{4-2}$$

Table 4-2: Urea Concentration (ppm) versus Absorbance (Au)

Sr. No.	Concentration (ppm)	Absorbance (Au)
1	0	0
2	20	0.024
3	40	0.051
4	60	0.072
5	80	0.096
6	100	0.12

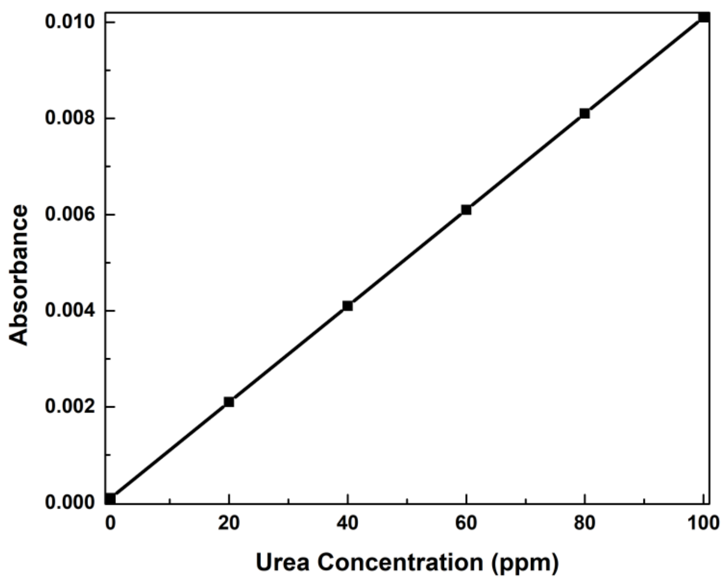


Figure 4-2: Calibration curve of analytical grade urea

4.1.6.2 Scanning Electron Microscopy

The technique of scanning electron microscopy (SEM) was used to study the morphology of nanoparticles and prepared samples. SEM gives higher resolution micrographs which are helpful to get an insight of the morphology of the surface and particle size. For SEM analysis, gold sputtering was carried out on all the samples using JEOL-1500 machine. The surface, structure and size evaluation of bSNPs along with coated urea was carried out on S 4700, Hitachi, Japan at 20 kV [94].

4.1.6.3 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared spectroscopy (FTIR) is a non-destructive technique used for identifying the nature of chemical bonds present in the test sample. When IR radiation is transmitted through the test sample, FTIR spectrums are obtained as either absorbed or transmitted radiations. The infrared radiation produces unique patterns of test material which are subsequently utilized in the analysis of the composition and chemical nature of the compounds. The bSNPs samples are examined using the dried potassium bromide method by making pellets. The test was carried out on FTIR PerkinElmer Spectrum 100 spectrometer in the range of wavelenths, 4000-400 cm^{-1} [94].

4.1.6.4 X-ray Diffraction

X-ray diffraction analysis is used to identify the crystallinity of unknown samples. Additionally, the structural parameters associated with the prepared samples are also determined with the help of this analysis. The synthesized bSNPs were tested on XRD machine STOE Germany. During the testing of nanoparticles, the step size was maintained at 0.05 seconds and scan ratio was maintained at 0.5 seconds. The scan angle was fixed in the range of 0-90° at 40 kV applied voltage [3].

4.1.6.5 Crushing Strength

The crushing strength of fertilizer is very important to predict its shelf life during the different phases in its life cycle, including production, bagging, shipping, and marketing. Higher values of crushing strength improve the shelf life of the product as well as its ability to withstand different stresses and harsh environmental conditions, including humidity and temperature. The coating improves the crushing strength, which substantially increases the shelf life of the product. The test is conducted on a Universal Testing Machine (AGX Plus). The urea particles are placed between metal plungers, and force is applied to them. The force in Newton (N) is noted when the particles fragment into fine powder. This measured value is referred to as the crushing strength of coated particles [95].

4.2 Machine Learning Methodology:

4.2.1 Data Collection

In this research study, data is gathered from a comprehensive literature review of experimental studies that have been reported on the release of nitrogen from coated urea fertilizer. Coated urea fertilizer, coating thickness, and release time comprised the primary criteria for data selection. Relevant articles were searched in Google Scholar, and Science Direct by employing a variety of keywords, including coated urea fertilizer, slow-release urea, coating material, coating thickness, release time, and percent release. The features data extraction and categorization were done to build and evaluate machine learning models after the reclamation of data from related papers.

A full set of 122 release time data points were gathered from 31 resaerch papers. The sample's data were obtained from the nitrogen release experiment on the composition of coated urea fertilizer, as well as the nitrogen release time. The literature was consulted for pertinent figures, tables, and supplementary data. Data regarding the release rate of coated urea fertilizers was gathered, including the granular radius, coating thickness, coating material, and release time. Polymers, additives, granular radius and coating thickness were used as input parameters in the nitrogen release from coated urea fertilizers. The output parameter of this process was the release time. **Table 4-3** shows the data distribution of the data all.

Table 4-3: Coated urea fertilizer data distribution

	Polymer	Additives	Radius (cm)	Coating Thickness (cm)	Release Time (days)
mean	120.786885	870.688525	0.334867	0.131925	34.800796
std	133.059126	1014.665096	0.504720	1.021408	49.275850
min	0.000000	0.000000	0.050000	0.000880	0.016664
25%	10.000000	0.000000	0.150000	0.003790	0.614825

50%	70.000000	0.000000	0.200000	0.008987	19.931818
75%	202.250000	1950.000000	0.300000	0.014709	49.826087
max	420.000000	3250.000000	2.600000	10.000000	280.000000

4.2.2 Overview of Developed Models:

This study employed Gaussian Process Regression, Ensembled Tree, Support Vector machine, and Decision Tree algorithms to develop models for accurately predicting the release of urea from coated surfaces, taking into account the coating material, granule radius, and coating thickness. The machine learning models in this work were constructed, trained, and evaluated using the MATLAB software. Further enhancement of the release time was achieved by the application of genetic algorithms and particle swarm optimization techniques.

4.2.2.1 Genetic Algorithm:

A genetic algorithm (GA) is an evolutionary algorithm that attempts to replicate the process of biological evolution. In 1975, Holland proposed a theory for genetic algorithms. Darwin's theory of evolution, which simulated the preservation of better species and their genes, had an impact on GA. Numerous researchers have utilized generalized estimating equations [96] to assess the resolution of challenging issues whose performance parameters lack the qualities of continuity and differentiability [97].

A genetic algorithm is a feature selection method that operates on a set of solutions instead of selecting a single optimum solution. At the start, the population is selected, and each solution is represented as a chromosome consisting of genes or bits. A population is a collection of solutions formed by combining the fitness values of individual chromosomes. A generation refers to a specific population at a particular time. The fitness function is a crucial element in the Genetic Algorithm as it defines the specific problem that needs to be optimized. The reproductive success of a chromosomal pair is determined by their fitness [98].

It is an inhabitant's algorithm that is built on the ideas of genetic inheritance and natural selection. Each solution stands in for a chromosome, and each parameter denotes a gene. GA measures each population member's fitness using an objective function called fitness. A selection technique is used to arbitrarily select the best options in order to enhance poor solutions. Because probability and fitness are related, this operator is a little more likely to choose the optimal options (objective value). Additionally, there is a higher likelihood to avoid local optima while choosing incorrect answers. It suggests that excellent alternatives can be removed with the aid of other solutions if they get trapped in a local solution. Until an optimal solution is established, an extreme integer of repetitions or population is comprehended, or a variation between solutions is smaller than a predetermined limit, this process is repeated [99], [100].

A genetic algorithm can drastically alter the search process in order to obtain the best potential solution by using the likelihood of genetic crossover and mutation. GA has the ability to change encoded genes. GA can examine numerous individuals and generate various optimal solutions. As a result, GA provides enhanced worldwide search capabilities. Babies born via chromosomal exchange between parents are likely to ruin magnificent genetic architecture, and the crossover formula is as follows:

$$\boldsymbol{K} = \frac{\boldsymbol{G} + 2\sqrt{\boldsymbol{g}}}{3\boldsymbol{G}} \tag{4-3}$$

$K = dynamically\ changing, and\ depends\ on\ the\ number\ of\ evolutionary\ generations$

$g\ =\ number\ of\ generations\ of\ the\ algorithm$

$G\ =\ total\ number\ of\ evolutionary\ generations$.[101]

4.2.2.2 Particle Swarm Optimization:

Particle swarm optimization (PSO) is a population based, self-adaptive, stochastic optimization method that finds the best position and calculates the optimal function value for every particle at that position. This algorithm calculates new velocities based on the current velocities, each particle's optimal position, and the optimal positions of its neighbors [102].

In the PSO algorithm, each solution is referred to as a "bird" or "particle" in the search space. These particles move in a swarm as they look for the ideal position. In N-dimensional problems, the particle includes both the position and velocity vectors [103].

The velocity field vector is represented by:

$$V_i = V_{i1}, V_{i2}, V_{i3}, V_{i4}, V_{i5}, \ldots\ldots\ldots, V_{iN} \tag{4-4}$$

And the position field vector is given by **Equation (4-5)**:

$$X_i = X_{i1}, X_{i2}, X_{i3}, X_{i4}, X_{i5}, \dots \dots \dots, X_{iN} \tag{4-5}$$

N is the number of unknown variables, and *i* represents the ith particle. The equations below are used to update the particle's velocity and position.

$$V_i^k = \omega . V_i^k + c_1 r_1 \left(pbest_i^k - X_i^k \right) + c_2 r_2 \left(gbest^k - X_i^k \right) \tag{4-6}$$

$$X_i^{k+1} = X_i^k + V_i^{k+1} \tag{4-7}$$

Here "gbest" represent the optimal location search of the swarm and "pbest" represent the best position of the *ith* particle individually. The impact of the previous velocity vector on the second vector is quantified by the inertia weight *w*. An upper bound is imposed on the velocity vector in all dimensions, denoted as V_{max}. Each time the method is iterated, the current position is evaluated as a possible solution to the problem. If the location in question is deemed more favorable than all previously determined locations, the coordinates are then included into the second position vector, X_i [104]. In order to simplify the comparison in subsequent rounds, the result of the optimal function is saved in a variable called *pbest*. The aim is to further explore more ideal locations and improve $pbest_i^k$ and X_i. The approach is implemented by modifying V_i, which can be conceptualized as a variable size, and selecting new locations by appending V_i coordinates to X_i.

4.2.2.3 Gaussian Process Regression

Gaussian Process Regression is a highly efficient learning model employed for addressing nonlinear regression problems. This method not only predicts but also calculates the coefficient of determination for each prediction point, which quantifies the uncertainty of the forecast. Statistical probability distributions can be regarded as Gaussian processes. The computed probability of an input vector is derived from both the variance and the average of a Gaussian distribution. Rather than a scalar mean and variance, the GPR model generates a mean and correlation vector [105].

Gaussian Process Regression (GPR) is a non-parametric and stochastic approach in machine learning that is employed to estimate the probability distribution across all feasible functions [106]. In Gaussian Process Regression (GPR), a Gaussian process prior is assumed. This prior can be defined by utilizing a mean function m(x) and a covariance function k (x, x’). Gaussian

Process Reanalysis (GPR) is based on the assumption of a Gaussian process prior, which can be defined as the average of the covariance function k (x, x') and function m(x).

$$f(x) \sim GP(m(x), k(x, x')) \quad \textbf{(4-8)}$$

When selecting a Gaussian process model, the form of the covariance kernel and mean function are determined. There exist several choices for kernel functions, including square, linear, and constant with multiple kernels composition. A kernel composition is a fixed kernel generated by the radial basis kernel function, which represents the smooth function. A constant times radial basis kernel function (RBF) is defined by the following equation:

$$k(x, x^{/}) = {\sigma_f}^2 \; exp(-\frac{1}{2l^2} \|x - x^{/}\|^2) \quad \textbf{(4-9)}$$

This study examines two hyperparameters: kernel length scale l and signal variance σ^2. After careful consideration, it is evident that GPR has several benefits, such as its capacity to handle small datasets and its capability to assess prediction uncertainty.

4.2.2.4 Support Vector Machine:

The Support Vector Machine (SVM) is a computer-generated machine learning algorithm used for both classification and regression problems [107]. In regression and classification issues, the support vector machine employs the kernel function to establish a mathematical link between the input and output variable. MATLAB allows users to specify custom kernels for Support Vector Machine (SVM) decision processes by defining kernel functions. This functionality enables the SVM method to address linear classification and regression problems effectively, eliminating the requirement for hyperparameter adjustment. Support Vector Machines (SVMs) has a distinctive capability to deliver well-balanced predicted outcomes, especially in study with limited sample sizes [108]. The optimization objective in this work is to determine the nitrogen release time. Precision tuning of Support Vector Machine (SVM) parameters is crucial for a target-optimization problem. Initially, the performance assessment index for SVM parameter optimization is established, and subsequently, the optimal parameter is determined using the MATLAB application [109].

Structural Vector Machines (SVM) were initially developed to address classification difficulties and subsequently extended to regression problems. To differentiate between distinct data sets, this method relies on the creation of a hyperplane in a space with a high (or infinite) number of dimensions. To optimize the separation, it is advisable to position the hyperplane at a considerable distance from the closest training data points. In the feature space, Support Vector Regression (SVR) produces a linear regression function as provided by an equation using a dataset of feature vectors. $x = \ x_i \ \in \ R^P; \ i = 1,,,n$, and a target value $Y \ \in \ R^n$.

$$f(x) \ = w^T\varphi(x) + b \qquad \textbf{(4-10)}$$

w = weight vector and b = bias

The following equations are solved to estimate these terms.

$$min \ \frac{1}{2}w^T w + C\sum_{i=1}^{n}(\xi_i + \xi_i{}^*) \qquad \textbf{(4-11)}$$

Subject to constraints:

$$yi - w^T \ \Phi(xi) - b \quad \leq \xi + \ \xi_i \qquad \textbf{(4-12)}$$

$$w^T \ \Phi(xi) + b \quad \leq \ \xi_i + \xi_i{}^* \qquad \textbf{(4-13)}$$

$$\xi_i, \xi_i{}^* \geq 0 \qquad \textbf{(4-14)}$$

ξ = error of models distant from the hyperplane where $\xi_i{}^*$, ξ depend on the sample position, below or above the $\boldsymbol{\varepsilon}$ tube, C represents the plenty term. The key hyperparameters are C and $\boldsymbol{\varepsilon}$, in which, a low value of C is recommended for datasets with high levels of noise. The prediction of Support vector regression by the lagrangian dual technique can be analyzed by following **Equation (4-15).**

$$f(x) = \sum_{i=1}^{n}(\alpha_i + \alpha_i{}^*)\,K(x_i + x_j) + b \qquad \textbf{(4-15)}$$

α = Lagrang multiplier of dual form,

K = Kernel function [95]

$$K(x_i + x_j) = \Phi(x_i)^T\Phi(x_j) \qquad \textbf{(4-16)}$$

4.2.2.5 Decision Tree:

The advanced algorithm known as Random Forest was developed using the multi-decision tree (DT) architecture. Each decision tree (DT) arises autonomously after acquiring a random subset of the input data, commonly known as a bootstrap sample. Although individual decision trees in the random forest are widely regarded as ineffective learners, the collective performance of the RF can attain superior levels of competence and accuracy when they collectively make predictions [110]. As the samples with desired values are grouped together, a decision tree systematically divides the feature space, (x), by employing a randomly selected set of data d(x,y). The dataset is denoted as dm, with nm samples at node (m) as illustrated in **Equation (4-17)** **&** **(4-18)**.

$$d_m^{left} = \{(x, y)|x_p \leq t_m\} \tag{4-17}$$

$$d_m^{right} = \frac{d_m}{d_m^{left}} \tag{4-18}$$

The dataset dm is partitioned into two subsets, namely dmleft and dmright. The candidate is divided into two variables, p and tm, where p represents a feature and tm represents a threshold. These subsets are preserved until the maximum reachable depth is achieved. The development of RF prediction is indicated in **Equation (4-19).**

$$f(x) = \frac{1}{K}\sum_{K=1}^{K} DT_t(x) \tag{4-19}$$

whereas K =number of DTs. ('n estimators') in the random forest.

4.2.2.6 Ensembled Learning Tree:

The ensemble learning method is an approach that combines numerous learners using predefined combination protocols. When compared to earlier black-box algorithms, tree-based machine learning models are more easily comprehensible and capable of addressing both linear and non-linear issues [111]. In order to generate efficient diagnostic criteria, the tree ensemble approach employed multi-objective optimization. The suggested approach utilizes two models: base learners for predicting the posterior class probabilities of a sample, and a meta-learner for predicting the label of the final class by combining the basic learners. The construction of a model involves a critical examination of model combination and model selection from several perspectives. To achieve an accurate and comprehensible ensemble, we employ a multi-objective method for selecting models. This method aims to optimize both accuracy and ensemble complexity simultaneously. The tree ensemble approach use the hillclimbing technique to identify a stable collection of rules, dependent on the selection of rules and their accuracy [112].

The machine learning process used for the data analysis and optimization in illustrated in the **Figure 4-3**.

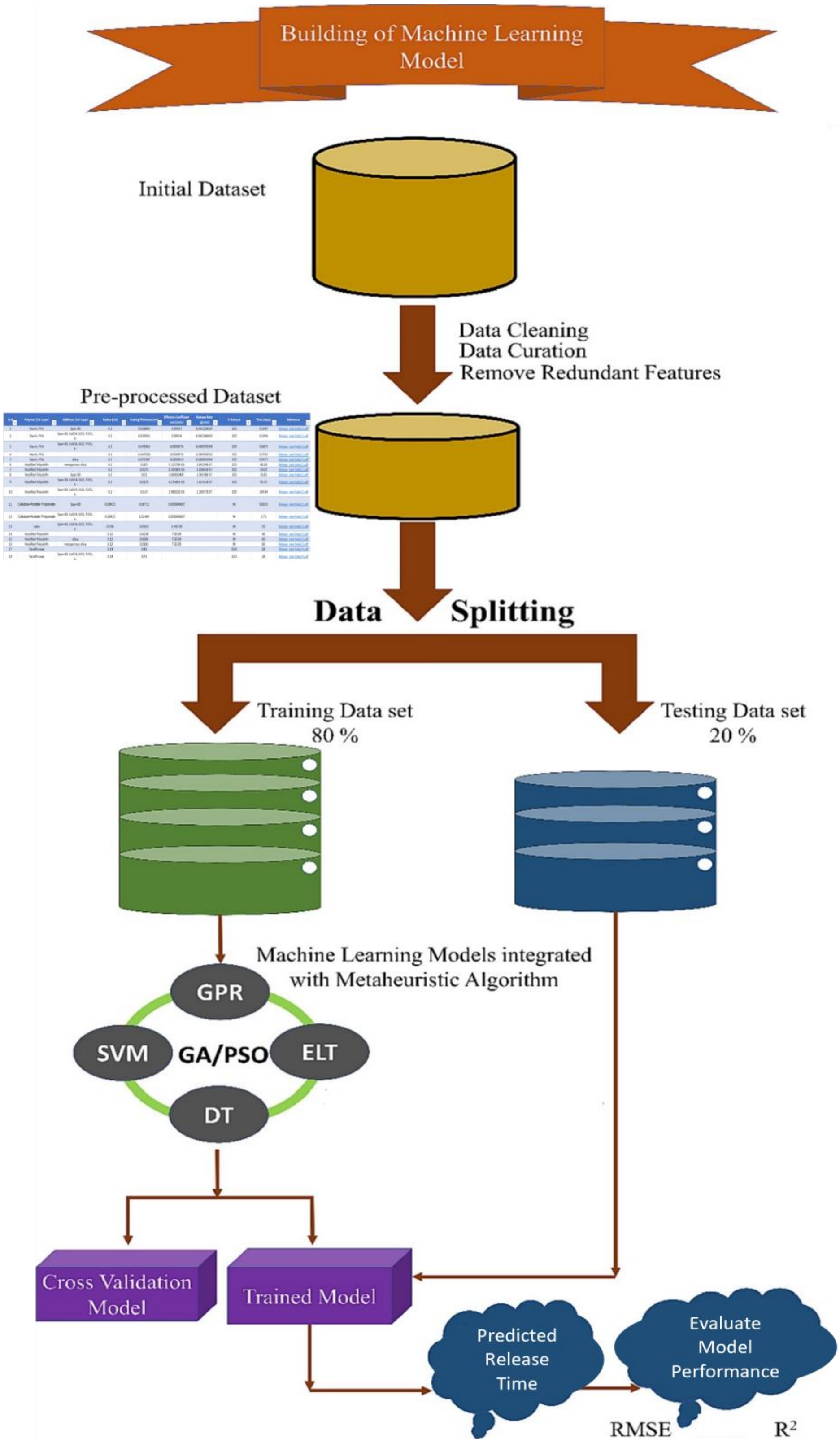


Figure 4-3: Machine learning workflow for data pre-processing, model development, and nitrogen release optimization.

CHAPTER 5: RESULTS & DISCUSSIONS

This chapter covers the key findings, which include both experimental data and machine learning predictions. The study focuses on the synthesis, characterization, and nitrogen release properties of chitosan-functionalized biogenic silica-coated urea fertilizer. In parallel, machine learning models were used to anticipate and optimize nitrogen release rates using experimental data.

5.1 Experimental Results:

5.1.1 Nitrogen Release Rate:

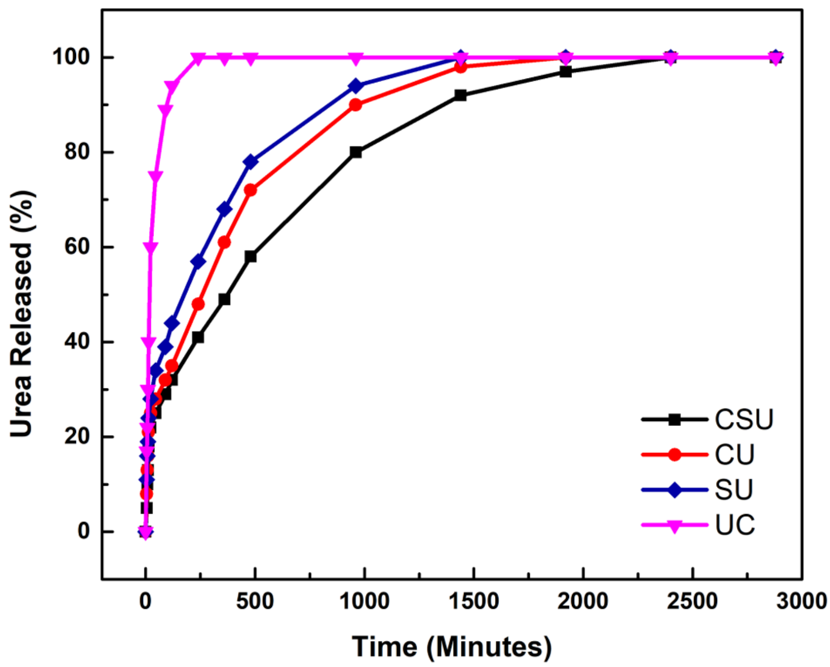
The purpose of this method of analysis was to measure the rate of urea release following the application of the coating on urea granules. The test was conducted by immersing the urea granules that had been coated in de-ionized water. In addition, uncoated granules were examined for comparison with coated ones.

Table 5-1: Concentration of coated and uncoated urea granules

Sr. No.	Time (minutes)	UC (ppm)	SU (ppm)	CU (ppm)	CSU (ppm)
1	4	0	220	160	100
2	8	340	320	260	200
3	12	440	380	320	260
4	15	600	480	420	360
5	30	800	560	500	440
6	45	1200	680	560	500
7	90	1500	780	640	580
8	120	1780	880	700	640
9	240	1880	1140	960	820
10	360	2000	1360	1220	980
11	480	2000	1560	1440	1160
12	960	2000	1880	1800	1600
13	1440	2000	2000	1960	1840
14	1920	2000	2000	2000	1940
15	2400	2000	2000	2000	2000

The release rate of urea granules exhibited the similar behavior of coated urea upon contact with water. Furthermore, this test assesses the effectiveness of coating materials that slow down the liberation of urea. Release experiments were conducted using various combinations of coated urea granules. The results of the tests were reported in terms of urea concentration in parts per million (ppm) using **Equation (4-1)**. The effectiveness of each combination was determined by comparing the urea content at 15 minutes of the untreated sample with the coated sample using **Equation (4-2)**. An analysis of the concentration of uncoated and coated urea granules at various time intervals is presented in **Table 5-1**.

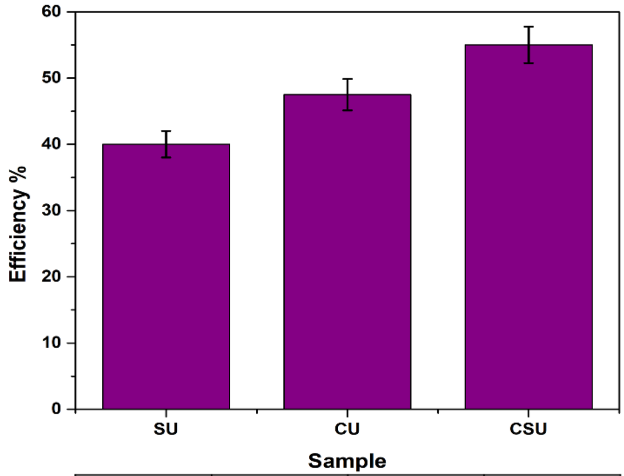
Figure 5-1 exhibited the release of uncoated and coated urea fertilizers. Uncoated urea granules (UC), release entirely in water after 240 minutes. Without coating, the UC will adhere to the burst flow mechanism. This occurred because of the exposed surface that enables water molecules to penetrate more easily. bSNPs coated urea granules (SU), completely release in water after 960 minutes. Chitosan coated urea (CU), completely release in water after 1440 minutes and Cs-bSNPs coated urea (CSU), released in 2400 minutes. This is because of the resistant layer provided by Cs-bSNPs. It lets water penetrate through it and results in swelling of coating layer with gradual release of nutrients.



df	F-value	P-value	η^2
3	15.67	<0.001	0.923

Figure 5-1: Cumulative release of urea from UC, SU, CU and CSU

Figure 5-2 exhibited the efficiency of coated urea fertilizers SU, CU and CSU which was calculated using the efficiency **Equation (4-2)**. Concentrations of Coated as well as uncoated urea granules at 15 minutes were used to calculate the efficiency of coated urea.



df	F-value	P-value	η^2
2	12.34	0.002	0.85

Figure 5-2: Efficiency of coated urea fertilizers: SU, CU and CSU

5.1.2 Surface Morphology:

The morphology of all the samples were investigated using scanning electron microscope. bSNPs were scanned to examine the morphology of the surface and dimensions of the bSNPs. Analysis was carried out on the coating surface to assess the shape, uniformity and structure of coating layer applied on urea.

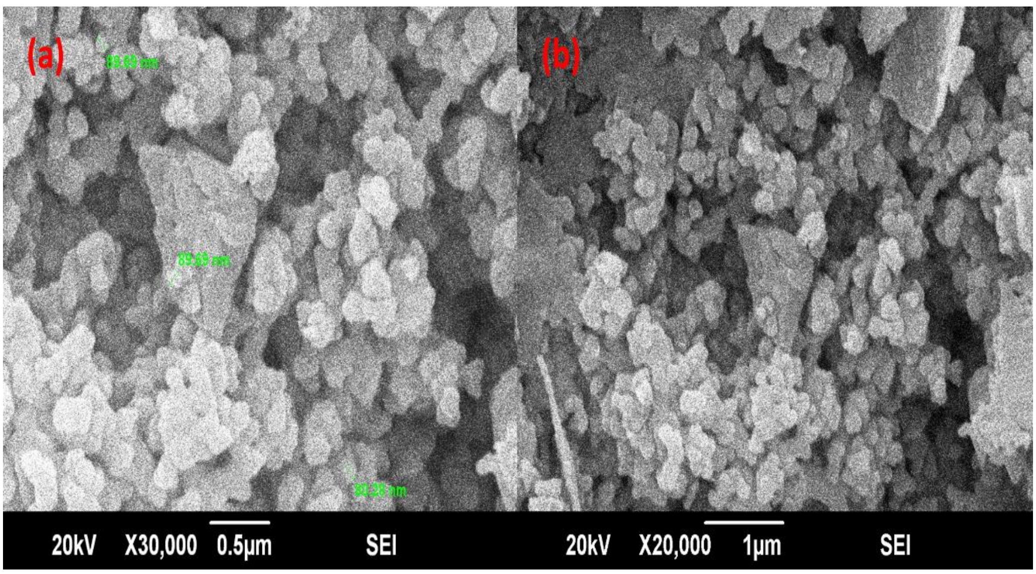


Figure 5-3: SEM Micrograph of bSNPs at different magnifications (a) X30000 and (b) X20000

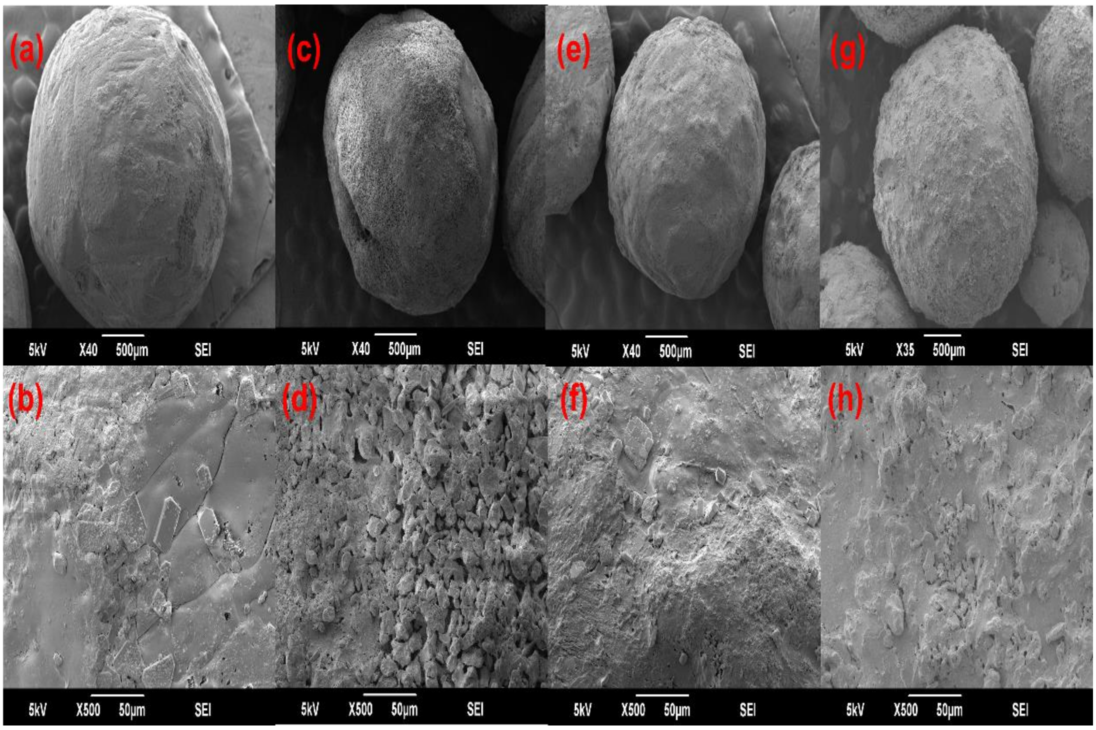


Figure 5-4: SEM Micrograph of (a) UC at X40, (b) UC at X500, (c) CU at X40, (d) CU at X500, (e) SU at X40, (f) SU at X500, (g) CSU at X40 and (h) CSU at X500

The SEM images of bSNPs showed spherical configuration of nanoparticles in **Figure 5-3**. The nanoparticles in SEM micrograph exhibited minimal agglomeration. As depicted in the figure, the average size of bSNPs ranged between 80 to 90 nm.

The SEM images of coated and uncoated urea are shown in **Figure 5-4**. The UC shows rough and crystalline structure leading to rapid nitrogen release. The CU shows rough and porous surface allowing for moderate nitrogen release. SU has a thin and uneven layer which slightly slows the release. CSU has a smooth and compact coating providing more controlled release.

5.1.3 Fourier Transform Infrared Spectroscopy:

The **Figure 5-5** presents the FTIR spectrum of bSNPs and Cs-SNPs. In bSNPs spectrum, the peak at 463 cm^{-1} corresponds to O-Si- bending. A stretching vibration arising from the Si-O-Si group is observable at 1105 and 810 cm^{-1}. Furthermore, there are peaks observed at 1625 and 3437 cm-^{1}. The stretching and bending vibrations may indicate that adsorbed water molecules are present on the surface of nano-silica particles. Modifying silica with chitosan increases the intensity of 3437 peak. Intensity of peaks at 1105, 810 and 463 cm^{-1} also increases [113], [114], [115].

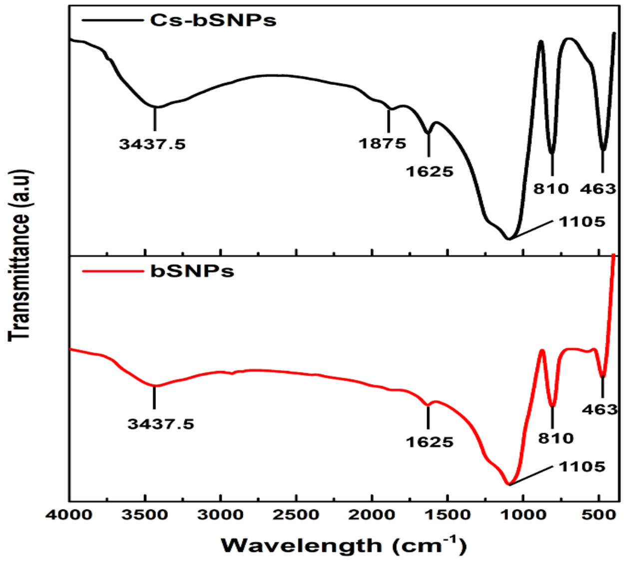


Figure 5-5: FTIR Spectra of bSNPs and Cs-bSNPs

The **Figure 5-6** presents the FTIR spectrum of uncoated and coated urea. Uncoated urea exhibits both asymmetric and symmetric vibrations of NH_2, within the wavelength range of 3430 and 3340 cm^{-1}. The peak at 1625 cm^{-1} corresponds to a carbonyl (CO) molecule, while the peak at 1465 cm^{-1} corresponds to NH and CH and stretching vibration of compound O=C-NH_2. There is also a stretching seen at 1465 cm^{-1} due to –CN bonds. A stretching vibration mode arising from the –C-O-C group is observable at 1150 cm^{-1}. Also, at this peak stretching vibrations from C-H group are detected.

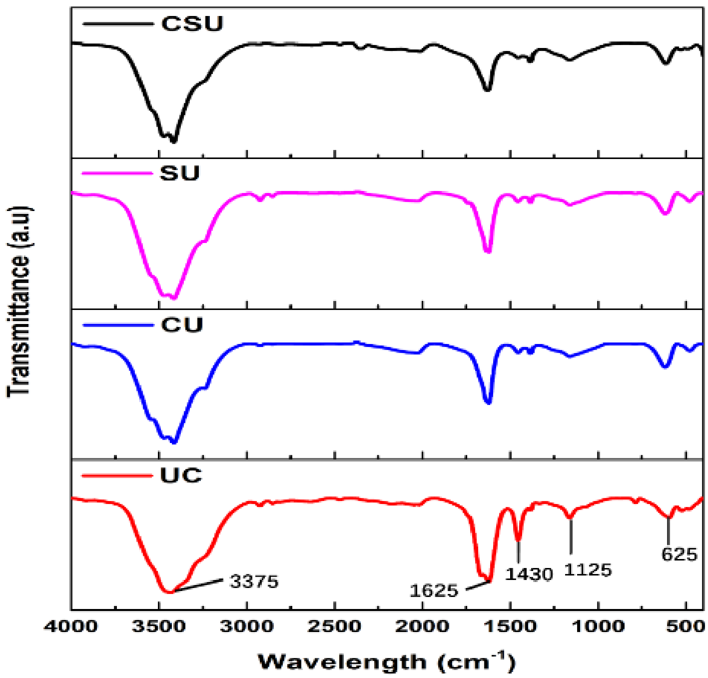


Figure 5-6: FTIR Spectra of UC, CU and SU

The spectra of all coated and uncoated urea appeared identical, with just a few modifications. The peaks at 2100 and 2010 cm^{-1} indicates C≡N stretching vibration and C≡C stretching vibration [116].

5.1.4 X-Ray Diffraction:

The **Figure 5-7** presents the XRD pattern of bSNPs and Cs-bSNPs. According to the pattern of b-SNPs the most evident amorphous curve appears at 25° in the 2θ angle. It exhibits an amorphous state of silica. In Cs-bSNPs pattern, curve broadening is observed. And the curve appears between 25 to 35° [117], [118].

The **Figure 5-8** represents the XRD patterns of uncoated and coated urea fertilizers. The prominent diffraction peaks are observed at 2θ values of 22°, 24.5°, 29.5° and 35.5°, corresponding to 110, 101, 111 and 210 planes respectively. The more prominent peaks are observed between 20 to 25°. The XRD patterns of coated urea also exhibited dominant peaks in this range. In the XRD pattern of CU, slight changes occurred due to addition of chitosan, so peaks at 29.5°, 31° and 36° become more prominent. In XRD patterns of SU and CSU no prominent peak except the 22° is observed [94].

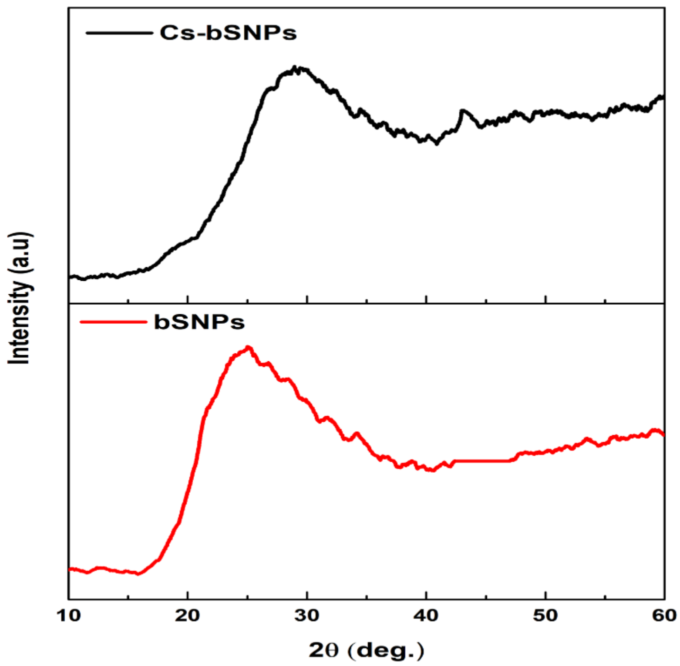


Figure 5-7: XRD pattern of bSNPs and Cs-bSNPs

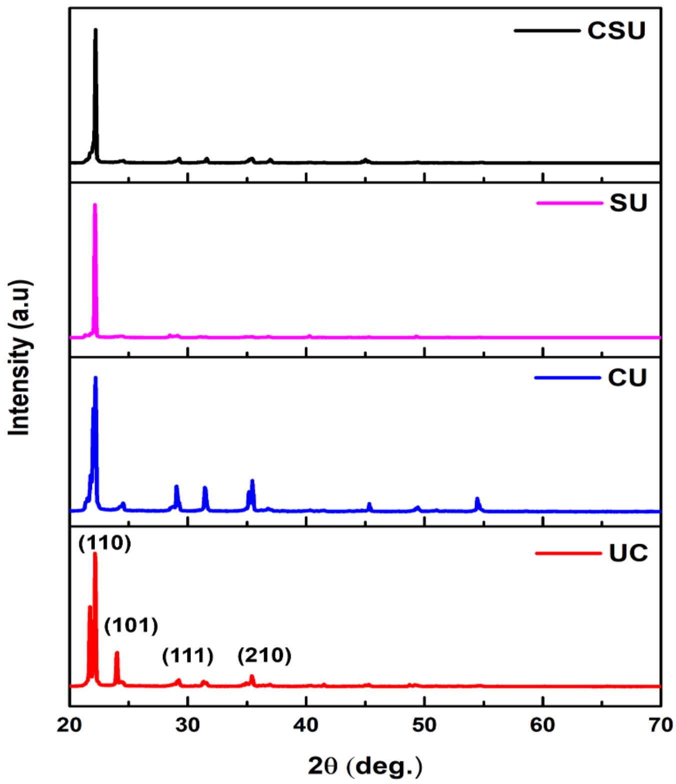


Figure 5-8: XRD patterns of UC, CU, SU and CSU

5.1.5 Crushing Strength:

After the application of the coating, if the granular urea fractures, the availability of nutrient nitrogen would be comparable to granules without the coating material. Preference will be given to samples that exhibit greater impact resistance against all anomalous forces, considering storage, bagging, and transportation points [95]. In this research, several coating formulations were employed to granular urea and subjected to pressure testing utilizing a tensile tester till fracture occurred.

Figure 5-9 depicted the crushing strength outcomes after undergoing testing using the universal testing machine. The final measurement is recorded when the urea granules are completely compressed into fine powder. Uncoated granules were crushed with a force of 7.03 N. The CSU exhibited the greatest crushing strength of 9.38 N. This is because of the presence of Cs-bSNPs. The three coating formulations have shown almost the same crushing strength. The average force required to crush coated urea granules is almost 45% more than the uncoated commercial fertilizer. Hence, the crushing strength of granules enhanced when three coating substances were utilized.

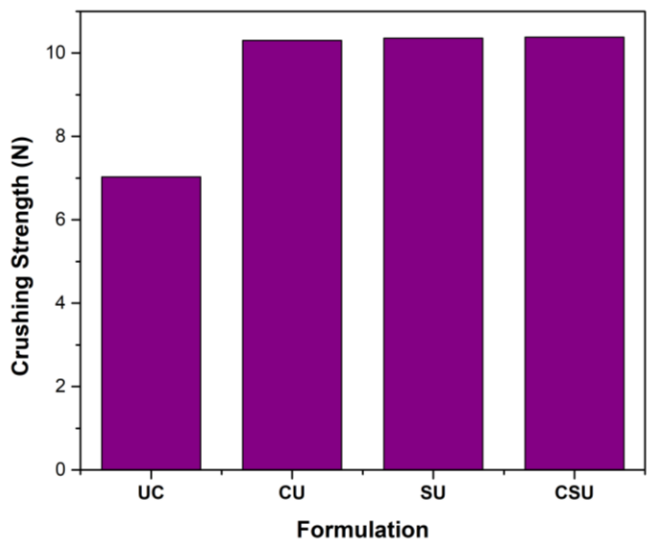


Figure 5-9: Crushing Strength of Uncoated and Coated Urea

5.2 Machine Learning Results:

5.2.1 Box Plot Presentation:

A Box Plot is an approach employed to visually represent the distribution of a dataset. The shown parameters include the maximum and lowest range, median, mean, tolerance, as well as the lower and upper quartiles. A comprehensive grasp of the structure and origin of the box plot enables the assessment of data and its applications [119]. **Figure 5-10** displays a box plot illustrating the distribution of radius and coating thickness, against their distinct values. The radius and coating thickness varied between 0.05cm and 2.6cm, 0.088cm and 0.71 cm, respectively.

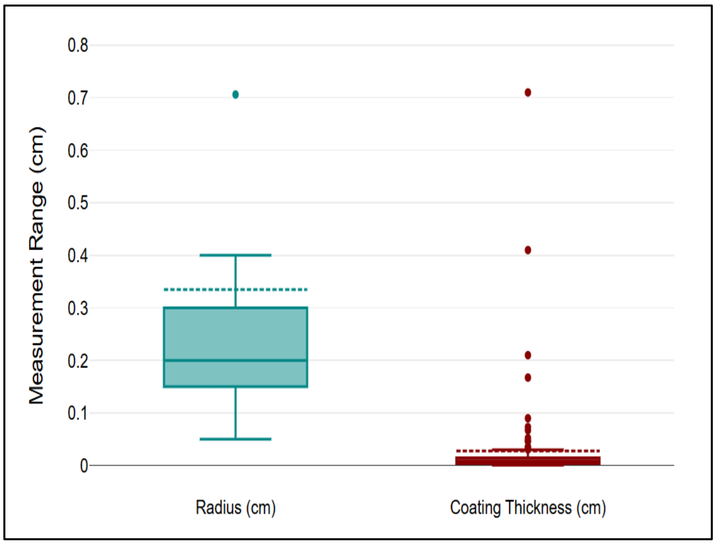


Figure 5-10: Box plot representation of the numerical data

5.2.2 *Count Plot Presentation:*

A count plot visualizes the frequency distribution of categorical data [120]. In this work, count plots were used to assess and compare the occurrence of various polymers and additives employed in coating formulations. The x-axis depicts the various types of polymers and additives, while the y-axis shows their corresponding counts. This enables for a simple comparison of the usage of different materials. **Figure 5-11** exhibits the count plot presentation of data.

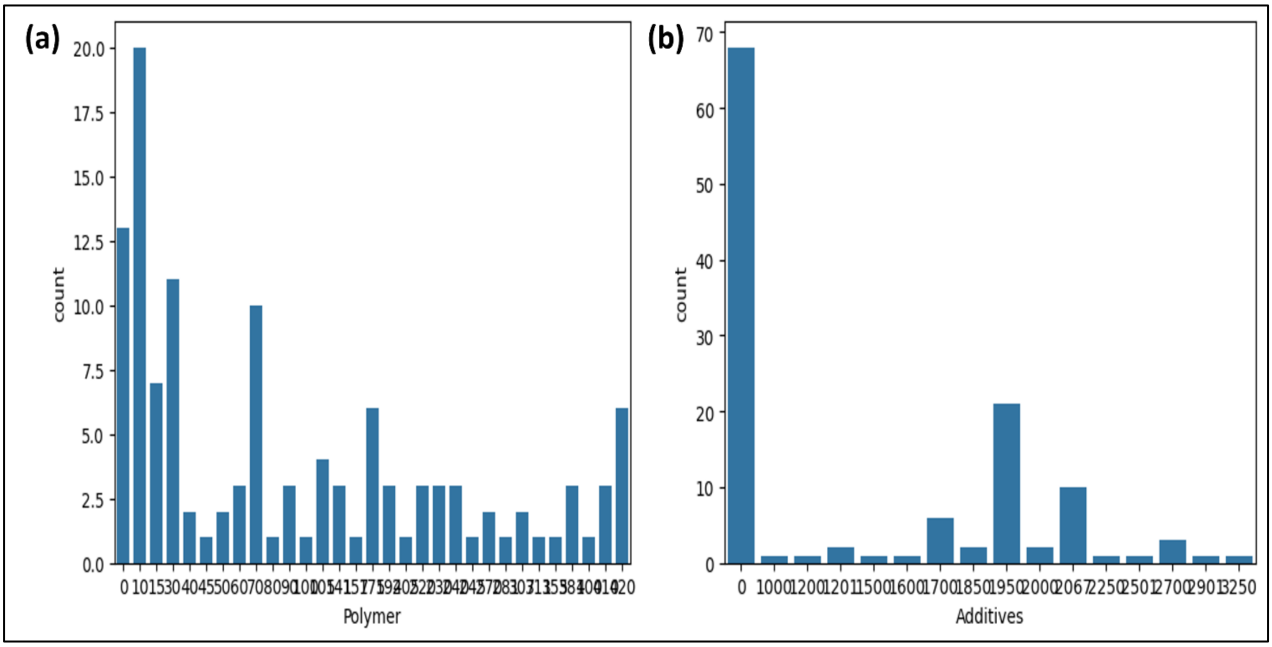


Figure 5-11: Count plot representation of categorical data: (a) Polymers (b) Additives

5.2.3 *Performance Evaluation Criteria:*

The GPR, DT, ELT, and SVM algorithms from the MATLAB package were pre-processed using the predefined hyperparameter specifications. Statistical measures of RMSE and R^2 were used to assess preprocessing methods. In order to preprocess and thoroughly model the variables, the datasets were randomly partitioned into training datasets (80%) and testing datasets (20%). To reduce data wastage and overfitting, the developed models were validated using 5-fold cross-validation. The hyperparameter tuning ranges were determined using the Regression model toolbox of each model and subsequently optimized using Genetic Algorithm (GA) and Particle Swarm Optimization (PSO). Once established, these hyperparameters were employed to construct and evaluate models. The mean values of the statistical indices were used to assess the performance of the validation phase in comparison to the modelling process.

Two specific criteria were utilized to evaluate the prediction performance of each final machine learning model:

1) RMSE (Root Mean Squared Error)

2) R^2, coefficient of determination

Presented below are the R^2 and RMSE equations:

	$$R^2 = 1 - \frac{\sum_{i=1}^{n}(Y_i^{exp} - Y_i)^2}{\sum_{i}^{n}(Y_i^{exp} - Y_i^{exp})^2}$$	**(5-1)**
	$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Y_i^{exp} - Y_i)^2}$$	(5-2)

Y_i^{exp} *is experimental value,* Y_i *is predicted data and* n *represent number of test sample*

5.2.4 Prediction Performance:

Predictions of the Release Time were made using various ML models, including GPR, ELT, DT, and SVM. The nitrogen release was properly predicted by all four machine learning models based on GA and PSO. Furthermore, we employed optimization methodologies such as Genetic Algorithms (GA) and Particle Swarm Optimization (PSO) to enhance the efficiency of these predictive models. We employed key metrics to assess the effectiveness of the predictive models. The following **Table 5-2,**

Table 5-3 and **Table 5-4** represent the performance outcomes of each model before and after the implementation of optimization methods, namely Genetic Algorithms (GA) and Particle Swarm Optimization (PSO).

Table 5-2: A Comparison of different ML Models

Models	**Training**		**Testing**	
	R^2	**RMSE**	**R^2**	**RMSE**
GPR	0.75	26.107	0.25	33.826
DT	0.55	34.703	0.15	35.878
ELT	0.65	30.626	0.13	36.384
SVM	0.03	50.942	0.12	36.602

Table 5-3: A Comparison of different ML models combined with GA

Models	Training		Testing	
	R^2	RMSE	R^2	RMSE
GPR	0.9976	0.0173	0.9766	0.1215
DT	0.9727	7.8056e-14	0.6431	3.0458e-14
ELT	0.8971	1.2428	0.5211	0.7540
SVM	0.9638	8.5285	0.3961	4.8953

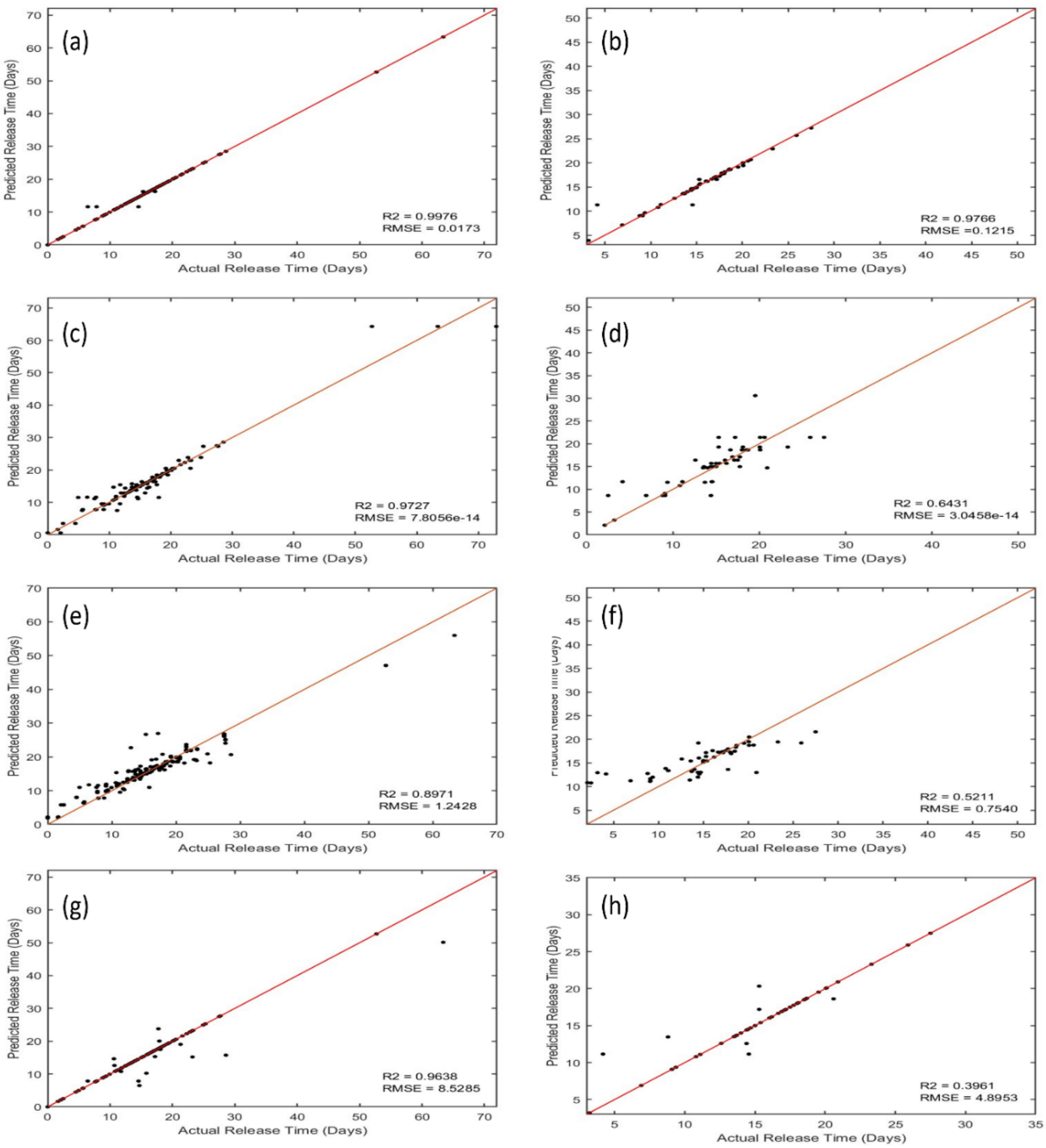


Figure 5-12: Comparison of training and testing graphs of different models combined with GA: (a) GPR Training, (b) GPR Testing, (c) DT Training, (d) DT Testing, (e) ELT Training, (f) ELT Testing, (g) SVM Training and (h) SVM Testing

Table 5-4: A Comparison of different ML models combined with PSO

Models	Training		Testing	
	R^2	RMSE	R^2	RMSE
GPR	0.6706	0.2434	0.9766	0.1215
DT	0.9838	1.2274e-13	0.6431	3.0458e-14
ELT	0.8478	3.079	0.5312	0.8828
SVM	0.9649	7.6991	0.4284	5.1348

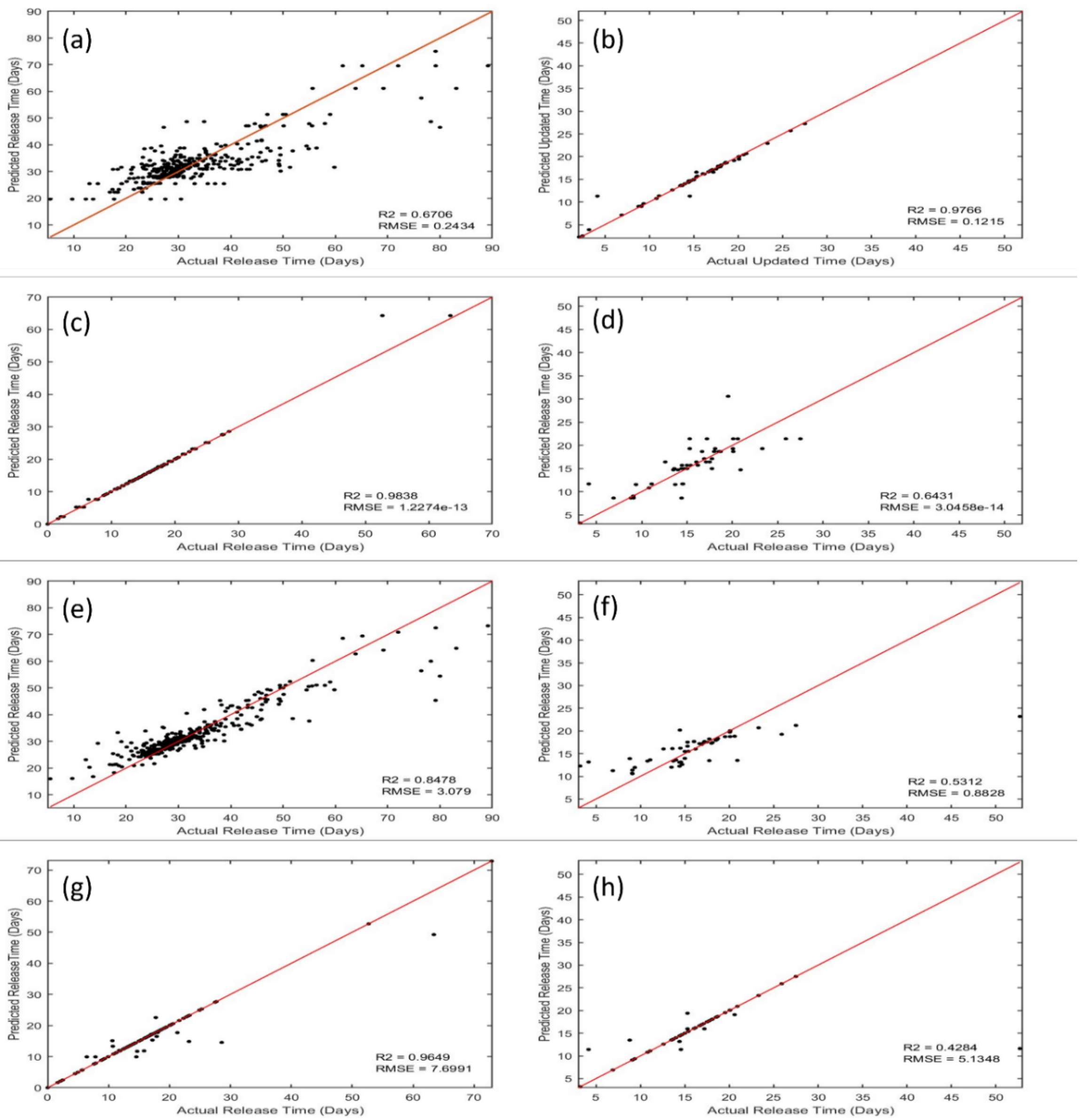


Figure 5-13: Comparison of training and testing graphs of different models combined with PSO: (a) GPR Training, (b) GPR Testing, (c) DT Training, (d) DT Testing, (e) ELT Training, (f) ELT Testing, (g) SVM Training and (h) SVM Testing

An analysis of the four machine learning models is shown in Table 5. The outcomes indicate that the performance of GPR, ELT, and DT models was acceptable when compared to the SVM model for predicting release time. Performance of the GPR model with GA surpassed that of that of all other models in both the training and testing phases. Furthermore, the DT model with PSO outperformed all other models in both the training and testing phases. Performance of machine learning models has been assessed using performance coefficient (R2) and root mean square error (RMSE) values. The performance trends for training and testing are as follows: GPR>DT>ELT>SVM.

5.2.5 Features Importance:

The correlation between input parameters and Release time can be well described by the GPR model with the Shapley technique. An operational principle of the Shapley method is the quantification of feature attribution. The present study utilized this approach to evaluate the relative significance of different input parameters on the release time of coated urea fertilizers.

The impact of coating materials and coating thickness on release time is depicted in **Figure 5-14**. Significant impact on release time was observed with additives polymers and coating thickness, whereas the influence of radius on nitrogen release time was found to be less significant.

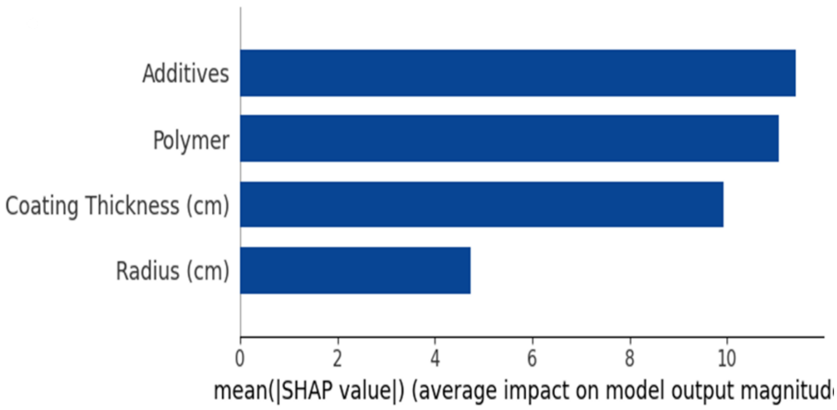


Figure 5-14: Shapley analysis of GPR Model

5.2.6 Effect of Parameters on Release Time:

Parametric analysis of partial dependent plots (PDPs) is a statistical technique employed to evaluate the impact of input factors on output. Within the PDPs, only the factors that exert an impact on the outcome were chosen. **Figure 5-15 (a)** demonstrates the influence of granular radius on release time. An upward trend in release time was seen as the radius was extended from 0 to 0.18 cm. Machine learning models propose that the release time can be enhanced by increasing radius but up to a certain limit.

The relationship between the thickness of the coating and the release time of coated urea fertilizer is shown in **Figure 5-15 (b)**. Release time shows an increasing trend when coating thickness was increased but up to a certain limit. The combined influence of coating thickness and radius was demonstrated by three-dimensional PDP in **Figure 5-16**.

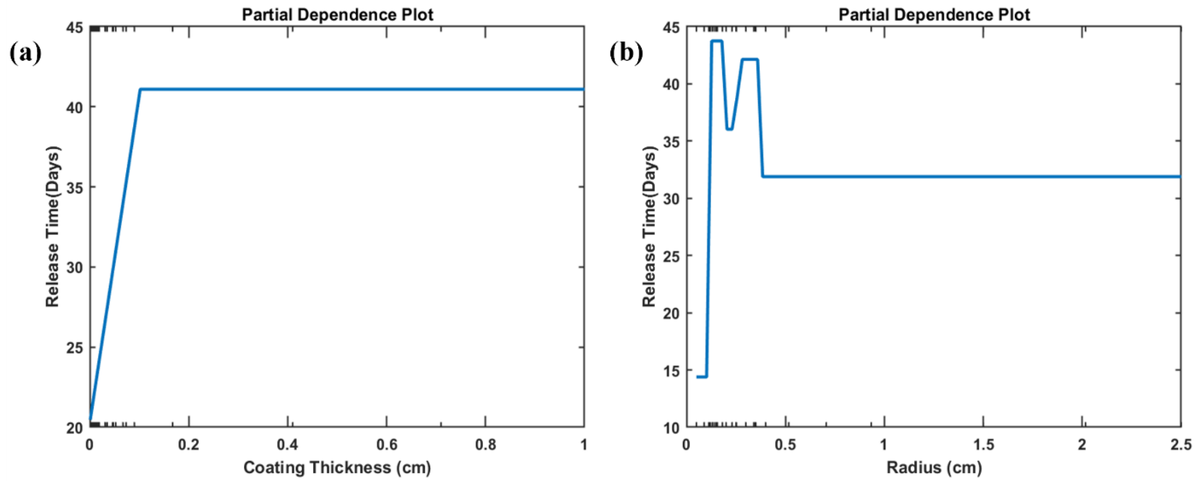


Figure 5-15: 2D Plots for release time using radius and coating thickness

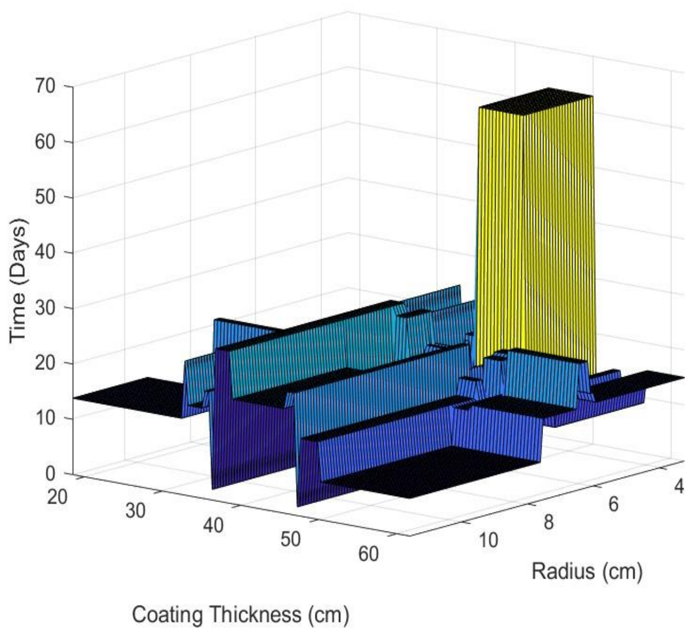


Figure 5-16: 3D PDPs for release time using radius and coating thickness

5.2.7 Graphical User Interface:

A Graphical User Interface (GUI) is a technology interface that enables individuals to engage with electronic devices by means of graphical icons, symbols, and user-friendly software implemented through a command driven interface. The GUI shown in **Figure 5-17** offered customers the ability to enter information on coating materials, such as polymer, additives, granular radius, and coating thickness. The GUI uses the GPR prediction tool to estimate the Release Time.

Figure 5-17: GUI for Release Time Prediction

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions:

The main research objective behind this research study was to experimentally evaluate the nitrogen release of chitosan functionalized biogenic silica nanoparticles and predict the nitrogen release using machine learning models trained on data collected from literature. The primary findings are as follows:

- The research demonstrated that encapsulating urea granules with biogenic silica nanoparticles functionalized with chitosan reduced nitrogen release significantly. This illustrates the promise of sustainable materials like biogenic silica in reducing the rapid nitrogen loss caused by traditional urea fertilizers.
- Data collected from the literature on coated urea fertilizers were utilized to train four machine learning models: GPR, DT, ELT and SVM to predict nitrogen release time. The GPR model performed best with the highest R^2 and lowest RMSE.
- The trained models were validated with experimental data, showing strong alignment between the predicted and observed nitrogen release time. This highlighted the value of employing data from literature to build predictive algorithms capable of accurately estimating nutrient release behavior.
- This research successfully combines experimental results with machine learning approaches. This integration offers a viable approach for increasing fertilizer efficiency while reducing environmental effect.

6.2 Recommendations:

The following conclusions are proposed based on this study's conclusion:

- Excessive pot tests to be conducted on various plants with different soils to check the impact of coating on plant growth.
- Future research should focus on increasing the dataset by incorporating more literature-based data to improve model predictions.
- Alternative biodegradable materials in coating formulations should be investigated to increase the sustainability and efficiency of slow-release fertilizers.

- Future research should focus on developing environmentally sustainable fertilizers that reduce nitrogen loss and improve nitrogen use efficiency, thus facilitating the global shift to more sustainable farming practices.

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