

Controlled Release of Herbicide Acetochlor from Clay/Carboxymethylcellulose Gel Formulations

JIANFA LI, YIMIN LI,* AND HUAPING DONG

Department of Chemistry, Shaoxing University, Zhejiang, 312000, P. R. China

Controlled-release formulations of the herbicide acetochlor were prepared by using carboxymethylcellulose (CMC) gel and different types of clay, which were obtained by acid activation, pillared with metal hydroxides, or saturated with organic cations. The effect of formulation parameters (amount and type of clay used, cross-linking time, and drying of the hydrogel formulations) on the acetochlor release rate from different formulations was evaluated by water-release studies. The time taken for 50% of acetochlor to be released, t_{50} , showed a wide variation (151–522 h) for dried gel formulations, the largest value corresponding to the formulation incorporating aluminum hydroxide pillared clay into CMC gels. The release rate of acetochlor from clay/CMC hydrogel formulations decreased with the increase of the hydrogels' cross-linking time (t_{50} values ranged from 2.18 to 14.0 h for cross-linking times ranging from 2.0 to 120 min). The performance of inorganic clays in dried gel formulations on slowing the release of acetochlor is related to their sorption capacities, but the addition of organic clay did not lead to the slowest release despite its highest sorption capacity. According to the parameters of an empirical equation used to fit herbicide-release data, the release of acetochlor from clay/CMC gel formulations is controlled by diffusion mechanism.

KEYWORDS: Acetochlor; controlled release; clay; carboxymethylcellulose; gel

INTRODUCTION

Acetochlor (2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide) is a herbicide that inhibits the protein synthesis of weeds in cropland. This herbicide is widely used in China and many other countries. Its use in China exceeds 10 000 tons per year (1). Acetochlor is considered as a herbicide with a high-leaching potential (2), and it is easily transported into water bodies (3). Studies have shown that acetochlor could lead to the reduction of fertility (4) and increase the occurrence of nasal adenomas in rats, although such acetochlor-induced nasal tumors in rats do not represent a hazard for humans (5). Recent studies indicated that acetochlor had potential toxicity to nontarget organisms in the field; it could influence the growth and reproduction of earthworms (6) and cause a dose-related increase in oxidative stress and DNA damage on tadpoles (7). Therefore, the development of controlled-release formulations (CRFs) of acetochlor could be very useful and advantageous for commercial formulations, because CRFs can provide an improvement in safety to the user and nontarget organisms and a reduction of the herbicide application rates and leaching in soils (8–10).

Clay minerals have high specific surface areas associated with their small particle size. Through surface modification with inorganic or organic cations, the derivatives are excellent sorbents for many organic compounds, including some toxic

or environmentally hazardous herbicides such as atrazine (11), chloridazon (12), alachlor (13), and so forth. In recent years, there has been much interest in using such clay sorbents to control the release of herbicides in water. For example, the hexazinone formulations based on inorganic or organic montmorillonites displayed slow-release properties in water and soil/water suspensions (14). The organically modified clays could also reduce the leaching of norflurazon (15) and were used for the controlled release of herbicide fenuron (16). Adsorption of metolachlor on bentonites and their pillared forms also provided the possibility to develop slow-release formulations (17).

Natural polymers are easily degradable and plentiful in resource, and they are considered as good carriers for the controlled release of herbicides. For example, early reports showed that starch xanthate was an effective substance for encapsulating agrochemicals (18–20), and alginate gels have been reported as matrices for the controlled release of herbicides over the past two decades (21–23). The cellulose derivative ethylcellulose was used to encapsulate norflurazon for its controlled release (10). Carboxymethylcellulose (CMC), another cellulose derivative containing many carboxyl and hydroxyl groups in its macromolecules, can be easily gelled in solutions of multivalent cations, such as aluminum or iron cations, to produce hydrogels, which have also been used to prepare CRFs of pesticides (24, 25) and fertilizers (26). These natural polymers or their derivatives can be easily processed into granular forms, which are much safer and easier to handle in agricultural operation than the powder form of clay-based formulations. By

* To whom correspondence should be addressed. Tel: +86 575 8834 2811. Fax: +86 575 8834 2911. E-mail: liym@zscas.edu.cn.

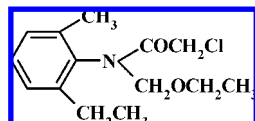


Figure 1. Chemical structure of acetochlor.

adding clays or their modified forms into the alginate matrices, one can make use of both the gelation property of alginate and the sorption capacity of clays. This also provides a practical choice as carriers for the controlled release of herbicides (9, 27, 28).

The present work is aimed to develop CRFs of acetochlor by using clay/CMC gel formulations. For this purpose, the effect of some preparation conditions (cross-linking time, type and amount of clay used, and drying of the hydrogels) on the controlled release of acetochlor into water was evaluated. In addition, the kinetics of the herbicide release has been studied and related to the sorption capacities of the clays employed, which were obtained by modifications of a Na^+ -saturated bentonite from China. The organic derivatives of this clay have been used to remove organic pollutants from water (29), which makes its inclusion in these formulations more attractive.

MATERIALS AND METHODS

Materials. The raw clay used in this study was Na^+ -saturated bentonite (Na-clay) from Zhejiang, China. Its cation-exchange capacity (CEC) was determined to be $55.3 \pm 0.2 \text{ cmol} \cdot \text{kg}^{-1}$. Food-grade sodium CMC was obtained from Suzhou Weiyi Chemicals of China. Its 2% (w/w) solution in water has a viscosity of $750 \pm 50 \text{ mPa} \cdot \text{s}$ at 25°C , and its content of sodium is $9.23 \pm 0.15\%$ (w/w). Technical grade herbicide acetochlor (96.2%) and a commercial formulation of emulsible acetochlor oil (50%) were purchased from Hangzhou Qingfeng Agrochemicals Co. Ltd., China. Figure 1 shows the chemical structure of this compound. Cetyltrimethylammonium bromide (CTAB) and other reagents used in clay modifications were all of analytical grade. HPLC-grade acetonitrile was purchased from Merck, and pure water was obtained by using a Milli-Q system.

Preparation of Modified Clays. Acid-activated clay (Su-clay) was prepared by heating 10 g of Na-clay in 30 mL of a 2.0 M H_2SO_4 solution at 80°C for 2 h. Then, the acid-activated sample was washed, centrifugally separated, and dried at 70°C to constant weight (8.9 g). Pillared clay with aluminum hydroxide (Al-clay) was prepared by making a Na-clay suspension of 10 g in 500 mL of distilled water. This step was followed by dropwise addition of 1000 mL of a 0.1 M solution of aluminum hydroxide, which was prepared by dropwise addition of a NaOH solution into a solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ until a $[\text{OH}^-]/[\text{Al}^{3+}]$ molar ratio of 2.2 was obtained. The resulting suspension was heated at 70°C for 48 h, and the modified clay was washed, separated, and dried at 70°C to constant weight (9.6 g). Pillared clay with iron hydroxide (Fe-clay) was prepared with a similar procedure, except that the 0.2 M solution of iron hydroxide was prepared by mixing a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a Na_2CO_3 solution at a $[\text{CO}_3^{2-}]/[\text{Fe}^{3+}]$ molar ratio of 1.

Organic derivative (Cta-clay) was prepared by adding 2.02 g of CTAB to a 1% (w/w) aqueous suspension of 10 g of Na-clay under continuous stirring for 1.5 h at 70°C . For this purpose, the molar amount of CTAB added was equal to the CEC of raw clay. Finally, the suspension was centrifuged, and the solid sample was washed and dried at 70°C to constant weight (10.5 g).

All clay samples were mechanically ground to less than 100 mesh and heated at 115°C for 2 h before use. The Brunauer–Emmett–Teller (BET) surface areas were obtained from nitrogen adsorption data at 77 K in an accelerated surface area and porosimetry system, ASAP 2020 (Micromeritics). The clay samples were degassed at 115°C for 4 h under vacuum prior to adsorption. The pH of the samples was determined in a 1:2.5 (w/w) clay/water suspension by using a glass electrode (27). The organic carbon content of the samples was chemically determined by using an oxidation method with potassium dichromate (29).

Table 1. Composition of Suspensions Used for Preparing Clay/CMC Gel Formulations

sample	clay type	CMC ^a (%)	clay ^a (%)	herbicide ^{a,b} (%)
FN0	Na-clay	3.0	0	1.65(0.03)
FN1	Na-clay	3.0	1.0	2.01(0.01)
FN2	Na-clay	3.0	2.0	2.00(0.02)
FN3	Na-clay	2.0	3.0	1.96(0.03)
FF2	Fe-clay	3.0	2.0	2.02(0.05)
FS2	Su-clay	3.0	2.0	2.01(0.00)
FL2	Al-clay	3.0	2.0	1.98(0.02)
FC2	Cta-clay	3.0	2.0	2.02(0.03)

^a Percentage (by weight) of components added in water suspensions to prepare the gel beads (the balance is water). ^b Values in parentheses represent the standard deviation of triplicates.

Sorption Studies. As in previous reports (14, 28), the sorption isotherms were determined by batch equilibration of 0.2 g of each clay sample with 50 mL of aqueous solutions of acetochlor of varied initial concentrations, C_0 ($15\text{--}160 \text{ mg} \cdot \text{L}^{-1}$). Experiments were carried out in a thermostatic shaker bath at $25 \pm 0.1^\circ\text{C}$ for 24 h. Preliminary experiments were conducted for various time intervals to determine when sorption equilibrium was reached. The sorption equilibrium time required for acetochlor was less than 24 h.

After equilibration, the suspension was centrifuged, the supernatant was filtered, and the herbicide concentration in the supernatant (C_e) was measured on an Agilent 1100 HPLC system equipped with an ultraviolet detector and a HP Hypersil C18 column ($150 \text{ mm} \times 4.6 \text{ mm}$ i.d., particle size $5\mu\text{m}$). The mobile phase used was an acetonitrile–water mixture (70:30), and the acetochlor was analyzed at 225 nm. The retention time of acetochlor was 4.9 min when the flow rate of the mobile phase was kept at $1.0 \text{ mL} \cdot \text{min}^{-1}$. The amount of acetochlor in solution was calculated with the peak area, and the detection limit for the acetochlor estimation was $0.2 \mu\text{g} \cdot \text{mL}^{-1}$.

The amount sorbed (Q_e) was calculated from the difference in concentration between the initial and the final or equilibrium solutions. Blanks without acetochlor and triplicates of each sorption point were used for each series of experiments.

Preparation and Characterization of Clay/CMC Gel Formulations. The clay sample, acetochlor, and CMC were added one by one into water and vigorously mixed into a viscous suspension. The composition of the suspensions used for preparing the various formulations is presented in Table 1. The mixed suspension was added dropwise into a 100 mL gellant bath of a 0.08 M $\text{Fe}(\text{NO}_3)_3$ solution ($\text{pH} = 1.64$) with a 5 mL injector. The hydrogel beads were obtained at various cross-linking times (2.0, 10, 30, and 120 min) and directly used in release experiments as indicated in the text. In order to obtain the dried gels, the hydrogel beads were dried in an oven (40°C) to constant weight.

In order to characterize the gel formulations, the encapsulation efficiency, size, weight, and swelling ratio were determined. The encapsulation efficiency was calculated with the following formula: encapsulation efficiency (%) = (amount of acetochlor in gel formulations/total amount added in suspensions) $\times 100$. The amount of acetochlor encapsulated in the gel formulations (M_0) was measured with an extraction procedure. The gel samples were extracted with a methanol–water mixture (80:20) more than three times until no residual acetochlor was detected, and the acetochlor concentration in the total extractive solution was determined by HPLC as mentioned above. The swelling ratio of the dried gels was measured by a conventional gravimetric procedure (23, 26). The preweighed dry sample (W_1) was immersed in distilled water, and the swollen gels were taken out at predetermined time intervals, pressed gently in between two filter papers, and weighed on an analytical balance (W_2). The swelling ratio was calculated as W_2/W_1 . The characterization data and swelling kinetics were obtained in triplicate.

Water Release Studies. The release of acetochlor from gel formulations was monitored in water as described in previous reports from other authors (14, 27, 28).

The hydrogel formulations containing about 10 mg of acetochlor (active ingredient) were added to distilled water (300 mL) in stoppered

Table 2. Characteristics of Clays

	clay type				
	Na-clay	Fe-clay	Su-clay	Al-clay	Cta-clay
surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	15.2	29.8	30.5	32.6	12.0
organic carbon content (%)	0.08	0	0	0	10.5
pH in water suspension	10.59	5.05	3.20	4.56	9.72

conical flasks. Experiments were carried out in a thermostatic shaker bath at 25 ± 0.1 °C. At selected time intervals (20 min, 1, 3, 6, 12, 24, 48, 72, 96, 120, 144, and 168 h) after herbicide application, a solution of 1.0 mL was sampled with an injector, and the acetochlor content in the sample solution was determined by HPLC as mentioned above. The sample solution was replaced with distilled water to keep the volume of the release system constant. The cumulative amount of acetochlor released at different time interval (M_t) was calculated according to the acetochlor concentrations in the various sample solutions.

The release experiments for dried gel formulations were similar to those for hydrogels. The sampling occurred at selected time intervals (1, 6, 24, 48, 72, 120, 192, 240, 312, 384, 480, 576, 672, 768, 864, and 960 h) after herbicide application. After the 240 h sampling, all the water was replaced with fresh water immediately after each sampling operation to minimize the influence of possible acetochlor degradation.

M_0 was calculated according to the sample content of same formulation, which was measured by the extraction procedure mentioned above. The cumulative percentage of acetochlor released at different times was calculated as $(M_t/M_0) \times 100$. For each gel formulation, the acetochlor release kinetics was obtained in triplicate.

RESULTS AND DISCUSSION

Surface Areas and Organic Carbon Content of Clays. The analytical results of raw clay and its modified derivatives are shown in **Table 2**. The inorganic derivatives (Fe-clay, Su-clay, and Al-clay) have distinctly increased surface areas compared to the raw clay (Na-clay). The acid activation results in the partial dissolution of the octahedral layers (Al–O layers) and the substitution of interlamellar cations such as Na^+ and Ca^{2+} with H^+ , so the bonding force between mineral layers is weakened, which results in enlarged surface areas (30). The pillared modification of the raw clay also results in enlarged surface areas by intercalating metal hydroxides in the interlayer spaces of bentonites, which has been reported by many other authors (31, 32).

The organic carbon content of Cta-clay is proportional to the amount of CTAB intercalated into the mineral layers. According to our experimental results (not shown), at a lower amount of intercalation, the surface area was increased because of the enlarged layer spacings. After the increase of the amount of CTAB intercalated, the long alkyl chains of CTAB molecules may cover many surface positions and plug the entrance of N_2 molecules, which gives smaller measured values of the surface areas, as reported by other authors (33). These changes on surface areas and organic carbon content form the basis of the different sorption properties of the various clays to organic herbicides.

Characteristics of Clay/CMC Gel Formulations. When the liquid mixtures of CMC, clay, and acetochlor were added dropwise into the solution of iron cations, hydrogel beads of a size of about 2.5 mm were immediately formed. The dried gels were spherical granules with diameters between 0.90 and 1.28 mm. **Table 3** presents the characteristics of the various dried gel formulations. The average weight of each granule varied between 1.86 and 3.12 mg depending on the amount and type of clay used in the different formulations. Generally, the addition

Table 3. Characteristics of Dried Gel Formulations

sample	average weight (mg/granule)	average size ^a (mm)	encapsulation efficiency ^a (%)	maximum swelling ratio ^a
FN0	1.86(0.06)	0.90(0.04)	91.3(0.5)	2.26(0.09)
FN1	2.53(0.12)	1.09(0.03)	94.5(0.8)	1.93(0.05)
FN2	2.72(0.15)	1.15(0.08)	95.6(0.3)	1.58(0.06)
FN3	3.12(0.06)	1.28(0.05)	90.2(0.8)	1.30(0.03)
FF2	2.78(0.12)	1.21(0.06)	95.0(0.3)	1.89(0.04)
FS2	3.02(0.20)	1.23(0.08)	96.8(0.6)	1.70(0.09)
FL2	2.85(0.09)	1.21(0.07)	97.2(0.5)	1.69(0.07)
FC2	2.33(0.16)	1.13(0.04)	97.5(0.1)	1.66(0.04)

^a Values in parentheses represent the standard deviation of triplicates.

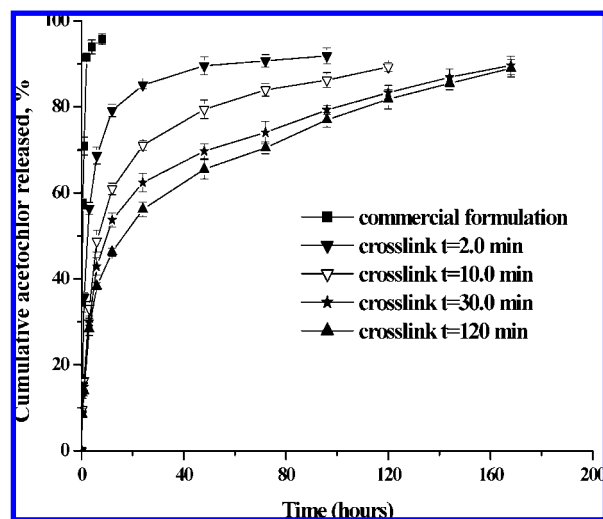


Figure 2. Release of acetochlor from FN2 hydrogels at different cross-linking times (error bars represent the standard deviation of triplicates).

of clay to the CMC gel led to heavier and larger granules, which dried more quickly than pure CMC gels. In our experiments, the FN0 sample was dried completely after 3 h, and the FN2 sample was dried completely within 2 h. This may result from the higher hydrophilicity of CMC than clay, which also led to the higher swelling ratio of pure CMC gel (FN0 formulation) than that of other clay/CMC gel formulations (**Table 3**). The lowest values of encapsulation efficiency were observed in FN0 and FN3 formulations, whereas the highest ones were observed in FL2 and FC2 formulations.

Influence of Cross-Linking Time on the Release Rate of Acetochlor from Hydrogel Formulations. In these release experiments, the hydrogel formulations with the same composition as that of the FN2 sample at different cross-linking times were directly used without further drying. The release profiles of acetochlor from these hydrogels are shown in **Figure 2**. As can be seen, 95.0% of acetochlor is released from the commercial formulation in less than 4 h, whereas at least 48 h is needed to release 90% of acetochlor from the clay/CMC hydrogel formulations. The longer the cross-linking time, the slower the acetochlor is released. This can be easily explained by the fact that a longer cross-linking time gives a more compact hydrogel structure, which results in a closer and stronger bonding of acetochlor to both CMC macromolecules and clay minerals. In such clay/CMC hydrogel formulations, hydrogen bonds play a very important role for the interaction between acetochlor and the carrier. The plentiful hydroxyl groups on cellulose macromolecules act as proton donors for hydrogen bonds, and the oxygen atoms of acetochlor act as acceptors. The hydration water molecules around the interlayer cations in the clay minerals can also form hydrogen bonds with acetochlor

Table 4. Fitting Results of Acetochlor Release from FN2 Hydrogels

cross-link time (min)	K^a (h^{-1})	n^a	R^b	t_{50} (h)
2.0	0.297 ± 0.006	0.668 ± 0.009	0.978	2.18
10.0	0.173 ± 0.003	0.537 ± 0.006	0.995	7.21
30.0	0.158 ± 0.005	0.521 ± 0.015	0.996	9.11
120	0.149 ± 0.003	0.459 ± 0.014	0.988	14.0

^a These values are presented with standard errors. ^b Significant at the 0.001 probability level.

(34). The stronger bonding of acetochlor to the hydrogel carrier hinders its release and makes the release slower.

To further compare the differences on the release of acetochlor from different gel formulations, the release data were analyzed by applying the empirical eq 1 proposed by Ritger and Peppas (35):

$$M_t/M_0 = Kt^n \quad (1)$$

M_t/M_0 is the ratio of active ingredient released at time t , K is a constant that incorporates the characteristics of the carrier and the active ingredient, and n is a parameter that is indicative of the transport mechanism. Equation 1 works well for analyzing the data of the initial 60% of herbicide released from bentonite-polymer composite carriers (27, 28).

Table 4 presents the fitting results with the linear form of eq 1 for the release of acetochlor from the above hydrogel formulations. The release data fit well to the empirical equation, as shown by the values obtained for the correlation coefficients ($R > 0.97$). The decrease of the K values with the increase of the cross-linking time indicates a stronger and stronger interaction between acetochlor and the carrier.

The n values also gradually decrease from 0.668 for the formulation cross-linked for 2.0 min to 0.459 for the formulation cross-linked for 120 min. Values of n close to 0.43 are indicative of Fickian diffusion in spherical monolithic matrices (35), and the n values may be higher for a release process from a swellable gel system (36). For example, for a drug release from a physically entangled CMC hydrogel, the n value is close to 1.0 and indicates a release mechanism of pseudocase II transport that mainly associates with the disentanglement of hydrogel network (37). In the release process from a swellable polymer hydrogel, the polymer relaxation plays a very important role. In our experiments, the clay/CMC hydrogels were chemically cross-linked with multivalent cations, and no apparent swelling of the hydrogels was observed in water. This means that the swelling capacity of these hydrogels is restrained by the cross-linked network structure, and the relaxation of the hydrogel network will not play a very significant role in this release study. As the n values indicate, when the hydrogel is cross-linked for 120 min, the release is dominated by a mechanism of Fickian diffusion ($n = 0.459$). When the cross-linked structure of hydrogel is not very tight at 2.0 min, the release of acetochlor may be influenced by both diffusion and polymer relaxation ($n = 0.668$).

Influence of the Amount of Clay on the Release Rate of Acetochlor from Na-Clay/CMC Gel Formulations. The cumulative release of acetochlor from such formulations is shown in **Figure 3**. As can be seen, the release rate of acetochlor from the pure CMC gel formulation (FN0) is the quickest, whereas the release of acetochlor from the clay/CMC gel formulations FN1, FN2, and FN3 is somewhat slower.

Table 5 presents the fitting results with the empirical eq 1 for the release data of acetochlor from Na-clay-based formulations. As can be seen from the values obtained for the correlation

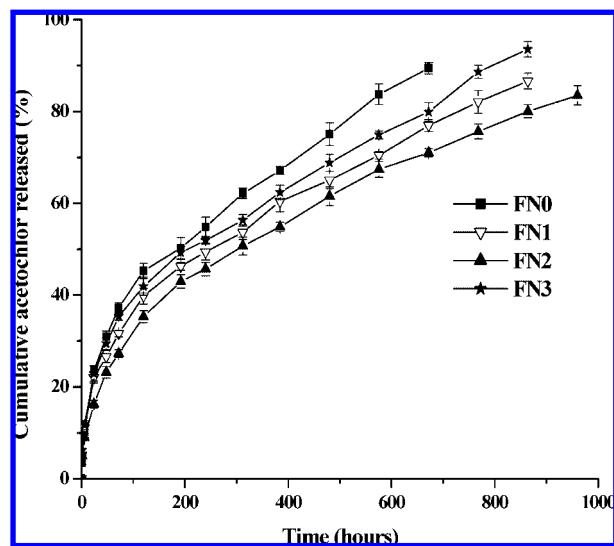


Figure 3. Release of acetochlor from dried gel formulations based on Na-clay of various amounts (error bars represent the standard deviation of triplicates).

Table 5. Fitting Results of Acetochlor Release from Dried Gel Formulations

sample	K^a (h^{-1})	n^a	R^b	t_{50} (h)
FN0	0.0401 ± 0.0025	0.504 ± 0.017	0.992	151
FN1	0.0537 ± 0.0018	0.411 ± 0.003	0.998	228
FN2	0.0460 ± 0.0024	0.418 ± 0.008	0.998	302
FN3	0.0614 ± 0.0028	0.396 ± 0.006	0.995	199
FF2	0.0488 ± 0.0034	0.399 ± 0.016	0.996	345
FS2	0.0405 ± 0.0026	0.412 ± 0.011	0.995	449
FL2	0.0429 ± 0.0024	0.393 ± 0.009	0.998	522
FC2	0.0352 ± 0.0006	0.432 ± 0.006	0.998	463

^a These values are presented with standard errors. ^b Significant at the 0.001 probability level.

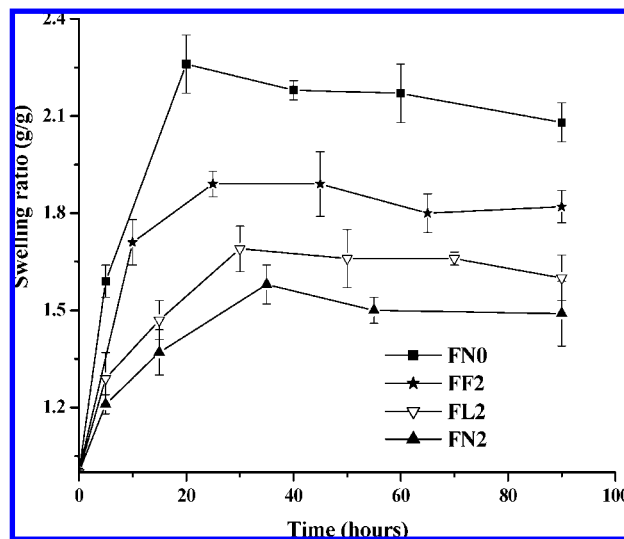


Figure 4. Swelling behavior of clay/CMC gels based on various clays (error bars represent the standard deviation of triplicates).

coefficients ($R > 0.99$), the release data fit well to the empirical eq 1. The n values range from 0.396 for the FN3 formulation up to 0.504 for the FN0 formulation. This means that the release of acetochlor from clay/CMC gel formulations is mainly controlled by a mechanism of Fickian diffusion. According to our experimental results, as shown in **Figure 4**, the swelling ratios of the dried clay/CMC gels remained below 2.5, and the swelling process was very quick and completed within 35 min.

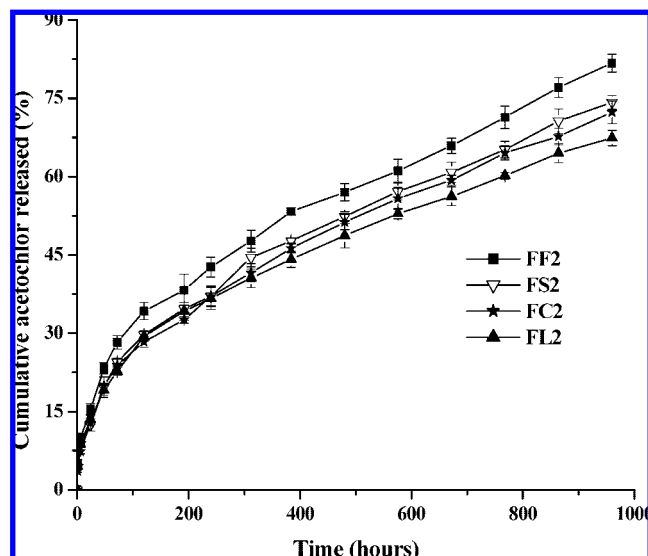


Figure 5. Release of acetochlor from dried gel formulations based on modified clays (error bars represent the standard deviation of triplicates).

The swelling performance of the clay/CMC gels is consistent with that of clay/alginate composites (28). The higher percentage of clay yielded lower swelling ratios, which had also been observed by other authors (38). In comparison, the release process of herbicide (Figure 3) is so slow that the influence of the quick swelling process can be neglected.

The time taken for 50% of the acetochlor to be released, t_{50} , can be calculated from the K and n parameters in empirical eq 1, and it is often used to evaluate the performance of CRFs. As can be seen in Table 5, the t_{50} values ranged from 151 h for the pure CMC gel formulation (FN0) to 302 h for the FN2 formulation. This indicates that the addition of some raw clay is beneficial to slow the release of herbicide from CMC gels. A higher clay percentage results in a dense and viscous clay/CMC suspension, which would give tailed hydrogel beads in gelation. For the FN3 formulation with the highest clay percentage, the CMC percentage was lowered to 2.0% to obtain spherical gels. The t_{50} value of 199 h for the FN3 formulation indicates that CMC in the composite formulations could be replaced partly with raw clay.

For the FN2 formulation with the same composition, the drying treatment greatly prolonged t_{50} . According to the results in Table 4, the t_{50} values for the FN2 hydrogel formulations ranged from 2.18 to 14.0 h. After drying treatment, the t_{50} value is increased to 302 h (Table 5). This result may be explained by the fact that the drying process vaporizes the free water in the hydrogel network and makes the acetochlor bind to the carrier more tightly through the contraction of the gel volume.

Influence of the Type of Clay on the Release Rate of Acetochlor from Clay/CMC Gel Formulations. Raw clays are often modified through acid activation, pillared with metal hydroxides, or saturated with organic surfactants to improve their performance as sorbents for organic compounds. In our research, the clays modified by the above methods (Su-clay, Al-clay, Fe-clay, and Cta-clay) were added in the CMC gel to prepare clay/CMC gel formulations of herbicide. The cumulative release of acetochlor from these formulations is shown in Figure 5. From these curves, we can see that the release of acetochlor from the FL2 formulation based on Al-clay is the slowest, and the release from the FF2 formulation based on Fe-clay is the quickest.

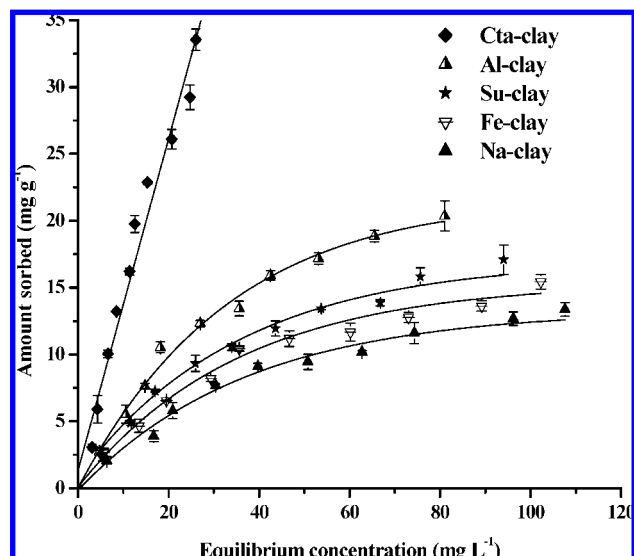


Figure 6. Sorption isotherms of acetochlor on various clays from water at 25 °C (error bars represent the standard deviation of triplicates).

The release data were also analyzed by applying the empirical eq 1, and the analytical results are listed in Table 5. The correlation coefficients ($R > 0.99$) indicate that the release of acetochlor from the dried gel formulations based on modified clays fits well to the empirical equation. The n values close to 0.43 imply a release mechanism of Fickian diffusion. The t_{50} values in Table 5 are clearly indicative of slow release rate resulting from the replacement of raw clay with modified clays in gel formulations. The formulations based on modified clays can be ranked in order of decreasing t_{50} values as follows: FL2 > FC2 > FS2 > FF2, and their t_{50} values are all larger than that of the FN2 formulation. In comparison to the t_{50} value of FN0, the pure CMC gel formulation, it can be concluded that the addition of modified clays in CMC gel can distinctly slow the release of acetochlor, and the t_{50} values are 2–3 times larger. This result can be due to the clays' sorption capacities, according to the results reported by other authors (14, 28, 39).

Sorption isotherms of acetochlor at 25 °C on various clays are shown in Figure 6. Among these curves, the sorption isotherm for Cta-clay shows the greatest slope. The sorption capacities of acetochlor on inorganically modified clays (Al-clay, Su-clay, and Fe-clay) are also apparently improved in comparison with the raw clay (Na-clay).

The sorption equilibrium of organic materials on the solid clays from the solution phase is often described by Langmuir and Freundlich equations that can be presented respectively as:

$$Q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (2)$$

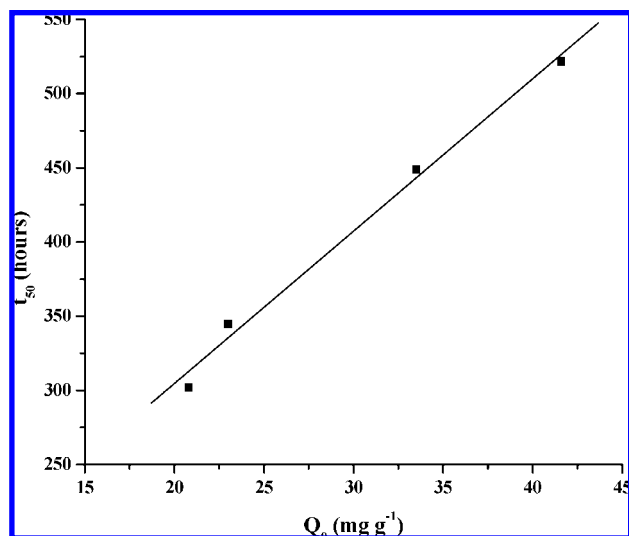
$$Q_e = K_f C_e^n \quad (3)$$

where Q_e is the amount of acetochlor sorbed on the clays ($\text{mg} \cdot \text{g}^{-1}$), C_e is the acetochlor concentration at equilibrium ($\text{mg} \cdot \text{L}^{-1}$), Q_0 and b are Langmuir constants which are the measurements of monolayer (maximum) adsorption capacity and energy of adsorption, respectively, and K_f and n are Freundlich constants which indicate the sorption capacity and sorption effectiveness, respectively. Table 6 presents the analytical results with both models for sorption isotherms of acetochlor on various clays.

Table 6. Analytical Data with Langmuir and Freundlich Models for Sorption Isotherms of Acetochlor on Various Clays

clay type	Q_0^a (mg·g ⁻¹)	b^a (L·mg ⁻¹)	$R_{(L)}^b$	K_f^a (mg ¹⁻ⁿ ·g ⁻¹ ·L ⁿ)	n^a	$R_{(F)}^c$
Na-clay	20.8 ± 2.1	0.0178 ± 0.0035	0.987	0.715 ± 0.019	0.651 ± 0.014	0.978
Fe-clay	23.0 ± 3.3	0.0202 ± 0.0042	0.996	0.923 ± 0.014	0.623 ± 0.006	0.983
Su-clay	33.5 ± 6.5	0.0148 ± 0.0051	0.995	0.933 ± 0.011	0.666 ± 0.003	0.985
Al-clay	41.6 ± 3.9	0.0150 ± 0.0020	0.996	1.062 ± 0.043	0.709 ± 0.012	0.980
Cta-clay	-48.5 ± 4.9	-0.0216 ± 0.0054	0.970	1.261 ± 0.089	1.030 ± 0.026	0.981

^a These values are presented with the standard errors. ^b Correlation coefficients to Langmuir model significant at the 0.001 probability level. ^c Correlation coefficients to Freundlich model significant at the 0.001 probability level.

**Figure 7.** Correlation study with t_{50} of clay/CMC gel formulations and Q_0 of inorganic clays.

The sorption data of acetochlor on inorganic clays (Fe-clay, Su-clay, and Al-clay) fit better to the Langmuir model than to the Freundlich model, as seen by comparing the correlation coefficients $R_{(L)}$ (0.995–0.996) with $R_{(F)}$ (0.980–0.985). The Langmuir isotherm model is based on monolayer adsorption on the surface of sorbents. The acid activation and pillared modification applied to the clay increased its surface area by a factor of about 2 (Table 2) and provided more sites for sorption interactions between clay minerals and herbicide molecules. According to the Q_0 values in Table 6, the inorganic clays can be ranked in order of decreasing sorption capacity as follows: Al-clay > Su-clay > Fe-clay > Na-clay. The Al-clay has the highest sorption capacity for acetochlor among the inorganic clays investigated in this research. This result could be explained by a strong coordination interaction formed between aluminum cations and functional polar groups (–OH, =O, and –Cl) on acetochlor molecules (34). Acid treatment leaches out inorganic ions in the octahedral sheet, resulting in numerous acid centers on the bentonite surface (40). Acetochlor, a weak basic herbicide, could be sorbed on the acid-activated Su-clay by the formation of acid–base pairs. The surface area of Fe-clay was close to that of Al-clay, but the sorption capacity of Fe-clay was much lower. This might result from the weak interaction between iron cations and acetochlor.

The above ranking of sorption capacities is consistent with the decreasing ranking of the t_{50} values for the release of acetochlor from clay/CMC gel formulations based on inorganic clays: FL2 > FS2 > FF2 > FN2 (Table 5). Figure 7 shows the plot of t_{50} vs Q_0 of inorganic clays. The higher the Q_0 values, the stronger the interaction between acetochlor and clays, which produces higher t_{50} values that indicate a slower release of herbicide from the formulations based on such clays. The equations of linear regression and correlation

coefficients were obtained by applying the least-squares method to the data.

$$t_{50} = 10.3Q_0 + 99 \quad (4)$$

where $R = 0.996$. Equation 4 may be useful for predicting the release profiles of herbicide from similar clay/CMC gel formulations.

Despite the decreased surface area (see Table 2), the organic clay Cta-clay provided the highest sorption capacity to acetochlor (Figure 6). As indicated by the correlation coefficients in Table 6, the sorption data of acetochlor on Cta-clay fit better to the Freundlich model. The n value close to 1 indicates a linear relationship of the distribution between solid clay and the solution interface. In contrast to inorganic clays, the sorption of organic materials on organic clays is mainly due to the partition in the organic phase derived from the cationic surfactant (29). For this study, the CTAB cations sorbed by clay minerals form a hydrophobic organic phase derived from their alkyl chains. This phase acts as a partition medium for the herbicide acetochlor, which is very hydrophobic with a low water solubility of 223 mg·L⁻¹ (20 °C) and a partition coefficient $\log K_{ow}$ of 4.14 (20 °C) in an octanol/water system. This result is in agreement with other research results concerning the sorption of pesticides by organic clays (41, 42).

The addition of Cta-clay in CMC gels also prolonged the release of acetochlor, but the increase of the t_{50} value was not as distinct as the improvement on the sorption capacity. At the same equilibrium concentration of acetochlor in water, the sorption amount on Cta-clay is 2–3 times higher than that on Al-clay (Figure 6), which provides the highest sorption capacity among inorganic clays. But the t_{50} value for the release of acetochlor from the gel formulation based on Cta-clay (463 h for FC2) was somewhat lower than that based on Al-clay (522 h for FL2) (Table 5). This might be explained by the different sorption mechanisms between organic and inorganic clays. The interaction between organic clay and acetochlor is mainly due to the van der Waals force between their hydrophobic moieties (34), whereas acetochlor is sorbed on inorganic clays mainly through coordination interaction. In the clay/CMC gel formulations, the van der Waals force might play a role not as important as that in pure Cta-clay and leads to a smaller improvement on slowing the release of the herbicide.

In conclusion, the clay/CMC gel formulations can be a practical choice as carriers for the controlled release of herbicides. The release rate of acetochlor can be adjusted through changing the amount and type of clays used in the formulations. This formulation form is useful to reduce the contamination due to herbicide and to improve the herbicide's efficiency on crop protection.

ACKNOWLEDGMENT

The authors express their thanks to Chinese Academy of Forestry for measurement of BET surface areas of clays.

LITERATURE CITED

- (1) Ye, C. Environmental behavior of the herbicide acetochlor in soil. *Bull. Environ. Contam. Toxicol.* **2003**, *71*, 919–923.
- (2) Balinova, A. M. Acetochlor—a comparative study on parameters governing the potential for water pollution. *J. Environ. Sci. Health, Part B* **1997**, *32*, 645–658.
- (3) Rebich, R. A.; Coupe, R. H.; Thurman, E. M. Herbicide concentrations in the Mississippi River Basin—the importance of chloroacetanilide herbicide degradates. *Sci. Total Environ.* **2004**, *321*, 189–199.
- (4) Ashby, J.; Tinwell, H.; Lefevre, P. A.; Williams, J.; Kier, L.; Adler, I. D.; Clapp, M. J. Evaluation of the mutagenicity of acetochlor to male rat germ cells. *Mutat. Res.* **1997**, *393*, 263–281.
- (5) Green, T.; Lee, R.; Moore, R. B.; Ashby, J.; Willis, G. A.; Lund, V. J.; Clapp, M. J. L. Acetochlor-induced rat nasal tumors: further studies on the model of action and relevance to humans. *Regul. Toxicol. Pharmacol.* **2000**, *32*, 127–133.
- (6) Xiao, N.; Jing, B.; Ge, F.; Liu, X. The fate of herbicide acetochlor and its toxicity to *Eisenia fetida* under laboratory conditions. *Chemosphere* **2006**, *62*, 1366–1373.
- (7) Liu, Y.; Zhang, Y.; Liu, J.; Huang, D. The role of reactive oxygen species in the herbicide acetochlor-induced DNA damage on *Bufo raddeitadpole* liver. *Aquat. Toxicol.* **2006**, *7*, 21–26.
- (8) Mogul, M. G.; Akin, H.; Hasirci, N.; Trantolo, D. J.; Gresser, J. D.; Wise, D. L. Controlled release of biologically active agents for purposes of agricultural crop management. *Resour., Conserv. Recycl.* **1996**, *16*, 289–320.
- (9) Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticides into soils from clay-polymer formulations. *J. Agric. Food Chem.* **1998**, *46*, 3797–3802.
- (10) Sopena, F.; Cabrera, A.; Maqueda, C.; Morillo, E. Controlled release of the herbicide norflurazon into water from ethylcellulose formulations. *J. Agric. Food Chem.* **2005**, *53*, 3540–3547.
- (11) Neitsch, S. L.; McInnes, K. J.; Senseman, S. A.; White, G. N.; Simanek, E. E. Melamine-based organoclay to sequester atrazine. *Chemosphere* **2006**, *64*, 704–710.
- (12) González-Pradas, E.; Socías-Viciano, M.; Ureña-Amate, M. D.; Cantos-Molina, A.; Villafranca-Sánchez, M. Adsorption of chloridazone from aqueous solution on heat and acid treated sepiolites. *Water Res.* **2005**, *39*, 1849–1857.
- (13) Yaron-Marcovich, D.; Nir, S.; Chen, Y. Fluridone adsorption-desorption on organo-clays. *Appl. Clay Sci.* **2004**, *24*, 167–175.
- (14) Celis, R.; Hermosín, M. C.; Carrizosa, M. J.; Cornejo, J. Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone. *J. Agric. Food Chem.* **2002**, *50*, 2324–2330.
- (15) Undabeytia, T.; Nir, S.; Rubin, B. Organo-clay formulations of the hydrophobic herbicide norflurazon yield reduced leaching. *J. Agric. Food Chem.* **2000**, *48*, 4767–4773.
- (16) Hermosín, M. C.; Calderón, M. J.; Aguer, J.-P.; Cornejo, J. Organoclay for controlled release of the herbicide fenuron. *Pest Manage. Sci.* **2001**, *57*, 803–809.
- (17) Nennemann, A.; Nir, S.; Rubin, B.; Polubesova, T.; Bergaya, F.; van Damme, H.; Lagaly, G. Clay-based formulations of metolachlor with reduced leaching. *Appl. Clay Sci.* **2001**, *18*, 265–275.
- (18) Stout, E. I.; Shasha, B. S.; Doane, W. M. Pilot-plant process for starch xanthide encapsulated pesticides. *J. Appl. Polym. Sci.* **1979**, *24*, 153–159.
- (19) Wing, R. E.; Shasha, B. S. Encapsulation of organic chemicals within a starch matrix. *J. Chem. Educ.* **1983**, *60*, 247–248.
- (20) Doane, W. M. Encapsulation of pesticides in starch by extrusion. *Ind. Crops Prod.* **1992**, *1*, 83–87.
- (21) Bahadi, M. Safe formulations of agrochemicals. *Chemosphere* **1987**, *16*, 615–621.
- (22) Pepperman, A. B.; Kuan, J.-C. W. Controlled release formulations of alachlor based on calcium alginate. *J. Controlled Release* **1995**, *34*, 17–23.
- (23) Kulkarni, A. R.; Soppimatha, K. S.; Aminabhavi, T. M.; Dave, A. M.; Mehta, M. H. Glutaraldehyde crosslinked sodium alginate beads containing liquid pesticide for soil application. *J. Controlled Release* **2000**, *63*, 97–105.
- (24) Kök, F.; Arica, M.; Gencer, O.; Abak, K.; Hasirci, V. Controlled release of aldicarb from carboxymethyl cellulose microspheres: In vitro and field applications. *Pestic. Sci.* **1999**, *55*, 1194–1202.
- (25) Mathew, N.; Kalyanasundaram, M. Development of biodegradable aluminum carboxymethylcellulose matrixes for mosquito larvicides. *Pest Manage. Sci.* **2004**, *60*, 685–690.
- (26) Bajpai, A. K.; Giri, A. Water sorption behaviour of highly swelling (carboxymethylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical. *Carbohydr. Polym.* **2003**, *53*, 271–279.
- (27) Fernández-Pérez, M.; Villafranca-Sánchez, M.; González-Pradas, E.; Martínez-López, F.; Flores-Céspedes, F. Controlled release of carbofuran from an alginate-bentonite formulation: Water release kinetics and soil mobility. *J. Agric. Food Chem.* **2000**, *48*, 938–943.
- (28) Fernández-Pérez, M.; Flores-Céspedes, F.; González-Pradas, E.; Villafranca-Sánchez, M.; Pérez-García, S.; Garrido-Herrera, F. J. Use of activated bentonites in controlled-release formulations of atrazine. *J. Agric. Food Chem.* **2004**, *52*, 3888–3893.
- (29) Zhu, L.; Li, Y.; Zhang, J. Sorption of organobentonites to some organic pollutants in water. *Environ. Sci. Technol.* **1997**, *31*, 1407–1410.
- (30) Yang, T.; Wen, X.-D.; Li, J.; Yang, L. Theoretical and experimental investigations on the structures of purified clay and acid-activated clay. *Appl. Surf. Sci.* **2006**, *252*, 6154–6161.
- (31) Ramesh, A.; Hasegawa, H.; Maki, T.; Ueda, K. Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Sep. Purif. Technol.* **2007**, *56*, 86–96.
- (32) Elmchaouri, A.; Mahboub, R. Effects of preadsorption of organic amine on Al-PILCs structures. *Colloids Surf., A* **2005**, *259*, 135–141.
- (33) Yilmaz, N.; Yapar, S. Adsorption properties of tetradecyl- and hexadecyltrimethylammonium bentonites. *Appl. Clay Sci.* **2004**, *27*, 223–228.
- (34) Lagaly, G. Pesticide-clay interactions and formulations. *Appl. Clay Sci.* **2001**, *18*, 205–209.
- (35) Ritger, P. L.; Peppas, N. A. A simple equation for description of solute release I. Fickian and anomalous release from nonswellable devices in the form of slabs, spheres, cylinders or discs. *J. Controlled Release* **1987**, *5*, 23–36.
- (36) Ritger, P. L.; Peppas, N. A. A simple equation for description of solute release II. Fickian and anomalous release from swellable devices. *J. Controlled Release* **1987**, *5*, 37–42.
- (37) Conti, S.; Maggia, L.; Segalea, L.; Ochoa Machiste, E.; Conte, U.; Grenier, P.; Vergnault, G. Matrices containing NaCMC and HPMC 2. Swelling and release mechanism study. *Int. J. Pharm.* **2007**, *333*, 143–151.
- (38) Garrido-Herrera, F. J.; González-Pradas, E.; Fernández-Pérez, M. Controlled release of isoprotruron, imidatoprid, and cyromazine from alginate-bentonite-activated carbon formulations. *J. Agric. Food Chem.* **2006**, *54*, 10053–10060.
- (39) González-Pradas, E.; Fernández-Pérez, M.; Villafranca-Sánchez, M.; Martínez-López, F.; Flores-Céspedes, F. Use of bentonite and humic acid as modifying agents in alginate-based controlled-release formulations of imidacloprid. *Pestic. Sci.* **1999**, *55*, 546–552.
- (40) Christidis, G. E.; Kosiri, S. Decolorization of vegetable oils: A study of the mechanism of adsorption of β -carotene by an acid-activated bentonite from Cyprus. *Clays Clay Miner.* **2003**, *51*, 327–333.
- (41) Yaron-Marcovich, D.; Nir, S.; Chen, Y. Fluridone adsorption-desorption on organo-clays. *Appl. Clay Sci.* **2004**, *24*, 167–175.
- (42) Sanchez-Martin, M. J.; Rodriguez-Cruz, M. S.; Andrades, M. S.; Sanchez-Camazano, M. Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides: Influence of clay type and pesticide hydrophobicity. *Appl. Clay Sci.* **2006**, *31*, 216–228.

Received for review August 22, 2007. Revised manuscript received January 1, 2008. Accepted January 2, 2008. Funding was provided by the Natural Science Foundation of Zhejiang Province (contracts Y506288 and Y307106) and the Science and Technology Bureau of Shaoxing City (contract 2006A32004) of China.