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Ethylcellulose and lignin as bearer polymers in controlled release formulations of chloridazon

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ABSTRACT

Polymeric materials like ethylcellulose and lignin have been used to improve the application of the herbicide chloridazon, preparing controlled release formulations (CRFs). The lignin-based formulations prepared were coated in a Wurster-type fluidized-bed equipment using ethylcellulose and dibutylsebacate.

Chloridazon has been successfully trapped, with values of encapsulation efficiency (EE) higher than 94% in all cases. FT-IR and DSC studies indicate the compatibility between polymers and chloridazon in lignin based CRFs. SEM pictures show a homogeneous film in ethylcellulose coated CRFs.

Using experimental equations, 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 chloridazon can be mainly controlled either by selecting the granule size of controlled release lignin matrixes, or by changing the thickness of the coating film and modifying its surface properties adding a plasticizer for ethylcellulose coated CRFs.

1. Introduction

Polymeric matrixes have been vastly used in different fields: as drug delivery vehicles, in protection of functional ingredients, as sensing devices, in biomaterials, and for catalysis (Varshosaz, Tavakoli, & Eram, 2006). The polymeric matrix can be made of both synthetic and natural polymers. Natural polymers such as dextrans, gelatin, chitosan, sodium alginate, lignin and cellulose derivate are more interesting than synthetic polymers for food and biomedical applications due to their higher biodegradability and biocompatibility (Beneke, Alvaro, Viljoen, & Hamman, 2009). These polymers can be also used to prepare controlled release formulations (CRFs) of pesticides. The primary objectives of controlled release technology, in crop protection, include improved performance on the desired target and the effectiveness of the agents which protect the crop, allowing a reduction of the environmental problems associated with its implementation.

CRFs regulate the supply of pesticides, allowing a lower and continued concentration of them in soil. Therefore, they reduce the losses caused by leaching and evaporation (Mogul et al., 1996), always maintaining their concentration between the limits of toxicity and the effectiveness. In CRFs, pesticides are trapped, that is, they are integrated into a polymer matrix, where they are dissolved or linked to it physically or chemically. In this way, the active ingredient is released through controlled diffusion processes achieving minimal losses. In this research, new CRFs of chloridazon have been developed using natural biodegradable polymers such as ethylcellulose and lignin.

Chloridazon, 5-amino-4-chloro-2-phenylpyridazin-3(2H)-one, is used as a selective systemic herbicide which inhibits photosynthesis and it is used for general weed control (Flores-Céspedes, Villafranca-Sánchez, Pérez-García, & Fernández-Pérez, 2007). Although results are conflicting, chloridazon appears to be mobile in some soils. Several researches reported the K_{oc} of chloridazon as 89–340 (Tomlin, 2002). According to a classification by Cohen (1990), these K_{oc} values indicate that chloridazon would generally have high mobility in soil. The use of this product in areas where soils are permeable and water tables are shallow could result in leaching to ground water leading to potential pollution. However using polymeric CRFs of chloridazon can reduce this risk.

The lignin polymer is a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap, and an underutilized resource nowadays. The use of the lignin by-product produced in the pulping of soft wood (kraft lignin) has been reported in other papers (Fernández-Pérez, González-Pradas, Ureña-Amate, Wilkins, & Lindup, 1998; García, Díez, Vallejo, García, & Cartagena, 1996; Zhao & Wilkins, 2003). Polyethylene glycol (PEG) was used in some of the formulations due to its characteristics such as hydrophobicity, low density, lack of reactivity with the other components within the system, suitability for

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melting and low cost (Harris, 1992). Ethylcellulose (EC) is one of the most widely-used polymers in film coating because of many advantages it offers as formulator, such as good film formability, excellent physical–chemical stability and minimum toxicity (Rao & Murthy, 2001). Plasticizers are commonly incorporated with the polymeric film, to change flexibility, tensile strength and adhesion properties of the resulting film (Lin, Cheng, & Liang, 2000). Dibutylsebacate (DBS) has been used in previous researches due to its lipophilic character (Lecomte, Siepmann, Walther, MacRae, & Bodmeier, 2004) and also due to a minimum pollution potential for the environment (Pérez-García, Fernández-Pérez, Villafranca-Sánchez, González-Pradas, & Flores-Céspedes, 2007). DBS is an insoluble plasticizer which combined with the ethylcellulose polymer can control the release rate of the herbicide into the CRFs.

The objectives of this study were:

i. To design, prepare and characterize controlled release formulations of chloridazon using biodegradable polymers like ethylcellulose and lignin.
ii. To evaluate chloridazon CRFs in water through kinetic studies.

The lignin-based CR granules were prepared by mixing the herbicide with kraft lignin and polyethylene glycol under melting conditions. The EC coated granules were prepared by coating lignin-based granules in a Wurster-type fluidized-bed equipment.

In order to investigate the physical and chemical compatibility of the materials used in the preparation of the formulations, pure polymers, chloridazon and blends were analyzed by Fourier transformed infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Materials

The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco Corp., Charleston, SC). To improve the properties of homogeneity of the formulation, polyethylene glycol (PEG) (molecular weight, 1000 g mol^{-1}) was used; the film-forming material of polymer coating was ethylcellulose (EC) (Ethocel®; ethoxy content, 48.0–49.5%; viscosity, 9–11 cP); and the plasticizer selected for the study was dibutylsebacate (DBS) (≥97%, $d = 0.936$ g mL^{-1}). These products were supplied by FlukaChemie AG (Buchs, Switzerland).

Technical grade chloridazon (94.1%) was kindly supplied by BASF Agro Spain (Barcelona, Spain). Its molecular formula and selected properties are as follows (PPDB, 2009; Tomlin, 2002): molecular formula, $C_{10}H_8ClN_3O$; molecular weight, 221.64 g mol^{-1}; melting point, 206 °C; degradation point, 306 °C; vapor pressure (20 °C), <0.01 mPa; water solubility (20 °C), 0.34 g L^{-1}; octanol/water partitioning ($\log K_{ow}$) (20 °C), 1.19; stable up 50 °C for ≥2 years; stable in aqueous media at pH 3–9.

2.2. Lignin based formulations

The CR granules were formed by mixing the lignin (L), polyethylene glycol (PEG) and chloridazon (C) in the optimized ratio [65:20:15 (w/w)] using a glass reactor inserted in a thermostatic bath (model Tectron L by Selecta S.A., Barcelona, Spain) filled with silicone oil. The mixture was heated under melting conditions at 206 °C for 20 min. On cooling, the matrixes were crushed in a hammer mill and then sieved to obtain granules of size between: 0–0.2 mm; 0.2–0.5 mm; 0.5–1 mm; 1–2 mm and 2–3 mm. The resulting products are labelled in the text as CPEL ($0 < d < 0.2$ mm), CPEL (0.2 mm $< d <$ 0.5 mm), CPEL (0.5 mm $< d <$ 1 mm), CPEL (1 mm $< d <$ 2 mm), and CPEL (2 mm $< d <$ 3 mm). The numbers in brackets represent the size range (mm). Additionally, lignin based granules without chloridazon (PEL) were also prepared to evaluate compatibility and interactions through DSC and FT-IR studies.

2.3. Ethylcellulose coated granules

2.3.1. Preparation of coating solutions

Appropriate quantities of ethylcellulose and plasticizer were combined and dissolved in ethanol (Table 1) to obtain the coating solutions with two different polymer levels and, in one case, with a plasticizer. The coating film consists of 10% and 20% ethylcellulose of the weight of the dry granules (20 g) and, for the coating solution containing a plasticizer, the coating film consist of 20% EC and 2.25% DBS of the weight of the dry granules.

2.3.2. Preparation of coated granules

To prepare coated granules, 20 g of CPEL formulation, granules of size between 0.2 mm $< d <$ 1 mm were loaded into a fluidized-bed coater (Mini-Glatt, Glatt AG, Pratteln l, Switzerland) assembled with a Wurster insert. The bed temperature was adjusted to 60 ± 2 °C. The granules were preheated at this temperature for 10 min. The coating solution was delivered with a peristaltic pump (Watson-Marlow, Model 1B-1003/R) and sprayed into the fluidized-bed via spray nozzle at the atomizing pressure of 1.2 bar. The coating solutions were pumped with a flow rate of 2.5 mL min^{-1} to prepare CPEL + EC_{10} and a flow rate of 5 mL min^{-1} for both CPEL + EC_{20} and CPEL + EC_{20} + DBS granules. The total spraying time was 40 min. The coated granules were then dried in the same device at 60 °C for 10 min and sieved, selecting the granules of size between 0.2 mm $< d <$ 1 mm.

2.4. Granules characterization

2.4.1. Determination of chloridazon content in the CRFs

The actual concentration of chloridazon in the granules was determined by dissolving 20 mg of the granules in 50 mL of methanol in an ultrasound bath for 15 min, which led to the complete disintegration of the granules. The volume was made up to 100 mL with ultra-pure water. This solution was placed in stoppered conical flasks and shaken in a thermostatic bath at 25 °C ± 0.1 °C for 24 h, then the resulting extract was filtered using nylon filters (0.20 μm). The concentration of chloridazon in the solution was determined by high-performance liquid chromatography (HPLC) using a Beckman Coulter Inc, System Gold HPLC (Fullerton, CA, USA) equipped with a diode-array detector and 32 Karat data station.

The HPLC operating conditions to analyze chloridazon were described previously by other authors (Carabias-Martínez, Rodríguez-González, Fernández-Laespada, & Sánchez-San Román, 2000; Traub-Eberhard, Kördel, & Klein, 1994). The mobile phase used was an acetonitrile–water (purity suitable for HPLC) mixture 35:65 at a flow rate of 1 mL min^{-1}, chloridazon was analyzed at its wavelength of maximum absorption, 229 nm, by injecting a volume of 20 μL. Separation by isocratic elution was performed on a 150 mm × 3.6 mm NOVA PACK C18 column, supplied by Waters Assoc. Three replications were carried out for each formulation.

2.4.2. Particle mean size

The average diameter of CR granules was determined using a Stereoscopic Zoom Microscope from Nikon, model SMZ1000, provided with a camera PixelLINK (*Megapixel FireWire Camera*) model PL-A662. Each measure was taken through the analysis of a basis of two hundred particles using the software *Image Pro-Plus* 6.0.

2.4.3. Differential scanning calorimetry

DSC scans of chloridazon, lignin, polyethylene glycol, PEL and CPEL were taken with a DSC from *TA Instruments*, model *DSC Q20*. The samples (6 mg) were preheated to 120 °C for water evaporation. The heat evolved during the heating process (10 °C/min) from room temperature to 300 °C was recorded as a function of temperature. Nitrogen atmosphere was used at a steam of 20 mL/min.

Table 1
Coating solutions composition for the preparation of CR granules containing chloridazon.

CR granules	Weight of CPEL granules (g)	Coating solution composition				
		EC (g)	DBS (g)	Ethanol (mL)	EC (%)[a]	DBS (%)[b]
CPEL + EC_{10}	20	2	–	100	10	–
CPEL + EC_{20}	20	4	–	200	20	–
CPEL + EC_{20} + DBS	20	4	0.45	200	20	2.25

CPEL + EC_{10}: chloridazon–polyethylene glycol–lignin–ethylcellulose 10%.
CPEL + EC_{20}: chloridazon–polyethylene glycol–lignin–ethylcellulose 20%.
CPEL + EC_{20} + DBS: chloridazon–polyethylene glycol–lignin–ethylcellulose 20%–dibutyl sebacate 2.25%.
[a] EC (%) = (EC (g)/weight of CPEL granules (g)) × 100.
[b] DBS (%) = (DBS (g)/weight of CPEL granules (g)) × 100.

2.4.4. Fourier transform infrared measurements

Fourier transform infrared (FT-IR) spectra of the PEG, lignin, empty lignin based granules (PEL) and chloridazon lignin based granules (CPEL) were taken with a FT-IR Raman Vertex 70 from Bruker. FT-IR spectra of samples (5% (w/w) sample in KBr) were recorded between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.4.5. Scanning electron microscopy

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

2.5. Water release kinetics

For each formulation and technical chloridazon (two replicates), an accurately weighed quantity of granules containing 8 mg of chloridazon was added to 500 mL of distilled water and placed into stoppered conical flasks. Flasks were kept in a thermostatic bath at 25 (±0.1) °C. At different time intervals, aliquots of 0.5 mL were removed to determine chloridazon and 0.5 mL fresh water was added to the flasks to maintain sinking conditions.

3. Results and discussion

3.1. Granule characterization

The results of practical chloridazon loading and encapsulation efficiency (EE) were calculated using Eqs. (1) and (2). These results are shown in Table 2:

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

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

The value of encapsulation efficiency for the CPEL system is 94.84%, which highlights the efficacy of melting process using lignin and PEG to formulate chloridazon. For EC coated granules, the EE values ranged between 93.13% for the CPEL + EC_{20} + DBS system and 94.70% for the CPEL + EC_{10} formulation.

Table 2
Characteristics of controlled release granules (0.2 mm < d < 1 mm) containing chloridazon.

Formulation	Theoretical chloridazon loading (%)[a]	Practical chloridazon loading (%)	Solids recovery (%)[b]	EE (%)	Mean thickness of film (μm)
CPEL	15.00	14.27 (0.36)		94.84	
CPEL + EC_{10}	12.91	12.24 (0.26)	94.83	94.70	10.11 (0.39)
CPEL + EC_{20}	11.83	11.07 (0.84)	97.20	93.40	22.06 (0.98)
CPEL + EC_{20} + DBS	11.64	10.82 (0.47)	99.97	93.13	13.67 (0.45)

Values in parentheses represent the standard deviation.

[a] Theoretical chloridazon loading (%) = (total amount of chloridazon used to prepare the formulations/total amount of solid components used in the formulation process) × 100.

[b] Solids recovery (%) = (total amount of formulation recovered/total amount of solid components used in the formulation process) × 100.

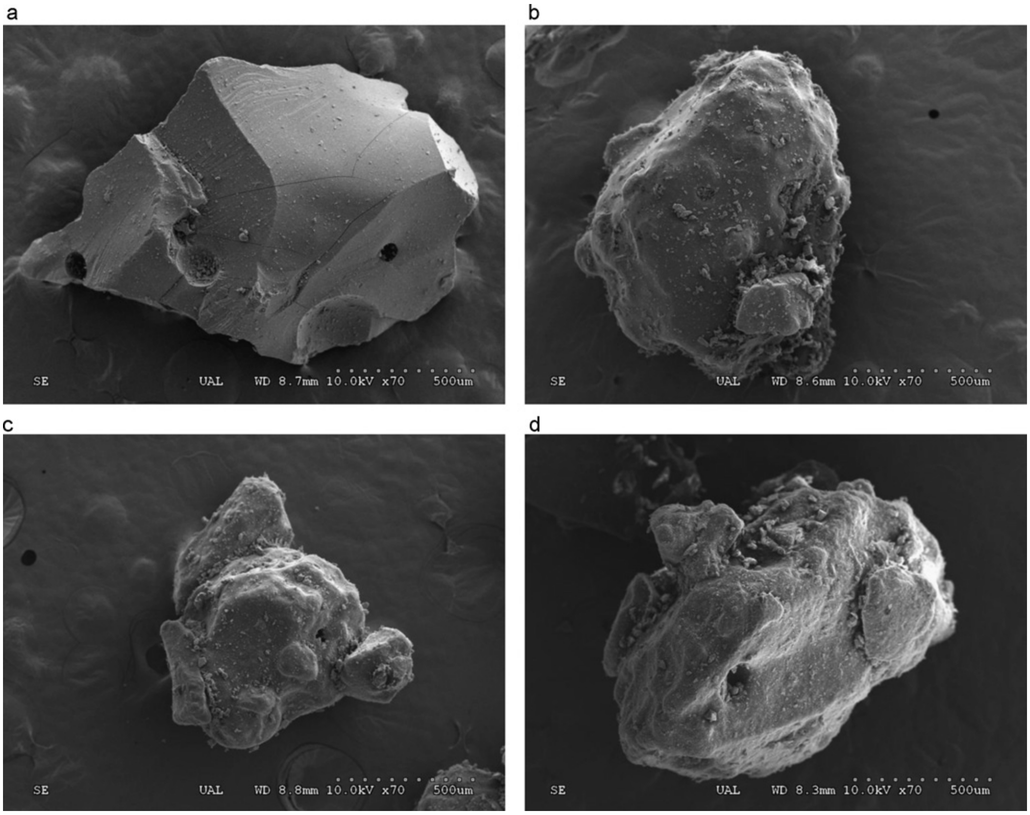

Fig. 1. SEM of shape and external morphology (70× magnifications): (a) CPEL, (b) CPEL + EC_{10}, (c) CPEL + EC_{20}, and (d) CPEL + EC_{20}DBS.

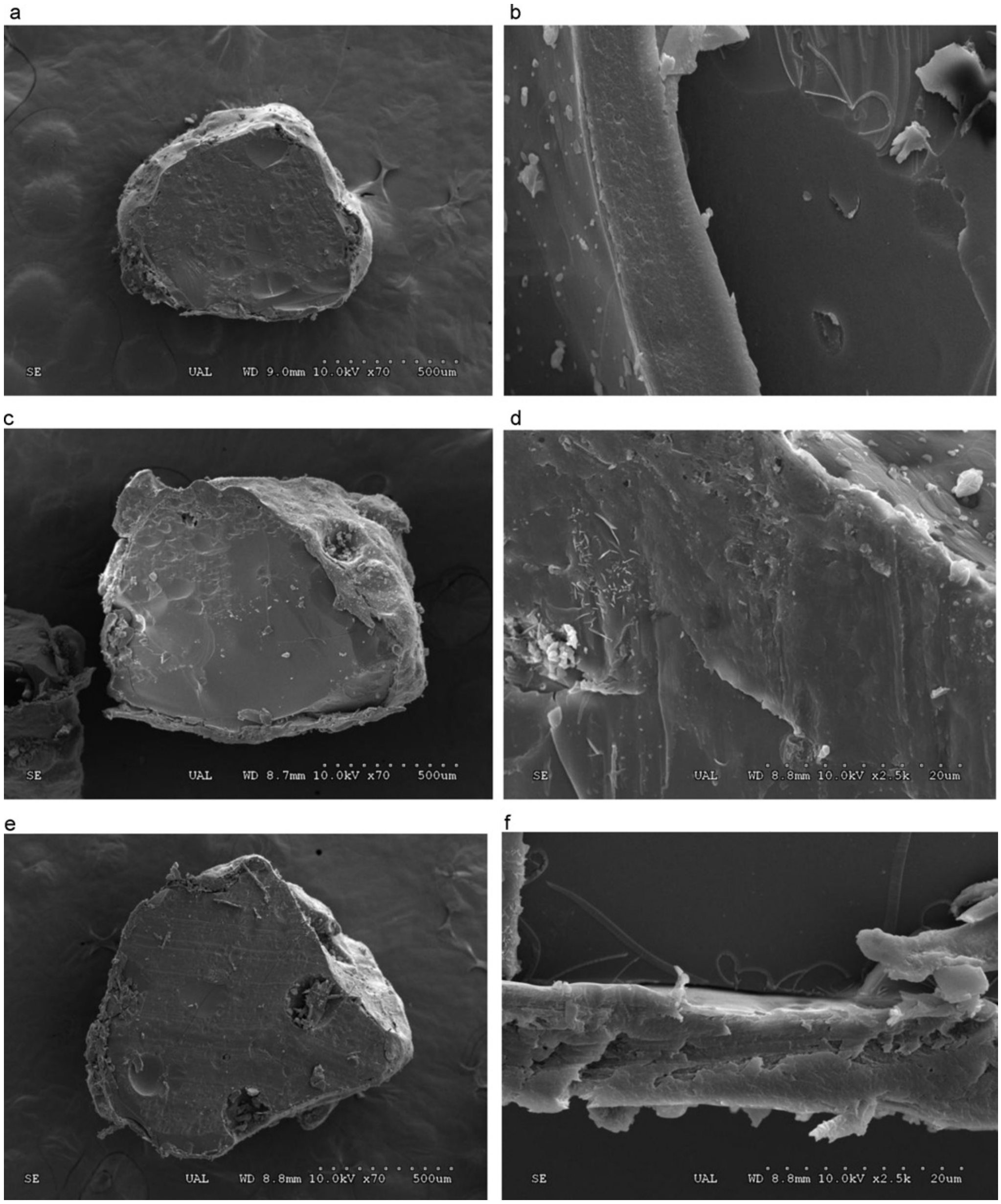

Fig. 2. SEM of the internal morphology (70× magnifications): (a) CPEL + EC_{10}, (c) CPEL + EC_{20}, and (e) CPEL + EC_{20} + DBS. The other ones show the detail of the coating film (2500× magnifications): (b) CPEL + EC_{10}, (d) CPEL + EC_{20}, and (f) CPEL + EC_{20} + DBS.

The practical chloridazon loading oscillate between 10.82% for the CPEL + EC_{20} + DBS system and 14.27% for the CPEL system, being the active ingredient of the granules suitable for agricultural practices.

SEM pictures from CR granules (Fig. 1) show the disappearance of the wrinkled aspect that the external surface of CPEL granules possesses (Fig. 1a) and the existence of a uniform and intact film in the coated formulations (Fig. 1b–d). The cross-section on coated formulations (Fig. 2) shows the porous core structure with a coherent film at the boundary, observing a bigger homogeneity and adherence in the coating film for the system that contains a plasticizer. This fact is also observed by other authors, who explain that the plasticizer, incorporated normally with polymers, modifies the properties of adhesion, flexibility, and tensile strength of the coating film (Frohoff-Hülsmann, Schmitz, & Lippold, 1999; Lin et al., 2000).

The thickness of the coating film was estimated using SEM photographs (Table 2). The thickness of the coating film ranged between 10.11 μm for the CPEL + EC_{10} system and 22.06 μm for the CPEL + EC_{20} system.

As expected, the highest amount of EC in the coating solution applied for the CPEL + EC_{20} system increases the thickness of the membrane in relation to the CPEL + EC_{10} system. The presence of the plasticizer in the CPEL + EC_{20} + DBS system leads to a decreasing in the thickness of the film compared to the CPEL + EC_{20} system.

DSC curves of chloridazon, lignin, PEG, PEL and CPEL are shown in Fig. 3. DSC thermogram of chloridazon showed the clear endothermic peak at a temperature of 200.38 °C, which is associated with the melting point of the technical product of chloridazon (Tomlin, 2002) (Fig. 3a). Fig. 3b shows both T_g and T_m which means that lignin has a partially crystalline structure as is also showed by Corradini et al. (1999) in lignin–poly(vinyl alcohol) blends studied by thermal analysis. For PEG (Fig. 3c) no T_g has been appreciated, which indicate a crystalline structure. As it is observed in Fig. 3d, the end point temperature of endothermic peak of the PEL granules shifted to higher temperature, in relation to the T_m of pure com-

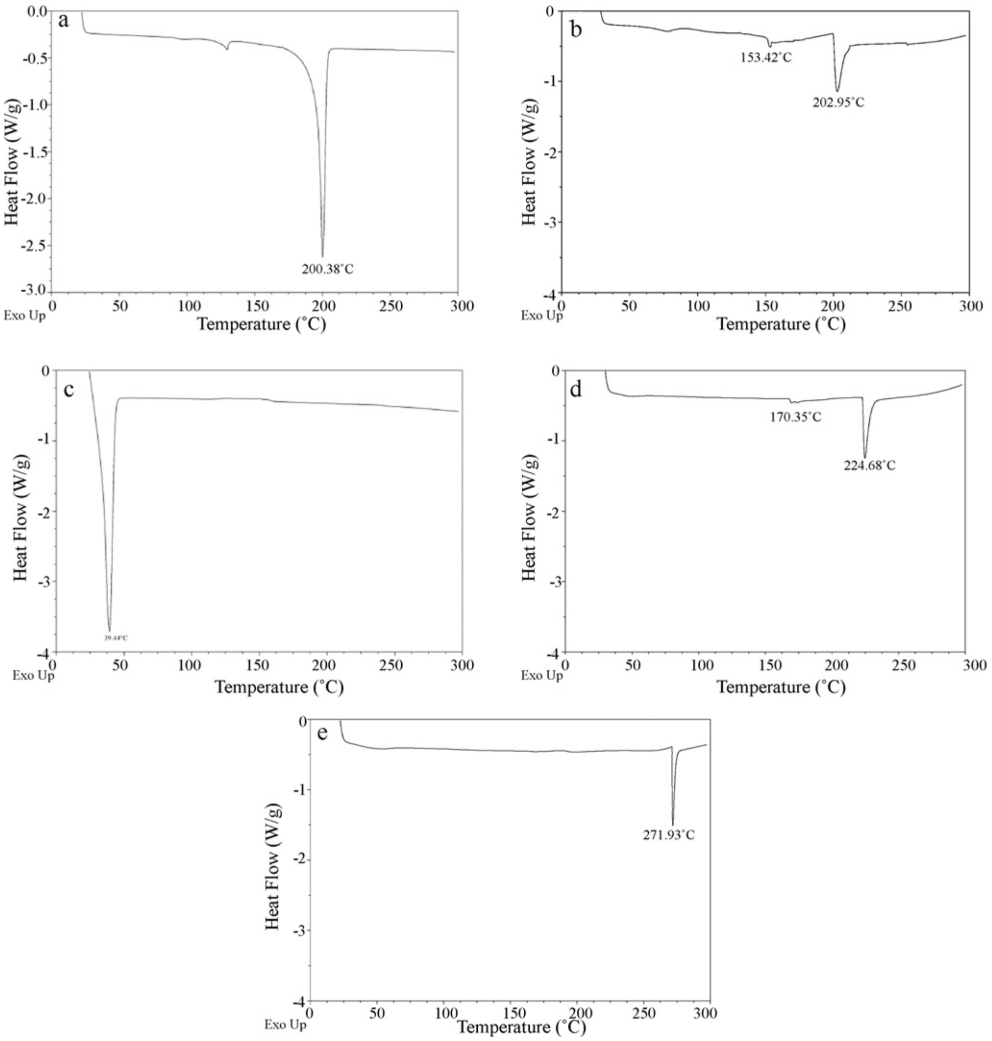

Fig. 3. DSC curves of chloridazon (a), lignin (b), polyethylene glycol (c), PEL granules (d) and CPEL granules (e).

ponents, due to the blending and crosslinking of PEG and lignin. The detection of a single T_g value in PEL granule higher than that corresponding to lignin can be attributed to the formation of a more rigid polymer matrix due to the interaction between the ether groups of the PEG and the hydroxyl and carbonyl groups of lignin as is discussed below in FT-IR studies. The DSC thermogram of CPEL showed a sharp endothermic peak at 271.93 °C (Fig. 3e) corresponding to the melting point of the formulation. The shift to higher temperature of the melting point of the formulation in relation to the T_m of pure components and PEL granules indicates chloridazon–polymers interaction. Besides, no characteristic peak of chloridazon was observed in DSC curves of the CPEL granules, suggesting that the chloridazon is molecularly dispersed in the polymer matrix.

FT-IR spectra of lignin (a), PEG (b), PEL (c) and CPEL (d) were shown in Fig. 4. The FT-IR spectra for lignin and PEG (Fig. 4a and b) were similar to those described previously by others for kraft lignin (Boeriu, Gosselink, & van Dam, 2004; Tejado, Peña, Labidi, Echeverria, & Mondragon, 2006) and PEG (Wang, Yang, Fang, Ding, &Yan, 2009).

The FT-IR spectrum for PEL granules shows a little shift of the broad center band at 3398 cm^{-1}, attributed to the hydroxyl groups in phenolic and aliphatic structures of lignin, which leads to a lower wavenumber in the presence of PEG (3392 cm^{-1}). A related effect is observed in the asymmetric C—O—C stretching ($\nu_{asC-O-C}$) region (1050–1150 cm^{-1}). For PEG this band appears at 1106 cm^{-1}, whereas this band shifted to a lower wavenumber region when PEG is blended with lignin, as shown in Fig. 4c. This is consistent with the observed effect in the ν_{O-H} region and can be due to the fact that new specific hydrogen-bonding interactions are formed between the ether group of the PEG and the hydroxyl groups of the lignin when thermal blending of PEG with lignin is carried out. The existence of hydrogen-bonding interactions is an important factor in the formation of miscible lignin-based polymer blends (Kubo & Kadla, 2004). The FT-IR spectrum of CPEL granules showed only an additional band at 1636 cm^{-1} which is characteristic of chloridazon (Rouchaud, Neus, & Hermann, 1997; Sánchez-Martín & Sánchez-Camanzano, 1987), along with all the characteristics bands of the PEL granules.

3.2. Water release kinetics

The cumulative release of chloridazon from CPEL granules with different sizes and the solubility curve of technical grade chloridazon are shown in Fig. 5a. For the technical grade product, 90% of the chloridazon was dissolved in less than 2 h. The rate of chloridazon release from CPEL granules diminished in all cases in relation to the technical grade product, being necessary at least 330 h to release 90% of chloridazon from CPEL (2 mm < d < 3 mm) granules. This fact is due to the lignin formulations contain finely divided chloridazon particles, which are uniformly dispersed within the matrix phase as it has been shown by SEM studies (Fig. 1a). For

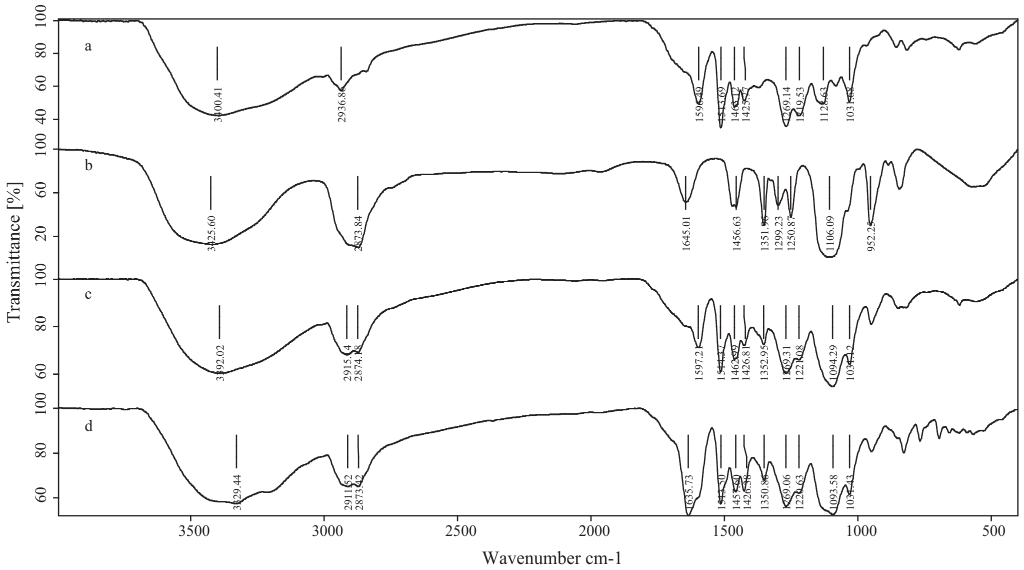

Fig. 4. FT-IR spectra of lignin (a), polyethylene glycol (b), PEL granules (c) and CPEL granules (d).

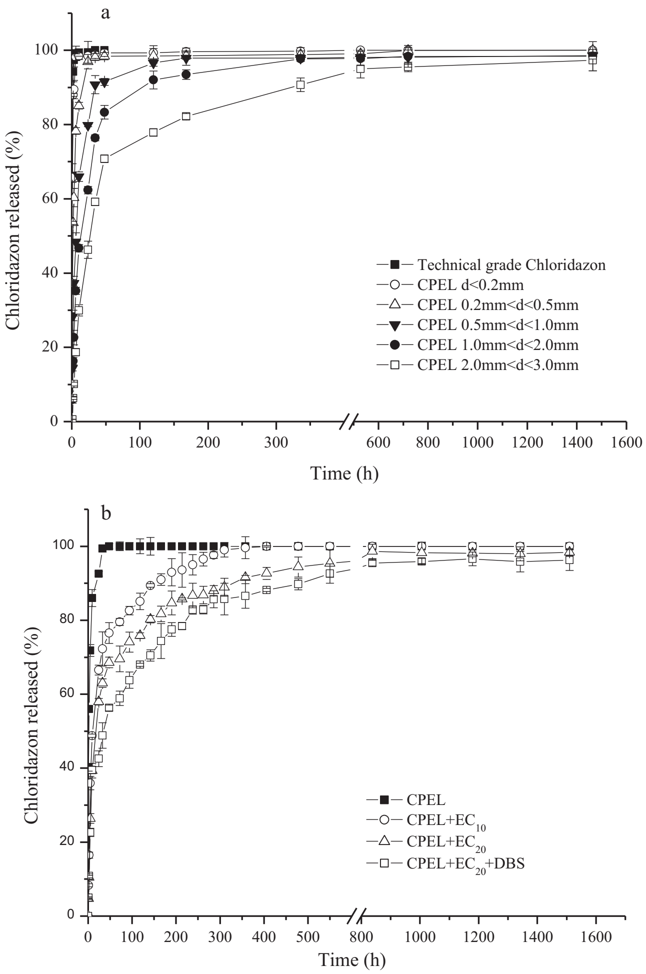

Fig. 5. Water release kinetics from different size fractions of CPEL (a) and from EC coated granules containing chloridazon and CPEL (0.2 mm < d < 1.0 mm) granules (b).

all formulations, a decrease in the release rate of chloridazon over time was observed. This result is due to an increase in the distance where dissolved molecules of chloridazon have to diffuse as the depleted zone advances to the center of the matrix. As it can be seen in Fig. 5a, an important decrease in the release rate of chloridazon is observed as the size of CPEL matrixes increases from CPEL (0 < d < 0.2 mm) up to CPEL (2 mm < d < 3 mm). This happened as expected due to a lower surface area of the matrix being exposed to water, with a longer distance over which the chloridazon must be diffused from the center of the matrix. Similar results were obtained for the release of different pesticides from granules based on a lignin matrix system (Cotteril, Wilkins, & da Silva, 1996; Fernández-Pérez et al., 1998).

In order to obtain a parameter to compare the behavior of CR granules prepared as lignin matrixes, the kinetic release data of chloridazon in water were analyzed applying the empirical equation proposed by Ritger and Peppas (1987):

$$\frac{M_t}{M_\infty} = K_1 t^n \qquad (3)$$

M_t/M_∞ is the percentage of active ingredient released at time t, K_1 is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and n is a diffusional parameter which is indicative of the transportation mechanism.

The values of K_1 and n obtained from initial 90% chloridazon released in water are presented in Table 3. There was good correlation of the release profiles of CR matrixes of chloridazon with the empirical equation, with the correlation coefficient (r) being greater than 0.93.

The time corresponding to release 50% of chloridazon, T_{50}, was calculated for the matrixes using the constants from Table 3. For uncoated granules (different fraction size) the T_{50} values ranged from 0.34 h for CPEL (d < 0.2 mm) granules up to 39.08 h for CPEL (2 mm < d < 3 mm) granules. By observing the T_{50} values obtained for lignin CR matrixes, it is possible to notice that the T_{50} value increases as the matrix size increases, showing the CPEL (2 mm < d < 3 mm) granule the highest T_{50} value, which means the slowest chloridazon release. This behavior is related to the results of studying imidacloprid and urea release from lignin matrix, (Fernández-Pérez et al., 1998; Garrido-Herrera, Daza-Fernández, González-Pradas, & Fernández-Pérez, 2009) where the T_{50} values increase as the diameter of the matrixes grows.

As commented above, it seems that the size of non-coated lignin matrixes is the most influential factor that affects the release rate of chloridazon. So, the T_{50} values of lignin CR granules (Table 3) were related to the average diameter of granules (D) which are 0.023, 0.32, 0.78, 1.29 and

Table 3
Constants from fitting the empirical equations the release data of controlled release systems into static water.

Equation	Formulation	K_1 ($\times 10^2$ h^{-n})	n	r	T_{50} (h)
$M_t/M_\infty = K_1 t^n$	CPEL $d < 0.2$ mm	67.47	0.28	0.93	0.34
	CPEL 0.2 mm < d < 0.5 mm	42.85	0.32	0.99	1.62
	CPEL 0.5 mm < d < 1 mm	22.96	0.40	0.98	7.00
	CPEL 1 mm < d < 2 mm	12.80	0.51	0.99	14.46
	CPEL 2 mm < d < 3 mm	13.86	0.35	0.94	39.08
	CPEL[a] 0.2 mm < d < 1 mm	41.82	0.32	0.98	1.74

Equation	Formulation	K_2 ($\times 10^2$ h^{-n})	r	T_{50} (h)
$M_t/M_\infty = 1 - e^{K_2 t}$	CPEL + EC_{10}	4.45	0.96	15.58
	CPEL + EC_{20}	2.21	0.92	31.34
	CPEL + EC_{20} + DBS	1.06	0.92	65.39

[a] This fraction is used to compare the lignin based formulation with ethylcellulose coated formulations.

2.26 mm for CPEL ($0 < d < 0.2$ mm), CPEL (0.2 mm < d < 0.5 mm), CPEL (0.5 mm < d < 1 mm), CPEL (1 mm < d < 2 mm) and CPEL (2 mm < d < 3 mm), respectively. The equation of linear correlation and correlation coefficient were obtained by applying the least-squares method to the data:

$$T_{50} = 17.50 \times D - 3.86 \quad (r = 0.974; \quad p = 0.005) \qquad (4)$$

This proves that the release of active ingredient from the systems based on lignin polymeric matrix is notably depleted through the increase of the granule size (average diameter, D). In this way, it can be stated that it is possible to foresee, under an early approach and an acceptable degree of reliability, the T_{50} values for chloridazon formulations from the average granule diameter.

In Fig. 5b, the cumulative release curves of chloridazon from CPEL granules size fraction between 0.2 mm < d < 1 mm and EC coated granules are shown. The coated CR granules CPEL + EC_{10}, CPEL + EC_{20} and CPEL + EC_{20} + DBS produce a decrease in the process of dissolution of the active ingredient in relation to the CPEL granules. From the release curves of the coated CR granules, we can observe a short initial part of the curve during which a constant release rate is observed, followed by an extended stage of gradual decay of release rate. Similar behavior was reported by other authors with polymer coated chemicals (Flores-Céspedes, Daza-Fernández, Villafranca-Sánchez, & Fernández-Pérez, 2009; Pérez-García et al., 2007). The highest delay in release rate is observed in the CPEL + EC_{20} + DBS system. Besides, as expected, the highest quantity of EC in the CPEL + EC_{20} formulation compared to CPEL + EC_{10} causes a delay in the release rate of chloridazon. This fact can be explained if we take into account that the diffusion of water through the membrane is slowed down as the thickness of the membrane increases. This behavior has also been observed by other authors (Jarosiewicz & Tomaszewska, 2003; Rao & Murthy, 2001; Tashima, et al. 2000).

To compare the behavior of EC coated granules, the following first order mathematical model was used for the evaluation of the dissolution profiles of the non-disintegrating coated pellets. The herbicide quantity within the reservoir is assumed to decline exponentially and the release rate is proportional to the residual quantity (Fekete et al., 2006):

$$\frac{M_t}{M_\infty} = 1 - e^{K_2 t} \qquad (5)$$

where M_t is the dissolved amount (%) at time "t" (h), M_∞ is the dissolved amount (%) at infinite time and K_2 is the dissolution rate constant (h^{-1}).

The values of K_2 obtained from initial 90% chloridazon released in water are presented in Table 3, beside the K_1 and n values for CPEL granules obtained by applying Eq. (3). There was a good correlation between the release profiles of CR matrixes of chloridazon and the empirical equation, the correlation coefficient (r) being greater than 0.92. T_{50} values were also calculated using the constants from Table 3. The values ranged from 1.74 h for CPEL (0.2 mm < d < 1.0 mm) granules up to 65.74 h for CPEL + EC_{20} + DBS granules. The variation order is:

$$\text{CPEL} < \text{CPEL} + \text{EC}_{10} < \text{CPEL} + \text{EC}_{20} < \text{CPEL} + \text{EC}_{20} + \text{DBS}$$

The presence of an uniform film of EC and/or plasticizer in the coated granules causes a delay in chloridazon release rate. When the data of T_{50} referring to the coated systems without plasticizer, CPEL + EC_{10} and CPEL + EC_{20}, are assessed, it can be seen that the T_{50} value is slightly higher in the system with a greater ethylcellulose percentage (CPEL + EC_{20}), which is in agreement with the low difference in the thickness of the coating. The addition of plasticizer in the coating process produces an increase of T_{50} values, which can be due to the higher homogeneity, less porosity and more hydrophobicity of the coating film in the CPEL + EC_{20} + DBS formulation (Frohoff-Hülsmann et al., 1999; Lecomte et al., 2004).

The new set of CR formulations obtained in this research lead to: firstly, improve the miscibility between chloridazon and lignin, which let us obtain a higher variety of active ingredient contents; secondly, an important retard in the release rate of chloridazon, which was achieve with the use of EC in coated CRFs. These improvements lead to achieve an optimum applicability of chloridazon in agronomic practices.

4. Conclusions

Chloridazon has been successfully trapped using lignin and EC to obtain chloridazon monolithic systems and coated granules respectively. In both, high encapsulation efficiency values for chloridazon have been obtained. FT-IR and DSC studies indicate the miscibility between lignin and polyethylene glycol mainly through hydrogen-bonding and the compatibility between polymers and chloridazon in lignin based CRFs. SEM studies demonstrate the existence of a uniform film in the CR coated formulations prepared, observing a higher homogeneity and adherence in the coating film for the system that contains a plasticizer. The kinetic water release experiments show that the use of CR granules reduces the release rate of chloridazon in comparison with the technical grade product, showing the EC coated granules release profiles slower than lignin matrixes. The release rate of chloridazon can be controlled by selecting the granule size for uncoated CR lignin matrixes. For EC coated granules, the chloridazon release rate can be controlled by adjusting the EC content, but mainly by adding a plasticizer as DBS, which decreases the delivery rate.

The use of polymeric materials, such as lignin and ethylcellulose in CRFs, could help to increase the efficiency of delivery of the bioactive material and prevent the environmental pollution derived from pesticide use.

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