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Synthesis and release behavior of bactericides intercalated Mg–Al layered double hydroxides

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ABSTRACT

In this paper, two charge-neutral and poorly water-soluble bactericides (BC), hexaconazole and triadimenol, were first encapsulated in micelles derived from anionic surfactant, calcium dodecylbenzenesulfonate (DBS), and then were successfully intercalated into the gallery of Mg–Al layered double hydroxides (LDHs) by using ion exchange, coprecipitation and reconstruction methods, respectively, to obtain BC–LDHs nanohybrids. The loading amounts of hexaconazole-LDHs nanohybrids are obviously higher than those of triadimenol-LDHs nanohybrids. The release kinetics of bactericides from the nanohybrids was investigated. It was found that the bactericide release kinetic processes of the nanohybrids can be described with pseudo-second-order model. The initial release rates and equilibrium percent releases of the nanohybrids are obviously dependent of synthesis methods. The nanohybrids can well control the release of bactericides, showing they are a potential pesticide controlled-release formulation.

1. Introduction

Hexaconazole and triadimenol, as bactericides extensively used, play an important role in agricultural activities. But there is residue in water and soil, which have made it a serious environmental problem and a primary source of pollution. This problem is exacerbated in the case of highly soluble pesticides because the risk of offsite movement from the intended target area increases as the pesticide is quickly dissolved in the soil solution [1]. Most herbicide formulations in current use deliver the bulk, if not all, of the active ingredient in an immediately available form that is readily released to the environment [2]. One approach to minimize the use of bactericides is to employ an efficient controlled release system. In the controlled-release formulations, the bulk of the herbicide is trapped in an inert formulation matrix, while only a part of the active ingredient is in an immediately available form. The constituents trapped in the controlled-release matrix would be expected to be less subject to environmental losses. A variety of systems have been used to control herbicide release. These include alginate encapsulation [3] and microencapsulation [4,5]. More recently, intense research interests have been paid on pesticide-layered double hydroxides (LDHs) nanohybrids because the nanohybrids may be used as controlled-release formulations (CRFs) of pesticides. Hussein et al. reported that LDHs can be used as a carrier for an active agent and the chemical structure of the intercalated moiety can be used to tune the desired release kinetics of the beneficial agent [6,7]. LDHs also could be used as removal agent of pesticides [8–10]. LDHs are less frequent or rare in nature than cationic clays but relatively inexpensive and simple to synthesize [11].

LDHs, or the so-called hydrotalcite-like compounds (HTlc), are a family of layered inorganic materials with structurally positively charged layers and interlayer balancing anions. LDHs may be represented by the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]\,[A^{n-}]_{x/n}\cdot mH_2O$, where M^{II} is a divalent cation; M^{III} is a trivalent cation, A^{n-} is a gallery anion, x is equal to the ratio $M^{III}/(M^{II}+M^{III})$, and m is the number of moles of co-intercalated water per formula weight of the compound. The interlayer region (or gallery) of LDHs may be considered as a microvessel in which organic molecules may be stored, *i.e.*, some organic molecules may be intercalated into the gallery of LDHs to form organic-HTlc nanohybrids [12-15]. The pesticide-LDHs nanohybrids may evidently inhibit the release of pesticide molecules stored in LDHs, therefore, LDHs may be potentially used in pesticide controlled-release.

Many methods for synthesis of pesticide-LDHs nanohybrids were developed, such as coprecipitation [16], ion exchange [17] and reconstruction [18]. For anionic pesticides, the nanohybrids are usually synthesized simply by above methods, while for charge-neutral and poorly water-soluble pesticides, it is usually needed to modify LDHs with surfactants to form a hydrophobic region in the gallery of HTlc, and then target pesticide molecules are intercalated into the hydrophobic region of HTlc [19,20]. Tyner et al. [14] developed a novel method to synthesize charge-neutral and poorly water-soluble drugs (camptothecin)-LDHs nanohybrids. Camptothecin was first incorporated into micelles derived

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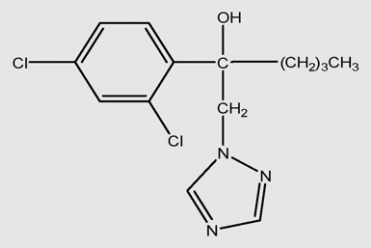
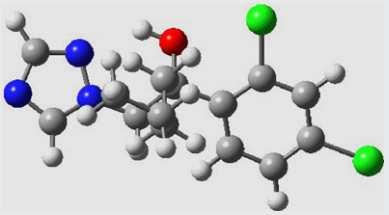
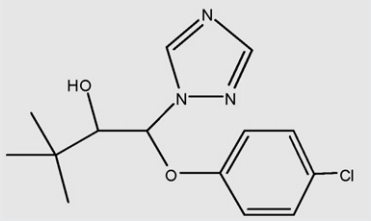
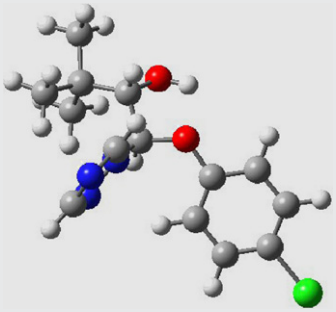
Table 1
Molecular structure of bactericides used.

Bactericides	Molecular structure scheme	Optimized molecular structure
Hexaconazole		
Triadimenol		

from negatively charged surfactants, and the negatively charged micelles were then encapsulated in nanoparticles of Mg–Al LDHs by an ion exchange process. Consulting Tyner's method [14], we synthesized charge-neutral and poorly water-soluble bactericides (hexaconazole and triadimenol)-LDHs nanohybrids in this paper. The charge-neutral and poorly water-soluble bactericides were first incorporated into micelles derived from negatively charged surfactants (dodecylbenzenesulfonic acid calcium), then the negatively charged micelles were intercalated into the gallery of Mg–Al LDHs by ion exchange method (IEM), coprecipitation method (CM) and reconstruction method (RM), respectively. The release behaviors of the obtained BC–LDHs nanohybrids were investigated, showing that the BC–LDHs nanohybrids are a potential controlled-release formulation (CRF) of the pesticide.

2. Materials and methods

2.1. Reagents

Hexaconazole (Adv Tech & Ind, HK) and triadimenol (Huachang, Jiangsu) were used as received without further purification. The molecular structure of bactericides is shown in Table 1.

All other chemical reagents used were A.R. grade.

2.2. Synthesis of micelle containing bactericides

0.244 g of anionic surfactant, calcium dodecylbenzenesulfonate was dispersed in 50 ml water. 20 ml methanol solution containing 0.05 mol bactericide was added to the surfactant mixture and stirred under N_2 at room temperature. After the methanol was evaporated the micelle containing bactericide was obtained as reported by Tyner et al. [14].

2.3. Synthesis of BC–LDHs nanohybrids

The BC–LDHs nanohybrids were synthesized by ion exchange method (IEM), coprecipitation method (CM) and reconstruction method (RM), respectively.

2.3.1. Ion exchange method

The pristine LDHs were prepared by the following procedures [21]. Under a N_2 atmosphere, the mixed solutions containing 1.0×10^{-2} mol/l of $Mg(NO_3)_2$ and 5.0×10^{-3} mol/l of $Al(NO_3)_3$ were prepared. Then the metal ion solution and 2 mol/l NaOH solution were added dropwise to water under vigorous stirring. The final pH value was at 9.5. The precipitate was aged for 72 h in the mother solution at 75 °C under vigorous stirring. Then it was filtered and washed with methanol and deionized water. The filter cakes held in a glass bottle were dried at a constant temperature of 80 °C in an oven for about 24 h to obtain pristine Mg–Al–NO_3 LDHs sample.

1.0 g Mg–Al–NO_3 LDHs was added to 250 ml of an aqueous solution containing 1.5×10^{-2} mol of the bactericide in micelles. The suspension was kept at 75 °C for 72 h under vigorous stirring. The resulting material was filtered and washed with methanol and deionized water. The filter cakes held in a glass bottle were dried at a constant temperature of 80 °C in an oven for about 24 h to obtain BC–LDHs nanohybrids. The obtained BC–LDHs nanohybrid samples were denoted as IEM nanohybrids.

2.3.2. Coprecipitation method

The BC–LDHs nanohybrids were prepared by coprecipitation method (CM) as the same route as pristine LDHs preparation, except that the metal ion solution and NaOH solution were added dropwise to an aqueous solution containing 5.0×10^{-2} mol/l of the bactericide in micelles under vigorous stirring, instead of adding to water. The obtained BC–LDHs nanohybrid samples were denoted as CM nanohybrids.

2.3.3. Reconstruction method

The pristine Mg–Al–CO_3 LDHs sample was synthesized as the same route as pristine Mg–Al–NO_3 LDHs preparation, except substituting 2 mol/l NaOH solution with 0.1 mol/l Na_2CO_3 solution. The Mg–Al–CO_3 LDHs sample was calcined in a muffle furnace at 500 °C for 4 h to obtain calcined-LDHs sample [22].

1.0 g of the calcined LDHs sample was added to 250 ml of aqueous solution containing bactericide micelle, and the suspension was kept under vigorous stirring at 75 °C for 72 h. The resulting