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Lignin-based formulations to prevent pesticides pollution

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ABSTRACT

The pesticides isoproturon, imidacloprid and cyromazine, identified as groundwater pollutants, were incorporated in lignin-based formulations to obtain controlled release (CR) properties. The formulations were prepared by mixing the pesticide with a commercially available pine kraft lignin under melting conditions. A high efficiency of the preparations was therefore reached; it oscillated between 93.36% and 98.20% for the cyromazine and the isoproturon formulations. Kinetic-release experiments carried out in water showed that the release rate of isoproturon, imidacloprid and cyromazine from CR granules diminished in all cases in relation to the technical products. From the analysis of the time taken for 50% of the active ingredient to be released into water (T_{50}), it can be deduced that the release rates were much higher in cyromazine CR formulations than in those prepared with isoproturon. However, imidacloprid showed an intermediate release rate. The obtained linear regression between T_{50} values and granule size can be suitable to select the most appropriate formulation to avoid the isoproturon, imidacloprid and ciromazine tendency to leach.

1. Introduction

The steadily increased use of pesticides for crop protection in the last decades, besides the progressive increase of intensive agricultural practices, more aggressive to the environment, has lead to greater detection of problems associated to these agrochemicals. The loss of effectiveness of conventional pesticides formulations are about 30%, derived from the immediate release of the active ingredients which compose them. The result of trying to compensate such loss is a tendency showing the use of excessive quantities of these dangerous chemical substances [1]. This situation is an important economic loss and, at the same time, it is perilous for human health as well as for environment. However, pesticides have become a key element of modern intensive agricultural systems. In this way, the Food and Agriculture Organization of the United Nations (FAO) has promoted a set of reasonable and responsible behaviours in agriculture that has been defined as Agricultural Good Practices (AGP) developing the code of international attitudes about pesticides distribution and use. This code establishes rules to assess that the application of phytosanitary products may not damage farmers, consumers or the environment.

The aims of controlled release formulations (CRFs) not only in drugs [2,3] but also in pesticides [4–6], nutrients [7–9] or other substances are to diminish the active ingredient costs, to allow the release of the agent to the target at a controlled rate, and to maintain its concentration in the system within an optimum limit, over a specified period of time, thereby providing great specificity, minimizing the adverse effects and optimizing its effectiveness [10,11].

CRFs of agrochemicals previously developed using biodegradable polymers and modifiers [12–14] have shown that the pesticide chemical structure, stability and properties such as water solubility and polarity, among others, do not only affect the pest control efficiency and environmental behaviour of the active ingredients. But it also has a great importance in the efficiency of the formulation process. Besides, they will be very important to optimize CRFs of pesticides. So, with this paper, we try to continue advancing in the development of more effective agricultural technologies, to improve the pesticide application and to mitigate the environmental pollution derived from its use, through the design, preparation and testing of controlled release (CR) systems of pesticides as an alternative to the conventional formulations commonly distributed in the market.

The main objective of this work was to encapsulate isoproturon, imidacloprid and cyromazine using a polymeric matrix of lignin. Lignin is a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap, and a currently underutilized resource that has shown potential in preparing controlled release formulations [15,16].

Isoproturon [3-(4-isopropyl-phenil)-1,1-dimethylurea], imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] and cyromazine [*N*-cyclopropyl-1,3,5-triazine-2,4,6-triamine] are systemic pesticides which have been identified as potential leachers when we use the groundwater ubiquity score

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(GUS) modeling technique [17]. In relation to the previous idea, isoproturon, imidacloprid and cyromazine have been found to be leachable [18–20].

In the present research, CR formulations were prepared by mixing the pesticides with kraft lignin under melting conditions. Moreover, the influence of CR granules size on the rate of pesticides release was evaluated. We also intended to obtain a further understanding of the release mechanism of the pesticides from the investigated formulations. In addition, the correlation between the characteristic release parameter (T_{50}) and properties of granules was studied.

2. Materials and methods

2.1. Chemicals

The lignin used in this study was a commercially available pine kraft lignin, Indulin AT (Westvaco Corp., Charleston, SC, USA). The material is labelled in the text as L. Thermal behavior of lignin was determined by using thermogravimetric analysis (TGA) (TA instruments, TGA 2950). TGA measurements were carried out at a 20 °C/min heating rate in the range of 25–700 °C under air atmosphere with a flow rate of 50 mL/min.

Technical grade isoproturon (98.0%), imidacloprid (99.0%) and cyromazine (99.0%) were kindly supplied by Rhône-Poulenc Agrochimie (Lyon, France), Bayer Hispania Industrial S.A. (Barcelona, Spain), and Industrias Afrasa S.A. (Valencia, Spain), respectively. The selected properties of isoproturon, imidacloprid and cyromazine are shown in Fig. 1 [21]. Solvents used in the mobile phase for high-performance liquid chromatography (HPLC) determinations were HPLC grade acetonitrile from Merck (Darmstadt, Germany), demineralized Milli-Q quality water from Millipore (Billerica, United States), and analytically pure KH_2PO_4 from Panreac S.A. (Barcelona, Spain).

2.2. Preparation of controlled release formulations

The CR granules were formed by mixing the lignin kraft (L) and the technical grade pesticide in the ratio [1:1] (w/w) (shown in Table 1) using a glass reactor inserted in a thermostatic bath filled with silicone oil (model Tectron L by Selecta S. A., Barcelona, Spain). The mixtures were heated and stirred under melting conditions for 20 min using temperatures slightly higher than the pesticide melting point (shown in Table 1) [22]. On cooling the glassy matrices were crushed in a hammer mill and then sieved to obtain granules of size between 0 and 0.5 mm, between 0.5 and 1.0 mm, between 1.0 and 2.0 mm, and between 2.0 and 3.0 mm. The resulting products are labelled in the text as $Is_{50}L_{50}$(<0.5), $Is_{50}L_{50}$(0.5–1.0), $Is_{50}L_{50}$(1.0–2.0) and $Is_{50}L_{50}$(2.0–3.0) for CRFs containing isoproturon (Is), $Im_{50}L_{50}$(<0.5), $Im_{50}L_{50}$(0.5–1.0), $Im_{50}L_{50}$(1.0–2.0) and $Im_{50}L_{50}$(2.0–3.0) for CRFs containing imidacloprid (Im); and $Cy_{50}L_{50}$(<0.5), $Cy_{50}L_{50}$(0.5–1.0), $Cy_{50}L_{50}$(1.0–2.0) and $Cy_{50}L_{50}$(2.0–3.0) for CRFs containing cyromazine (Cy). Number 50 is the percentage of lignin kraft and technical grade pesticide in dry mixture, and the numbers in brackets represent the size range (mm).

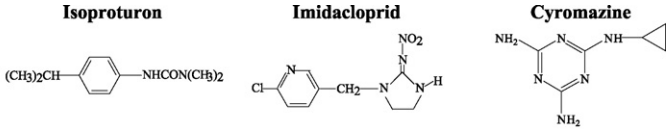
Table 1
Percentage (by weight) of component of controlled release formulations containing pesticides.

Formulation	Technical pesticide (%)	Kraft lignin (%)	Melting point (°C)
Isoproturon – kraft lignin ($Is_{50}L_{50}$)	49.14	49.86	158
Imidacloprid – kraft lignin ($Im_{50}L_{50}$)	49.39	49.91	143
Cyromazine – kraft lignin ($Cy_{50}L_{50}$)	49.57	49.93	220

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. The density was determined using a pycnometer of He from Micromeritics, model AccuPyc 1330.

2.3. Analysis of pesticides in granules

Granules (20 mg) were treated with methanol (50 mL) in an ultrasound bath for 15 min. After 24 h at 25 ± 0.1 °C and 200 rpm in a thermostatic bath to obtain the complete disintegration of the granules, the mixture was then filtered quantitatively through a syringe filter (0.2 μm). The volume was made up to 100 mL with water, and the resulting extract was filtered using nylon filters (0.45 μm), and the pesticide concentration was determined by HPLC. The HPLC operating conditions were as follows: the separation, by isocratic elution, was performed on a 150 mm × 3.9 mm Nova-Pack LC-18 bonded-phase column from Waters for isoproturon and imidacloprid and on a 250 mm × 4.6 mm SUPELCOSIL™ LC-SCX bonded-phase column from Supelco Co. for cyromazine; sample volume, 20 μL for isoproturon and imidacloprid and 50 μL for cyromazine; flow rate, 1.0 mL min^{-1} for isoproturon and imidacloprid and 2.0 mL min^{-1} for cyromazine; and the mobile phase, an acetonitrile–water mixture 60:40 for isoproturon, 35:65 for imidacloprid, and an acetonitrile–aqueous solution of KH_2PO_4 15 mM (pH 3.0) mixture 25:75 for cyromazine. Pesticides were analyzed at their wavelength of maximum absorption (239, 269 and 214 nm for isoproturon, imidacloprid and cyromazine, respectively). External standard calibration was



	Isoproturon	Imidacloprid	Cyromazine
Molecular formula	$C_{12}H_{18}N_2O$	$C_9H_{10}ClN_5O_2$	$C_6H_{10}N_6$
Molecular weight (g mol^{-1})	206.3	255.7	166.2
Melting point (°C)	158	143	220
Vapour pressure (mPa)	$3.30 \cdot 10^{-3}$ (20 °C)	$2.00 \cdot 10^{-4}$ (20 °C)	$4\,48 \cdot 10^{-4}$ (25 °C)
Water solubility (mg L^{-1})	55 (20 °C)	510 (20 °C)	13000 (25 °C)
Log K_{ow}	2.5	0.57	-0.061

Fig. 1. Structure and physico–chemicals properties of isoproturon, imidacloprid and cyromazine.

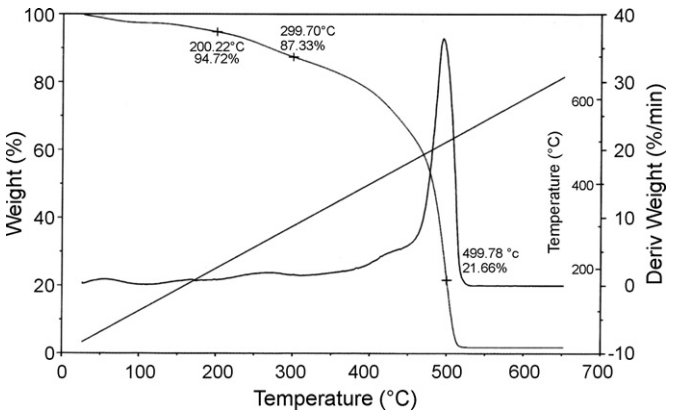


Fig. 2. TGA curve of the kraft lignin Indulin AT.

used, and three replicates were carried out for each formulation.

2.4. Pesticide release kinetics

An accurately weighed quantity of CRFs containing 8.0 mg of pesticide was added for each sample (three replicates) to 500 mL of distilled water and placed into stoppered conical flasks. The systems were shaken in a thermostated bath at 25 ± 0.1 °C. At different time intervals, aliquots of 1 mL were removed for determination of pesticides by HPLC using the methods described above (analysis of pesticides in granules), and 1 mL of fresh water was added to the flasks to maintain constant volume.

3. Results and discussion

3.1. Controlled release formulations

To predict compatibility of the pesticides with lignin, solubility parameter, determined according to a group contribution method [23] has been used. Solubility parameters of the pesticides were estimated to be 23.84, 34.26 and 51.42 $mPa^{1/2}$ for isoproturon, imidacloprid and cyromazine, respectively. On the other hand, the value for kraft lignin showed by Barton [24] ranged between 20–24 $mPa^{1/2}$. On the basis of these values, it can indicate that the lignin shows an excellent compatibility with isoproturon, acceptable compatibility with imidacloprid and lesser compatibility with cyromazine. Nevertheless, according to Schuerch [25], the most important solvent property for lignin solubility is the hydrogen bonding capacity. Functional groups such as amino and nitrogen atoms in the ring, present in cyromazine, are capable of forming hydrogen bonds with hydroxyl, ether and carbonyl groups of lignin increasing the compatibility between cyromazine and lignin. From Fig. 2, where the lignin thermogram is shown, we can observe that the maximum of thermal decomposition appears at approximately 500 °C, so at the temperature of lignin matrix preparations (143 °C for imidacloprid, 158 °C for isoproturon and 220 °C for cyromazine) no thermal decomposition was carried out.

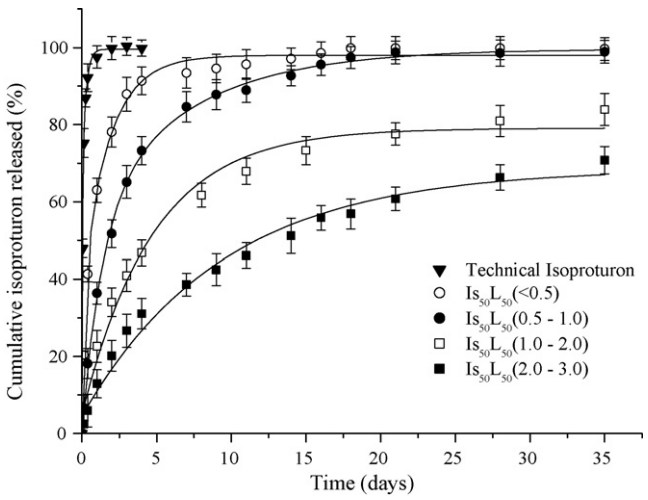


Fig. 3. Cumulative release of isoproturon from granules into static water (error bars represent the standard deviation of three replicates).

Characteristics of lignin-based CR granules containing isoproturon, imidacloprid and cyromazine are shown in Table 2. The percentages of active ingredient oscillate between 46.28% for the system $Cy_{50}L_{50}$(1.0–2.0) and 48.50% for the system $Im_{50}L_{50}$(1.0–2.0), being the active ingredient of the granules adequate for agricultural practice [26]. The average weight of the matrices are very similar, ranged the values between 2.87 mg/granule for the system $Is_{50}L_{50}$(1.0–2.0) and 3.47 mg/granule for the system $Cy_{50}L_{50}$(1.0–2.0). The average densities of lignin-based CR granules are less than that of kraft lignin (~1.4 g cm^{-3}) and also less than those of active ingredients (1.20, 1.54 and 1.35 g cm^{-3} for isoproturon, imidacloprid and cyromazine, respectively). This fact can be explained by the presence of small holes or pores in the melting matrices difficult to observe in the microscope. Finally, we can notice that the values of encapsulation efficiency range between 93.36% for the system $Cy_{50}L_{50}$(1.0–2.0) and 98.20% for the system $Im_{50}L_{50}$(1.0–2.0). These data highlight the efficacy of the method used for encapsulation of the pesticides.

3.2. Release studies

In Figs. 3–5 the cumulative release of isoproturon, imidacloprid and cyromazine from lignin-based CR granules and the solubility profile for technical grade pesticides are shown. By observing these figures the following behaviours can be deduced. Firstly, all granules prepared, independently from their size lead to a decrease of the release process of the active ingredients in relation to the solubility process of the technical products. As an example, in Fig. 3, 100% of technical grade isoproturon is dissolved in less than 3 days, although it takes at least 20 days to release the same percentage of active ingredient from the lignin-based CR formulation $Is_{50}L_{50}$(0.5–1.0). Secondly, the granule size influence is clearly defined in all CR systems prepared despite the active ingredient tested. Therefore the increase of the granules size is relevant

Table 2
Characteristics of controlled release granules containing pesticides.

Formulations	Pesticide (%)	Average Weight (mg/granule)	Average density (g cm^{-3})	Encapsulation efficiency[a] (%)
$Is_{50}L_{50}$(1.0–2.0)	46.47 (0.42)[†]	2.87 (0.05)	1.21 (0.03)	94.57
$Im_{50}L_{50}$(1.0–2.0)	48.50 (0.47)	3.46 (0.04)	1.35 (0.03)	98.20
$Cy_{50}L_{50}$(1.0–2.0)	46.28 (0.31)	3.47 (0.06)	1.23 (0.07)	93.36

[a] Encapsulation efficiency = (amount of pesticide in matrix/amount of pesticide fused) × 100.
[†] Values in brackets represent standard deviation.

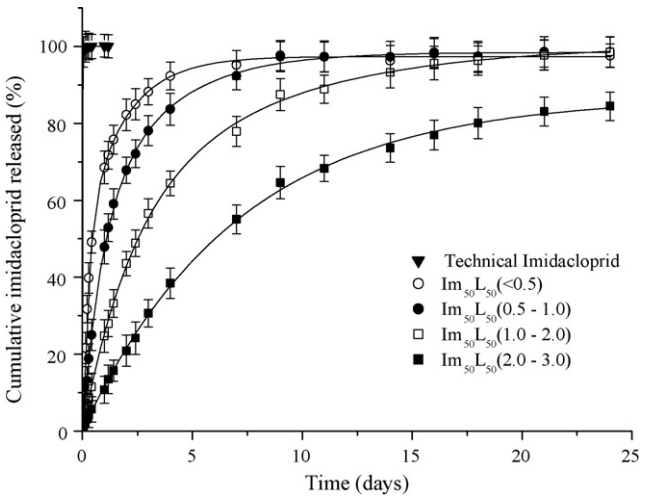


Fig. 4. Cumulative release of imidacloprid from granules into static water (error bars represent the standard deviation of three replicates).

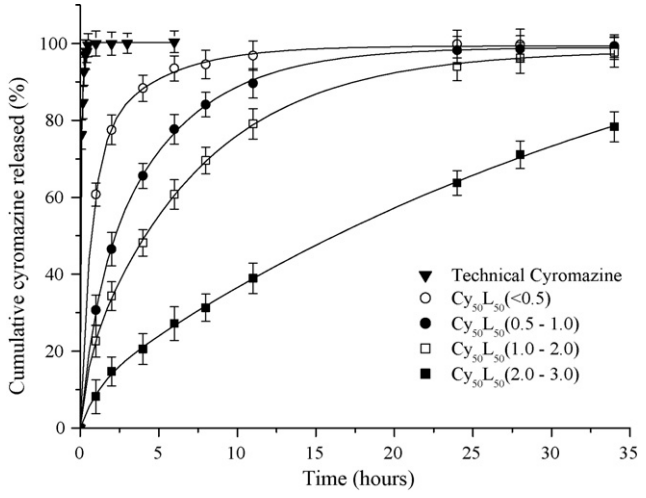


Fig. 5. Cumulative release of cyromazine from granules into static water (error bars represent the standard deviation of three replicates).

in the active ingredient release. This increase in size affects the prepared systems behaviour, obtaining a major decrease in releasing for larger granule systems (size between 2 and 3 mm) for the three pesticides. Finally, drop in the release of pesticide over time was observed in all formulations. This result is probably due to an increase in the distance where dissolved molecules have to diffuse as the depleted zone advances to the center of the matrix.

The release data of pesticides in water were analyzed by applying the empirical equation proposed by Ritger and Peppas [27]:

$$\frac{M_t}{M_0} = Kt^n \quad (1)$$

M_t/M_0 is the percentage of active ingredient released at time t, K is a constant that incorporates characteristics of the macromolecular network system and the active ingredient, and n is a diffusional parameter, which shows the transporting mechanism.

The values of K and n obtained from 90% of maximum released pesticide, in each curve (Figs. 3–5), were obtained using the nonlinear curve-fitting utility of SigmaPlot software. These values and the correlation coefficients are presented in Table 3 for isoproturon and imidacloprid, and in Table 4 for cyromazine. There was good correlation of the release profiles of CR pesticides granules with the empirical equation, the correlation coefficient (r) being higher than 0.98. The K values oscillate between 8.7×10^{-2} h^{-n} for $Cy_{50}L_{50}$(2.0–3.0) formulation and 66×10^{-2} $days^{-n}$ for $Im_{50}L_{50}$(<0.5) formulation. In each group of CR formulations the K values are diminished while the granules sizes are increased. This behaviour is shown again when evaluating the data referred to T_{50} parameter (the time taken for 50% of the pesticides to be released). The T_{50} values calculated from K and n constants are also presented in Tables 3 and 4. First, the values of the T_{50} parameter are observed to be much lower in cyromazine systems than in those prepared with isoproturon and imidacloprid, being the resulting order cyromazine formulations ≪ imidacloprid formulations < isoproturon formulations. This variation order shows the loss of speed in the releasing process of the active ingredient from the polymeric matrices of lignin as long as the active ingredient solubility decreases from 13,000 mg L^{-1} in cyromazine to 55 mg L^{-1} in isoproturon. The variation order in this parameter for the three groups of prepared systems is (<0.5 mm) < (0.5–1.0 mm) < (1.0–2.0 mm) < (2.0–3.0 mm). A

Table 3
Constants from fitting the empirical equation $M_t/M_o = Kt^n$ to release data of isoproturon and imidacloprid in water.

	Formulation	$K \times 10^2$ (days)$^{-n}$	n	r	T_{50} (days)
Isoproturon	$Is_{50}L_{50}$(<0.5)	57.9 ± 0.007§	0.45 ± 0.009	0.987*	0.73
	$Is_{50}L_{50}$(0.5–1.0)	30.5 ± 0.006	0.64 ± 0.013	0.986*	2.17
	$Is_{50}L_{50}$(1.0–2.0)	22.3 ± 0.004	0.48 ± 0.011	0.991*	5.36
	$Is_{50}L_{50}$(2.0–3.0)	11.2 ± 0.003	0.61 ± 0.014	0.990*	11.42
Imidacloprid	$Im_{50}L_{50}$(<0.5)	66.9 ± 0.006	0.55 ± 0.008	0.982*	0.59
	$Im_{50}L_{50}$(0.5–1.0)	40.6 ± 0.007	0.71 ± 0.013	0.991*	1.34
	$Im_{50}L_{50}$(1.0–2.0)	22.1 ± 0.005	0.76 ± 0.016	0.993*	2.94
	$Im_{50}L_{50}$(2.0–3.0)	11.3 ± 0.003	0.79 ± 0.015	0.998*	6.54

§ These values represent standard error.
* Significant at the 0.001 probability level.

Table 4
Constants from fitting the empirical equation $M_t/M_o = Kt^n$ to release data of cyromazine in water.

	Formulation	$K \times 10^2$ (h)$^{-n}$	n	r	T_{50} (h)
Cyromazine	$Cy_{50}L_{50}$(<0.5)	60.7 ± 0.007§	0.35 ± 0.009	0.985*	0.58
	$Cy_{50}L_{50}$(0.5–1.0)	32.7 ± 0.005	0.45 ± 0.010	0.989*	2.54
	$Cy_{50}L_{50}$(1.0–2.0)	23.2 ± 0.005	0.53 ± 0.014	0.999*	4.32
	$Cy_{50}L_{50}$(2.0–3.0)	8.7 ± 0.004	0.63 ± 0.013	0.998*	16.23

§ These values represent standard error.
* Significant at the 0.001 probability level.

Table 5
Average diameter (D) for each size of lignin-based granules.

Granule size (mm)	D (minimum average diameter (mm))		
	$Is_{50}L_{50}$	$Im_{50}L_{50}$	$Cy_{50}L_{50}$
<0.5	0.30 (0.05)[†]	0.29 (0.03)	0.38 (0.06)
0.5–1.0	0.73 (0.03)	0.68 (0.06)	0.90 (0.05)
1.0–2.0	1.40 (0.04)	1.69 (0.07)	1.40 (0.03)
2.0–3.0	2.94 (0.07)	2.83 (0.08)	2.92 (0.06)

[†] Values in brackets represent standard deviation.

decrease in release rate is observed as consequence of both lengthening of the diffusional pathway through the lignin and a decrease in the superficial area exposed to the dissolution medium as granule size increase. This is determining to understand the evolution of T_{50} values considering each particular group of systems containing the same active ingredient. The higher variability of T_{50} values might also be useful for selecting the most appropriate formulation depending on the soil environments, especially to avoid the cyromazine, isoproturon and imidacloprid tendency to leach [20,28,29].

There are various agronomic practices in which pesticides are used and in which it is necessary to control the release rate of pesticides to the environment. Thus, it is interesting to find a relationship between the main parameter in the release process (T_{50}) and some main properties of the granules that allow us predict the kinetic behaviour of prepared systems. As related above, it seems that the size of lignin matrices is the most influential factor that affects the release rate of pesticides. So, the T_{50} values of lignin CR granules were correlated with the average diameter of granules (D) (Table 5). Figs. 6–8 show the plot of the T_{50} values for isoproturon, imidacloprid and cyromazine, respectively versus the D values of the matrices. The analysis indicates that T_{50} values are well-correlated with the D values of formulations. The equations of linear correlation and correlation coefficients were obtained by applying the minimum-squares method to the data.

$$T_{50} = 4.10 \times D - 0.58 \quad (2)$$

where $r = 0.999$ and $p = 0.001$

$$T_{50} = 2.29 \times D - 0.30 \quad (3)$$

where $r = 0.986$ and $p = 0.01$ and

$$T_{50} = 6.39 \times D - 3.07 \quad (4)$$

where $r = 0.987$ and $p = 0.01$.

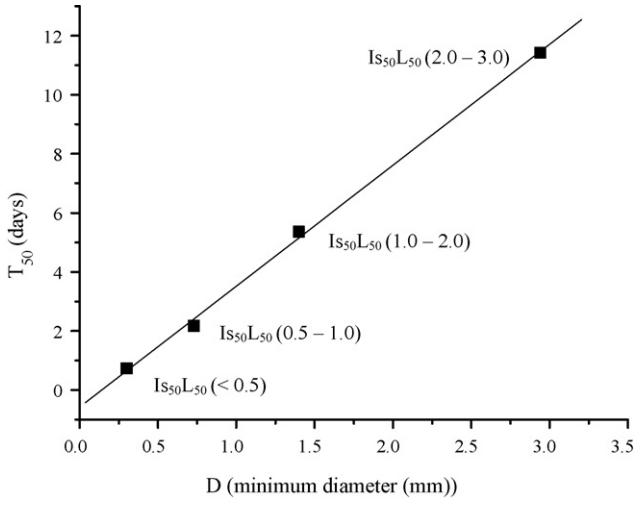


Fig. 6. Correlation study with T_{50} and the minimum diameter (D) of isoproturon granules.

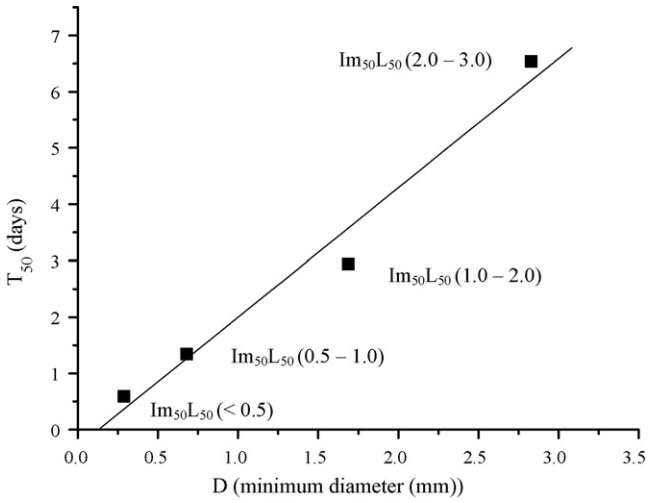


Fig. 7. Correlation study with T_{50} and the minimum diameter (D) of imidacloprid granules.

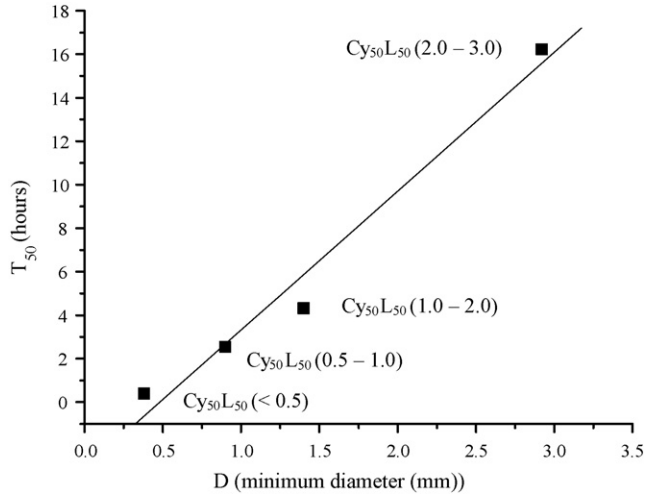


Fig. 8. Correlation study with T_{50} and the minimum diameter (D) of cyromazine granules.

It is easy to prove that the release of isoproturon (Eq. (2)), imidacloprid (Eq. (3)) and cyromazine (Eq. (4)) from the systems based on lignin polymeric matrix is notably depleted though 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 from the D values used in the prepared formulations. As indicated before, these T_{50} values will be used to predict kinetic behaviour of the prepared systems and therefore to design a suitable profile of the release of the active ingredient from granules in each particular pesticide and agro-environmental situation.

4. Conclusions

Controlled release systems of isoproturon, imidacloprid and cyromazine have been obtained by mixing the pesticide and kraft lignin under melting conditions. In this way, high encapsulation efficiency was obtained for the three pesticides.

The kinetic experiments of release in water have shown that: (i) the use of CR granules reduces the release rate of isoproturon, imidacloprid and cyromazine in comparison to the technical products; (ii) the release rates are higher in cyromazine CR formulations than in those prepared with isoproturon, however imidacloprid shows

an intermediate behavior; and (iii) for each pesticide CR formulating group the release rate can be controlled by selecting the granule size.

A linear regression of the T_{50} values and the granule size (D) was finally obtained. From the D values of granules, it is possible to obtain a rough estimation of the release rate of, which can be useful to supply the appropriate concentration of pesticide in each agronomic practice into the soil solution.

Therefore, the use of a unique method to encapsulate pesticides with different physical–chemical properties can mean a wide improvement in preparation of pesticide formulations. Moreover, the use of these CR formulations would have the potential to make the pesticides easier to use and reduce the required dose, both of which will decrease environmental exposure of isoproturon, imidacloprid and cyromazine

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