Controlled Release of 2,4-D from Granule Matrix Formulations Based on Six Lignins

André Ferraz, Josefina A. Souza, Flávio T. Silva, Adilson R. Gonçalves, Roy E. Bruns, and André R. Cotrim*

Departamento de Biotecnologia, Faculdade de Engenharia Química de Lorena, CP 116, 12600-000 Lorena, SP, Brazil

Richard M. Wilkins

Department of Agricultural and Environmental Science, Newcastle University, Newcastle upon Tyne, NE1 7RU, U.K.

Six lignins were used to obtain granular controlled release matrix formulations of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid). The water insoluble lignins were sourced from sugar cane (S*accharum officinarum*) bagasse and *Eucalyptus* sp. and *Pinus* sp. woods. Each lignin was characterized by its functional groups and molecular weight distributions. The formulations were prepared by melting the 2,4-D and mixing in the lignins individually and then granulating (to 0.7−1.0 mm) the glassy matrix. Release rates determined in static water were correlated to a diffusion-controlled mechanism according to the square root of time. Principal component regression of the slopes of these lines showed that these depend inversely on the molecular weight and the total and aliphatic hydroxyls of the lignins. For the other functional groups (aromatic hydroxyls, methoxyls, and carbonyls), the higher their contents, the higher the diffusion and release rates.

Keywords: *Controlled-release; 2,4-D; lignin; chemical structure; release rates*

INTRODUCTION

Delivery of pesticides through controlled release (CR) systems has gained increased interest, since these can reduce their environmental impact. Furthermore, the use of biodegradable polymers in these formulations is desirable, since no residues of the polymer remain and consequently no pesticide can persist trapped within the polymer. Lignin is a degradable macromolecule with appropriate physical and chemical properties and widely available at low cost. It is a polyfunctional material that can protect the pesticide against environmental processes such as photodegradation, air oxidation, leaching, runoff, and biodegradation (Wilkins, 1990).

Lignin has been used as a polymeric matrix for CR systems with a large number of pesticides (Wilkins, 1990). Most of the work has been focused on a commercially available pine kraft lignin (Indulin AT) or on other modified pine kraft lignins (Riggle and Penner, 1987, 1988, 1992, 1994; Dellicolli, 1977). Among the pesticides compatible with lignin is 2,4-D, a widespread foliar herbicide (in ester and salt forms) used for broad leaf weed control in cereals, pastures, lawns, parks, and golf courses. Although not conventionally used as a soil-applied herbicide, a controlled release granular formulation of 2,4-D based on a kraft lignin matrix has been developed (Allan and Neogi, 1975). This has been approved (EPA, 1988) for use in the establishment of Douglas fir (*Pseudotsuga menziesii*) through long-term weed control and growth stimulation of the tree. Apparently, two controlled release mechanisms may operate in this formulation: the faster by diffusion of the 2,4-D through the solid matrix and a slower by hydrolysis of ester links formed adventitiously from the carboxylic group of 2,4-D and the phenolic lignin during preparation. This provided weed control of 1−2 years after transplanting in British conditions (Wilkins, 1981). It is also noteworthy that up to 27% of wood volume increase could be achieved in a 6 year old plantation treated with these formulations compared to a mechanically controlled weed-free plantation (Allan et al., 1978).

It is thus likely that the kinetics of release from such 2,4-D granular formulations may be influenced by the nature of the lignin. Recently, we have demonstrated that lignins isolated from various lignocellulosic materials by several methods provide different release profiles of some herbicides (Cotrim et al., 1993; Silva and Wilkins, 1992). By assessment of the potential of such 2,4-D formulations for weed control in tropical conifer plantations, the effect of lignin properties on release kinetics has been investigated. We report here the release rates of 2,4-D from matrix granules based on lignins from various sources and of a range of structural properties. By assessment of the effects of these properties on controlled release, they have been correlated with release kinetics.

MATERIALS AND METHODS

Chemicals. The 2,4-D used in the formulations was of technical grade. For calibration of the HPLC system, technical 2,4-D was previously recrystallized from toluene solutions to give a purity higher than 99%.

Six lignins were used: two soda lignins extracted from steam-exploded sugar cane bagasse, recovered by precipitation with HCl (SEBL-HCl) and with H_2SO_4 (SEBL-H_2SO_4), and three kraft eucalyptus lignins from the black liquor of the pulp and paper industry. One of them was precipitated with H_2SO_4 from kraft liquor containing 14% of solids (KEL 14%-H_2SO_4) and the other two precipitated with H_2SO_4 and HCl from kraft liquor containing 37% of solids (KEL 37%-H_2SO_4 and KEL 37%-HCl, respectively). For comparison, a com-

* Author to whom correspondence should be addressed (e-mail: arc@sbq.org.br).

S0021-8561(96)00487-6 CCC: $14.00

mercial kraft pine lignin (INDULIN-AT) provided by Westvaco Co. was also used. The lignins used in this work were characterized, as previously described (Ferraz et al., 1992), by their carbon, hydrogen, and nitrogen contents (CHN), hydroxyl, methoxyl, and carbonyl group contents as well as by their molecular weight distributions.

Preparation of Lignin-Based Formulations. Formulations were prepared by mixing 2,4-D and lignins in percentages of 25−45% 2,4-D. The herbicide was melted in stainless steel cups immersed in a silicone oil bath at a nominal temperature of 170 °C. Lignin was then added and thoroughly mixed for 10 min. After cooling, the final formulation was ground and sieved to select a fraction of granule size ranging from 0.71 to 1.00 mm.

FTIR Analysis of Formulations. Fourier transform IR spectra of 2,4-D, lignin matrix, and lignin-based formulations were recorded using KBr pellets containing 0.7% sample on a NICOLET 520 spectrometer. Facilities of the "Advantage" software were used to obtain subtraction spectra.

Determination of 2,4-D in the Formulations. Matrix granules (approximately 30 mg) were immersed in 25 mL of methanol and disrupted for 10 min in an ultrasonic bath. The suspension was filtered and the filtrate analyzed by HPLC using a 1.8 mm × 200 mm C-18 column (HP-RP18). 2,4-D was eluted with a methanol/H_2SO_4 5×10^{-3} M aqueous solution (70:30) at 1.0 mL min^{-1} and detected at 276 nm. Releasable 2,4-D was calculated as the amount solubilized in methanol divided by the initial amount added to the formulation.

Release of 2,4-D in Water Immersion Experiments. The formulation granules (three replicates) were weighed to ensure a minimum amount of 25 mg of 2,4-D and kept immersed in 30 mL of deionized water. The flasks were closed and maintained at 22−30 °C. In the first 10 days sampling was performed daily by changing all the water contents of the flasks. Further sampling was performed at intervals of 3−7 days. The concentrations of 2,4-D in samples were determined by HPLC as described above. Released 2,4-D was expressed as a percentage of the initial amount added to the formulation.

An additional experiment was also carried out to estimate the reproducibility of 2,4-D release from five replicate formulation batches produced with 45% 2,4-D and SEBL. Release experiments were carried out on each formulation batch in triplicate. For this set of experiments the flasks were maintained in a controlled-temperature chamber at 30 °C.

Principal Component Regression. A data set of functional group contents and average molecular weights of lignins were analyzed by principal component analysis (PCA) (Mardia et al., 1979; Sharaf et al., 1986). Before the PCA analysis, the data were autoscaled to allow treatment of variables with different units. Scores for each lignin sample calculated by PCA were regressed against release rate constants by linear least squares. The principal components were calculated using software previously described (Scarminio and Bruns, 1989).

RESULTS AND DISCUSSION

Compatibility of 2,4-D and Lignin. 2,4-D was found to be compatible with all six lignins used in this work. Totally homogeneous formulations were obtained by mixing melted 2,4-D and lignin with a 45:55 (w/w) ratio. Homogeneous formulations were still obtained at 2,4-D/lignin ratios of 25:75 for kraft lignins from eucalyptus, 30:70 for kraft pine lignin (INDULIN-AT), and 35:65 for steam-exploded bagasse lignins. To ensure the homogeneity of all formulations used in this work, a 2,4-D/lignin ratio of 45:55 was chosen as the standard condition to obtain formulations.

Releasable 2,4-D from all the formulations is given in Table 1. Releasable 2,4-D ranged from 74.1 to 81.1% of the initial amount used in the formulation. However, the proportion of herbicide released in the water immersion experiments was around 95% of the initial amount. This result indicates that some extension of water labile linkages has occurred between the acid group of 2,4-D and the hydroxyl groups of the lignins. The formation of ester linkages in lignin-based formulations of 2,4-D has been reported and may result from the heating process during manufacture (Wilkins, 1990).

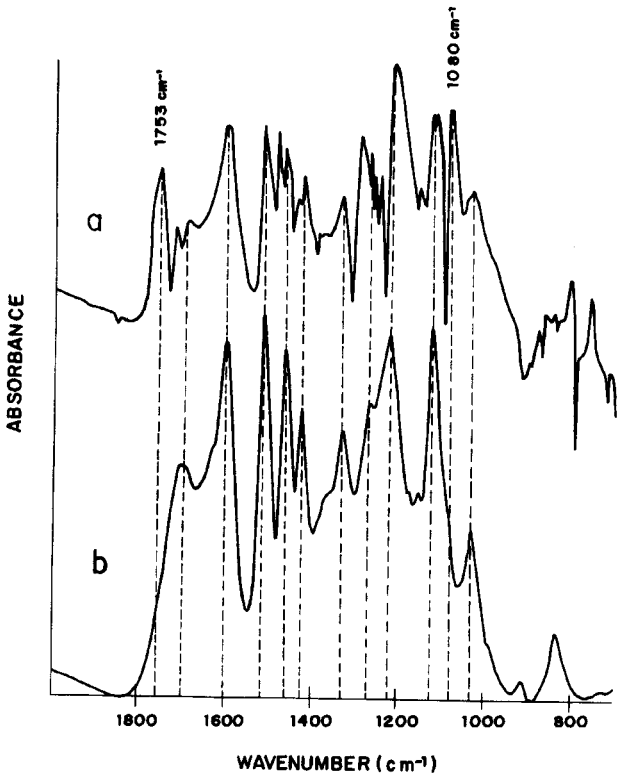

Figure 1. Differential FTIR spectrum of SEBL-HCl formulation subtracted from 2,4-D (a) and the spectrum of SEBL-HCl (b).

Table 1. Releasable Amounts of 2,4-D from Lignin-Based Formulations

formulation	initial 2,4-D added to the formulation (%)	methanol-extracted 2,4-D (%)	releasable 2,4-D (%)
SEBL-H_2SO_4	46.0	34.1	74.1
SEBL-HCl	46.1	37.4	81.1
INDULIN AT	45.8	35.0	76.4
KEL 14%-H_2SO_4	45.3	35.3	77.9
KEL 37%-H_2SO_4	46.2	36.4	78.9
KEL 37%-HCl	45.9	35.8	77.9

Subtracting the FTIR spectra of the formulation from the one of pure 2,4-D resulted in the spectrum a (Figure 1). This spectrum showed two bands, at 1753 and 1080 cm^{-1}, that were absent in the lignin spectrum b (Figure 1). These bands were assigned, respectively, to carbonyl and C−O stretching and are typically found in ester groups (Schrader, 1995). This corroborates with the formation of ester linkages between 2,4-D and the lignin matrix.

Kinetics and Reproducibility of 2,4-D release. The reproducibility of 2,4-D release from lignin-based formulations was estimated using five replicate batches of SEBL-HCl formulations containing 45% 2,4-D. The cumulative release of 2,4-D into water as a function of time is shown in Figure 2.

Release of pesticides from lignin-based formulations has been reported to follow a diffusion-controlled mechanism in which a linear response of released pesticide as a function of the square root of time is observed (Wilkins, 1983). Treatment of data for the release of

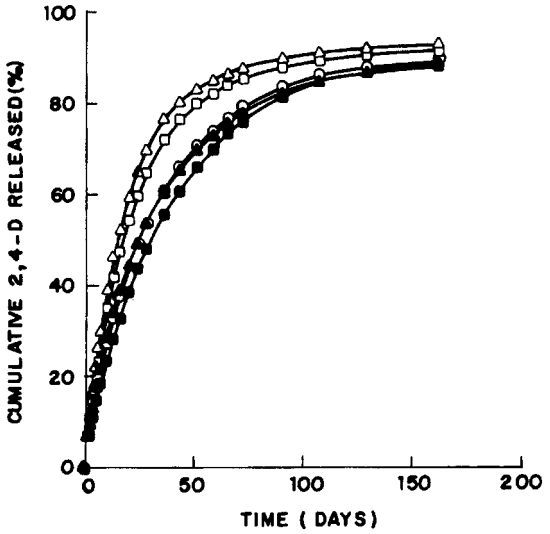

Figure 2. Amount of 2,4-D released into water as a function of time for five SEBL-HCl formulations containing 45% 2,4-D.

2,4-D from lignin matrices confirmed that the rate-determining process is diffusion (Souza, 1994). Equation 1 (Schwartz et al., 1968), which describes the diffusion-controlled release from an insoluble, inert matrix is given by

$$Q = \sqrt{\frac{D\epsilon}{\tau(2A - \epsilon C_s)C_s t}} \quad (1)$$

where Q is the amount of active ingredient (AI) released per unit area (A) of the formulation exposed to the solvent, D is the AI diffusion coefficient in the solvent, ϵ is the porosity of the matrix, τ is the tortuosity of the matrix, C_s is the AI solubility in the solvent, and t is time (Schwartz et al., 1968). This equation can be reduced to

$$Q' = K\sqrt{t} \quad (2)$$

where

Q' = percent amount released = 100 QS/m

m = mass of AI present in the formulation

S = surface area of the granule

K = rate constant = $100[D\epsilon/(\tau\,(2A - \epsilon C_s)C_s)]^{1/2}/S/m$

A plot of released 2,4-D against the square root of time is shown in Figure 3. A linear response for up to 65% of 2,4-D released was observed. A linear regression of this part of the curve furnished the slope K, the rate constant for the release process. K values for each formulation are reported in Table 2 along with the times required to release 50% of the initial 2,4-D (T_{50}).

The average rate constant for the five replicate batches of the 2,4-D/SEBL-HCl formulations was 13 ± 2 days$^{-1/2}$. The variance observed for the K values (15%) was lower than that observed for the T_{50} values (27%). As such, the former seems to be a better parameter for the study of the effect of various lignins on the release rates of 2,4-D.

Influence of Various Lignins on the Release Rate of 2,4-D. Cumulative release of 2,4-D into water from the six formulations obtained with various lignins

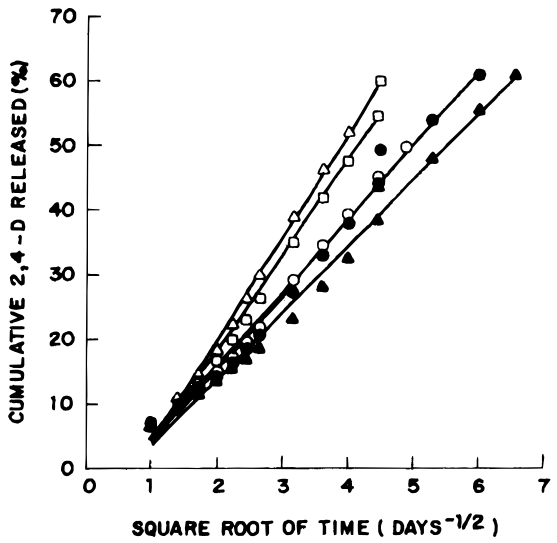

Figure 3. Amount of 2,4-D released into water as a function of square root of time for SEBL-HCl formulations containing 45% 2,4-D.

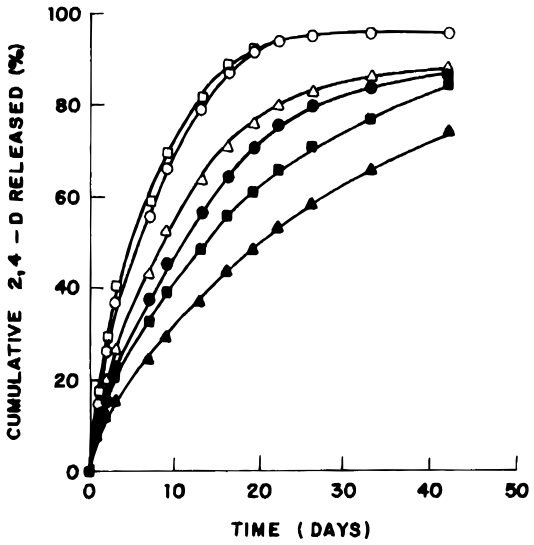

Figure 4. Amount of 2,4-D released into water for six different formulations: (□) KEL 14%-HCl; (○) KEL 37%-H_2SO_4; (△) KEL 14%-H_2SO_4; (●) INDULIN AT; (■) SEBL-HCl; (▲) SEBL-H_2SO_4.

Table 2. Rate Constants (K) and Times Required To Release 50% of 2,4-D (T_{50}) from Five Replicate Formulation Batches with Steam-Exploded Sugar Cane Bagasse Lignin

formulation batch	K (days$^{-1/2}$)	T_{50} (days)
1	11.5	24.0
2	15.0	17.3
3	15.8	15.0
4	10.2	29.8
5	11.4	24.0
average ± std	13 ± 2	22 ± 6

is shown in Figure 4. Various 2,4-D release profiles were observed, indicating that the properties of each lignin influence the release rate of the active ingredient. The effect of a number of lignins on release rates from adhesive matrices of the herbicides ametryn, 2,4-D, and diuron was also reported recently (Silva and Wilkins, 1992; Cotrim et al., 1993).

The rate constant K and T_{50} values for each formulation are shown in Table 3. According to these results, we can establish an increasing order of 2,4-D release rates for the formulations based on the lignins: SEBL-

Table 3. Rate Constants (K) and Times Required To Release 50% of 2,4-D (T_{50}) from Six Different Formulations with Kraft Eucalyptus Lignins, INDULIN-AT, and Steam-Exploded Sugar Cane Bagasse Lignin

formulation	K (days$^{-1/2}$)	T_{50} (days)
SEBL-H_2SO_4	12.1	19.6
SEBL-HCl	15.4	13.7
INDULIN-AT	18.2	10.3
KEL 14%-H_2SO_4	20.1	7.4
KEL 37%-H_2SO_4	24.7	5.4
KEL 37%-HCl	25.2	4.5

H_2SO_4 < SEBL-HCl < INDULIN < KEL14%-H_2SO_4 < KEL37%-H_2SO_4 < KEL37%-HCl.

Linear regressions between the functional group contents and the weight-average molecular weight (M_w) of each lignin and the release rate constant K of each formulation were performed by the least-squares method. The M_w and functional group contents of the six lignins used in this study are presented in Table 4.

The linear regression results for the K values, the functional group contents, M_w's, and F values from the analysis of variance are given in Table 5. The correlations between K values and the carbonyl and methoxyl contents were not statistically significant (95% confidence level). The other structural characteristics gave F-test results higher than those tabulated for the 95% confidence level (total hydroxyls, M_w, and aliphatic hydroxyls) and for the 99% confidence level (aromatic hydroxyls). Aliphatic and aromatic hydroxyls produced antagonistic effects on the release rate of 2,4-D, since slopes of opposite signals were observed.

To correlate the release rates of 2,4-D with all the structural characteristics of the lignins in a single model, a principal component regression (PCR) was performed. Autoscaling of the data presented in Table 4 permitted the treatment of the structural characteristics of the lignins with different units at the same time. The principal component analysis (PCA) of the scaled data showed that the first principal component explained 81% of the data variance. Regression of K values as a function of the scores, χ, of each lignin matrix, using only the first principal component, yielded the following model:

$$K = 19.3 + 4.6\chi \quad (3)$$

where

$$\chi = +0.4107\,(\%\ \text{methoxyl}) - 0.4354\,(\%\ \text{total OH}) - 0.4357\,(\%\ \text{aliphatic OH}) + 0.4099\,(\%\ \text{aromatic OH}) + 0.2927\,(\%\ \text{carbonyl}) - 0.4452\,(M_w)$$

represents the sample scores of the first principal component.

The F-test result for this regression (16.13) was higher than the value required for the 95% confidence level (7.71). Furthermore, the correlation coefficient (r^2) of 0.89 demonstrated a good fit to the experimental data. The low residuals for the experimental and calculated K values reported in Table 6 show the usefulness of this model for predicting rate constants for various lignin matrix formulations. However additional release rate data for other lignin matrices are necessary to extend the usefulness of this model.

On the basis of the coeficients (loadings) of the first principal component, it is possible to predict that methoxyl, aromatic hydroxyl, and carbonyl groups, which have positive signals, contribute to an increase of the diffusion constant values. Nevertheless, carbonyl groups are less important than the other groups, since its loading is lower. On the other hand, total hydroxyl, aliphatic hydroxyl, and weight-average molecular weight, which have negative coefficients, contribute to a decrease in K.

CONCLUSIONS

The release rates of 2,4-D into static water varied depending on the type of lignin matrix used. The time for the total release of the herbicide varied from 15 to 40 days, and the increasing release rates followed the order SEBL-H_2SO_4 < SEBL-HCl < INDULIN < KEL14%-H_2SO_4 < KEL37%-H_2SO_4 < KEL37%-HCl.

The release of 2,4-D into water showed square root kinetics (for up to 65% of 2,4-D release) controlled by diffusion. Based on the diffusion mechanism, the rate constants for each formulation were calculated. PCR analysis correlating the structural characteristics of the lignins and the rate constant values demonstrated that

Table 4. Weight-Average Molecular Weight (M_w) and Functional Group Contents of the Lignins Used as Matrices for Controlled Release Formulations of 2,4-D[a]

		functional group contents (%, w/w)				
lignin matrix	M_w (Da)	methoxyl	total hydroxyl	aromatic hydroxyl	aliphatic hydroxyl	carbonyls
SEBL-H_2SO_4	4364	14.7 ± 0.9	13 ± 2	2.9 ± 0.3	10 ± 2	3.3 ± 0.1
SEBL-HCl	3999	14 ± 1	13 ± 1	2.9 ± 0.3	10 ± 1	2.4 ± 0.1
INDULIN-AT	4032	13 ± 1	13 ± 2	4.0 ± 0.1	9 ± 2	3.2 ± 0.3
KEL 14%-H_2SO_4	932	17.7 ± 0.7	11 ± 2	4.5 ± 0.1	6 ± 2	3.6 ± 0.1
KEL 37%-H_2SO_4	940	19 ± 1	11 ± 2	4.6 ± 0.4	7 ± 2	4.0 ± 0.1
KEL 37%-HCl	1057	17 ± 1	11 ± 2	5.7 ± 0.2	5 ± 2	3.2 ± 0.1

[a] For use in eq 3, all the values in this table have to be firstly autoscaled.

Table 5. Linear Regression Equations of Rate Constants as a Function of Structural Characteristics of Lignins[a]

structural characteristics	equation	r^2	F statistics
% methoxyls	$K = 1.6(\%\ OCH_3) - 5.8$	0.74	4.64
% total hydroxyls	$K = -4.1(\%\ OH_{tot}) + 68.3$	0.84	9.38
% aromatic hydroxyls	$K = 4.5(\%\ OH_{aro}) + 1.0$	0.92	23.28
% aliphatic hydroxyls	$K = -2.3(\%\ OH_{aliph}) + 37.1$	0.91	18.94
% carbonyls	$K = 5.1(\%\ C{=}O) + 2.5$	0.54	1.36
weight-average molecular weight (Da)	$K = -0.026(M_w) + 25.9$	0.87	13.1

[a] $F_{4,1,0.05} = 7.71$.

Table 6. Experimental and Calculated Rate Constant Values of 2,4-D Released from Six Different Controlled Release Formulations

formulation	exptl K value ($days^{-1/2}$)	calcd K value ($days^{-1/2}$)	deviation ($days^{-1/2}$)
SEBL-H_2SO_4	12.1	15.0	−2.9
SEBL-HCl	15.4	14.4	+1.0
INDULIN-AT	18.2	16.0	+2.2
KEL 14%-H_2SO_4	20.1	22.9	−2.9
KEL 37%-H_2SO_4	24.7	23.1	+1.6
KEL 37%-HCl	25.2	24.3	+0.9

the higher the total hydroxyl, aliphatic hydroxyl, and the average molecular weight values, the lower the diffusion constants. Therefore, the release rates of 2,4-D are also lower. On the other hand, PCR predicts higher release rates for higher aromatic hydroxyl, methoxyl, and carbonyl contents.

ABBREVIATIONS USED

2,4-D, 2,4-dichlorophenoxyacetic acid; CR, controlled-release; SEBL, steam-exploded sugar cane bagasse lignin; KEL, kraft eucalyptus lignin; CHN, carbon, hydrogen, and nitrogen; IR, infrared; HPLC, high-performance liquid chromatography; PCA, principal components analysis; PCR, principal components regression; AI, active ingredient; χ, score of a principal component; Q, amount of AI released per unit area; D, diffusion coefficient; ϵ, porosity of the matrix; τ, tortuosity of the matrix; C_s, AI solubility in the solvent; t, time; Q', percent amount released = 100 QS/m; M_w, weight-average molecular weight; m, mass of AI present in the formulation; S, surface area of the granule; K, rate constant; T_{50}, time required to release 50% of AI; r^2, correlation coefficient; A, surface area of the granule.

ACKNOWLEDGMENT

The authors thank J. S. Canilha, J. C. S. Tavares, and M. E. M. Coelho for technical assistance.

LITERATURE CITED

Allan, G. G.; Beer, J. W.; Cousin, M. J. Growth enhancement of a juvenile conifer forest six years after application of a controlled release herbicide. *Int. Pest Control* **1978**, *15*, 6−13.

Allan. G. G.; Neogi, A. N. German Offen. DT 2501808, 24/7/75.

Cotrim, A. R.; Souza, J. A.; Ferraz, A.; Silva, F. T.; Wilkins, R. M. The Influence of Different Lignins on the Controlled-Release of 2,4-D and Ametryn Herbicides. *Proc. Braz. Symp. Chem. Lignins Other Wood Compon., 3rd* **1993**, *4*, 278−281.

Dellicolli, H. T. Controlled Release of Pesticides from Kraft Lignin Carriers. In *Controlled Release Pesticides*; Herbert, B. C., Ed.; ACS Symposium Series 53; American Chemical Society: Washington, DC, 1977; pp 84−93.

EPA Est. No. 45083-WA-1 EPA Reg. No. 43740-1. For reproduction of label see Wilkins, R. M. 1990, p 136.

Ferraz, A.; Souza, J. A.; Silva, F. T. Characterization of Lignins Used as Matrix in Controlled-Release Formulations: Steam Explosion Sugar Cane Bagasse and Kraft Eucalyptus Lignins. *Proc. Braz. Symp. Chem. Lignins Other Wood Compon., 2nd* **1992**, *3*, 173−177.

Mardia, K. V.; Kent, J. T.; Bibby, J. M. *Multivariate Analysis*; Academic Press: London, 1979; Chapter 8.

Riggle, B. D.; Penner, D. Controlled Release of Three Herbicides With the Kraft Lignin PC940C. *Weed Sci.* **1988**, *36*, 131−136.

Riggle, B. D.; Penner, D. Evaluation of Pine Kraft Lignins for Controlled Release of Alachlor and Metribuzin. *Weed Sci.* **1987**, *35*, 243−246.

Riggle, B. D.; Penner, D. Kraft Lignin Adsorption of Alachlor and Cloramben as a Controlled-Release Function Evaluation. *J. Agric. Food Chem.* **1994**, *42*, 2631−2633.

Riggle, B. D.; Penner, D. Kraft Lignin Adsorption of Metribuzin as a Controlled-Release Function Evaluation. *J. Agric. Food Chem.* **1992**, *40*, 1710−1712.

Scarminio, I. S.; Bruns, R. E. An Adaptation of ARTHUR for Microcomputers. *Trends Anal. Chem.* **1988**, *8*, 326−328.

Schrader, B. Vibrational Spectroscopy of Different Classes and States of Compounds - Organic Substances. In *Infrared and Raman Spectroscopy*; Schrader, B., Ed.; VCH: Weinheim, 1995; pp 188−222.

Schwartz, J. B.; Simonelli, A. P.; Higuchi, W. I. Drug release from wax matrices I: analysis of data with first-order kinetics and with a diffusion-controlled model. *J. Pharm. Sci.* **1968**, *57* (2), 274−277.

Sharaf, M. A.; Illman, D. L.; Kowalski, B. R. *Chemometrics*; Wiley: New York, 1986.

Silva, F. T.; Wilkins, R. M. Use of Lignins as Support for Herbicides in Controlled Release Formulations. *Proc. Braz. Symp. Chem. Lignins Other Wood Compon., 2nd* **1992**, *3*, 165−171.

Souza, J. A. Utilização de ligninas para obtenção de formulações de liberação controlada de 2,4-D. MSc Thesis, State University of Campinas, Campinas, Brazil, 1994.

Wilkins, R. M. Biodegradable polymer methods. In *Controlled Delivery of Crop-protection Agents*; Wilkins, R. M., Ed.; Taylor & Francis: London, 1990; pp 149−165.

Wilkins, R. M. Determination of release rates. In *Controlled-Release Technology - Bioengineering Aspects*; Das, K. G., Ed.; John Wiley & Sons: New York, 1983; pp 143−178.

Wilkins, R. M. The use of controlled release herbicides in the establishment of conifer plantations. *Proceedings of Crop Protection in Northern Britain*; BCPC: London, 1981; pp 261−267.

Received for review July 8, 1996. Accepted November 18, 1996.[⊗] Financial support from the European Community, fixed contribution Contract TS2* 0293-C (SMA), CNPq, FAPESP, GTZ, and Faculdade de Engenharia Química de Lorena is acknowleged.

JF960487O

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.