

Controlled Release of the Herbicide, Fluometuron, from Matrix Granules Based on Fractionated Organosolv Lignins

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An organosolv lignin and several of its fractions were used to prepare controlled release matrix granules with fluometuron using a melt process. Release profiles of fluometuron from these granules and a commercial granular formulation were studied in vitro. The release rates of fluometuron were considerably reduced from all lignin-based granules as compared to the commercial formulation. The release rates markedly varied with the lignin fraction used in the fluometuron–lignin matrix systems with the corresponding times for 50% release (T_{50}) values ranging from 2.37 to 11.2 days. The variation in release rate of fluometuron was related to the high proportion of low molecular weight lignin and its associated water soluble lignin in the lignin-based granules, in terms of the hydrophobicity of matrix, the content, and release rate of soluble lignin. The release kinetics were fitted to the generalized model for up to 60% release of fluometuron; the kinetics of fluometuron were of the anomalous type for all matrixes in which release rates increased following a delay.

KEYWORDS: Controlled release; fluometuron; organosolv lignin; matrix; granules

INTRODUCTION

Controlled release formulations of pesticides have been well-known to have many advantages over conventional formulations, particularly in terms of reducing active ingredient application rates and leaching potentials in soils. Matrix granular formulations based on biodegradable polymers can reduce the leaching and improve the efficiency of pesticides. Lignin, a polyphenylpropane macromolecule, is the most abundant natural aromatic polymer in the world and a byproduct from many wood pulping processes. Because of its protective and biodegradable properties plus low cost, lignin has been intensively studied as a carrier or sorptive filler in the controlled release matrix formulations of pesticides (1–7).

The focus has been on soda and, especially, kraft lignins and their modified products from sulfur-based wood pulping processes. More recently, an organosolv lignin (Alcell lignin) (8) and its fractionated lignins have been reported as a carrier to formulate matrix granules with bromacil. It was found that the high proportion of low molecular weight lignin and its associated water soluble lignin has a profound influence on both the release rate and the release mechanism (9–10). Apart from the physicochemical properties of the lignin used in the matrix system, the properties of active ingredients, in particular water solubility (S) and octanol–water partition coefficient (K_{ow}), also have a strong influence on the release rate of lignin-based granules (4).

Fluometuron (*N,N*-dimethyl-*N'*-[3-(trifluoromethyl)phenyl]-urea) has a lower water solubility and a higher partition coefficient (110 mg L⁻¹; 25 °C; K_{ow} , 171) than those of bromacil (807 mg L⁻¹; 25 °C; K_{ow} , 75.2) (11), which has been studied in organosolv lignin-based matrix granules. Fluometuron is a pre- and postemergence herbicide used widely as water dispersible (WG) and suspension concentrate formulations for the control of grass and broadleaf weeds in cotton and sugarcane. The major problems associated with its application are losses due to leaching by rainfall and irrigation water, adsorption to soil particles, volatilization, and photochemical and microbial degradation (12–15). Leaching into subsurface soil from no tillage was most severe, and losses could be up to 53% of applied fluometuron (12, 15–16). These existing problems make fluometuron an ideal model compound to formulate matrix formulations with lignins.

The objectives of this study were (i) to obtain controlled release of fluometuron from various fractionated lignin-based matrixes and (ii) to investigate whether low molecular weight lignin and its associated water soluble lignin affect the release of the pesticide. Fluometuron was used in the formulation of matrix granules with various fractionated organosolv lignins using a melt process. The release characteristics of those lignin-based matrix granules were investigated in vitro and related to the properties of the fractionated lignins and the fine structure of the matrixes. The results gained would provide further understanding of the remarkable controlled release characteristics of organosolv lignin.

MATERIALS AND METHODS

Materials. The hardwood organosolv lignin (Alcell lignin) (8) was provided by Repap Technologies Inc (Valley Forge, PA). Alcell lignin

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Table 1. Details of the Fractionated Organosolv Lignins Examined in This Study

| code | solvent system | water soluble lignin content (w/w, %) \pm SD ^a | $M_n^{b,c}$ (g mol ⁻¹) | $M_n^{b,d}$ (g mol ⁻¹) | $d^{b,e}$ |
|-------------------------------|--------------------------|---|------------------------------------|------------------------------------|-----------|
| L ₀ | none | 16.5 \pm 0.79 | 3300 | 900 | 3.7 |
| sequential solvent extraction | | | | | |
| L _{Fr1} | diethyl ether | 39.1 \pm 0.31 | 720 | 480 | 1.5 |
| L _{Fr2} | methanol | 14.1 \pm 0.13 | 2410 | 1040 | 2.3 |
| L _{Fr3} | insolubles | 0.79 \pm 0.05 | 6950 | 2400 | 2.9 |
| solvent mixture precipitation | | | | | |
| L _{WAT} | deionized water | 16.4 \pm 0.26 | | | |
| L _{HCl} | 2 M HCl | 16.2 \pm 0.43 | | | |
| L _{ACE} | acetone–water (1:10) | 12.5 \pm 0.49 | | | |
| L _{HAC} | acetic acid–water (1:10) | 8.1 \pm 0.17 | | | |

^a The data were measured in deionized water at 30 °C (10). ^b Values were taken from Thring et al. (17). ^c Weight average molecular weight. ^d Number average molecular weight. ^e Polydispersity.

was fractionated by sequential solvent extraction with diethyl ether and methanol according to the method of Thring et al. (17) and by solvent-diluted HCl mixture precipitation according to the method reported previously (10). The details of the fractionated lignins are summarized in **Table 1**. All analytical grade solvents were obtained from Fisher Scientific, U.K., and used as received without further purification. Fluometuron was recrystallized from the commercial product Cotoron (WG, 87%) using acetone, and the purity was 99% by HPLC analysis. Fluometuron standard (99.8%) was purchased from Greyhound (Birkenhead, U.K.).

Methods. Preparation of Fluometuron–Lignin Granules. The lignin (Alcell lignin or a fraction) (1 g) and fluometuron (1 g) were weighed, thoroughly mixed, and then heated on a hot plate at 150–160 °C for 10 min. After it was cooled, the solid glass was granulated and sieved to the granule size of 0.7–1.0 mm. The granules were analyzed for fluometuron content by extracting with acetone (sonicated) in quadruplicate, filtered through a nylon membrane, and analyzed using HPLC. A code for each lignin-based matrix was used, FLx, where F represents fluometuron and Lx is the original or a fractionated lignin.

Measurement of Herbicide Release. Fluometuron release from the lignin-based granules (three replicates, 50 mg) was studied at 30 °C in reagent bottles using a controlled environment incubator orbital shaker at 150 rpm. Immersion water was sampled at intervals and completely replaced with fresh deionized water (300 mL) in order to maintain “sink” conditions. The samples collected were filtered and then analyzed by HPLC using a Phenomenex column (Spherisorb 5 ODS 2, 150 mm \times 3.2 mm, 5 μ m) and a diode array detector (Gilson 170) at 254 nm. An isocratic regime of 55% acetonitrile in water was used as a mobile phase at a flow rate of 1 mL min⁻¹.

Measurement of Release of Water Soluble Lignins. The water samples were also analyzed for water soluble lignin content using a UV/vis spectrometer (Umicam 8625) at 254 nm. The water soluble lignin content in the solution was calculated on the difference between the total absorbance and the absorbance contributed by fluometuron at 254 nm. The total release of water soluble lignin during the course of the release of fluometuron was determined using the gravimetric analysis reported previously (10).

Electron Scanning Microscopy. The lignin-based granules before and after the release experiment were carefully cut to expose the cross-section without deformation of the granules. The cut granules were mounted with the cross-section facing upward on double-sided tape, sputter-coated with gold, and examined in a Cambridge Stereoscan (model S240, U.K.) microscope.

RESULTS AND DISCUSSION

Compatibility of Fractionated Lignins with Fluometuron.

The compatibility for blending lignins with pesticides is

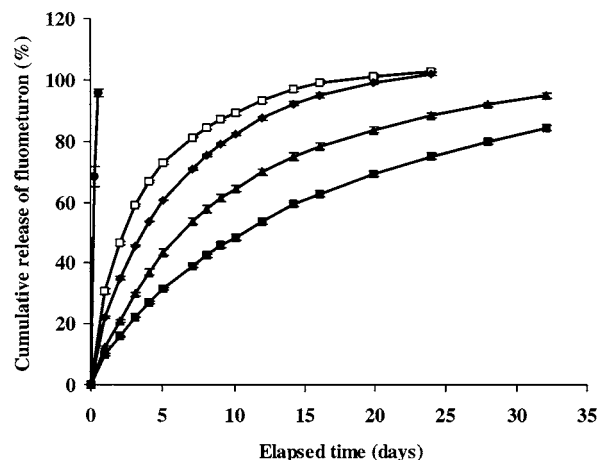


Figure 1. Release of fluometuron from matrix granules based on sequential solvent-extracted lignins and the original Alcell lignin in comparison with a commercial formulation. Cotoron (●), 87% fluometuron WG; FL_{Fr1} (□), 44.43% fluometuron; FL₀ (◆), 43.73% fluometuron; FL_{Fr3} (●), 38.60% fluometuron; FL_{Fr2} (■), 41.66% fluometuron. Error bars represent the standard deviation of three replicates. Where error bars are not shown, the values of standard deviation are smaller than the data points.

normally considered from the solubility parameter (δ) of each of the components in the matrix (2). Polymers have a maximum solubility in solvents with δ values closest to their own. All of the lignins had solubility parameters ranging from 20.5 to 26.5 MPa^{1/2} and moderate hydrogen-bonding capacity (10). The solubility parameter (δ value) of Alcell lignin was reported as 28 MPa^{1/2} based on the lignin molecular formula (18). The δ value of fluometuron was calculated as 27.1 MPa^{1/2} by using the method of Meusburger (19). The similarity in the solubility parameters of fractionated lignins and fluometuron signifies compatibility. As expected, a homogeneous combination was observed by a scanning electron microscope for all fluometuron–lignin matrixes except the FL_{Fr1} matrix (data not shown), which had a rough and heterogeneous combination. The FL_{Fr1}–fluometuron matrix was also different from the other matrixes in appearance and hardness, showing a hard, brittle, and nonglossy appearance.

Release of Fluometuron from Matrix Granules. The release of fluometuron from the matrix granules based on the sequential solvent-fractionated lignins and original Alcell lignin, which were very different in molecular weight and water soluble lignin content (**Table 1**), is compared with that from the commercial granular formulation Cotoron (WG, 87%) in **Figure 1**. The release of fluometuron from the commercial formulation was almost immediate, 95% of the initial amount of fluometuron released within 13 h, while the release rate of fluometuron was dramatically reduced from the granules based on all sequential solvent-fractionated lignin-based. During the same time interval, only 5–12% of the initial amount of fluometuron was released. Similarly, the release rates of fluometuron were reduced from the matrix granules based on all solvent–mixture precipitated lignins as compared to that of the original Alcell lignin, as shown in **Figure 2**.

To facilitate comparison, the T_{50} values (time required for 50% release of fluometuron) were calculated from the constants obtained by fitting the release data to the generalized model, $M_t/M_\infty = kt^n$ (20). M_t/M_∞ is the fraction of pesticide released at time t , k is a constant incorporating the structural and geometric characteristics of the release system, and n is the release exponent indicative of the mechanism of release. The curve-

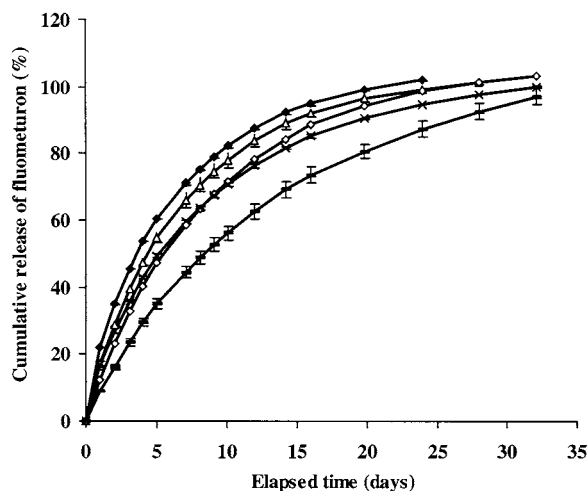


Figure 2. Release of fluometuron from the matrix granules based on solvent mixture precipitated lignins and the original Alcell lignin: FL₀ (◆), 43.73% fluometuron; FL_{wat} (△), 42.16% fluometuron; FL_{HCl} (◇), 41.22% fluometuron; FL_{ace} (×), 41.99% fluometuron; FL_{HAc} (—), 38.84% fluometuron. Error bars represent the standard deviation of three replicates. Where error bars are not shown, the values of standard deviation are smaller than the data points.

Table 2. Constants from Fitting the Generalized Model $M_t/M_\infty = kt^n$ to the Release Data of Fluometuron from the Matrix Granules Based on Fractionated Organosolv Lignins^a

| matrix | k (day ⁻ⁿ) | n | r^b | T_{50}^c (days) | $T_{50-FL_0}/T_{50-FL_0}^d$ |
|-------------------|--------------------------|-------------|--------|-------------------|-----------------------------|
| FL ₀ | 23.31 ± 0.72 | 0.62 ± 0.02 | 0.9998 | 3.68 | 1 |
| FL _{Fr1} | 30.59 ± 0.90 | 0.58 ± 0.03 | 0.9999 | 2.33 | 0.63 |
| FL _{Fr2} | 10.65 ± 0.40 | 0.65 ± 0.02 | 0.9992 | 10.80 | 2.93 |
| FL _{Fr3} | 13.02 ± 0.51 | 0.72 ± 0.02 | 0.9990 | 6.48 | 1.76 |
| FL _{wat} | 17.82 ± 0.63 | 0.69 ± 0.02 | 0.9994 | 4.46 | 1.21 |
| FL _{HCl} | 13.80 ± 0.55 | 0.75 ± 0.02 | 0.9990 | 5.56 | 1.51 |
| FL _{ace} | 17.36 ± 0.60 | 0.64 ± 0.02 | 0.9996 | 5.22 | 1.42 |
| FL _{HAc} | 10.04 ± 0.33 | 0.75 ± 0.02 | 0.9993 | 8.50 | 2.31 |

^a The generalized model was fitting to the data up to 60% release of fluometuron.

^b Correlation coefficient, significant at the probability level of 0.001. ^c The time required for 50% release of fluometuron. ^d The ratio of T_{50} values of various fractionated lignins-based granules to that of Alcell lignin-based granules.

fitting results are summarized in **Table 2**. The greater the T_{50} values, the slower the release. The release rates of fluometuron varied considerably with the lignin fraction used in the matrixes, as suggested by the T_{50} values. The release rates of fluometuron decreased in the order FL_{Fr1} > FL₀ > FL_{wat} > FL_{HCl} ≈ FL_{ace} > FL_{Fr3} > FL_{HAc} > FL_{Fr2}. The greatest reduction in release rates was found for the matrix granules based on the medium molecular weight lignin fraction L_{Fr2} ($M_w = 2400$, **Table 2**).

The low molecular lignin fraction had a high proportion of water soluble lignin (**Table 1**), which had a relatively high solubility of 1100 mg L⁻¹ in water at 30 °C (10). As the water soluble lignin content varied with lignin fraction (**Table 1**), the difference in release rates of fluometuron could be related to the release of water soluble lignin from the matrix. However, there was no simple linear relationship between the T_{50} values and the water soluble lignin content of the granules as found for bromacil–lignin granules based on solvent–mixture precipitated organosolv lignins (10). This discrepancy was attributed to the great difference in water solubility and hydrophobicity (K_{ow}) between fluometuron and bromacil (S , 110 as compared to 807 mg L⁻¹; 25 °C; K_{ow} , 171 to 75.2).

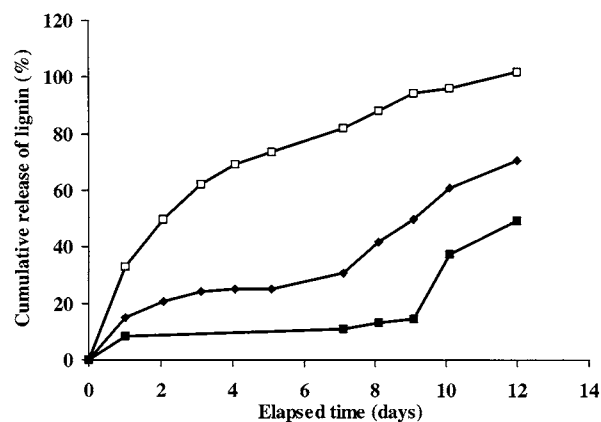


Figure 3. Release of water soluble lignin from the fluometuron–lignin matrix granules based on sequential solvent-extracted lignins and the original Alcell lignin: FL₀ (◆), 9.28% water soluble lignin; FL_{Fr2} (■), 8.22% water soluble lignin; FL_{Fr1} (□), 21.73% water soluble lignin.

As previously mentioned, n is the release exponent indicative of the mechanism of release. The value of n varies with the geometry of the release devices. For a sphere, the value of n is equal to 0.43 for Fickian diffusion, >0.43 and <0.85 for anomalous diffusion. The release mechanism of fluometuron from the granules based on all fractionated lignins was anomalous, as indicated by the n values ranging from 0.58 to 0.75 (**Table 2**).

Release of Water Soluble Lignin from Matrix Granules.

Figure 3 shows the release of water soluble lignin from the granules based on the original and sequential solvent-extracted lignins except for FL_{Fr3} as it had an extremely low water soluble lignin content. As seen in **Figure 3**, the release of water soluble lignin was fastest from the granules FL_{Fr1}, which were based on the low molecular weight lignin fraction with a water soluble lignin content of 21.73% of the matrix (**Table 1**). The release pattern of water soluble lignin from the granules FL_{Fr1} was distinctly different to that of the matrix granules FL₀ and FL_{Fr2} based on Alcell lignin (L₀) and medium molecular weight fraction (L_{Fr2}). The FL_{Fr1} granules had an initial burst while the FL₀ and FL_{Fr2} granules had initial slow release followed by a fast release (i.e., delayed release).

Surprisingly, the release of water soluble lignin from all of the solvent mixture precipitated lignin-based matrix granules (**Figure 4**) followed a similar release pattern as for FL₀ and FL_{Fr2}. These release patterns, however, were different from that of fluometuron for the corresponding granules. The release rates of water soluble lignin decreased with the soluble lignin content but were not directly proportional to soluble lignin content. The results suggested that the release of water soluble lignin could be influenced by the release of fluometuron considering the difference in the water solubility and content in lignin matrixes between fluometuron and soluble lignin.

Correlation of the Release of Fluometuron with Water Soluble Lignins. The release of fluometuron was correlated with the release of water soluble lignin by plotting the cumulative percentage releases against each other at the same time intervals. The plots are shown in **Figure 5** for the granules based on the sequential solvent extracted and in **Figure 6** for the solvent mixture precipitated lignins. As shown in **Table 3**, the cumulative release of fluometuron correlated well with that of water soluble lignin in a nonlinear (i.e., a power law model) and linear relationship at the early and late release stages, respectively.

Although the granules FL_{Fr1} had a ratio of water soluble lignin to fluometuron of 0.49 in the matrix, the n value was 1.09 for

Table 3. Constants from Fitting a Power Law Model $y = kx^n$ and a Linear Model $y = mx + b$ to the Plots of the Cumulative Release of Fluometuron vs the Cumulative Release of Water Soluble Lignin

| matrix | matrix composition (%) | | soluble lignin/ fluometuron ratio | nonlinear part in the curves ($y = kx^n$) ^a | | | linear part in the curves ($y = mx + b$) ^b | | | inflection point ^c ratio |
|-------------------|------------------------|---------|--------------------------------------|---|-------------|---------------------|--|--------------|---------------------|--|
| | fluometuron | soluble | | k | n | r^d | m | b | r^d | |
| FL ₀ | 43.73 | 9.28 | 0.212 | 0.10 ± 0.03 | 1.95 ± 0.09 | 0.9863 | 0.41 ± 0.03 | 58.27 ± 1.70 | 0.9962 | 0.41 |
| FL _{Fr1} | 44.43 | 21.73 | 0.490 | 0.67 ± 0.11 | 1.09 ± 0.04 | 0.9995 | 0.60 ± 0.06 | 31.95 ± 6.06 | 0.9920 | 1.01 |
| FL _{Fr2} | 41.66 | 8.22 | 0.197 | 0.17 ± 0.05 | 2.16 ± 0.12 | 0.9474 ^e | 0.26 ± 0.03 | 40.19 ± 1.07 | 0.9486 ^e | 0.30 |
| FL _{WAT} | 42.16 | 9.48 | 0.225 | 0.02 ± 0.01 | 2.25 ± 0.10 | 0.9902 | 0.42 ± 0.03 | 50.76 ± 1.82 | 0.9948 | 0.55 |
| FL _{HCl} | 41.22 | 9.52 | 0.231 | 0.03 ± 0.01 | 2.48 ± 0.12 | 0.9947 | 0.38 ± 0.04 | 44.18 ± 2.48 | 0.9996 | 0.39 |
| FL _{ACE} | 41.99 | 7.25 | 0.173 | 0.19 ± 0.04 | 2.07 ± 0.07 | 0.9875 | 0.44 ± 0.03 | 53.69 ± 1.19 | 0.9886 ^f | 0.27 |
| FL _{HAc} | 38.84 | 4.95 | 0.127 | | | | 0.30 ± 0.04 | 43.29 ± 0.98 | 0.9737 ^e | 0.19 |

^a The power law model was fitting to the nonlinear part of the curves at the early release stage. ^b The linear model was fitting to the linear part of the curves at the late release stage. ^c The inflection points of the curves were represented by the ratio of the percentage release of water soluble lignin to fluometuron in the plots of the cumulative release of fluometuron vs the cumulative release of water soluble lignin (Figures 6 and 7). ^d Correlation coefficient, significant at the probability level of 0.001 where the data are not labeled. ^e Correlation coefficient, significant at the probability level of 0.05. ^f Correlation coefficient, significant at the probability level of 0.01.

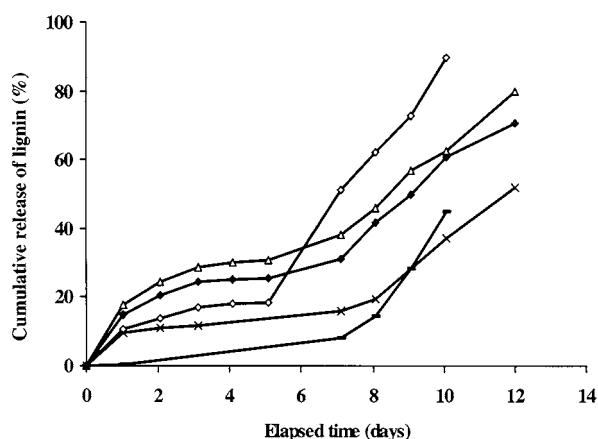


Figure 4. Release of water soluble lignin from the fluometuron–lignin matrix granules based on solvent mixture precipitated lignins and the original Alcell lignin: FL₀ (◆), 9.28%; FL_{WAT} (△), 9.48%; FL_{HCl} (◇), 9.52%; FL_{ACE} (×), 7.25%; FL_{HAc} (○), 4.95% of water soluble lignins.

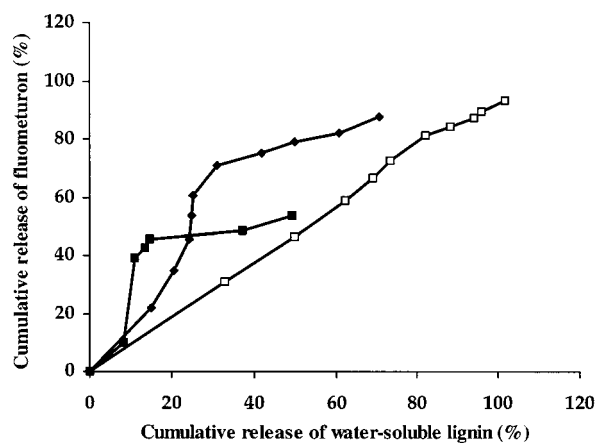


Figure 5. Plots of the cumulative release of fluometuron vs the cumulative release of water soluble lignin for the matrix granules based on sequential solvent fractionated lignins and the original Alcell lignin: FL₀ (◆), 43.73% fluometuron, 9.28% water soluble lignin; FL_{Fr2} (■), 41.66% fluometuron, 8.22% water soluble lignin; FL_{Fr1} (□), 44.43% fluometuron, 21.73% water soluble lignin.

the matrix granules, indicating that water soluble lignin released almost as fast as that of fluometuron possibly due to the aqueous solubility of soluble lignin being 10 times higher than that of fluometuron (1100 as compared to 110 mg L⁻¹). For the other granules with much lower ratios of soluble lignin to fluometuron

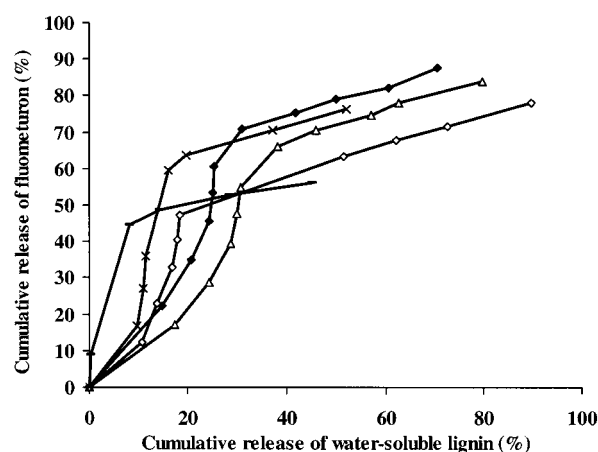


Figure 6. Plots of the cumulative release of fluometuron vs the cumulative release of water soluble lignin for the matrix granules based on solvent mixture precipitated lignins and the original Alcell lignin: FL₀ (◆), 43.73, 9.28%; FL_{WAT} (△), 42.16, 9.48%; FL_{HCl} (◇), 41.22, 9.52%; FL_{ACE} (×), 41.99, 7.25%; FL_{HAc} (○), 38.84, 4.95% of fluometuron and water soluble lignin, respectively.

(0.13–0.23), the release of soluble lignin was much slower than that of fluometuron during the early release stage. As a result, the ratio of soluble lignin to fluometuron remaining in the matrix then increased, producing a subsequent release of soluble lignin faster than that of fluometuron at the late release stage, as indicated by the slope (m) less than 1 (Table 3).

These biphasic patterns were explored by plotting the point of inflection (the point where the extrapolated lower and upper lines intersect) of the curves in the plots (Figures 5 and 6) vs the water soluble lignin content of granules in Figure 7. A highly significant linear relationship ($P = 0.001$) was observed between the ratio (at the inflection point) of the cumulative release of lignin to fluometuron and the water soluble lignin content in the matrix granules. This indicated that the ratio of the release rates of water soluble lignin to fluometuron was proportional to the water soluble lignin content. The lower the soluble lignin contents, the slower the release of soluble lignin as compared to the release of fluometuron.

The above results suggested that the release rate of soluble lignin could only exceed that of fluometuron when the lignin-based matrix granules contained a high proportion of water soluble lignin or after a sufficient amount of fluometuron had been released. The lower the water soluble lignin contents, the greater the amount of fluometuron released before the inflection point occurred.

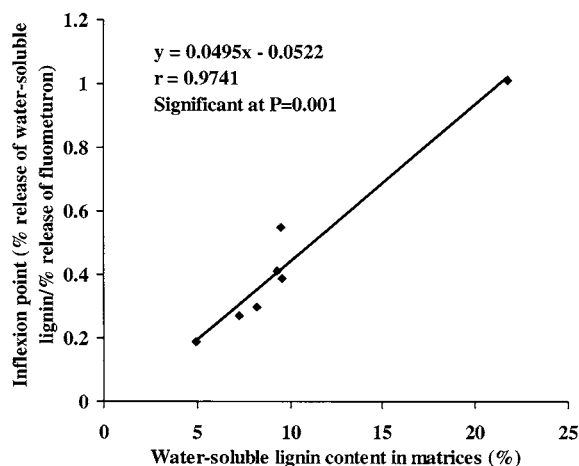


Figure 7. Plot of the inflexion points of the curves in **Figures 6** and **7** vs the water soluble lignin content in the fluometuron–lignin matrix granules.

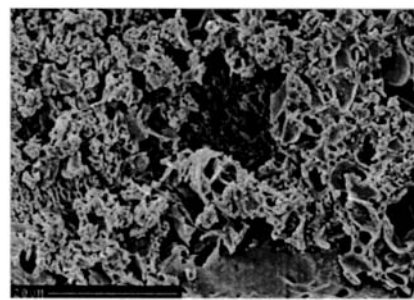
All of the matrix granules had similar fluometuron contents but different water soluble lignin contents (**Table 1**). The presence of water soluble lignin affected the hydrophobicity of fluometuron–lignin matrixes and the release of soluble lignin, leading to the different release rates of fluometuron from various fractionated lignin-based granules.

The release of water soluble lignin affected the release of fluometuron only when the former released at a substantial amount or a high rate (**Figures 5** and **6**). The influence of soluble lignin on the release of fluometuron could be varied with the different release rates of soluble lignin at the late stage (*m* values, **Table 3**). This was different from the previously reported results where the release of bromacil was primarily affected by the soluble lignin content in the granules and less by the release rates of lignin (*10*).

As water soluble lignin was released, more pores were created in the matrix, leading to an increase in release rate. In this case, the soluble lignin acted as a “channelling agent” in the matrix, resulting in a shortened diffusion pathway for fluometuron to release from the matrix. Therefore, the faster the soluble lignins released, the faster fluometuron released. As shown in **Figure 8**, more extensive and larger contiguous pores were found in the granules FL_{F1} (**Figure 8a**) with 21.73% of water soluble lignin than in the granules FL₀ (**Figure 8b**) with 9.28% of water soluble lignin. The contiguous porous structure with larger pore size of the FL_{F1} granules would facilitate the diffusion of fluometuron out of the matrix, resulting in the high release rates of soluble lignin and fluometuron.

The release rate of soluble lignin (**Figure 7**) and the amount of fluometuron released were highly dependent on the soluble lignin content. Therefore, the presence of water soluble lignin had a considerable influence on the release characteristics of fluometuron as compared to bromacil. The release rate of an active ingredient having a water solubility much lower than that of soluble lignin was related to not only the soluble lignin content in the matrix granules but also the hydrophobicity of matrix and release rate of soluble lignin.

This study shows that the release profile of fluometuron from a granular formulation can be controlled by using an organosolv lignin (Alcell lignin) and its various lignin fractions as a formulating agent. The release characteristics of fluometuron lignin granules were related to the water soluble lignin in the lignin-based matrix granules through the change of hydropho-



8 a)



8 b)

Figure 8. Scanning electron micrographs of the cross-section of fluometuron–lignin matrixes after release: (a) FL_{F1} (44.43% fluometuron, 21.73% water soluble lignin) after 100% release of fluometuron and water soluble lignin and (b) FL₀ (43.73% fluometuron, 9.28% water soluble lignin) after 100% release of fluometuron and 60% release of water soluble lignin.

bicity of the matrix and the release of soluble lignin. These results also emphasize the importance of both the content and the release rate of water soluble lignin in altering the release rates of hydrophobic active ingredients from the matrix granules. The release mechanism of fluometuron was found to be anomalous for all of the lignin-based granules. The results obtained in this study, showing a considerable reduction in the amount of fluometuron available in the release medium from the organosolv lignin-based matrixes, provided a promising way to minimize the potential environmental risks associated with its application. In addition, the results obtained could provide useful information for designing appropriate organosolv lignin-based formulations for hydrophobic pesticides.

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