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Estimation of Solubility Effect on the Herbicide Controlled-Release Kinetics from Lignin-Based Formulations

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Abstract

Understanding the main phenomena involved in the controlled-release kinetics of herbicides in a water bath is a very important requisite for diffusive-parameter estimation, because, some mathematical models based on Fick's second law for diffusion have been developed to describe the controlled-release kinetic data. However, the validity of these models is restricted to the following assumptions: (1) the formulation is an isothermal slab; (2) the release occurs through the two faces of the slab; (3) the herbicide is dissolved in the water contained in the slab pores at a concentration less than the saturation concentration (c_{is}); (4) the total sum of the individual volumes of the pores is εAL (ε is the slab porosity, A is the slab area, and L is the slab thickness); and (5) the initial concentration of herbicide in the pores is $M_0/\varepsilon AL$ (M_0 is the initial amount of herbicide in the matrix). The fourth assumption may be invalid for mathematical description of systems in which the herbicide concentration in the slab may be above the saturation concentration. If this were true, the final assumption would also be invalid, because the initial concentration of herbicide in the pores is c_{is} in this case. This work presents a study of the solubility effect on the controlled-release kinetics of herbicides from lignin matrices.

Index Entries: Mathematical modeling; controlled-release; lignin; herbicide; diffusion; solubility.

Introduction

The technology of controlled-release of herbicides is proving to be very attractive as a solution to the problems with defensive application and

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contamination. Polymeric and macromolecular matrices are often utilized as supports for the herbicide, and among the various materials used as support, lignin is an interesting alternative since it can be obtained from most agroindustrial residues such as sugarcane bagasse, kraft liquor, rice, and wheat straws *(1)*.

To understand the main phenomena involved in controlled-release systems, mathematical models for describing the transport of herbicide through the matrix and the soil, and the herbicide degradation by chemical and biologic processes have been developed.

Some mathematical models based on Fick's second law for diffusion (Eq. 1) have been presented in order to describe the controlled-release kinetics data in water bath experiments *(2–5)*.

$$\frac{\partial c_{iw}}{\partial t} = D_{eff} \frac{\partial^2 c_{iw}}{\partial x^2} \tag{1}$$

in which c_{iw} is the herbicide concentration into the matrix (g/cm^3), D_{eff} is the effective diffusion coefficient (g/[cm^2 day]), t is the time (d), and x is the spatial coordinate (cm).

To solve the partial differential equation, two alternative boundary conditions were assumed for the matrix surface: (1) a herbicide concentration equal to zero *(2,5)*, and (2) the existence of a stagnant unstirred layer of herbicide solution *(2–4)*. The second boundary provided a good fit of the model to the experimental data *(2–4)*. However, if the herbicide concentration in the matrix is above the herbicide solubility, Eq. 1 is invalid for describing the release kinetics. Since, in some cases, the herbicide solubility in the water is relatively low, and the concentration in the matrix is high, a model considering the solubility effect is more realistic.

Materials and Methods

Herbicides Formulations

The formulations of the herbicides (2,4-D) dichlorophenoxyacetic acid, ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine), and diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) with lignin extracted from several sources were prepared by a melting process. After melting, the final formulation was ground and sieved to select a fraction granule size range from 0.71 to 1.00 mm. The main characteristics of controlled-release formulations (CRFs) obtained are presented in Table 1.

Release Experiments in Static Water Bath System

The formulation granules were weighed and immersed in 30 mL of deionized water. The flasks were closed and maintained at 30°C. In the first 10 d sampling was performed by changing all the water contents in the flasks. The concentration of herbicide in the samples was determined by high-performance liquid chromatography (HPLC). Released herbi-

Table 1
Main Characteristics of Formulation Used in Runs Conducted in Water Bath

Symbol	Herbicide	Lignin source	Lignin production process	Precipitant agent
CRF1	2,4-D	Bagasse	Steam explosion	HCl
CRF2	2,4-D	Bagasse	Steam explosion	H_2SO_4
CRF3	2,4-D	Eucalyptus[a]	Kraft	H_2SO_4
CRF4	2,4-D	Eucalyptus[b]	Kraft	H_2SO_4
CRF5	2,4-D	Eucalyptus[b]	Kraft	HCl
CRF6	2,4-D	Pinus	Kraft	[c]
CRF7	Diuron	Bagasse	Steam explosion	HCl
CRF8	Ametryn	Bagasse	Steam explosion	HCl

[a] From kraft liquor containing 14% solids.
[b] From kraft liquor containing 37% solids.
[c] Pinus kraft lignin (INDULIN AT; Westvaco).

cide was expressed as a percentage of the initial amount added to the formulation: M_t/M_0. The release experiments in a static water bath system were conducted with the formulations CRF1, CRF2, CRF3, CRF4, CRF5, CRF6, and CRF7.

Release Experiments in Dynamic Water Bath System

The CRF samples were weighed and allocated in 40-mm-long by 18-mm-diameter glass columns containing sintered disks in the top and bottom. The system was maintained at 30°C and fed from the bottom with deionized water at a flow rate of 2 mL/min. The effluent was collected on the top and stored in glass flasks and was changed periodically. The herbicide content in the flasks was determined by HPLC. The release experiments in the dynamic water bath system were conducted with the formulations $CRF7_d$ and $CRF8_d$, where the subscript d indicates that the formulation was assayed in the dynamic water bath system.

Mathematical Modeling

When the herbicide concentration in the matrix is above the herbicide solubility, two different mechanisms occur: diffusion and dissolution. The dissolution rate is proportional to the difference between the herbicide solubility (c_{is}) and its local concentration (c_{iw}) *(5)*. Thus, the release kinetics is described by Eq. 2.

$$\frac{\partial c_{iw}}{\partial t} = D_{eff}\frac{\partial^2 c_{iw}}{\partial x^2} + k\left(c_{is} - c_{iw}\right) \tag{2}$$

in which k is the dissolution rate constant.

Table 2
Results of Parameter Estimation

CRF	D^* (d^{-1}) × 10^5	k (d^{-1}) × 10^3	C^* × $10^{3\,a}$	F_{calc}[a]	F_{tab}[b]	R^2
CRF1	2.1 ± 0.8	2 ± 1	8 ± 1	[c]	[c]	0.9968
CRF2	2.3 ± 0.9	0.0001 ± 0.03	0.07 ± 0.01	[c]	[c]	0.9966
CRF3	0.72 ± 0.2	28 ± 9	1.4 ± 0.1	[c]	[c]	0.9952
CRF4	0.9 ± 0.4	50 ± 20	2.5 ± 0.4	[c]	[c]	0.9920
CRF5	0.4 ± 0.3	70 ± 40	30 ± 20	[c]	[c]	0.9939
CRF6	0.3 ± 0.2	34 ± 21	1.3 ± 0.7	[c]	[c]	0.9950
CRF7	0.17 ± 0.03	0.56 ± 0.08	0.085 ± 0.003	[c]	[c]	0.9986
$CRF7_d$	0.17 ± 0.02	0.1 ± 0.06	0.106 ± 0.001	1.055	1.583	0.9990
$CRF8_d$	0.14 ± 0.05	40 ± 8	2.0 ± 0.7	0.73	1.739	0.9990

[a] F_{calc} is the calculated value of F for the lack of fit of the model to experimental data.
[b] F_{tab} is the tabulated value of F for a confidence level of 95%.
[c] Experiments without replicates.

The initial and boundary conditions are given by Eqs. 3 and 4, respectively.

$$c_{iw}\left(x,t=0\right)=c_{is} \tag{3}$$

$$c_{iw}\left(0,t\right)=c_{iw}\left(L,t\right)=0 \tag{4}$$

The solution of Eq. 2 using the initial and boundary conditions is given by *(6)*

$$\frac{M_t}{M_0}= C^*\left(\sqrt{D^*k}\,\tanh\left[\frac{\pi}{2}\sqrt{\frac{k}{D^*}}\right]+\frac{4}{\pi}\sum_{n=0}^{\infty}\left[\frac{\{2n+1\}^2D^{*2}}{\{k+(2n+1)^2D^*\}^2}\left(1-\exp\left\{-\left[k+(2n+1)^2D^*\right]t\right\}\right)\right]\right) \tag{5}$$

in which $C^* = 2\varepsilon AL\,c_{is}/(\pi M_0)$ and $D^* = \pi^2 D_{eff}/L^2$. The D^*, k, and C^* parameters were estimated using the Marquardt's *(7)* method.

Results and Discussion

The results of parameter estimation are presented in Table 2, which Table 2 shows inaccurate parameter estimates for 2,4-D CRF1–CRF6 according to Student's *t*-test. This result can be explained by the high solubility of the 2,4-D in water (620 ppm). For high solubility, the herbicide concentration in the matrix is below saturation, and the estimation of the dissolution rate constant (*k*) is inaccurate, because, in this case, the rate-limiting mechanism is diffusion.

For the formulation containing the herbicide diuron (low solubility in water—42 ppm), assayed in static (CRF7) and dynamic ($CRF7_d$) bath systems, the mathematical model fit was very good for $CRF7_d$ according to Fisher's test providing significant parameter estimates according to

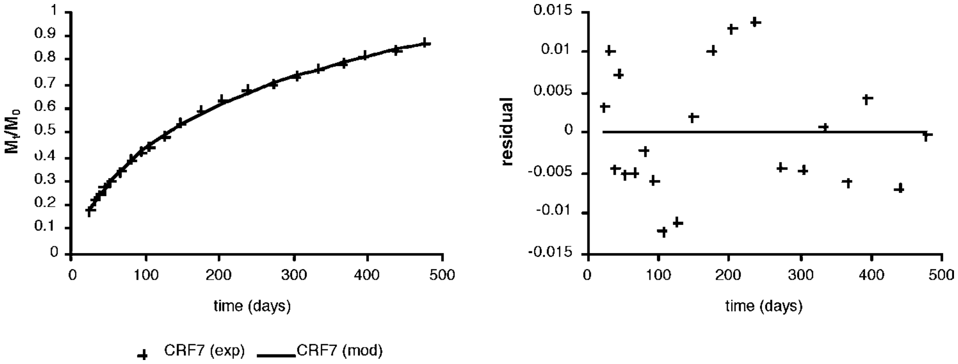

Fig. 1. Plot of experimental (exp) data vs model (mod) predictions and residual values (residual = experimental value – predicted value) for CRF7.

Student´s *t*-test. The estimated values of D^* (1.70×10^{-6} d^{-1}) and C^* (approx 1.0×10^{-4}) were close for diuron formulation assayed in both static and dynamic systems. This result indicates that the model has a physical meaning, because these parameters correlate only with the formulation, independently of the assay type. This result was not observed in previous works using the models based on Eq. 1 *(2–5)*.

The *k* parameter estimated for CRF7 (5.6×10^{-4} d^{-1}) is lesser than for $CRF7_d$ (1.0×10^{-3} d^{-1}). This can be explained by the fact that in the static-bath system, the volume of water changed daily was less than in the dynamic bath system. Thus, the concentration of herbicide in the static bath medium was higher than that in the dynamic bath, and the dissolution rate in the static system was less than that in the dynamic system.

For the CRF containing the herbicide ametryn (intermediate solubility in water—185 ppm), the fit of the mathematical model was very good according to Fisher test and provided significant parameters according to student's *t*-test.

Figures 1–3 present plots of the experimental data versus model predictions, and the distribution of the residual values for CRF7, $CRF7_d$, and $CRF8_d$. A good fit of the model to the experimental data was observed for these formulations. Moreover, the residuals distribution obtained for CRF7, $CRF7_d$, and $CRF8_d$ indicate a randomized behavior.

Conclusion

The model considering the solubility effect on the controlled-release of herbicide in a water bath was able to describe the experimental data for formulations containing herbicides with intermediate (ametryn) and low (diuron) solubilities in water. One important result obtained in this work was the estimation of an equal diffusivity parameter for the diuron formulation assayed in two different water bath systems.

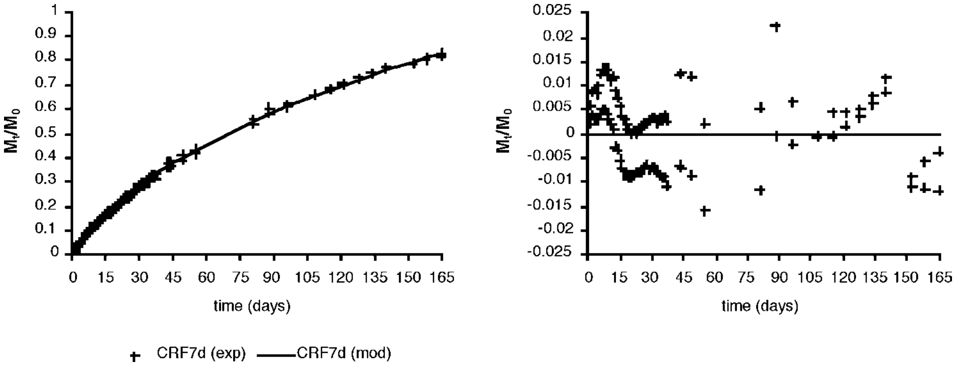

Fig. 2. Plot of experimental (exp) data vs model (mod) predictions and residual values (residual = experimental value – predicted value) for $CRF7_d$.

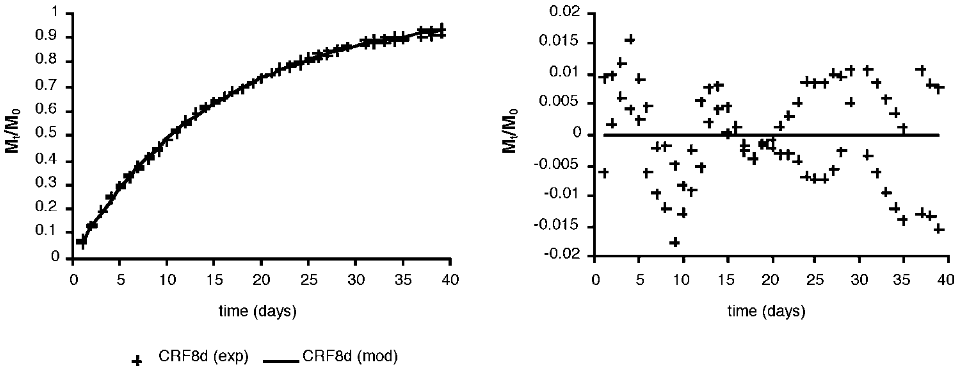

Fig. 3. Plot of experimental (exp) data vs model (mod) predictions and residual values (residual = experimental value – predicted value) for $CRF8_d$.

For the herbicide with high solubility in water (2,4-D), the parameter estimates obtained were not statistically significant according to student's *t*-test. This fact may be ascribed to the high solubility of 2,4-D, rendering a herbicide concentration in the matrix less than its solubility in water.

The next step in the validation of the current model is determination of the volume of the matrix pores (εAL), in order to obtain an experimental value for C^*. With the use of an experimental value for C^* in the model, the estimation of D^* and k will be more accurate.

Acknowledgments

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