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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).

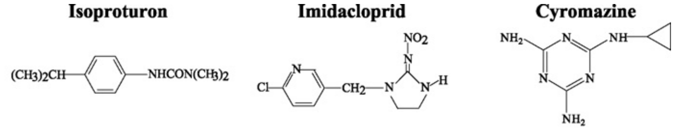
Table 1
Percentage (by weight) of component of controlled release formulations containing pesticides.

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 (ºC)	158	143	220
Vapour pressure (mPa)	$3.30 \cdot 10^{-3}$ (20 ºC)	$2.00 \cdot 10^{-4}$ (20 ºC)	$4\ 48 \cdot 10^{-4}$ (25 ºC)
Water solubility (mg L^{-1})	55 (20 ºC)	510 (20 ºC)	13000 (25 ºC)
Log K_{ow}	2.5	0.57	-0.061

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