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Research paper

Lignin and ethylcellulose in controlled release formulations to reduce leaching of chloridazon and metribuzin in light-textured soils

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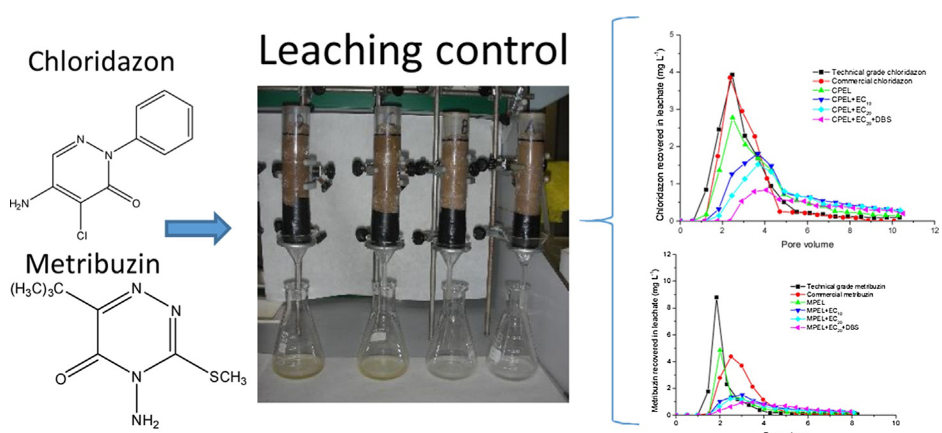
HIGHLIGHTS

- The use of CRFs reduces the presence of chloridazon and metribuzin in the leachate.
- CRFs coated with EC and DBS provides the lowest percentages of herbicides leached.
- The use of CRFs leads to increase the herbicide effectiveness in soil.
- A correlation between herbicide recovered in leachates and T_{50} values was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, controlled release formulations (CRFs) of the herbicides chloridazon and metribuzin, identified as potential leachers, have been evaluated in soils with different texture. To prepare the CRFs, ethylcellulose (EC) and dibutylsebacate (DBS) have been used as coating agents in lignin-polyethylene glycol based formulations.

Mobility experiments have been carried out in two light textured soils (sandy and sandy-loam). Breakthrough curves have shown that the use of CRFs reduces the presence of chloridazon and metribuzin in the leachate compared to technical and commercial products, being the lignin CRF coated with EC and DBS the most efficient to diminish the herbicide leaching.

Mass balance study has shown a higher amount of chloridazon and metribuzin recovered in soils when these herbicides were tested as CRFs compared to technical and commercial products. The gradual release of herbicides from the CRFs resulting in a rather available levels of chloridazon and metribuzin in soil for a longer time. A good correlation between percentages of herbicide recovered in leachates and T_{50} values (time corresponding to 50% release of herbicide in water)

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was obtained, which allows to select the most appropriate CRF in each agro-environmental practice to reduce the potential pollution of groundwater by chloridazon and metribuzin.

1. Introduction

Nowadays, the use of large amount of herbicides for the control of weeds in crops represents a major challenge to maintain welfare. The proper use of these chemicals can contribute to protect natural resources and to avoid environmental pollution and damage on the public health [1].

Different fates have been observed when herbicides are applied in the field. Among others, uptake by plants, degradation process, movement, out-target, immobilization and unintentional discharge in the environment. Effectively control weeds with few or no adverse environmental must be observed in a well-planned management system. However, the high amount of herbicides used in agronomic practices leads to the existence of contaminated groundwater sources, mainly through the leaching process [2–4]. The most important parameters that determine herbicide capacity to leach, and so capable to reach groundwater, are the herbicide properties, being persistence in soil and sorption the most relevant ones. To calculate the leaching potential of a substance, the Groundwater Ubiquity Score (GUS) can be used. This index can be calculated from its organic carbon normalized sorption coefficient (K_{oc}) and the parameter of soil persistence halftime (DT_{50}) by the next equation. [5]:

$$\text{GUS} = \log(\text{DT}_{50}) \times (4 - \log(K_{oc}))$$

According to GUS index, the herbicides chloridazon and metribuzin (2.78 and 2.57, respectively) have been identified as potential leachers [6].

Chloridazon (5-amino-4-chloro-2-phenylpyridazin-3(2H)-one), which is used as a selective systemic herbicide that inhibits photosynthesis and is used for the general control of weeds [7]. The herbicide chloridazon is considered as a mobile molecule in some soils despite the existence of contradictory results. The K_{oc} values for chloridazon ranged from 89 to 340 according to several investigations [8]. These K_{oc} values shows that this herbicide could have an important tendency to leach in soils, in agreement to the Cohen classification [9].

Metribuzin, 4-amino-3-methylthio-6-ter-butyl-1,2,4-triazin-5(4H)-one, is a selective systemic herbicide, being well absorbed both by root and foliar routes with translocation to all plants parts. This herbicide is used for the control of annual broadleaf weeds in field crops and vegetables. The herbicide metribuzin is a very soluble compound in water (water solubility = 1050 mg L^{-1} at 20 °C) and therefore tends to adsorb little in most soils [10].

The development of CRFs based on polymeric materials for its use in agriculture will allow to apply highly soluble herbicides such as chloridazon and metribuzin in an efficient way and with a minimum pollution risk resulting from rapid runoff and leaching. Controlled-release technology of agrochemicals is based on the use of existing active ingredients and selected natural materials. The aim of this technique is to develop formulations that allows the precise and quantitative release of the active ingredients, and finally to achieve the most economic, safe and effective control of pests and weeds and reducing the environmental contamination [11,12]. Encapsulation of agrochemicals into polymeric carriers has attracted emerging interests. The polymeric matrix prevents direct exposure of the active ingredient to environment, reducing loss of degradation and evaporation [13–15].

The nature and type of polymeric material are the parameters that affect the properties of controlled release formulations. Different polymers have been used in the preparation of controlled release systems. Natural polymers such as alginate, lignin, starch, ethylcellulose, chitosan and so on, have been preferably used instead synthetic polymers due to their biodegradability characteristics, low cost, free availability, and non-toxicity [14,16–19].

One of the polymers widely used in CRFs synthesis is the lignin, a low-cost waste product in the paper pulp manufacturing process, which is readily available, cheap and a currently underutilized resource [20–22]. Several encapsulation methods and different agrochemicals have been used to obtain lignin-based controlled release systems. Polyethylene glycol (PEG) and ethylcellulose (EC) have been used to optimize lignin-based formulations prepared with highly water soluble herbicides, such as chloridazon and metribuzin, and increase their release efficiency [18,23]. These previous papers were focused on synthesis, characterization and evaluation in water of the controlled release systems.

In this paper, we investigate the potential use of these CRFs to control the release and leaching behavior of both herbicides in soils. These studies could lead to obtain a higher knowledge of herbicides behavior as leacher in soils when there are uses as CRFs.

The purposes of this study were to evaluate the capacity of the CRFs based on lignin to control release rate and leaching of metribuzin and chloridazon in soils. The mobility of herbicides from CRFs was compared to those of technical grade and commercial products in soil column experiments. Furthermore, the influence of physico-chemical properties of two soils on the herbicides distribution from CRFs, technical grade and commercial products has been also researched.

2. Materials and methods

2.1. Chemicals and soils

Metribuzin (93.0%) and chloridazon (93.5%) technical grade (TG) were nicely provided by Industrias Afrasa, S. A. (Valencia, Spain). Their molecular formula and selected properties are as follows [6]. For metribuzin, molecular formula: $C_8H_{14}N_4OS$; water solubility (20 °C): 1165 mg L^{-1}; octanol/water partition coefficient ($\log K_{ow}$) (20 °C), 1.60. For chloridazon, molecular formula: $C_{10}H_8ClN_3O$; water solubility (20 °C): 422 mg L^{-1}; octanol/water partition coefficient ($\log K_{ow}$) (20 °C), 1.19.

Commercial formulation of chloridazon (65%) in the form of water-dispersible granules (Pyramin DF) was supplied by BASF Crop Protection (Barcelona, Spain). Commercial formulation of metribuzin (70%), in the form of water-dispersible granules (Eclipse 70 WG) was supplied by Makhteshim Agan España S.A. (Valencia, Spain).

Indulin AT commercially available pine kraft lignin, used for CRFs preparation, was kindly supplied by Westvaco Corp., Charleston, SC. Polyethylene glycol with a molecular weight of 1000 g mol^{-1} was used to improve the formulation homogeneity; ethylcellulose (Ethocel®; ethoxy content, 48.0–49.5%; viscosity, 9–11 cp) was used as film-forming material of polymer coating; and finally, dibutylsebacate, (DBS), (≥97%, d = 0,936 gm L^{-1}) was selected as plasticizer. These chemical were provided by Fluka Chemie AG (Buchs, Switzerland).