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Use of Kraft Pine Lignin in Controlled-Release Fertilizer Formulations

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Lignin was used as a majority component in a controlled-release fertilizer coating, since this waste product displays properties that make it an ideal substance for application in soil together with conventional mineral fertilizers. Pine lignin marketed under the name of Indulin AT and obtained by the Kraft process was used. Insoluble in water for all pH values that may occur in soil, this product was employed for coating pelleted urea. Seven series of fertilizer were obtained, which also contained various types of rosins and in some cases linseed oil as additives. The physical–chemical evaluation of these fertilizers showed that the most efficient are those whose coating embodies a mixture of dimerized, esterified, and natural rosins, as well as lignin. It was also demonstrated that the efficiency of the products noticeably increases by adding linseed oil as a sealing agent.

Introduction

The efficiency of nitrogenous controlled-release fertilizers (CRFs) is usually greater than that of conventional fertilizers in media where major water losses occur through drainage (Vallejo et al., 1993). One way to prepare CRFs is to coat soluble fertilizers with an insoluble material. The nutrient is released slowly through surface pores or cracks (Jiménez, 1992). Coatings used for this purpose must have two additional properties: they must be biodegradable in soil and not leave toxic substances behind which will affect crops (Hignett, 1985).

As a low-cost waste product in the paper pulp manufacturing process, lignin is a material that may be ideal for application to soil together with soluble fertilizers (Truskin and Kadyrov, 1978) since, according to Martin and Haider (1992) and Stevenson (1982), when embodied into soil, it acts as a humic acid precursor substance. Flaig (1984) proved that lignin reduces the nitrification rate of urea, enabling this compound to remain in the soil longer.

The purpose of this paper was to study the possibility of using lignin as a coating for soluble fertilizers in preparing more controlled-release fertilizers. Seven series of CRFs were prepared by coating pelleted urea with Kraft pine lignin, several types of rosin, and, in some cases, linseed oil. An additional aim was to evaluate the influence of the type of coating and its percentage on the product's solubilization rate and on physical properties related to the handling, transport, and subsequent use of the fertilizer (More, 1978).

Materials and Methods

Lignin-coated controlled-release fertilizers were prepared in the laboratory per the process described in Spanish Patent No. 536567 (Jiménez et al., 1984). The base fertilizer used was pelleted urea with 46% nitrogen richness. The lignin embodied into the coating is marketed under the name of Indulin AT and is a purified Kraft pine lignin completely free of hemicellulose products and water insoluble for all possible pH values a soil may display. Natural, dimerized (Residys Polymer) and esterified (Resiester T) rosins were used as the lignin's adhesive. Linseed oil was used as an adhesive or sealant in preparing some products.

Components of the products obtained were separated by selective solubilization processes. Urea was water solubilized and its content was determined by the Kjeldhal method (AOAC, 1990). Benzene-dissolved rosins were jointly evaluated by visible–ultraviolet spectrophotometry using a UV-160 Model Shimadzu spectrophotometer. The same method was employed to analyze the lignin content by using dioxane as solvent.

The urea release curve was characterized in each of the products obtained as a function of time, at a constant temperature of 20 °C (Jiménez et al., 1993). To do so, 0.5 g of each fertilizer was placed in test tubes and 10 mL of distilled water was added. When the time for each test had elapsed, the samples were filtered and the urea content was analyzed in each filtrate by visible spectrophotometry using *p*-(dimethylamino)benzaldehyde in a hypochlorite medium (AOAC, 1990). All tests were performed in triplicate, and the average value was taken as the result.

The type of release kinetics and the constant of release rate for the urea release process were determined in each case by mathematically processing the experimentally obtained data. It is thus possible to characterize and compare the different fertilizers with each other.

Physical properties were studied by performing tests on some of the fertilizers prepared: grain size (Kelly, 1974), crushing strength (TVA, 1970), apparent density (USDA, 1977), critical relative humidity (Hoffmeister, 1979), humidity absorption rate, and microphotographic study of the coating, enabling its thickness to be measured and its surface to be examined by metal coating the fertilizer pellets and using an ISI Sx-25 electron scanner microscope.

Results and Discussion

1. Composition of the Fertilizers. Table 1 shows the composition of all fertilizers prepared, expressed as a percentage of their components. A figure has been inserted in the nomenclature of each product referring to its coating percentage.

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Table 1. Description of the Composition of the Base Urea Fertilizer Products Expressed as % of Their Components

series	fertilizer	coating	nitrogen	lignin	total rosin	Residis polymer[a]	Resiester T[a]	natural rosin	oil
ULI	ULI-20	20	36.2	12.3	7.7	7.7			
	ULI-25	25	33.9	15.2	9.8	9.8			
	ULI-32	32	30.7	22.3	9.7	9.7			
	ULI-40	40	27.0	24.1	15.9	15.9			
ULII	ULII-20	20	36.2	11.3	8.7	4.3	4.3		
	ULII-25	25	33.9	13.7	11.3	5.6	5.6		
	ULII-30	30	31.6	17.5	11.5	5.7	5.7		
ULIII	ULIII-16	16	38.0	9.6	6.4	2.1	2.1	2.1	
	ULIII-22	22	35.3	13.9	8.1	2.7	2.7	2.7	
	ULIII-29	29	32.0	19.2	10.1	3.3	3.3	3.3	
ULIIA	ULIIA-31	31	31.2	17.5	11.5	5.7	5.7		2.0
	ULIIA-33	33	30.2	18.1	11.5	5.7	5.7		3.4
ULIIIA	ULIIIA-18	18	37.1	10.2	6.4	2.1	2.1	2.1	2.0
	ULIIIA-34	34	29.8	19.8	10.1	3.3	3.3	3.3	5.0
ULA	ULA-12	12	39.8	6.6					5.4
	ULA-16	16	38.0	9.2					7.0
ULCA	ULCA-13	13	39.5	7.1	3.0	1.0	1.0	1.0	2.9
	ULCA-19	19	36.6	11.1	3.9	1.3	1.3	1.3	4.0
	ULCA-23	23	35.0	13.4	4.8	1.6	1.6	1.6	4.8

[a] Commercial products from Unión Resinera Española, S.A.

2. Urea Release Rates in Water at a Constant Temperature of 20 °C. 2.1. Series ULI, ULII, and ULIII. Figure 1 shows urea release from the series ULI, ULII, and ULIII, respectively, as a function of time. The rate of urea release diminishes in all cases as the percentage of each series' coating increases. As an exception, the ULI series is seen to behave in a fairly similar way to the two thickest coated products: ULI-32 and ULI-40. This may be due to the fact that, when the coating percentage reaches this order of magnitude, further increase barely alters the nutrient's rate of release.

The release pattern for all of the fertilizers conforms to a first-order law. The release rate in this case is proportional to the mass of active agent contained within the device. The release rate is then given as

$$dM_t/dt = K(M_0 - M_t) \tag{1}$$

where M_0 is the mass of agent in the device at $t = 0$.

Table 2 shows the values obtained for the first-order release constant (K_1) obtained for all fertilizers in the series ULI, ULII, and ULIII, as well as their coefficients of correlation (r). As was to be expected, the value of K_1 diminishes when the percentage of fertilizer coating in each series increases. Series ULIII fertilizers show considerably lower K_1 values than fertilizers in other series with similar coating percentages.

Urea release in series ULIII fertilizers also conforms to a zero-order law. The release rate remains constant until the device is exhausted of active agent. Mathematically the release rate, dM_t/dt, from this device is given as

$$dM_t/dt = K \tag{2}$$

where K is a constant, time is t, and the mass of active agent released is M_t (Baker, 1987).

Zero-order release rate constants (k_0) obtained for the ULIII-16, ULIII-22, and ULIII-29 products are 3.73, 2.69, and 2.07 days^{-1}, respectively. Their coefficients of correlation are significant at 0.001%, and k_0 reduces with the percentage of coating, corroborating the fact that coatings improve when this percentage is increased and release the nutrient more slowly.

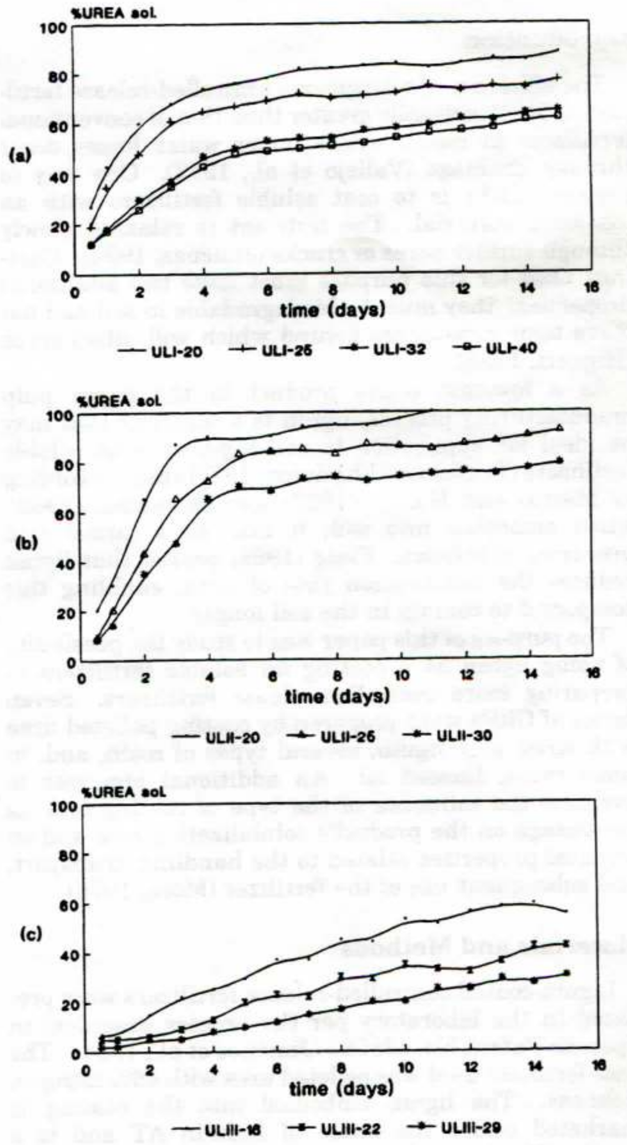

Figure 1. Urea release in water, as a function of time, at a constant temperature of 20 °C for (a) series ULI fertilizers with different coating percentages; (b) series ULII fertilizers with different coating percentages; (c) series ULIII fertilizers with different coating percentages.

Table 2. Values of First-Order Release Constants and Their Correlation Coefficients (*r*) Obtained by Simple Linear Regression for the Series ULI, ULII, ULIII, ULCA, and ULA Fertilizers ($n = 15$)

series	fertilizer	K_1 (days^{-1})	r^a
ULI	ULI-20	0.099	−0.91***
	ULI-25	0.067	−0.87***
	ULI-32	0.059	−0.93***
	ULI-40	0.051	−0.94***
ULII	ULII-20	0.316	−0.92***
	ULII-25	0.141	−0.90***
	ULII-30	0.089	−0.88***
ULIII	ULIII-16	0.059	−0.98***
	ULIII-22	0.035	−0.97***
	ULIII-29	0.025	−0.99***
ULCA	ULCA-13	0.06	−0.90***
	ULCA-19	0.05	−0.94***
	ULCA-23	0.043	−0.94***
ULA	ULA-12	0.048	−0.98***
	ULA-16	0.035	−0.97***

[a] ***, significant at <0.001% level.

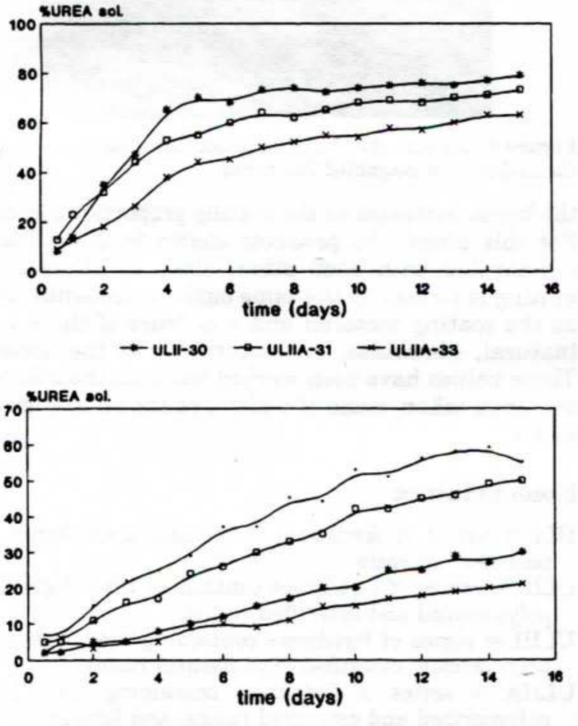

Figure 2. Urea release in water, as a function of time, at a constant temperature of 20 °C for (a) the ULII-30 fertilizer and the series ULIIA fertilizers; (b) series ULIII and UlIIIA fertilizers.

The fact that the release kinetics of series ULIII components may be either a first- or zero-order pattern is explained by taking into account the low magnitude of the first-order release constants, involving small variations in the active agent's release rate.

It may be concluded that the most efficient coating from a kinetic point of view is that of the series ULIII and that the fertilizers releasing urea at the fastest rates are those of series ULII.

2.2. Series ULIIA and ULIIIA. Series ULIIA and ULIIIA fertilizers were obtained by adding an external lignin and linseed oil coating on series ULII and ULIII products. In fact, ULII-30 acted as a base for preparing two series ULIIA fertilizers. ULIIIA-18 and ULIIIA-34 were prepared from ULIII-16 and ULIII-29, respectively. Figure 2 shows that series ULIIA and ULIIIA fertilizers have slower solubilization process than the ULII-30, ULIII-16, and ULIII-29 from which they originate.

Table 3. Values of the Release Rate Constant and the Coefficient of Correlation Obtained by Simple Linear Regression for Series ULIIA and ULIIIA Fertilizers ($n = 15$)

		first order		zero order	
series	fertilizer	K_1 (days^{-1})	r^a	K_0 (days^{-1})	r^a
ULIIA	ULIIA-31	0.072	−0.94***	3.58	−0.89***
	ULIIA-33	0.061	−0.96***	3.46	−0.96***
ULIIIA	ULIIIA-18	0.046	−0.99***	3.25	−0.98***
	ULIIIA-34	0.015	−0.98***	1.32	−0.97***

[a] ***, significant at <0.001% level.

Table 4. Crushing Strength of Prepared Fertilizers

fertilizer	crushing strength (kg/grain)	standard deviation
urea	1.10	0.42
ULI-20	1.17	0.35
ULI-25	1.41	0.37
ULI-32	1.71	0.38
ULI-40	1.78	0.38
ULII-20	1.13	0.40
ULII-25	1.18	0.39
ULII-30	1.40	0.40
ULIIA-31	1.40	0.38
ULIIA-33	1.42	0.38
ULIII-16	2.35	0.30
ULIII-22	2.56	0.31
ULIII-29	2.73	0.31
ULIIIA-18	2.40	0.30
ULIIIA-34	2.75	0.29
ULA-12	1.10	0.36
ULA-16	1.11	0.38
ULCA-13	1.10	0.35
ULCA-19	1.12	0.33
ULCA-23	1.14	0.36

Table 3 demonstrates that the release rate constants of oil-sealed fertilizers also diminish when the coating percentage increases and that the coefficients of correlation of zero-order constants obtained from ULIIA and ULIIIA fertilizers are comparable to those of the first-order constants.

2.3. Series ULCA and ULA. The series of products called ULCA was prepared by using a mixture of the ethanol solution of three rosins used in the series ULIII and linseed oil, in equal parts, for adhering lignin to urea. The adhesive is made of linseed oil only in the series ULA fertilizer.

The linear regression analysis of these two series (Table 2) provides a better correlation by processing the data according to a first-order pattern. The values of the release rate constants thus obtained are between 0.06 and 0.035 days^{-1}. They are therefore of the same order of magnitude as those obtained for series ULIII products. Nevertheless, the physical properties of these fertilizers related to their coating strength did not prove satisfactory.

3. Physical Tests. Once the products prepared were evaluated by determination of their release rate in water at a constant temperature, it was necessary to also consider their physical properties since handling and transport operations depend on such. The properties studied were as follows.

3.1. Grain Size. Grain size tests showed that the fertilizer grain size in all cases is between 1 and 4 mm, in accordance with current Spanish legislation, which requires 85% of a fertilizer to be between these limits.

3.2. Crushing Strength. In Table 4, uncoated urea gives a compressive strength of 1.10 kg/pellet, which is

Table 5. Coating Thickness of Some Series ULIII and ULIIIA Fertilizers

fertilizer	mean thickness (μm)	extreme values
ULIII-16	125	104−139
ULIII-29	196	160−210
ULIIIA-18	139	125−149
ULIIIA-34	238	205−245

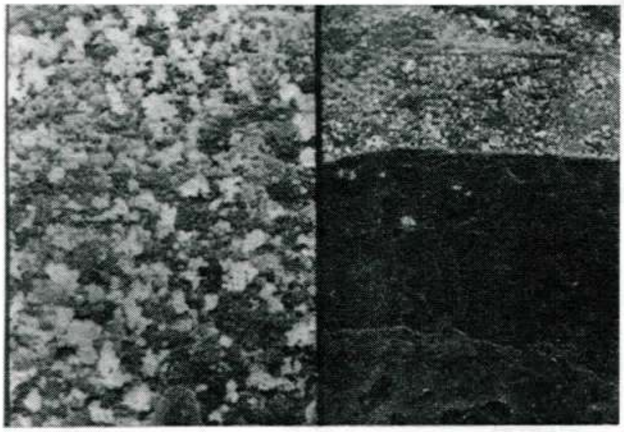

Figure 3. Surface and cross section of a ULIII-29 pellet (29% coating) magnified 1000 times (left) and 200 times (right).

less than the minimum value of 2.3 kg/pellet recommended by the TVA. The latter figure is reached only in the case of ULIII and ULIIIA products, in which the increase in coating means an increase in this value. In the case of ULIIIA-34, the 2.75 value obtained is the highest of all and represents an increase of 59% over that of the uncoated base substance.

In the light of such results, it may be concluded that, except for these fertilizers, the remaining products prepared by coating urea pellets do not meet the physical hardness properties required for handling and transport, despite some of them having raised good expectations from the kinetic standpoint.

3.3. Apparent Density. Coated products have a higher apparent density than uncoated products. This density increases with the coating percentage, and products with a similar percentage have the same apparent density.

3.4. Critical Relative Humidity and Humidity Absorption Rate. In the case of uncoated urea, humidity absorption commences at a critical relative humidity of 80.5%. This figure agrees with reference results (Hoffmeister, 1979). The fertilizer's coating increased the value of the critical relative humidity to 88% in all cases.

The percentage of water absorbed by the different products tested is differentiated according to the type of coating and decreases with increasing coating percentage. The highest values are those of series ULII products by far, according to the kinetic results obtained in water solubilization tests. ULIII and ULIIIA show the smallest water absorption percentages. Water absorption as a function of time is noticeably higher in uncoated urea and in series ULII fertilizers.

3.5. Microphotographic Coating Study. This study enables the coating's thickness and homogeneity to be determined and was carried out with ULIII and ULIIIA fertilizers, which proved to be the most interesting in their overall physical−chemical properties. The extreme values and average thicknesses of the microphotographically studied fertilizer coatings are given in Table 5. It can be deduced from these data that the thickness increases as the coating proportion increases. For this effect, the products shown in this table are comparable with each other, since in all cases the coating is formed by the same basic components: lignin as the coating material and a mixture of three rosins (natural, dimerized, and esterified) as the adhesive. These values have been worked out from the microphotographs taken, some of which are shown in Figures 3 and 4.

Figure 4. Surface of a ULIIA-18 pellet (18% coating) cut through the middle and magnified 250 times.

Nomenclature

ULI = series of fertilizers containing urea, lignin, and polymerized rosin
ULII = series of fertilizers containing urea, lignin, and polymerized and esterified rosins
ULIII = series of fertilizers containing urea, lignin, and polymerized, esterified, and natural rosins
ULIIA = series of fertilizers containing urea, lignin, polymerized and esterified rosins, and linseed oil
ULIIIA = series of fertilizers containing urea, lignin, polymerized, esterified, and natural rosins and linseed oil
ULA = series of fertilizers containing urea, lignin, and linseed oil
ULCA = series of fertilizers containing urea, lignin, polymerized, esterified, and natural rosins, and linseed oil

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