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Investigating the biodegradation pattern of an ecofriendly pesticide delivery system based on wheat gluten and organically modified montmorillonites

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ABSTRACT

An organically modified montmorillonite (C30B) was introduced within a wheat gluten (WG)-based formulation containing ethofumesate (as model pesticide) with the aim to enhance its slow release properties by modulating both biodegradation and release properties. For this purpose, biodegradation pattern in soil and release properties in model system have been investigated for ethofumesate alone, WG-ethofumesate and WG-C30B-ethofumesate formulations. Respirometric experiments undertaken with ethofumesate in soil have evidenced a non-biodegradable behavior whereas the incorporation of 0.26% of ethofumesate in WG-based formulation did not affect the final biodegradability of WG-based material in spite of a slight but significant delayed biodegradation pattern. This delaying effect, attributed to the ecotoxic effect of ethofumesate, was shown to disappear when introducing C30B in the formulation. The use of WG-based materials to formulate ethofumesate also resulted in a slow release effect (in water) that could be significantly enhanced by adding organoclays in the materials in spite of a very poor dispersion of the nanoclays within the matrix. Indeed, the presence of clay aggregates evidenced by TEM in the WG matrix would result in the entrapment of ethofumesate taking into account the huge affinity of this pesticide for this nanoclay. This hypothesis appeared fully consistent with the assumption that ethofumesate would be less available to reduce microorganisms respiration and also potentially less subjected to transport mechanisms. As a result, WG-based formulations appeared as a suitable ecofriendly strategy to design slow release delivery system for pesticides with the objective to reduce pesticide leaching in the environment.

1. Introduction

Agrochemicals such as pesticides have been extensively used for decades and have substantially increased the food production. However a large amount of applied pesticides often never reach their intended target due to their degradation, volatilization and leaching, leading to serious ecological problems [1]. Their impact on surface and ground water is a major concern along with their potential health hazards to the general population. In the context of agrochemical uses limitation, increasing attention is given to controlled release systems in which the pesticide is gradually delivered over time, thus limiting the amount immediately available for transport processes [2].

Organic matrices have been regarded as pesticide carriers worthy of attention. Even if studies have already been carried using synthetic polymers matrix as carriers (urea-formaldehyde resins, acrylic acid polymers, polyurethane…) [3], bio-sourced polymers are considered as more ecofriendly due to their biodegradability and non-ecotoxicity and are often preferred to design controlled release formulations. Indeed, the use of polymers stemming from renewable resources to develop bioplastics constitutes one of the many strategies to minimize the environmental impact of petroleum-based plastics.

Among bio-sourced matrices already tested as support for controlled release formulations, the most frequently used are chitosan [4,5], pectin [6], polylactic acid [7], starch [8,9], alginate [10], starch-alginate [6,11–13], alginate-gelatin [14,15], lignin and/or cellulose derivatives [16–19] and wheat gluten [20,21]. Wheat gluten, a by-product of the starch industry with a high protein content (>75 wt%), could be considered as suitable for such applications owing to its good thermoplastic properties and processability by extrusion at temperatures as low as 60 °C [22], and its remarkable biodegradability [23,24]. Moreover, the use of protein

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as raw material offers a wide spectrum of chemical functionalities due to the large variety of amino acids, and also represents a significant source of nitrogen (around 17 wt%) for the crops nutrition, a huge advantage for agricultural applications.

However, to extend the use of bio-sourced polymer matrix in a wider range of applications, their water resistance and mechanical properties often require to be improved. Nanoreinforcement through the incorporation of nanoclays appears to be an efficient way to enhance these latter properties and also bring additional functionalities such as controlled release properties. Indeed, several studies have already reported that interesting slow release properties could be brought by combining clay fillers with a bio-sourced polymer matrix such as cellulose derivatives [25], chitosan [26] or alginate [6,27–29]. This slow release behavior was often attributed to clay sorption properties. Nevertheless, in the case of a good affinity between the clay and the polymer, an exfoliated nanocomposite structure might be obtained that would be expected to modulate diffusion through a tortuosity effect [30,31].

We recently designed new pesticide formulations by combining wheat gluten, three contrasted montmorillonites (MMT) and ethofumesate (as model pesticide) using a bi-vis extrusion process with the objective to evaluate the potential use of nanoclays for modulating transfer properties of active agents in bio-sourced polymers [32]. With such formulation, associating polymer and nanoclays, the bioavailability of the active substance in soil would result from concomitant complex phenomena including (i) its desorption from the clay particles depending on its affinity for the fillers, (ii) its diffusion through the material, and (iii) the matrix biodegradation rate. Thus, a better knowledge of each mechanism contribution would enable to better control the release pattern of a pesticide.

In the present study, Cloisite®30B (C30B), an organically modified montmorillonite (OMMT) was used to design controlled release systems based on a biodegradable wheat gluten (WG) matrix and a hydrophobic herbicide (ethofumesate) using a bi-vis extrusion process. The interest of selecting this OMMT is the presence on its surfactant of apolar (tallow chain and methyl group) and polar (hydroxyl groups) groups, which result in an intermediary affinity for both ethofumesate [32,33] and wheat gluten [24,32]. The targeted effect of this OMMT was to delay the herbicide delivery in environment by controlling (i) its sorption on nanoclays, (ii) its diffusion via a tortuosity effect and/or (iii) the WG matrix biodegradation rate. The objective of this study was to investigate the effect the concomitant presence of both ethofumesate and C30B on the properties of wheat gluten-based controlled release formulation of pesticide. For this purpose, biodegradation pattern in soil and release properties in model system have been investigated for ethofumesate alone, WG-ethofumesate and WG-C30B-ethofumesate formulations.

2. Material and methods

2.1. Materials

Commercial vital wheat gluten (WG) was kindly supplied by Syral (Belgium) under the reference AMYGLUTEN 110. Its moisture and protein content was approximately 10% and 80%, respectively. Technical ethofumesate [5-Benzofuranol, 2-ethoxy-2,3-dihydro-3,3-dimethyl-, methanesulfonate, (±)] 97% pure was a crystalline solid kindly supplied by Bayer Crop Science (France). Analytical ethofumesate (99.5% pure) was purchased from SIGMA Aldrich to compare with calibration standards. A commercial formulation of ethofumesate (Tramat® F) was provided by Bayer Crop Science (France). The molecular mass of ethofumesate was 286.3 g mol^{-1} and its solubility in water ranged from 44 to 57 mg L^{-1} depending on the pH. Cloisite®30B (noted C30B), a commercial nanoclay purchased by Southern Clay (Gonzales, Texas), is an organically modified montmorillonite, carrying a methyl, tallow, bis-2-hydroxyethyl alkylammonium salt. Its interlayer distance d_{001} was 18.3 Å and its CEC value (cation exchange capacity) was 93 meq. 100 g^{-1}. Further information on this OMMT (organic content, organic cation saturation, 3D models of organic cations) are given in Chevillard et al. [33]. Chemicals, unless specified separately, were purchased from Sigma Aldrich in per analytical quality.

2.2. Preparation of wheat gluten-based materials

Extrusion was performed using a co-rotating twin screw extruder (Coperion, ZSK25, Stuttgart, Germany) connected to a computer interface and controller unit (Brabender, O.H.G, Duisburg, Germany). The barrel consisted of twelve zones, each zone being equipped with an independent temperature control and a die head constituted of two 5-mm diameter holes. The total length of the screw was 42D. The first and second heating zones were constantly set at 40 °C and the other heating zones at 60 °C. The screw speed was set at 150 rpm. Wheat gluten and nanoclays powders were fed using two distinct weight feeders (Brabender, Duisburg, Germany) leading to a cumulate powder feed rate of 4.5 kg h^{-1}. The ratio nanoclays/wheat gluten was adjusted to have a final inorganic filler content corresponding to 5 wt%. Water was fed with a weight pump (Movacolor, WL Sneek, Netherlands) at a flow rate of 2 kg h^{-1}. Immediately after extrusion, extrudates were cooled and air-dried in ambient conditions during approximately 30 min before being cut using a Scheer SGS 50E pelletizer (Scheer Reduction Engineering GmbH, Stuttgart, Germany). Granulates were allowed to dry in ambient room conditions until constant weight. Water content of final granulates was 9 wt% (measured after drying 24 h at 105 °C). They were characterized by a height of 2.3 ± 0.2 mm, a diameter of 5.1 ± 0.4 mm, and a weight of 53 ± 2 mg. Samples were packed in polyethylene hermetic bags and stored in dark room at 4 °C until experiments.

2.3. Material structural characterization by transmission electron microscopy (TEM)

Small pieces of material (about 1 mm^3) were fixed in glutaraldehyde 2.5% (v/v), dehydrated in an ethanol gradient, then impregnated in propylene oxide and finally embedded in epoxy resin epon-812 substitute, (Electron Microscopy Science, England). After three days of incubation at 60 °C, ultra-thin sections of 70 nm were cut with an ultramicrotome diamond and mounted on 100 mesh grids covered by a colodion film. Samples were examined with a Jeol JEM-1200EX II TEM (Jeol ltd., Tokyo, Japan) using magnifications from 10 to 100 K.

2.4. Ethofumesate release kinetics in water

Appropriate amounts of granulates, corresponding to 16 mg of ethofumesate, were added to 0.8 L of deionized water with 0.2% (w/v) of sodium azide (to prevent microbial growth) in closed glass bottles of 1 L. Bottles were placed under magnetic stirring (200 rpm). At selected times, from 0 to 15 days, samples (500 μL) were taken, then passed through nylon filters (0.45 μm) and the amount of ethofumesate was analyzed by HPLC. The same experiments were conducted with the commercial formulation (Tramat) used as control. Experiments were conducted at 8, 25 and 40 °C. Tests were performed in triplicate. All data were considered for data analysis whereas average values were used for plotting.