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Slow-Release Urea Prills Developed Using Organic and Inorganic Blends in Fluidized Bed Coater and Their Effect on Spinach Productivity

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Abstract: The application of urea-based fertilizers in developing countries has gained significant momentum over time. Urea usage is to meet demand and supply gap of food resources as world population is increasing at a fast pace. Urea contains largest content of nitrogen (46%) among all the solid nitrogenous fertilizers. However, main drawback of urea is its higher dissolution rate. After soil application, most of urea nitrogen is lost through a leaching, runoff, nitrification-denitrification and ammonia volatilization. To tackle urea related environmental pollution, development of slow-release urea fertilizer is a need of the hour and this would also increase product use efficiency in terms of crop productivity and its N uptake. We studied the usage of polymeric materials in combination with inorganic substances like sulfur and plaster of Paris as effective and biodegradable coating substances for urea prills. For coating on urea prills, fluidized bed coater was used whereas paraffin wax and molasses were used as binding agents. The urea was coated with four different formulations, i.e., C-1: PVA 5% + plaster of Paris 10% + sulfur 5% + paraffin wax 2%, C-2: PVA 5% + starch 10% + sulfur 5% + paraffin wax 2%, C-3: gelatin 5% + plaster of Paris 10% + sulfur 5% + paraffin wax 2% and C-4: PVA 5% + starch 10% + sulfur 5% + paraffin wax 2.5% + molasses 2.5%. Each formulation along with uncoated urea prills (C-0) were evaluated for characterization and N release kinetics. All the formulations along with uncoated urea were applied to spinach crop in pot experiment. A control (No N: untreated) was also kept. Spinach biomass yield and N uptake were determined. The formulation C-1 yielded highest urea-N release efficiency and spinach N uptake of 6.87% and 1.93 g N/pot, respectively. The modified Schwarz and Sinclair formula gave the excellent representation of release of nutrient-N from coated urea prills. It is concluded that coating urea prills with organic and inorganic blends is better option to slow down N release kinetics and improve spinach productivity. Therefore, by using coated fertilizers, farmers can improve agro-environmental value of urea, worldwide.

Keywords: slow release fertilizer; release rate; coated urea prills; polymeric and inorganic substances; nitrogen uptake
1. Introduction

Nitrogen (N) is a vital constituent for any crop to complete its lifecycle and therefore forms basics of sustainable agriculture [1]. Within soil environment, inorganic N compounds mostly exist in the form(s) of ammonium, nitrite and nitrate ions [2]. In all cases, crop plants utilize the N ions as nitrate and/or ammonium to fulfill their N demand [3]. Natural and synthetic fertilizers are being used since decades to replenish the soil with essential plant nutrients. crop residues, feces, animal dung, urea and other NPK fertilizers are examples of natural and synthetic fertilizers [4]. After application of various N fertilizers in soil, mineralization process starts. In case urea is applied to soil, urea–nitrogen starts loosening from the fertilizer core and is taken up by crops as well assoil microorganisms, present within the soil environment after due process of nitrification [5]. Conversely, the process of mineralization/nitrification is affected by many ambient conditions like soil moisture content, soil types, fertilizer granule structure, atmospheric temperature, presence and type(s) of microorganism and enzymes [6]. Therefore, breakdown of N fertilizers into various constituents is a result of above mentioned factors including oxidation and reduction.

After soil application of urea fertilizer, N is discharged into the surrounding environment through ammonification, nitrification and denitrification [1]. Inorganic nitrogen ($NH_4^+$ and nitrate ($NO_3^-$) ion forms) is readily taken up by crops whereas nitrite ($NO_2^-$) is formed as an intermediate during mineralization of $NH_4^+$ to $NO_3^-$. Generally $NO_2^-$ does not accumulate in soils because of its rapid transformation into $NO_3^- [7]. If not utilized by the plants then this useful N is lost to the environment. However, these losses are highly dependent on type(s) of fertilizer. For example, N losses are higher from urea prills compared to urea super granules when applied to soil under flooding conditions [8]. This is due to higher solubility of prills in water and its fragile nature in comparison to urea super granules. Small size of prills enhances its solubility within soil environment under moist and/or flooded conditions [9]. The higher solubility of urea prills contributes towards environmental pollution at global scale as the extra N is lost through leaching, runoff, denitrification and volatilization [10]. Leaching and runoff of $NO_3^-$ affects underground water bodies, lakes, streams and seas. Denitrification causes emission of greenhouse gases such as nitrous oxide ($N_2O$) and volatilization of ammonia creates acidification and eutrophication of oligotrophic habitats [10].

There is a strong evidence that links extreme losses of nitrogen from soil environment with ecological issues [11]. As per recent global assessment, four of nine planetary boundaries have now been crossed as a result of human activity including pollution caused by N fertilizers [11]. These boundaries include climate change, ocean acidification, fresh water pollution and ozone depletion [11]. Therefore, to protect the environment and avoid N losses various technologies are being introduced especially by researchers working with fertilizer industry [12]. Development of slow release urea fertilizer could be a promising option to minimize the N losses since such products would release urea based N in a controlled manner to meet sequential needs of crops [13]. crop N uptake from conventional (un-coated) urea ranged between 30–50% of the total applied N whereas it could be doubled through development of economical coatings over urea prills. Such slow releasing fertilizers can further safeguard the environment in case biodegradable polymeric materials are employed as raw material to develop the coating [14]. Since urea is an easily available cheap source of solid inorganic fertilizer with high N content up to 46%therefore, it was chosen for evaluation of N release kinetics and crop N uptake after coating with cheapest sources of organic and inorganic blends.

In recent past, many polymeric materials with different composition have been used to slow down the urea dissolution within soil environment followed by irrigation. Controlled-release fertilizer comprises of inorganic and organic polymeric materials with very moderate solubility in water, carrying urea as a base foundation material [15]. Coated layers of these polymeric materials manipulate the dissolution rate of fertilizers and slows-down its solubility in soil to match crop N requirement [13]. Many studies have been performed to check the N release and control-release behavior of the combined organic and inorganic blends of coating [12–14]. Blend of organic and inorganic material form complexes that greatly extend the release rate of N from urea fertilizer. Latest research work has been
focusing on cheaper membrane forming biodegradable substances, which would retard solubility within soil environment [16]. In addition, these inorganic coating materials would also act as a source of secondary micronutrients for crops that is an added advantage [17]. This may be the reason that urea blends containing calcium, magnesium and sulfur are claimed to effectively enhance urea fertilizer efficiency [18]. Most of the coating materials used in recent past although could reduce the release rate of N, but may damage the soil environment and whole eco-system due to their non-degradability [18]. A serious concern over this aspect has recently been shown by International Fertilizer Industry Association (IFA) during its meeting in Montreal in June 2019. Therefore, more emphases should be put on utilization of only those coating materials which are cheap, environment friendly and easily biodegradable within soil environment [19].

In our study, fluidized bed coater was used to produce biodegradable coatings over urea prills to manufacture controlled release fertilizer. The novelty/focus of this research is development of new coating materials, which are low cost, environmentally friendly (in terms of biodegradability) thus having potential to slow down the release rate of N from urea prills. The objectives of the study are (i) to evaluate the characterization and N release kinetics of urea prills coated with biodegradable polymers and (ii) study the effect of these coated fertilizers on N uptake and foliage yield of spinach.

2. Materials and Methods

2.1. Materials

Commercial grade urea prills having 46\% N (Manufacturer and Supplier: Fauji fertilizer Company Limited, Sadiqabad, Pakistan) were sieved through a 1-mm sieve in order to obtain uniform size. Coating test materials of analytical grades, i.e., sulfur, starch, polyvinyl alcohol, gelatin and paraffin wax were purchased from Daejung-Korea. Molasses were sourced from a local sugar mill. Concentrated HCl and P-dimethyl amino benzaldehyde of analytical purity were purchased from Daejung-Korea for release rate measurement during the experiment.

2.2. Synthesis of Spray Coating Solutions

For synthesis of spray coating solutions, 10 g of starch was mixed with 100 mL of deionized water at constant temperature of 80 °C for 30 min. Then, purposed quantities of polyvinyl alcohol, sulfur and Paraffin wax were added to the starch based deionized water solution while maintaining the solution temperature at 80 °C. Thus, final solution was ready for its application as a coating material over urea prills. Due to smaller particle size, handling of urea prills was very difficult during coating process. Similar methodology was adopted for synthesis of all fertilizer formulations as mentioned in Table 1.

Table 1. Composition of Coating solutions used in the study.

| Treatment Code | Sulphur (g) | Starch (g) | PVA (g) | POP ** (g) | Molasses (g) | Gelatin (g) | Paraffin Wax (g) |
|----------------|-------------|------------|---------|------------|--------------|-------------|------------------|
| C-1            | 5           | 5          | 10      | -          | -            | 2           |                  |
| C-2            | 5           | 10         | 5       | -          | -            | -           | 2                |
| C-3            | 5           | -          | -       | 10         | -            | 5           | 2                |
| C-4            | 5           | 10         | 5       | -          | 2.5          | -           | 2.5              |

* PVA = poly vinyl alcohol, ** POP = plaster of Paris.

2.3. Apparatus

For coating of urea prills, a mini spray granulator (Manufacture: Shanghai Pilotech Instrument & Equipment Co., Ltd., Shanghai, China; Model: YC-1000) was used as shown in Figure 1. Spray nozzle of the equipment was located just below fluidized bed containing the feed of urea prills. About 0.5 kg of product batch was run at a time. The prills were fluidized using hot fluidization air blown at 45 Hz through the heater at temperature of 80 °C. The built-in peristaltic pump was utilized for
movement of hot solution. The hot coating solution was atomized using pressurized air through compressor before showering on fluidized prills in the bed. The coating procedure was only started once steady state temperature conditions were achieved and finished after a drying period of 15 min after coating. After drying, the coated urea prills were removed from the bed and analyzed using different characterization techniques.

![Figure 1. Pictorial view of an operational fluidized bed coater.](image)

2.4. Scanning Electron Microscopy (SEM)

A SEM (S-4700 Hitachi, Japan) was employed to study the surface morphology of coated urea samples. Urea prills without coating were also cross examined earlier in comparison to coated samples for reference. Prior to examination, coated prills were developed in anion sputtering machine (JFC-1500 of JEOL, Ltd. (Akishima, Tokyo Japan). Gold coating was done up to 250 angstroms on the prills. The sample prills’ surface was analyzed with a secondary electron detector using the accelerating voltage of 20 kV.

2.5. Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform infrared spectroscopy of coated and uncoated urea prills was carried out using FTIR (Perkin Elmer Spectrum 100 spectrometer) technique. The urea prills were crushed into powder form for analysis in the range of 400 to 4000 cm\(^{-1}\). The FTIR absorption spectrum was utilized to evaluate the bonding nature and chemical structure associated by the result of cross linking between different polymer material chains.

2.6. X-ray Diffraction

X-ray diffraction (XRD) characterization of polymeric and inorganic blended coated urea was performed using equipment STOE, Germany. The XRD was carried out to check crystallinity of polymeric and inorganic films formed. The 2-theta angle was varied from 20° to 70° to get more prominent peaks. Step size and step time was taken as 0.4 degree and 1 s, respectively. Radiation used for characterization was of Cu K α-1 [20].
2.7. Crushing Strength

The crushing strength of urea formulations were measured to assure that the coated urea prills can survive without breakage from product manufacturing phase till its sales and marketing. Due to excessive physical impacts, the coated as well as uncoated urea prills may start to disintegrate and thus convert into fines. These fines are known as “urea dust” and have no acceptability at farmer end due to the difficulty in fertilizer broadcasting and chances to stay on surface of leaves. The crushing testing on coated urea prills was performed using a universal testing machine (AGX Plus). The coated urea prills used in the testing exercise were randomly selected from each of the sample batch. During the test, urea prills were introduced against a calculated amount of stress by means of metal plunger. The force at which the urea prills got cracked was noted as a measure of its strength [19].

2.8. UV-Visible Spectrophotometry

Release rate and Efficiency [19] of each coated urea formulation along with uncoated urea was evaluated by P-methyl amino benzaldehyde method. Initially, calibration curve was drawn using analytical grade urea prills (99.9% purity) by utilizing GENESYS™20 UV-Visible spectrophotometer. Standardized solutions of analytical grade urea (20, 40, 60, 80 and 100 ppm) were pre-arranged to get the slope from drawn calibration curve. Subsequently, calibration curve was drawn by plotting graph between known urea concentration and absorbance. To evaluate the dissolution rate of various combinations (C-1 to C-4) including uncoated (C-0) treatment, following test protocol was developed.

2.9. Test Protocol

A 10 g of sample urea prills was taken in a 5-L glass beaker filled with deionized water. A 10 mL of sample aliquot was taken from the center of beaker at time intervals of 3, 6, 9, 12, 30, 60, 120 min followed by dilution to 50 mL for absorbance measurement using UV-Visible Spectrophotometer method. A 10 mL sample was collected from 50 mL flask containing diluted sample into another 50 mL volumetric flask to which 1 mL of HCl(1:1) and 5 mL of p-Dimethyl amino benzaldehyde solutions were added while deionized water was used to make the final volume to 50 mL. Finally, absorbance was noted using wavelength of 418 nm to calculate the unknown concentration of coated urea test batch, its release rate and efficiency.

\[
\text{urea (ppm)} = \frac{\text{Absorbance} - \text{Y intercept}}{\text{Slope of calibration curve}} \quad (1)
\]

\[
\text{Efficiency (\%) } = \frac{C_u - C_{cu}}{C_u} \times 100 \quad (2)
\]

where \(C_u\) and \(C_{cu}\) are the concentrations of urea (ppm) in the uncoated and coated samples at 15 min, respectively.

2.10. Pot Experiment

Response standard pot experiment was carried out to evaluate crop productivity and its N uptake after soil application of coated versus uncoated urea prills using spinach as a test crop [21]. Experiment was conducted at Fauji Fertilizer Company (FFC) Fertilizer Research Center, Faisalabad Pakistan (latitude 31.56° N and longitude 73.12° E). The top 30 cm of soil was collected from the research field of the above center and sieved through a 2-mm mesh in order to remove plant debris, gravels and non-soil materials. The soil texture was sandy clay loam and classified as typic camborthids (Govt. of Pakistan, 1974). The soil had an initial pH of 8.1, EC 0.19 dS m\(^{-1}\), total organic carbon 0.16% and dissolved organic carbon of 4.9 mg kg\(^{-1}\) and mineral nitrogen of 4.1 mg kg\(^{-1}\). After sieving, earthen pots were filled with soil. There were in total 24 pots having 6 treatments each with four replicates arranged in randomized complete block design. Each pot had internal diameter of 17.1 cm filled with 8 kg of soil. Treatments were: No N: Untreated control with no fertilizer applied (only soil nitrogen as source of
N for crop), C-0: uncoated urea prills, C-1: urea prills coated with PVA 5% + plaster of Paris 10% + sulfur 5% + paraffin wax 2%, C-2: urea prills coated with PVA 5% + starch 10% + sulfur 5% + paraffin wax 2%, C-3: urea prills coated with gelatin 5% + plaster of Paris 10% + sulfur 5% + paraffin wax 2% and C-4: urea coated with PVA 5% + starch 10% + sulfur 5% + paraffin wax 2.5% + molasses 2.5%. Spinach seeds were sown in each pot. Both coated and uncoated urea prills were applied at the recommended rate of 100 kg N/ha in three splits, i.e., before sowing and immediately after the 2nd and 3rd cuttings of spinach plants. Coated urea application was corrected for weight of coating materials on their surfaces. Phosphorous (P) and potassium (K) fertilizers were applied as basal doses of 75:100 kg PK/ha as per their source as triple-super-phosphate and muriate of potash, respectively. Pots were placed in an open field to provide natural conditions for spinach plants. Each pot was regularly irrigated to maintain the soil water holding capacity at 60%; excess moisture was measured by using low-cost moisture meter (FY-901, Hangzhou FCJ I&E Co., Ltd., Hangzhou, China).

The spinach crop was harvested four times during the experimental period. Immediately after each harvest, the fresh spinach biomass was measured. The leaves samples collected from the last (4th) harvest were washed with deionized water and dried in oven at 70 °C for 48 h until constant weight to get dry foliage yield. Afterwards, these were ground to pass 1 mm sieve and analyzed for nitrogen content. Total N in leaves was determined using Kjeldahl method [22,23]. Leaves- N analysis was performed by a commercial lab at Faisalabad, Pakistan. Foliage N uptake of last harvest was calculated by using equation as follows:

\[ FNU = NC \times DFY \]  \tag{3}

where \( FNU \) is foliage N uptake in g N/pot, \( NC \) is N content of spinach in g N \((100 \text{ g DM})^{-1}\) and \( DFY \) is spinach dry foliage yield in g/pot.

2.11. Release Kinetics

Urea Release Kinetics

In present work, the release kinetics of coated and uncoated urea prills was carried out to check how urea-N gets dissolves/releases from urea prills when it is applied to soil followed by surface irrigation. Water dissolution experiment was used to obtain the reading in terms of concentration of urea versus time. The urea concentration versus time data were first converted into fractional urea release as shown in Table 2 and then applied to the Sinclair and Peppas formula, modified hyperbola formula, modified Schwartz formula and Schwartz and Sinclair formula. All the above mentioned formulas explain diffusion mechanism associated with nutrient release when coated and uncoated urea prill samples get in contact with water, i.e., dissolution experiment [19,20].

| Model Equation | Sample Name | Adjusted R Square | Value of “k” | Value of “n” | Reduced Chi-Squared |
|----------------|-------------|-------------------|--------------|--------------|--------------------|
| \( Q_t = k t^n \) | uncoated    | 0.2072            | 0.947        | 0.015        | 0.0008             |
|                | C-1         | 0.6332            | 0.160        | 0.417        | 0.0619             |
|                | C-2         | 0.6197            | 0.317        | 0.269        | 0.0383             |
|                | C-3         | 0.5680            | 0.192        | 0.381        | 0.0787             |
|                | C-4         | 0.6582            | 0.387        | 0.321        | 0.0541             |

1) Sinclair and Peppas formula, which has the following form:

\[ Q_t = k t^n \]  \tag{4}

The above equation is also known as Power equation, where \( k \) and \( n \) are power equation constants.

This simple equation provided by Sinclair and Peppas, explains the phenomena behind the release of dynamic controlling agent of nutrient by enlargement of coating films.
2) modified hyperbola formula, represented by the following type:

\[ Q_t = \frac{at}{1 + bt} \]  \hspace{1cm} (5)

Small values of time represented first-order kinetics whereas by increasing time of experiment the kinetics shows zero order.

3) Schwartz and Sinclair formula represented by following forms:

\[ Q_t = (1 - e^{-bt}) \]  \hspace{1cm} (6)

4) modified Schwartz formula, explained below with following form:

First-order kinetics explains the release of nutrients from the coating films when matrices were formed.

\[ Q_t = a(1 - e^{-bt}) \]  \hspace{1cm} (7)

In all of the above mentioned relations, \( Q_t \) is the fractional urea release at time \( t \), while \( a \) and \( b \) are the release constants. Curve fitting technique was employed to check whether the experimentation data best fit each equation as mentioned above \([24,25]\).

2.12. Statistical Analysis

Univariate analysis was done to check treatment effect by using SPSS statistics version 20 (IBM, Armonk, NY, USA). Main effect of fertilizers formulations was analyzed through analysis of variance (ANOVA) at 5% probability level. If treatment effect was significant then multiple comparisons was done by Tukey-HSD test.

3. Results and Discussion

3.1. Scanning Electron Microscope

Effect of Coating on Surface Morphology

The SEM images represent the uncoated urea prill at 2 different magnification levels that are *30 and *2000, respectively. The surface in Figure 2(b1) looked rough with spot patches and nonuniformities on it \([21,26]\). The Figure 2(a2,b2) depicted uniform coating of plaster of Paris and PVA as coating material with sulfur and paraffin wax \([27,28]\). Irregular structures were formed probably because of molasses and sulfur. PVA coating was clear and visible on back. Agglomeration was observed on some places over the prill surface. The rod like long fibrous structures was formed due to plaster of Paris \([26]\). Pores and voids were observed almost everywhere on the coated surface which reduces the efficiency. The Figure 2(a3,b3) represents uniform coating of starch and PVA as coating material along with sulfur and paraffin wax. Uniform coated film of PVA could be seen with pointy sulfur crystals. The crystals contain interlaced parallel long crystals with agglomeration. The Figure 2(a4,b4) represented nonuniform coating of plaster of Paris and gelatin as coating material along with sulfur and paraffin wax \([29]\). Uniform coated film of gelatin could be observed behind the fibrous bone like crystal structure due to POP and sulfur \([19]\).

The Figure 2(a5,b5) depict uniform coating of PVA and starch as coating material along with sulfur and wax. Irregularities appeared in the coating with agglomerated structure. The structure obtained for formulation C-1 appeared to be the best structure since it was compact enough to retard the release rate of urea. The hydrophobic PVA film helped further to reduce the solubility of urea which would yield longer release time.
Figure 2. SEM micrographs of uncoated and coated urea (1: uncoated urea, 2: C-1 coated, 3: C-2 coated, 4: C-3 and 5: C-4 coated) (a = at 30 magnification and b = at 2000).

3.2. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of uncoated and coated urea are shown in Figure 3. The FTIR characterization reveals bonding nature and chemical structure associated by the result of cross linking between different polymer material chains when polymeric solution is coated on urea. A comparison was made between the coated and uncoated one test batches. At wavelength of 3438 and 3344 cm\(^{-1}\), uncoated urea depicted asymmetric and symmetric vibrations of NH\(_2\) [30,31]. At peak 1626 cm\(^{-1}\) is a carbonyl (CO) and at peak of 1465 cm\(^{-1}\) is a bending vibration NH and CH stretching vibration of O = C-NH\(_2\) [32]. In addition, the band which appeared at 1465 cm\(^{-1}\) is attributed to —CN stretching [33–36]. At 1154 cm\(^{-1}\), a stretching vibration mode resultant from the—C-O-C group can be seen. C-H overtone stretching vibrations are observed at 1154 cm\(^{-1}\). At peak 2100 cm\(^{-1}\) is a Nitrile (C≡N) stretching vibration and peak 2010 cm\(^{-1}\) is an Alkyne (C≡C) stretching vibration [33]. All spectra of uncoated and coated urea looked similar with slight modifications. All the peaks were detected with minute changes. All the peaks of the uncoated urea prill and, the coated prills looked very much alike [33,34]. For better
nitrogen release, 2100 cm\(^{-1}\) Nitrile (C≡N) stretching and 2010 cm\(^{-1}\) Alkyne (C≡C) stretching vibrations were desired as observed for test batch formulations C-1 and C-3.

3.3. X-ray Diffraction (XRD)

In XRD pattern of uncoated urea fertilizer, the dominant diffraction peaks were observed at 2\(\theta\) = 22°, 2\(\theta\) = 24.5°, 2\(\theta\) = 29.5° and 2\(\theta\) = 35°. The more prominent peaks were observed in the range of 22° to 25° that is the reason we selected the range from 20 to 70. All the XRD spectra of prepared formulations (Figure 4) of coated urea prills showed sharp peaks similar to the uncoated urea [25,37]. There were no necessary differences in the location and strength of the peaks between the spectrum of uncoated urea and coated urea prills. By taking into consideration the reason behind that no new peaks were seen in the synthesized urea prill with coated materials, it may be inferred that no new phases were formed or deformation in structure took place during coating process [25]. When new phases are formed during coating process, solubility of end product gets compromised which can affect the release rate of coated urea [37].
3.4. Crushing Strength

Effect of Coating on the Crushing Strength

After the application of coating, if prilled urea is fractured, the availability of urea-N will be similar like that of uncoated prills [19]. From storage, bagging and shipping point of view, the samples (finished marketable product) having superior impact resistance against all odd forces is preferred [27]. In this study, diverse coating materials were employed to prilled urea and were tested by applying pressure while using tensile tester until breakage occurred. Figure 5 depicts the crushing strength of prills randomly selected from sample batches. Three readings were performed for each sample and then average was plotted after passing through universal testing machine. The final reading was noted at the point when the urea prills completely got crushed into fine powder. Uncoated prills got crushed at a force of 7.03N whereas C-4 showed highest crushing strength (21.83 N) among the coated ones. This depicts superiority of the coated product as criteria for its marketing and ease in uniform spread infield over standard urea.

![Crushing strength of uncoated and coated urea](image)

**Figure 5.** Crushing strength of uncoated and coated urea. Error bars represent standard error of the means. Different small letters above bars show significant variations among treatments at 5% probability level.

It is clear from the bar graph that upon replacement of coating materials like gelatin/POP/sulfur over urea prills there was a considerable impact noted for the crushing test. For all the combinations, sulfur content was same. Among all coated urea combinations, C-1 showed lowest value due to poor integration of PVA and plaster of Paris as coating material(s) along with paraffin wax used as a sealant [38,39]. The C-4 combination showed highest value of 21.83 N. starch and PVA formed excellent coating layer on urea prills, which enhanced its strength [27]. The enhancement in crushing strength by effective coating materials would lead towards better storage and shipping functionalities [19]. The average force needed to crush coated prills was more than three times than the force required to crush industrial grade marketed product (uncoated urea prills). Hence, the compressive resistance of prills was significantly enhanced when three coating substances were utilized.

3.5. Effect of Coating on the Rate of Urea–Nitrogen Release

The aim behind this analytical technique was to check the rate at which urea-N is released/dissolved after the application of coated versus uncoated urea prills. The test was carried out by simply adding the coated urea prills in DI water. Uncoated prills were also tested to make comparison with coated ones. All coated urea prills combinations were tested as separate treatment/test batch and the results are reported in terms of concentration of urea (ppm) by using equation (A) as shown in Figure 6a.
The efficiency [19] of each combination was calculated by comparing the urea concentration at 15 min of uncoated with that of coated one using formula (B) and displayed in the Figure 6b.

![Figure 6](image)

**Figure 6.** (a) Effect of coating on release rate and (b) efficiency of coated urea formulations. Error bars represent standard error of the means. Different small letters above bars show significant differences among treatments at 5% probability level.

The C-0, i.e., uncoated urea prills quickly dissolved (i.e., released urea-N) in DI water completely. In just 3 min and 57 s, the uncoated prills vanished and could not be seen with naked eye [21]. The C-0 followed the burst release mechanism in absence of any coating over its surface [40]. All coating materials over urea prills managed to slow down the nutrient (urea-N) release to some extend depending upon the nature of coating material used. The starch, PVA, sulfur combination with paraffin wax (C-2) depicted 1.875% efficiency. For paraffin wax combination, due to fragile nature of sulfur, cracks formed on the surface of coated urea prills allowed water to penetrate thus reduced efficiency of this test formulation [38]. The coating layer gradually disintegrated to a point where a burst release occurred like the one observed during uncoated urea exposure to DI water.

On the other hand, POP, PVA and sulfur combinations with Paraffin wax (C-1) depicted efficiency of 6.87%. The binding ability of POP with wax was stronger and compatible and this ultimately resulted into a reliable coating as shown in SEM Figure 2(a2,b2). The SEM micrograph of C-3 coated urea also supported this release, probably because of poor coating which looked like fibrous rod like structure formed because of presence of POP and paraffin wax which possessed poor compatibility against each other [38]. The samples composed of POP depicted better efficiency compared to others formulations probably due to sparingly soluble property of POP [29].

The blend consisting of POP, gelatin sulfur and paraffin wax (C-3) coating blend enhanced the efficiency only by 1.125% [39]. Probably, POP was boundless effectively with sulfur and gelatin in presence of paraffin wax to form coating as seen SEM micrograph Figure 2(a4,b4). With this coating, the urea prills sustained up to 16 min and 11 s physically and it was less sensitive towards water. In actual, the gelatin starts to swell which creates a barrier between water and the fertilizer core. This swelled layer restricted the penetration of water to ingress the coating and delayed the discharge of urea-N from urea prills core [39].

Compared to paraffin wax, the presence of molasses retarded the release rate more efficiently due to its adhesive nature. The adhesion property in molasses helps out to join up all the materials together which assist in uniform coating around each urea prill. In combination with containing wax,
the blocking of possible surface cracks occurred during coating which delayed the release/dissolution
time due to perfect sealing in addition to its hydrophobic nature as shown for formulation C-4.

The high speed burst release mechanism was followed by uncoated urea prills (10 g urea completely
dissolved in water or 99% of the urea-N in prill got released) [40]. This whole process occurred within 
237 s. In contrast to above, notably slower and constant release of urea-N was noticed by the application
of different combinations of coating materials. The analysis results for C-1 showed that 93% of urea
(9.3 g) was released within the period of 1500 s. The remaining 0.7 g released urea-N slowly within
prolonged duration of 2 h until coating was dissolved [33].

3.6. Spinach Biomass Yield and N Uptake

To measure crop productivity and plants N uptake after application of coated and uncoated urea, 
spinach was sown as a test crop [21]. Application of both coated and uncoated urea fertilizers increase 
spinach fresh biomass yield (total of 4 cuts) between 21–54% than untreated control. It was higher in 
coated urea formulations than uncoated urea prills. Coating of urea prilled enhanced fresh biomass yield by 11%, 23%, 10% and 28% after application of C-1, C-2, C-3 and C-4 formulations than uncoated urea, respectively (Figure 7a). The highest biomass was harvested in C-4; and C-2 followed by C-1. Dry biomass yield of last harvest (4th cut) was the highest in C-1 while lowest in C-4 treatments (Figure 7b). Interestingly, finally harvest C-4 produced lower biomass than other fertilized treatments. Plant N uptake also followed same trend. Coated fertilizer treatment C-1 has 87% higher N uptake than control while respective increment of 53% was noticed when compared with uncoated urea (Figure 7b).

![Figure 7](image_url)

**Figure 7.** (a) Spinach fresh biomass yield, (b) dry biomass yield and N uptake of last harvest (4th cut) after application of coated and uncoated urea prills. Error bars represent standard error of the means. Under Figure 7a, different letters on bars for each separate/specific cut depict significant difference(s) among treatments at 5% probability level. Under Figure 7b, different letters (small or capital) on bars show significant difference(s) among treatments at 5% probability level.

Similar findings, i.e., increase in spinach biomass with the use of coated fertilizers have also been 
reported by other researchers (Tachibana, 2007 reported by Trenkel [41,42]. Zhaohui Li [42] concluded 
that compared to the conventional fertilizer, with the same amount of nutrients applied, higher spinach
yields could be achieved when zeolite coated/blended fertilizer was used even though, the difference was statistically not significant. Similarly, results from three-year trials carried out by Tachibana (2007) indicate that using a controlled release N fertilizer (Dd-Meister) allowed a substantial reduction (30%) in the amount of N fertilizer applied, while obtaining high-quality leaves, equal spinach yields and reducing adverse environmental effects [41]. In leafy vegetables, particularly spinach, the use of Dd-Meister had considerably reduced the nitrate-N content of leaves.

3.7. Release Kinetics

After transition of release data into fractional urea release (Figure 8), curve-fitting technique was applied to check whether the experimentation data best fit each model [37]. The fitting results of the four equations are displayed in Tables 2–5, respectively. As reported in Table 4, release data best fit the model equation in comparison to all other equations. The results after fitting are best than others obtained from other three equations [25,43]. The data fitting results when applied to Schwartz and Sinclair formula yielded the correlation constants values very high in terms of precision and considerably superior to Sinclair and Peppas formula, modified hyperbola and modified Schwartz and Sinclair formula. It may be concluded that the Schwartz and Sinclair formula utilized in this work is the excellent equation to represent the release of urea-N from coated urea prills. The Schwartz and Sinclair formula best explained the release of active agents from applied coating by first-order kinetics [43]. At smaller time periods, the release of urea followed zero order kinetics while by applying slow release technology the order of release increased from zero to first-order [25].

![Figure 8.](Image)

**Table 3.** Release kinetics 25 °C: modified hyperbola formula.

| Model Name                  | Sample Name | Adjusted R Square | Value of “a” | Value of “b” | Reduced Chi-Squared |
|-----------------------------|-------------|-------------------|--------------|--------------|--------------------|
| $Q_t = a(1+bt)$             | uncoated    | 0.9975            | 3.709        | 3.652        | 0.0002             |
| modified hyperbola          | C-1         | 0.8183            | 0.060        | 0.045        | 0.0334             |
|                             | C-2         | 0.8824            | 0.125        | 0.107        | 0.0169             |
|                             | C-3         | 0.7985            | 0.075        | 0.058        | 0.0404             |
|                             | C-4         | 0.8912            | 0.112        | 0.099        | 0.0289             |

**Table 4.** Release kinetics at 25 °C: Schwartz and Sinclair formula.

| Model Name                  | Sample Name | Adjusted R Square | Value of “b” | Reduced Chi-Squared |
|-----------------------------|-------------|-------------------|--------------|--------------------|
| $Q_t = (1-e^{-bt})$         | uncoated    | 0.9999            | 0.8043       | 0.000008           |
| Schwartz and Sinclair       | C-1         | 0.8657            | 0.054        | 0.0247             |
| formula                     | C-2         | 0.9239            | 0.093        | 0.0109             |
|                             | C-3         | 0.8548            | 0.066        | 0.0291             |
|                             | C-4         | 0.9192            | 0.084        | 0.0201             |
### Table 5. Release kinetics data at 25 °C modified Schwartz and Sinclair formula.

| Model Name                        | Sample Name | Adjusted R Square | Value of “a” | Value of “b” | Reduced Chi-Squared |
|-----------------------------------|-------------|-------------------|--------------|--------------|--------------------|
| Q$_t$ = a(1 – $e^{-bt}$)         | uncoated    | 0.9999            | 1.001        | 0.7999       | 0.000008           |
| modified Schwartz and Sinclair formula | C-1         | 0.8532            | 1.070        | 0.0484       | 0.02699            |
|                                   | C-2         | 0.9156            | 1.032        | 0.0881       | 0.01213            |
|                                   | C-3         | 0.8398            | 1.062        | 0.0599       | 0.03211            |
|                                   | C-4         | 0.9011            | 1.041        | 0.0679       | 0.02013            |

### 4. Conclusions

Uniform coating barrier layers were developed on the surface of urea prills to control the discharge of urea–nitrogen by spraying different combinations of polymeric materials with sulfur in fluidized bed coater. Coating of urea prills C-1: with polyvinyl alcohol (5%), plaster of Paris (10%) sulfur (5%) and paraffin wax (2%) improved N release pattern with efficiency of 6.87% which was four times higher than other coated fertilizers. Application of coatings on urea prills improved crushing strength by 3 times relative to uncoated urea, which may increase acceptability at farmer end with minimum breakage of prills during its handing and processing. Coating of urea prilled enhanced spinach fresh biomass/yield between 10–28% after application than uncoated urea. Based on variety of parameters tested and their outcome combinations, it could be concluded that C-1 and C-2 coated samples were the best and therefore, could be opted for commercial scale production of biodegradable and environmentally friendly N fertilizers.

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**Nomenclature**

| Symbols | Description                                      |
|---------|--------------------------------------------------|
| SEM     | Scanning electron microscope                     |
| UV—VIS | Ultraviolet Visible (UV) spectroscopy            |
| FTIR    | Fourier transform infra-red                     |
| XRD     | X-ray diffraction                                |
| POP     | Plaster of Paris                                 |
| PVA     | Poly vinyl alcohol                               |
| N       | Nitrogen                                         |
| C-0     | Uncoated urea                                    |
| C-1     | Urea coated with PVA 5%, plaster of Paris 10%, sulfur 5%, paraffin wax 2% |
| C-2     | Urea coated with PVA 5%, starch 10%, sulfur 5%, paraffin wax 2% |
| C-3     | Urea coated with gelatin 5%, plaster of Paris 10%, sulfur 5%, paraffin wax 2% |
| C-4     | Urea coated with PVA 5%, starch 10%, sulfur 5%, paraffin wax 2.5%, molasses 2.5% |

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