



## Research paper

## Controlled release of phoxim from organobentonite based formulation

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## ABSTRACT

Organobentonite, prepared by employing dodecyl trimethyl ammonium chloride (DTMAC) and hexadecyl trimethyl ammonium chloride (HTMAC) as modifying agents, was used as carrier of phoxim to obtain controlled release granule. The structure of organobentonite was investigated by XRD, and utilized to reveal the effects on the sorption and release of phoxim. The results indicated that organobentonite was an excellent sorbent towards phoxim and greatly reduced the release of phoxim. It was found that the sorbed quaternary ammonium aggregates together to form organic phase in bentonite interlayer to accommodate the pesticide molecules. The average loading percentages for organobentonite modified with DTMAC and HTMAC at the loading level of 50, 100 and 150% of the clay's cation exchange capacity were 70.8, 75.3, 71.0% and 91.8, 93.9, 90.3%, and the time taken for 50% of phoxim to be release,  $T_{50}$ , for the CRF based on the organobentonites was 3.7, 11.8, 10.7 times and 3.4, 10.4, 8.2 times of the value for the formulation without organobentonite, respectively. An enhancement of the release of phoxim could be achieved by increasing the carbon chain of quaternary ammonium. The results also showed that an increase of quaternary ammonium loading via electrostatic interaction significantly slowed down the release of phoxim, whereas that via hydrophobic interaction showed little effect. The results suggested the feasibility of regulating the release of phoxim via controlling the structure of organobentonite.

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## 1. Introduction

Organophosphorus pesticides are major alternatives to organochlorine for pest control in agriculture since 1980's. At present, more than 70% of the total 1.7 million tons pesticides production in China is an organophosphorus one (Jin et al., 2010). Phoxim, an organophosphorus pesticide with relatively high efficiency and low toxicity, is frequently employed in soil and foliage, and also as a seed dressing to control unwanted insects and underground pests worldwide and up to 1000 tons phoxim is applied in China per year (Jin et al., 2010; Ni et al., 2007). As a result of wide applications, it is one of the frequently detected pesticides in agriculture effluent and river water, causing concerns about its impact on the environment and humans (Liang et al., 2005; Lin et al., 2011). In southern China, phoxim is applied to control underground pests in fields of sugar cane. Owing to the feature of the plant of sugar cane, pesticides are commonly used once per year. However, as a consequence of hydrolysis and photodegradation, a large amount of phoxim is required to maintain efficacy, bringing up a great risk to the environment and human health.

The use of controlled release formulations (CRFs) is one of the best strategies to reduce the use and impact of pesticides in the environment. CRFs make a gradual and controlled release of the pesticide over time, which allows a lower, but enough concentration of active ingredients against the pest. This fact also reduces losses by evaporation

and filtration of the active ingredient that does not reach the target and diminish the intrinsic risk and those derived from the application by farmers (Guo, 2004). To date, many types of CRFs have been proposed by using natural or synthetic polymer as matrix. However, the higher cost compared with the conventional formulation hinders its widespread application. It is of special interest to develop CRFs with a matrix of relatively low cost, such as clay minerals.

Bentonite is a natural silicate mineral with a lamellar structure containing montmorillonite as a major constituent and is considered as a potential sorbent or carrier for many chemicals due to the high specific surface area. Bentonite has been used in CRFs of pesticides and herbicides, and succeeds in reducing the leaching of active ingredients in soil (Cornejo et al., 2008; Mishael et al., 2003; Polubesova et al., 2001, 2003; Rytwo et al., 2005, 2008). However, the intrinsic hydrophilicity of bentonite makes it an ineffective sorbent for hydrophobic organic molecules. In most cases, bentonite is taken as the additive of polymer-based CRF (Fernandez-Perez et al., 1999, 2005; Flores-Céspedes et al., 2007; Gonzalez-Pradas et al., 1999; Li et al., 2009; Singh et al., 2009, 2010; Villafranca-Sanchez et al., 2000).

In this work, organobentonite, prepared by employing dodecyl trimethyl ammonium chloride (DTMAC) and hexadecyl trimethyl ammonium chloride (HTMAC) as modifying agents, was used as carrier of phoxim and blended with kaolin, a common inert filler in agricultural chemical industry, to obtain controlled release granule and the release behavior of phoxim was studied in water. The structure of organobentonite was investigated by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) and was utilized to reveal the influence on the

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sorption and the release of phoxim. The primary focus of this study was to determine the feasibility of controlling phoxim release kinetics via regulating the structural property of bentonite.

## 2. Experimental

### 2.1. Materials

The Ca-Bentonite used was obtained from Guangxi Ninning Minerals Co. (China). The cation exchange capacity (CEC) was  $0.82 \text{ mmol} \cdot \text{g}^{-1}$  clay. Methanol (AR, Shantou Xilong Chemical Co., China), DTMAC (AR, Shanghai Chemical Regent Co., China Medicine Group), HTMAC (AR, Shanghai Chemical regent Co., China Medicine Group) and Kaolin (Shanghai Chemical regent Co., China Medicine Group) were used as received. Technical grade phoxim (The chemical structure is showed in Fig. 1.) was kindly supplied by Guangxi Tianyuan Biochemical Co. (China). Stock solution of phoxim ( $0.5 \text{ g} \cdot \text{mL}^{-1}$ ) was prepared by dissolving technical grade phoxim into methanol and stored at  $0\text{--}5 \text{ }^\circ\text{C}$ . Deionized water was used throughout the experiment.

### 2.2. Methods

#### 2.2.1. Sorption of quaternary ammonium

Batch experiments were used to determine the equilibrium sorption of DTMAC and HTMAC on bentonite. Aqueous dispersions of 2% bentonite content were mixed with DTMAC and HTMAC of the amount ranging from 0 to 2 times of the clay's CEC and kept at  $25 \pm 1 \text{ }^\circ\text{C}$  in an overhead shaker for 24 h (Xu and Zhu, 2009). The dispersions were then centrifuged at  $3000 \times g$  for 30 min and the residual surfactant in supernatants was analyzed with TOC analyzer, to determine the amount of DTMAC and HTMAC sorbed.

In the following text, the organobentonites modified with DTMAC and HTMAC were denoted as DTMA- and HTMA-bentonite, respectively, and labeled as  $\text{BD}_x$  and  $\text{BH}_x$ , whereas the number  $x$  is the quantity of DTMAC (D) and HTMAC (H) used and presented as the times of the clay's CEC. Similarly, organobentonites incorporating phoxim (P) were labeled as  $\text{BD}_x\text{P}_y$  and  $\text{BH}_x\text{P}_y$ , and the organobentonite-based granules with kaolin (K) were labeled as  $\text{BD}_x\text{P}_y\text{K}$  and  $\text{BH}_x\text{P}_y\text{K}$ . For the convenience, the number  $y$  is presented as the weight ratio of phoxim to bentonite used in the preparation procedure, instead of the actual quantity of phoxim loading on organobentonite.

#### 2.2.2. Kinetics of phoxim sorption on organobentonite

Following the procedure described in Subsection 2.2.1, organobentonite  $\text{BD}_{1.0}$  and  $\text{BH}_{1.0}$ , prepared from 5 g raw bentonite, were dispersed again into 250 mL water and 10 mL phoxim stock solution (containing 5.0 g a. i.) was added under stirring at  $25 \pm 1 \text{ }^\circ\text{C}$ . At preset time intervals, 10 mL dispersion was removed and filtered under vacuum immediately. The organobentonite incorporating phoxim was washed with 50 mL water for 4 times and extracted by 25 mL methanol for 4 times. The extract was analyzed by HPLC to evaluate the amount of phoxim sorbed on organobentonite. The experiment was run in duplicate.

#### 2.2.3. HPLC analysis of phoxim

For analysis, resulting extracts were passed through nylon filters of  $0.22 \text{ } \mu\text{m}$  pore diameter. Phoxim was 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  $1.0 \text{ mL} \cdot \text{min}^{-1}$ .

#### 2.2.4. Phoxim sorption on organobentonite

Phoxim sorption on organobentonite was investigated by batch experiment. Briefly, the organobentonite samples  $\text{BD}_{0.5}$ ,  $\text{BD}_{1.0}$ ,  $\text{BD}_{1.5}$ ,  $\text{BH}_{0.5}$ ,  $\text{BH}_{1.0}$ , and  $\text{BH}_{1.5}$ , prepared from 0.2 g raw bentonite, were dispersed again into 25 mL water and phoxim stock solutions of the amount required were added. The dispersions were kept at  $25 \pm 1 \text{ }^\circ\text{C}$  in an overhead shaker for 4 h, and then filtered under vacuum immediately. The organobentonite incorporating phoxim was washed with 50 mL water for 4 times to remove the phoxim on the surface of the organobentonite particle and then extracted by 25 mL methanol for 4 times. The extract was analyzed by HPLC to evaluate the amount of phoxim sorbed on organobentonite.

#### 2.2.5. FTIR measurement

FTIR measurements were conducted with an accumulation of 20 scans and a resolution of  $4 \text{ cm}^{-1}$  on a Shimadzu FTIR-8400S Fourier transform infrared spectrometer by the method of transmission. The samples of bentonite and organobentonite were dried at  $45 \text{ }^\circ\text{C}$ , ground with KBr at a weight ratio about 2:100 and compressed into a pellet, before the performance.

#### 2.2.6. XRD measurement

XRD patterns of bentonite, organobentonite and that incorporating phoxim were recorded on a Rigaku D/Max-2500V diffractometer by the method of reflection. The Ni-filtered  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) was used as X-ray source at 40 kV and 200 mA. All scans were performed in the range of  $2\theta = 2\text{--}30^\circ$  at a speed of  $4^\circ \cdot \text{min}^{-1}$ , with a step size of  $0.02^\circ$ . The samples were dried at  $45 \text{ }^\circ\text{C}$ , ground in an agate motor and sifted through a  $48 \text{ } \mu\text{m}$  mesh sieve, before the measurement.

#### 2.2.7. Preparation of organobentonite-based phoxim granules

Organobentonite samples  $\text{BD}_{0.5}$ ,  $\text{BD}_{1.0}$ ,  $\text{BD}_{1.5}$ ,  $\text{BH}_{0.5}$ ,  $\text{BH}_{1.0}$ , and  $\text{BH}_{1.5}$ , prepared from 5 g raw bentonite, were dispersed again into 250 mL water and 10 mL phoxim stock solution (ca 5.0 g a. i.) was added. The dispersions were kept at  $25 \pm 1 \text{ }^\circ\text{C}$  under stirring for 4 h, separated by vacuum filtration and washed with 625 mL water for 4 times. Resulting organobentonite incorporating phoxim was sampled and dried to weight constant at  $45 \text{ }^\circ\text{C}$ . The water content was determined by weight and phoxim content by HPLC following an extraction procedure.

Organobentonites incorporating phoxim were blended with kaolin and water of the amount predetermined and turned into grain by an extrusion granulating method. After drying at  $45 \text{ }^\circ\text{C}$  to weight constant, organobentonite-based granules containing ca. 10% phoxim were obtained. A conventional formulation granule, taken as a control, was prepared by mixing phoxim with kaolin and water, using a similar procedure.

#### 2.2.8. Phoxim release in water

The investigation of phoxim release from granules into water was carried out in a thermostatic bath with continuous water supply at a flow rate of  $50 \text{ mL} \cdot \text{min}^{-1}$ . Accurately weighted quantities of granules containing 50 mg a. i. for each sample were sealed in small packages made of filter cloth of the pore size  $38 \text{ } \mu\text{m}$  and immersed in water at  $25 \pm 1 \text{ }^\circ\text{C}$ . At preset time intervals, 3 samples were collected and analyzed for phoxim residual by HPLC following an extraction procedure. The amount of released pesticide from each sample was evaluated and divided by the total amount to obtain cumulative release value.

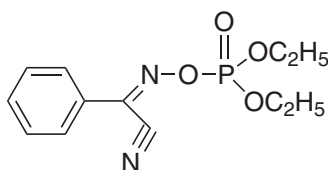


Fig. 1. Chemical structure of phoxim.

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