USE OF CLAY/β-CYCLODEXTRIN FORMULATIONS TO OBTAIN A SLOW RELEASE OF A HYDROPHOBIC HERBICIDE

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ABSTRACT

The study aimed to prepare slow release formulations of the hydrophobic herbicide norflurazon (4-chloro-5-methylamino-2-(α,α,α)-trifluoro-m-tolopyridazin-3-(2H)-one) based on a standard montmorillonite, a pillared montmorillonite and an organo-montmorillonite. For this purpose, a β-cyclodextrin-norflurazon solution was used, due to its ability to form an inclusion complex which yields an increase in norflurazon solubility in water (up to 5 times). The amount of herbicide adsorbed on the standard montmorillonite was directly proportional to the herbicide concentration in solution, obtaining an herbicide adsorption 5 times higher when β-cyclodextrin-norflurazon solutions were used. The organo-clay was prepared modifying the surface of montmorillonite from hydrophilic to hydrophobic preadsorbing an organic cation (phenyltrimethylammonium), at a loading yielding the highest affinity of adsorption for norflurazon. Pillared clay used was an alumina pillared montmorillonite which showed a similar affinity by norflurazon adsorption than the untreated montmorillonite. Water release experiments were also performed in order to test the slow release capacity of the different matrices selected in this study. Pillared montmorillonite formulations showed a similar norflurazon release profile compared with the untreated montmorillonite. Likewise, release profiles of the pillared clay with two different herbicide loadings were obtained revealing the influence of the herbicide loading on the release rate from the formulations. The release profile corresponding to the organo-clay sample showed the slowest release rate, reaching only a 24% of the herbicide loaded released after 3 days of experiment. The results of this study indicate that the use of selectively-modified clays could be useful for the preparation of herbicide slow release formulations, where the increase of the hydrophilic character of the montmorillonite using an organic cation is a critical property when slow release formulations of herbicide want to be prepared. The use of these formulations can be advantageous, because they can minimize the risk of groundwater contamination and permit herbicide use reduced rates, maintaining the desired concentrations of herbicide in the topsoil layer for longer periods of weed control.

KEYWORDS: Norflurazon; phenyltrimethylammonium; montmorillonite; pillared clay; controlled release.

INTRODUCTION

The risk of environment contamination by pesticides and their degradation products has encouraged the interest in the development of new formulations for pesticide application. Slow release formulations (SRFs) of pesticides maintain the threshold concentration of the active ingredient for pest control in soil or plant by its release at the required rate, reducing its level in the environment because lower amounts are required for biological effect with the economical and environmental advantages [1]. Clays and clay minerals are excellent materials, since their high adsorption power, the ease with which they are modified, and their particular colloidal properties make them suitable materials for designing solid laden pesticide formulations [2]. Most of the works have been focused on the use of modified montmorillonite by preadsorbing organic cations. By the nature of the organic cation, the organoclays may be classified as either organophilic or adsorptive [3]. Organophilic montmorillonites are formed by sorbing bulky quaternary amine cations, with long alkyl chains of 10 carbon atoms at least. Once the cations are adsorbed on the clay, the alkyl chains interact between themselves forming an organic phase with a very high affinity for hydrophobic compounds. Adsorption of the fungicides metalaxyl and penconazole on hexadecylpyridinium-exchanged montmorillonite was directly related to the hydrophobicity of the herbicide and the organic matter content [4]. Organoclay complexes of metalaxyl and metribuzin prepared using hexadecyltrimethylammonium (HDTMA) reduced their downward mobility in soil [5]. On the other hand, pillared clays are likely employed as matrices for preparation of SRFs, especially due to their adsorptive properties and low cost. Pillared clays have been used for water detoxification [6], and especially for organic pollutants in solution.

Cyclodextrins (CDs) are a class of microbially produced compounds that are able to form inclusion complexes with organic compounds in solution, increasing their water solubility. The most important structural feature of these compounds is their toroid shape, with hydrophobic interior cavity and hydrophilic faces [6]. The application of CDs as solubility-enhancing agents has been broadly investigated. Many synthetic pesticides can form inclusion complexes with CDs, often resulting in improvements in their chemical and physical properties, such as enhancement of solu-
MATERIALS AND METHODS

Materials

The clays used were a standard montmorillonite from Wyoming (SWy-1) [13] supplied by the Clay Minerals Society (Source Clay Minerals Repository), and an aluminia pillared montmorillonite (M-PIL) supplied by FLUKA. The organo-clay (M-FTMA) was prepared by dropwise addition of aliquots of 0.1 M of FTMA to aqueous suspension g L⁻¹ of the clay under continuous stirring. The final suspension was 1% (w/v). After being stirred for 24 hours, the suspensions were centrifuged at 12000 rpm for 15 minutes, the supernatant was discarded, and the samples were freeze-dried. The final load was 0.5 mmol/g for the organic cation. Commercial (Zoral) and technical grade NFL (80 and 97.8% purity, respectively) were kindly supplied by Novartis A. G. (Basel, Switzerland). Norflurazon (NFL) is a fluorinated pyridazone herbicide that inhibits photosynthesis and is registered for soil-applied use in cotton, soybean, tree fruit and nut crops, citrus and cranberries. NFL, with a molecular weight of 303.67, has a water solubility of 28 mg L⁻¹ and a vapour pressure of 2.7x 10⁻⁶ Pa at 20°C. The organic cation phenyltrimethylammonium (FTMA) was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). β-CD was purchased from cyclolab Roquette (F-Lestrem). The structural formulas of the herbicide, β-CD and the organic cation are shown in Figure 1.

Methods

For the preparation of the β-CD-NFL solutions, the herbicide was added to a 0.01 M β-CD solution in order to obtain a final concentration of 100 mg L⁻¹ of herbicide [12]. These solutions were stirred for 24 hours in a platform shaker at 20 ± 1°C.

NFL adsorption experiment was carried out on the standard montmorillonite in the presence of β-CD, reaching a NFL concentration of 100 mg L⁻¹, and in the absence of β-CD 0.01 M, (reaching only 20 mg L⁻¹ of NFL concentration). 20 mL of the herbicide solutions were added to 1g of SWy-1 under continuous stirring in 30 mL polycarbonate tubes. Afterwards, the tubes were shaken for 24 hours at 20 ± 1°C, the suspensions were centrifugated at 12000 rpm for 12 minutes, and the NFL in the supernatant was determined by HPLC, Shimadzu SIL-6B, with the following conditions: mobile phase 50:50 acetonitrile:water; flux 0.6 mL min⁻¹; diode array detector (Shimadzu, SPD-M10A...
Saturation of the original (SWy-1) and modified clays (M-FTMA and M-PIL) with NFL was achieved using 1g of each clay selected and 10 mL of β-CD-NFL solution (100 mg L⁻¹), using polypropylene centrifuge tubes, under continuous shaking in a platform shaker at 25°C, withdrawing 5 mL and adding another 5 mL from the stock solution, every 24 hour during 24 days of experiment, till the NFL concentration was kept constant.

**Release experiments**

To compare the release behaviour of the different clay formulations obtained, dissolution tests of commercial NFL and all the clay formulations were performed in triplicate with a rotating paddle apparatus (SOTAX AT 7 Smart). The operating conditions were as follows: a quantity of formulation containing 0.65 mg of NFL was added to 1000 mL of deionised water as dissolution medium at 25 ºC and with stirring at 50 rpm. At appropriate time intervals during the experiment time (72 hours), 1 mL samples were taken and analysed by HPLC.

**RESULTS AND DISCUSSION**

NFL adsorption on SWy-1 was studied in the presence and absence of β-CD 0.01 M. In the absence of β-CD, the maximum concentration employed was of 20 mg L⁻¹, since it is difficult to obtain higher concentrations due to the proximity of its product solubility. However, in the presence of β-CD it could get easily a concentration 5 times higher (100 mg L⁻¹), according to previous results [12]. The amount of NFL adsorbed was directly proportional to the herbicide concentration in solution, obtaining an herbicide adsorption 5 times higher in the case of using β-CD-NFL solutions, from a NFL adsorption of 0.12 mg/g, in the absence of β-CD, to 0.57 mg/g in the presence of β-CD. For this reason, to prepare the clay formulations, 100 mg L⁻¹ β-CD-NFL solutions were used, in order to obtain the highest clay-saturation percentages with NFL.

The SWy-1, M-PIL and M-FTMA samples underwent consecutive additions of the NFL solutions until no increase in the adsorption was observed. In Figure 2, it could be observed the different behaviours among the clays under study, where a similar saturation profile was obtained for SWy-1 and M-PIL, either in the maximum amount of herbicide adsorbed (1.72 and 1.89 mg g⁻¹, respectively) and in the number of additions needed to reach it. On the other hand, M-FTMA sample showed a quite different saturation profile, since 24 additions were needed to reach the maximum saturation, which was around 4 times higher than that obtained in the case of M-PIL (7.05 mg g⁻¹).

NFL adsorption on SWy-1 can occur via ion-dipole interactions of the pyridazine ring of the herbicide and the cations saturating the interlayer space, as described for chloridazon, another related pyridazinone herbicide [14]. In the case of M-PIL its large porous structure is responsible for the adsorption of NFL as a zeolite-like molecular sieve [15, 16], in addition to its acidic nature, mainly due to its high Lewis acidity [17, 9], concluding that the main mechanism of adsorption was due to the interaction with Lewis acid sites, based on the Lewis base character of this herbicide due to the presence of an aromatic ring in its structure (Figure 1) and a pyridazine ring attached to two electron-donor groups (chloride and methylamine).

NFL adsorption on SWy-1 preadsorbed with the organic cation FTMA increases dramatically when compared to that of SWy-1 or M-PIL (Figure 2). The mechanism involved in this case is based on the likely interactions between the corresponding rings of NFL and the organic cation. The hydrophilic character of SWy-1 is due to the strongly hydrated exchangeable cations [18]. The replacement of the interlayer cations by less hydrated small quarternary ammonium cations increases the hydrophobicity of the clay and the adsorption of non-ionic organic compounds [19]. Undabeytia et al. [20] suggested that another mechanisms for the NFL adsorption on the organo-clay should be also inferred, since they found that the highest adsorption of NFL did not take place on the SWy-1 preloaded with the organic cation up to cation exchange capacity (CEC, 0.8 mmol/g), but at a loading of 5/8 of the CEC (0.5 mmol/g), which is employed in this work. Xu et al. [21] also observed that the adsorption capacity of FTMA-smectite for aromatic hydrocarbons increased dramatically when the fraction of exchange sites occupied by FTMA reached 65-75% of the CEC, and further increase of FTMA loading decreased its adsorption capacity. The adsorption of the herbicide on the organo-clay should also be dependent on the existence of specific interactions between the phenyl rings of the herbicide and the organic cation pre-loading the clay [22].

NFL release rate profiles from the SWy-1, M-PIL and M-FTMA samples are shown in Figure 3. In all cases, the release of NFL from the clay formulations was retarded regarding that corresponding to the commercial herbicide, where 100% of NFL was released after the first hours of experiment (release profile not shown). The release of NFL from all formulations was nonlinear, characterized by an initial fast release in the first few hours. Sopěňa et al. [23] observed a similar behaviour for NFL release from ethyl-cellulose formulations. However, it would be desirable that a high concentration of herbicide is released during the first days after its application, in which most of the weeds are in the germination process, followed by a constant release of lower concentrations over a longer period of time. The release profile corresponding to the M-FTMA sample showed the slowest release rate, reaching 24% of the herbicide loading after 3 days, despite being the formulation with the highest load (7.05 mg g⁻¹). M-PIL and SWy-1 formulations showed a similar NFL release profile, being slightly slower that corresponding to the pillared formulation, what does not mean a great advantage regarding to the untreated montmorillonite.
The results of this study indicate that both the herbicide load and the type of matrix are critical properties when SFRs of herbicide want to be prepared. The amount of NFL adsorbed was directly proportional to the herbicide concentration in solution, therefore, β-CD was shown as a potential adjuvant to obtain new SRFs with a higher load of herbicide, since in the presence of β-CD it was possible to get a NFL concentration 5 times upper (100 mg L⁻¹). Likewise, the use of β-CD would mean a reduction in the contact toxicity to humans regarding to the use of organic solvents, which has a great risk of contamination. Besides, these formulations showed a desirable release profile where a high concentration of herbicide is released during the first days after its application, in which most of the weeds are in the germination process, followed by a constant release of lower concentrations over a longer period of time.

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