

Carboxymethylcellulose/Bentonite Composite Gels: Water Sorption Behavior and Controlled Release of Herbicide

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ABSTRACT: The composite gels were prepared by adding bentonite or its acid-activated derivative into the carboxymethylcellulose (CMC) gel, and the resulted products were characterized with infrared spectroscopy. Different from ordinary swellable hydrogels, the CMC/bentonite hydrogel beads shrank in water. The water sorption of dried gels was limited below 120% of their own weight, and a sorption equilibrium reached quickly within 20–40 min. The water of swollen gels exists mainly in bound status according to the DSC analysis. The release experiments in water were carried out to evaluate the release of herbicide metolachlor from gel formulations. The release mech-

anism dominated by a Fickian diffusion might be related to the quick and limited swelling of dried gels. Addition of bentonites in CMC gel is beneficial for slowing the release of metolachlor, especially when the acid-activated bentonite was added. The time taken for 50% of metolachlor to be released, t_{50} was prolonged to 158 h for the composite gel formulation based on acid-activated bentonite from the 61.1 h for pure CMC gel formulation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 261–268, 2009

Key words: cellulose; clay; hydrogel; controlled release; herbicide

INTRODUCTION

Natural polymers are easily degradable and plentiful in resource, and used widely in many industrial fields. Through proper modifications, their derivatives can be used as carriers for the controlled release of agrochemicals, which can offer many advantages over conventional means of applications. The principal advantage is that the controlled release formulations (CRFs) can maintain the effective level of active ingredients for a longer period at a much less consumption of agrochemicals, so as to reduce the potential contamination of pesticides or fertilizers to the water system. Early reports showed that starch xanthate was applicable for encapsulating agrochemicals,^{1–3} and alginate gels have been reported as matrices for the controlled release of herbicides since decades ago.^{4–6} The cellulose derivatives were also used to encapsulate herbicide for its sustained release.⁷ Carboxymethylcellulose (CMC), a water-soluble cellulose derivative that is easily crosslinked in solutions of multivalent metal cations to produce hydrogels, is a practical carrier for pesticides.^{8,9} The swellable hydrogels prepared by graft-

ing crosslinked polyacrylamide chains onto CMC could control the release of fertilizer.¹⁰

The bentonite is a kind of layered clay mineral and composed primarily of montmorillonite. The bentonite has high specific surface area associated with its small particle size and can be used as adsorbent and carrier for many kinds of chemicals. Surface modifications can further improve its adsorption capacity to organic compounds, and the resulted products can be used to control the release of those organic agrochemicals in water.^{11–13} Addition of clays in the gel-forming alginate polymer can produce an excellent matrix for the controlled release of herbicides.^{14,15} In such a composite matrix, the polymer acts as a shaped carrier and clays as the adsorbent for herbicides, and their difference on chemical affinity make such matrix suitable for different herbicides with various structures and properties.

In this article, a new composite matrix for the controlled release of herbicides was prepared by adding bentonite or its acid-activated form into CMC gel. The water sorption behavior of these composite gels and their performance on controlling the release of herbicide metolachlor were investigated. The metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] is a selective pre-emergence herbicide widely used in irrigated crops. Because of its relatively high solubility in water (530 mg L⁻¹), the metolachlor has a high potential to leach and migrate through the soil profile and contaminate the ground water.

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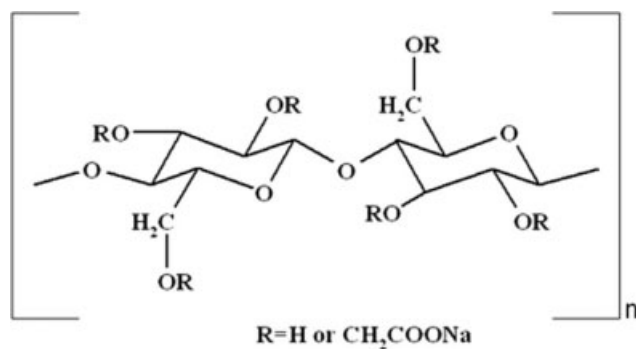


Figure 1 Chemical structure of Na-CMC.

EXPERIMENTAL

Materials

Food-grade Na-CMC (the chemical structure is shown in Fig. 1) was obtained from Suzhou Weiyi Chemicals of China. Its 2.0% (w/w) solution in water has a viscosity of 1250 ± 50 mPa s at 25°C, and its Na content is $8.6 \pm 0.15\%$ (w/w). The original bentonite used in this study was Na⁺-saturated bentonite (denoted as Na-bent) from Zhejiang, China. The Na-bent is chemically composed of SiO₂: 67.8%, Al₂O₃: 14.9%, Fe₂O₃: 1.3%, Na₂O: 2.3%, CaO: 1.5%, MgO: 1.9%, K₂O: 1.8%, and other residual minerals. Its cation-exchange capacity (CEC) was determined to be 55.3 ± 0.2 cmol kg⁻¹, with surface area 15.2 m² g⁻¹ (N₂-BET method). Technical grade herbicide metolachlor (96.2% pure) was purchased from Hangzhou Qingfeng Agrochemicals Co. Ltd., China. Other reagents used were all of analytical grade. HPLC-grade acetonitrile was purchased from Merck, and HPLC grade water was obtained using a Milli-Q system.

Preparation of acid-activated bentonite

The acid-activated bentonite (denoted as H-bent) was prepared by heating 10 g of Na-bent in 30 mL of 2.0M H₂SO₄ solution at 80°C for 2 h. Then the acid-activated sample was washed, centrifugally separated, and dried to constant weight (8.9 g). The dried H-bent sample was mechanically ground to less than 100 mesh (<0.15 mm in diameter) and heated at 115°C for another 2 h before use. The surface area (N₂-BET method) of H-bent was determined to be 30.5 m² g⁻¹.

Preparation of CMC/bentonite composite gels

The composite gels were prepared by adding bentonite samples in the 1.5%–2.5% (w/w) solution of Na-CMC in water and vigorously mixed into a viscous suspension (the compositions of suspensions

for various samples were listed in Table I). The mixture was dropwise added into a solution of 0.08M Fe(NO₃)₃ (the crosslinking agent) with a 5 mL injector. The hydrogel beads with diameter of 2.0–2.5 mm were obtained after 10 min. The hydrogels could be dried in an oven (40°C) to produce dried granular gels. The average size of dried gels was measured, ranged between 0.85–1.05 mm in diameter, and varied depending on the amount and type of bentonites used.

Fourier transform infrared spectral studies

Fourier transform infrared (FTIR) spectral data were taken on a Nicolet Nexus instrument to identify the formation of composite gels. For this purpose, the films of composite gels were prepared by mixing Na-CMC 0.5 g, Na-bent or H-bent 0.5 g, Fe(NO₃)₃ · 9H₂O 0.08 g, and distilled water 25 g into a uniform suspension, then the suspension is poured on a flat dish, followed by crosslinking and drying at 80°C in an oven. The film samples with thickness of 0.3–0.5 mm were used for the analysis of FTIR spectroscopy. The film sample of CMC gel crosslinked with Fe(NO₃)₃ was also prepared in the same way except that no bentonite was added in the suspension. The film sample of Na-CMC was prepared by drying on a flat dish and used for the comparison study. To characterize clearly the composite gels, the mechanically mixed powder of Na-CMC, H-bent, and Fe(NO₃)₃ · 9H₂O with a dosage as aforementioned was analyzed on a KBr disk. The FTIR spectra of Na-bent and H-bent were also obtained in the powder form on KBr disks. The spectral scanning was done in the range between 4000 and 675 cm⁻¹.

Shrinkage of hydrogel beads in water

The preweighed hydrogel sample (M_0) was immersed in deionized water, and then taken out at predetermined time intervals. The water on bead surface was wiped away using filter papers. The beads were weighed in an analytical balance (M_w).

TABLE I
Compositions of Suspensions for Preparing Gels

Gel sample	Bentonite type	Bentonite percentage ^a (%)	CMC percentage ^a (%)
CMC control	–	0	2.5
Na-bent 2.0	Na-bent	2.0	2.0
H-bent 1.5	H-bent	1.5	2.0
H-bent 2.0	H-bent	2.0	2.0
H-bent 3.0	H-bent	3.0	1.5

^a The balance is water.

Water sorption behaviors of dried gels

The water sorption of dried gels was measured by conventional gravimetric procedure. The preweighed sample (M_0) was immersed in deionized water, and the swollen gels taken out at predetermined time intervals, pressed gently in between two filter papers and weighed in an analytical balance (M_w). The water sorption was calculated by: Water sorption (%) = $(M_w - M_0) \times 100/M_0$.

Thermal analysis of swollen gels

The swollen gels were analyzed using differential scanning calorimetry (DSC) to investigate the water status in them. The analysis was carried out using a Perkin–Elmer Diamond apparatus under air atmosphere. Samples were put into aluminum pans and covered with lids. The conditions were as follows: heating rate, $10^\circ\text{C min}^{-1}$; temperature scanning range from 40 to -40°C .

Preparation of gel formulations of herbicide

The procedure for preparing the gel formulations of herbicide metolachlor was similar as that for preparing CMC/bentonite composite gels, except that the herbicide was added in the viscous suspension and accounted for the 2.5% of total suspension weight. The dried gel formulations were prepared for the release study.

Herbicide release study from gel formulations into water

The release of metolachlor from the gel formulations was monitored in water as described by previous reports.^{15,16} The dried gels containing 8 mg of metolachlor (active ingredient) were added to distilled water (300 mL) in stoppered conical flasks. Experiments were carried out in a thermostatic shaker bath at $25 \pm 0.1^\circ\text{C}$. At selected time intervals after herbicide application (3 h, 12 h, 24 h, 48 h, 96 h, 144 h, 216 h, 288 h, 360 h, 456 h, 552 h, 648 h), the solution of 1 mL was sampled, the metolachlor concentration was determined on an Agilent 1100 HPLC system equipped with an ultraviolet detector and HP Hypersil C18 column (150 mm \times 4.6 mm i.d., particle size 5 μm). The mobile phase used was an acetonitrile–water mixture (75 : 25, V/V) and the metolachlor analyzed at 218 nm. The retention time of metolachlor was 4.6 min when the flow rate of the mobile phase was kept at 1.0 mL min^{-1} . The amount of metolachlor in solution was calculated with the peak area. The sample solution was replaced with distilled water after each sampling operation, so as to keep the constant volume of the release system. The cumulative amount of metolachlor released at

different time interval (M_t) was calculated according to the metolachlor concentration in sample solutions.

After the last sampling, the residue amount of herbicide in gel formulations (M_r) was extracted with a methanol–water mixture (80 : 20, V/V) for three times, and the metolachlor concentration in the extractive solution was determined. Preliminary experiments confirmed the complete extraction of metolachlor from the gel formulations with above procedure. The cumulative amount of metolachlor released into solutions (M_t) plus the residue amount in gel formulations at the end (M_r) were considered as the total amount of metolachlor initially present in the gels (M_0). The cumulative percentage of metolachlor released at different time was calculated as $(M_t/M_0) \times 100\%$. The release kinetics was described as the cumulative percentage of metolachlor released at various time. For each gel formulation, metolachlor release kinetics was obtained in triplicates. The release kinetics were analyzed by applying the empirical eq. (1) proposed by Ritger and Peppas:¹⁷

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

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

RESULTS AND DISCUSSION

Characterizations of composite gels by FTIR spectroscopy

The infrared spectroscopy was used for identifying the formation of composite hydrogels. The FTIR spectra of original bentonite Na-bent, Na-CMC, crosslinked CMC gel, and composite gel of CMC with Na-bent are shown in Figure 2. The absorption at 3620 cm^{-1} , found in the spectrum of Na-bent [Fig. 2(a)], can be ascribed to the structural OH groups of bentonites. The broad band near 3448 cm^{-1} and the sharp peak at 1638 cm^{-1} indicate the bonded water in bentonite samples. The peaks at 1090 and 1043 cm^{-1} are characteristic of Si–O stretching vibrations of bentonites.¹⁸ The weak peak at 1458 cm^{-1} might result from the residual carbonates in the original bentonite sample. In the spectrum of Na-CMC [Fig. 2(b)], the peaks were observed at 1109 , 1058 , and 1030 cm^{-1} due to C–O stretching vibrations. Two strong peaks were observed at 1593 and 1415 cm^{-1} due to the asymmetrical and symmetrical stretching of $-\text{COO}^-$ groups. The broad band from 3200 to 3450 cm^{-1} belongs to the characteristic absorption of hydroxyl groups of CMC.¹⁹

There are a large number of carboxyl groups on CMC macromolecules, which can interact with

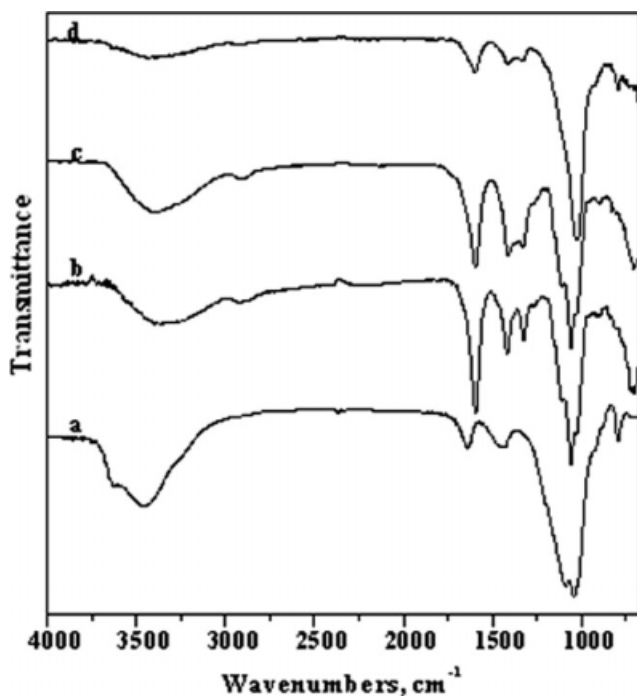


Figure 2 FTIR spectra of (a) Na-bent, (b) Na-CMC, (c) crosslinked CMC gel, and (d) composite gel of CMC with Na-bent.

multivalent cations such as Al^{3+} or Fe^{3+} to form a crosslinked network.²⁰ Figure 3 shows the scheme of crosslinking of CMC with Fe^{3+} cations. In this way, the water-soluble Na-CMC is transformed into an insoluble gel form. In the spectrum of crosslinked CMC gel [Fig. 2(c)], the two peaks at 1410 and 1328 cm^{-1} are overlapped by the peak at 1385 cm^{-1} due to the NO_3^- stretching vibration, and the NO_3^- may come from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the crosslinking agent.

In the spectrum of the composite gel of CMC with Na-bent [Fig. 2(d)], the absorption peaks of Si—O groups of Na-bent are overlapped with peaks of C—O groups of CMC, and form a strong band with peak value at 1030 cm^{-1} . The diminish of absorption at 1593 cm^{-1} indicates the reduced ratio of CMC in the composite gel in comparison with the pure CMC gel.

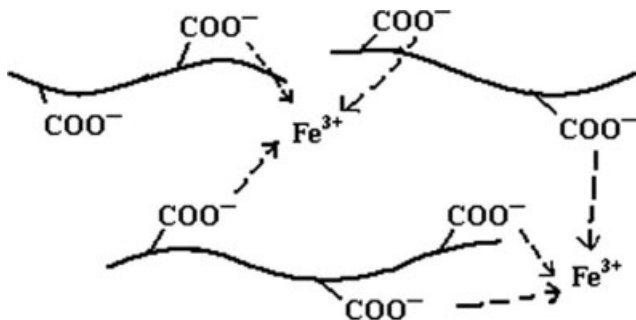


Figure 3 Scheme of crosslinking of CMC with Fe^{3+} cations.

The FTIR spectra of H-bent and its composite gel with CMC are shown in Figure 4. The spectrum of the mechanically mixed powder of CMC, H-bent, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is also included in Figure 4. In the spectrum of H-bent [Fig. 4(a)], the absorption peaks of Si—O groups moved at 1087 and 1045 cm^{-1} , the disappearance of weak peak at 1458 cm^{-1} indicates the purification of bentonite sample. The obvious difference on absorption profiles between Figure 4(b,c) confirms that the composite gel is not a simple mixture of CMC and bentonite. In the spectrum of the mixed powder of CMC and H-bent [Fig. 4(b)], the peaks at 1087 and 1045 cm^{-1} are still indicative of H-bent, and the sharp peak at 1385 cm^{-1} due to the NO_3^- stretching vibration is ascribed to the unreacted $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. But in the spectrum of the composite gel of CMC with H-bent [Fig. 4(c)], the absorption peaks of Si—O groups of H-bent are overlapped with peaks of C—O groups of CMC, and form a strong band with peak value at 1038 cm^{-1} . The spectral profile is similar as that observed in the composite gel of CMC and Na-bent [Fig. 2(d)]. In these spectra of composite gels, the strong overlapped bands may imply the interactions between CMC and bentonites.

Shrinkage of composite hydrogels in water

When the liquid mixtures of CMC and bentonites were added dropwise into the solution of Fe^{3+} cations, the hydrogel beads were formed immediately. Following the progress of crosslinking, the hydrogel

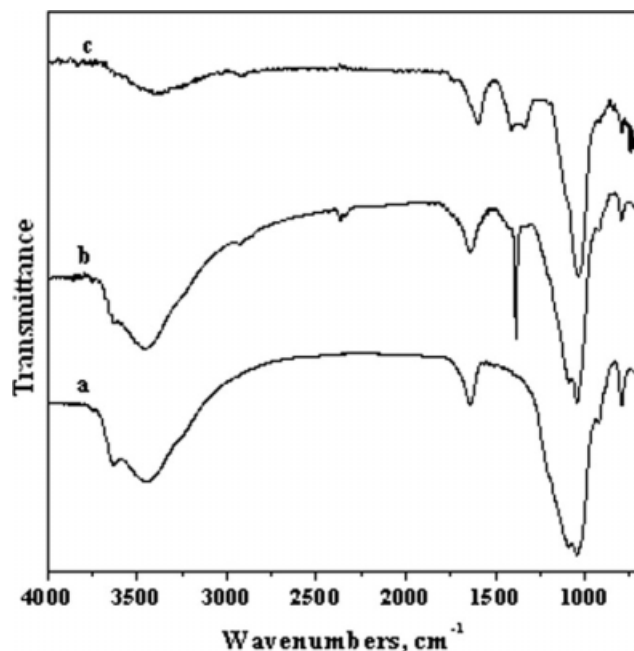


Figure 4 FTIR spectra of (a) H-bent, (b) mixture of Na-CMC, H-bent, and $\text{Fe}(\text{NO}_3)_3$, and (c) composite gel of CMC with H-bent.

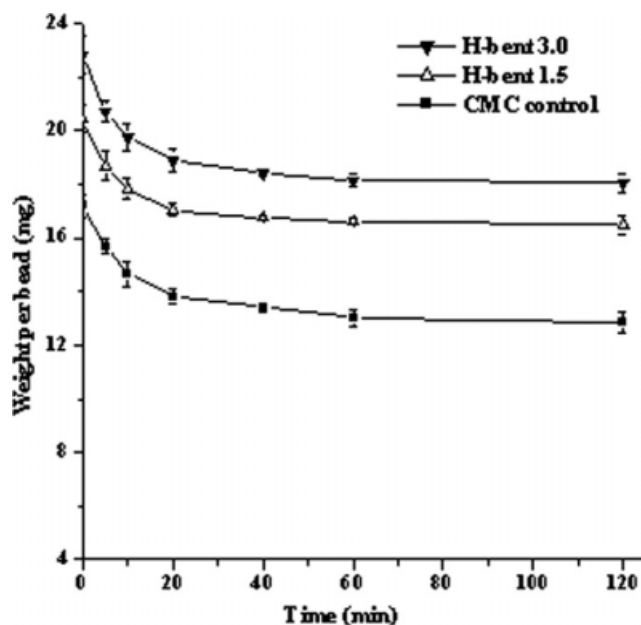


Figure 5 Change of weight per bead of various hydrogels in water (error bars represent the standard deviation of triplicates).

beads became smaller and lighter. The reason may be due to loss of free water in beads during crosslinking, and the water was compressed out by the tightening network formed with the penetration of Fe^{3+} ions into the beads. The hydrogel beads obtained after 10 min of crosslinking were put into the deionized water. Surprisingly no swelling was observed on the hydrogel beads, but instead a slight shrinkage was testified by weighing the beads at a specified time interval after immersing them in water. The change of average weight per bead of various hydrogels is shown in Figure 5. As can be seen, the average weight per bead is apparently reduced in the initial 30 min of immersion.

Such shrinkage is not ordinary for CMC hydrogels, for example, the physically entangled CMC hydrogels could swell in water by several times.²¹ In this research, the CMC-based hydrogels were fabricated by chemical crosslinking with multivalent cations. Different from physically entangled hydrogels, the chemically crosslinked hydrogels have irreversible network structures that constrain their swelling in water. The shrinkage may be resulted from the particular core-shell structure of hydrogel beads that could be observed through dissection. The shell is an elastic gel and the core still a viscous solution. The shrinkage might be explained by a suggested process as: when the core-shelled beads were put into the deionized water, the Fe^{3+} ions enriched in the shell might further penetrate slowly into the core, and more CMC macromolecules were crosslinked to form a thicker shell layer, which would

compress the free water in the core out and result in the reduced weight per bead.

Water sorption behavior of dried composite gels

The average weight each granule of dried gels was various between 2.0 and 2.6 mg depending on the amount and type of bentonites added. Generally the addition of bentonites to CMC gel led to heavier and larger granules. The water sorption process of various dried gels was shown in Figure 6. The sorption was very quick and reached the maximum at about 20–40 min, then the sorption equilibrium reached. The water sorption of pure CMC gel (CMC control) is limited below 120% because of the strong chemical bonds. The water sorptions of CMC/bentonite composite gels were lower than that of pure CMC gel, and the maximum value ranged from the 58% for Na-bent 2.0 gel to the 83% for H-bent 1.5 gel. The maximum water sorption of H-bent 3.0 gel was 56% (not shown in Fig. 6) and close to that of Na-bent 2.0 gel. The lower water sorption of composite gels may be explained by the higher hydrophilicity of CMC than bentonites.

DSC analysis of water in swollen gels

Generally, the bonding status of water sorbed in hydrogels can be analyzed with thermodynamic methods. Representative DSC cooling curves for the water-sorbed swollen gels based on various bentonites are shown in Figure 7. The cooling curve of Na-bent containing 40% of water [Fig. 7(a)] is also included for comparison.

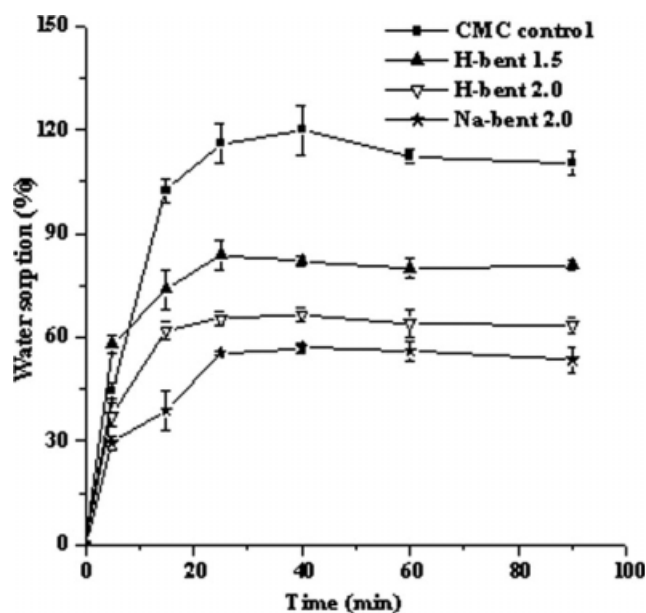


Figure 6 Water sorption of dried gels (error bars represent the standard deviation of triplicates).

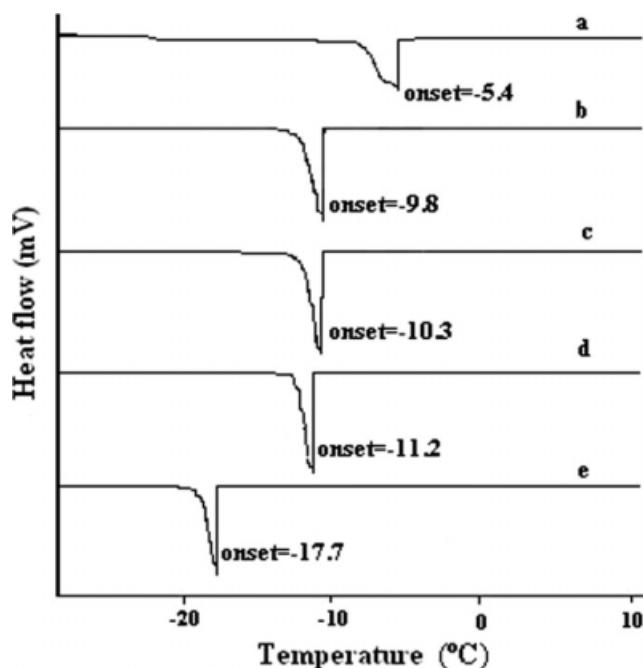


Figure 7 DSC cooling curves for (a) Na-bent powder and the swollen gels of (b) Na-bent 2.0, (c) H-bent 2.0, (d) H-bent 1.5, and (e) CMC control.

Hysteresis is observed for the freezing of water in every samples, and there is significant depression of the freezing temperature with $\Delta T = 5.4\text{--}17.7^\circ\text{C}$. It has been suggested that only nonfreezable water exists in the polymer network up to a certain percentage of water uptake before freezable water can be detected. Generally, there are two types of freezable water existing in the hydrogels: the freezable bound water and freezable water (free water).²² The existence of freezable bound water is often testified by a sharp peak on DSC curves, which appears at lower freezing temperature than pure water. The free water, if existed simultaneously, is displayed by another peak or a broad peak with shoulder on DSC curves.²³ According to the single-peaked cooling curves of CMC/bentonite composite gels, the water sorbed in these swollen gels exists mainly in a bound status. The largest depression of the freezing temperature was observed on the pure CMC gel ($\Delta T = 17.7^\circ\text{C}$), which confirmed the higher hydrophilicity of CMC than bentonites.

Release of metolachlor from gel formulations

The dried granular formulations prepared by encapsulating metolachlor into the composite CMC/bentonite gels were similar in appearance as the composite gels themselves. The encapsulation efficiencies of all samples were higher than 90%. The cumulative release of metolachlor from some gel for-

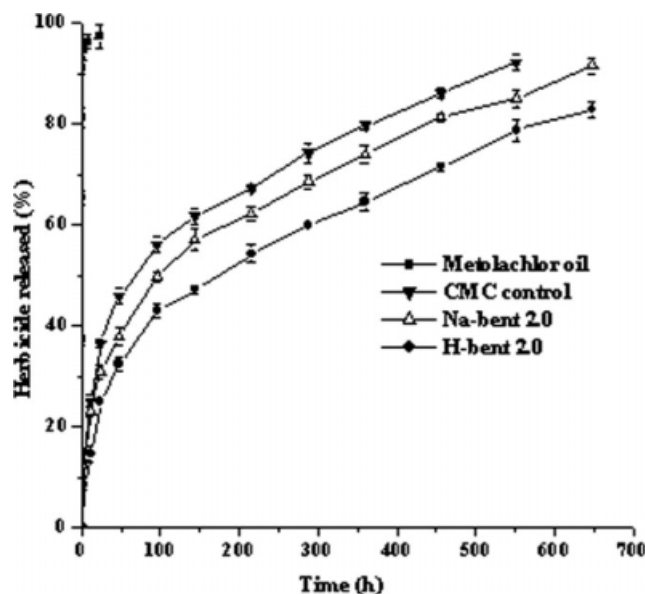


Figure 8 Release of metolachlor from gel formulations (error bars represent the standard deviation of triplicates).

mulations is shown in Figure 8. Compared with the commercial formulation of emulsible metolachlor oil (72%, w/w) (see the curve denoted as Metolachlor oil in Fig. 8), the release of metolachlor is distinctly slowed by encapsulated in gel formulations. A total of 95.0% of metolachlor is released from commercial formulation in less than 4 h, whereas at least 500 h is needed to release 90% of metolachlor from the gel formulations. Among these gel formulations, the release rate of metolachlor from pure CMC gel formulation (CMC control) is quicker than that from the composite Na-bent 2.0 gel formulation. Replacement of Na-bent with H-bent in the gel formulation can further slow the release of metolachlor (see the curve denoted as H-bent 2.0).

To further compare the difference on the release of metolachlor from different gel formulations, the release data were analyzed by applying the linear form of empirical eq. (1). The fitting results are presented in Table II. As can be seen from the values obtained for the correlation coefficients ($R \geq 0.99$), the release data fit well to the empirical eq. (1). The

TABLE II
Fitting Results of Release Data From Gel Formulations

Gel sample	K^a (h) ⁻¹	n^a	R^b	t_{50} (h)
CMC control	0.085 ± 0.002	0.43 ± 0.010	0.993	61.1
Na-bent 2.0	0.084 ± 0.002	0.39 ± 0.005	0.996	95.2
H-bent 1.5	0.066 ± 0.003	0.43 ± 0.009	0.990	113
H-bent 2.0	0.054 ± 0.004	0.44 ± 0.015	0.992	158
H-bent 3.0	0.076 ± 0.003	0.41 ± 0.016	0.994	103

^a These values are presented with standard errors.

^b Significant at the 0.001 probability level.

n values range from 0.39 for the Na-bent 2.0 gel formulation up to 0.44 for the H-bent 2.0 gel formulation. The n value close to 0.43 is characteristic for a Fickian diffusion of active ingredient from a spheric carrier.¹⁷ That means the release of metolachlor from CMC/bentonite composite gels is mainly controlled by a mechanism of Fickian diffusion. In swellable matrices for the controlled release of drugs, the polymer relaxation plays an important role on the release mechanism, which often leads to a higher n value even close to 1.^{22,24} For our CMC/bentonite composite matrices, the gel carriers swelled by very limited ratios (<2.2) and the swelling completed quickly as indicated in Figure 6. In this controlled release system, the time taken for gel relaxation (20–40 min) is much shorter than the release process of herbicide (>550 h), so the polymer relaxation or swelling of gels has little effect on the release.

The time taken for 50% of metolachlor to be released, t_{50} , can be calculated from K and n constants in empirical eq. (1), and often used to evaluate the performance of CRFs.^{11,15} As can be seen in Table II, the t_{50} values range from 61.1 h for the pure CMC gel formulation to 95.2 h for the Na-bent 2.0 gel formulation, and then to 158 h for the H-bent 2.0 gel formulation. This indicates that the addition of bentonites is beneficial to slow the release of herbicide from CMC gel, especially when the acid-activated bentonite (H-bent) was used. The performance of bentonites on slowing the release of herbicide can be associated with their adsorption capacity.^{11,16,25,26} The isothermal adsorption experiments in water confirmed that Na-bent could adsorb a certain amount of metolachlor. The utmost adsorption of metolachlor on Na-bent was estimated to be 29.5 mg g⁻¹ by fitting the adsorption data with Langmuir equation. The acid activation of bentonite leaches out inorganic ions in the octahedral sheet, resulting in numerous acid centers on the bentonite surface. The metolachlor, a weak basic herbicide, could be adsorbed on the acid-activated H-bent by the formation of acid–base pairs. The experimental results of N₂-BET adsorption also showed that the activated bentonite had apparently increased surface area (30.5 m² g⁻¹ for H-bent) compared with the original bentonite (15.2 m² g⁻¹ for Na-bent), which provide more space for the adsorption of herbicide. All these factors are in favor of the H-bent's performance as adsorbent for metolachlor. The utmost adsorption of metolachlor on H-bent was estimated to be 42.6 mg g⁻¹ by isothermal adsorption experiments, higher than that on Na-bent. When the bentonites were added in CMC gel formulations of herbicide, the release of herbicide was constrained by the adsorption on bentonite. The higher adsorption capacity of herbicide on bentonites results in a slower release of herbicide from formulations based on bentonites.

In the pure CMC gel formulation, hydrogen bonds play a very important role for the interaction between metolachlor and the carrier. The numerous hydroxyl groups on cellulose macromolecules can act as proton donors for hydrogen bonds, and the oxygen atoms of metolachlor as acceptors. The herbicide may also be associated with CMC macromolecules through other weak intermolecular actions. So that pure CMC gel itself is also capable for controlling the release of herbicide metolachlor. When the ratio of CMC/H-bent used in the gel formulations was changed, the release rate of metolachlor was also changed. For example, at the same amount of CMC used in formulations, when the amount of H-bent was reduced, the t_{50} for the release of herbicide declined from the 158 h for H-bent 2.0 gel formulation to the 113 h for H-bent 1.5 formulation (see Table II). But when the amount of CMC used in gel formulations was reduced (see the H-bent 3.0 gel sample in Table I), the t_{50} for the release of herbicide is also shortened to 103 h in comparison with the 158 h for H-bent 2.0 gel formulation (see Table II). This means that the adequate amount of CMC in composite gels is important for achieving good performance on controlling the release of herbicide.

CONCLUSIONS

The new CMC/bentonite composite gels were prepared by crosslinking with Fe³⁺ cations, and characterized with FTIR spectroscopy. The composite gels have low water sorption capacity, and the swelling equilibrium is quickly reached within 40 min, so the water sorption process has little effect on the release of herbicide from these gels. Experimental results indicated that the composite gels could be an useful carrier for the controlled release of herbicide metolachlor. The inclusion of proper amount of acid-activated bentonite in the CMC gel provided the best performance on controlling the release of herbicide.

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