ABSTRACT: Thermodynamics and kinetics of pretilachlor adsorption on organobentonites modified with hexadecyltrimethyl ammonium chloride were investigated to reveal the structural effects of organobentonites on the interaction with pretilachlor and the diffusion of the herbicide and were related to the controlled release from organobentonites. The adsorption of pretilachlor was entropically driven by hydrophobic interaction. The entropy change dropped with increasing surfactant loading from 0.4 to 1.50 times the cation exchange capacity (CEC) of the bentonite used, corresponding to a decrease in the degree of freedom of pretilachlor molecules due to the enhanced order of surfactant in the interlayer. The kinetics of pretilachlor adsorption was well fitted to the pseudo-second-order model and related to the structural features of organobentonites. The enhanced packing density of the surfactant in the interlayer generally resulted in a reduction of the rate constant of the pretilachlor adsorption onto organobentonites. However, the stepwise increase in the basal spacing due to the surfactant arrangement transition, from lateral-monolayer to lateral-bilayer at a loading level of more than 0.8 × CEC, benefitted the diffusion of pretilachlor and diminished the influence of the increase in surfactant packing density. The release of pretilachlor from organobentonites was predominated by Fickian diffusion, which could be understood from the adsorption thermodynamics and kinetics. The time taken for the release of 50% of active ingredient was 16–23 times that for the control formulation and exhibited a linear increase with the relative value of the equilibrium constant to the rate constant of pretilachlor adsorption.

1. INTRODUCTION

Herbicides are the most commonly used agrochemicals for impeding the growth of weeds and improving the yield of crops. However, only part of herbicides reaches their target, whereas the rest remains attached to the soil colloids or undergoes degradation and transfer process such as migration to surface and groundwater, which has been reported to be one of the main sources of water pollution. In the past decades, many efforts have been made to minimize the use and impact of herbicides on the environment by developing controlled release formulations (CRFs). The success of CRFs in agriculture practice is critically dependent on the development of the matrix of high loading efficacy and controllable release properties. Clay minerals have been considered as good candidates for CRF because of their potential adsorbent properties in addition to their abundance and low cost. Bentonite is a natural material containing montmorillonite as a major constituent and has been considered as a potential platform for CRF of insecticides and herbicides due to the high specific surface area. Moreover, the surface properties and nanostructure in the interlayer of bentonite was readily regulated by organic modifications, which improved the adsorption capability toward several herbicides and reduce leaching in soil.

The knowledge of the structural effects of the matrix on the release behavior of pesticides would be helpful in developing new formulations to fulfill the actual requirement of environmental control. The release of pesticides from the CRFs was usually understood from the adsorption capability and the permeability of the matrix. A higher adsorption capability and a lower permeability usually resulted in a slower release. In the past decades, much attention has been paid to the development of organobentonites with high adsorption capacity and feasibility to regulate the adsorption capacity of organobentonites. However, little is known about the effects of structural features, such as molecular structure, loading level, and orientation of modifying agents in the interlayer space, on the permeability of organobentonites. The release behavior from organobentonites was qualitatively interpreted from the adsorption capacity of the matrix.

In a previous work, organobentonites modified with dodecyltrimethyl ammonium chloride (DTMA) and hexade-
Cyltrimethyl ammonium chloride (HTMA) were used as carriers of pretilachlor [2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl) acetamide], a selective pre-emergent herbicide widely applied to control annual grasses and broadleaf weeds in rice field, to obtain controlled release granules. The results indicated that the time taken for 50% of active ingredients to be released from organobentonites with surfactant loading level from 0.6 to 1.2 times the cation exchange capacity (CEC) increased with increasing adsorption coefficient by the Freundlich equation and is seemed to be related to the interlayer spacing and packing density of the surfactant in the interlayer. Unfortunately, the mechanism of structural effects of organobentonites on pretilachlor release remained unclear due to the lack of the physical significance of adsorption coefficient by the Freundlich equation and a suitable method to evaluate the permeability of the matrix.20

To get a further insight into the release properties of organobentonites, equilibrium adsorption of pretilachlor onto organobentonites with HTMA loading level from 0.4 to 1.5 × CEC was investigated. The adsorption thermodynamic parameters were used to reveal the interaction between the matrix and the herbicide. Kinetics of pretilachlor adsorption was also studied to illustrate the structural effects of organobentonites on the diffusion of pretilachlor molecules in the interlayer gallery. The release behavior of pretilachlor from organobentonites was understood from the thermodynamics and kinetics of pretilachlor adsorption. The results were helpful to evaluate the release properties of organobentonites and explore the organobentonite-based CRFs.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of Organobentonites. Organobentonites modified with HTMA at a feeding level in the range from 0.4 to 1.5 × CEC were prepared. The proportion of HTMA adsorbed on the bentonite used was found to drop dramatically when the feeding level was more than 1.5 × CEC.21 While those with a surfactant loading level less than 0.4 × CEC were subjected to suspension and blocked the filter membrane in the stirred-flow reactor system used in the adsorption kinetics and release of pretilachlor.

X-ray powder diffraction (XRD) is a useful method to characterize the arrangement model of the intercalated surfactants of organoclay, based on the basal spacing and the dimensions of the surfactant molecule. XRD patterns for the natural bentonite and organobentonites are presented in Figure 1, and the basal spacing \(d_{001}\) is listed in Table 1. The bentonite used was a typical Ca\(^{2+}\)-bentonite, of which the \(d_{001}\) value was 1.48 nm.22 A small quantity of HTMA of less than 0.8 × CEC slightly decreased the basal spacing of the bentonite. The interlayer separation, ca. 0.46 nm, agreed with the size of the head group of the quaternary ammonium, indicating that HTMA\(^+\) had intercalated into the interlayer of bentonite and replaced the exchangeable Ca\(^{2+}\) ion and water molecules adsorbed.23 A stepwise increase in the basal spacing to about 1.8 nm for organobentonites with higher surfactant loading indicated that the intercalated HTMA\(^+\) underwent a transition from a lateral-monolayer (\(d_{001} = 1.45−1.47\) nm) to a lateral-bilayer orientation (\(d_{001} = 1.75−1.85\) nm) (Figure S1 in the Supporting Information).

Fourier transform infrared spectroscopy (FTIR) has been widely used to probe the conformation of the adsorbed surfactant on clay minerals. The frequency of the CH\(_2\) absorption is sensitive to the ordering and packing density of the surfactants, the environment, and interactions between alkyl chains. The FTIR spectra of organobentonites are presented in Figure 2. The CH\(_2\) asymmetric stretching (\(\nu(CH_2)\)) and symmetric stretching vibrations (\(\nu(CH_3)\)) of the adsorbed surfactant were found to be around 2927 and 2854 cm\(^{-1}\) and slightly shifted to 2921 and 2850 cm\(^{-1}\) due to the increasing surfactant loading level up to 1.5 × CEC, close to those of pure HTMA (around 2919 and 2848 cm\(^{-1}\), respectively), indicating that the adsorbed surfactant developed from a less ordered conformation of low packing density to an ordered one of high packing density.25−28 An increase in hydrophobicity of organobentonite was also observed, as indicated by the decrease in the relative absorption of the adsorbed hygroscopic water around 3450 cm\(^{-1}\) to the structural \(\text{OH}\) of organobentonites at 3630 cm\(^{-1}\).10

2.2. Adsorption Isotherms. The isotherms of pretilachlor adsorption are shown in Figure 3. The linear increase of pretilachlor adsorption on organobentonites with the equilibrium concentration in the solution indicated that the adsorption was predominated by the partition of pretilachlor between the aqueous phase and the organic phase created by long hydrocarbon chain surfactant in the interlayer.29,30 The apparent adsorption equilibrium constant \(K_0\) was thus derived from the slope of isotherms and found to increase from 0.68 × 10\(^3\) mL·g\(^{-1}\) for BH\(_{1,5}\) to 3.30 × 10\(^3\) mL·g\(^{-1}\) for BH\(_{1,5}\) much more than that for bentonite (Table 1).

The adsorption capability was usually related to the organic carbon content of the clay. To evaluate the impact of organic carbon on the adsorption capability of organobentonites toward pretilachlor, the organic carbon contents \(f_{oc}\) were determined by elemental analysis (Table 1). The adsorption equilibrium constants \(K_0\) of pretilachlor normalized to the carbon content of the organoclay \(K_{oc}\) were derived by the following equation

\[
K_{oc} = K_0/f_{oc}
\]

\(K_{oc}\) values of HTMA-benton first increased and then slightly decreased with increasing surfactant loading level, reaching a maximum of around 0.8 × CEC (Table 1 and Figure S2 in the Supporting Information). Similar results were obtained for the adsorption of other organic compounds on organobentonites modified with quaternary ammonium surfactants. It has been suggested that the increase of the surfactant benefits the formation of the organic phase in the interlayer gallery. However, quaternary ammonium surfactant in molecule form
appeared in the interlayer via a hydrophobic interaction when the loading exceeded 0.8 × CEC. In the confined clay interlayer, the available space to accommodate the organic solutes reduced when the surfactant loading increased to a higher level. Moreover, the ammonium heads and the counterions of the surfactant interfered with the hydrophobic interaction between the surfactant molecules, resulting in a reduction of the adsorption capability of organobentonite toward hydrocarbon organic compounds.30−32

2.3. Adsorption Thermodynamics. To gain further insight into the structural effects of organobentonites on pretilachlor adsorption, equilibrium adsorption was conducted for different temperatures at 293, 303, and 313 K. The equilibrium constant ($K_a$) was obtained from the equilibrium concentration of pretilachlor in the solutions ($c_e$) and the adsorbed amount onto organobentonites ($q_e$). The thermodynamic parameters of pretilachlor adsorption were determined from Van’t Hoff equation by plotting ln $K_a$ vs 1/T (Figure 4)

$$\ln K_a = -\Delta H/R + \Delta S/R$$

(2)

$$\Delta G = -RT \ln K_a$$

(3)

$$K_a = q_e/c_e$$

(4)

where $T$ and $R$ are the thermodynamic temperature and gas constant, respectively; $\Delta G$, $\Delta H$, and $\Delta S$ are the changes in Gibbs free energy, enthalpy, and entropy, respectively. The results are listed in Table 2.

The negative value of $\Delta G$ at all temperatures indicated that pretilachlor adsorption on HTMA-bent was spontaneous and that the solute was favored to stay in the stationary phase rather than in the mobile phase. Generally, the physisorption was characterized by a standard Gibbs free energy change ($\Delta G^\circ$) of the absolute magnitude between 0 and $-20$ kJ·mol$^{-1}$, while for chemisorption $\Delta G^\circ$ is in the range from $-80$ to $-400$ kJ·mol$^{-1}$.33 In the temperature range studied, $\Delta G$ for pretilachlor adsorption on HTMA-bent was found to be between $-15.8$ and $-21.9$ kJ·mol$^{-1}$, indicating that the adsorption was physical in nature. The noncovalent binding usually originated from hydrophobic interaction, electrostatic interaction, hydrogen bond, or van der Waals interaction, which was reflected by the thermodynamic parameters. Hydrophobic interactions between two apolar molecules have been known as entropy-driven processes with a favorable entropy and unfavorable enthalpy ($\Delta H > 0$, $\Delta S > 0$, $\Delta H < T\Delta S$), opposite to the enthalpy-driven hydrogen bond and van der Waals interaction ($\Delta H < 0$, $\Delta S < 0$, $|\Delta H| > |T\Delta S|$). The interaction dominated by electrostatic attraction is characterized by a positive entropy and a minor unfavorable enthalpy.
The adsorption of pretilachlor on organobentonites via partition can be considered as a transfer from the aqueous phase to the organic phase in the interlayer gallery. The decrease in the degree of freedom of the adsorbed species was usually accompanied by a negative entropy change. However, the strong hydrophobicity of pretilachlor (octanol–water partition coefficient log \(K_{ow} = 4.08\)) made it a structure maker to induce an enhancement in the hydrogen-bonding network in the hydration cosphere, as compared to the bulk. The transfer of pretilachlor to the organic phase in the interlayer gallery of organobentonite would release the solvating water molecules to the bulk, bringing about an increase in the entropy of the whole system, which can be attributed to the positive entropy change for pretilachlor adsorption (Table 2). Since the intercalation of quaternary ammonium surfactants was dominated by ion exchange at the loading level less than \(1.0 \times \text{CEC}\), an increase in surfactant loading usually resulted in an enhanced hydrophobicity of organobentonite, as illustrated by the decreased relative IR absorption intensity of the adsorbed water to that of the structural –OH of organobentonites (Figure 2). However, the value of \(\Delta S\) dropped dramatically with increasing surfactant loading up to \(0.8 \times \text{CEC}\) (Table 2), indicating that the hydrophobicity of organobentonite had little influence on the dehydration of pretilachlor molecules. The reduction of entropy change may be related to the decrease in the degree of freedom of pretilachlor molecules due to the enhancement in structure order and packing density of surfactant in the interlayer gallery. Following the suggestion by Xu et al., quaternary ammonium surfactant in molecular form intercalated in the clay via hydrophobic interaction when the loading exceeded \(0.8 \times \text{CEC}\). The ammonium heads and the counterions would interfere with the hydrophobic interaction of the surfactant and destroyed the close packing in clay galleries. As a result, the entropy decrease due to the solidification of pretilachlor in the organic phase of HTMA-bent became less evident and quickly leveled off when the surfactant loading level was more than \(0.8 \times \text{CEC}\) (Table 2 and Figure S3 in the Supporting Information).

**2.4. Adsorption Kinetics.** Adsorption kinetics of pretilachlor on HTMA-bent is presented in Figure 5. The profiles were fitted to two commonly used kinetics models, pseudo-first-order (eq 5) and pseudo-second-order (eq 6).

\[
\ln (q_t - q) = \ln q_1 - k_1 t \\
\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{t}{q_2}
\]

where \(q_t\) (mg·g\(^{-1}\)) is the amount of pretilachlor adsorbed at time \(t\) (min); \(q_1\) (mg·g\(^{-1}\)) and \(q_2\) (mg·g\(^{-1}\)) are the maximum adsorption capacities for the pseudo-first-order adsorption and pseudo-second-order adsorption, respectively; and \(k_1\) (min\(^{-1}\)) and \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) are rate constants for the pseudo-first-order adsorption and pseudo-second-order adsorption, respectively. The values of the maximum adsorption capacity and rate constant were obtained by a nonlinear fit using the least-squares method and are summarized in Table 3. Based on the \(R^2\) values, both pseudo-first-order and pseudo-second-order models could be well used to describe the kinetics of pretilachlor adsorption onto organobentonites. The maximum adsorption capacity obtained by both models increased, while the rate constant decreased and leveled off with increasing surfactant loading. However, a further comparison showed that the latter generally provided better results than the former. The adsorption capacity \(q_2\) agreed well with those from adsorption isotherms (Table S1 in the Supporting Information). Thus, the structural effects of organobentonites on the kinetics of adsorption and the release of pretilachlor were discussed based on the results from the pseudo-second-order model in the following text.

Several rate-limiting steps and mechanisms were involved in the kinetics of adsorption onto organobentonites, including (1) diffusion of adsorptive from the bulk solution to the surface of clay particles, (2) migration into the interlayer gallery, and (3) binding to the active site. It was apparent that an increase of basal spacing would result in an increase of interface between the bulk solution and the organic phase created by the surfactant and thus benefit the diffusion of the active ingredient into the interlayer gallery of organobentonite. However, the increase in surfactant packing density would slow

**Table 2. Thermodynamic Parameters for Pretilachlor Adsorption on HTMA-Bent**

| sample | \(\Delta H/\text{(kJ·mol}^{-1}\)) | \(\Delta S/\text{(J·mol}^{-1}·\text{K}^{-1}\)) | \(\Delta G/\text{(kJ·mol}^{-1}\)) |
|--------|-------------------------------|---------------------------------|---------------------------------|
| BH0.4  | 16.0 (1.2)                    | 166.3 (4.3)                    | −10.2 (0.2)                     |
| BH0.6  | 20.6 (1.0)                    | 118.9 (3.8)                    | −15.2 (0.5)                     |
| BH0.8  | 20.6 (0.8)                    | 100.1 (2.6)                    | −19.5 (0.3)                     |
| BH1.0  | 7.7 (1.2)                     | 93.2 (3.8)                     | −19.6 (0.3)                     |
| BH1.25 | 19.0 (2.2)                    | 69.0 (7.4)                     | −20.0 (0.3)                     |
| BH1.5  | 6.6 (0.3)                     | 91.0 (1.1)                     | −21.0 (0.3)                     |

\(\Delta H \sim 0\) or \(\Delta H > 0, \Delta S > 0\). The positive values of enthalpy and entropy change indicated that pretilachlor adsorption was driven by entropy through hydrophobic interaction. Despite the decrease in entropy change, the reduction of the unfavorable enthalpy change led to an enhancement of the adsorption capability of HTMA-bent with increasing surfactant loading, as indicated by an increase in \(\Delta G\) (Table 2).
The release of pretilachlor from HTMA-bent in water. Inset: dissolution profile of pretilachlor in water.

Table 3. Kinetic Parameters for Pretilachlor Adsorption onto HTMA-Bent

| sample  | \(q_1/(\text{mg} \cdot \text{g}^{-1})\) | \(k_1 \times 10^5/\text{min}^{-1}\) | \(R^2\) | \(q_1/(\text{mg} \cdot \text{g}^{-1})\) | \(k_2 \times 10^5/(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})\) | \(R^2\) |
|---------|----------------------------------|-------------------------------|------|----------------------------------|----------------------------------|------|
| BH0.4   | 25.8 (0.4)                       | 13.5 (0.7)                    | 0.996| 31.5 (0.3)                       | 45.8 (2.1)                       | 0.999|
| BH0.6   | 43.0 (0.7)                       | 11.6 (0.5)                    | 0.997| 53.6 (0.6)                       | 22.2 (1.0)                       | 0.999|
| BH0.8   | 57.0 (0.5)                       | 11.1 (0.3)                    | 0.999| 72.5 (1.9)                       | 14.5 (1.4)                       | 0.995|
| BH1.0   | 67.7 (0.9)                       | 10.6 (0.4)                    | 0.998| 85.8 (1.6)                       | 12.1 (0.8)                       | 0.997|
| BH1.25  | 72.3 (0.5)                       | 10.5 (0.2)                    | 0.999| 93.2 (2.0)                       | 10.4 (0.8)                       | 0.997|
| BH1.5   | 78.1 (0.9)                       | 10.3 (0.3)                    | 0.998| 100.3 (1.9)                      | 9.4 (0.7)                        | 0.997|

Values in brackets represent the standard deviation.

The release of pesticides from CRF was usually understood from the adsorption capability and the permeability of the matrix. A higher adsorption capability would result in a slower release, a consequence of the lower equilibrium concentration in the medium. The \(T_{50}\) values for the pretilachlor release from organobentonites totally increased with increasing adsorption equilibrium constant \(K_a\) (Tables 1 and 4). However, the upward curvature of the \(T_{50}\) vs \(K_a\) plot suggested a possible alteration of matrix permeability induced by the structural change in the interlayer (Figure S6 in the Supporting Information).

The value of the diffusion exponent \(n\) from 0.50 to 0.59 (Table 4) indicated that the pretilachlor release from organobentonites was predominated by a Fickian diffusion mechanism. In an aqueous environment, the active ingredient migrated in the interlayer space and diffused into the release medium due to the concentration gradient and was sustained by the lamellar of bentonite and surfactant molecules intercalated. Thermodynamic studies have indicated that the adsorption of pretilachlor on HTMA-bent is physical and thus a reversible process of the release. The rate constant of adsorption \(k_a\) and that of desorption \(k_d\) could be related to the equilibrium constant \(K_a\)

\[
k_a = k_d/K_a
\]
organobentonite was also observed, although much less evident than that for organobentonites with lower surfactant loading, as the stepwise increase in the basal spacing benefited the diffusion of pretilachlor into the interlayer gallery of organobentonite and reduced the influence on the increase in surfactant packing density.

The release of pretilachlor was greatly retarded by incorporating it into HTMA-bent. The release was dominated by Fickian diffusion, which could be understood from the thermodynamics and kinetics of pretilachlor adsorption on the matrix. The time taken for the release of 50% of active ingredient from organobentonites was 16–23 times that for the control formulation and increased linearly with the relative value of the equilibrium constant to the rate constant of pretilachlor adsorption.

4. MATERIALS AND METHODS

4.1. Materials. Bentonite was obtained from Guangxi Ningming Minerals Co. (China). The cation exchange capacity (CEC) of the bentonite was about 0.82 mmol·g⁻¹. Analytical grade hexadecyltrimethyl ammonium chloride (HTMA) and methanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Technical grade pretilachlor (95%) was kindly supplied by Guangxi Tianyuan Biochemical Co. (China).

4.2. Methods. 4.2.1. Preparation of Organobentonites. Organobentonites were prepared following the process described in previous work.²¹ Briefly, a stock solution containing HTMA of the amount equivalent to 0.4–1.5 × CEC of the clay was added to the dispersion containing ca. 2% bentonite under agitation and kept at 60 °C for 24 h. The resulting organobentonites were then separated by vacuum filtration, dried to constant weight at 60 °C, ground in an agate mortar and sifted through a 150 μm mesh sieve. The organobentonite is denoted as HTMA-bent and labeled as BHx, where x is the quantity of HTMA used and presented as BH, μmol·g⁻¹.

The carbon content of organobentonites was determined on a PerkinElmer PE2400II elemental analyzer. Organobentonites was determined on a Rigaku D/Max-2500V diffractometer. The Ni-filtered Cu Kα radiation (λ = 1.5405 Å) was used as the X-ray source. All scans were performed in the range of 2θ = 3–10° at a speed of 4°·min⁻¹, with a step size of 0.02°. The basal spacing of organobentonites was calculated from the (001) plane, using the Bragg equation.

4.2.2. FTIR. FTIR spectra were collected from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ on a Shimadzu FTIR-8400S FTIR spectrometer in the transmission mode. Organobentonites were ground with KBr in the weight ratio of 1:50. The FTIR spectra were obtained from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The FTIR spectra were obtained from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.
about 2:100 and compressed into pellets before the performance.

4.2.4. HPLC. The concentration of pretilachlor in the solutions was determined by a Shimadzu SPD-10A high-performance liquid chromatograph equipped with a UV–vis detector set at 225 nm and an ODS column (250 mm × 4.6 mm, 5 μm). The mobile phase was a methanol–water mixture (volume ratio of 90:10) at a flow rate of 1.0 mL min\(^{-1}\). Solutions containing pretilachlor were passed through nylon filters of 0.22 μm pore diameter before the performance.

4.2.5. Adsorption Isotherms. Fifty milligrams of organobentonite was mixed with 50 mL of the aqueous solution of pretilachlor of concentration ranging from 5 to 40 μg·mL\(^{-1}\). The dispersions were kept on a multichannel magnetic stirrer equipped with a water bath thermostated to 25 °C for 4 h to reach an equilibrium. The equilibrium concentration of pretilachlor in the solution was determined by HPLC, and the adsorbed amount of pretilachlor was calculated to reach an equilibrium. The supernatants were analyzed by HPLC and the adsorbed amount of pretilachlor was calculated from the difference between initial and final concentrations. The performance was carried out duplicate, and the average results were used to obtain the adsorption isotherms of pretilachlor on organobentonites.

4.2.6. Adsorption Thermodynamics. Similar to the performance of adsorption isotherms, 50 mL of a solution containing pretilachlor in ca. 40 μg·mL\(^{-1}\) concentration was mixed with 50 mg of organobentonite under agitation and kept for 4 h to reach an equilibrium. The equilibrium concentration of pretilachlor in the solution was determined by HPLC, and the adsorption equilibrium constant was evaluated. The performance was carried out at 20, 30, and 40 °C and for at least 5 times under the same conditions. The average results were used to evaluate the thermodynamic parameters of pretilachlor adsorption on organobentonites.

4.2.7. Adsorption Kinetics. Adsorption kinetics of pretilachlor was carried out on a stirred-flow reactor system made in our laboratory (Figure S7 in the Supporting Information). The ca. 0.1 cm\(^{3}\) propylene stirred-flow reactor had a side inlet at the bottom and was connected to an LC-10AD pump (Shimadzu, Japan) by 0.5 mm i.d. poly(tetrafluoroethylene) tube. The outlet in the lid was covered with a nylon filter membrane of pore size 0.45 μm to retain the samples in the reactor. The reactor carrying 25 mg of organobentonite and a magnetic stirring bar was immersed in a water bath thermostated to 25 °C. The stock solution containing pretilachlor in the concentration of ca. 40 μg·mL\(^{-1}\) was circulated at a flow rate of 1 mL·min\(^{-1}\). The output solution fractions were collected in predefined time duration, and the mass was determined on a Mettler AE200 analytical balance. The herbicide was analyzed by HPLC, and the adsorbed amounts were obtained from the concentration difference between the input and the output solutions.

4.2.8. Preparation of Pretilachlor-Loaded Organobentonites. A stock solution of 1 g of pretilachlor (a.i.) dissolved in 5 mL of methanol was dropped into aqueous dispersions containing 5 g of organobentonites under rigorous agitation. The dispersions were kept at room temperature for 12 h and separated by vacuum filtration. The resulting pretilachlor-loaded organobentonites were dried to a constant weight at 60 °C, ground in an agate mortar, and sifted through a 150 μm mesh sieve. Fifty milligrams of pretilachlor-loaded organobentonites were extracted by 50 mL of methanol 2 times. The extract was separated by centrifugation, and the supernatant was analyzed by HPLC to evaluate the amount of pretilachlor loaded. Organobentonites incorporating pretilachlor were labeled as BH\(_{P}\).

4.2.9. Pretilachlor Release in Water. The release of pretilachlor from organobentonites in water was conducted in the stirred-flow reactor system using a method similar to that used for adsorption kinetics. Twenty-five milligrams of pretilachlor-loaded organobentonite was placed in the reaction chamber kept at 25 °C and water was circulated at a flow rate of 1 mL·min\(^{-1}\). The output solution fractions were collected in predefined time duration. The herbicide was analyzed by HPLC and the amount released was calculated to obtain a cumulative release profile.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.9b04025.

A comparison of maximum adsorption capacity of HTMA-bent toward pretilachlor calculated from adsorption isotherms and kinetics (Table S1); dependence of interlayer space \(d_{001}\) on surfactant feeding of organobentonites (Figure S1); plot of adsorption equilibrium constants of pretilachlor normalized to the carbon content of the organoclay, \(K_{a}\), against surfactant feeding (Figure S2); dependence of entropy change, \(\Delta S\), on surfactant feeding of organobentonites (Figure S3); dependence of adsorption rate constant from pseudo-second-order model, \(k_{p}\), on surfactant feeding of organobentonites (Figure S4); dependence of \(T_{50}\) value for pretilachlor release from HTMA-bent on the surfactant loading level (Figure S5); dependence of \(T_{50}\) value for pretilachlor release from HTMA-bent on equilibrium constant \(K_{a}\) for pretilachlor adsorption (Figure S6); and schematic representation of the stirred-flow reactor system (Figure S7) (PDF)

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### Notes

The authors declare no competing financial interest.
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