

## Use of Ethylcellulose To Control Chlorsulfuron Leaching in a Calcareous Soil

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Controlled release formulations (CRFs) have been researched to reduce the water-polluting risk derived from the use of conventional formulations of chlorsulfuron. Coated chlorsulfuron granules were produced in a Wuster-type fluidized-bed equipment using two different amounts of ethylcellulose. The highest one was modified by the addition of a plasticizer such as dibutyl sebacate. The encapsulation efficiency and morphological properties of coated granules having been studied, the chlorsulfuron kinetic release in water was studied. In addition, the mobility of chlorsulfuron in a calcareous soil was finally carried out. High encapsulation efficiency was obtained, being nearly 100% in all cases. SEM pictures show a homogeneous film in coated CRFs; thickness oscillates between 23.32  $\mu\text{m}$  for the system prepared with a 10% of ethylcellulose and 32.61  $\mu\text{m}$  for the system prepared with a 20% ethylcellulose plus plasticizer. The rate of chlorsulfuron release from coated CRFs is diminished in all cases in relation to chlorsulfuron commercial formulation, the latter being completely dissolved in <1 h, but it took at least 50 days to release 90% of chlorsulfuron from the formulation coated with a 20% ethylcellulose plus plasticizer. Using a generic equation, the time taken for 50% of the active ingredient to be released into water ( $t_{50}$ ) was calculated. From the analysis of the  $t_{50}$  values, it can be deduced that the release rate of chlorsulfuron can be mainly controlled by changing the thickness of the coating film, by modifying the surface properties of the coating film, and by adding a plasticizer. Mobility experiments carried out in calcareous soil show that the use of coated CRFs reduces the presence of chlorsulfuron in the leachate compared to commercial formulation.

**KEYWORDS:** Chlorsulfuron; ethylcellulose; controlled release; fluidized bed; coating

### INTRODUCTION

Chlorsulfuron [1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea] is a sulfonylurea herbicide used as a pre- and postemergent herbicide to control a variety of weeds on cereal grains, pasture and rangeland, industrial sites, and turf grass (1). Chlorsulfuron is likely to be persistent and highly mobile in the environment. It may be transported to nontarget areas by runoff and/or spray drift. Degradation by hydrolysis appears to be the most significant mechanism for degradation of chlorsulfuron, but is significant only in acidic environments (23 day half-life at pH 5); it is stable to hydrolysis at neutral to high pH. Degradation half-lives in soil environments range from 14 to 320 days (2). Chlorsulfuron is a weak acid ( $\text{p}K_{\text{a}} = 3.6$ ) with water solubilities ranging from 0.587  $\text{g L}^{-1}$  at pH 5 to 31.8  $\text{g L}^{-1}$  at pH 7. The mobility of chlorsulfuron (3, 4) was found to be enhanced at higher soil pH and/or relatively lower organic matter content, reflecting the influence of these soil properties on herbicide adsorption. The slow rate of chlorsulfuron degradation coupled with its high potential

mobility in soils suggests a high potential for transport below the root zone with subsequent movement into groundwaters, especially in soils with shallow groundwater tables.

The risk of contamination resulting from rapid runoff and leaching of highly soluble pesticides such as chlorsulfuron can be minimized through the application of the pesticide in controlled release formulations (CRFs). Besides, the use of CRFs has beneficial effects related to the reduction in the amount of chemical required for pest control, increased safety for the pesticide applicator, and a general decrease in nontarget effects (5).

The parameters that affect the properties of CRFs depend on the nature and type of polymer used. Despite several polymers employed in CRFs in agriculture, natural polymers such as starch, ethylcellulose, lignin, chitosan, and alginate are preferred over synthetic polymers because of their nontoxic, low-cost, wide availability, and biodegradability characteristics (6–10).

Previous encapsulation studies of agrochemicals using biodegradable polymers and modifiers (5, 6, 8) showed that it was necessary to develop and optimize the preparation of CRFs to encapsulate active ingredients with high water solubility values such as the herbicide chlorsulfuron.

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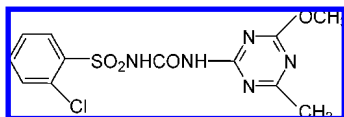


Figure 1. Chemical structure of chlorsulfuron.

Table 1. Coating Solution Composition for the Preparation of CR Granules Containing Chlorsulfuron

| CR granules <sup>a</sup> | wt of CF granules (g) | coating solution composition |         |              |                     |                      |
|--------------------------|-----------------------|------------------------------|---------|--------------|---------------------|----------------------|
|                          |                       | EC (g)                       | DBS (g) | ethanol (mL) | EC <sup>b</sup> (%) | DBS <sup>b</sup> (%) |
| CFEC <sub>10</sub>       | 20                    | 2                            |         | 100          | 10                  |                      |
| CFEC <sub>20</sub>       | 20                    | 4                            |         | 200          | 20                  |                      |
| CFEC <sub>20</sub> DBS   | 20                    | 4                            | 0.45    | 200          | 20                  | 2.25                 |

<sup>a</sup> CFEC<sub>10</sub>, commercial chlorsulfuron formulation, ethylcellulose 10%; CFEC<sub>20</sub>, commercial chlorsulfuron formulation, ethylcellulose 20%; CFEC<sub>20</sub>DBS, commercial chlorsulfuron formulation, ethylcellulose 20%, dibutyl sebacate 2.25%. <sup>b</sup> Based on the weight of CF granules.

The purpose of this paper was to research the preparation and characterization of chlorsulfuron coated CR granules using a natural polymer such as ethylcellulose (EC) and a plasticizer such as dibutyl sebacate (DBS). Ethylcellulose is one of the most widely used film coatings because of the many advantages it affords formulators, such as good film formability, excellent physical–chemical stability, and minimum toxicity (11). Plasticizer is commonly incorporated with the polymeric film, to change the flexibility, tensile strength, and adhesion properties of the resulting film (12). DBS has been used in previous research due to its lipophilic character (13) and also due to a minimum pollution potential for the environment (14).

In the present study, CRFs were prepared by coating a commercial chlorsulfuron formulation with ethylcellulose. Therefore, coated chlorsulfuron granules were produced in a Wuster-type fluidized-bed equipment, using an ethanolic solution of EC on two different polymer levels. The highest one was modified by the addition of a plasticizer such as dibutyl sebacate. The characteristics of the CR chlorsulfuron herbicide granules were tested, and kinetic-release experiments were carried out in water to determine the release characteristics of the CR granules. Besides, mobility experiments were also performed to determine the leaching characteristics of chlorsulfuron in a calcareous soil from CR granules and the commercial product.

## MATERIALS AND METHODS

**Chemicals.** The chlorsulfuron used in this study was a commercially available formulation (CF), Glean (75% w/w) (DuPont Ibérica, SL, Barcelona, Spain) supplied as water dispersible granules. Its molecular formula and selected properties are as follows (1): molecular formula, C<sub>12</sub>H<sub>12</sub>ClN<sub>5</sub>O<sub>4</sub>S; molecular weight, 357.8; melting point, 174–178 °C; vapor pressure (25 °C), 3 × 10<sup>-6</sup> mPa; water solubility (25 °C), 0.587 g L<sup>-1</sup> (pH 5), 31.8 g L<sup>-1</sup> (pH 7); pK<sub>a</sub>, 3.6. The chlorsulfuron structure is shown in Figure 1.

The film-forming material of polymer coating was ethylcellulose (EC) (Ethocel; ethoxy content, 48.0–49.5%; viscosity, 9–11 cP). This product was supplied by Fluka Chemie AG (Buchs, Switzerland). The plasticizer selected for the study was dibutyl sebacate (DBS), (≥97%, *d* = 0.936 g mL<sup>-1</sup>), supplied by Fluka Chemie AG (Buchs, Switzerland).

**Formulations.** (a) *Preparation of Coating Dissolution.* Appropriate quantities of ethylcellulose and plasticizer were combined and dissolved in ethanol (Table 1) to obtain coating dissolutions with two different polymer levels and, in one case, with a plasticizer. The coating film consists of 10 and 20% ethylcellulose, respectively, of the weight of the commercial chlorsulfuron formulation (20 g). For the coating

Table 2. Characteristics of Commercial Formulation and Controlled Release Granules (0.2 mm < *d* < 1 mm) Containing Chlorsulfuron

| formulation            | theoretical chlorsulfuron loading (%) <sup>a</sup> | practical chlorsulfuron loading (%) | solids recovery (%) <sup>b</sup> | EE (%) | mean thickness of film (μm) |
|------------------------|--|-------------------------------------|----------------------------------|--------|-----------------------------|
| CF                     |  | 78.00 (2.21) <sup>c</sup>           |                                  |        |                             |
| CFEC <sub>10</sub>     | 70.90  | 72.17 (1.33)                        | 84.31                            | 101.79 | 23.32 (3.53)                |
| CFEC <sub>20</sub>     | 65.00  | 63.60 (1.69)                        | 85.58                            | 97.84  | 30.26 (3.59)                |
| CFEC <sub>20</sub> DBS | 63.80  | 64.01 (0.50)                        | 91.41                            | 98.67  | 32.61 (2.05)                |

<sup>a</sup> Theoretical chlorsulfuron loading (%) = (total amount of chlorsulfuron used to prepare the formulations/total amount of solid components used in the formulation process) × 100. <sup>b</sup> Solids recovery (%) = (total amount of formulation recovered/total amount of solid components used in the formulation process) × 100. <sup>c</sup> Values in parentheses represent the standard deviation.

dissolution containing a plasticizer, the coating film consists of 20% EC and 2.25% DBS of the weight of the commercial chlorsulfuron formulation.

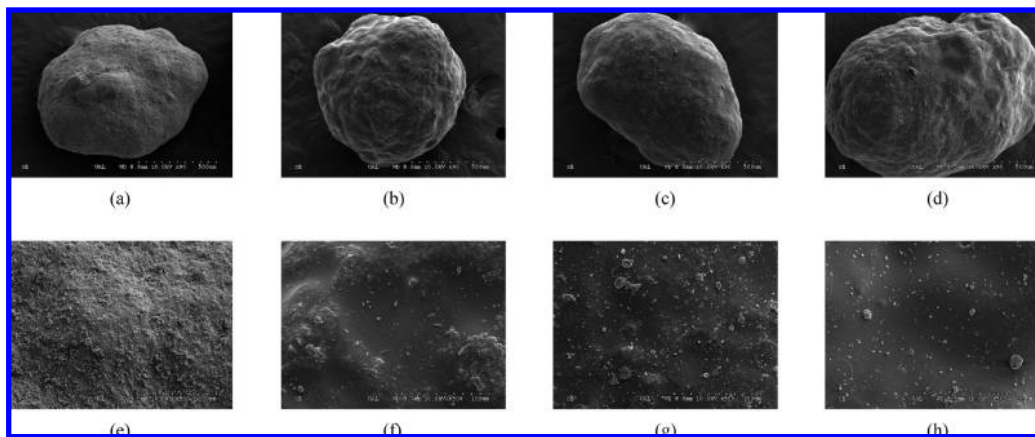
(b) *Preparation of Coated Formulations.* The commercial chlorsulfuron formulation (CF) was sieved to obtain granules between 0.20 and 1.0 mm, and 20 g of this fraction was loaded into a fluidized-bed coater (Mini-Glatt, Glatt AG, Pratteln 1, Switzerland) assembled with a Wuster insert. The bed temperature was regulated to 60 ± 2 °C. The granules were preheated at this temperature for 10 min. Coating dissolution was delivered by a peristaltic pump (Watson-Marlow, model 1B-1003/R) and sprayed into the fluidized bed via a spray nozzle at the atomizing pressure of 1.2 bar. Coating dissolutions were pumped at a flow rate of 2.5 mL min<sup>-1</sup> to prepare CFEC<sub>10</sub> and at a flow rate of 5 mL min<sup>-1</sup> for both CFEC<sub>20</sub> and CFEC<sub>20</sub>DBS granules. The total spraying time was in all cases 40 min. The coated granules were then dried in the same equipment at 70 °C for 10 min. Coated granules were sieved, selecting the granules of size between 0.2 and 1 mm.

**Coated Granules Characterization.** The actual concentration of chlorsulfuron in the granules was determined by dissolving 20 mg of the granules in 50 mL of methanol in an ultrasound bath for 15 min. This led to a complete disintegration of the granules. The volume was made up to 100 mL with water. The concentration of chlorsulfuron in the solution was determined by high-performance liquid chromatography (HPLC) using a Beckman Coulter Inc., System Gold HPLC (Fullerton, CA) equipped with a diode array detector and 32 Karat data station. The HPLC operating conditions to analyze chlorsulfuron were described by Bernal et al. (15). The mobile phase used was an acetonitrile/aqueous solution of H<sub>3</sub>PO<sub>4</sub> (0.1% w/w) (pH 2.2) mixture 40:60 at a flow rate of 1 mL min<sup>-1</sup>; chlorsulfuron was analyzed at its maximum absorption of wavelength, 227 nm, by injecting a volume of 50 μL. Separation by isocratic elution was performed on a 150 × 3.9 mm Nova-Pak LC-18 bonded-phase column (Waters, Millipore Corp.). The results of percent chlorsulfuron loading and encapsulation efficiency (EE) were calculated using eqs 1 and 2. These results are shown in Table 2.

$$\text{practical chlorsulfuron loading (\%)} = \left( \frac{\text{wt of chlorsulfuron CR granules}}{\text{wt of CR granules}} \right) \times 100 \quad (1)$$

$$\text{encapsulation efficiency (\%)} = \left( \frac{\text{practical chlorsulfuron loading}}{\text{theoretical chlorsulfuron loading}} \right) \times 100 \quad (2)$$

The morphological and structural surface of coated granules was examined with the aid of a Hitachi S-3500-N scanning electron microscope (SEM) at the required magnification at room temperature. The granules were settled on brass hold and sputtered with a thin coat of gold under vacuum. The acceleration voltage used was 10 kV with secondary electron image as a detector. To examine the internal morphology of the polymeric films, coated granules were carefully cut with the aid of a chisel, and their cross sections were photomicrographed. The thickness of the prepared films was measured. Each film sample was measured at 10 different points.



**Figure 2.** Scanning electron microscopic photographs of chlorsulfuron granules ( $0.2 \text{ mm} < d < 1 \text{ mm}$ ), CF granule (magnification  $\times 90$ ) (a), surface morphology of CF granule (magnification  $\times 500$ ) (e), CFEC<sub>10</sub> granule (magnification  $\times 90$ ) (b), surface morphology of CFEC<sub>10</sub> granule (magnification  $\times 500$ ) (f), CFEC<sub>20</sub> granule (magnification  $\times 90$ ) (c), surface morphology of CFEC<sub>20</sub> granule (magnification  $\times 500$ ) (g), CFEC<sub>20</sub>DBS granule (magnification  $\times 90$ ) (d), and surface morphology of CFEC<sub>20</sub>DBS granule (magnification  $\times 500$ ) (h).

**Water Release Kinetics.** For each sample (two replicates), an accurately weighed quantity of granules containing about 8 mg of chlorsulfuron was added to 500 mL of Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffer (pH 8.2) and placed into stoppered conical flasks. Flasks were maintained in a thermostated bath at  $25 \pm 0.1 \text{ }^\circ\text{C}$ . At different time intervals, aliquots of 0.5 mL were removed for determination of chlorsulfuron, and 0.5 mL of fresh buffer was later added to the flasks to maintain sinking conditions.

**Soil Mobility Experiments.** The soil used was a calcareous soil (Calcareous Regosol) with a pH of 8.7, previously described by Flores-Céspedes et al. (16) and representative of soils from the Almería area (southeastern Spain).

The columns were made using a polyvinyl chloride (PVC) pipe (4.4 cm internal diameter, 24 cm length) and applying 2 mm thick silicone ridges around the inside of the column at 5 cm increments to minimize boundary flow (17). Nylon mesh with an effective 60  $\mu\text{m}$  pore diameter and lined with a layer of wool-looking fiberglass was sealed to the bottom of each column to prevent displacement of the soil from the columns and minimize the dead-end volume (18). Each column contained, from the bottom to the top, soil (20 cm) and a layer of acid-washed sand (1 cm). The soil, screened through a 2 mm sieve, was added to the column in small increments to minimize particle size segregation, obtaining a final bulk density of  $1.53 \text{ g cm}^{-3}$ . This bulk density resulted in a pore volume of approximately 100 mL. Prior to application of the herbicide treatments, the columns were saturated with distilled water via capillarity and then left to be drained for 1 day.

The pesticide treatments were applied at a rate of  $7 \text{ mg of ai kg}^{-1}$ . Each pesticide treatment was applied to duplicate soil columns. The formulations were uniformly distributed on the soil surface. After that, 1 cm of acid-washed sand was added to the top of the column. Next, the columns were eluted with approximately 1000 mL of distilled water by using a Watson-Marlow model 1B-1003/R peristaltic pump with a flow rate of  $4 \text{ mL h}^{-1}$ . The leachate was collected in fractions of about 100 mL every day. Aliquots were taken from the leachates, then passed through  $0.45 \text{ }\mu\text{m}$  PTFE filters, and finally injected directly in the HPLC system. At the end of the leaching procedure, the columns were allowed to drain for 24 h. The soil, acid-washed sand, and granules were removed from the columns. Each sample was dried at room temperature and homogenized. Subsamples of each were extracted in conical flasks, placed in a shaking bath for 24 h with a methanol/water (80:20) mixture, and analyzed by HPLC, as described above. The herbicide content of CFEC<sub>10</sub>, CFEC<sub>20</sub>, and CFEC<sub>20</sub>DBS were determined by dissolving the granules in 50 mL of methanol in an ultrasound bath for 15 min. The volume was made up to 100 mL with water and analyzed by HPLC.

## RESULTS AND DISCUSSION

**Coated Granules Characterization.** Characteristics of controlled-release granules ( $0.2 \text{ mm} < d < 1 \text{ mm}$ ) containing chlorsulfuron are presented in **Table 2**.

The percentages of active ingredient oscillate between 72.17% for the system CFEC<sub>10</sub> and 63.60% for the system CFEC<sub>20</sub>, the active ingredient content of the coated granules being suitable for agricultural practice.

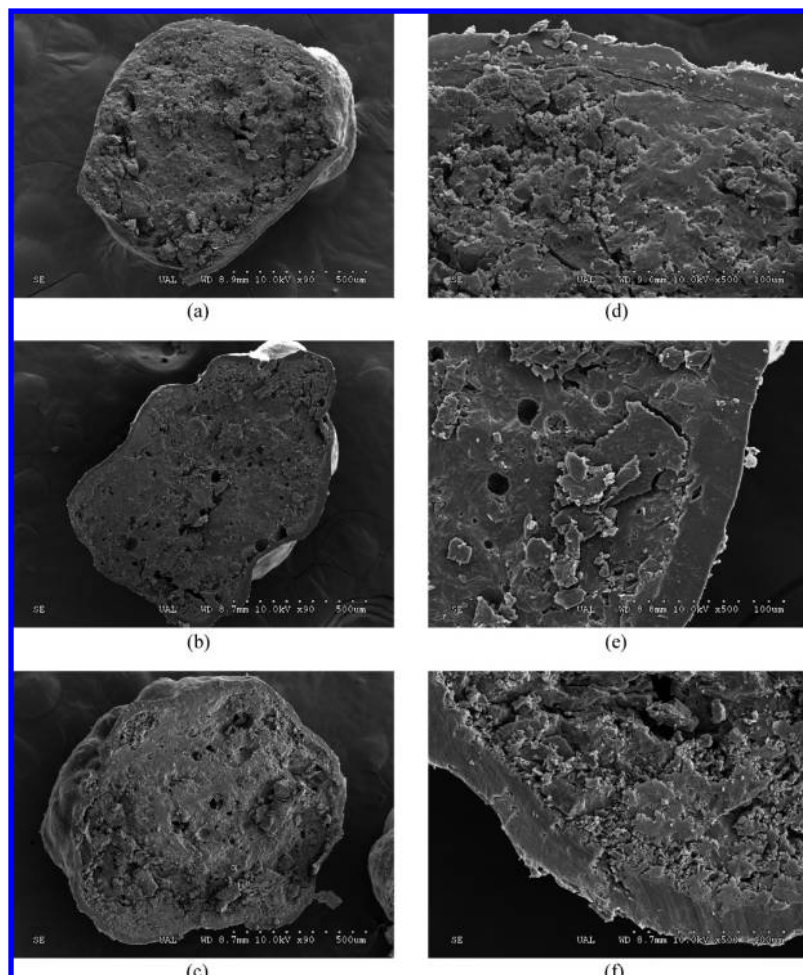
It can be observed that the values of encapsulation efficiency (EE) range between 97.84% for the system CFEC<sub>20</sub> and 101.79% for the system CFEC<sub>10</sub>. These data highlight the efficacy of the method used for the encapsulation of chlorsulfuron. For the formulation CFEC<sub>10</sub>, the EE value obtained indicates that the herbicide content in the granules is slightly higher than the theoretical content, suggesting a minimal solids loss during the formulation process.

SEM pictures (**Figure 2**) show a uniform and intact coating of ethylcellulose and plasticizer. In panels e–h of **Figure 2** (magnification  $\times 500$ ) a gradual disappearance of the wrinkled aspect of the external surface is observed from CF to CFEC<sub>20</sub>DBS granules.

The cross section (**Figure 3**) shows the porous core structure with a fine and coherent film at the boundary in the coated formulations. The thickness of the coating material, covering the herbicide granule, was estimated using SEM photographs. The thickness of the coating film (**Table 2**) varied between  $23.32 \text{ }\mu\text{m}$  for the system CFEC<sub>10</sub> and  $32.61 \text{ }\mu\text{m}$  for the system CFEC<sub>20</sub>DBS.

As expected, the highest amount of EC in the coating dissolution applied for the system CFEC<sub>20</sub> increases the thickness of the membrane in relation to the system CFEC<sub>10</sub>. The presence of the plasticizer in the system CFEC<sub>20</sub>DBS leads to a slight increase in the film thickness compared to the system CFEC<sub>20</sub>.

**Water Release Kinetics.** The effects of ethylcellulose percentage on the release behavior of chlorsulfuron are shown in **Figure 4**. Percentages in ethylcellulose coating aside, these formulations produce a diminishing process of release of the active ingredient in relation to the commercial formulation. As an example, 100% of chlorsulfuron is released in  $<1 \text{ h}$  for the CF; meanwhile, about 35 days is necessary to release the same active ingredient percentage for CFEC<sub>20</sub>. This figure also shows that the influence of ethylcellulose percentage appears clearly defined by means of the two CR systems CFEC<sub>10</sub> and CFEC<sub>20</sub>. The highest quantity in polymer of the CFEC<sub>20</sub> formulation causes a pronounced delay in release rate in relation to CFEC<sub>10</sub>. Only a slight decrease in chlorsulfuron release rate from the system CFEC<sub>20</sub>DBS is observed in relation to the system CFEC<sub>20</sub>.



**Figure 3.** Scanning electron microscopic photographs of cross section for coated chlorsulfuron granules ( $0.2 \text{ mm} < d < 1 \text{ mm}$ ), CFEC<sub>10</sub> granule (magnification  $\times 90$ ) (a), surface morphology of CFEC<sub>10</sub> granule (magnification  $\times 500$ ) (d), CFEC<sub>20</sub> granule (magnification  $\times 90$ ) (b), surface morphology of CFEC<sub>20</sub> granule (magnification  $\times 500$ ) (e), CFEC<sub>20</sub>DBS granule (magnification  $\times 90$ ) (c), and surface morphology of CFEC<sub>20</sub>DBS granule (magnification  $\times 500$ ) (f).

For all formulations, an exponential decrease in the release of chlorsulfuron was observed over time. This result is probably due to an increase in the distance over which dissolved molecules have to be diffused as the depleted zone advances to the core of the matrix. The release data of chlorsulfuron were analyzed by applying the exponential equation (19)

$$\frac{M_t}{M_0} = 1 - e^{-kt}$$

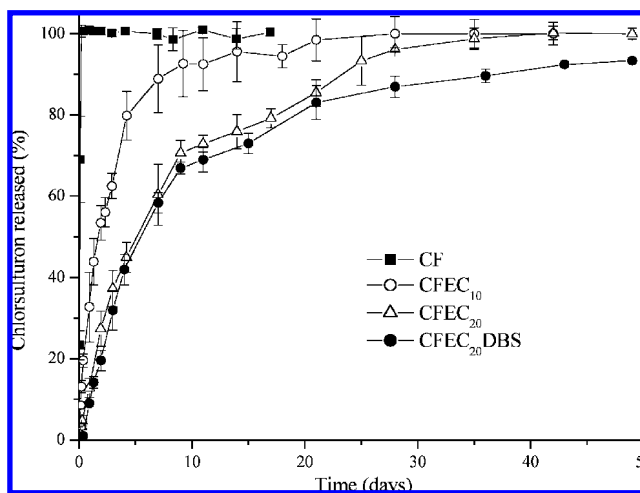
where  $M_t/M_0$  is the released fraction at time  $t$  (days) and  $k$  is the dissolution rate constant ( $\text{days}^{-1}$ ).

The  $k$  values and correlation coefficients were obtained by applying the model to predict the release rate, using the nonlinear curve-fitting utility of SigmaPlot software (version 9.0, Systat Software, Inc.). These values are presented in **Table 3**.

There was very good correlation of the release profiles of CR chlorsulfuron granules with the empirical equation, the correlation coefficient ( $r$ ) being  $>0.99$ .

The values of  $k$  ranged from 0.108 for CFEC<sub>20</sub>DBS granules to 10.98 for CF granules. The time range to release 50% of chlorsulfuron,  $t_{50}$ , was calculated for the granules using constants from **Table 3**. The values ranged from 0.06 day for CF granules to 6.41 days for CFEC<sub>20</sub>DBS granules. The variation order is

$$\text{CF} < \text{CFEC}_{10} < \text{CFEC}_{20} < \text{CFEC}_{20}\text{DBS}$$



**Figure 4.** Cumulative release of chlorsulfuron from EC-coated granules into water (error bars represent the standard deviation of two replicates).

This variation order shows that the presence of plasticizer in the formulation retards the release of chlorsulfuron in relation to those without plasticizer. This fact could be due to the formation of films without cracks when plasticizers have been added with ethylcellulose that can diminish the permeability as shown by Lecomte et al. (13). From the  $t_{50}$  data for systems

**Table 3.** Constants from Fitting the Empirical Equation  $M_t/M_0 = 1 - e^{(-kt)}$  to Release Data of Chlorsulfuron into Static Water

| CR granules            | $k$ (days <sup>-1</sup> )  | $r$   | $t_{50}$ (days) |
|------------------------|----------------------------|-------|-----------------|
| CF                     | 10.98 ± 0.945 <sup>a</sup> | 0.990 | 0.06            |
| CFEC <sub>10</sub>     | 0.379 ± 0.019              | 0.993 | 1.74            |
| CFEC <sub>20</sub>     | 0.124 ± 0.005              | 0.994 | 5.59            |
| CFEC <sub>20</sub> DBS | 0.108 ± 0.004              | 0.991 | 6.41            |

<sup>a</sup> These values represent the 95% confidence limits.

**Table 4.** Percentages of Chlorsulfuron Recovered from the Granules, Soil, and Leachates

| CR granules            | chlorsulfuron recovered |                 |                 |           |
|------------------------|-------------------------|-----------------|-----------------|-----------|
|                        | in soil (%)             | in leachate (%) | in granules (%) | total (%) |
| CF                     | 0.00                    | 100.00          | 0.00            | 100.00    |
| CFEC <sub>10</sub>     | 7.65                    | 89.96           | 1.78            | 99.39     |
| CFEC <sub>20</sub>     | 16.81                   | 73.44           | 8.18            | 98.43     |
| CFEC <sub>20</sub> DBS | 18.87                   | 63.62           | 17.25           | 99.74     |

without plasticizer, CFEC<sub>10</sub> and CFEC<sub>20</sub>, we see that the value of  $t_{50}$  is higher in the system with a superior ethylcellulose percentage (CFEC<sub>20</sub>). This is because of a higher coating thickness. Other studies have found that  $t_{50}$  in the delivery of coated fertilizers is lineally increased with coating thickness (11, 14).

The addition of plasticizer in the coating process produces an increase of  $t_{50}$  values; this can be due to higher homogeneity, less porosity, and more hydrophobicity of the coating film in the CFEC<sub>20</sub>DBS formulation (20). Besides, the coating film is thicker in the CFEC<sub>20</sub>DBS formulation than in either the formulations of CFEC<sub>10</sub> or CFEC<sub>20</sub>.

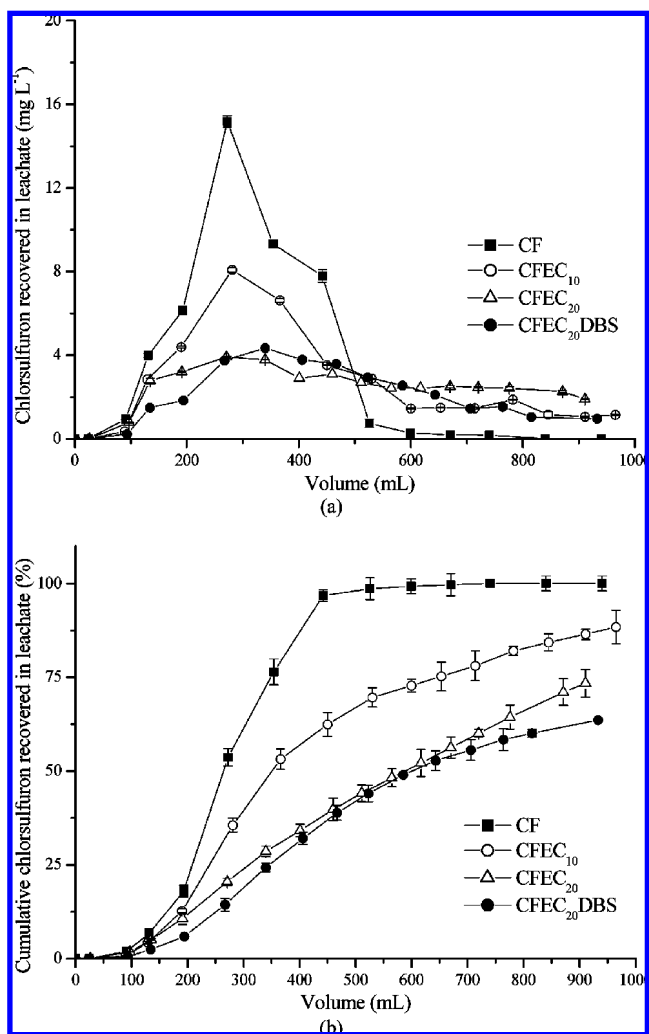
**Mobility of Chlorsulfuron in Soil Columns.** The amounts of chlorsulfuron recovered in soil, leachate, and granules referred to the total amount of herbicide applied in the experiments are indicated in **Table 4**.

As can be seen, 100% of the herbicide was present in the leachate when chlorsulfuron was applied as CF. The presence of this high amount of chlorsulfuron in the leachate was expected according to its relatively high solubility in water (31.8 g L<sup>-1</sup> at 25 °C, pH 7) and the low value of  $K_{ow}$  (0.10) (1), which means a potential mobility capacity in soil. When chlorsulfuron was applied as EC-coated CR formulations (CFEC<sub>10</sub>, CFEC<sub>20</sub>, and CFEC<sub>20</sub>DBS), the amount of active ingredient recovered in the leachates was lower than that obtained in columns treated with commercial product (89.96 for the treatment with CFEC<sub>10</sub> granules, 73.44% for the treatment with CFEC<sub>20</sub>, and 63.62% for the columns treated with CFEC<sub>20</sub>DBS granules, respectively). These results clearly highlight the efficiency of EC formulations in reducing the leaching of chlorsulfuron in comparison to commercial formulation. Several researchers have reported that the use of CRFs reduces the leaching of pesticide in soil columns (21, 22). The chlorsulfuron recovered in soil and granules is increased from CF to CFEC<sub>20</sub>DBS in the following order:

$$CF < CFEC_{10} < CFEC_{20} < CFEC_{20}DBS$$

This variation order and the percentage of chlorsulfuron recovered in the leachate are in agreement with the  $t_{50}$  values obtained from release kinetics in water. This means that higher  $t_{50}$  values lead to a low percentage of chlorsulfuron recovered in the leachate and higher values of chlorsulfuron recovered in granules.

The total percentage of total chlorsulfuron recovered (soil + granules + leachate) is nearly 100% in all cases. This is so

**Figure 5.** Chlorsulfuron recovered in the leachate from EC-coated granules: (a) breakthrough curves; (b) cumulative percentage curves (error bars represent the standard deviation of two replicates).

because of the basic pH of the soil used (pH 8.7), where no degradation is expected to occur as deduced from its physical–chemical properties.

The breakthrough curves and cumulative chlorsulfuron leached from soil columns treated with commercial chlorsulfuron and EC coated granules (CFEC<sub>10</sub>, CFEC<sub>20</sub>, and CFEC<sub>20</sub>DBS) are shown in **Figure 5**. Significant differences were noted in the leaching patterns of the formulations researched. The ranking of the formulations tested in terms of percentage leached was as follows:

$$CF > CFEC_{10} > CFEC_{20} > CFEC_{20}DBS$$

For the commercial grade product, chlorsulfuron was first spotted in the leachate at approximately 0.10 L (first pore volume). The amount of leached chlorsulfuron increased steadily over time to approximately 100% of the total applied by the time of the fifth column leachate sample. For the CRFs, a smoother lixiviation profile can be appreciated, which indicates that the use of CRFs reduces leaching of chlorsulfuron to a very acceptable level during the entire process of the experiment compared to the commercial product.

**Conclusions.** Controlled release formulations of chlorsulfuron have been obtained by coating a commercial product with a biodegradable polymer such as ethylcellulose. Nearly 100%

encapsulation efficiency was obtained. Uniform and intact films were observed in coated granules by SEM.

The release rate in water can be controlled mainly by adjusting the thickness of the coating film and by modifying the surface properties of the coating film by adding a plasticizer such as DBS.

Mobility experiments in soil show that the use of coated CRFs reduces the presence of chlorsulfuron in the leachate. This can be useful to prevent the polluting environmental risk derived from the use of chlorsulfuron mainly in soils, as the one studied here, with a low organic carbon content and high pH, where this herbicide shows a greater potential to cause groundwater pollution.

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