A Biopolymer Coating Strategy for the Slow Release of Urea from Urea Fertiliser

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Abstract
Due to the rapid dissolution of urea fertilisers in water, leaching and evaporation from the soil cause approximately 70 % of the urea to be lost to the atmosphere and groundwater without being used by plants. It is known that a significant portion of urea fertiliser is released into the atmosphere as ammonia gas, and into groundwater as nitrate and nitrite, resulting in nitrogen losses. To mitigate these losses, various studies have been conducted on coating urea fertiliser with different materials. Biopolymers, in addition to providing controlled release, also act as soil conditioners by increasing the water-holding capacity of the soil and providing necessary moisture to plants during dry periods. In this study, three different types of biopolymers – chitosan, pectin, and xanthan gum – at two different concentrations (1 % and 3 %), were used to coat urea fertiliser aiming for controlled release. Biopolymer solutions and their cross-linkers were prepared, and the urea fertiliser was coated using a laboratory-scale coating drum. The chemical structure of the coated urea fertiliser was determined using Fourier-Transform Infrared Spectroscopy, and its morphology was examined with a Scanning Electron Microscope. The water-holding capacity in the soil and the ammonia released into the atmosphere were also analysed. The results indicated that the most effective biopolymer coating type for the slow-release mechanism of urea was pectin at a 1 % coating ratio on the fertiliser granules. The concentration of ammonia released from the soil and the water-holding capacity of the soil treated with biopolymer-coated urea fertiliser were tested through various experiments, and the results were analysed statistically. According to the statistical analysis, the 1 % pectin-coated urea fertiliser yielded the best results in both experiments, with an ammonia release value of 246.66 ppm and an evaporation rate of 67.84 % at the end of 30 days.

Keywords
Biopolymer, slow release, urea fertiliser, chitosan, pectin, xanthan gum

1 Introduction

The world population has grown exponentially, reaching approximately 8.0 billion today and is expected to approach 9.5 billion by 2050.[1] With this increase, global food requirements have also risen, and per capita food demand is projected to double by 2050.[2]

In recent years, the world has experienced severe environmental changes, evident in the increased frequency of heavy rains and floods, forest fires, the emergence and spread of new diseases caused by various pathogens and viruses, abnormal bacterial growth, and a rise in insect pests. Greenhouse gas emissions are now recognised as the primary cause of global climate change. The agricultural sector is directly affected by changes in temperature, precipitation, and atmospheric carbon dioxide (CO_2) concentration.[3]

Mineral fertilisers are crucial products for the agricultural industry. They enhance crop growth by providing essential nutrients and play an important role in regulating soil pH and fertility. With the increasing human population and the growing need for food production, the production and consumption of mineral fertilisers has risen accordingly.[4]

Urea fertiliser, formed by the reaction of ammonia and carbon dioxide gas under certain pressure and temperature conditions, contains the highest level of nitrogen, with 46 % nitrogen. It is white, odourless, and has a prill or granular structure.[5]

Urea fertiliser dissolves very easily in water, and rapid dissolution and hydrolisation of urea can result in most of the nitrogen leaching into groundwater without benefiting the soil and plants.[6] Furthermore, bacteria convert the nitrogen in fertilisers into ammonium, a nitrogen form that plants can uptake, but it also releases ammonia gas into the atmosphere.[7]

To reduce the loss of nutrients and enhance nutrient use efficiency (NUE) of fertilisers used in agriculture, recent efforts have focused on developing slow and controlled-release fertilisers (SRF, CRF).[2]

The synthesis of these fertilisers involves various physical or chemical methods, both aimed at slowing nutrient release by controlling diffusion or dissolution.[8]

For urea fertiliser to be as efficient as possible, it should be delivered to plants in a controlled manner. Uncontrolled release can result in nitrogen losses of up to 70 % through evaporation and leaching into groundwater in the form of nitrite and nitrate.[9] Many studies have been conducted in

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recent years on coating urea fertilisers with slow-release polymers to control nutrient release. The goal is not only to reduce nitrogen losses but also prevent greenhouse gas emissions associated with high urea fertiliser consumption.[10] Previous studies have used various polymers to coat urea fertilisers to enhance their slow or controlled release of urea and investigate the release mechanisms in the soil.

The fertilisers are coated with various natural polymers to develop environmentally friendly controlled-release fertilisers. Natural polymers, such as starch, are commonly used due to their low cost and accessibility.[11] In this study, chitosan, pectin, and xanthan gum were chosen as the natural polymers for coating urea fertiliser to determine their effects on urea dissolution by examining the ammonia release from the soil, and the water-holding capacities of the soil.

Chitosan is a linear aminopolysaccharide derived from the (partial) deacetylation of chitin, an essential component of the exoskeleton of crustaceans such as crabs and shrimp.[12] Chitosan is a versatile biopolymer that can be developed in various forms, such as gels, films, nano/microparticles with its features such as biocompatibility, biodegradability and low toxic effect.[13]

Pectin is a high molecular weight carbohydrate polymer known for its very high viscosity. It is valued as a hydrocolloid for its versatile applications in the food and beverage industry (as a gelling, emulsifying, and stabilising agent), the manufacturing industry (for improving composite adhesive coating performance), and the cosmetics industry.[14]

Xanthan gum is a polysaccharide formed by the aerobic fermentation of the sugar of the *Xanthomonas campestris* bacteria species. It is widely used as a food additive due to its properties as a hydrocolloid rheology modifier.[15] Xanthan gum is suitable for a wide variety of applications because of its high stability over a broad temperature and pH range.[16]

In this study, three different types of biopolymers at two different doses were used to coat urea fertiliser granules to determine the most suitable biopolymer and its appropriate dose for the slow release of urea fertiliser in the soil.

2 Experimental

2.1 Materials and methods

Chitosan (low molecular weight, Sigma Aldrich, Germany, CAS number 9012-76-4), pectin from apple (Sigma Aldrich, Germany, CAS number 9000-69-5), and xanthan gum (CP Kelco, Denmark, CAS number 11138-66-2) were used as the coating biopolymers. Epichlorohydrin (Acar Chemicals, Turkey, CAS number 106-89-8) was used as a cross-linker of chitosan and xanthan gum biopolymers. Calcium chloride dihydrate (Merck, Germany, CAS number 10035-04-8) was used as a cross-linker of pectin biopolymer.

Table 1   – Amount of biopolymers and their cross-linkers

Type of biopolymer	Concentration of the biopolymer / %	Cross-linker, ratio / g cross-linker / g biopolymer	Solvent
Chitosan	1	Epichlorohydrin, 0.26	1 % acetic acid solution
	3	Epichlorohydrin, 0.78	
Pectin	1	$CaCl_2$ $2H_2O$, 0.03	Water
	3	$CaCl_2$ $2H_2O$, 0.09	
Xanthan gum	1	Epichlorohydrin, 0.26	
	3	Epichlorohydrin, 0.78	

2.2 Preparation of the biopolymer solutions

100-ml solutions were prepared from chitosan, xanthan gum, and pectin biopolymers at 1 % and 3 % w/w concentrations, respectively. The cross-linkers, which help to manage a more rigid and superabsorbent coating surface on urea granules,[17,18] and solvents suitable for each biopolymer type are listed in Table 1. Solutions were prepared according to Table 1 and placed in a shaker at 70 °C. The solutions were mixed on the shaker at 300 rpm for 3 h.

2.3 Coating of urea fertiliser

The urea fertiliser was prepared for coating by heating it in an oven at 70 °C for 1 h. A laboratory-scale coating drum (Fig. 2), equipped with mixing wings mounted on the inner stainless steel cylindrical surface and a heating system, was used for the coating procedure to simulate the coating mechanism of a large-scale fertiliser coating process. The coating drum was also heated to 70 °C before the coating procedure to maintain the fluidity of the coating solutions, which could easily become lumpy at lower temperatures. Urea fertiliser granules were coated using the biopolymer solutions prepared as described previously and adding a red food colourant to ensure the homogeneity of the coating on the urea granules. The urea fertiliser granules were weighed and placed in the laboratory-scale coating drum, and the biopolymer solutions were injected slowly during rotation through a central hole in the drum. After the entire solution was injected, the hole was plugged closed. The coating drum kept rotating until the entire system cooled to room temperature. After the coating procedure, the coated urea granules were dried in an oven at 70 °C for 4 h to ensure solidification of the biopolymers and remove excess water from the biopolymer solutions.

Table 2 provides information on the concentrations of materials used in the coating of urea fertiliser granules. As indicated in Table 2, for the first experiment, a total of 100 g of coated urea fertiliser was obtained by coating 99 g of urea fertiliser with 1 % chitosan biopolymer solution, aiming to cover the urea fertiliser granules with 1 % chitosan biopolymer. The urea granules before and after coating are shown in Fig. 1.

Table 2 – Materials and quantities used in coating experiments

Sample no.	Type of biopolymer	Amount of biopolymer / g/100 g coated urea fertiliser	Amount of urea fertiliser / g/100 g coated urea fertiliser
1C	chitosan, (C)	1	99
3C		3	97
1P	pectin, (P)	1	99
3P		3	97
1X	xanthan gum, (X)	1	99
3X		3	97

Fig. 1 – Uncoated urea (left) – xanthan gum-coated urea (right). The general appearance of biopolymer-coated urea granules is the same due to the colouring agent used to check the homogeneity of the coatings
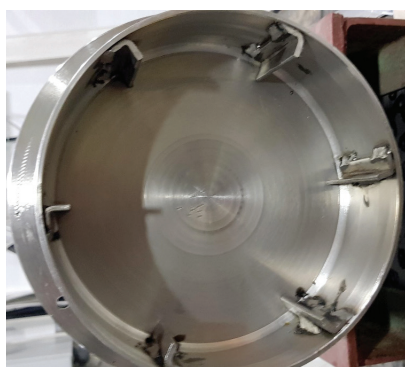

Fig. 2 – Laboratory-scale coating drum

2.4 Measuring equipment

A Fourier transform infrared spectrophotometer (FTIR) (Jasco, FT/IR-6700, Japan) was used to examine the coating efficiency of the coated urea fertilisers. Solid samples were homogenised by mixing them with KBr in a certain ratio. Since KBr does not absorb in the infrared region, it is suitable for use in FTIR measurements.

A scanning electron microscope (SEM) (FEI, Quanta 650 FEG-SEM, USA) was used to observe the coating thickness of the coated fertilisers. The fertiliser samples to be analysed in SEM are gently divided into two with the help

of a razor blade, without damaging the coating. One half of the split fertiliser was covered with a thin metal layer (usually gold or gold-palladium). The coated fertiliser grain was placed in the device, and the coating thickness was measured.

2.5 Method of measurement of released ammonia

The Draeger tubes were used to determine the amount of ammonia released by the material they contain.[19] In plastic containers, the middle of the soil was disinterred and the specified amount of the fertiliser was added, and then the top of the fertilizer was covered with the soil. Subsequently, 30 ml of water was added and the plastic cups were closed with perforated lids. The Draeger tubes were inserted into a hole centred on the cap.

In this experiment, four retests of each sample were conducted. In the experimental system set up with Draeger tubes, the amount of ammonia released every five days was noted in ppm for 30 days.
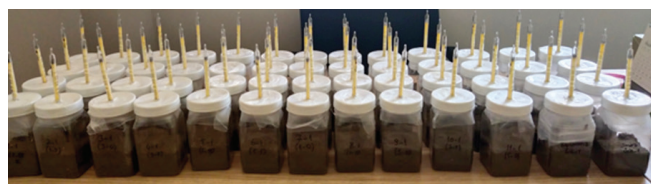

Fig. 3 – Experimental set-up with Draeger tubes

Fig. 4 – (a) View of the Draeger tube, (b) View of the perforated support structure of the Draeger tube

The Draeger tube operates by absorbing the evaporated ammonia and indicating the amount of ammonia evaporated on the Draeger tube in ppm. A photograph of the Draeger tube is provided in Fig. 4(a). The tube has a data range of 20–1500 ppm, as shown. In Fig. 4(b), the tube was broken below the 20 ppm line, and placed in plastic sample cups. Ammonia in the air passing through the tube

is absorbed by the carrier material of the Draeger tube, and the ammonia value in ppm is read directly from the tube.

2.5.1 Measurement of water-holding capacity in soil

Two grams (2 g) of biopolymer-coated urea fertiliser were thoroughly mixed with 200 g of dry sandy soil weighed into a plastic cup, followed by the slow addition of 200 g of tap water into the container. After these processes, the plastic containers opened to the atmosphere were weighed (T1) at 25 °C. The plastic containers were weighed (at 25 °C) on day 4, day 8, day 12, day 16, day 20, day 25, and day 30 (Ti). The evaporation rate ($T\%$) of water in the soil was calculated using the following equation(1).[20]

$$T\% = 100 \cdot (T1 - Ti)/200 \qquad (1)$$

In this experiment, three retests of each sample were conducted.

3 Results and discussion

3.1 Investigation of FTIR and SEM results of biopolymer-coated urea fertiliser

The FTIR spectrum (Fig. 5) of the urea shows a C=O stretching at 1667.16 cm^{-1}, N−H stress and deformation at 3428.81 cm^{-1} and 1589.06 cm^{-1}, and C−N stretching at 1414.53 cm^{-1}.[21] The FTIR spectrum of the chitosan displays an −OH bond at 3283.21 cm^{-1}, a C−H bond at 2868.59 cm^{-1}, and C=O and N−H bond at 1644.02 and 1556.27 cm^{-1}, respectively. In addition, there is a C−O bond at a wavenumber of 1023.05 cm^{-1}.[22] These peaks are also observed in the FTIR spectra of chitosan-coat-

ed urea, with a slight shift confirming the coating of urea fertiliser granules with 1 % and 3 % chitosan biopolymer (Fig. 4).

The wavenumber 3355.53 cm^{-1} in the FTIR spectrum of pectin (Fig. 6), corresponds to the presence of free and intermolecular bonded hydroxyl groups, associated with high amounts of OH groups, as well as symmetrical and asymmetric stretching vibrations related to H_2O molecules. The band at 1730.80 cm^{-1} is attributed to free carboxyl groups. Bands between 1100 and 1200 cm^{-1} represent R-O-R ether and cyclic C−C bonds in the pectin ring structure.[23] The sharp peak at 829 cm^{-1}, observed in both the pectin and pectin-coated urea FTIR spectra, is attributed to the C−H bending of pectin molecules. Peaks in the range of 3000 to 3600 cm^{-1} wavenumber correspond to stretching vibrations of hydroxyl (−OH) groups.[24] Additionally, peaks at wavenumbers 3316 and 3446.17 cm^{-1} correspond to the N−H bonds found in urea fertiliser.[21]

Fig. 6 – Comparative FTIR plots of urea fertilisers coated with 1 % and 3 % pectin, pectin biopolymer, and uncoated urea fertiliser

Upon examination of the FTIR spectrum of the xanthan biopolymer in Fig. 7, the OH stretch is observed at wavenumber 3281.29 cm^{-1}. The characteristic absorption band of xanthan gum, the −OH bond, appears at wavenumber 1015.34 cm^{-1}, which is also evident in the spectra of xanthan gum-coated urea with a blue shift of 8 cm^{-1}. The peak at 1402.96 cm^{-1} in xanthan gum spectra is attributed to the bending of the OH group, which shifts to 1410 cm^{-1} in the spectra of xanthan gum-coated urea. The peak at 1603.52 cm^{-1} wavenumber represents the C=C stretching of the cyclic alkene group.[25] The peak at 1270.86 cm^{-1} is attributed to the stretching of the C−N bond in aromatic amine groups of xanthan gum, which shifts to 1265 cm^{-1} in the spectra of xanthan gum-coated urea.

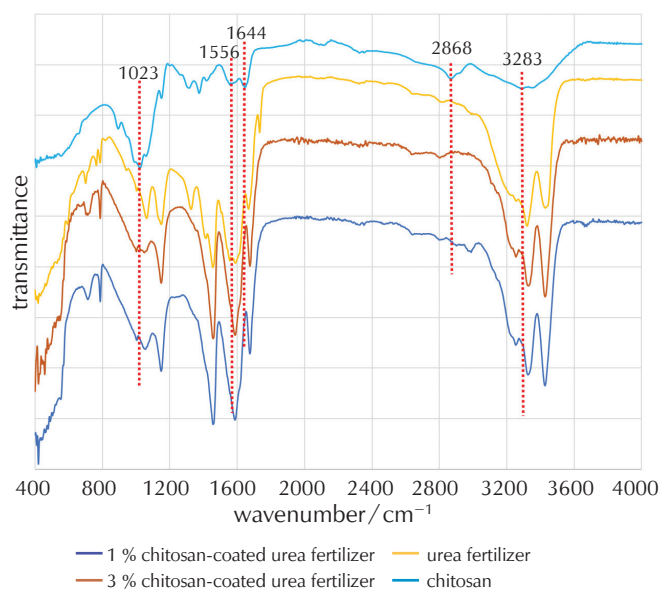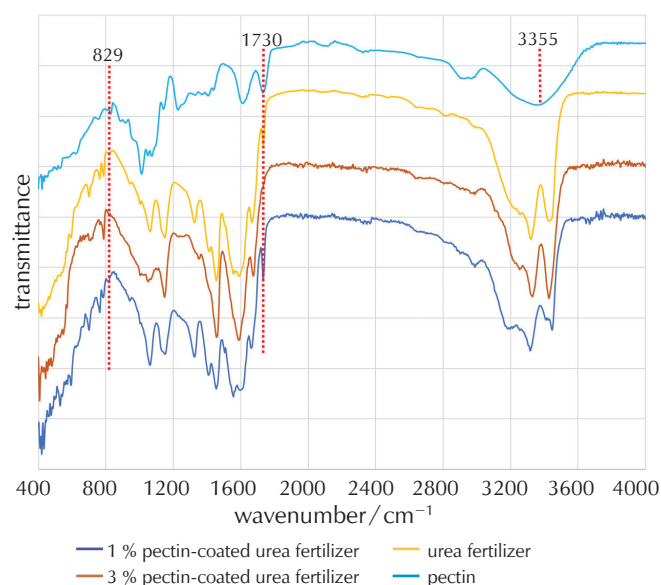*Fig. 5* – Comparative FTIR plots of urea fertilisers coated with 1 % and 3 % chitosan, chitosan biopolymer, and uncoated urea fertiliser
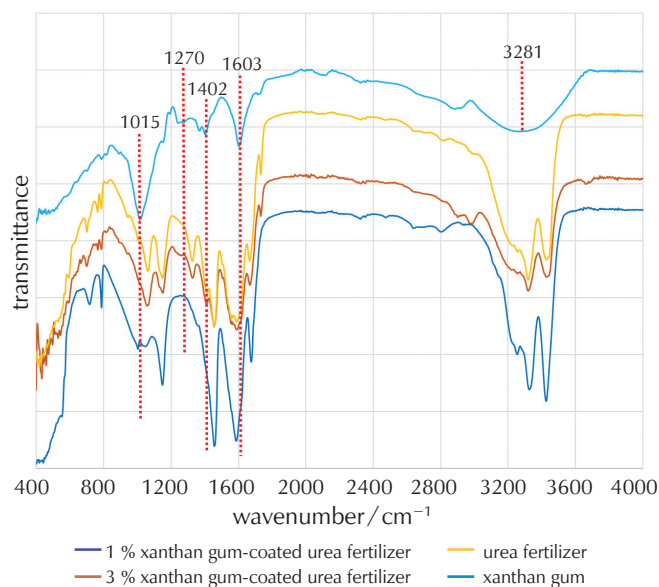
Fig. 7 – Comparative FTIR plots of urea fertilisers coated with 1 % and 3 % xanthan gum, xanthan gum biopolymer, and uncoated urea fertiliser

Fig. 9 – SEM images of urea fertilisers coated with (a) 1 % and (b) 3 % pectin

Upon examination of the SEM images in Fig. 10, it is observed that the average coating thickness of the urea fertiliser granules coated with 1 % and 3 % xanthan gum biopolymer is 4.2 µm and 10 µm, respectively. The poor adhesion of xanthan gum biopolymer to the urea fertiliser is likely due to incompatible surfaces interactions.[27]

Fig. 10 – SEM images of urea fertilisers coated with: (a) 1 % and (b) 3 % xanthan gum

Upon examination of the SEM images in Fig. 8, it is evident that the average coating thickness of the urea fertiliser granules coated with 1 % and 3 % chitosan biopolymer is 40 µm and 61 µm, respectively. The SEM images indicate that the coating thickness of chitosan on urea granules increased with higher coating percentage, but not at a consistent ratio.

3.2 Ammonia release tests

Ammonia release data on different days of all samples examined within the scope of Draeger tube experiments are presented in Table 3. The abbreviations C for chitosan, X for xanthan gum, and P for pectin are used in the table.

The coating type exhibiting the lowest ammonia release after 30 days was 1 % pectin-coated urea fertiliser. Another low ammonia release was observed with 3 % chitosan-coated urea fertiliser. However, higher levels of ammonia release were observed with the other coating types and percentages compared to the uncoated urea fertiliser. The reason why the biopolymer-coated urea fertiliser released more ammonia than uncoated urea fertiliser may be attributed to the water retention properties of the biopolymers as discussed in previous sections. As biopolymers retain water in the soil, it is hypothesised that the water held by the biopolymers aids the faster dissolution of the urea fertiliser encapsulated in the biopolymer coating, thereby increasing ammonia release.
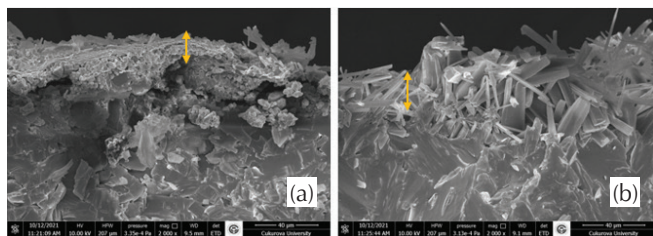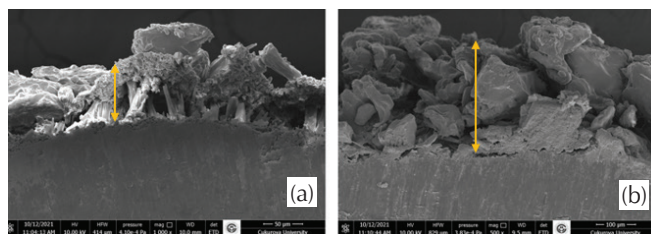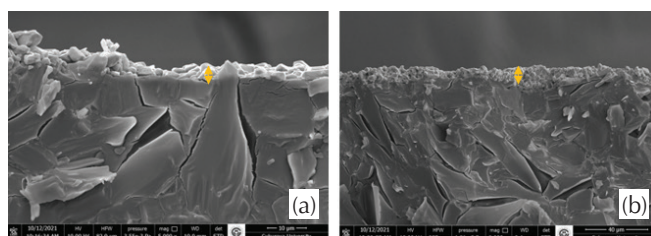

Fig. 8 – SEM images of urea fertilisers coated with (a) 1 % and (b) 3 % chitosan

Upon examination of the SEM images in Fig. 9, it is evident that the average coating thickness of the urea fertiliser granules coated with 1 % and 3 % pectin biopolymer is 98 µm and 306 µm, respectively. The significant adhesion of pectin biopolymer to the urea fertiliser is attributed to its strong adhesion properties.[26]

Table 3   – Ammonia release values obtained during the Draeger tube experiment

Trial types	Day 5 / ppm avg ± std	Day 10 / ppm avg ± std	Day 15 / ppm avg ± std	Day 20 / ppm avg ± std	Day 25 / ppm avg ± std	Day 30 / ppm avg ± std
urea	87.50 ± 25.00	160.00 ± 53.54	227.50 ± 63.44	330.00 ± 95.92	352.50 ± 89.95	372.50 ± 89.95
1C	151.25 ± 79.62	210.00 ± 105.20	297.50 ± 112.66	397.50 ± 124.47	400.00 ± 127.54	430.00 ± 138.80
3C	86.25 ± 30.38	122.50 ± 61.31	193.75 ± 88.07	272.50 ± 129.20	292.50 ± 149.08	312.50 ± 171.93
1P	93.33 ± 40.41	153.33 ± 72.34	201.67 ± 109.81	240.00 ± 121.66	216.67 ± 144.34	246.67 ± 127.02
3P	256.67 ± 183.39	338.33 ± 228.93	386.67 ± 205.02	460.00 ± 191.57	490.00 ± 149.33	500.00 ± 147.99
1X	117.50 ± 63.97	185.00 ± 93.99	262.50 ± 115.00	337.50 ± 121.21	412.50 ± 154.78	432.50 ± 147.28
3X	155.00 ± 69.46	210.00 ± 95.39	283.33 ± 90.74	383.33 ± 119.30	380.00 ± 157.16	406.67 ± 136.50

Table 4   – Evaporation rates of water from the soil

Trial Type/ Time	Day 4 / %	Day 8 / %	Day 12 / %	Day 16 / %	Day 20 / %	Day 25 / %	Day 30 / %
urea	9.58	22.00	32.42	41.41	51.67	64.17	70.09
1C	11.08	25.79	38.99	49.46	59.53	71.58	77.63
3C	9.99	21.67	31.73	40.82	50.54	63.55	69.61
1P	11.82	24.34	33.04	43.58	52.98	63.04	67.80
3P	9.34	24.92	35.37	45.74	56.28	69.68	74.51
1X	11.58	23.53	35.69	46.07	57.84	73.87	79.57
3X	9.90	22.75	33.63	44.52	53.71	67.37	72.30

3.3 Measurement of water-holding capacity of the soil

Polymer-coated fertilisers possess the ability to absorb water in the soil, thus protecting moisture, and facilitating controlled release. This property is attributed to the chemical structure of the polymer, and may vary among different polymers. The goal is to absorb and store the water in the soil, releasing it gradually as soil moisture decreases. Polymer-coated fertilisers that store water act as an additional nutrient reservoir for the plant-soil system, partially extending irrigation cycles, reducing irrigation frequencies, and enhancing drought resistance.[28]

Soil water-holding capacity is crucial for efficient water usage, particularly in arid regions, thereby increasing soil productivity.

In the soil water-holding capacity test, results are expressed in terms of evaporated water. Higher amounts of water evaporation indicate lower water-holding capacity of the soil (Table 4).

The higher the water evaporation rate, the lower the water-holding capacity of the biopolymer used. Upon examination of the data in Table 4, it is evident that 1 % pectin-coated urea fertiliser exhibited the highest water retention capacity among chitosan-coated urea fertilisers after 30 days. The 1 % xanthan gum-coated urea fertiliser displayed the lowest water-holding capacity.

3.4 Statistical analysis of the results

As the results of ammonia release and evaporation rate experiments showed some high standard deviations, statistical analysis was conducted to further examine the experimental results.

General full factorial DOE regression analysis was performed using Minitab 21 statistical software, based on the results of the ammonia release and the water retention experiments, as well as the polymer type and coating ratio.

During the variance analysis, the P-values were examined to represent the probability of obtaining a result at least as extreme as the observed one, assuming the null hypothesis (which suggests no effect or difference) is true.[29] According to the P-values for the coating ratio and polymer type, ammonia release does not depend on either factor individually. However, these two factors are effective when considered together with interaction at a 95 % confidence level (Tables 5-7, and Eq. (2)).

Table 5 – Factor information of ammonia release statistical analysis

Factor	Levels	Value
coating ratio / %	2	1; 3
polymer type	3	chitosan; pectin; xanthan gum

Table 6 – Analysis of variance of ammonia release statistical analysis

Source	DF	Adj SS	Adj MS	F-value	P-value
model	5	126967	25393	1.96	0.157
linear	3	14994	4998	0.39	0.765
coating ratio/%	1	6050	6050	0.47	0.507
polymer type	2	8944	4472	0.35	0.715
2-way interactions	2	111973	55987	4.33	0.038
coating ratio/% *polymer type	2	111973	55987	4.33	0.038
error	12	155299	12942		
total	17	282266			

Table 8 – Analysis of variance of evaporation rate statistical analysis

Source	DF	Adj SS	Adj MS	F-value	P-value
model	5	386.47	77.295	11.34	0.000
linear	3	124.91	41.636	6.11	0.009
coating ratio/%	1	56.23	56.228	8.25	0.014
polymer type	2	68.68	34.341	5.04	0.026
2-way interactions	2	261.57	130.783	19.18	0.000
coating ratio/% *polymer type	2	261.57	130.783	19.18	0.000
error	12	81.81	6.81 7		
total	17	468.28			

Table 7 – Coefficients of ammonia release statistical analysis

Term	Coef	SE Coef	T-value	P-value	VIF
constant	388.0	26.8	14.47	0.000	
coating ratio/%1	−18.3	26.8	−0.68	0.507	1.00
polymer type (chitosan)	−16.8	37.9	−0.44	0.665	1.33
polymer type (pectin)	−14.7	37.9	−0.39	0.706	1.33
coating ratio/% *polymer type					
%1 chitosan	77.2	37.9	2.03	0.065	1.33
%1 pectin	−108.3	37.9	−2.86	0.014	1.33

Table 9 – Coefficients of evaporation rate statistical analysis

Term	Coef	SE Coef	T-value	P-value	VIF
constant	73.476	0.615	119.39	0.000	
coating ratio/%1	1.767	0.615	2.87	0.014	1.00
polymer type (chitosan)	−0.643	0.870	−0.74	0.475	1.33
polymer type (pectin)	−2.005	0.870	−2.30	0.040	1.33
coating ratio/% *polymer type					
%1 chitosan	2.721	0.870	3.13	0.009	1.33
%1 pectin	−5.391	0.870	−6.19	0.000	1.33

Ammonia release (ppm) =
= 388.0 − 18.3 coating ratio $(\%)_1$ + 18.3 coating ratio $(\%)_3$ − 16.8 polymer type$_{chitosan}$ − 14.7 polymer type$_{pectin}$ + 31.5 polymer type$_{xanthangum}$ + 77.2 coating ratio (%)

*polymer type$_{1chitosan}$ − 108.3 coating ratio (%)
*polymer type$_{1pectin}$ + 31.2 coating ratio (%)
*polymer type$_{1xanthangum}$ − 77.2 coating ratio (%)
*polymer type$_{3chitosan}$ + 108 .3 coating ratio (%)
*polymer type$_{3pectin}$ − 31.2 coating ratio (%)
*polymer type$_{3xanthangum}$

(2)

Evaporation rate (%) = 73.476 + 1.767 coating ratio $(\%)_1$ + 1.767 coating ratio $(\%)_3$ − 0.643 polymer type$_{chitosan}$ − 2.005 polymer type$_{pectin}$ +2.648 polymer type$_{xanthangum}$ + 2.721 coating ratio (%)

*polymer type$_{1chitosan}$ − 5.391 coating ratio (%)
*polymer type$_{1pectin}$ + 2.67 coating ratio (%)
*polymer type$_{1xanthangum}$ − 2.721 coating ratio (%)
*polymer type$_{3chitosan}$ + 5.391 coating ratio (%)
*polymer type$_{3pectin}$ − 2.67 coating ratio (%)
*polymer type$_{3xanthangum}$

(3)

Upon examination of the variance analysis, it can be said that the evaporation rate depends on both the coating rate and the polymer type at a 95 % confidence level (Tables 8 and 9, and Eq. (3)).

As the P-values demonstrate, the polymer type (chitosan) has a P-value higher than 0.05, indicating that if chitosan coating is assumed to be effective on the evaporation rate, the risk taken is more than 5 % (the risk value at a 95 % confidence level).

Statistical analysis was performed to evaluate the effect of biopolymers and coating doses used in this research on the slow release mechanism of urea fertilisers. After the variance analysis, a response optimisation analysis was conducted to determine the best formulation that results in the minimum ammonia release and the minimum water evaporation rate (Fig. 9).
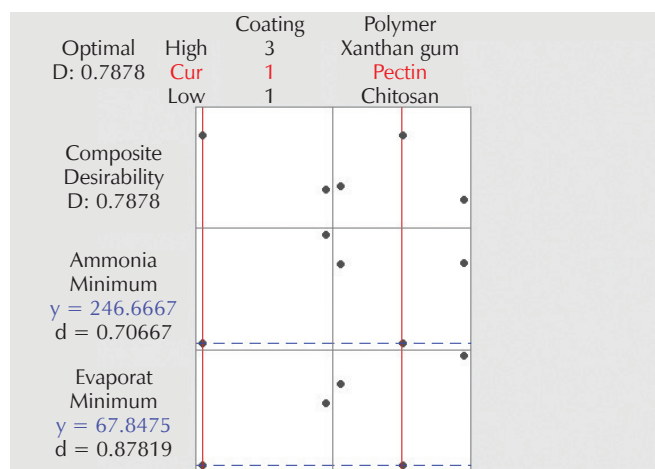
Fig. 9   – Optimisation according to evaporation rate and ammonia release values

The results demonstrate that 1 % pectin-coated urea fertiliser exhibited the best results in both experiments, with an ammonia release value of 246.66 ppm, and an evaporation rate of 67.84 % at the end of 30 days.

4 Conclusion

Coating with biopolymer solutions presents a significant challenge due to the sudden solidification of the polymer solutions, which can cause lumps on the inner surface of the coating drum. Given that a laboratory-scale coating drum was used to simulate the industrial-scale coating process, these lumps could have caused blockage and system failures in larger-scale operations. Therefore, in this study, the coating procedure on a laboratory-scale coating drum was optimised to achieve homogenously coated granules with fewer lumps in the coating drum. This optimisation involved applying different solvents, temperatures, and total material amounts. The optimal coating solution formulas and coating temperature were determined for laboratory-scale drums with a batch capacity of around 200 g. Although the laboratory-scale parameters showed successful results, transitioning to larger-scale studies should be done with detailed consideration.

In this study, urea fertiliser granules were coated with three different biopolymers (chitosan, pectin, and xanthan gum). The chemical properties of the obtained structures were examined using FTIR, and their morphological properties were examined with SEM. The ammonia release from the developed fertilisers was investigated, and their water-holding capacity in soil was measured. Statistical analysis of the results revealed that 1 % pectin-coated urea fertiliser had the lowest ammonia release value and evaporation rate. Additionally, the 1 % pectin-coated urea had a higher nitrogen content compared to the 3% pectin-coated urea, making it advantageous for maintaining higher total fertiliser nitrogen. This resulted in a urea fertiliser with higher nitrogen and a slower release rate.

According to many studies in the literature, slow release of the controlled-release fertilisers is enhanced by coating them with synthetic polymers. However, the use of synthetic polymers in agriculture can cause environmental pollution due to residue accumulation in the soil from long-term use. Therefore, biopolymers are being used to enhance controlled-release properties of fertilisers as an environmentally friendly alternative to synthetic polymers.

The goal of controlled-release fertiliser studies is to minimise the effects of agricultural applications on climate change and contribute to a sustainable economy. This is especially relevant in developing and using environmentally friendly products in the agricultural sector, which aligns directly with the European Union Green Deal Strategy.

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SAŽETAK

Strategija primjene biopolimerne obloge za polagano otpuštanje uree iz gnojiva na bazi uree

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Zbog visoke topljivosti urea gnojiva u vodi, oko 70 % uree biva neiskorišteno od strane biljaka bilo da odlazi u atmosferu (isparavanje) ili podzemne vode (ispiranje tla). Značajan dio uree iz gnojiva otpušta se u atmosferu kao amonijak, dok se u podzemne vode prenosi kao nitrat i nitrit. S ciljem smanjenja tih gubitaka, provedena su brojna istraživanja vezana uz oblaganje gnojiva na bazi uree različitim materijalima. Biopolimeri, osim što omogućuju kontrolirano otpuštanje, oplemenjuju tlo povećavajući njegov kapacitet zadržavanja vode i osiguravajući biljkama prijeko potrebnu vlagu tijekom sušnih razdoblja. U ovom istraživanju, s ciljem postizanja kontroliranog otpuštanja, za oblaganje uree upotrijebljena su tri biopolimera: kitozan, pektin i ksantan guma, u udjelima 1 i 3 %. U tu svrhu pripremljene su biopolimerne otopine i aditivi za poprečno umrežavanje te je gnojivo na bazi uree obloženo pomoću bubnja za oblaganje. Infracrvenom spektroskopijom s Fourierovom transformacijom analizirana je kemijska struktura obloženog gnojiva, dok je morfologija ispitana pretražnom elektronskom mikroskopijom. Analizirani su i kapacitet zadržavanja vode u tlu te količina amonijaka otpuštenog u atmosferu. Količina amonijaka oslobođena iz tla i kapacitet zadržavanja vode u tlu tretiranom gnojivom na bazi uree obloženim biopolimerom ispitani su raznim eksperimentima, a rezultati su podvrgnuti statističkoj analizi. Rezultati su pokazali da je oblaganje granula gnojiva biopolimerom pektinom u udjelu od 1 % najdjelotvornije s 246,66 ppm oslobođenog amonijaka i stopom isparavanja od 67,84 % nakon 30 dana.

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