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Modeling of 2,4-Dichlorophenoxyacetic Acid Controlled-Release Kinetics from Lignin-Based Formulations

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Abstract

The second Fick´s law of diffusion, considering boundary conditions that at both slab faces the concentration of herbicide is equal to zero (sink conditions), has been adequate to describe our kinetic data obtained from experiments on 2,4-dichlorophenoxyacetic acid, (2,4-D) released from lignin-based formulations in a water static bath system. However, the same model proved to be invalid in describing the experimental data obtained with ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine) and diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) formulations in a water dynamic bath system. For ametryn and diuron formulations, because of the lower aqueous solubility of these herbicides, it was necessary to model a stagnant film at the formulation surface to describe better the release kinetics because the model incorporating sink conditions is insufficient. This study presents a new mathematical modeling of experimental data obtained with 2,4-D formulations in a water static bath system. The new model incorporates a stagnant film as the boundary condition at the formulation surface, and its diffusion coefficient value is more precise than the one estimated by the model employing sink conditions.

Index Entries: Mathematical modeling; controlled release; lignin; herbicide; 2,4-dichlorophenoxyacetic acid; diffusion.

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Introduction

Herbicides are usually applied as sprays in excessive amounts implying risks for the environment, agriculturists, and consumers owing to losses occurred by many processes *(1)*.

The controlled release of herbicides is a technology that is proving to be very attractive for solving problems with herbicide application and contamination. Polymeric and macromolecular matrices are often utilized as supports for the herbicide, and among the various materials used as supports, lignin is an interesting alternative since it can be obtained from most agroindustrial residues, such as sugarcane bagasse, kraft liquor, rice, and wheat straw *(1)*.

Controlled-release formulations (CRF) using lignins obtained from different sources (*Pinus*, *Eucalyptus*, sugarcane bagasse), production processes (kraft, pretreatment by steam explosion), and several herbicides have been evaluated in the past few years *(2–9)*. The interest in understanding the main phenomena related to herbicide release in such systems has stimulated the development of mathematical models describing the transport of herbicide through the matrix and the soil, and herbicide degradation by chemical and biologic processes.

Oliveira et al. *(10)* presented a review of mathematical models for controlled release systems of herbicides using lignin as matrices. Two models based on the second Fick's law were presented to describe the release kinetics: an early time approximation, acceptable until 60% of release (Eq. 1), and a rigorous model (Eq. 2). Both models were developed considering boundary conditions that at both slab faces the concentration of the herbicide is equal to zero (sink condition) *(10)*:

$$\frac{M_t}{M_0} = \frac{4}{\pi}\left(\frac{D^*}{\pi} t\right)^{1/2} \tag{1}$$

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left(\frac{exp\left[-(2n+1)^2 D^* t\right]}{(2n+1)^2} \right) \tag{2}$$

In Eqs. 1 and 2, $D^* = \pi^2 D_{eff} / L^2$ (d^{-1}), *Deff* is the effective diffusion coefficient ($cm^2\ d^{-1}$), L is the slab thickness (cm), M_0 is the initial amount of herbicide in the slab (g), M_t is the cumulative amount of herbicide released at the time (g), and t is the release time (d).

The sink condition was shown to be suitable to describe the herbicide release kinetic data obtained with formulations containing 2,4-dichlorophenoxyacetic acid (2,4-D). However, this boundary condition proved to be invalid for describing the experimental data obtained with the herbicides ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine) and diuron (3-[3,4-dichlorophenyl]-1,1-dimethylurea) formulations in a water dynamic bath system. For ametryn and diuron formulations, because of the

lower aqueous solubility of these herbicides, it was necessary to model a stagnant film at the formulation surface to describe better the release kinetics because the model incorporating sink conditions is insufficient.

In the present study, a stagnant film model was fitted to data from 2,4-D experiments. In the experiments, 2,4-D was released from lignin-based formulations assayed in a water static bath system.

Materials and Methods

The formulations of herbicides with lignin extracted from several sources were prepared by melting equal amounts of lignin and 2,4-D in concave stainless steel recipients immersed in a silicon bath at 170°C. The mixture was homogenized, and after complete homogenization, the recipients were cooled at room temperature. After cooling, the formulations were ground and sieved to select a range of granule size from 0.71 to 1.00 mm. Table 1 presents the main characteristics of CRF obtained *(5,6)*.

The formulation granules were weighed to ensure an amount of 25 mg of herbicide and were kept immersed in 30 mL of deionized water. The flasks were closed and maintained at 30°C. In the first 10 d, sampling was performed daily by changing all the water contents of the flasks. Further sampling was performed at intervals of 3–7 days. The concentration of 2,4-D in the samples was determined by high-performance liquid chromatography *(5,6)*. Released herbicide was expressed as a percentage of the initial amount added to the formulation: M_t/M_0.

Results and Discussion

Equations 1 and 2 were used for the treatment of release kinetic data of CRFs containing the herbicide 2,4-D. The results shown in Table 2 indicate an equivalence between these equations with respect to the values of D^* estimated. In fact, the values of D^* estimated using the early time approximation were close to the ones estimated using the rigorous model. For the herbicide 2,4-D, Eq. 2 was able to describe the release kinetics in all its extension, and the estimates of the parameter D^* were statistically significant at a 95% confidence level. Figure 1 shows good agreement between the model predictions (Eq. 2) and the experimental data; however, a nonrandomized residual distribution is also observed. For the CRF containing the herbicides ametryn and diuron, Eqs. 1 and 2 did not fit the well experimental data obtained in runs carried out in a water dynamic bath system. This poor fit is related to the low solubility of these herbicides in water at room temperature (ametryn: 185 ppm; diuron: 42 ppm) in comparison with the solubility of the 2,4-D (620 ppm). As a consequence, a stagnant film is established at the interface between the formulation and the release acceptor medium. Thus, the models considering a sink condition at the surface are unsuitable for describing kinetic data obtained with formulations containing the less-soluble herbicides (ametryn and diuron).

Table 1
Main Characteristics of 2,4-D CRF Assayed in Water Static Bath System

Symbol	Lignin source	Lignin production process	Precipitant agent	Herbicide concentration
CRF1	Bagasse	Steam explosion	HCl	45%
CRF2	Bagasse	Steam explosion	H_2SO_4	45%
CRF3	Eucalyptus[a]	Kraft	H_2SO_4	45%
CRF4	Eucalyptus[b]	Kraft	H_2SO_4	45%
CRF5	Eucalyptus[b]	Kraft	HCl	45%
CRF6	Pinus	Kraft	[c]	45%

[a] from kraft liquor containing 14% solids,
[b] from kraft liquor containing 37% solids,
[c] pinus kraft lignin (INDULIN AT, Westvaco).

Table 2
Parameter Estimation for 2,4-D CRF Using
Early Time Approximation and Rigorous Model

	Early time approximation		Rigorous model	
CRF	D^* (d^{-1})	R^2	D^* (d^{-1})	R^2
CRF1	0.035 ± 0.002	0.9976	0.037 ± 0.001	0.9983
CRF2	0.022 ± 0.001	0.9935	0.023 ± 0.001	0.9960
CRF3	0.055 ± 0.003	0.9982	0.058 ± 0.002	0.9901
CRF4	0.092 ± 0.007	0.9837	0.107 ± 0.005	0.9911
CRF5	0.078 ± 0.009	0.9891	0.097 ± 0.005	0.9913
CRF6	0.043 ± 0.003	0.9956	0.047 ± 0.002	0.9908

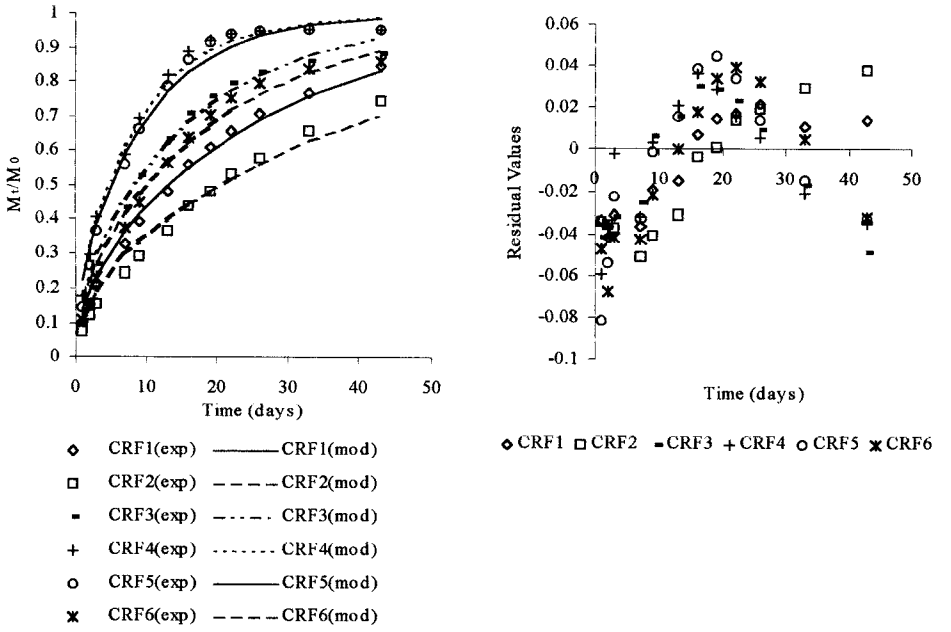

Fig. 1. Plot of experimental data and calculated values by model incorporating sink condition at CRF surface.

Pereira et al. *(11)* developed a mathematical model for controlled-release kinetic data of the herbicides ametryn and diuron obtained in runs carried out in a water dynamic bath system. In the development of the mathematical model, a stagnant film of herbicide solution was considered as the boundary condition at the CRF surface. The final model using this boundary condition is given by Eq. 3 *(11)*:

$$\frac{M_t}{M_0} = 1 - \sum_{n=0}^{\infty} \frac{2Bi^2 \exp\left(-4\beta_n^2 D^* t/\pi^2\right)}{\beta_n^2\left(\beta_n^2 + Bi^2 + Bi\right)} \quad (3)$$

in which β_n are the values of the positive roots of the equation $\beta\tan(\beta) = Bi$, Bi is the Biot number ($Bi = Lk/D_{eff}$) and k is the mass transfer coefficient by convection (cm·d^{-1}). The D^* and Bi parameters of Eq. 3 were estimated using the Marquardt method *(12)* and the β_n values were determined using the Newton-Raphson method *(13)*.

Equation 3 provided a good fit of the experimental data obtained in runs employing the formulations containing ametryn and diuron. The lack of fit was insignificant at a 95% confidence level, and the distribution of the residues was randomized *(11)*.

To test further the applicability of the boundary condition, Eq. 3 was fitted to experimental data of 2,4-D controlled release in a water static bath system; Table 3 presents the results. The values of R^2 presented in Table 3 are closer to 1 than those presented in Table 2. Figure 2 presents

Table 3
Parameter Estimation for 2,4-D CRF Using
Model Incorporating Stagnant Film as Boundary Condition at CRF Surface

CRF	D^* (d^{-1})	*Bi*	R^2
CRF1	0.0081 ± 0.0003	11 ± 2	0.9990
CRF2	0.0062 ± 0.0004	7 ± 1	0.9977
CRF3	0.012 ± 0.001	12 ± 6	0.9928
CRF4	0.024 ± 0.003	8 ± 4	0.9944
CRF5	0.028 ± 0.005	4 ± 2	0.9952
CRF6	0.012 ± 0.002	6 ± 2	0.9941

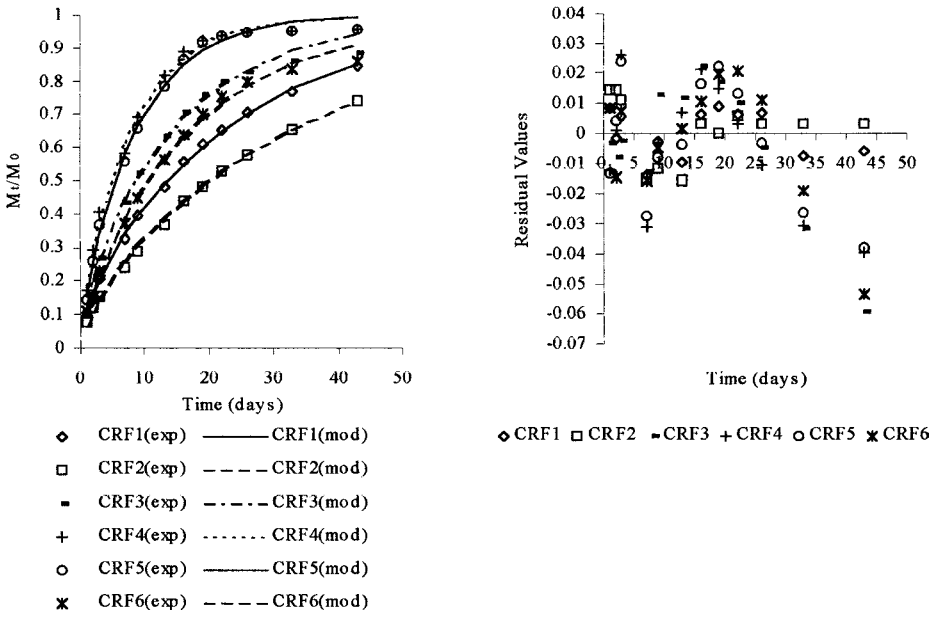

Fig. 2. Plot of experimental data and calculated values by model incorporating stagnant film as boundary condition at CRF surface.

a plot of the experimental data and model predictions, and the distribution of the residual values. A good fit and a more randomized distribution of the residues is observed. Thus, the fit of Eq. 3 to experimental data is better than the fit of Eq. 2.

The *Bi* values estimated for the formulations containing 2,4-D (*Bi* = 4.0–12.0) were higher than ones estimated for the CRF containing ametryn (*Bi* = 2.8) and diuron (*Bi* = 2.0) herbicide *(11)*. The sink condition is a more realistic assumption for high *Bi* values. In fact, when the *Bi* value is high, the external resistance to mass transfer can be neglected, and Eq. 3 is equivalent to Eq. 2 *(11)*. This verifies that the 2,4-D CRF should have the high *Bi* values.

Conclusion

The model incorporating a stagnant film as the boundary condition at the CRF surface (Eq. 3) was able to describe the release kinetic data of 2,4-D in an acceptor medium containing water better than models assuming a sink condition. High *Bi* values were estimated for these formulations, explaining why the model considering a sink condition fits reasonably well to the experimental data. A high *Bi* values means a low external resistance to mass transfer, rendering the sink condition more realistic.

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