



Chemical fertilizer release control using encapsulation in polymer matrix by electrospinning

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 Encapsulation;
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Abstract. This study investigates the control of the release of urea fertilizer from the nanofiber substrate of cellulose acetate polymer to increase the release time of fertilizer. First, cellulose acetate solution was prepared at concentrations of 13, 14, and 15% and their nanofibers were produced via electrospinning. By checking the diameter and filamentation of fibers based on FESEM (Field Emission Scanning Electron Microscopy) images, the concentration of 14% was selected as the optimal one. Then, cellulose acetate solution of 14% (weight/volume) containing urea fertilizer with concentrations of 17, 21, and 23% (weight/weight, w/w) was prepared, compared to the weight of cellulose acetate. Nanofibers of cellulose acetate solutions containing urea were produced by electrospinning. The produced fibers were evaluated by FTIR. The results showed that the urea fertilizer was well loaded in the nano fiber substrate and no chemical reaction was formed between the fertilizer and the polymer. As demonstrated by the results, the DSC test, in which fertilizer was loaded on the bed of nanofibers, increased the degradation of cellulose acetate nanofibers. In addition, the release rate of urea fertilizer into distilled water was monitored using a UV-vis spectrophotometer and the outcome indicated that the release time increased to 15 days, which is significant.

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1. Introduction

Fertilizers are inorganic materials with high analytical value and definite composition and they can supply nutrients and trace elements, usually applied to the soil to encourage the growth of crops. Chemical fertilizers are prepared by combining the three essential nutrients needed by the plant (nitrogen, phosphorus, and potassium) with appropriate concentrations. Nitrogen helps increase leaf growth and causes protein and chlorophyll formation while phosphorus facilitates the growth of root and fruit and potassium promotes shoot growth,

root growth, and protein synthesis [1–3]. Among the most widely used fertilizers is urea fertilizer with 46% nitrogen, which is one of the important sources of this element in the world [4,5]. However, the use of this fertilizer requires good and efficient farming operations to prevent it from being absorbed into the air by ammonia gas. The results show that 90% of nitrogen fertilizer is washed off at high ambient temperature and humidity, being a major economic blow to producers but also detrimental to the environment. Therefore, researchers are trying to control the release rate of fertilizer at the time of fertilization to inject fertilizers at a slower rate into production [6]. Release-controlled fertilizers are typically coated or encapsulated with inorganic or organic materials that control the rate, pattern, and duration of plant nutrient release [7]. The use of biodegradable materials to coat urea reduces not only the environmental pollution but also the harmful effects

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of conventional coatings on the proper functioning of soil and plant ecosystems. These materials slow down *N* release from urea that could be synchronized with crop *N* demand during the growing season. Moreover, their high biodegradability and renewability derived from natural products are the reasons why researchers and industrialists search for innovatively sustainable bio-based materials that could further reduce the cost of coated fertilizer production while providing high-efficiency and superior properties of controlled *N* release from urea fertilizer on a local scale [8]. Da Costa et al. (2019) studied urea granule coating through a suspension of biodegradable polymers, glycerol, distilled water, and talc. This study aimed to evaluate the rate of nitrogen loss by volatilization, which is the principal in-field urea deprivation and is associated with urea hydrolysis and depends on the physical-chemical soil characteristics. Up to 50% reduction of *N* loss by volatilization route compared to uncoated granules was reported, and the coating layer exhibited higher effectiveness in accordance with its homogeneity and diminished porosity [9]. Similar studies were developed by Qiao et al. (2016) [10] and Yu and Li (2019) [11] which reduced the rate of urea release by coating with biopolymers and paraffin. One of the mechanisms for controlling the release of substances is encapsulation of the active substance in the polymer substrate. In this method, active substances are loaded onto a polymer substrate, which are usually on micro and nanometer scales. Then, the substances are released from the fiber substrate into the environment [12]. Today, electrospinning is the best and most efficient way to produce nanofibers. Electrospinning is a method for generating fibers through the formation of a jet from a charge polymer or non-polymeric system in an electric field. Generally, electrospinning consists of four main parts: high-voltage power supply, syringe and needle, pump, and collector, as shown in Figure 1 [13–15]. In the electrospinning process, first, the polymer solution is poured into the syringe and then, the syringe is inserted into the syringe pump and the needle and

collector are connected to one of the power supply poles. By placing the collector at the fixed distance from the needle and applying voltage and starting the injection, the electrospinning process begins.

As the process begins, syringe pump must inject very small amounts of the solution accurately and uniformly. The solution reaches the end of the metal needle and is charged by a pole attached to it. Because of the two unnamed poles, an electrostatic field is formed between the needle head and the collector plate. The charged polymer solution is then pulled to the collector and produces fibers with a diameter in the micro and nanometer range [16]. The release behavior of urea encapsulated in St-g-PVAc and St-g-PVAc/urea composite film was studied. The experimental results indicate that the introduction of hydrophobic PVAc reduces the swellability of the starch matrix; the urea nitrogen slow-release time can reach 28 h in water. The St-g-PVAc/urea composite films could be biodegraded in the soil environment [17]. Slow fertilizer release from core-shell electrospun fibers (poly-hydroxybutyrate/polylactic acid (PLA) mixed with fertilizers) was investigated by Kampeerappun and Phanomkate. These core-shell structures offer the potential to control the manner and timing of fertilizer delivery. The results demonstrated that core-shell electrospun mats released fertilizers for a month and were biodegradable within 3 months [18]. The objective of this work is to prepare urea encapsulated by Cellulose Acetate (CA) nanofibers as a simple and cheap method to increase the release time of fertilizer and to investigate the effect of the preparation method on the microcapsules' characteristics and their biodegradability. Moreover, the potential use of the microcapsules as controlled-release systems aiming to avoid the ecological problems caused by excessive urea release in the environment is certainly a primary objective.

2. Materials and methods

2.1. Materials

Polymer CA (in powder form, Mw = 30000 Da percent steel with 39.8% w/w) was purchased from Aldrich Sigma Co.; pure acetic acid purchased from Merck Co. (Germany); urea chemical fertilizer with chemical formula $\text{CO}(\text{NH}_2)_2$ donated by the (Khoda-bande city Jahad Keshavarzy); and deionized water provided by the Faculty of Engineering Laboratory, University of Engineering.

2.2. Preparation of solutions for the electrospinning process

A mixture of two organic solvents including acetic acid and distilled water at a ratio of 90 to 10 was used to prepare the cellulose acetate polymer solution at concentrations of 13, 14, and 15% (weight/volume).

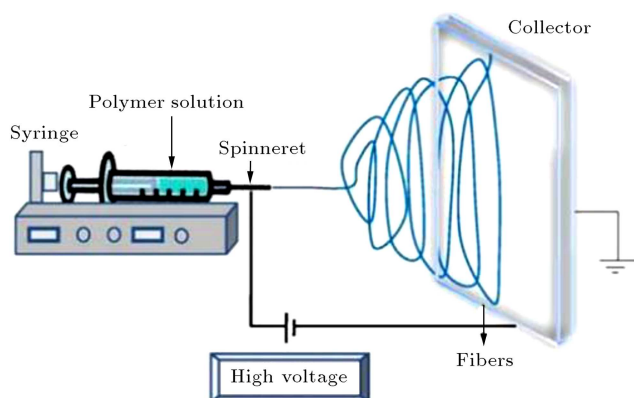


Figure 1. Electrospinning machine image.

Table 1. Conditions applied to the electrospinning machine to determine the optimal electrospinning conditions.

No.	Changes				
	Solution concentration (weight/volume)	Feeding rate (ml/h)	Voltage (kV)	Relative humidity (%)	Distance (cm)
1	13%	0.5	25	20	10
2	13%	1	25	20	10
3	13%	1.5	25	20	10
4	14%	0.5	25	20	10
5	14%	1	25	20	10
6	14%	1.5	25	20	10
7	15%	0.5	25	20	10
8	15%	1	25	20	10
9	15%	1.5	25	20	10

Acetic acid was used as a CA solvent and since we needed a solvent to transfer the electrostatic current well, distilled water was used. If the ratio of distilled water in the solvent mixture is high, the CA does not dissolve well in the solvent and the solvent does not dry during the jet flight, resulting in fibers sticking to the collector and forming improper nanofibers. Moreover, if the proportion of acetic acid in the mixing compound is high, in the electrospinning, the solution at the head of the needle is dried and does not form a jet due to the high volatility of the acetic acid [19]. The solutions were electroporated according to the experimental design in Table 1 to determine the optimum conditions using a high-voltage electrospinning machine manufactured at the University of Guilan, School of Chemical Engineering.

After determining the optimum solution, the optimum solution of CA polymer containing 17%, 21%, and 23% (w/w) urea fertilizers was prepared relative to CA weight. Then, the solutions were electrospun according to the optimum conditions obtained from the first-phase laboratory experiments.

2.3. Investigation of structure and morphology of nanofibers

In this study, the field emission scanning electron microscope (S-Hitachi 4160) made in Japan was used to study the morphology, surface properties, and diameter of nanofibers. In this study, the fibers were cast on an aluminum foil with a perfectly smooth and clean surface. Samples of fibers were separated from the aluminum foil and laminated for 15 minutes by the film deposition device. Then, photographs were taken at different magnifications using FESEM equipment

and by using image-j software, fiber diameter and its diameter distribution were investigated. A voltage of 25 cm and a distance of 10 cm between the needle tip and the collector were considered.

2.4. Infrared spectroscopy with Fourier transformation (FT-IR)

To identify the functional groups and verify the loading of the fertilizer on the nanofiber substrate and to investigate the presence or absence of chemical reaction between the urea fertilizer and the polymer substrate, the FT-IR Spectrometer was obtained with a Thermo Nicolet Model 370 (made in U.S.A) using KBr mode.

2.5. Differential Scanning Calorimeter (DSC) Device

The thermal properties of the specimens were measured by a PerkinElmer STA6000 differential scanning calorimeter (DSC) made in the United States. In this study, 3.252 mg of pure CA and the CA containing 21% urea in aluminum thigh were exposed to N₂ gas with a flow rate of 50 ml per minute. The samples were heated from 25 to 250°C with a scan rate of 10°C/min.

2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) emerged as an alternative, less expensive, fast, and more convenient technique for measuring the thermal stability of materials including polymers. In this method, the weight change for a substance was monitored as a function of temperature or time as the specimen was subjected to a controlled temperature program in a controlled atmosphere.

2.7. Evaluation of release rate of urea fertilizer from nanofiber substrate

To determine the release rate of urea fertilizer from the polymer substrate by a UV-Vis Model Varian Cary 50 (made in U.S.A) spectrophotometer, a single beam was used. To this end, first, a certain concentration of urea fertilizer, which is soluble in distilled water, was prepared and then, the absorbance of each solution in the range of 200 to 800 nm was read by a UV spectrophotometer to determine the maximum wavelength. The curves of these concentrations were then plotted against light absorption to obtain a calibration curve. Then, 0.01 g of the fibers were carefully separated from the aluminum foil at which the fibers were collected and placed in 5 ml distilled water at 25°C. In order to determine the release rate of urea fertilizer, the sample was discharged at a specified time into another container containing 5 ml distilled water. This operation continued for some time until the amount of urea fertilizer inside the container resulted in a detectable absorption peak in the maximum absorption wave, while the adsorption rate was equal to the acceptable calibration curves for concentration at the same time. After calculating the amount of urea fertilizer extracted from the nanofibers at each stage, the percentage of urea fertilizer released from the sample at the sampling interval was finally calculated via Eq. (1):

$$\text{Urea released (\%)} = \frac{M_t}{M_\infty} \times 100, \quad (1)$$

where M_t is the amount of fertilizer released from the nanofiber substrate at time t and M_∞ is the amount of fertilizer released from the nanofiber substrate at time ∞ .

3. Results and discussion

3.1. Morphology of nanofibers produced by electrospinning

This study investigates the effect of changes in two important parameters, namely concentration of polymer solution and dissolved feed rate, on nanofiber production by electrospinning.

3.1.1. Concentration

Polymer solution concentration is one of the factors influencing the electrospinning process for high-quality fibers. In order to produce high-quality fibers, an appropriate concentration of solution must be provided to allow sufficient viscosity for the electrospinning process. At concentrations that allow sufficient chain contention, continuous uniform nanofibers can be reached in a strong electric field from the polymer solution. When the jet leaves the tip of the needle and is pulled toward the collector plate, during solution elongation, the bond between the molecular chains avoids a cutoff

by driven electric forces. Therefore, a continuous jet producing a flawless structure and a knot in the fiber is produced. The concentration of polymer in the solution often determines the electrospinning. Decreasing the concentration of the solution causes nodules in the fibers, and increasing the concentration of the solution increases the fiber diameter and heterogeneity of the fiber diameter [20]. FESEM images of CA are produced according to Table 1 and the test scheme in Figure 2 is given. Based on Figure 2, by reducing the concentration of the polymer solution (Samples 1, 2, and 3), the rate of node formation in the fibers increases due to inadequate interference between the polymer molecular chains, thus increasing the number of nodes on the nanofiber surface. On the other hand, by increasing the concentration of the polymer solution (Samples 7, 8, and 9), the electrostatic force cannot overcome the viscoelastic force and the fibers are produced in a large and heterogeneous diameter. In addition, if the concentration of the solution exceeds a limit, it prevents continuous electrospinning. The results are similar to those obtained by Ewalds et al. [21].

3.1.2. Feeding rate

Another effective factor is feed rate, and if the target is to have a Taylor cone, a proper feed rate should be applied to the electrospinning system. As the feeding rate increases, there is a reciprocal increase in fiber diameter and vertebral size, because if the feed rate is high, greater volume is removed from the needle tip and it takes a long time for the jet to dry and the filaments stick together [22]. As shown in Figure 2, changing the feed rate causes changes in the fiber properties and if the feed rate is high (Samples c, e, f, h), the bulk of the solution is removed from the needle and it takes a long time for the jet to dry; therefore, the filaments stick together. As a result, fibers are formed with a heterogeneous diameter and are attached together. Therefore, in order to produce fibers with good quality, there must be a proper relationship between the factors influencing the electrification process.

In Table 2, descriptions of nanofiber images produced by electrification are given based on Figure 2.

The examination of FESEM images shows that specimen no. d is a nodule-free fiber with a proper diameter distribution. The average fiber diameter is about 87 nm and the percentage of fiber diameter in the range of 60 to 100 nm is very high, indicating the high quality of the fibers produced (Figure 3).

Therefore, according to the above, the nanofibers produced in a condition characterized by 25 kV, 0.5 ml/h feed rate, 14% concentration, and 10 cm distance between the needle and the collector were of good quality. Figure 4 shows the FESEM image and the diameter distribution of CA nanofibers containing urea fertilizer at concentrations of 17, 21, and 23% (w/w)

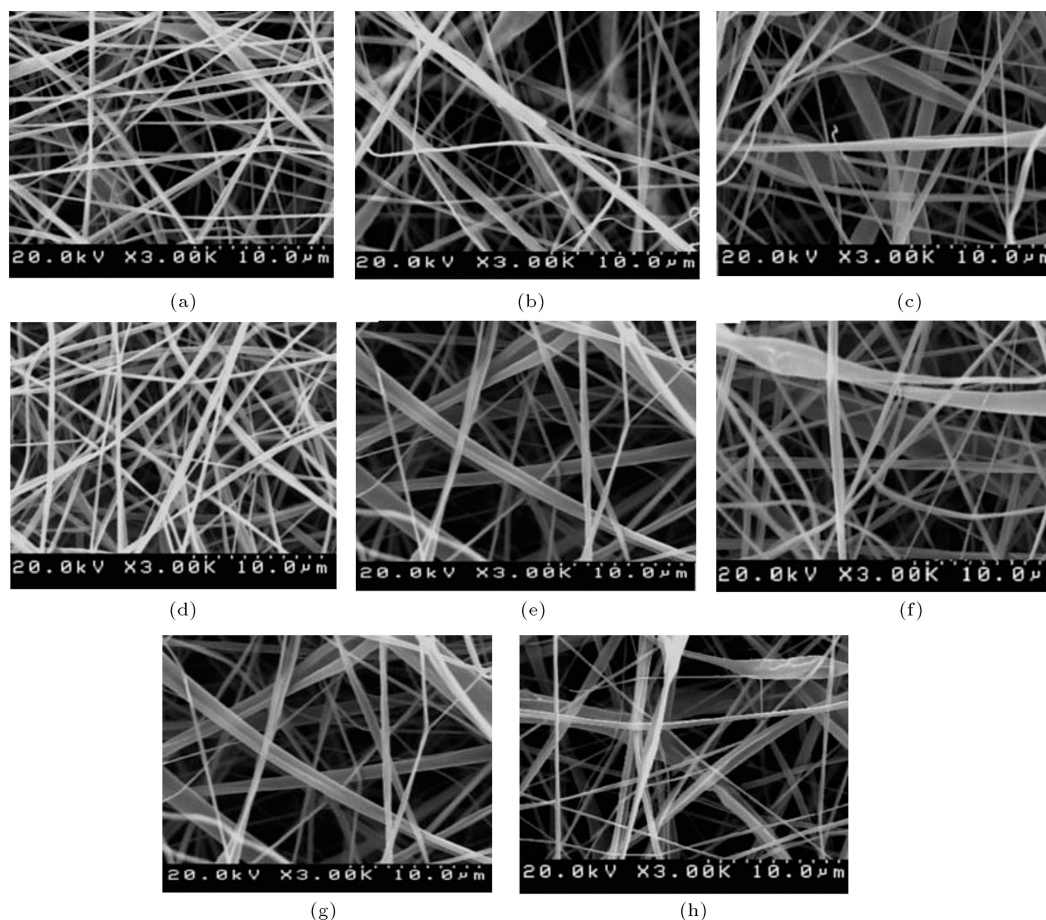


Figure 2. FESEM images of cellulose acetate polymer nanofibers.

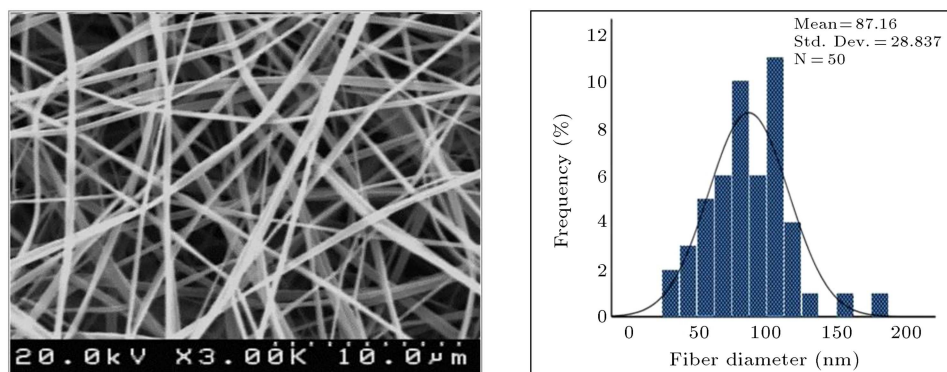


Figure 3. FESEM image and diameter distribution of fiber Sample no. 4.

with respect to the weight of CA at an optimum concentration (14%). According to Figure 4, it can be mentioned that as the concentration of urea fertilizer in the polymer solution increases, the fiber diameter increases due to the swelling of the produced fibers.

3.2. Investigation of infrared spectrometer with Fourier transform

Figure 5 shows the infrared spectrum of cellulose acetate and urea fertilizer. The most important cellulose acetate peaks are as follows: carbonyl group

(C=O) at 1751 wavelengths, methyl group ($-\text{CH}_3$) at 1373 wavelengths, and 1241.24 wavelengths at tensile vibrations for the ether functional group (C-O-C), and 1049 adsorbents in the (C-O) group at the same adsorption peak. 3525.29 relates to stretching types of hydroxyl groups (O-H) [23]. The most significant peaks in the FTIR urea spectrum include the absorption peak at 3440.44 cm^{-1} and 3340.16 cm^{-1} wavelengths for the tensile vibrations of the amine group (N-H), the peak absorption at a wavelength of 1666.22 cm^{-1} for the carbonyl group (C=O), the absorption peak at a

Table 2. Specifications of cellulose acetate nanofibers according to the experiment design.

No.	Specifications	Description
1	Thin knit fibers	Because of the low concentration of the solution, the node is composed of fibers.
2	Thin knit fibers	Due to the high concentration of the solution, nodular fibers are formed.
3	Knot fibers with heterogeneous diameter	Due to the high soluble feed rate as well as the low soluble concentration, inhomogeneous and knot fibers are formed.
4	Thin fibers with homogeneous diameter without knot	Due to proper proportionality among concentration, feed rate, and voltage, homogeneous and thin fibers are formed.
5	Fibers with heterogeneous diameter	Due to the high feeding rate of the solution, fibers with a heterogeneous diameter are formed.
6	Fibers with heterogeneous diameter	Due to the high feeding rate of the solution, fibers with a heterogeneous diameter are formed.
7	Fibers with heterogeneous diameter	Due to the high feeding rate of the solution, fibers with a heterogeneous diameter are formed.
8	Fibers with heterogeneous diameter	Due to the high feeding rate of the solution, fibers with a heterogeneous diameter are formed.
9	Fibers with heterogeneous diameter	Due to the high feeding rate of the solution, fibers with a heterogeneous diameter are formed.

wavelength of 1619.94 cm^{-1} for the tensile vibrations of the amine group (N-H), and the absorption peak at a wavelength of 1457.94 cm^{-1} for the tensile band (C-N). The results are similar to the findings of Manivannan and Rajendran [24]. Figure 6 shows FTIR spectra of CA nanofibers containing urea fertilizer at 17, 21, and 23% (w/w) concentrations with respect to the weight of CA at 14%.

The results show no change in the peak of cellulose acetate and urea fertilizer indices, including the peak removal or the appearance of new ones. In fact, this phenomenon reflects the fact that there is no chemical reaction between the urea fertilizer and the substrate. Therefore, urea fertilizer is well loaded on the nanofiber substrate.

3.3. Effect of urea fertilizer on physical properties of cellulose acetate using DSC

Figure 7 shows the differential scanning calorimetry graphs of pure cellulose acetate polymer and CA containing 21% urea fertilizer (CA-U). According to the figure, pure CA does not have a large peak at temperatures 25 to 250°C , but CA containing fertilizer at 132.71°C has a large heating peak due to its thermal degradation. The reason that the CA-U nanofibers have a melting temperature in the range of 25 to 250 while the CA nanofibers do not have melting temperatures in this range is that the fertilizer loaded on the cellulose

acetate substrate has weakened the CA molecular bond chains.

TGA curve of pure CA and CA containing 21% urea fertilizer (CA-U) in Figure 8 shows the weight loss (%) with respect to the temperature increase. As shown in Figure 8, weight percentage decreases due to different reactions taking place following increase in the temperature. It means that mass is constantly changing due to thermal treatment. Analysis of the cellulose acetates revealed a weight loss in the region of 0 to 50°C corresponding to the loss of water. The second event occurring at around $130\text{--}150^{\circ}\text{C}$ is characteristic of thermal degradation of cellulose acetate. Thus, in TGA curve, the first decomposition begins at a lower temperature and continues up to high temperatures with change in weight percentage. CA-U weight loss is noticeable at a temperature limit of 132°C .

3.4. Investigation of fertilizer release profile

In this study, the UV-Vis spectrophotometric method was used to measure the concentration of released urea fertilizer at a given time. The use of this method requires that the absorption of light by a solution containing urea at varying concentrations follow the Beer-Lambert law. In other words, there is a linear relationship between the absorption of light by the solution containing urea and its concentration. In order to use the UV-Vis spectrophotometer device, it is first

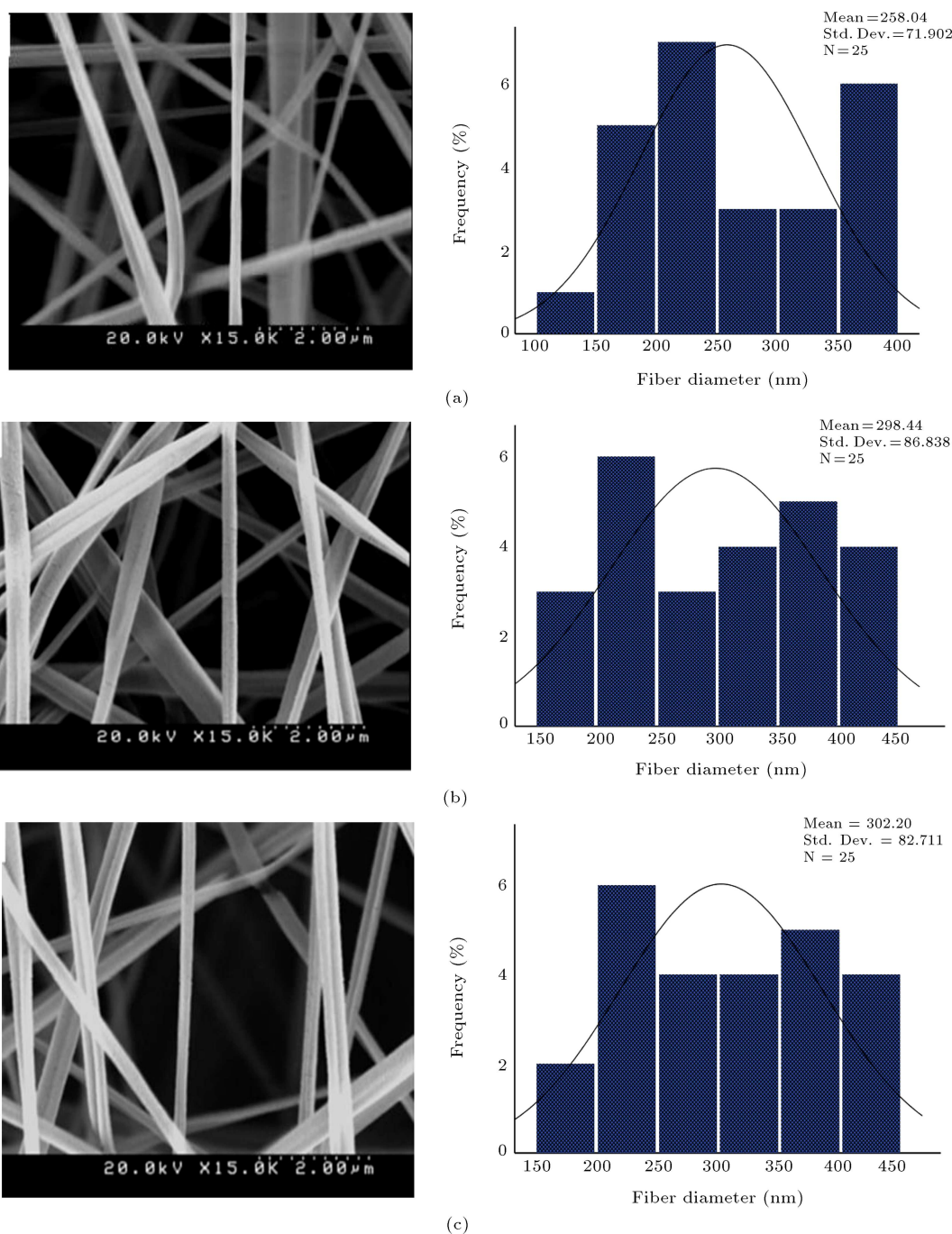


Figure 4. FESEM image of cellulose acetate nanofibers containing urea fertilizer with concentrations of: (a) 17% (w/w), (b) 21% (w/w), and (c) 23% (w/w) relative to cellulose acetate weight at an optimum concentration.

necessary to draw a calibration curve between certain concentrations of the solution containing the substance in question and the light absorption of the solution. Then, one should examine whether it is linear or non-linear, or if it follows Bayer-Lambert law or not. The calibration curve used to measure the amount of urea fertilizer release in distilled water was obtained by preparing the mother solution at a concentration of 1000 $\mu\text{g/ml}$ of urea fertilizer in distilled water and, then, diluting it with solutions 5, 11, 17, and 23

$\mu\text{g/ml}$ made in distilled water. Then, the amount of light absorbed by the UV-Vis spectrophotometer was measured in the range of 200 to 800 nm and was characterized by a maximum wavelength of 220 nm (Figure 9).

Then, the absorbance of all concentrations at this wavelength was repeated three times at each concentration, and the average and standard deviation of absorbance of solutions with different concentrations at the maximum wavelength were calculated in Table 3.

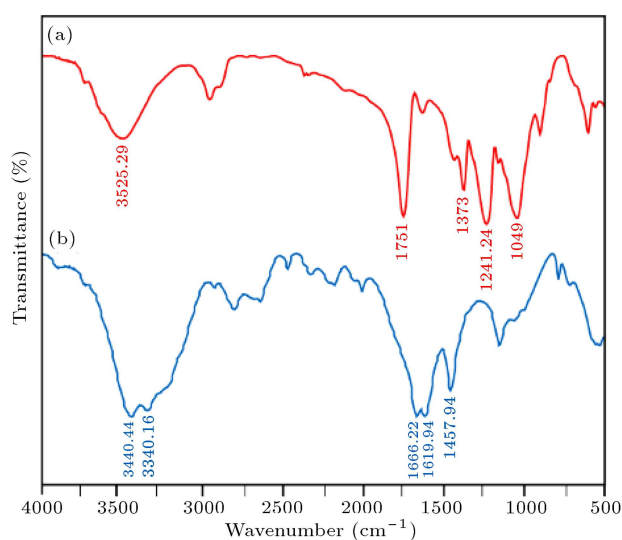


Figure 5. FTIR spectra of nanofibers: (a) Pure cellulose acetate and (b) urea fertilizer.

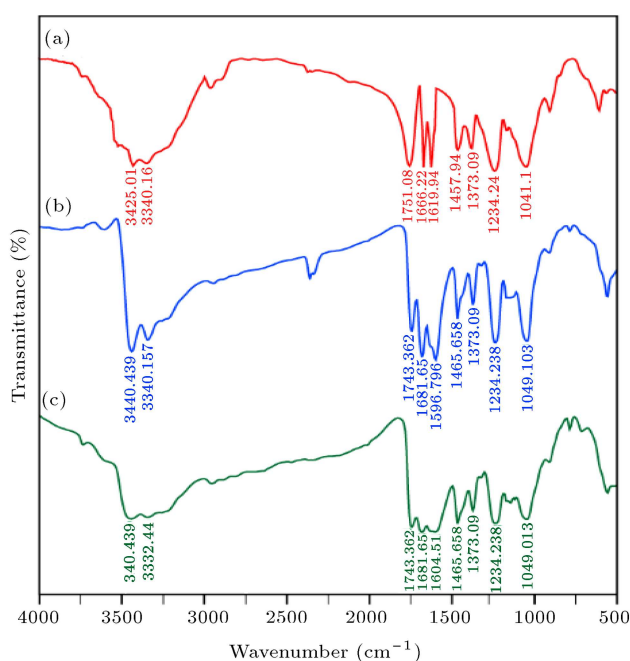


Figure 6. FTIR image of cellulose acetate nanofibers containing urea fertilizer with concentrations of (a) 17% (w/w), (b) 21% (w/w), and (c) 23% (w/w) relative to the weight of cellulose acetate at optimum concentration.

Finally, the absorption calibration curve against urea fertilizer concentration was plotted using these mean values (Figure 10). Given the value of R^2 , the linearity of the calibration curve is confirmed, and the linearity of the relationship between UV-V absorption and urea fertilizer concentration indicates compliance with the Beer-Lambert law.

In order to evaluate the release of urea fertilizer from the CA nanofibers, the amount of urea released into the medium at specific time intervals was measured

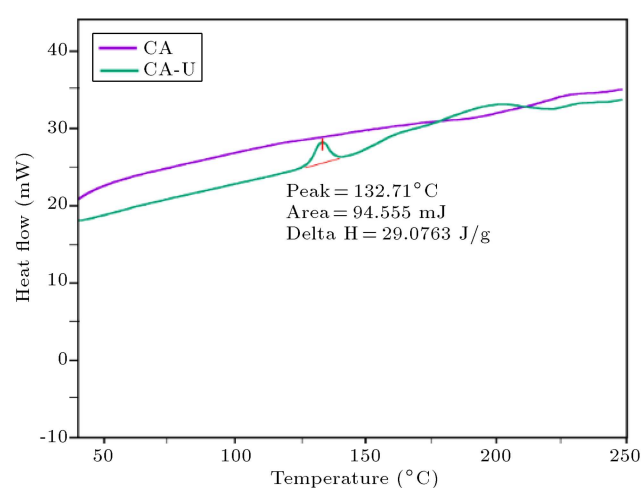


Figure 7. DSC image of pure Cellulose Acetate (CA) and cellulose acetate nanofibers containing fertilizer Urea at concentrations of 17% (w/w) relative to cellulose acetate at an optimum concentration (CA-U).

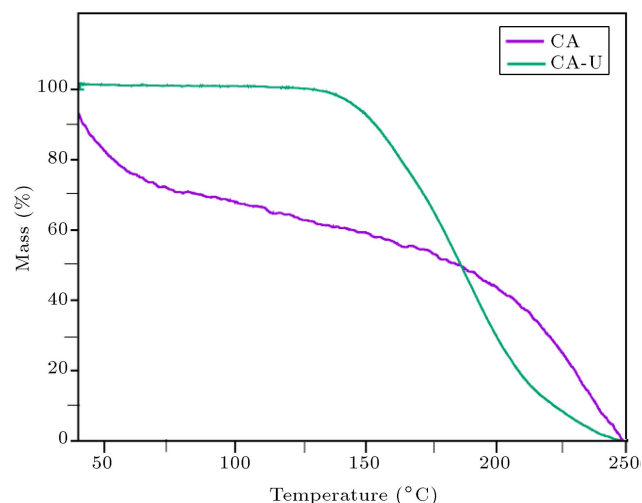


Figure 8. TGA image of pure Cellulose Acetate (CA) and cellulose acetate containing 17% (w/w) urea fertilizer relative to cellulose acetate at an optimum concentration (CA-U).

by UV-vis spectrophotometry and the results of these experiments were evaluated. The controlled release of urea was due to its solubility in water; however, when the fertilizer is in the CA nanofiber bed, the chain of acetyl cellulose molecules is weakened and the degradation rate of potency increases. Figure 11 shows the release profile of urea fertilizer from the cellulose nanofiber substrate with different urea percentages. Upon increasing fiber diameter and urea fertilizer percentage, more fertilizer is released from the CA substrate. The graph shows nanofibers containing 17% urea fertilizer. In this case, the amount of fertilizer released from the polymer substrate is lower than other percentages (21% and 23%). Similarly, the release rate of the fertilizer is also slower in the early days and may

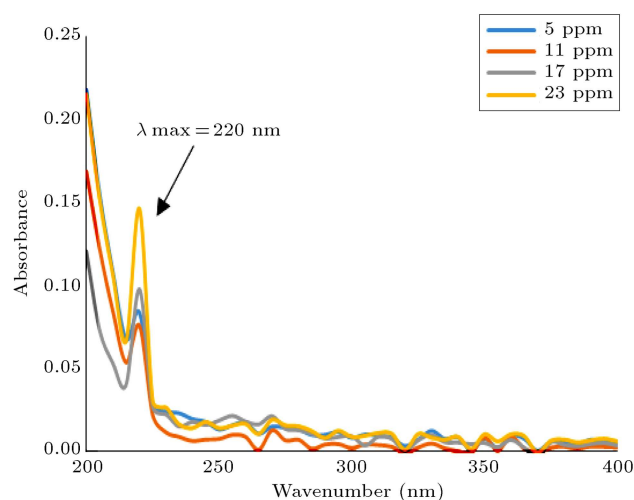


Figure 9. Maximum wavelength diagram for measuring urea fertilizer release rate from cellulose acetate nanofibers.

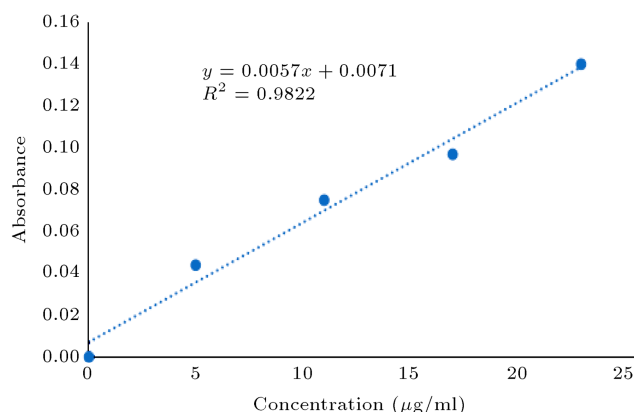


Figure 10. UV absorption calibration curve of solution containing urea fertilizer in water for a maximum of 220 nm to measure release.

Table 3. Adsorption results of solution containing urea fertilizer in distilled water at maximum wavelength 220 nm to draw the calibration curve.

Sample	Concentration of urea ($\mu\text{g/ml}$)			
	5	11	17	23
1	0.043	0.074	0.097	0.14
2	0.046	0.075	0.098	0.149
3	0.044	0.076	0.096	0.145
Average	0.044	0.075	0.097	0.14
Standard deviation	0.001	0.001	0.001	0.002
Coefficient of variation (%)	2.2	1.3	1.03	1.42

be due to more urea compression inside the nanofibers. It is also observed in nanofibers containing 23% urea fertilizer that the release rate is initially higher than 17% and 21% due to the increase in the diameter and percentage of fertilizer loaded on the nanofiber

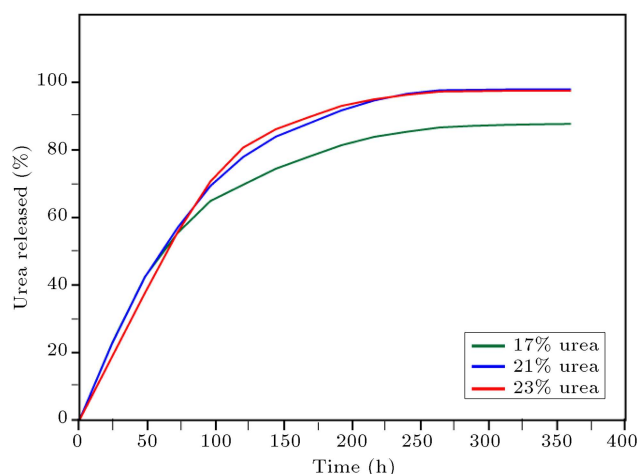


Figure 11. Release profile of urea fertilizer from cellulose acetate nanofibers substrate.

substrate. However, the nanofibers containing 21% urea fertilizer outperform the other 2 samples and the release rate is faster.

4. Conclusion

The results of the present study determined appropriate conditions for the production of nanofibers containing urea fertilizer to increase the duration of fertilizer release from the nanofibers substrate. The results demonstrated the application of the production conditions including constant voltage of 25 kV, feed rate of 0.5 ml/h, needle to collector distance of 10 cm, and humidity of 20% in a CA polymer solution containing urea fertilizer with 21% (w/w) concentration, compared to cellulose weight. Acetate at a concentration of 14% results in the production of suitable fibers, which can increase the release time of fertilizer from the nanofiber substrate to 15 days. Under these conditions, the FT-IR test illustrated that the fertilizer was loaded onto the nanofibers substrate and no chemical reaction was carried out between urea and CA. The DSC test also illustrated that the fertilizer loaded on the nanofiber substrate increased the degradability of CA nanofibers under optimum conditions. The results illustrated that the fiber diameter and the amount of fertilizer loaded on the fiber substrate affected the release rate of fertilizer and it was directly related to the diameter and amount of the fertilizer loaded.

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