

Addition of Modified Bentonites in Polymer Gel Formulation of 2,4-D for Its Controlled Release in Water and Soil

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Carboxymethylcellulose (CMC) gel was used for encapsulating anionic herbicide 2,4-D for its controlled release. The slower release rate of 2,4-D in water and soil was obtained by adding in the gel formulation some modified bentonites, which were prepared by intercalating inorganic or organic cations in interlayers of Na⁺-saturated bentonite. The higher encapsulation efficiencies of 2,4-D were observed on the bentonite/CMC gel formulations due to the sorption of 2,4-D on modified bentonites. The time taken for 50% of 2,4-D to be released in water, *t*₅₀, showed a variation (8.8–19.8 h) for these gel formulations, the largest value corresponding to the formulation incorporated with hydroxy-iron intercalated bentonite that has the highest sorption capacity to 2,4-D. The gel formulations could also control the release of 2,4-D when applied to a thin soil layer and demonstrated potential to reduce leaching of such anionic herbicides in soil.

KEYWORDS: 2,4-D; controlled release; clay; carboxymethylcellulose; gel

INTRODUCTION

Pesticides, the most cost-effective means of pest and weed control in agriculture, are also recognized as a source of potential adverse environmental impact due to their mobility (1). Among them, 2,4-dichlorophenoxyacetic acid (2,4-D) is an anionic herbicide widely used on wheat, maize, and rice to control broad-leaf weeds. Due to its relatively high water solubility, 2,4-D is weakly adsorbed by soil particles and has a high leaching potential and then poses a threat of surface and groundwater contamination (2, 3). Therefore, the development of controlled release formulations (CRFs) of 2,4-D could be advantageous, because CRFs can provide a slower release of active ingredients in water and soils and a reduction of pesticide contamination (4).

The performance of CRFs on controlling the release of pesticides is directly related to carrier materials. Among those investigated, some natural polymers such as alginate, lignin, starch, and cellulose derivatives have shown to be good carriers for active ingredients (5–11). These natural polymers are easily degradable and plentiful in resource, so their use as carriers for pesticides is of special interest in terms of both economic and sustainable development. Carboxymethylcellulose (CMC), a cellulose derivative containing carboxyl and hydroxyl groups on its macromolecules, can be easily gelled in solutions of multivalent cations such as Al³⁺ or Fe³⁺ cations. The resulting gels have also been used to prepare CRFs of pesticides (12, 13). These gel formulations based on natural polymers can be easily processed into granular forms and are safer and easier to handle

in agricultural operation than most of liquid or powder formulations.

The release of pesticides from CRFs based on natural polymers can be further retarded by incorporating some sorbents in polymer gel formulations. In such a mixed matrix, the release of active ingredients is influenced by both polymer and sorbents (14, 15). Among the sorbents, clay minerals are advantageous in terms of cost due to their cheap price. Fernández-Pérez and his group added clays in the alginate polymer to control the release of herbicides such as alachlor, carbofuran, atrazine, and metribuzin, etc. (16–18). Bentonite is a kind of expandable clay mineral composed primarily of montmorillonite, with permanent negative charges on its surface resulting from the isomorphous substitution of central atoms in the octahedral/tetrahedral by cations of lower valence. Such structure enables bentonite or montmorillonite to be intercalated by organic cations or hydroxy-metal cations, and the resulting products are good sorbents for many organic compounds (19, 20), including some environmentally hazardous pesticides (21–24). Therefore, it is interesting to investigate the use of modified bentonites in polymer gel formulations of pesticides. The authors have reported the slower release of active ingredient by incorporating bentonites in CMC gel formulations of nonionic herbicide acetochlor (25).

In comparison with most nonionic herbicides, the anionic herbicides such as 2,4-D are highly water soluble and easily diffuse from soils or carriers into water, so it is always challenging to control their release in water and soil. The aim of this work is to evaluate the bentonite/CMC matrices for the controlled release of herbicide 2,4-D. For this purpose, various kinds of modified bentonites are prepared and incorporated into

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Table 1. Characterization Parameters of Various Bentonites

sample	surface area (m ² g ⁻¹)	basal spacing (nm)	organic carbon contents (%)	pH in water suspension
Na-bentonite	15.2	1.27	0	10.4
Al-bentonite	32.6	1.66	0	5.64
Fe-bentonite	57.0	1.63	0	3.63
CTMA ₆₀ -bentonite	13.6	1.67	6.52	9.80
CTMA ₁₀₀ -bentonite	11.6	2.02	10.8	9.52

the CMC gel formulations of 2,4-D through gelation in the solution of Al³⁺ cations. The effects of the type and amount of modified bentonites on the release of 2,4-D into water and soil are investigated.

MATERIALS AND METHODS

Materials. Technical grade herbicide 2,4-D (acid form) with purity of 98.2% was purchased from Hangzhou Qingfeng Agrochemicals Co. Ltd., China. Food-grade sodium carboxymethylcellulose was obtained from Suzhou Weiyi Chemicals of China. Its 2% (w/w) solution in water has a viscosity of 750 ± 50 mPa s at 25 °C, and its content of sodium is 8.5 ± 0.1% (w/w). The original bentonite (denoted Na-bentonite) composed primarily of Na⁺-montmorillonite was purchased from Zhejiang, China. It was washed and dried before use. The cation-exchange capacity (CEC) of dried Na-bentonite was determined to be 0.570 ± 0.002 mmol g⁻¹. The organic cation cetyltrimethylammonium (CTMA) and other reagents used for bentonite modifications were all of analytical grade. The soil used for release tests was collected locally from the top layer of red soil (a kind of ferrallitic soil in southern China). The pH of the soil is 4.8, organic matter content 0.6%, and CEC 0.11 mmol g⁻¹. The soil was air-dried and sieved through a 2 mm screen before use.

Preparation and Characterization of Modified Bentonites. Inorganically modified bentonites were prepared from Na-bentonite by intercalation with hydroxyaluminum(III) or hydroxyiron(III) cations (25). The resulting products were denoted Al-bentonite or Fe-bentonite, respectively. Al-bentonite was prepared by making a Na-bentonite suspension of 10 g in 500 mL of distilled water. This step was followed by dropwise addition of 500 mL of 0.2 mol L⁻¹ solution of aluminum hydroxide, which was prepared by dropwise addition of NaOH solution into a solution of AlCl₃·6H₂O until a [OH⁻]/[Al³⁺] molar ratio of 2.2 was obtained. The resulting mixture was heated at 70 °C for 48 h, and the modified bentonite was washed, centrifugally separated, and dried to constant weight. Fe-bentonite was prepared with a similar procedure, except that the 0.2 mol L⁻¹ solution of iron hydroxide was used as the modifying agent, which was prepared by adding slowly a solution of Fe(NO₃)₃·9H₂O in Na₂CO₃ solution at 60 °C until a [CO₃²⁻]/[Fe³⁺] molar ratio of 1 was reached.

Organically modified bentonites were prepared by adding CTMA to a 10% (w/w) aqueous suspension of 10 g of Na-bentonite under continuous stirring, and the suspension was heated for 1.5 h at 70 °C. The molar amount of CTMA added was equal to 60 or 100% of the CEC of Na-bentonite (0.570 mmol g⁻¹ as mentioned above). Then the suspension was centrifuged, and the solid sample was washed and dried at 70 °C to constant weight. The resulting products were identified as CTMA₆₀-bentonite and CTMA₁₀₀-bentonite, respectively.

All bentonite 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 samples were degassed at 115 °C for 4 h under vacuum prior to adsorption. The organic carbon content of bentonite samples was determined by using the solid module on a LIQUI TOC system. The basal spacings were measured by X-ray in a Rigaku D/MAX 3A equipment with Cu Kα radiation and a goniometer rate of 4 ° min⁻¹. The pH of bentonites was determined in a 1:10 (w/w) sample/water suspension using a glass electrode. The characterization parameters for the bentonite samples are listed in **Table 1**.

Sorption of 2,4-D on Bentonites. The sorption isotherms were determined by batch equilibration of 0.2 g of each bentonite sample

Table 2. Compositions of Suspensions for Preparing Bentonite/CMC Gel Formulations

sample	CMC ^a (%)	bentonite type	bentonite amount ^a (%)
GC3.0	3.0		0
GC2.0N2.0	2.0	Na-bentonite	2.0
GC2.0A2.0	2.0	Al-bentonite	2.0
GC2.0A4.0	2.0	Al-bentonite	4.0
GC2.0F2.0	2.0	Fe-bentonite	2.0
GC1.5F3.0	1.5	Fe-bentonite	3.0
GC3.0F1.0	3.0	Fe-bentonite	1.0
GC2.0C ₁₀₀ 2.0	2.0	CTMA ₁₀₀ -bentonite	2.0
GC1.5C ₁₀₀ 3.0	1.5	CTMA ₁₀₀ -bentonite	3.0
GC1.5C ₆₀ 3.0	1.5	CTMA ₆₀ -bentonite	3.0

^a Percentage (in weight) of components added in water suspensions to prepare the gel formulations (in all suspensions, 2.0% of 2,4-D was added, and the balance was water).

with 50 mL of aqueous solutions of 2,4-D of varied initial concentrations, C₀ (25–200 mg L⁻¹). Experiments were carried out in a thermostatic shaker bath at 25 ± 0.1 °C for 8 h. Preliminary experiments had been conducted to determine that the sorption equilibrium time required for 2,4-D was <4 h. After equilibration, the suspension was centrifuged, and the herbicide concentration in supernatant (C_e) was measured. The amount sorbed (Q_e) was calculated from the difference in concentration between the initial (C₀) and the equilibrium (C_e) solution. Blanks without 2,4-D and triplicates of each sorption point were used for each series of experiments.

Preparation and Characterization of Bentonite/CMC Gel Formulations. The bentonite sample, 2,4-D, and CMC were added one by one into water and vigorously mixed into a viscous suspension. **Table 2** presents the compositions of suspensions, in which 2.0% (in weight) of 2,4-D was added for all formulations. The mixed suspension was added dropwise into 100 mL of gellant bath of 0.03 M Al₂(SO₄)₃ solution with a 5 mL injector. The hydrogel beads were obtained after 10 min of gelation and were dried in an oven (40 °C) to obtain the bentonite/CMC gel formulations.

To characterize the gel formulations, the weight per gel granule, content of active ingredient, and encapsulation efficiency were determined. The content of active ingredient was calculated as content of active ingredient (%) = (amount of 2,4-D in gel formulation/total weight of gel formulation) × 100. The encapsulation efficiency was calculated as encapsulation efficiency (%) = (amount of 2,4-D in gel formulations/total amount added in suspensions) × 100. The amount of 2,4-D encapsulated in the gel formulations (M₀) was measured with an extraction procedure. That is, the gel samples were extracted with a methanol/water mixture (70:30) for more than three times until no residual 2,4-D detected, and the 2,4-D concentration in the total extractive solution was determined. The characterization data were obtained in triplicates.

Fourier transform infrared (FTIR) spectra were taken on a Nicolet Nexus instrument to characterize the bentonite/CMC gel formulations. For this purpose, the film of formulation GC2.0F2.0 was prepared by mixing 0.5 g of 2,4-D, 0.5 g of Na-CMC, 0.5 g of Fe-bentonite, 0.04 g of Al₂(SO₄)₃, and 23.5 g of water into a uniform suspension, then the suspension was poured on a flat dish, followed by cross-linking and drying at 80 °C in an oven. The resulting film sample was used for FTIR analysis. The film sample of Na-CMC was prepared by drying on a flat dish and used for the comparison study. The FTIR spectra of 2,4-D and Fe-bentonite were obtained in the powder form on KBr disks. The spectral scanning was done in the range between 4000 and 675 cm⁻¹.

Herbicide Release in Water. The release experiment of 2,4-D in water from gel formulations was carried out in a thermostatic shaker bath at 25 ± 0.1 °C (16–18). The gel formulations containing 2,4-D of 5 mg (M₀) were added to distilled water (300 mL) in stoppered conical flasks, which were put in the shaker bath for continuous shaking. At selected time intervals (1, 3, 9, 12, 24, 48, 72, 96 h, respectively) after herbicide application, a supernatant solution of 0.5 mL was filtered and the 2,4-D concentration was determined. Then the amount of 2,4-D released into water at time *t* (M_t) was calculated, and the release kinetics

Table 3. Characteristics of Dried Gel Formulations

sample	av wt (mg/granule)	content of 2,4-D (%)	encapsulation efficiency (%)
GC3.0	1.41 (0.09) ^a	22.2 (0.7)	55.5 (1.7)
GC2.0N2.0	1.44 (0.12)	22.6 (0.3)	67.7 (0.9)
GC2.0A2.0	1.88 (0.11)	25.8 (0.4)	77.3 (1.3)
GC2.0A4.0	2.34 (0.16)	22.5 (0.3)	90.2 (1.2)
GC2.0F2.0	1.70 (0.05)	26.6 (0.3)	79.8 (0.9)
GC1.5F3.0	1.96 (0.09)	26.2 (0.2)	85.3 (0.5)
GC3.0F1.0	1.55 (0.14)	25.2 (0.5)	75.5 (1.5)
GC2.0C ₁₀₀ 2.0	1.69 (0.10)	23.7 (0.2)	71.2 (0.5)
GC1.5C ₁₀₀ 3.0	2.07 (0.11)	22.5 (0.3)	73.2 (1.0)
GC1.5C ₆₀ 3.0	1.93 (0.08)	21.7 (0.2)	70.6 (0.6)

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

is described by the change of release percentage (M_t/M_0) with time t . In all cases, 2,4-D release kinetics was obtained in triplicates. The release data were analyzed by applying the equation proposed by Ritger and Peppas (26):

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

M_t/M_0 is the ratio of active ingredient released at time t , K is the constant that incorporates characteristics of the carrier and the active ingredient, and n is a parameter that is indicative of transport mechanism.

Herbicide Release through a Thin Soil Layer. The leaching of 2,4-D through a thin soil layer was carried out in a Buchner funnel (27–29). First, a thin layer of red soil of 50 g was deposited on a nylon filter cloth in a funnel (with diameter of 8 cm). The gel formulations containing 2,4-D of 1 mg (M_0) were applied on the top of soil and then covered by another piece of nylon filter cloth. The funnels were irrigated three times a day at 2 h intervals, the volume of one irrigation being 40 mL. The leachate was collected after each irrigation. The amount of 2,4-D leached at each time (M_t) was calculated from the 2,4-D concentration in leachate. Each sample was irrigated for a total of nine times and preformed in triplicates.

2,4-D Analysis by HPLC. The amounts of 2,4-D in water solutions were analyzed on an Agilent 1200 HPLC system equipped with an ultraviolet detector and a HP Hypersil C18 column (150 mm × 4.6 mm i.d, particle size = 5 μm). The mobile phase used was a methanol/water mixture (70: 30, pH 2.0), and the 2,4-D was analyzed at 282 nm.

RESULTS AND DISCUSSION

Characteristics of Bentonite/CMC Gel Formulations. The dried gel formulations of 2,4-D are varied in shape depending on the type and amount of bentonites added. The dried gel granules of pure CMC formulation (GC3.0) are small flat cakes with a diameter of nearly 2.0 mm, but the dried gels of bentonite/CMC formulations of higher bentonite content (GC1.5F3.0, for example) appear to be spherical. Other formulations have transitional shapes from the flat cakes to spherical granules. Therefore, it is difficult to compare the size of different bentonite/CMC formulations. **Table 3** presents other characteristic parameters of various formulations. The average weight of each granule varied between 1.41 and 2.34 mg depending on the amount and type of bentonites added in gel formulations. Generally, the addition of bentonites in the CMC gel led to heavier granules, which were dried more quickly than the pure CMC gel. The content of 2,4-D in the gel formulations varied from 21.7 to 26.6%, depending on the initial amount of 2,4-D added and the encapsulation efficiency. Higher encapsulation efficiencies were observed in the bentonite/CMC gel formulations in comparison with the pure CMC gel formulation. The highest encapsulation efficiency belongs to the formulation GC2.0A4.0, which has the highest content of bentonite. Therefore, it can be concluded that the incorporation of

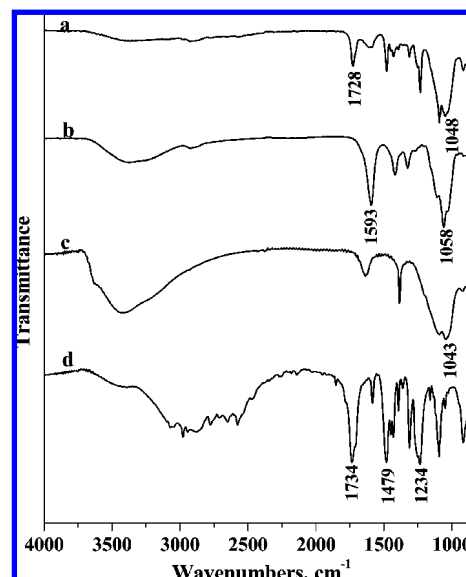


Figure 1. FTIR spectra of (a) formulation GC2.0F2.0, (b) Na–CMC, (c) Fe–bentonite, and (d) 2,4-D.

bentonites in CMC gel formulations of 2,4-D is beneficial for the improved encapsulation efficiency, which may be attributed to the sorption of 2,4-D on bentonites.

FTIR spectra were used for spectroscopically characterizing the bentonite/CMC gel formulations and investigating the interactions between 2,4-D and formulation components. **Figure 1** shows the FTIR spectra of formulation GC2.0F2.0, polymer Na–CMC, bentonite Fe–bentonite, and herbicide 2,4-D. In the spectrum of formulation GC2.0F2.0 (**Figure 1a**), the band at 1728 cm⁻¹ can be ascribed to C=O groups of 2,4-D encapsulated in the formulation. The same C=O stretching vibration was observed at 1734 cm⁻¹ for the free 2,4-D (**Figure 1d**). The shift of C=O stretching vibration to the lower wavenumber implies that hydrogen bonds may be formed between 2,4-D and formulation components, in which the hydroxyl groups on both CMC macromolecules and Fe–bentonite can act as proton donors for such hydrogen bonds. The band at 1593 cm⁻¹ was observed in spectra of both formulation GC2.0F2.0 (**Figure 1a**) and polymer Na–CMC (**Figure 1b**) and can be assigned to the asymmetrical stretching of –COO⁻ groups on CMC (30). In **Figure 1b**, the strong band at 1058 cm⁻¹ belongs to C–O–C absorption of CMC and shifted to the lower wavenumber at 1048 cm⁻¹ in the spectrum of gel formulation (**Figure 1a**). In **Figure 1c**, the bands at 1092 and 1043 cm⁻¹ are characteristic of Si–O stretching vibrations of bentonite, but in the spectrum of gel formulation (**Figure 1a**), the band at 1043 cm⁻¹ is merged into the band at 1048 cm⁻¹. This mergence of C–O–C and Si–O absorption bands for the CMC/clay composite has also been reported by Qiu et al. (31), and coordination interactions between CMC and clay were suggested. That is, oxygen atoms on C–O bonds of CMC and Si–O/Al–O bonds of bentonite may form coordination interactions with multivalent cations such as Al³⁺ in bentonite. Therefore, in the bentonite/CMC gel formulation of 2,4-D, complicated interactions may exist between herbicide and formulation components, as well as between bentonite and CMC.

Sorption Isotherms of 2,4-D on Modified Bentonites. Sorption isotherms of 2,4-D on modified bentonites at pH 6 are shown in **Figure 2**. All modified bentonites displayed higher sorptions to 2,4-D than the original Na–bentonite. As an organic acid, 2,4-D (pK_a = 2.6–3.0 at ionic strength of 0–0.05) may dissociate easily in water and exists mainly as the anionic

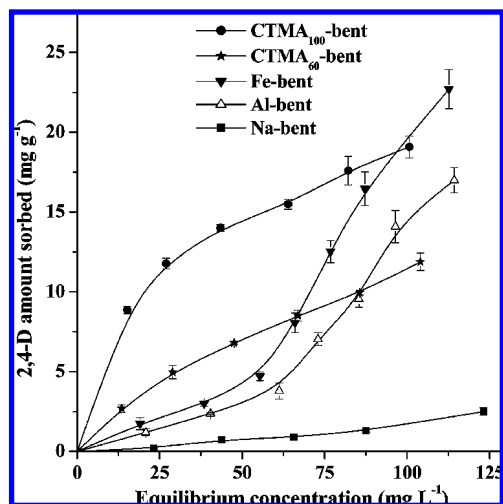


Figure 2. Sorption isotherms of 2,4-D on modified bentonites (error bars represent the standard deviation of triplicates).

species. Due to the repulsion by negatively charged surface of original Na-bentonite, its sorption to anionic 2,4-D is very low. For inorganically modified bentonites (Al-bentonite and Fe-bentonites), the negative charge on bentonite surface is reduced by intercalation with hydroxy-metal cations. In the meantime, the increased specific surface areas and basal spacings (see **Table 1**) provide sufficient space and sites for interactions formed between 2,4-D and bentonites. The interactions may involve hydrogen bonds formed between carbonyl groups of 2,4-D and hydroxyl groups on modified bentonites and coordinations of carboxyl groups of 2,4-D to the multivalent metal cations intercalated in bentonites (32, 33). In comparison with Al-bentonite, Fe-bentonite has higher specific surface area (see **Table 1**), which may be a reason for its higher sorption to 2,4-D compared with Al-bentonite. **Figure 2** also presents the sorption isotherms of 2,4-D on organically modified bentonites (CTMA₆₀-bentonite and CTMA₁₀₀-bentonite). Similar to results reported previously (34, 35), the organic modification of bentonite improved its sorption to the anionic herbicide, and the greater amount of CMTA cations intercalated into the bentonite led to the higher sorption.

In **Figure 2**, the difference in isotherm profiles can be observed between inorganically and organically modified bentonites. The L-type isotherms on organically modified bentonites (CTMA₆₀-bentonite and CTMA₁₀₀-bentonite) indicate the high sorption even at low 2,4-D concentrations. That means the organically modified bentonites have good affinity to 2,4-D, because the intercalation of organic CTMA cations converted the hydrophilic surface of original Na-bentonite into hydrophobic. In contrast, the sorption on inorganically modified bentonites (Al-bentonite and Fe-bentonite) was very low when the 2,4-D concentration in solution was lower than 50 mg L⁻¹. This implies the poor affinity of inorganically modified bentonites to 2,4-D in dilute solutions. However, in the concentrated solutions, the bentonite surface became more hydrophobic upon the sorption of some 2,4-D molecules, so the affinity of bentonites to 2,4-D increased and the sorption was obviously enhanced (36). Therefore, S-type isotherms were obtained for the inorganically modified bentonites.

2,4-D Release from Gel Formulations Mixed with Different Types of Bentonites. In these release experiments, gel formulations of the same bentonite/CMC ratio (1: 1) but with different types of bentonites were used. The release profiles of 2,4-D from some formulations are shown in **Figure 3**. As can be seen, free 2,4-D was mostly dissolved in water within 1 h,

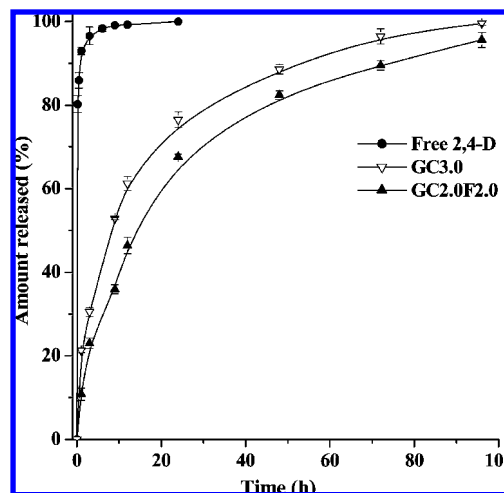


Figure 3. Release of 2,4-D from gel formulations in water (error bars represent the standard deviation of triplicates).

Table 4. Fitting Results of 2,4-D Release from Various Formulations

sample	K^a (h ⁻¹)	n^a	R^b	t_{50} (h)
GC3.0	0.214 ± 0.004	0.390 ± 0.007	0.992	8.8
GC2.0N2.0	0.171 ± 0.003	0.440 ± 0.008	0.996	11.4
GC2.0A2.0	0.158 ± 0.008	0.463 ± 0.012	0.991	12.1
GC2.0F2.0	0.122 ± 0.009	0.499 ± 0.020	0.990	16.9
GC2.0C ₁₀₀ 2.0	0.135 ± 0.005	0.500 ± 0.012	0.989	13.6
GC1.5C ₁₀₀ 3.0	0.123 ± 0.008	0.508 ± 0.018	0.990	15.9
GC1.5C ₆₀ 3.0	0.145 ± 0.001	0.482 ± 0.003	0.987	13.1
GC2.0A4.0	0.128 ± 0.007	0.500 ± 0.011	0.995	15.4
GC1.5F3.0	0.098 ± 0.006	0.545 ± 0.015	0.991	19.8
GC3.0F1.0	0.160 ± 0.006	0.430 ± 0.008	0.988	14.1

^a Presented with standard errors. ^b Significant at the 0.001 probability level.

whereas at least 48 h was needed to release 90% of 2,4-D from the gel formulations. When herbicide was encapsulated in the solid polymer formulation, the diffusion from the inner solid to the surface is a necessary step for its release into water (9). In this study, 2,4-D molecules were encapsulated in the cross-linked CMC gel; the increased tortuosity in gel formulations resulted in longer diffusion paths, so the release of 2,4-D is obviously delayed. The interactions between CMC and 2,4-D molecules (as indicated in FTIR spectra in **Figure 1**) may also partly contribute to the delayed release. Addition of modified bentonite Fe-bentonite in the gel formulation (see curve GC2.0F2.0) further slowed the release of 2,4-D in comparison with the pure CMC gel formulation (GC3.0). The slower release may be due to the sorption of herbicide on bentonite, which results in the lower solution concentration.

The release kinetics of 2,4-D from bentonite/CMC gel formulations by adding other modified bentonites are not shown in **Figure 3**, because some curves may overlap or cross each other and make the figure confusing. **Table 4** presents the fitting results with eq 1 for release data of 2,4-D from these gel formulations. As can be seen from the values obtained for the correlation coefficients ($R > 0.98$), the release data fit well to eq 1. The n values ranged from 0.390 for the GC3.0 formulation to 0.500 for the GC2.0C₁₀₀2.0 formulation. Values of exponent n close to 0.43–0.50 are indicative of Fickian diffusion from polymer matrices (26), so the fitting results imply that the release of 2,4-D from bentonite/CMC gel formulations is dominated by a mechanism of Fickian diffusion. This is similar to that obtained on the release of herbicide acetochlor from such mixed matrices (25).

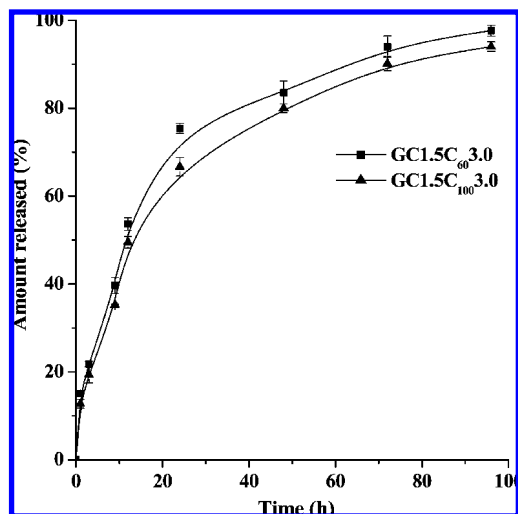


Figure 4. Release of 2,4-D from gel formulations mixed with organically modified bentonites (error bars represent the standard deviation of triplicates).

The time taken for 50% of the herbicide to be released, t_{50} , can be calculated from K and n parameters in eq 1 and often used to evaluate the performance of CRFs. As can be seen in **Table 4**, the t_{50} values were obviously prolonged by the addition of bentonites in the CMC gel formulations. Among the formulations of the same bentonite/CMC ratio (1: 1), the highest t_{50} value was obtained for the release of 2,4-D from formulation GC2.0F2.0, corresponding to the highest sorption of 2,4-D on Fe-bentonite. The smaller t_{50} value for the herbicide release from formulation GC2.0N2.0 corresponds to the lower sorption on the original Na-bentonite.

Gel formulations with another bentonite/CMC ratio (2: 1) were prepared by mixing with organically modified bentonites. The release kinetics of 2,4-D from these formulations are shown in **Figure 4**. According to the curves, the release of 2,4-D from formulation GC1.5C₁₀₀3.0 is slower than that from formulation GC1.5C₆₀3.0. The same result may also be obtained by comparing the calculated values of t_{50} for the two formulations (see **Table 4**). The slower release from formulation GC1.5C₁₀₀3.0 corresponds to the higher sorption of 2,4-D on CTMA₁₀₀-bentonite, so it can be concluded that, in the bentonite/CMC gel formulations, the higher sorption of herbicide on bentonites results in a slower release of active ingredient (25). Similar results have also been reported by researchers using other clay/polymer matrices (14–18).

2,4-D Release in Water from Gel Formulations Mixed with Various Amount of Modified Bentonites. The influence of the amount of modified bentonites shall be investigated, considering the improvement on slowing herbicide release by adding them in gel formulations. **Figure 5** shows the release kinetics of 2,4-D from gel formulations mixed with the same modified bentonite Al-bentonite. The curve of formulation GC2.0A4.0 indicates a slower release of herbicide by adding a higher amount of Al-bentonite. The higher amount of bentonites used in preparing gel formulations results in the denser and more viscous suspension and, finally, the larger and heavier gel granules. This may be one reason for the slower release from formulation GC2.0A4.0, but another reason may be related to the sorption of 2,4-D on Al-bentonite.

Figure 6 shows the release kinetics of 2,4-D from gel formulations mixed with the same Fe-bentonite but with different bentonite/CMC ratios. The curve of formulation GC1.5F3.0 indicates a slower release of 2,4-D by using the

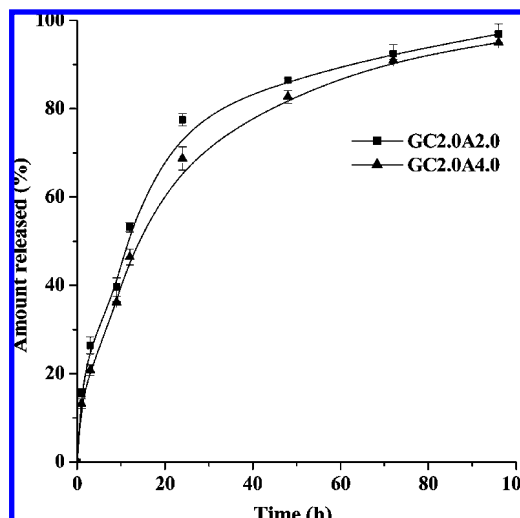


Figure 5. Release of 2,4-D from gel formulations mixed with various amount of Al-bentonite (error bars represent the standard deviation of triplicates).

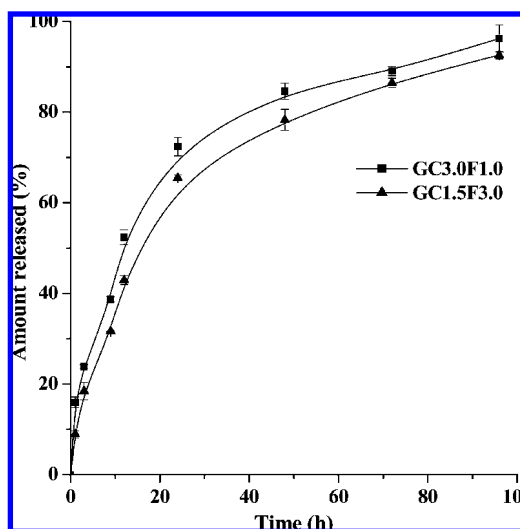


Figure 6. Release of 2,4-D from gel formulations mixed with various amount of Fe-bentonite (error bars represent the standard deviation of triplicates).

higher ratio of Fe-bentonite/CMC, and the same conclusion can be obtained by comparing the t_{50} values in **Table 4**. The formulations using the same Fe-bentonite can be ranked in order of increasing t_{50} values as follows: GC3.0F1.0 < GC2.0F2.0 < GC1.5F3.0, just the same as the ranking of increasing Fe-bentonite/CMC ratio from 1:3 to 2:1. The formulations using organically modified bentonite CTMA₁₀₀-bentonite have the same change of t_{50} values, which increased from 13.6 to 15.9 h with the increase of CTMA₁₀₀-bentonite/CMC ratio from 1:1 to 2:1. This may be explained by, in the bentonite/CMC gel formulations, the sorption interactions between bentonites and herbicide increasing with increasing amount of bentonites, which hinders the release of herbicide from such mixed matrices.

2,4-D Release in Soil from Polymer Gel Formulations. Herbicide release through a thin soil layer can be used to evaluate the herbicide's leaching potential when applied in field (27–29). **Figure 7** shows the 2,4-D release in soil from various gel formulations. The curves indicate slower release of herbicide 2,4-D in soil from the bentonite/CMC gel formulation (GC1.5F3.0) than from the pure CMC gel formulation (GC3.0).

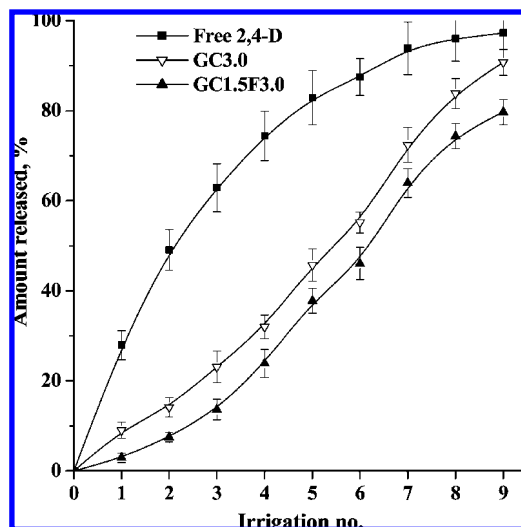


Figure 7. Release of 2,4-D from gel formulations in soil (error bars represent the standard deviation of triplicates).

This is consistent with the herbicide release in water from these formulations. In comparison, the release of free 2,4-D in soil was much quicker, and it was completely released through the soil layer within eight irrigations. The experimental results indicate that encapsulation of 2,4-D in CMC gel can control its release in soil, and addition of modified bentonite can further slow its release rate. This implies that the designed formulation could be useful for reducing the leaching of 2,4-D in soil.

In conclusion, the CMC gel can be used as a carrier for the controlled release of anionic herbicide 2,4-D. Addition of some modified bentonites in gel formulations can make the release slower, and the release rate in water changed when different amounts and types of bentonites were used. This formulation may be useful to reduce contamination due to the anionic herbicide and to improve the herbicide's efficiency on crop protection.

ABBREVIATIONS USED

CMC, carboxymethylcellulose; 2,4-D, 2,4-dichlorophenoxyacetic acid; CRF, controlled release formulation; CEC, cation-exchange capacity; CTMA, cetyltrimethylammonium; FTIR, Fourier transform infrared; HPLC, high-performance liquid chromatography.

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