



Research paper

Effects of organobentonites on imidacloprid release from alginate-based formulation



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ABSTRACT

To provide effective delay in release, organobentonites with different loading levels of dodecyltrimethylammonium chloride (DTMA) and hexadecyltrimethylammonium chloride (HTMA) were used as modifying agents in the alginate-based controlled release formulation (CRF) containing imidacloprid. The structure of organobentonites was characterized by FTIR and XRD, and adsorption toward imidacloprid was investigated. The results were utilized to reveal the effects of organobentonites on the release of imidacloprid as well as its mechanism, and to evaluate the potential use of organobentonites to modulate the release of imidacloprid. The results showed that organobentonites could reduce the release of imidacloprid from alginate-based granules, different from the natural bentonite that accelerated the release of imidacloprid. The time taken for 50% of the active ingredient to be released, T_{50} , for CRF incorporating organobentonites with DTMA at loading level of 50, 75, 100 and 125% of the clay's cation exchange capacity was 2.12, 1.59, 1.55 and 1.38 times of the value for the formulation without modifying agent, respectively. The values for those incorporating organobentonites with HTMA at the same loading level were 2.61, 2.20, 1.89 and 1.88 times. It was suggested that imidacloprid released via an anomalous transport kinetics predominated by Fickian diffusion and was influenced by the addition of bentonite and organobentonites due to the change of matrix permeability and the interaction with organobentonites. The enhancement of matrix permeability and imidacloprid release resulting from the addition of natural bentonite might be attributed to the lamellar structure and swellability of bentonite in water. In contrast, the matrix permeability and imidacloprid release decreased when organobentonites were used as modifier agents, as a consequence of the hydrophobicity of organobentonite. The results also suggested the feasibility of regulating imidacloprid release via controlling the structure of the organobentonites. An increase in loading level of quaternary ammonium ions could result in an enhancement of the release, while the extension of the alkyl chain slowed down the release of imidacloprid.

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1. Introduction

In the past decade, the use of neonicotinoids has been increasing faster than other insecticides such as carbamates, organophosphates and pyrethroids, mainly due to their excellent plant systemic activity coupled with the reduced effectiveness of other neuroactive insecticides. Imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitro-imidazolidin-2-ylideneamine] (the chemical structure is shown in Fig. S1 in the Supplementary data), the first member of neonicotinoids that has been commercially introduced to the market in 1991 by Bayer AG and Nihon Tokushu Noyaku Seizo KK, is used worldwide as an agricultural insecticide to control sucking and mining pests and as a flea control agent for domestic pets. Imidacloprid is a systemic insecticide used for seed treatment, soil and foliar applications, acting on the target species through ingestion or direct contact and blocking the nicotinic neuronal pathway (Matsuda et al., 2001; Tomizawa and Casida, 2005).

As nicotinic receptors are more abundant in insects than in warmblooded animals, neonicotinoids exhibit selective toxicity toward insects (Tomizawa and Casida, 2005). It is now considered as a possible replacement for the insecticides that are in the process of phased revocation (US EPA, 2004). However, the relatively high solubility and stability in water make imidacloprid a potential contaminant of surface and ground waters through drift, dissolved runoff or leaching (Gupta et al., 2002; Fossen, 2006; CCME, 2007; Jemec et al., 2007). It is increasingly found in aquatic systems, causing great concerns about its impact on the environment and humans. Recent studies have confirmed the toxicity effects of imidacloprid and its transformation products to non-target aquatic organisms, including invertebrate, crustacean, algae and fish (Pestana et al., 2009; Tişler et al., 2009; Chen et al., 2010; Hayasaka et al., 2012; Malev et al., 2012; Mohra et al., 2012).

The use of controlled release formulation (CRF) is one of the best strategies to reduce the use and the impact of pesticides on the environment. To date, many types of CRF of pesticides have been proposed, of which dispersion or dissolution of the active ingredient in a polymeric matrix is one of the most important technologies. Natural polymers

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like starch, neem, cellulose and alginate have been used as matrices for CRF due to their biodegradability (Li et al., 2009; Singh et al., 2009, 2010). Nevertheless, such a type of CRF often fails to reduce the release of small molecules of high solubility. Additional sorbents have been suggested to be incorporated in the formulation to provide effective delay in release. Using natural bentonite and activated carbon as modifying agents, the group of Pérez prepared alginate-based CRFs that exhibited a better encapsulation and reduction in the release rate of imidacloprid, isoproturon and cyromazine (Pérez et al., 2005; Herrera et al., 2006; Cespedes et al., 2007).

Bentonite is a natural material containing montmorillonite as a major constituent and has been considered as a potential sorbent for many chemicals due to the high specific surface area (Jiang and Zhang, 2005). Bentonite has been used in CRFs of pesticides to reduce the leaching of active ingredients in soils (Pradas et al., 1999a, 1999b). However, the intrinsic hydrophilicity of bentonite makes it an ineffective sorbent for organic molecules, setting great limits to the application of bentonite in CRFs. Actually, it is not the bentonite, but the activated carbon that plays a key role in the improved controlled release of active ingredients from alginate-based granules proposed by the group of Pérez (Pérez et al., 2005; Herrera et al., 2006; Cespedes et al., 2007).

Modification of bentonite with organic cation surfactants is a useful method to improve the adsorption capacity toward hydrocarbon organics (Mishael et al., 2003; Polubesova et al., 2003; Cornejo et al., 2008; Rytwo et al., 2008). In previous work, organobentonites prepared by modification with quaternary ammonium ions were used as carrier of phoxim to obtain CR granule (Huang et al., 2013). The results indicated that organobentonites were excellent sorbents toward phoxim and greatly reduced the release of phoxim in comparison to the formulation with natural bentonite. Also, the release of phoxim could be regulated via controlling the structure of the organobentonites. As an extension of the previous work, an attempt was made to evaluate the potential use of organobentonites to control the release of pesticide from CRFs based on a polymeric matrix. Organobentonites, loaded with dodecyl trimethyl ammonium chloride (DTMA) and hexadecyl trimethyl ammonium chloride (HTMA), were used as modifying agents in alginate-based granules of imidacloprid and the effects on the release of imidacloprid were evaluated. The adsorption capacity toward imidacloprid and the structure of organobentonites were also investigated, with the purpose to get a better insight into the mechanism of organobentonites acting on the release of pesticide from the CRF studied.

2. Experimental

2.1. Materials

The Ca-bentonite, of which the cation exchange capacity (CEC) was 0.82 mmol g^{-1} clay, was obtained from Guangxi Ninming Minerals Co. (China). Analytical grade DTMA, HTMA and disodium ethylenediamine tetraacetic acid (EDTA) from Sinopharm Chemical Reagent Ltd. (China) and chemical pure sodium alginate from Shantou Xilong Chemical Co. (China) were used as received. Technical grade imidacloprid was kindly supplied by Guangxi Tianyuan Biochemical Ltd. (China).

2.2. Methods

2.2.1. Preparation and characterization of organobentonite

Following the procedure described by Huang et al. (2013), aqueous dispersions of 2 wt.% of bentonite were mixed with DTMA and HTMA of the amount equivalent to 0.5 to 1.25 times the clay's CEC and kept at $25 \pm 1 \text{ }^\circ\text{C}$ in an overhead shaker for 24 h. The dispersions were then separated by vacuum filtration. Resulting organobentonites were dried to a weight constant at about $45 \text{ }^\circ\text{C}$, ground in an agate mortar and sifted through a $48 \text{ }\mu\text{m}$ mesh sieve. Total carbon content of

organobentonites was determined on a PE2400II elemental analyzer (PerkinElmer).

FTIR measurements were conducted from 400 to 4000 cm^{-1} with an accumulation of 20 scans and a resolution of 4 cm^{-1} on a Shimadzu FTIR-8400S Fourier transform infrared spectrometer in transmission mode. Samples of organobentonites were ground with KBr at a weight ratio about 2:100 and compressed into a pellet, before the analysis.

Samples of organobentonites were pressed in glass sample holders and XRD patterns were recorded on a Rigaku D/Max-2500 V diffractometer. The Ni-filtered Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) was used as X-ray source at 40 kV and 200 mA with 0.5° divergence slit, 0.5° antiscatter slit and 0.15 mm receiving slit. All scans were performed in the range of $2\theta = 2\text{--}30^\circ$ at a speed of 4° min^{-1} , with a step size of 0.02° .

In the following text, the organobentonites modified with DTMA and HTMA are denoted as DTMA- and HTMA-bentonite, respectively, and labeled as BD $_x$ and BH $_x$, whereas the number x is the quantity of DTMA (D) and HTMA (H) used and presented as the fraction of the clay's CEC.

2.2.2. HPLC analysis of imidacloprid

Solutions containing imidacloprid were passed through nylon filters of $0.22 \text{ }\mu\text{m}$ pore diameter and then analyzed by HPLC (Agilent 1100) equipped with a UV-vis detector set at 254 nm . The column was a LiChrospher 100 RP-18 ($5 \text{ }\mu\text{m}$), and the mobile phase was a methanol/water mixture (90:10) at a flow rate of 1.0 mL min^{-1} .

2.2.3. Kinetics of imidacloprid adsorption on organobentonite

Kinetic studies were performed to obtain the optimal conditions for imidacloprid adsorption on organobentonite. 0.2 g samples of organobentonites were weighed into 50 mL centrifuge tubes, dispersed in 25 mL aqueous solution of imidacloprid with concentration of $300 \text{ }\mu\text{g mL}^{-1}$, and kept at $25 \pm 1 \text{ }^\circ\text{C}$ in an overhead shaker. At preset time intervals, duplicate samples were collected and centrifuged at 3500 rpm on a Xiangyi L-50 centrifuge (Hunan Xiangyi Centrifuge Co., China) for 10 min . The supernatants were analyzed by HPLC to determine the amount of imidacloprid adsorbed.

2.2.4. Adsorption isotherms of imidacloprid on organobentonites

Adsorption experiments of imidacloprid were carried out using a batch equilibration technique. Duplicate 0.2 g samples of organobentonites were weighed into 50 mL centrifuge tubes and combined with 25 mL aqueous solution of imidacloprid with concentration ranging from 10 to $300 \text{ }\mu\text{g mL}^{-1}$. The dispersions were kept at $25 \pm 1 \text{ }^\circ\text{C}$ in an overhead shaker. After equilibration, the dispersions were centrifuged at 3500 rpm on a Xiangyi L-50 centrifuge for 10 min . The supernatants were analyzed by HPLC to determine the equilibrium concentrations of imidacloprid, while the adsorbed amounts were obtained from the difference between initial and final solute concentrations.

2.2.5. Preparation of CRFs

The CRFs containing imidacloprid were prepared following a common procedure (Pérez et al., 2005; Herrera et al., 2006; Cespedes et al., 2007). In brief, different amounts of imidacloprid (I), sodium alginate (A), bentonite (B) or organobentonite (BD $_x$ or BH $_x$) were made up in 50 mL water (the formulations are shown in Table S1 in the Supplementary data) and stirred slowly to form homogenous mixtures. The mixtures were added dropwise, by using a 50 mL syringe (needle size 1.2 mm), into 150 mL 0.1 M CaCl $_2$ solution under constant stirring, in about 10 min . The resulting beads were allowed to gel for 30 min , filtered and then dried to a constant weight at about $45 \text{ }^\circ\text{C}$. The average weight and diameter of the dry granules were determined using a METTLER AE200 balance and a micrometer from Guilin Measuring Instrument Co. (China), respectively. The products obtained were labeled as IA, IAB, IABD $_x$ and IABH $_x$.

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