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Environmental Effects of Inclusion Complexation between Methylated β-Cyclodextrin and Diclofop-methyl

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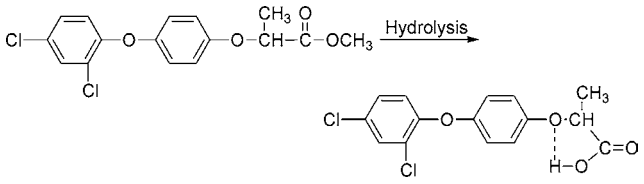
Diclofop-methyl (DM) is a broad-spectrum herbicide but often shows a reduced biological activity against the target grasses due to its poor water solubility and slow translocation within plant tissues. Randomly methylated β-cyclodextrin (MCD) is an effective inclusion complexation agent and, as a potential formulation additive, may thus improve the behavior of DM. We evaluated the complexing role of MCD by measuring the solubility and soil sorption of DM as a function of MCD concentration, as well as the dissolution rates of DM−MCD complexes. The complex was also extensively characterized by UV, fluorescence, Fourier transform infrared, nuclear magnetic resonance, and differential scanning calorimetry techniques. The apparent solubility of DM linearly increased with MCD concentration, indicating the formation of a 1:1 complex. In contrast, diclofop was not complexed by MCD. The DM−MCD complex appeared to have formed within the hydrophobic cavity of MCD. With the measured stability constant of 4740 L mol^{-1}, the complex was apparently stable, which resulted in DM resistant to hydrolysis, and hence the ratio of DM to the sum of DM and diclofop increased toward unity with increasing MCD concentration. The DM−MCD complex also quickly dissolved to a maximum within 5 min, due presumably to the hydrophilicity of MCD. The sorption of DM by soil was significantly reduced in the presence of MCD. All the results suggest that MCD may effectively improve the availability of DM to pests and for bioremediation.

KEYWORDS: Diclofop-methyl; inclusion complexes; MCD; solubility; sorption

INTRODUCTION

Diclofop-methyl {methyl 2-[4-(2,4-dichlorophenoxy) phenoxy] propionate, DM} is a postemergence herbicide registered by Farbwerke Hoechst AG for annual grass control in a variety of cereal, oil seed, and legume crops. Laboratory experiments and field studies have shown that in the presence of water pure DM hydrolyzes rapidly to diclofop, the acid form of DM (*1*−*4*):



The two chemicals differ in water solubility, mobility, and herbicidal activity. DM has a very low water solubility (3.0 mg L^{-1} at pH 7 and 25 °C), low mobility in soil, and low herbicidal activity (*5*), whereas diclofop has a comparatively higher solubility (23 mg L^{-1} at pH 7 and 20 °C), slight-to-moderate mobility, and stronger herbicidal activity. Currently, commercial DM is formulated as an emulsifiable concentrate to enhance its solubility and, more importantly, to chemically stabilize it in the form of DM, as its hydrophobic nature facilitates movement into target grasses through cuticles. DM is then rapidly converted to diclofop within the cells where it inhibits acetyl-CoA carboxylase for fatty acid synthesis to block the production of phospholipids.

Widespread use of pesticides has been a constant environmental concern. As both DM and diclofop are herbicidal, their environmental availability is of great interest. DM runoff and spray drift may be harmful to nontarget grasses, sedges, and aquatic plants. The herbicide also poses a potential risk of reproductive toxicity to mammals (*6*). Worse than all, DM is suspected of endocrine disrupting and diclofop is a peroximose proliferator that belongs to the group of nongenotoxic carcinogens and/or tumor promoters (*7*). Previous study indicated that, in four soils aerobically incubated, DM and diclofop degraded with estimated half-lives of 21 to 51.3 days (*1*). Diclofop appeared to undergo an increasing bounding or complexing to the soils, from which it could be liberated only by treatment with hot alkali. When DM was in soil, most of the bound

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residues were identified as diclofop, with only small fractions being DM (*8*).

Pesticides are formulated not only to improve their efficacy to pests but also to reduce the environmental risk associated with overdosing. While current formulation additives are chosen primarily on the basis of their ability to improve physicochemical properties of pesticides in, for example, solubility, bioavailability, soil sorption, and leaching (*9*), their environmental consequences should also be taken into consideration. In this regard, cyclodextrins (CDs) derived from natural starches seem promising, as they are biodegradable and nontoxic, harmless to microorganisms, and hence environmentally friendly (*10*). CDs are a group of cyclic oligosaccharides with a hydrophilic nature (the solubility of β-cyclodextrin, for example, at 25 °C is 18.8 g L^{-1}) but contain doughnut-shaped hydrophobic cavities. Random methylation of CDs further enhances their water solubility (*11*). These structural features allow size- and polarity-based selective formation of soluble inclusion complexes between methylated CDs and a variety of synthetic pesticides to improve their solubility. As to DM, the inclusion complexation may offer additional advantages over conventional additives by stabilizing its ester form and inhibiting hydrolysis. Addition of methylated CDs may thus result in a homogeneous delivery of DM formulations to target grasses and an increased herbicidal effectiveness.

The aim of this study was to confirm and characterize the formation of DM-methylated β-CD (MCD) inclusion complexes by phase-solubility determination and UV and fluorescence spectrometry, as well as Fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (NMR), and differential scanning calorimetry analysis (DSC) techniques. The DM−MCD inclusion complexes were prepared by kneading, heating, and colyophilization techniques. Their dissolution rates were also measured to examine their immediate availability. The second aim of this study was to investigate the effect of MCD on the sorption of DM in relation to its soil mobility, environmental availability, and in turn the environmental friendliness of CD-based formulations.

MATERIALS AND METHODS

Materials. Technical formulation DM was kindly supplied by Ningbo Jiema Chemical Engineering Co., Ltd., and further purified to a purity of ≥98% by column chromatography with silica gel as stationary phase and petroleum ether as mobile phase. Diclofop and MCD were prepared according to previous studies (*11*, *12*) and identified by HPLC-ESI-MS and ^{13}C NMR/^{1}H NMR.

Six methods were used for the preparation of DM−MCD solid inclusion complexes. Based on the phase-solubility analysis that indicated a 1:1 stoichiometric ratio for DM−MCD inclusion complexes (data shown later), equimolar DM and MCD were used. Samples of physical mixing (PM), kneading (KN), and sealed-heating (SH) were prepared according to Mura et al. (*13*). A kneaded-heating sample (KH) was obtained by adding appropriate CH_2Cl_2 to KN, followed by heating and grinding. A solution-inclusion sample (SI) was obtained by dissolving equimolar DM and MCD in CH_2Cl_2 for 2 weeks at 20 °C, evaporating at <37 °C, and grinding gently. A colyophilized sample (COL) was prepared by prechilling the CH_2Cl_2 solution of mixed MCD and DM for 24 h in a −20 °C freezer and colyophilizing for 24 h in a −40 °C freezer. All the samples were sieved to collect the <500-μm fractions.

HPLC. HPLC analyses were performed using a chromatographic system of American Spectra-Physics, equipped with Spectra 100 UV−vis detection and YWG C_{18} reversed-phase column (4.6 × 250 mm; Dalian Elite Analytical Instruments Co., Ltd., China). The mobile phase of 85% methanol and 15% water, in which the DM−MCD complex dissociated, with pH preadjusted to 3.1 by phosphate acid was used to elute DM and diclofop. The flow rate was 1 mL min^{-1}, and λ was set at 280 nm.

Phase Solubility. Solubility measurements were carried out in duplicate using the Higuchi and Connors method (*14*). Briefly, DM (25 mg) was added to 10 mL of aqueous solutions in glass tubes containing various concentrations of MCD ranging between 0 and 10 mmol L^{-1}. The tubes were sealed and shaken in the dark at 20 °C for 5 days. Half of each of the solutions was then filtered through 0.45-μm membrane filters and analyzed on a UV spectrophotometer at 280 nm. The presence of MCD was not found to interfere with the detection. To study the stability of DM in MCD solutions, the remaining solutions were further shaken for 21 days and analyzed for diclofop on HPLC. The 21-days shaking was sufficient that the concentration of diclofop no longer increased. No chemicals other than DM and diclofop were detected.

UV and Fluorescence of DM−MCD Inclusion Complexes. A 10- or 100-μL aliquot of the DM stock solution prepared in methanol (5000 mg L^{-1}) was added to each of four graduate tubes (total of eight tubes). To half of the tubes was added 1 mL of 3.49×10^{-3} mol L^{-1} of MCD solution to prepare the DM−MCD inclusion complexes. This design resulted in each of the samples in duplicate. All the tubes were filled with deionized water to bring the total volume to 25 mL, sealed with glass stoppers, well mixed, and kept in the dark at 20 °C for 5 days. The nominal concentration of DM was thus 2 or 20 mg L^{-1} and that of MCD was 1.4×10^{-4} mol L^{-1}. DM in all the tubes was then analyzed on HPLC as well as UV and fluorescence spectrophotometers. Tubes containing MCD or DM alone were also prepared as controls. No effect of methanol was found.

The UV spectra of DM were collected on a Shimadzu UV-2401 PC (scan speed, fast; slit width (nm), 1.0; sampling interval (nm), 0.5), and the fluorescence spectra were obtained on a Hitachi F-2500 fluorescence spectrophotometer (EX slit, 10.0 nm; EM slit, 10.0 nm; PMT voltage, 400 V).

FTIR, ^{1}H NMR, and DSC. The FTIR spectra were recorded using a Shimadzu 8900 spectrometer between wavenumbers of 400 and 2000 cm^{-1}. Samples were prepared as KBr disks. The NMR spectra were recorded using a Bruker Advance 400/500 DMX spectrometer (Switzerland) with working frequencies of 500 mHz. Samples were prepared in $CDCl_3$. Thermal analysis of DSC was carried out using a DSC Q100 equipped with an aluminum pan. The heating rate was 10 °C/min over the temperature range from 30 to 280 °C.

Dissolution Rates. The DM dissolution rates of the DM−MCD inclusion complexes were determined in deionized water at room temperature using the dispersed amount method. Each complex sample (total 72.7 mg or 15.6 mg of DM alone) was weighed into a 1000-mL beaker containing 500 mL of deionized water; the mixture was stirred with a magnetic stirrer. At various sampling times, aliquots were withdrawn, filtered through 0.45-μm membrane filters, and analyzed by HPLC for DM concentration at 280.0 nm.

Effects of MCD on Sorption of DM. Sorption measurements were conducted by weighing 2.0 g of a soil (% OC = 2.12) into glass tubes. The tubes were divided into four groups, with each group consisting of five tubes in triplicate, for different sorption schemes as follows: (first group) 25 mL of $CaCl_2$ solution; (second group) 1 mL of 3.49×10^{-3} mol L^{-1} MCD solution plus 24 mL of $CaCl_2$ solution; (third group) 1 mL of deionized water in each tube to prewet soil for 24 h, followed by 24 mL of $CaCl_2$ solution; (fourth group) 1 mL of MCD solution for soil to presorb MCD for 24 h, followed by 24 mL of $CaCl_2$ solution. The initial DM concentrations for each group were 0, 0.8, 1.6, 3.0, and 4.0 mg L^{-1}. All the tubes were shaken at 25 °C. At predetermined times, 10 mL of suspension from each tube was centrifuged; the supernatant was filtered through a 0.45-μm Nuclopore filter. The first 3 mL of filtrate was discarded, and the next 2 mL was collected for solution-phase DM analysis by HPLC. The sorbed DM was calculated by the following equation:

$$X/m = (C_0 - C_{AW})V_{STDS}/S \quad (1)$$

where X/m (μg g^{-1}) is the amount sorbed, C_0 (μg mL^{-1}) is the initial concentration in the liquid phase, C_{AW} (μg mL^{-1}) is the concentration

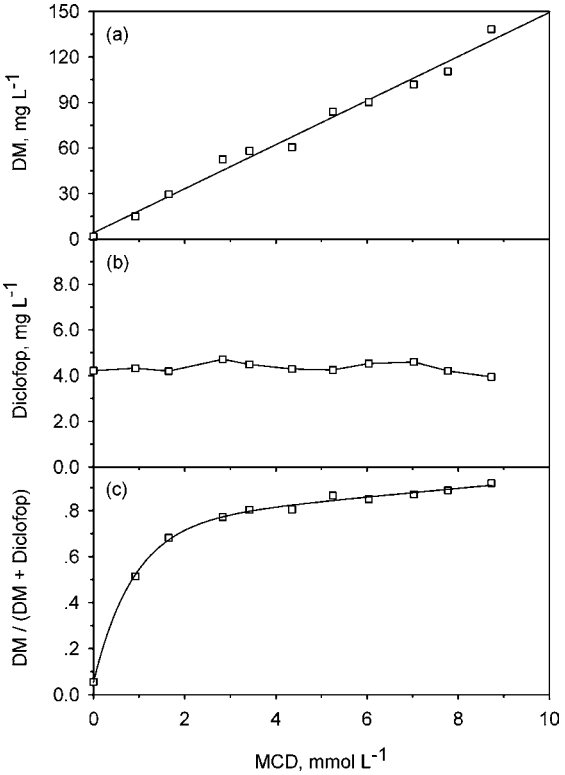

Figure 1. Phase-solubility diagram of DM in MCD-containing solutions: (**a**) effect of MCD on DM solubility; (**b**) effect of MCD on diclofop solubility; (**c**) ratio of DM to DM + diclofop as a function of MCD concentration.

in the liquid phase at given sampling time, V_{STDS} (mL) is the volume of the liquid phase (25 mL), and S (g) is the weight of soil (2.0 g).

RESULTS AND DISCUSSION

Phase Solubility. The solubility of DM in water increased linearly as a function of MCD concentration (**Figure 1a**). According to Higuchi and Connors (*14*), the phase-solubility curve of DM in the MCD solutions was classified as type A_L, indicating the formation of 1:1 inclusion complex over the tested MCD concentration range. The apparent stability constant for DM−MCD inclusion complex ($K_{1:1}$) can be calculated using

$$K_{1:1} = \text{slope}/S_0(1 - \text{slope}) \quad (2)$$

where S_0 is the solubility of DM in pure water. The determined apparent stability constant of 4740 L mol^{-1} suggests a strong affinity between DM and MCD in water and the high stability of the complex.

In contrast, the determined concentration of diclofop in water was 4.2 mg L^{-1} after 21 days in the absence of MCD and remained relatively constant between 4.0 and 4.5 mg L^{-1} in the presence of various concentrations of MCD (**Figure 1b**). The difference in diclofop concentration was not statistically significant ($P = 0.05$). This suggests that diclofop did not form an inclusion complex with MCD. This is due presumably to the relatively hydrophilic nature of diclofop that reduced its interaction with the hydrophobic cavity of MCD. Similar results have been reported with 2,4-D that the apparent stability constant for 2,4-D-(hydroxypropyl-β-CD) (HP-β-CD) complex was 98.6 L mol^{-1} (*15*), only about 1/50th of that of DM−MCD complex.

The high degree of complexation for DM and the lack of it for diclofop resulted in an enhanced proportion of DM in the solution in the presence of MCD, as illustrated in **Figure 1c** as the ratio of dissolved DM to the sum of DM and diclofop. The ratio showed an asymptotic increase in approach to unity with increasing MCD concentration. The increase in the ratio and the constant diclofop concentration over the tested MCD concentration range suggest that complexed DM was resistant to hydrolysis and MCD may thus be adequate as the formulation additive for DM.

Table 1. Influence of MCD on UV and Fluorescence Spectra of DM

	DM (2 mg L^{-1})	DM (2 mg L^{-1}) + MCD	DM (20 mg L^{-1})[a]	DM (20 mg L^{-1}) + MCD[b]
Λ_{max}[c]	276	277	276	283
Abs[d]	0.0293	0.0419	0.0697	0.1060
λ_{Ex}[e]	292	290.5	292	292.5
λ_{Em}[f]	351	351.5	350.5	350.5
FI[g]	235.5	149.8	250.1	309.2

[a] The dissolved concentration of DM was 3.20 mg L^{-1}. [b] The dissolved concentration of DM was 7.08 mg L^{-1}. [c] The maximum absorption wavelength (nm). [d] The absorbance at maximum absorption wavelengths (nm). [e] The maximum excitation wavelengths (nm). [f] The maximum emission wavelengths (nm). [g] The fluorescence intensity at corresponding maximum excitation/emission wavelengths.

UV Spectra of DM. When the nominal concentration of DM was 2 mg L^{-1}, the addition of MCD did not result in a significant change in the UV absorption spectrum of DM between 200 and 350 nm (**Table 1**). The differences between the experimentally recorded spectrum using pure DM and the calculated spectrum by subtracting the spectrum of MCD from that of MCD + DM did not exceed experimental error of about 3 absorbance units (±0.0045). However, the maximum absorption wavelength was shifted from 276 nm (DM) to 277 nm (DM + MCD). When the nominal concentration of DM was increased to 20 mg L^{-1}, the maximum absorption wavelength in the presence of MCD was further shifted to 283 nm. Together with the HPLC analysis that indicated 7.08 mg L^{-1} of dissolved DM in the solution in the presence of MCD in comparison to 3.20 mg L^{-1} in the absence of MCD, these results suggest the formation of the DM−MCD inclusion complex.

Fluorescence Spectra of DM. MCD had notable influences on the fluorescence spectra of DM. At the nominal DM concentration of 2.0 mg L^{-1}, the measured reference fluorescence intensity of DM at the maximum excitation/emission wavelengths of 292/351 nm was 235.5 units. The addition of MCD shifted the respective maximum wavelengths to 290.5/351.5 nm. At these wavelengths, the fluorescence intensity of the DM in the presence of the MCD was only 149.8 units, ∼64% of the reference value, as compared to ∼81% in the absence of MCD (pure DM) obtained in a separate measurement. These results illustrate that the formation of the DM−MCD inclusion complex contributed significantly to the variation in DM fluorescence spectrum, although the changes in the characteristics of MCD-containing solution such as refractive index, dielectric constant, and viscidity arising from solubility enhancement and the complex formation may also have been partially responsible. The maximum excitation/emission wavelengths were 292/350.5 nm at the nominal DM concentration of 20 mg L^{-1} with the measured dissolved DM concentration of 3.2 mg L^{-1}. These wavelengths were shifted to 292.5/350.5 nm when MCD was added where the dissolved DM concentration was 7.08 mg L^{-1}. These results reveal that the chromophores of DM moved near to or entered the hydrophobic cavity of MCD and that their quantum yield was greatly reduced. The shift in the maximum wavelengths also suggests that DM was included in MCD, bringing about the observed changes in the microenvironment of its chromophores.

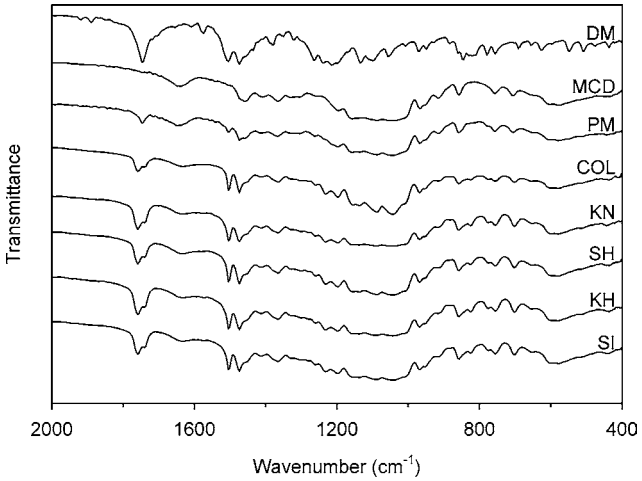

Figure 2. FTIR spectra of DM, MCD, and DM–MCD inclusion complex samples prepared by six methods.

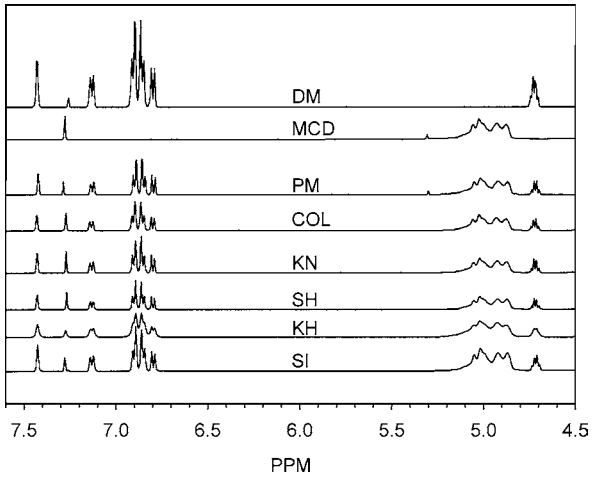

Figure 3. ^{1}H NMR spectra of DM, MCD, and DM–MCD inclusion complex samples prepared by six methods.

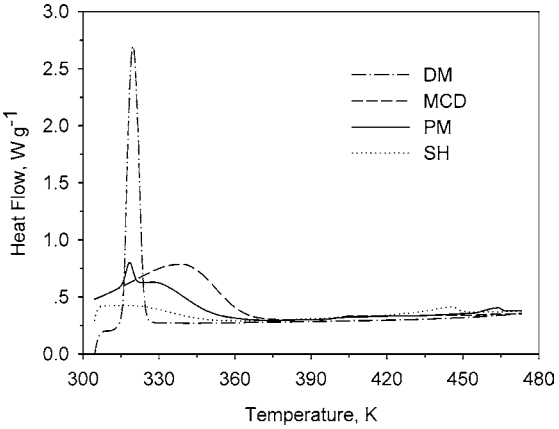

Figure 4. DSC thermograms of DM, MCD, physical mixture (PM), and SH inclusion complex.

FTIR. Figure 2 is the FTIR spectrum of pure DM, with the band(s) at 1747 cm^{-1} assigned to the carbonyl stretching of DM carboxyl ester, at 1365 and 1407 cm^{-1} to the methyl winding vibration, at 1238 cm^{-1} to the ether asymmetrical stretching, at 655 cm^{-1} to the aromatic phenyl ring wag, at 1041−1087 cm^{-1} to the aromatic C−Cl stretching vibration, and at 829−856 and 856−906 cm^{-1} to the single and adjacent hydrogens of the phenyl ring. The characteristics of the ester carbonyl stretching band (1747 cm^{-1}) of DM in PM appeared unchanged, indicating that physical mixing of solid DM, and MCD did not result in obvious direct interactions between the two. However, this band was shifted to higher frequency for the inclusion complex obtained by all of the other five methods. Furthermore, a new band at 1740 cm^{-1} appeared with the complex-containing samples and may be attributed to inclusion complexation within the cavity of MCD. The shift of the band corresponding to the methyl winding vibration from 1407 to 1411 cm^{-1} suggests the structural change of the methyl group, arising likely from new hydrogen bonding between the carbonyl of DM and the -OH of MCD. These observations are consistent with those reported by Mura et al. (*13*) who characterized the complexes of ketoprofen with β-CD and MCD.

^{1}H NMR. The ^{1}H NMR spectra show obvious chemical shift associated with DM methenyl structure in the samples of COL, KN, SH, KH, and SI, as compared to pure DM and the PM sample (**Figure 3**). The shift suggests that the methenyl structure of DM was most likely located at the entrance of the MCD cavity or entered the cavity. Some changes in the secondary structures of DM in SI, SH, and KH may have also occurred, as indicated by the bands at 6.80, 7.14, and 7.44 ppm (corresponding to chemical shifts of hydrogens of DM aromatic rings) with new splitting bands appeared and/or the characteristic splitting bands disappeared. These results are in agreement with the UV and fluorescence analyses. The relatively small changes in the chemical shift of DM observed here may be due to the overlapping effect of uncomplexed (free) DM and MCD. The solvent ($CDCl_3$) apparently competed with DM for the MCD cavity, which may have reduced the amount of DM−MCD complex formed. The solvent may have also made more labile the complex in which DM was only partially included and thus readily released.

DSC. Liberation of crystal water from amorphous MCD was observed as an endothermic effect and peaked at about 66 °C (**Figure 4**). The thermogram of DM showed a characteristic single endothermic fusion peak at about 47 °C. The endothermic fusion of DM maintained its main characteristics in the physical mixture (PM), although the thermogram was not a simple addition of those of DM and MCD. The inclusion complexation may have occurred during the analysis, due likely to the melting of the chemicals. Weaker dehydration of MCD in PM also suggests a lower amount of water in the cavity of MCD when DM was present. Disappearance of both DM peak and the MCD dehydration effect in SH indicates the formation of DM−MCD complex in the MCD cavity, where water molecules originally resided (*16*, *17*). Similar DSC results were obtained for the complexes of ketoprofen with β-CD and MCD by Mura et al. (*13*).

Dissolution Rates. Due to its hydrophobicity, DM is poorly soluble in water. The measured concentration of DM by itself in deionized water was only 0.28 mg L^{-1} 2 h after mixing (**Figure 5**). In contrast, the dissolved DM concentration reached the maximum (∼5 mg L^{-1}) 0.5 min after mixing PM in water and was 29.8 times higher than DM alone in deionized water. The large increase in apparent DM solubility indicates the rapid formation of soluble DM−MCD inclusion complex in water, due primarily to the great hydrosolubility of MCD and its high amorphizing, wetting, solubilizing, and complexation power toward DM (*14*). Under the same conditions, the apparent solubility of DM at 0.5 min was 65.2 times (KN), 87.1 times (KH), 74.5 times (SH), 74.6 times (SI), and 74.1 times (COL) that of DM alone. The apparent solubility of DM 0.5 min after dissolving these complex samples was also much higher as compared to the PM sample. The high preparation temperatures

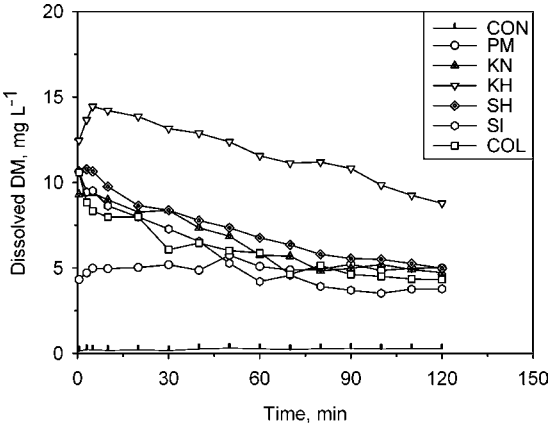

Figure 5. Dissolution of DM from DM–MCD complex samples prepared by different methods.

may have resulted in the greater-than-normal amounts of DM in the five complex samples. Slow decreases in apparent solubility with time suggest the release of DM from the complex samples toward 1:1 stoichiometry in DM−MCD.

Effects of MCD on Sorption of DM. Sorption of DM depended on its initial concentration, the contact time, and the treatment that the soil received prior to the sorption (**Figure 6**). The kinetics of DM sorption followed a biphasic model in which the sorption is described as an initially rapid process followed by a slow phase. The rapid process occurred within the first 30 min with 64.5−71.3% of the total DM sorbed from $CaCl_2$ solution, 25.4−31.7% from MCD solution, 48.9−57.6% from $CaCl_2$ solution with the soil prewet by water, and 34.7−39.8% from $CaCl_2$ solution with MCD presorbed on the soil. For the slow sorption, only 3−10% of the total DM was sorbed during the next 90 min for all the treatments. More DM remained in solution when MCD was added to the solution or presorbed on the soil than without MCD treatments. Prewetting of soil had little influence on sorption with two initial DM concentrations (1.6 and 3.0 mg L^{-1}) but reduced sorption with two other concentrations (0.8 and 4.0 mg L^{-1}).

To determine the effect of MCD on the sorption of DM, the sorption was assumed to have reached quasi-equilibrium after 30 min. All the sorption data collected after 30 min with four initial DM concentrations for each scheme were fit to the following Freundlich equation

$$\log X/m = \log K_f + (1/n)\log C_{AW} \quad (3)$$

where X/m is the amount of DM sorbed at its equilibrium concentration of C_{AW}, K_f is the Freundlich constant, and $1/n$ describes the degree of isotherm nonlinearity with unity indicating linear isotherms. The fitting parameters are listed in Table 2, in which K_{OC} was calculated from K_f divided by the organic carbon content of soil.

Table 2. the Freundlich Parameters for DM Sorption

	sample no.	R^2	$1/n$	K_f	K_{OC}
1[a]	12	0.965	1.410	23.684	1117
2[b]	12	0.975	1.226	5.056	238
3[c]	12	0.948	1.002	10.313	486
4[d]	12	0.992	1.004	7.974	376

[a] Sorption in 0.01 mol L^{-1} $CaCl_2$ solution. [b] Sorption in $CaCl_2$ solution containing 1.4×10^{-4} M MCD. [c] Sorption in $CaCl_2$ solution with soil prewet for 24 h. [d] Sorption in $CaCl_2$ solution with MCD–presorbed soil.

With $1/n > 1.0$, the DM sorption from $CaCl_2$ solution exponentially increased as the initial concentration increased. The nonlinearity of the isotherm suggests that DM competed against water for active adsorption sites of soil. Prewetting effectively eliminated such sites and thus adsorptive competition, as indicated by the $1/n$ value of about 1.0 with the prewet soil and the K_{OC} value decreasing from 1117 to 486. With a K_{OC} of 376, presorbed MCD appeared to better suppress the DM sorption. However, the role of MCD as suppressant of DM sorption may suffer from its complexation ability. Alternatively, MCD can be directly dissolved in solution for complexation and solubility enhancement. With the K_{OC} value of 238, it is clear that solution-phase MCD more effectively reduced the DM sorption. As such, DM would be highly mobilized in soil, which would increase its leachability. However, enhanced efficacy of DM by complexation would prevent its overdosing and in turn reduce its leaching potential. On the other hand, mobilization of DM by using dissolved MCD as its formation additive would enhance bioremediation of DM-contaminated soil. Facilitated mobilization has been reported in previous studies where

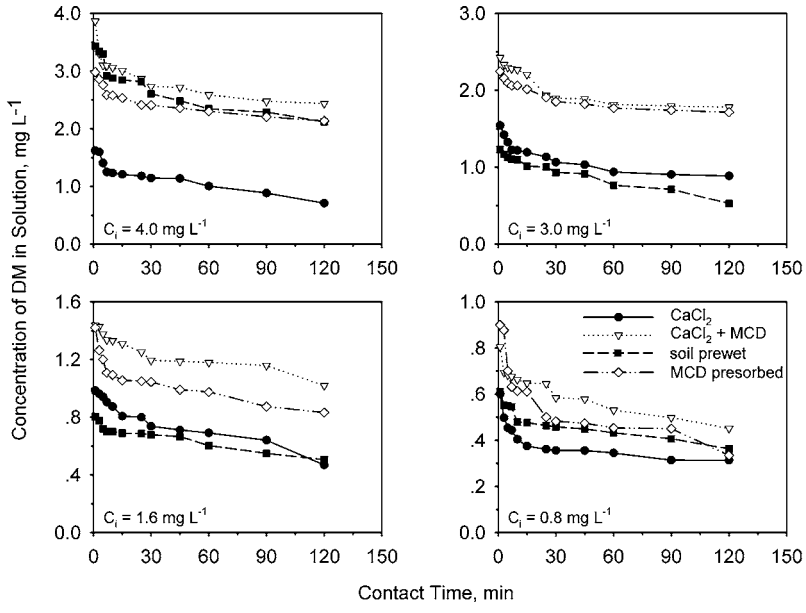

Figure 6. Sorption of DM on soil subjected to various treatments.

desorption and leaching of pesticides including both polar herbicides (e.g., 2,4-D) and low-polarity compounds (e.g., *p,p′*-DDT) in soils were enhanced by CDs (*15*, *18*−*20*).

CONCLUSIONS

As an environmentally friendly compound derived from natural starches, randomly methylated β-cyclodextrin (MCD) appears promising to be used as a future formulation additive for commertial diclofop-methyl (DM). MCD is hydrophilic in nature but also contains a hydrophobic cavity within its molecular structure. MCD forms a highly stable 1:1 inclusion complex with DM. The complexation occurs within the cavity of MCD, as verified by the techniques including UV, fluorescence, FTIR, NMR, and differential scanning calorimetry. By complexation, not only is the solubility of DM greatly enhanced, but also DM remains as the predominant form of the herbicide. This is due to the resistance of the complexed DM to hydrolysis that would otherwise convert DM to diclofop, a less herbicidal form. The DM−MCD complex also dissolves quickly in water and thus is immediately available to target grasses. The complexation reduces the sorption of DM by soil and may concurrently mobilize additional sorbed pesticides and other organic pollutants for enhanced biodegradation. MCD thus may offer several advantages over current additives in improving DM availability and enhancing bioremediation.

ABBREVIATIONS USED

DM, diclofop-methyl; CD, cyclodextrin; MCD, randomly methylated β-cyclodextrin; HP-β-CD, hydroxypropyl β-cyclodextrin.

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