

Lignin and Ethylcellulose as Polymers in Controlled Release Formulations of Urea

M. Fernández-Pérez, F. J. Garrido-Herrera, E. González-Pradas, M. Villafranca-Sánchez, F. Flores-Céspedes

Department of Inorganic Chemistry, University of Almería, La Cañada de San Urbano s/n Almería 04120, Spain

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ABSTRACT: Lignin and ethylcellulose (EC) have been used for the preparation of controlled release (CR) formulations of urea. The lignin matrixes were prepared by mixing the urea with kraft lignin (UL) under melting conditions. They were also crushed and sieved to obtain granules of size between 0.5–1, 1–2, 2–3 and 3–5 mm. The coated urea granules were produced in a Wurster-type fluidized-bed equipment, using an ethanolic solution of EC on two different polymer levels. Having researched the encapsulation efficiency (EE) and the homogeneity of the CR formulations, kinetic-release experiments were carried out in water. A high EE was reached, it oscillated between 95.12% for the system coated with 20% of EC and 97.18% for the $1 \text{ mm} < d < 2 \text{ mm}$ UL system. The rate of urea release from CR granules diminished in all cases in relation to nonformulated urea, being the latter completely dissolved in less than 0.5 h, but it took at least 48 h to

release the 90% of urea from the EC coated formulations. Using an empirical equation, the time taken for 50% of the active ingredient to be released into water (T_{50}) was calculated. From the analysis of the T_{50} values, we can deduce that the release rate of urea can be controlled mainly by selecting the granule size for lignin CR systems and changing the thickness of the coating film for EC coated granules. The variation order of T_{50} values, UL ($0.5 \text{ mm} < d < 1.0 \text{ mm}$) < UL ($1.0 \text{ mm} < d < 2.0 \text{ mm}$) < UL ($2.0 \text{ mm} < d < 3.0 \text{ mm}$) < UL ($3.0 \text{ mm} < d < 5.0 \text{ mm}$) < UEC₁₀ < UEC₂₀, showed that the presence of EC in formulations retarded the release of urea in relation to those prepared with lignin. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3796–3803, 2008

Key words: ethylcellulose; lignin; controlled release; urea

INTRODUCTION

The aims of controlled release (CR) formulations not only in drugs^{1–3} but also in pesticides,^{4–6} fertilizers,^{7–9} or other substances are to diminish the active ingredient cost, to allow the release of the chemical agent to the target at a controlled rate, and to maintain its concentration in the system within the optimum limit, over a specified period of time, thereby providing highly-improved specification, minimizing the adverse effects, and optimizing its effectiveness.^{10,11} The parameters that affect the properties of CR formulations depend on the nature and type of polymer used. In spite of several polymers employed in CR formulations in agriculture, natural polymers such as starch, ethylcellulose, lignin, chitosan, and alginate are preferred to synthetic polymers because of their nontoxic, low cost, free availability, and biodegradability characteristics.^{6,12–15}

The use of nitrogen and phosphorous fertilizers is an essential input for the sustainability of agriculture. Among the nitrogenous fertilizers, the most widely used is urea. The high solubility of urea causes several agronomic and environmental problems.^{16,17} One of the methods to effectively check these problems is to prepare CR polymers formulations.

Previous encapsulation studies of agrochemicals using biodegradable polymers and modifiers^{4,6,13,18} showed that it was necessary to develop and optimize the preparation of CR formulations to encapsulate active ingredients with high solubility water values such as nitrogen fertilizers.

The purpose of this article was to research the preparation and characterization of urea CR matrixes and urea coated CR granules using two natural polymers such as lignin and ethylcellulose (EC). Lignin is a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap, and a currently underutilized resource that has shown potential in preparing CR formulations.^{13,19–21} EC is one of the most widely-used polymers in film coating because of many advantages it affords formulators, such as good film formability, excellent physical-chemical stability, minimum toxicity, and so on.²²

Correspondence to: M. Fernández-Pérez (mfernand@ual.es).

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In the present study, CR formulation was prepared by mixing the urea with kraft lignin under melting conditions. Moreover, coated urea granules were produced in a Wurster-type fluidized-bed equipment, using an ethanolic solution of EC on two different polymer levels. The characteristics of the CR fertilizer granules were tested and kinetic-release experiments were carried out in water in order to determine the release characteristics of the CR granules.

EXPERIMENTAL

Materials

The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco Corp., Charleston, SC). Thermal behavior of lignin was determined by using thermogravimetric analysis (TGA) (TA instruments, TGA 2950). TGA measurements were carried out at a 20°C/min heating rate in the range of 25–700°C under air atmosphere with a flow rate of 50 mL/min. Technical grade urea (99%) was supplied by Panreac S.A. (Barcelona, Spain). Urea pellets (99%) were obtained from Fluka Chemie AG (Buchs, Switzerland). Urease, activity (urea; pH: 6.1; 30°C) ≥ 5 U/mg, was from Merck KGaA (Darmstadt, Germany).

The film-forming material of polymer coating was EC (Ethocel[®]; ethoxy content, 48.0–49.5%; viscosity, 9–11 cp). This product was supplied by Fluka Chemie AG (Buchs, Switzerland). Ethanol and methanol used were of analytical grade, purchased from Panreac S.A. (Barcelona, Spain).

Lignin-based formulations

The CR granules were formed by mixing the lignin and technical grade urea in the ratio [1 : 1 (w/w)] using a glass reactor inserted in a thermostatic bath filled with silicone oil (model Tectron L by Selecta S.A., Barcelona, Spain). The mixture was heated under melting conditions at 135°C for 20 min. On cooling, the glassy matrixes were crushed in a hammer mill and then sieved to obtain granules of size between 0.5–1, 1–2, 2–3 and 3–5 mm. A UL is a code used for the formulations, where U represents the active ingredient (urea) and L is the pine kraft lignin.

Ethylcellulose coated granules

Fifty grams of urea pellets U, (size fraction, 1–2 mm) were loaded into a fluidized-bed coater (Mini-Glatt, Glatt AG, Pratteln, Switzerland) assembled with a Wurster device. The bed temperature was adjusted at (60 \pm 2)°C. The granules were preheated at this temperature for 10 min. Coating solution was deliv-

ered by a peristaltic pump (Watson-Marlow, Model 1B-1003/R) and sprayed into the fluidized-bed via spray nozzle at the atomizing pressure of 1.2 bars. 100 or 200 mL of 5% EC solution in ethanol were pumped with a flow rate of 2.5 mL min⁻¹ or 5 mL min⁻¹, respectively. The total spraying time was 40 min. The coated granules were then dried in the same apparatus at 70°C for 10 min. The coating film consists of 10% EC (UEC₁₀) and 20% (UEC₂₀) from the weight of the dry granules.

Granules characterization

The actual concentration of urea in the UL granules was determined by dissolving 20 mg of the granules in 50 mL of methanol in an ultrasound bath for 15 min. This led to the complete disintegration of the granules. The volume was made up to 100 mL with ultra pure water, and 1 mL of the resulting solution was diluted with 25 mL of water and 5 mL of fresh urease solution 1% (w/v). This solution was placed in stoppered conical flasks and shaken in a thermostated bath at (25 \pm 0.1)°C. Preliminary experiments were conducted for various time intervals to determine when the total hydrolysis of urea to NH₄⁺ was reached. The time required for hydrolysis was 2 h. Then, the solution was diluted to 100 mL with water. The resulting extract was filtered using nylon filters (0.20 μ m), and ammonium concentrations were determined by capillary electrophoresis (CE) using a Beckman CE system (P/ACE 5000) equipped with a UV detector and data station. The CE operating conditions to analyze ammonium ions were described by Arce et al.²³ Electropherograms were recorded with indirect UV detection at 214 nm for ammonium ions. Three replications were carried out for each formulation.

For the coated granules, the urea concentration was determined by dissolving 20 mg of the granules in 5 mL of absolute ethanol followed by extraction into ultra pure water + ethanol (90 + 10 by volume). The resulting extract was treated as the same method described above to determine the ammonium concentration. Three replications were carried out for each formulation.

The average diameter of granules was determined using a Stereoscopic Zoom Microscope from Nikon, model SMZ1000, provided with a camera PixelLINK (Megapixel FireWire Camera) model PL-A662.

The morphological and structural surface of lignin matrix and EC coated granules were examined with the aid of a Hitachi S-3500-N scanning electron microscope (SEM) at the required magnification at room temperature. The granules were deposited on brass hold and sputtered with a thin coat of gold under vacuum. Acceleration voltage used was 10 kV with secondary electron image as a detector. To

TABLE I
Characteristics of Controlled Release Granules Containing Urea ($1\text{ mm} < d < 2\text{ mm}$)

Formulation	Urea (%)	Average Weight (mg/granule)	Average diameter (mm/granule)	EE ^a (%)
UL	48.11 (0.12) ^b	2.79 (0.11)	1.42 (0.06)	97.18
UEC ₁₀	88.59 (0.15)	3.92 (0.09)	1.71 (0.08)	97.02
UEC ₂₀	80.44 (0.32)	4.25 (0.13)	1.78 (0.03)	95.12

^a Encapsulation efficiency = (amount of urea in dry product/amount of urea in formulation processed) \times 100.

^b Values in brackets represent the standard deviation.

examine the internal morphology of the polymeric films, coated granules were carefully cut with the aid of a chisel and their cross sections were photomicrographed. The thickness of the prepared films was measured. Each film sample was measured at 10 different points.

Water release kinetics

For each sample (two replications), an accurately weighed quantity of granules containing about 150 mg of urea was added to 100 mL of ultra pure water and placed into stoppered conical flasks. Flasks were maintained in a thermostated bath at $(25 \pm 0.1)^\circ\text{C}$. At different time intervals, aliquots of 1 mL were removed for determination of urea and 1 mL of fresh water was added to the flasks.

RESULTS AND DISCUSSION

Granules characterization

Characteristics of CR granules ($1\text{ mm} < d < 2\text{ mm}$) containing urea are presented in Table I. The percentages of active ingredient oscillate between 48.11% for the system UL and 88.59% for the system UEC₁₀, being the active ingredient of the granules adequate for agricultural practice. It can be observed that the values of encapsulation efficiency (EE) are 95.12% for the system UEC₂₀, 97.02 for the system UEC₁₀ and 97.18% for the system UL. These data highlight the efficacy of the methods used for the encapsulation of urea.

From Figure 1, where the lignin thermogram is shown, we can observe that the maximum of thermal decomposition appears at $\sim 500^\circ\text{C}$, so at the temperature of lignin matrix preparations (135°C) no thermal decomposition was carried out. To predict compatibility of urea with lignin, the solubility parameter, determined according to a group contribution method²⁴ has been used. The solubility parameter of urea was estimated as being $43.95\text{ MPa}^{1/2}$, which is higher to that showed by Barton²⁵ for kraft lignin ($20\text{--}24\text{ MPa}^{1/2}$). Nevertheless, according to

Schuerch,²⁶ the most important solvent property for lignin solubility is the hydrogen bonding capacity. Functional groups such as carbonyl and amino, present in urea, are capable of forming hydrogen bonds with hydroxyl, ether, and carbonyl groups of lignin increasing the compatibility between urea and lignin.

To obtain further information about the morphology and distribution of urea in the urea-lignin matrix and EC coated granules SEM images of granules were obtained.

Figure 2 shows the surface evolution of UL ($1\text{ mm} < d < 2\text{ mm}$) matrix before water immersion [Fig. 2(a,d)] and after 0.5 h of water immersion [Fig. 2(b,e)] and after a total release of urea [Fig. 2(c,f)]. From Figure 2(a) it can be seen that the surface of UL matrix is coarse and porous, which it increased the surface area of UL matrix. Figure 2(d) shows a homogeneous distribution of urea crystals in the lignin matrix which were identified through an X-ray microanalysis in the intact granules. Figure 2(b,c,e,f) show a higher amount of crack, holes, and pores as release time increased. This fact could be due to the higher amount of urea released and the effect of swelling and dehydration process as suggested by Cotteril et al.²⁷

SEM pictures from coated granules (Fig. 3) shows a uniform and intact coating of EC. The disappear-

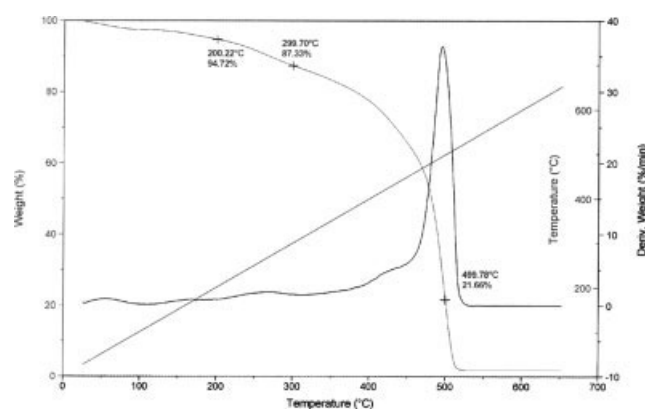


Figure 1 TGA curve of the kraft lignin Indulin AT.

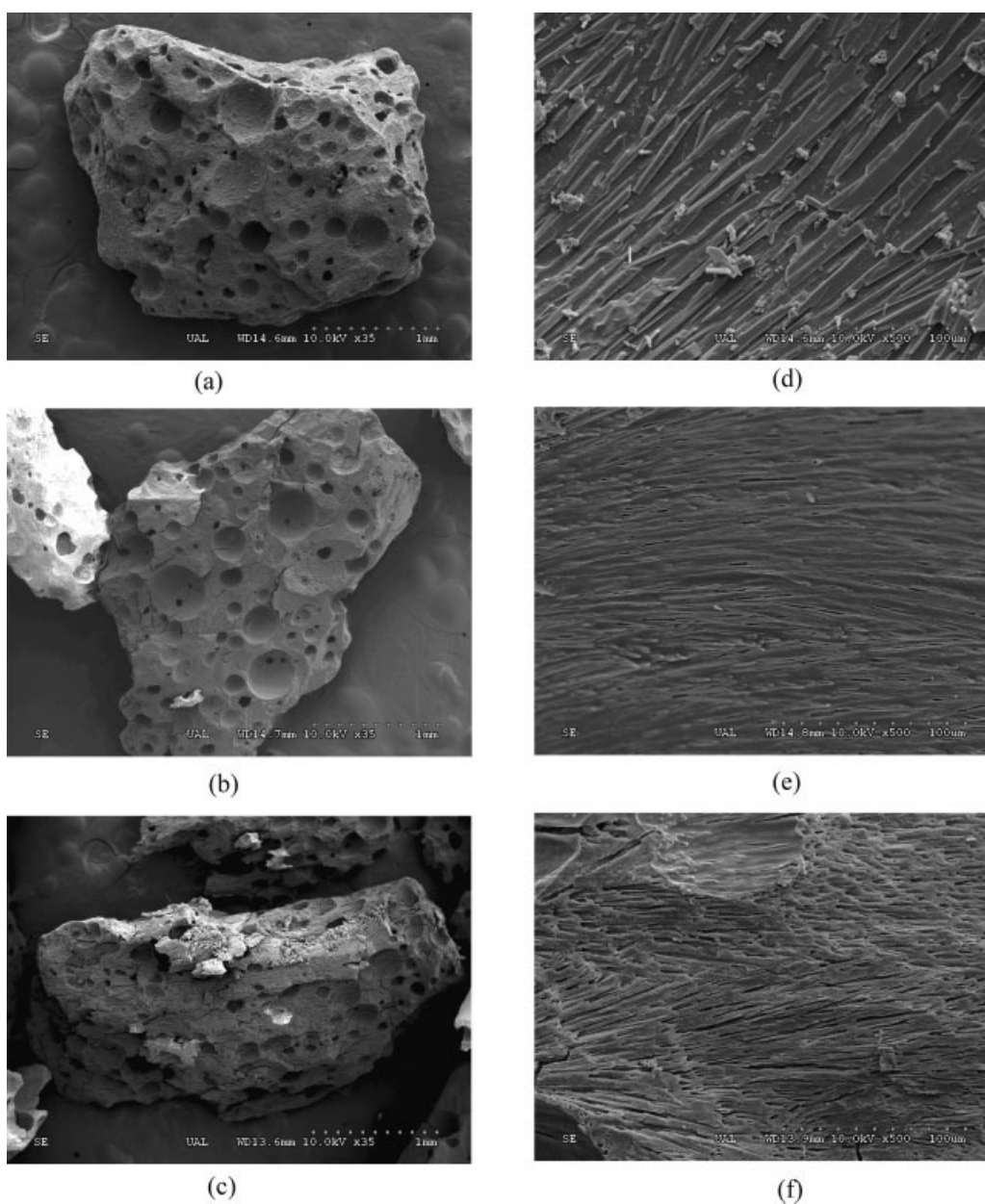


Figure 2 Scanning electron microscopic photographs of UL ($1 \text{ mm} < d < 2 \text{ mm}$), intact granule (magnification, $\times 35$) (a), surface morphology of intact granule (magnification, $\times 500$) (d), granule after 0.5 h water immersion (magnification, $\times 35$) (b), surface morphology of granule after 0.5 h water immersion (magnification, $\times 500$) (e), granule after total urea release (magnification, $\times 35$) (c) and surface morphology of granule after total urea release (magnification, $\times 500$) (f).

ance of the wrinkled aspect that the external surface of urea pellets possesses [Fig. 3(a)] and the existence of a fine film in the coated formulations can be observed in Figure 3(b,c). The cross-section on coated formulations showed the porous core structure with a coherent film at the boundary of the granules [Fig. 3(e,f)]. The thickness of the coating material, covering urea granule, was estimated using a SEM photographs. The thickness of the coating films are $33.3 \mu\text{m}$ for the system UEC_{10} and $55.6 \mu\text{m}$ for the system UEC_{20} , respectively.

Water release kinetics

The cumulative release of urea from lignin matrixes besides with the check out curve of technical grade urea are shown in Figure 4. The study carried out with technical grade urea showed that the urea was completely dissolved in less than 0.5 h. The rate of urea release from CR granules diminishes in all cases in relation to technical grade urea. This fact could be so because of the lignin formulations containing finely divided urea particles, which are

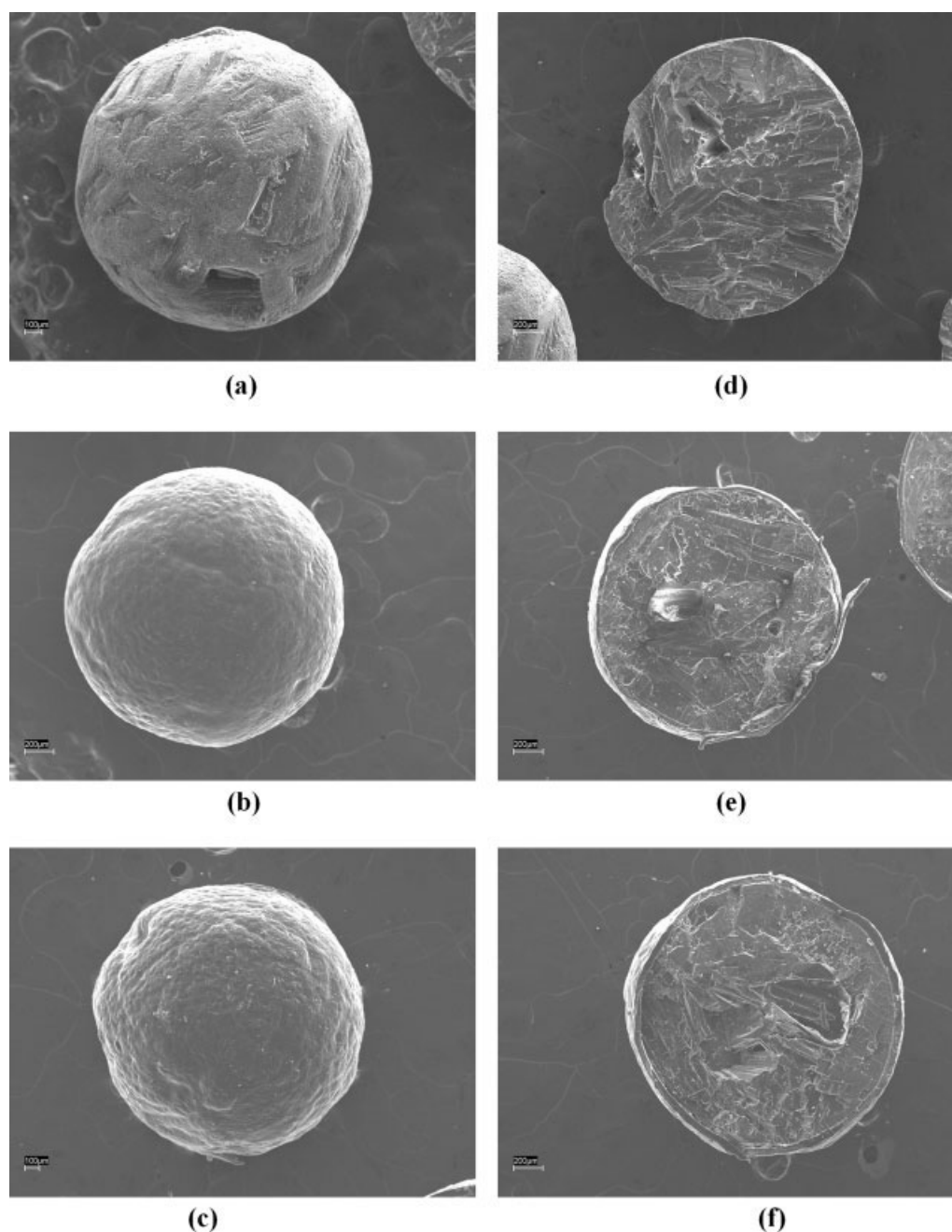


Figure 3 SEM of shape and external morphology: (a) urea pellets, (b) UEC₁₀, (c) UEC₂₀. The remaining ones show the internal morphology: (d) urea pellets, (e) UEC₁₀, (f) UEC₂₀.

uniformly dispersed within the matrix phase as it has been shown by SEM studies. For all formulations, a decrease in the release of urea over time was observed. This result is probably due to an increase in the distance where dissolved molecules have to diffuse as the depleted zone advances to the center of the matrix. As it can be seen from Figure 4, an important repercussion over the urea release rate is observed as the CR matrixes size increases from UL $0.5 \text{ mm} < d < 1.0 \text{ mm}$ up to UL $3.0 \text{ mm} < d < 5.0 \text{ mm}$. The bigger granule size (UL $3.0 \text{ mm} < d < 5.0 \text{ mm}$)

results in a slower release of urea. This was as expected due to a lower surface area of the matrix being exposed to water, with a longer distance over which the urea must be diffused from the center of the matrix. Similar results were obtained for the release of different pesticides from granules based on a lignin matrix system.^{13,27}

In Figure 5, the cumulative release of urea from pellets and EC coated granules are shown. The two CR granules UEC₁₀ and UEC₂₀ produce a decrease in the process of dissolution of the active ingredient

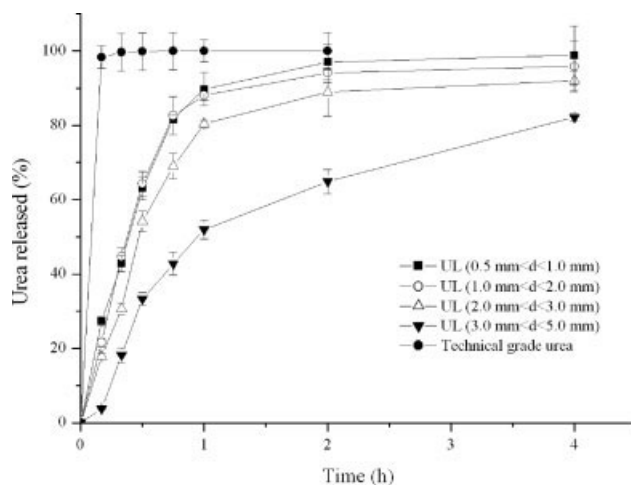


Figure 4 Cumulative release of urea from lignin matrix into water (error bars represent the standard deviation of two replicates).

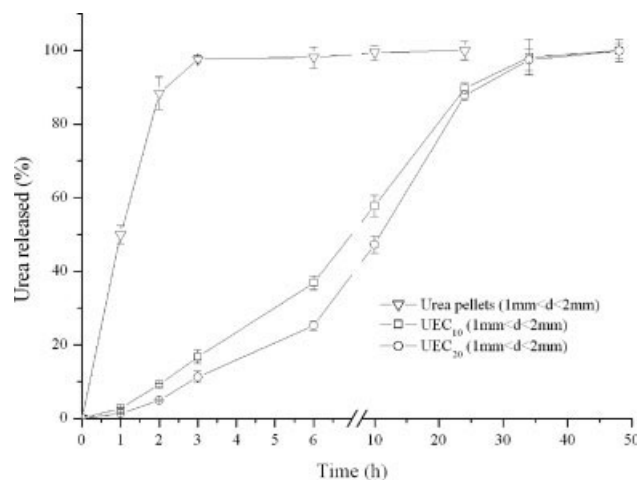


Figure 5 Cumulative release of urea from EC coated granules into water (error bars represent the standard deviation of two replicates).

in relation to the urea pellets. From the release curves of the two CR granules, we can observe an initial part of the curve during which low release rate is observed, followed by a constant release step and finally a stage of gradual decay of release rate. Similar behavior was reported by others with polymer coated chemicals.^{28–30} As expected, the highest quantity in polymer of the UEC₂₀ formulation increases the thickness of the coating film, and so causes the highest delay in release rate. Besides, the diffusion of water through the membrane is slowed down as membrane thickness increases. This behavior has also been observed by other authors.^{8,22,31}

To obtain a parameter to compare the behavior of CR granules prepared as lignin matrix and EC coated granules, the kinetics release data of urea in water were analyzed by applying the empirical equation proposed by Ritger and Peppas.³²

$$\frac{M_t}{M_0} = Kt^n$$

M_t/M_0 is the percentage of active ingredient released at time t , K is a constant that incorporates characteristics of the macromolecular network system and the

active ingredient, and n is a diffusional parameter which is indicative of the transport mechanism.

The values of K and n obtained from the 90% of the maximum urea released in water are presented in Table II. There was good correlation of the release profiles of CR urea granules with the empirical equation, the correlation coefficient (r) being higher than 0.98.

The time corresponding to release 50% of urea, T_{50} , was calculated for the granules using the constants from Table II. The values ranged from 0.40 h for UL ($0.5 \text{ mm} < d < 1.0 \text{ mm}$) granules up to 9.47 h for UEC₂₀ granules. The variation order is as it follows UL ($0.5 \text{ mm} < d < 1.0 \text{ mm}$) < UL ($1.0 \text{ mm} < d < 2.0 \text{ mm}$) < UL ($2.0 \text{ mm} < d < 3.0 \text{ mm}$) < UL ($3.0 \text{ mm} < d < 5.0 \text{ mm}$) < UEC₁₀ < UEC₂₀.

This variation order shows that the presence of EC in formulations retards the release of urea in relation to those prepared with lignin. This fact could be so because of the EC coated granules prepared in this research consist of homogeneous films of EC which coat urea pellets. These coated granules absorb water slowly and produce a retard in the check out process of urea in the granules. Later once urea has been dis-

TABLE II
Constants from Fitting the Empirical Equation $M_t/M_0 = Kt^n$ to Release Data of Urea in Water

Formulation	$K \cdot 10^2(\text{h})^{-n}$	n	r	$T_{50}(\text{h})$
UL ($0.5 \text{ mm} < d < 1.0 \text{ mm}$)	94.69 ± 0.025^a	0.70 ± 0.013	0.989^b	0.40
UL ($1.0 \text{ mm} < d < 2.0 \text{ mm}$)	86.68 ± 0.026	0.88 ± 0.017	0.990^b	0.53
UL ($2.0 \text{ mm} < d < 3.0 \text{ mm}$)	84.39 ± 0.014	0.93 ± 0.011	0.997^b	0.57
UL ($3.0 \text{ mm} < d < 5.0 \text{ mm}$)	67.51 ± 0.047	1.45 ± 0.020	0.985^b	0.81
UEC ₁₀	3.32 ± 0.016	1.31 ± 0.016	0.991^b	7.91
UEC ₂₀	1.65 ± 0.008	1.52 ± 0.021	0.993^b	9.47

^a These values represent the standard error.

^b Significant at the 0.001 probability level.

solved; it is diffused through the film and released in water. From the T_{50} data for systems with EC, UEC₁₀ and UEC₂₀, we see that the value of T_{50} is higher in the system with a major EC percentage (UEC₂₀). It is so due to the higher coated thickness. Others have found that in coated fertilizers, the time need for the delivery of active ingredient increases uniformly with the coated thickness.^{9,29}

If we observed the T_{50} values obtained for lignin CR matrixes, we would notice that the T_{50} value increases as the matrix size increases as well showing that the UL (3.0 mm < d < 5.0 mm) granule is the highest T_{50} value, which means the slowest urea release. This behavior is related to the results of studying imidacloprid release from lignin matrix,¹³ where the T_{50} values increase as the diameter of the matrixes grows.

As related earlier, it seems that the size of lignin matrixes is the most influential factor that affects the release rate of urea. So, the T_{50} values of lignin CR granules were correlated with the average diameter of granules (D) (Table III). Figure 6 shows the plot of the T_{50} values versus the D values of the matrixes. The analysis indicates that T_{50} values are well-correlated with the D values of formulations. The equation of linear correlation and correlation coefficient were obtained by applying the least-squares method to the data.

$$T_{50} = 0.10 \times D + 0.35 \quad (r = 0.971) \quad (P = 0.03) \quad (1)$$

From the linear correlation obtained, the release of urea from a system of similar structure to those used in our experiments could be readily predicted from the D values used in the formulations prepared.

Using the T_{50} values in water for lignin and EC urea CR granules besides with the equations proposed by Ali and Wilkins³³ and Pérez García et al.,⁹ where the characteristics of release into soil conditions were related to those obtained by release into water, we will note the behavior of CR formulations prepared in soils. And, therefore, this study might be useful for selecting the most appropriate formulation, depending on the environmental factor that affects urea release in soils.

TABLE III
Average Diameter for Each Size Fraction
of Lignin Based Granules

Formulation	Diameter (mm)
UL (0.5 mm < d < 1.0 mm)	0.68
UL (1.0 mm < d < 2.0 mm)	1.42
UL (2.0 mm < d < 3.0 mm)	2.85
UL (3.0 mm < d < 5.0 mm)	4.60

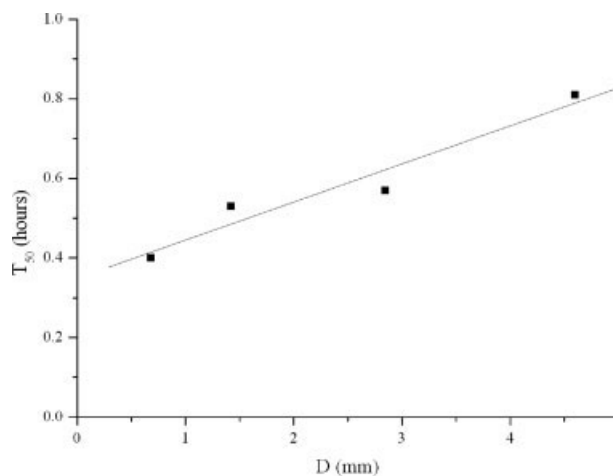


Figure 6 T_{50} values of UL matrixes obtained from water release kinetics versus average diameter of granules (D).

CONCLUSIONS

Urea has been successfully encapsulated using EC and lignin to obtain urea coated granules and monolithic systems respectively. In both, high EE values for urea have been obtained. The use of CR granules reduces the release rate of urea in comparison with the technical grade urea and commercial urea pellets. The EC coated granules have release profiles slower than lignin matrixes. The release rate can be controlled by adjusting the EC content in coated granules or by selecting the granule size for CR lignin matrixes. A linear regression of the T_{50} values and the granule size has been obtained in lignin matrixes.

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