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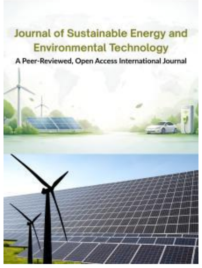

Synthesis and Characterization of Urea Encapsulated with Chitosan/Acetic Acid Composite to Control N2 Release, Water Dissolution Rate, and Enhance Soil Degradation Rate

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Abstract: Nitrogen is the most important nutrient for plants to grow effectively. Despite having a limited dispersion mechanism, urea contains the most nitrogen (46%) of any solid nitrogenous fertilizer. Urea is required to ensure that most plants get the nitrogen they need over their lifetimes. Various plants have different lifespans, so it's important to control the nitrogen release from urea. Using chitosan bio-composites, which are composed of renewable and biodegradable ingredients, granular urea fertilizer was encapsulated to create controlled release encapsulated urea (CREU).

In this work, urea was encapsulated using a biodegradable adhesive derived from a poly-condensation reaction between acetic acid and chitosan. This allowed for the regulation of nitrogen's rate of solubility in water as well as its breakdown in soil. Reaction temperatures of 140, 160, and 180 degrees Celsius, reaction durations of 2, 3, and 4 hrs, and chitosan to acetic acid mixing ratios of 5:1, 10:1, and 15:1 w/w were all employed for the condensation process. In terms of pH, release temperature, and release duration, the CREU's ideal nitrogen release property was evaluatedThe structural properties of the encapsulated and uncooked urea was determined by FTIR analysis. The kinetics of the release of nutrients from the different encapsulated urea were determined using the Kjeldahl method. When the medium's temperature rises and the amount of urea in the resulting acetic acid-grafted chitosan increases, the urea release rate increases; however, when the medium's pH rises, it decreases. As the grafting efficiency increased, the rate of acetic acid-grafted chitosan degradation reduced, and the results of the soil degradation test demonstrated that all of the CREUs were fully broken down in the soil.

The rates of soil degradation are significantly influenced by the amount of urea in the acetic acid-grafted chitosan. With appropriate correlation coefficients and release exponent (n) values for all CREUs between 0.45 and 0.89, the Korsmeyer-Peppas equation shows the best match among the four review kinetic model equations for the N2 release rate of CREUs in water. This suggests that for CREUs, anomalous transport (non-Fickian diffusion release) takes place.

Keywords: *Chitosan, Controlled Released Encapsulated Urea, Dissolution rate, Kinetics model, Nitrogen release rate.*

1. Introduction

Environmental concerns have taken center stage in discussions about materials and their uses. Materials used for surface coatings are no exception. Since surface coating is a broad term for any substance that may be continuously applied to a surface, it can be said that coatings are used in many aspects of our daily life (David et al., 2023). As consumer preferences and VOC laws change, the industry must lower the VOC in coatings. According to Sim et al. (2021), this has occasionally necessitated switching from solvent-based to water-based techniques. Control release urea (CRU) has been so successful that it is now more crucial than ever to investigate the practicality and feasibility of aqueous chitosan as an environmentally benign and sustainable coating material. Because chitosan is hydrophobic, the polymer must be constructed and modified in order to endure in a polar, watery environment. An ideal CRU contains a layer of eco-

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friendly, natural or semi-natural macromolecular substances that slow down fertilizer release to the point that a single soil application can provide all the nutrients that crop needs. Uncoated urea is vulnerable to losses via water eutrophication, denitrification, leaching, nitrous emission, and volatilization when it is applied to crops. Urea is the most widely used fertilizer worldwide because of its high nitrogen content (46%) and simplicity of usage (Xiaoyu et al., 2013). As a result, there has been interest in the development of CRCU for decades (Garc et al., 2023). Film-coated urea is used to increase the effectiveness of urea utilization. Conventional urea fertilizer is vulnerable to loss due to common outcomes of applying urea fertilizer without any coating, including nitrous emission, leaching, denitrification, and water eutrophication. The development of an appropriate controlled release system can more precisely meet the plant's nutritional needs, boosting output and reducing the risk of overdosing. Additionally, CRU reduces agricultural costs by reducing the amount of fertilizer needed and the labor and fuel costs associated with regular fertilizer applications. The release mechanism usually begins with a wetting phase where water penetrates through the fertilizer layer. Recently, there has been a lot of interest in using bio-based polymers such as cellulose, chitosan, and gum acacia to create fertilizers with a controlled or gradual release (Ali et al., 2023). Currently, bio-based polymers are often hydrophilic in their native forms, which limits their practical use. However, the polymers' potential applications are greatly expanded if they can be made into hydrophobic materials. Chitosan is a hydrophilic biopolymer by nature, but some structural modifications can make it hydrophobic, which makes it useful for applications involving nutrient encapsulation (Sadik et al., 2023). Additionally, it is appropriate for a controlled nutrient delivery system application since its hydrophobicity may be adjusted throughout its modification reaction. Here, chitosan was modified with acetic acid oligomers via a condensation reaction to create a hydrophobic and biodegradable adhesive. Additionally, urea was successfully encapsulated into the synthesized hydrophobic and biodegradable glue to create a controlled dissolution rate fertilizer with an enhanced soil degradation rate.

2. Materials and Methods

2.1 Materials

A variety of tools and materials were employed in the synthesis and characterization of acetic acid oligomer grafted chitosan, including an analytical balance, water bath, pH meter, spatula, boll mill, hot plate, sieve, measuring cylinder, beaker, fine mesh cloth, copper wire, oven, and mixer. Furthermore, the Automatic Kjeldhal Analyzer, Refractometer, and FTIR were used for analytical purposes. We bought commercial urea granules with a nitrogen content of roughly 46% from Ethiopian government fertilizer distributors. The reagents required to produce acetic acid oligomer grafted chitosan (i.e., 99% quality degradable monomer (acetic acid) and chitosan) were obtained from a local market; other chemicals, such as sodium phosphate dibasic, sodium bicarbonate, sodium carbonate, and citric acid, as well as solvents supplied by the laboratory, such as deionized water, were also utilized.

2.2. Methods

2.2.1. Synthesis of Acetic Acid Oligomers

The acetic acid oligomer was synthesized using a condensation technique. Using a convectional heating system, oligomerization of acetic acid by condensation was accomplished without the need of a catalyst by simply removing water from a 99wt% aqueous solution of acetic acid at 140°C for 30 minutes.

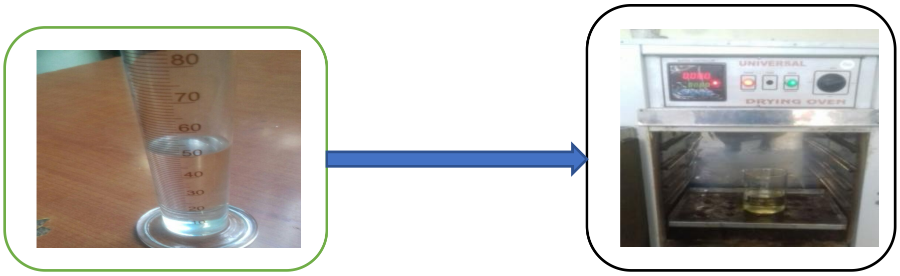


Figure 2.1. Production Process of Acetic Acid Oligomers

2.2.2. Synthesis of Acetic Acid Oligomer Grafted Chitosan

A reactor vessel (beaker) was initially filled with a predefined amount of acetic acid and chitosan, which were then mixed with a spoon to create a bio-based adhesive. A temperature-controlled reactor/oven was utilized to access the vessel that held the mixture of chitosan and acetic acid. The temperature and reaction time were predetermined, and a convectional heating system was used to conduct a poly-condensation reaction. Thus, after the process was finished, acetic acid grafted chitosan was produced.

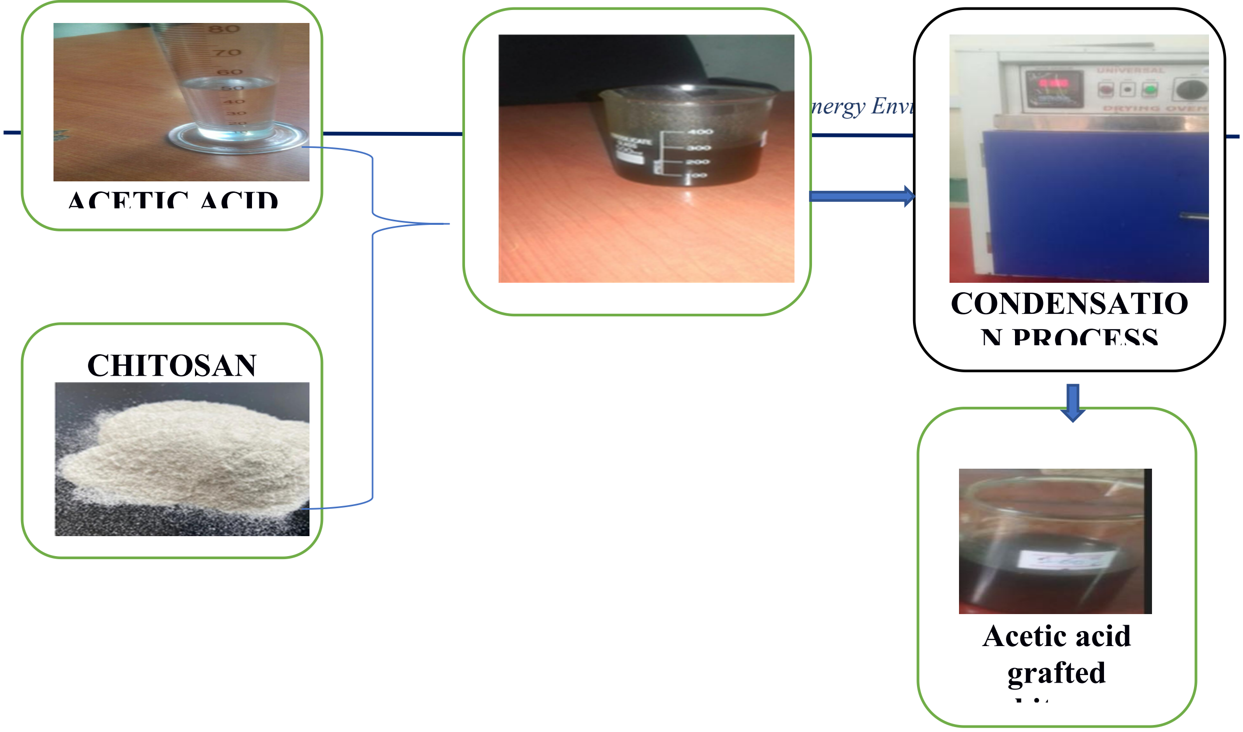


Figure 2.2. Poly-condensation reaction process to synthesis acetic acid grafted chitosan copolymer

2.2.3. FTIR Analysis for the Synthesized acetic acid grafted chitosan

FTIR analysis: The grafting of the acetic acid oligomer on the backbone of the chitosan and the existence of the anticipated functional groups were further confirmed using FTIR spectroscopy equipment. The attenuated total reflectance FTIR in the 4000–400 cm^{-1} range and the FTIR-6600 type A model, serial number A013861790, were used.

2.2.4. Encapsulation of Urea into a Synthesized LAO-g-GA

First, a ball mill grinder set at 300 rpm for 20 minutes was used to grind commercial urea granules. After that, the powder was sieved to a size of about 40 mesh. Then, urea powder and acetic acid oligomer grafted chitosan were combined to create either urea encapsulated acetic acid oligomer grafted chitosan or controlled release encapsulated urea (CREU). To properly disseminate it, it was constantly mixed at 50°C for about ten minutes. The mixing temperature was selected based on the preliminary experiment. The semisolid material was heated and then pelletized using a palletizing machine.

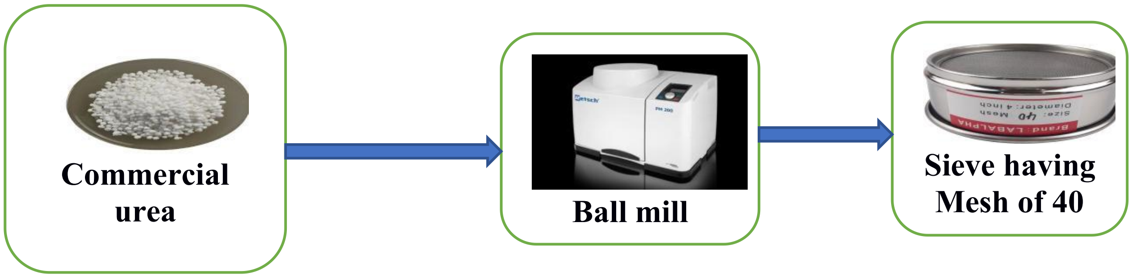


Figure 2.3. Urea powder preparation

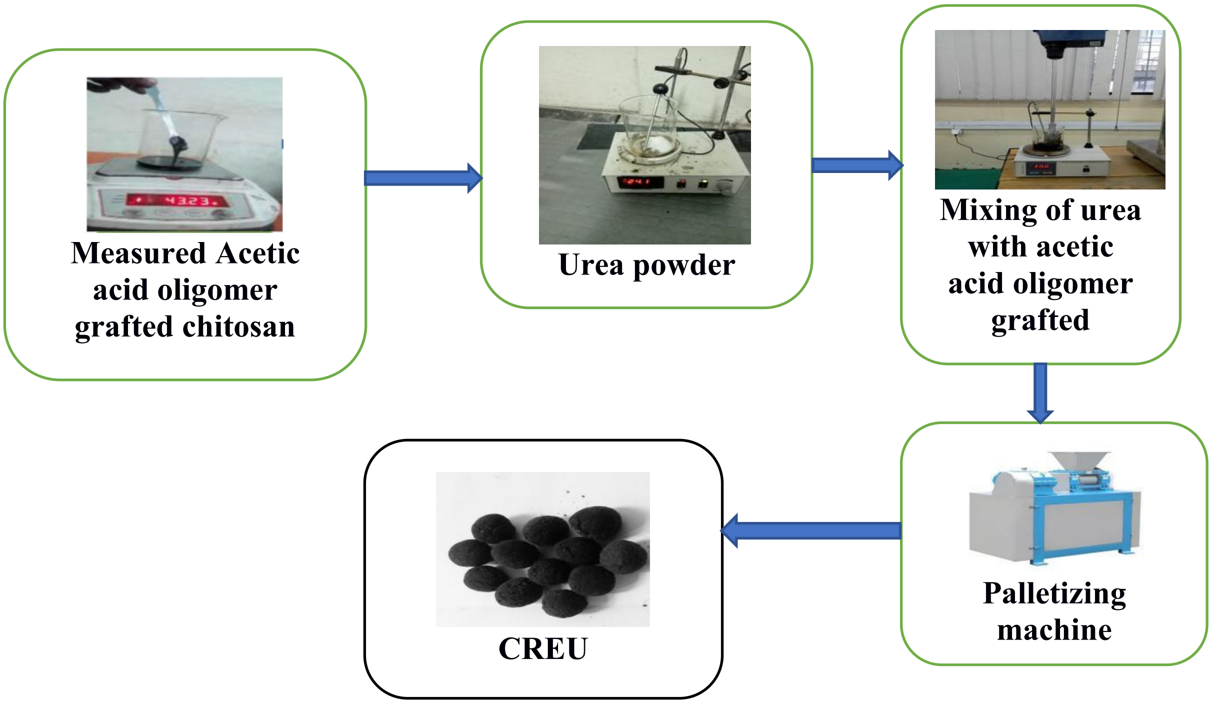


Figure 2.4. Procedure for the formulation of controlled release encapsulated urea

2.2.5. Effect of LAO-g-GA Synthesizing Factors on the Urea Release Rate

The rate of release of the CREU in deionized water has been evaluated. To investigate the impact of acetic acid oligomer grafted chitosan synthesizing factors (i.e., reaction time, reaction temperature, and chitosan to acetic acid mixing ratio) on the urea release rate, 20g of each CREU with the same urea concentration (65% urea) were placed in fine mesh cloth bags and immersed in 200mL of distilled water in a glass beaker which was properly covered at room temperature. To secure the bags, a copper wire was utilized. The samples were carefully withdrawn after 4 hours of incubation using the copper wire that had been previously attached, and the solutions were completely shacked. Then, after taking 20 mL of solution out of each beaker, the refractive index of each sample was measured using a Refractometer (Sim et al., 2021). The amount of urea released into a deionized water from each CREU was then computed utilizing the correlation between refractive index and concentration of pure urea. The correlation shown below can be used to calculate the urea release rate.

$$\text{urea release rate} = \frac{M_n}{M} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Mn is the concentration of urea released within a given time interval (i.e. after 4 hrs. of incubation for this test) of the experiment and M is the final concentration released in the experiment.

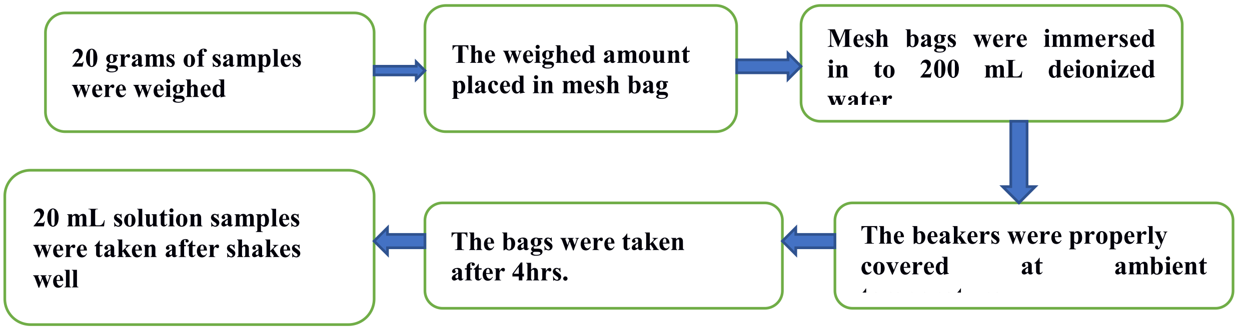


Figure 2.5. The process of preparing solutions to measure its refractive index

2.2.6. Effect of pH, Temperature, and Urea Concentration on the Urea Release Rate

The effect of pH, temperature, and urea concentration on urea release rate was determined by varying these factors on CREU selected from the urea release rate results of method 2.2.5. The release rate quality (highly, medium, and low released) after three hours of incubation in deionized water was the basis for selection. The water bath was set at three different temperatures (25, 40, and 55 °C) using glass beakers containing 100 mL of deionized water in order to evaluate the impact of temperature on the rate of urea release. Properly covering the glass beakers, each of the three selected CREU (10 g) with the identical urea content (65%) was placed in a fine mesh cotton bag and submerged separately. The cloth bags containing the samples were then taken out of the glass beakers at predetermined times (i.e., 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, and 23 hrs) and the solutions in each beaker were appropriately shacked using the copper wire that had already been attached. The refractive index was then measured using a Refractometer following the extraction of 20 mL of solutions from each beaker. The urea release rate from each sample was then calculated using the previously mentioned equation (3). Furthermore, the process for calculating the urea release rate was comparable to that for assessing the temperature effect, except that it was conducted at room temperature and substituted three different buffer solutions (pH 3, pH 7, and pH 11) for the deionized water as a medium. Furthermore, until the high-released sample achieved its equilibrium condition (29 hrs), the samples were taken out of the incubation period at intervals of 2 hrs (i.e. at 1, 3, 5, 7,9, 11, 13, 15, 17, 19, 21, 23, 25, 27, and 29 hrs). The effect of urea concentration on the urea release rate of these synthesized CREU was also examined by simply changing the amount of urea encapsulated in each of the three selected acetic acid oligomer grafted chitosan (i.e., 50%, 65%, and 80% urea concentration) at room temperature and pH 7. The samples in this instance were taken out of the incubation period for a maximum of 25 hrs (that is, at 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23 and 25 hrs.) (the high released sample approaches equilibrium).

2.2.7. Urea Release Rate Test in Soil

A CRCU was buried in soil at room temperature in order to perform the urea release rate test in soil in accordance with (Zafar et al., 2021). The rate of urea release from the soil was measured using plastic bottles with a hole of the same size at the bottom for each of the three selected CREU and pure urea. 300 g of soil with 20% moisture content was placed on top of the cleaned sand, which had been packed in separate plastic bottles, down to a depth of 10 cm in order to keep dirt from getting into the leachate. Then the sand was covered with a tiny mesh cloth. In the prepared plastic bottles, 10g of each of the CREU (which each contain a 65% urea concentration) and 6.5g of pure urea were buried 5 cm under soil in separate fine mesh fabric bags. During different incubation periods (i.e. 1, 5, 10, 15, 20, 25, and 30 days), 200 mL of deionized water was progressively poured over the prepared bottles, and the leachate was collected at the bottom of each plastic bottle. Following the measurement of the leachates' refractive index using a Refractometer to determine the percentage of urea released following each incubation period, the urea release rate (%) was then calculated using equation (1) above.

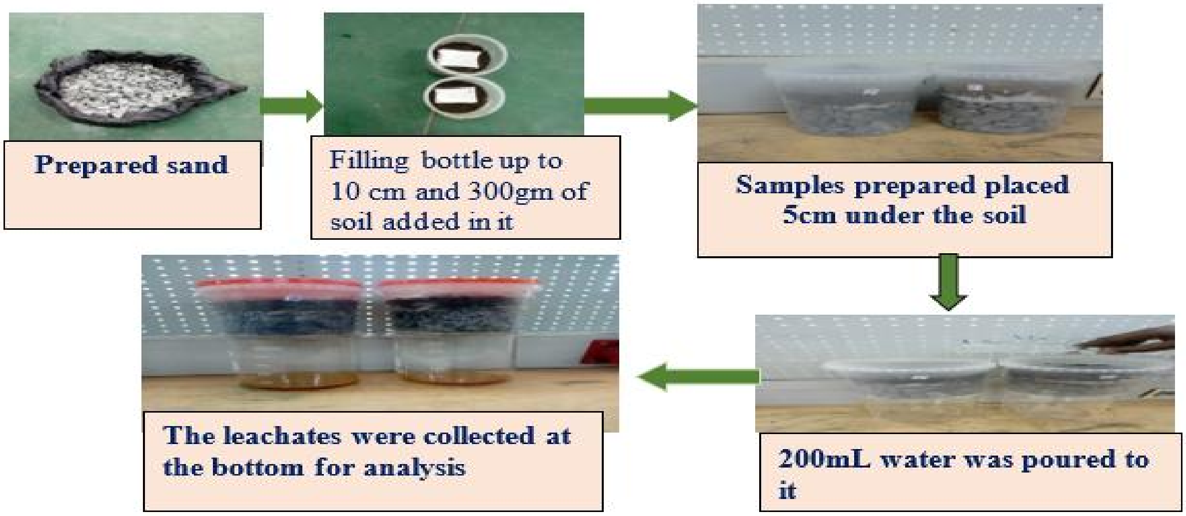


Figure 2.6. Procedural step to determine urea release rate of samples in soil

2.2.7. Studding the Nitrogen Release Rate and Its Release Kinetics Behavior

The method used to calculate the urea release rate in water was similar to the experimental process used to create a solution to ascertain the nitrogen release rate in water (see 2.2.5 above). Each sample's 10g of CREU were placed in fine mesh bags on a copper wire and fully submerged in 100ml of pH 7 aqueous medium in glass beakers with the same urea concentration (65% urea). The beakers were left with their lids on and at room temperature. The beakers were kept at room temperature with the lids on. The cloth bags holding the samples were then taken out at different intervals (i.e., 1, 2, 3, 4, 5, 10, 15, 20, and 25 hrs) and the solution was completely shacked using the copper wire that was attached. After obtaining 10ml of solution from each sample, the total nitrogen content was determined using the Kjeldahl method (Francolins & Domnic, 2018).

$$\text{Nitrogen release rate} = \frac{C * V}{M} * 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (2)$$

Where M is the total amount of nitrogen in a fertilizer (g), V is the leachate volume in each

sampling (mL), and C is the nitrogen concentration in leachate (g/mL) as determined by the

Kjeldahl method.

3. Result and Discussions

3.1. The Effect of Independent Variables on the Grafting Efficiency and Urea Release rate

3.1.1. Effect of Reaction time and Reaction temperature on the Grafting efficiency and Urea Release Rate

The grafting efficiency (%) of the synthesized acetic acid oligomer-grafted chitosan itself, as well as the urea release rate (%) of the CREU after three hours of water incubation. When the ratio of chitosan to acetic acid mixing is constant (10w/w%), the grafting effectiveness of acetic acid oligomer on the backbone of chitosan is positively impacted by the increase in reaction duration and temperature of the chitosan and acetic acid poly-condensation reaction. This effect starts to decline and reaches 58.5% at a reaction temperature of 180 °C and a reaction time of 4 hours after reaching its highest value (63.2%) at a reaction temperature of 160 °C and a reaction time of 2 hrs. This is because greater grafting is explained by the fact that the availability of more active sites speeds up the propagation of grafting chains as the reaction temperature and reaction length rise. However, if the reaction temperature and reaction time are increased above 160 °C and 3 hours, respectively, grafting efficiency may be decreased because forming chains may be mutually destroyed (Abdul & Wasaf, 2023). However, the combination between reaction temperature and reaction time negatively impacts the rate at which urea is released into a deionized water. The urea release rate decreases from 25.6% at a reaction temperature of 140 ^{0}C and 2 hours of reaction time to its lowest value of 14.9% at 160 ^{0}C and 3 hrs. The urea release rate then gradually increases as the reaction temperature and duration grow further, reaching 15.6% at 180 °C and 4 hrs. In the initial stage, the urea release rate decreases as grafting efficiency rises. The percentage of urea released from CREU decreases as grafting efficiency increases. Consequently, after 3 hrs. and 160°C. At high temperatures and longer reaction times, the acetic acid oligomer grafted chitosan copolymer's growing chains started to degrade, which caused the urea release rate to progressively rise. As a result, acetic acid oligomer grafted chitosan lost its wettability and even its capacity to encapsulate urea, resulting in a decline in quality.

3.1.2. Effect of Mixing Ratio and Reaction temperature on the Grafting Efficiency and Urea Release Rate

The increase in the chitosan to acetic acid mixing ratio and the reaction temperature of the chitosan and acetic acid poly-condensation reaction, when the reaction time is constant (3 hrs), have a beneficial effect on the grafting efficiency of the acetic acid oligomer on the backbone of chitosan. At a reaction temperature of 160 °C and a mixing ratio of 10 w/w% chitosan to acetic acid, this impact achieves its highest value of 63.2%. However, when the reaction temperature and chitosan to acetic acid ratio increase over 160 ^{0}C and 10 w/w%, respectively, the grafting efficiency starts to decline. At a reaction temperature of 180 ^{0}C and a chitosan to acetic acid mixing ratio of 15 w/w%, it reaches 57.3%. On the other hand, the chitosan to acetic acid mixing ratio and reaction temperature have an opposite effect on the urea release rate into deionized water as they do on the grafting efficiency. As the grafting efficiency increases, the rate of urea emitted decreases, and vice versa. At reduced reaction temperatures and chitosan to acetic acid mixing ratios of 180 °C and 5 w/w%, respectively, the amount of urea released peaked at 37.1%. The urea release rate gradually decreases as the reaction temperature and chitosan to acetic acid mixing ratio increase, reaching a minimum of 13.3% at 160 °C and 10 w/w% chitosan to acetic acid mixing ratio. As the reaction temperature and chitosan to acetic acid mixing ratio increase over 160 °C and 10 w/w%, respectively, the urea release rate (%) increases gradually. At 180 °C reaction temperature and 15 w/w% chitosan to acetic acid mixing ratio, it achieves 17.4%. This is because, in the initial step, the chitosan concentration rises with the reaction temperature, creating a number of chitosan active sites that are ready for the attachment of acetic acid oligomers. This boosts grafting efficiency and lowers the rate of urea release. However, raising the reaction temperature further degrades the grafted chitosan chains of the expanding acetic acid oligomer, and raising the chitosan further decreases the quantity of acetic acid oligomer available for chain (Ali et al., 2023), causes a decrease in grafting efficiency and increase in urea release rate.

3.1.3. Effect of Mixing Ratio and Reaction time on the Grafting efficiency and Urea Release Rate

When the reaction temperature is maintained at 160 ^{0}C, the chitosan to acetic acid mixing ratio and reaction time interact to improve grafting efficiency and decrease the urea release rate. Nevertheless, as reaction time and the chitosan to acetic acid mixture ratio increase, grafting efficacy declines and the urea release rate gradually increases. Both the chitosan to acetic acid mixing ratio and the duration of the chitosan and acetic acid poly-condensation reaction boost the grafting effectiveness of the acetic acid oligomer on the chitosan backbone. At 10 w/w% chitosan to acetic acid mixing ratio and 3 hours of reaction time, it reaches its highest value (63.75%). After that, it gradually starts to decrease and reaches 59.5% at 15 w/w% chitosan to acetic acid mixing ratio and 4 hours of reaction time. Reaction time and the chitosan to acetic acid mixing ratio both enhance the rate at which urea is released into a deionized water. Its lowest value, 12.6%, was attained at 10 w/w% chitosan to acetic acid mixing ratio and 3 hrs of reaction time. It began at 31.7% at 5 w/w% chitosan to acetic acid mixing ratio and 2 hrs of reaction time. When the reaction time and mixing ratio are increased to more than 10 w/w% and 3 hrs, respectively, the urea release rate gradually increases to 15.3% at 15 w/w% and 4 hrs. This is because more polar water is drawn from the functional groups of the chitosan backbone as the poly-condensation reaction's chitosan content and reaction time rise. Additionally, a large number of free radicals are generated on the chitosan backbone to facilitate the attachment of acetic acid oligomers. As a result, grafting efficiency rises and urea release rate falls. Acetic acid oligomer grafted chitosan's expanding chains are further hampered by longer reaction times, which reduces grafting efficiency and speeds up urea release. Meanwhile, further increases in chitosan content result in a scarcity of acetic acid oligomer for chain propagation.

3.1.4. FTIR Analysis for CREU and Pure Urea.

As illustrated in Figure 3.2 below, the FTIR spectra of CREU and pure urea demonstrate that urea and acetic acid oligomer grafted chitosan interact, especially because to the hydrogen bonding interaction. The O-H and N-H stretching peaks at 3425 cm-1 widen for LR-CREU and HR-CREU, respectively (Dimkpa et al., 2020). Similar to pure urea, the C=O stretching frequency for HR-CREU and LR-CREU is 1664 cm^{-1}(Francolins & Domnic, 2018), However, when acetic acid oligomer grafted chitosan was present, significant peak C=O stretching was seen at 1725 cm^{-1} for only HR-CREU and LR-CREU. Additionally, it is noted that the C-O stretching frequency is shifted from 1159 cm^{-1} for pure urea to 1161 cm^{-1} and 1201 cm^{-1} for LR-CREU and HR-CREU, respectively. This further implies that the amino groups of urea and the carboxylic groups of acetic acid oligomer grafted chitosan interact through hydrogen bonding(Garc et al., 2023). N-H deformation and C-N stretching are demonstrated by the peaks at the wavenumber of approximately 1628 cm^{-1} and 1456 cm^{-1} for all CREU and pure urea, respectively (Luthra, 2018).

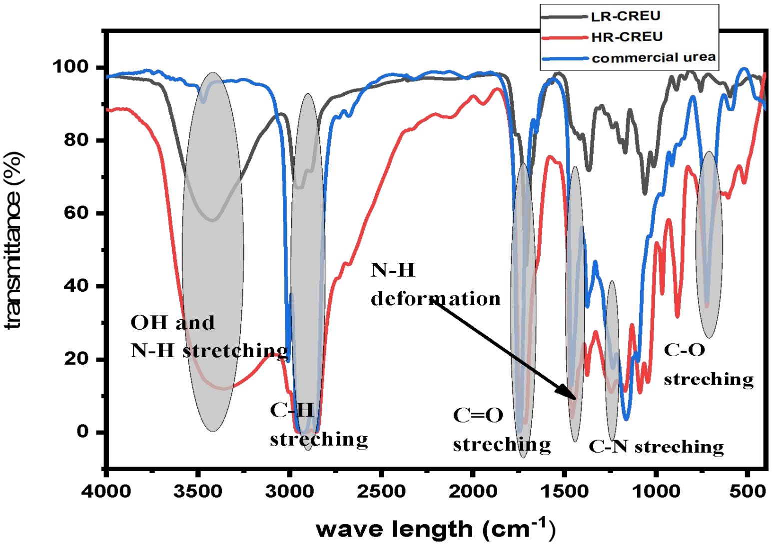


Figure: 3.2. FTIR graph for CREU and pure urea

3.1.5. The Effect of pH on the Urea Release Rate

The urea release rate of the three selected CREU (HR-CREU, MR-CREU, and LR-CREU) in buffer solutions at PH 3, 7, and 11 at room temperature was evaluated, as shown in Figure 3.3a, b, and c below. The graph showed that when the medium's pH increases, the rate of urea release decreases. Figure 3.3a shows that after 15 hours of incubation in a solution, the urea from a sample coded HR-CREU releases (93.89%) of its urea at pH 3. MR-CREU and LR-CREU samples had urea release percentages of 80.71% and 68.75%, respectively, over the same incubation period. As shown in Figure 3.3b, a highly released sample coded by HR-CREU needs to be incubated for 23 hours in order to release 96.33% of its urea at pH 7, whereas samples coded by MR-CREU and LR-CREU release 82.70% and 71.93% of their urea, respectively. Furthermore, as shown in Figure 4.4c, samples coded by MR-CREU and LR-CREU only release 83.22 % and 74.01 % of their urea, respectively, during this lengthy incubation time, but HR-CREU, a highly released sample, only 29 hrs of incubation to release 93.71% of its urea at pH 11.

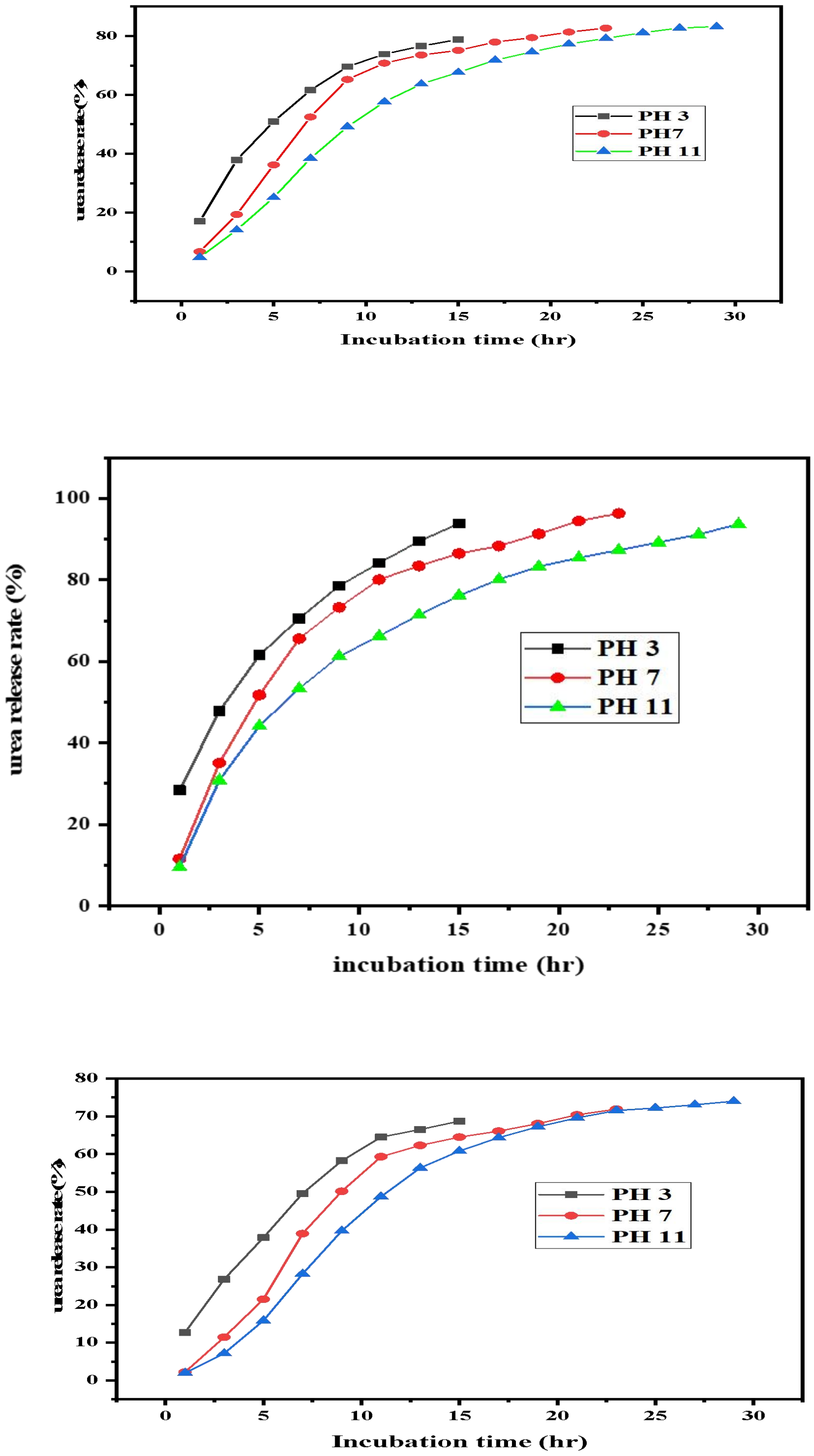
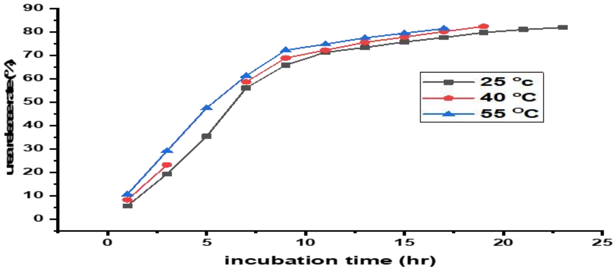


Figure 3.3: The percent of urea released as a function of time at different pH values, A) HR-CREU, B) MR-CREU and C) LR-CREU

The effect of pH on the rate of urea release from CREU is dependent on the protonation of the amino groups in urea. Depending on the pH of the medium, urea may either undergo protonation or deprotonation. More H+ was transferred into the solution when the pH of the solution medium decreased, protonating the amino groups in urea. Because the H^{+} in the solution occupies the bond sites of the urea's amino groups, the carboxyl groups of acetic acid oligomer-grafted chitosan cannot easily bind to urea molecules. As a result, at pH 3, the urea amino groups are in their ionized state ($NH3^{+}$). The charged amino groups ($NH3^{+}$) of urea and the non-ionized carboxyl groups (-COOH) of acetic acid oligomer grafted chitosan experience an electrical repulsion due to the bond sites being occupied by H ions, which results in fast release. Once the buffer solution reaches pH 7, the amine groups in the urea stay in their non-ionized condition (NH_2) (Nadiah et al., 2013), However, it is anticipated that the carbonyl groups in the acetic acid oligomer grafted chitosan will exist in both their ionized (-COO-) and non-ionized (-COOH) forms. As a result, the anime groups of urea and the carboxyl groups of acetic acid oligomer-grafted chitosan have a greater hydrogen bonding interaction. Consequently, urea is released at a slower rate. Since the amino groups of urea were not protonated and remained in the form of primary amine (NH_2), it was anticipated that the carboxyl groups of acetic acid oligomer grafted chitosan would adopt their ionized (-COO-) forms when the pH rose. Consequently, the hydrogen bonding interaction between the amine groups of urea and the carbonyl groups of acetic acid oligomer grafted chitosan increases as the medium's pH rises to 11. As the number of hydrogen bonds between urea and acetic acid oligomer-grafted chitosan increases, the amount of urea released into the media gradually decreases. The sample can release 78.83% at pH 3, 75.11% at pH 7, and 67.64% at pH 11 thanks to MR-CREU. The sample can release 68.75% at pH 3, 64.52% at pH 7, and 60.82% at pH 11 thanks to LR-CREU. This suggests that, in comparison to other samples, pH had a considerable effect on the sample classified by HR-CREU. Specifically, it rises by 17.73% when the pH is lowered from 11 to 3. At the same time, the MR-CREU and LR-CREU coded samples grew by 11.19% and 7.93%, respectively. Strongly grafted acetic acid oligomer grafted chitosan (LR-CREU) is produced by distributing urea into it, and its urea release rate is resistant to the effects of pH. One possible explanation for this could be because the urea in LR-CREU was enclosed in lengthy chains of acetic acid oligomer-grafted chitosan. The solution was unable to penetrate the incredibly tiny chain gaps or the robust surface of the highly grafted acetic acid oligomer grafted chitosan to readily reach the urea because of the excessively small distance between these long molecular chains and the resulting strong surface. The carboxyl groups of acetic acid oligomer grafted chitosan, which are found in the amino acids of chitosan, can easily form hydrogen bonds with the non-ionized amine groups of urea. This suggests that at lower pH values (i.e., pH 3), it takes a long time for the urea amino group to be protonated with the solution's H ion.

3.1.6. The Effect of Temperature on the Urea Release Rate

Figure 3.4 a, b, and c below show the effects of temperature on the urea release rate of the selected CREU (i.e., HR-CREU, MR-CREU, and LR-CREU) at 25 ^{0}C, 40 ^{0}C, and 55 ^{0}C, at that order. Because of the high nutritional release rate that was recorded over the 35 ^{0}C to 40 ^{0}C range, 25 ^{0}C and 55 ^{0}C were selected as extreme values to examine the nutrient release rate in this case. In all CREU, the urea release rate increases with temperature, as seen in Figure 3.4a, b, and c. In the acetic acid oligomer grafted chitosan, higher temperatures cause the kinetic energy of urea molecules to increase, increasing the average molecular diffusion rate of urea and speeding up its release rate. Furthermore, hydrogen bonds are more prone to disintegrate as the temperature rises since they have lower energies than traditional valence bonds (Sadik et al., 2023). Figure 3.4a shows that after 23 hrs of incubation at 25 ^{0}C, 96.77% of the urea in a sample coded by HR-CREU was released into deionized water. That means the urea was almost completely dissolved. Over the course of the 23-hour incubation period, however, samples coded with MR-CREU and LR-CREU produced 81.88% and 72.06%, respectively. MR-CREU and LR-CREU samples release 82.30% and 72.76% of their urea, respectively, at 40 °C over the same incubation period of 19 hrs, while HR-CREU samples took 19 hrs to release 96.73%. Furthermore, the HR-CREU-coded sample releases 95.6% of its urea in just 17 hours at 55 °C, as shown in figure 3.4c. In contrast, the MR-CREU and LR-CREU-coded samples release 81.36% and 74.17% of their urea in 17 hrs, respectively.



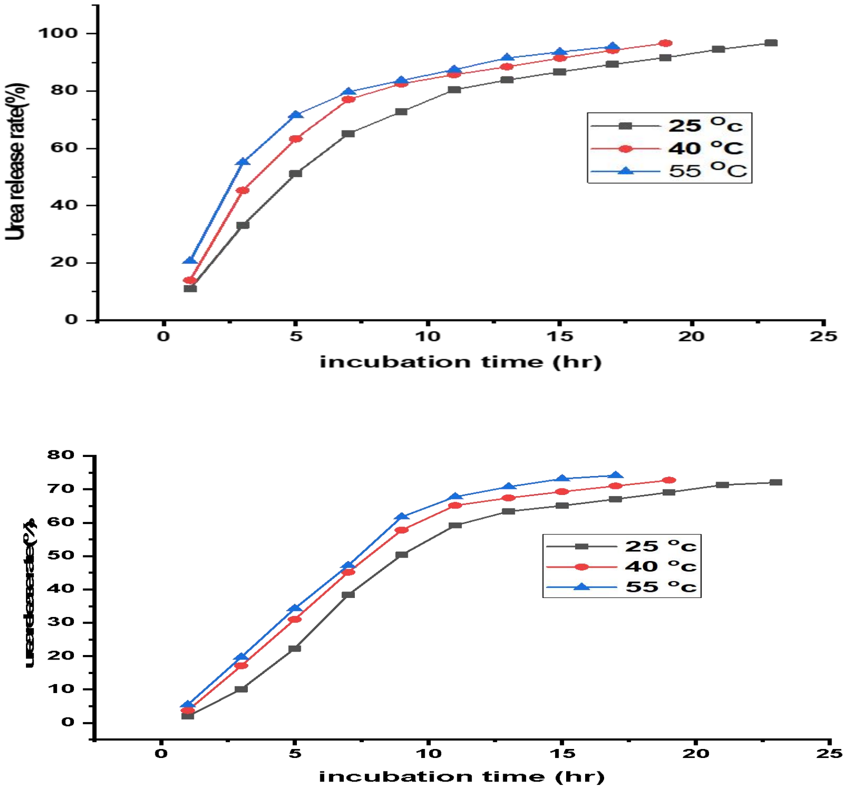


Figure 3.4: The percent of urea released as a function of time at different temperatures, A) HR-CREU, B) MR-CREU, C) LR-CREU.

As shown in Figure 3.4a, b, and c, temperature had the biggest effect on the rate of urea release during the first few hours of release periods. This phenomenon is explained by the system gaining more energy, which leads to the formation of a hydrogen bond between the amino group of urea and the carbonyl group of acetic acid oligomer grafted chitosan. This bond facilitates the dissociation of contacts and speeds up the release of urea. Furthermore, after around nine hours at each temperature condition, the urea release rates of all samples become incredibly slow, as shown in Figure 3.4a, b, and c. The experiment's conditions required the urea trapped in an insoluble component of acetic acid oligomer grafted chitosan to be broken down into soluble, which is a very lengthy procedure.

3.1.7. The Effect of Urea Concentration on Urea Release Rate

For the three selected CREU (HR-CREU, MR-CREU, and LR-CREU), Figure 3.5a, b, and c below illustrate how urea concentrations affect the urea release rate at 50%, 65%, and 80% of urea concentrations. The experiment shows that the urea content contained inside the generated acetic acid oligomer grafted chitosan increases in proportion to the pace at which urea is released from each CREU. The urea from the sample coded by HR-CREU releases almost all of its urea (96.78%) during 25 hours of incubation, as shown in Figure 3.5a, when all CREU contain 50% urea. However, over this prolonged incubation time (25 hrs), the percentage of urea released from samples coded by MR-CREU and LR-CREU was 82.03% and 71.74%, respectively. However, when the amount of urea contained in all CREU increases to 65%, samples coded by MR-CREU and LR-CREU release 82.88% and 72.32% of their urea, respectively, whereas a highly released sample coded by HR-CREU requires 23 hrs of incubation to release 95.91% of its urea (Figure 3.5b). Additionally, when the amount of urea contained in all CREU climbs to 80%, a highly released sample coded by HR-CREU releases 95.73% of urea in just 21 hrs. On the other hand, Figure 3.5c illustrates that samples coded by MR-CREU and LR-CREU release 82.23% and 72.83% of urea throughout the same incubation time (21 hrs). This is because as the amount of urea enclosed within each acetic acid oligomer-grafted chitosan molecular chain diminishes, the molecular chains' spacing widens and their surface strength deteriorates. Because more water could pass through the surface and the pores in acetic acid oligomer-grafted chitosan, the rate of urea release increased.

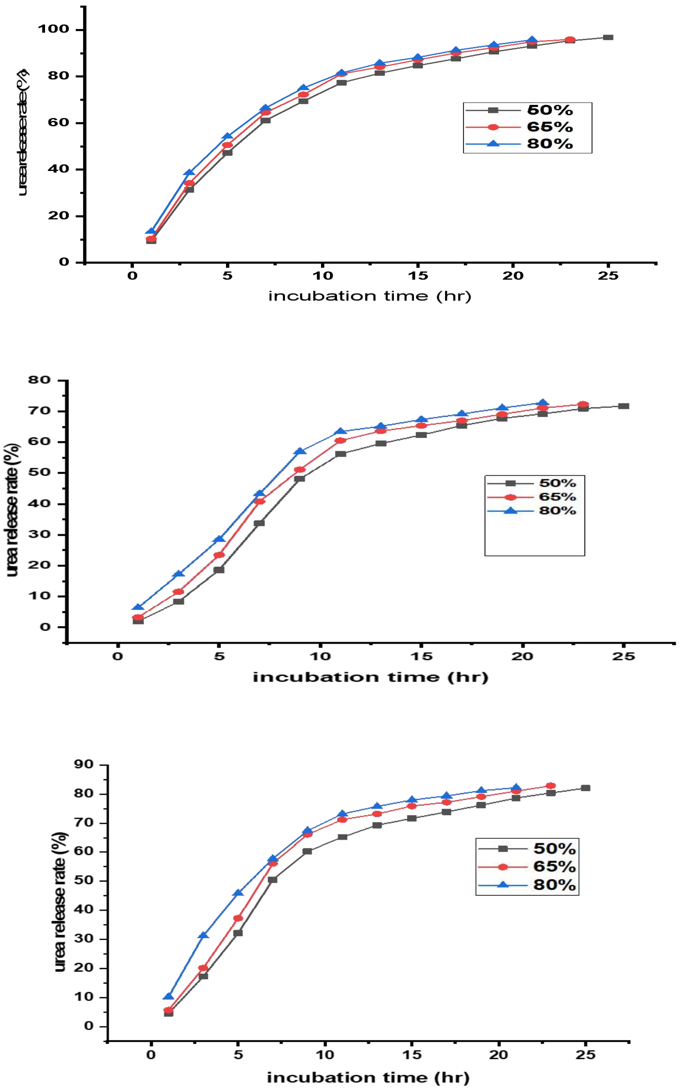


Figure 3.5: The percent of urea released as a function of time at different urea concentration, A) HR-CREU, B) MR-CREU, C) LR-CREU.

The urea release rate from all CREU rapidly increased when the urea concentration rose at the beginning of the urea release periods. This is because each CREU surface has a different amount of urea. As illustrated in Figure 3.5a, b, and c, the urea release rate was substantially faster at the beginning urea release periods in each CREU that contained 80% urea as compared to those CREU produced under the identical conditions, having 65% and 50% urea concentrations. The urea release rate differential steadily decreased once the maximum amount of urea on each individual CREU surface was released. The molecular chains' ability to absorb water and the rate at which soluble acetic acid oligomer grafted chitosan hydrolyzes to become soluble are then used to calculate the release rate of the remaining urea from each CREU. The remaining rate of urea release after the urea on the sample surfaces was released is usually determined by the grafting effectiveness of the acetic acid oligomer grafted chitosan in which the urea was encapsulated.

3.1.8. Soil Degradation Rate of U-e-LAO-g-GAs Relative to Pure Urea

CREU's rate of degradation was to be compared to that of commercial urea fertilizer in the soil degradation trials. The effect of grafting efficiency on the rate of CREU soil deterioration was also investigated during the data processing phase. Figure 3.6 below shows the results of the soil degradation rate of CREU and commercial urea fertilizer, which was plotted using the experimental result data shown in Appendix-9b. The weight loss of all CREU and pure urea was shown to rise with the incubation duration (Figure 4.8). The commercial urea (pure urea) completely degrades after three days of incubation in the soil, resulting in a 100% weight loss. However, over the first three days of incubation, those CREU, HR-CREU, MR-CREU, and LR-CREU only lose 40.8%, 25.5%, and 18.8% of their weights, respectively. Over the course of these 25 days of incubation, the LR-CREU fertilizer shows the lowest weight loss (66.22 % only), but the high urea released CREU (i.e., HR-CREU) releases 96.87% and MR-CREU releases 85.22%. Although it takes longer for them to fully degrade than commercial urea fertilizer, this shows that all CREU were broken down in the soil (Naz & Sulaiman, 2016).

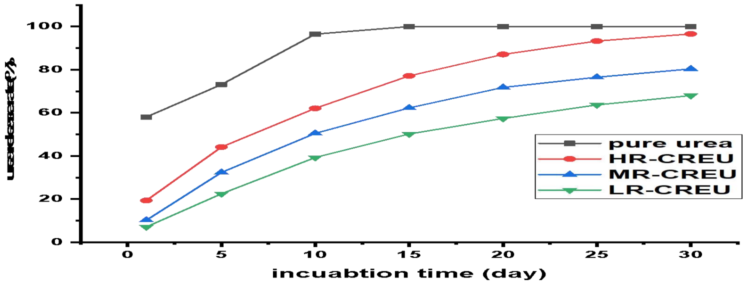


Figure 3.6: Weight loss (%) for the three selected CREU and pure urea exposed to soil for 25 days.

3.1.9. Total Nitrogen Release Rate and its Release Kinetics Behaviors in Water

The Kjeldhal method was used to assess the nitrogen release rate of CREU and commercial urea in water, as shown in Figure 3.7 below. Pure urea releases 95.11 % of its nitrogen content in an hour, as seen in figure 3.7 below, which is nearly identical to the findings reported in the literature (Kashyap et al., 2015) (97%), and (Piluharto et al., 2024) (980%). However, the nitrogen release rates for CREU coded by HR-CREU, MR-CREU, and LR-CREU were 10.45%, 5.74%, and 2.33%, respectively, following an hour of incubation in distilled water. LR-CREU releases more slowly than the other synthesized acetic acid oligomer grafted chitosan because the acetic acid oligomer grafted chitosan used to manufacture it has the highest grafting effectiveness. As mentioned earlier, the best grafting efficiency is linked to the lowest release rate. HR-CREU releases almost all of its nitrogen content (95.91%) from those CREU within 25 hours of incubation, whereas MR-CREU-coded fertilizer achieves 83.34% and LR-CREU releases only 73.44% of its nitrogen content over the same time frame.

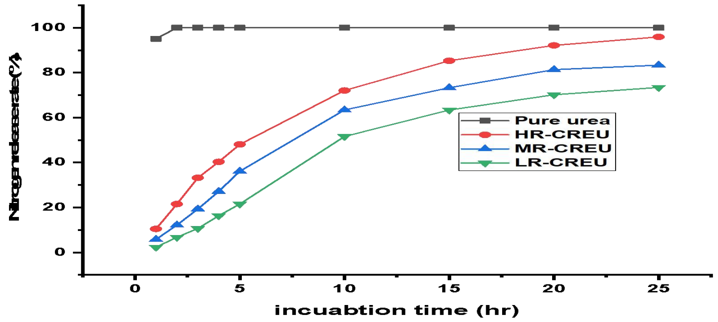


Figure 3.7: Nitrogen release rate in water

The Korsmeyer-Peppas model only used a nitrogen release percentage below 60% because the data from model calculations and experimental results differed significantly above 60% (Science et al., 2022). Nutrient release mechanisms can be divided into two categories: diffusion control, erosion control, or a combination of the two. If diffusion through water-filled matrix pores primarily regulates nutrient release and a good fit to the Korsmeyer–Peppas equation indicates that erosion and diffusion mechanisms cooperate to release nutrients, then the Higuchi model is suitable (Sarhan et al., 2024). In this case, the correlation coefficient for CREU (i.e., R^2= 0.9891 for MR-CREU) and the release kinetics suit the Higuchi equation both quite well. The correlation coefficient ($R^2 > 0.99$) for all CREU (i.e., $R^2 = 0.9732$ for HR-CREU and $R^2 = 0.9923$ for LR-CREU) suggests that the release mechanism was a combination of diffusion and erosion release processes rather than a pure diffusion driven release. Furthermore, as all CREU fit the Korsmeyer-Peppas equation well, the type of diffusion can be determined by determining the release exponent (n). When n is less than 0.45, Fichian diffusion release takes place; when n is between 0.45 and 0.89, anomalous transport (non-Fickian diffusion release) takes place; when n is 0.89, case II transport over swelling matrices takes place; and when n is greater than 0.89, super case II transport takes place (Saleem, 2024). The release exponent (n) values in all of the CREU were greater than 0.87 (i.e., n = 0.87919 for HR-CREU, n = 1.07012 for MR-CREU, and n = 1.37804 for LR-CREU), indicating that the nitrogen released from the CREU anomalous transport (non-Fickian diffusion release).

This suggests that the nitrogen released from the CREU in this instance followed the super case-II transport mechanism. This is accomplished by the acetic acid oligomer-grafted chitosan chains' macromolecular relaxation and erosion mechanism.

4. Conclusion

Urea was successfully encapsulated inside a biodegradable acetic acid oligomer grafted chitosan to create a novel kind of controlled dissolution rate fertilizer with an enhanced soil degradation rate. Several physiochemical methods were used to characterize the characteristics of controlled released encapsulated urea (CREU) and a synthetic acetic acid oligomer grafted chitosan. In respect to the grafting efficiency of acetic acid oligomer grafted chitosan and the urea release rate of controlled released encapsulated urea, the link between independent factors such as reaction temperature, reaction time, and chitosan to acetic acid mixing ratio was examined. The results show that the urea release rate of controlled released encapsulated urea and the grafting. When the grafting efficiency achieves its maximum of 60.14% at an acetic acid to chitosan mixing ratio of 10:1 w/w%, a reaction temperature of 160 °C, and a reaction duration of three hours, the urea is released. The rate gets to its lowest point at 12.0%. The FTIR analysis confirmed that the acetic acid oligomer chains were grafted at the O-H and N-H functional groups of the chitosan backbone. Additionally, the effects of the acetic acid oligomer grafted chitosan on its solubility were investigated. The urea release rate of controlled released encapsulated urea was also assessed in relation to pH, temperature, and urea concentration. When the temperature is raised, the urea release rate in acetic acid oligomer grafted chitosan increases due to an increase in the urea molecular diffusion rate. Similarly, if the acetic acid oligomer grafted chitosan's urea concentration rises, so does its urea release rate. The significant amount of urea in acetic acid oligomer-grafted chitosan causes its molecular chains to enlarge, which is what causes this. The pH of the medium rises, however, and less urea is produced from controlled released encapsulated urea. Because of the increased contact between the carboxyl groups of acetic acid oligomer grafted chitosan and the amine groups of urea, this is caused. We also looked into the rates of soil urea release and decomposition. During the first three days of incubation in the soil, the weights of the controlled released encapsulated urea's coded HR-CREU, MR-CREU, and LR-CREU decrease by 38.83%, 25.5%, and 18.8%, respectively, whereas commercial urea (pure urea) almost fails. The acetic acid oligomer grafted chitosan was broken down in the soil, although it takes longer for them to break down completely than commercial urea fertilizer. When acetic acid oligomer grafted chitosan's grafting effectiveness rises, the rate of degradation of the grafted chitosan falls. As the rate of soil degradation increases, it also increases the urea concentration in acetic acid oligomer grafted chitosan. Using the Kjeldhal method, the total nitrogen release rate of encapsulated urea that was regulated was compared to that of pure urea in water. Using four different kinetic models, we also examined the nitrogen release kinetics from controlled released encapsulated urea. All of those model equations are best matched by the Korsmeyer-Peppas equation, which has correlation coefficients ($R^2 > 0.98$) and release exponent (n) values between 0.45 and 0.89 for all controlled released encapsulated urea. The release kinetics, which included diffusion and erosion-controlled release processes, demonstrated that the nitrogen release from the controlled released encapsulated urea followed the anomalous transport (non-Fickian diffusion release). In summary, this study showed that a fertilizer with a controlled rate of dissolution does not leave behind residue that totally decomposes in the soil, putting the soil's structure and nitrogen balance at risk. The grafting efficiency of acetic acid oligomer grafted chitosan during the poly-condensation reaction of chitosan and acetic acid can be adjusted by varying the values of its synthesizing parameters, such as reaction temperature, reaction duration, and chitosan to acetic acid mixing ratio. As a result, by simply varying the grafting efficiency of acetic acid oligomer grafted chitosan, the nitrogen release rate in water could be changed because the two variables are inversely proportional.

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