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Organohydrotalcites as novel supports for the slow release of the herbicide terbuthylazine

F. Bruna [a], I. Pavlovic [a], R. Celis [b], C. Barriga [a], J. Cornejo [b], M.A. Ulibarri [a,*]

[a] *Departamento de Química Inorgánica e Ingeniería Química. Universidad de Córdoba. Campus de Rabanales, Edificio Marie Curie, 14071 Córdoba, Spain*
[b] *Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Avenida Reina Mercedes 10, Apartado 1052, 41080 Sevilla, Spain*

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Abstract

The design of slow release formulations of pesticides is the subject of increasing attention with the aim of prolonging the biological efficacy of pesticides and attenuating their adverse environmental effects. In this work, organohydrotalcites (OHTs) are proposed as novel supports for the slow release of terbuthylazine, a herbicide widely applied to agricultural land. Two different OHTs were prepared by intercalating dodecylsulfate (DDS) and sebacate (SEB) anions into Mg–Al hydrotalcite (HT). Adsorption experiments revealed that terbuthylazine was well adsorbed by both HT–DDS and HT–SEB, whereas terbuthylazine adsorption by unmodified (inorganic) Mg–Al HT was negligible. Different terbuthylazine–OHT complexes were prepared by mixing the herbicide with the OHTs, using different solvents to favor the adsorbent–herbicide interaction. The ability of the herbicide–OHT complexes to slow the release of the herbicide into water and to reduce the herbicide leaching losses in soil was evaluated through batch release and column leaching tests. Compared to a standard commercial formulation of the herbicide, the complexes prepared from both HT–DDS and HT–SEB retarded the release of terbuthylazine into aqueous solution and reduced the herbicide leaching through soil columns. These results indicated promising usefulness of OHTs as suitable supports for the design of pesticide slow release formulations with the aim of reducing the adverse effects derived from rapid transport losses of the chemical once applied to soils.

Keywords: Dodecylsulfate; Hydrotalcite; Pesticides; Sebacic acid; Terbuthylazine

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1. Introduction

The increase in the levels of pesticide residues in soils and ground waters is a current environmental problem. In order to compensate for the losses caused by transport and degradation processes, pesticides are applied to agricultural soils in amounts which greatly exceed those required for control of the target organisms, and the excessive quantities added increase the environmental impact of these compounds (Gerstl et al., 1998a,b). An approach to minimize the pesticide transport losses after soil application is the use of controlled release formulations, in which the pesticide is delivered gradually over time, thus limiting the amount immediately available for transport processes. Beneficial effects related to the use of controlled release formulations include reduction in rapid losses of pesticide by volatilization, runoff and leaching, savings in manpower and energy by reducing the number of applications required in comparison to conventional formulations, increased safety for the pesticide applicator, and a general decrease in non-target effects (Gerstl et al., 1998b; Celis et al., 2002a). Raw materials, process steps, release mechanisms, as well as information on existing controlled release formulation types and specific applications have been reviewed by Scher (1999).

Numerous natural and synthetic materials have been proposed as carriers in controlled release formulations of pesticides, although the use of natural materials has the advantage of reducing the environmental impact of the pesticide carrier once incorporated into the environment (Celis et al., 2002b). Natural clay minerals have been studied as pesticide carriers, because clay minerals have high specific surface areas, low cost, and ubiquitous occurrence in soils and sediments (Margulies et al., 1994; Gerstl et al., 1998b; Johnson and Pepperman, 1998; Gonzaléz-Pradas et al., 1999). In addition, the possibility exists to selectively modify the clay mineral surfaces, for instance through

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* Corresponding author. Tel.: +34 957218648; fax: +34 957218621.
E-mail address: iq1ulcom@uco.es (M.A. Ulibarri).

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the incorporation of organic cations in the clay mineral interlayers, to enhance their affinity for selected pesticides and to control the pesticide desorption rate once added to the environment (El Nahhal et al., 1998; Celis et al., 2000, 2002a; Hermosín et al., 2001, 2006; Nennemann et al., 2001).

Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTs) can be easily synthesized in the laboratory by varying the nature of the divalent (M^{II}) and trivalent (M^{III}) cations, the M^{II}/M^{III} molar ratio, and the nature of the interlayer inorganic anion (Miyata, 1983; Cavani et al., 1991; Inacio et al., 2001). Both the facility in the synthesis and the potential variety in the combination of the components result in promising usefulness of HTs for developing new types of materials for many applications (Rives, 2001; Kanezaki, 2004).

Because their interlayer anions can be exchanged, HTs are good adsorbents for anionic organic compounds (Meyn et al., 1990; Ulibarri et al., 1995; Celis et al., 1999; Inacio et al., 2001; del Arco et al., 2007). In fact, different HTs have successfully been assayed as supports in controlled release formulations of anionic pharmaceuticals, such as ibuprofen, citrate, salicylate, and aspartic and glutamic acids (Ambrogi et al., 2001; Tronto et al., 2001; del Arco et al., 2004), and also for the controlled release of anionic pesticides, such as glyphosate, α-naphthalene-acetate, 2,4-D, MCPA, and picloram (bin Hussein et al., 2002, 2005; Zhang et al., 2004; Cardoso et al., 2006).

Similarly to clay minerals, the inorganic anions of HTs can be exchanged by organic anions rendering organohydrotalcites (OHTs) (Meyn et al., 1990; Clearfield et al., 1991; Zhao and Vance, 1997). This simple modification changes the nature of the HT surface from hydrophilic to hydrophobic, increasing its affinity for nonionic organic compounds, including nonionic pesticides (Pavlovic et al., 1996; Villa et al., 1999; Celis et al., 2000; Bruna et al., 2006). Nonetheless, to our knowledge, there are no published reports on the applicability of OHTs for the development of pesticide slow release formulations.

The objective of this study was to test the possibility of using OHTs as supports for the development of slow release formulations of pesticides. Two different organic anions, dodecylsulfate (DDS) and sebacate (decanedioic acid anion) (SEB), were incorporated in the interlayers of a Mg/Al HT, as a strategy to increase the affinity of the mineral for the herbicide terbuthylazine. Then, OHT–terbuthylazine complexes were prepared and their ability to slow the release of the herbicide into aqueous solution and to retard the vertical movement of the herbicide through soil, as compared to a standard commercial formulation of the herbicide, was evaluated.

2. Materials and methods

2.1. Organic anions, herbicide and soil

The organic anions used for the preparation of the organohydrotalcites, dodecylsulfate (DDS) and sebacate (SEB), were supplied as soluble sodium salt and acid form, respectively, by Sigma-Aldrich (Spain). The acid form of SEB, i.e. sebacic acid, has a water solubility of 1 g/L (17 °C) and dissociation constants $pK_{a1}=4.6$ and $pK_{a2}=5.6$. Terbuthylazine (N^2-*tert*-butyl-6-chloro-N^4-ethyl-1,3,5-triazine-2,4-diamine) is a *s*-triazine herbicide widely used for selective weed control in citrus, olive, maize, pod forests and vineyards at 1.2–1.8kg/ha (Worthing and Hance, 1991). It has a water solubility of 8.5mg/L and weakly basic character ($pK_a=2.0$) (Worthing and Hance, 1991). Pure analytical terbuthylazine, purity= 99% (Dr. Ehrenstorfer Lab.), was used to prepare the external standards for terbuthylazine analysis, the initial herbicide solutions used in adsorption experiments, and the organohydrotalcite-based formulations of the herbicide. Commercial terbuthylazine (500g/L suspension concentrate, Spicam Inagra S.A., Spain) was used as a reference standard formulation in the release and leaching experiments. The molecular structures of the herbicide and organic anions used are shown in Fig. 1.

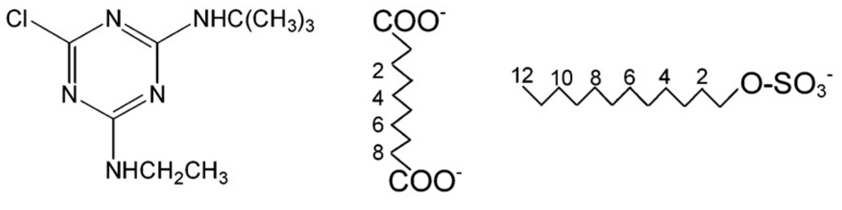
The soil used in the leaching experiments was a Typic Rhodoxeralfs soil from Coria del Río (Sevilla, Spain). The soil was sampled (0–20cm), air-dried, and sieved (2mm) prior to use. It had 73% sand, 7% silt, 20% clay, and 0.94% organic carbon. Soil pH was 8.2 in a 1:2 (w:w) soil:deionized water mixture.

2.2. Synthesis of the organohydrotalcites

Two organohydrotalcites (OHTs), $[Mg_3Al(OH)_8][CH_3(CH_2)_{10}CH_2SO_4]\ nH_2O$ and $[Mg_3Al(OH)_8]_2[OOC–(CH_2)_8–COO]\ nH_2O$ (HT–DDS and HT–SEB, respectively) were obtained by the coprecipitation method (Reichle, 1986), using N_2 atmosphere and CO_2-free water. A solution containing 0.06 mol of $Mg(NO_3)_2\ 6H_2O$ and 0.02 mol of $Al(NO_3)_3\ 9H_2O$ was added to an alkaline solution (0.16 mol of NaOH) containing 0.05 mol of dodecylsulfate (DDS) or sebacate (SEB). The organohydrotalcite suspensions thus obtained were hydrothermally treated at 80 °C for 24 h, and the precipitate washed with CO_2-free, distilled water and dried at 60 °C. For comparison purposes, a carbonate–Mg/Al hydrotalcite ($HT–CO_3$), $[Mg_3Al(OH)_8]_2CO_3\ nH_2O$, was prepared by the coprecipitation method, dropping a solution containing 0.75 mol of $Mg(NO_3)_2\ 6H_2O$ and 0.25 mol of $Al(NO_3)_3\ 9H_2O$ to a solution containing 1.7 mol of NaOH and 0.5 mol of Na_2CO_3. The resultant suspension was submitted to hydrothermal treatment by heating at 80 °C for 24 h, and the precipitate washed with distilled water and dried at 60 °C.

2.3. Adsorption and desorption of terbuthylazine on $HT–CO_3$ and OHTs

Terbuthylazine adsorption isotherms on $HT–CO_3$, HT–DDS, and HT–SEB were obtained by the batch equilibration procedure. Duplicate 20 mg adsorbent samples were equilibrated by shaking for 24 h at room temperature with 8 mL of terbuthylazine solutions with initial herbicide concentrations (C_{ini}) ranging between 0.4 and 26 μM. After equilibration, the suspensions were centrifuged at 5000×*g* for 15 min and 4 mL of the supernatant solution was removed, filtered with glass fiber filters of pore size 0.45 μm, and then analyzed by high performance liquid chromatography (HPLC) as described below. The amount of herbicide



Terbuthylazine Sebacate (SEB) Dodecylsulfate (DDS)

Fig. 1. Molecular structures of terbuthylazine, dodecylsulfate, and sebacate.