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Authors

Shirvani, Mehran
Farajollahi, Edris
Bakhtiari, Somayeh
[et al.](#)

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Mobility and efficacy of 2,4-D herbicide from slow-release delivery systems based on organo-zeolite and organo-bentonite complexes

MEHRAN SHIRVANI¹, EDRIS FARAJOLLAHI¹, SOMAYEH BAKHTIARI¹
and OLADELE A. OGUNSEITAN²

¹Department of Soil Science, College of Agriculture, Isfahan University of Technology, Isfahan, Iran

²Program in Public Health, Department of Population Health & Disease Prevention, University of California, Irvine, California, USA

This research aimed to develop slow-release formulations (SRFs) of 2,4-dichlorophenoxyacetic acid (2,4-D) using zeolite and bentonite minerals modified with cetyltrimethylammonium (CTMA) surfactant. Adsorption-desorption, greenhouse bioassay and column experiments were carried out to assess the potential of the SRFs to control weeds while reducing the herbicide leaching losses to deep layers of soil. The results showed that only 6.5 mmol 2,4-D kg⁻¹ was retained by Na-bent, and the herbicide was not adsorbed by Na-zeol at all. The surface modification with CTMA surfactant, however, improved the 2,4-D adsorption capacity of the zeolite and bentonite up to 207.5 and 415.8 mmol kg⁻¹, respectively. The synthesized organo-minerals slowly released the retained 2,4-D discharging 22 to 64% of the adsorbed 2,4-D to the solution phase within 7 days. The SRFs significantly ($P = 0.05$) reduced the herbicide mobility within the soil columns keeping a great portion of the herbicide active ingredient in the upper 5 cm soil layer. The SRFs were significantly ($P = 0.05$) as effective as the free technical herbicide in weed control without harming the ryegrass as the main plant. Therefore, the synthesized SRFs could be considered as useful tools for weed control in sustainable agriculture.

Keywords: Dichlorophenoxy acetic acid, bentonite, zeolite, modification, herbicide.

Introduction

The extensive use of herbicides in agriculture has contributed to significantly expand food production. Nevertheless, this has resulted in serious environmental pollution and ecological issues, because more than 95% of applied herbicides never reach the intended target, leading to soil, water, air, and food contamination.^[1,2]

2,4-dichlorophenoxyacetic acid (2,4-D) is a systemic herbicide widely used to control broad-leaf weeds.^[3] 2,4-D is anionic with low sorption efficiency to soil particles; consequently, it has a high potential mobility in wet soils.^[4] Therefore, residues of 2,4-D have been detected repeatedly in ground and surface waters in various regions of the world.^[5–7] Short-term exposure to 2,4-D can cause damage to the nervous system, while long-term exposure can be harmful to the liver and kidneys.^[8] Nevertheless, U.S.

EPA recently denied the petition filed by the Natural Resources Defense Council to revoke all tolerances and to cancel all registrations of 2,4-D. EPA confirmed previous finding that the 2,4-D tolerances are safe and decided not to ban 2,4-D.^[9]

To overcome the adverse impacts of herbicides on the environment, slow-release formulations (SRFs) have been developed to gradually deliver the herbicide active ingredients to limit the amounts immediately available for off-site transport and degradation processes.^[2] Substrates such as starch,^[10] chitosan,^[11] lignin,^[12] alginate^[13] and synthetic polymers^[2] have been examined for producing SRFs. Clays have also been investigated for SRFs synthesis due to their stability, adsorptive capacity and low cost.^[14,15] Despite these favorable characteristics, natural clay minerals are ineffective adsorbents for hydrophobic and anionic organic compounds because their negatively charged surfaces electrostatically retain hydrated inorganic cations and repel anions and nonpolar substances.^[16,17] To enhance sorption capacity of the clays for hydrophobic and anionic herbicides, the mineral surfaces can be pretreated with organic cations such as alkylammonium surfactants that have a positively charged head group and a hydrophobic tail.^[16–18]

Address correspondence to Mehran Shirvani, Department of Soil Science, College of Agriculture, Isfahan University of Technology 84156-83111, Isfahan, Iran; E-mail: shirvani@cc.iut.ac.ir; mehshirvani@yahoo.com
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Adsorption of these organic cations changes the mineral surface character from hydrophilic to hydrophobic and the net charge from negative to positive which increases adsorption capacity of the modified-clays for anions and nonpolar molecules particularly when surfactant amount is greater than the CEC of the clay.^[16]

Various surfactant-mineral complexes have been tested for preparing SRFs of different herbicides such as norflurazon,^[19,20] acetochlor,^[21] fenuron,^[22] metolachlor^[23] and diuron.^[24] Very few attempts have been made to synthesize and evaluate SRFs of 2,4-D using organo-minerals. For instance, Hermosín et al.^[4] used organo-montmorillonite as support to produce SRFs of 2,4-D. They showed that the SRFs reduced herbicide losses through leaching and biodegradation, while maintained a herbicidal efficacy similar to that of the free (technical) 2,4-D. But there are no further comparative studies to assess the characteristics and performance of preemergence applied SRFs developed using readily available mineral deposits. Therefore, this study was carried out to: (i) evaluate adsorption and desorption patterns of 2,4-D on/from Iranian zeolite and bentonite minerals modified with CTMA surfactant, (ii) develop SRFs of 2,4-D herbicide based on the synthesized organo-mineral complexes and (iii) assess the efficacy of the SRFs in weed control and reducing herbicide leaching within soil columns.

Materials and methods

Materials

Bentonite and zeolite minerals from Mehrejan (33°36'7" N, 55°10'4" E) and Aftar (35°38'31" N, 53°20'39" E) mines, respectively, were used in this study. Chemical composition (%) of the bentonite sample (%) was: SiO₂ 66.37, Al₂O₃ 13.24, Fe₂O₃ 2.04, MgO 2.37, CaO 1.79 and Na₂O 1.69 based on a XRF analysis. According to XRD analysis, the bentonite was composed of 86.5% montmorillonite, 9.5% quartz, 2.5% illite and 1.5% calcite.^[25] Chemical composition (%) of the zeolite was: SiO₂ 61.91, Al₂O₃ 11.02, Fe₂O₃ 0.99, MgO 0.79, CaO 0.32 and Na₂O 6.75. The zeolite was composed of 82.6% clinoptilolite, 8.6% quartz, 5.3% illite and 3.5% feldspar.

The clay samples were homogenized to pass through a 50 µm size (mesh #270) sieve. The clays were then saturated with Na⁺ using 0.1 M NaCl and washed free of salts with distilled, deionized water. Finally, the Na-saturated bentonite and zeolite (hereafter named Na-bent and Na-zeol, respectively) were dried and crushed to <50 µm. The cation exchange capacity (CEC) of the Na-bent and Na-zeol was 66 and 114 cmol_c kg⁻¹, respectively, as determined by ammonium acetate method.^[26]

Cetyltrimethylammonium (CTMA) bromide from Sigma-Aldrich (St. Louis, MO, USA) was used to modify the mineral surfaces and 2,4-D (purity 98%) from Merck (Darmstadt, Germany) was used as the model herbicide.

Preparation of the organo-mineral complexes

To prepare the organo-minerals, 10 g of each mineral was treated with 100 mL of an ethanol/water (50:50) solution containing an amount of CTMA⁺ equal to 100% or 200% of the CEC of the mineral. The suspensions were stirred constantly at 25°C for 48 h, centrifuged and washed with distilled water until the eluents were free from bromide ions. The produced organo-minerals were freeze-dried, ground (<50 µm) and kept in polystyrene tubes at room temperature until used.

Characterization of the organo-minerals

The organic carbon (OC) content of the minerals and organo-minerals was determined using a Skalar Primacs^{SLC} (Skalar Analytical BV, The Netherlands) carbon analyzer to estimate actual loading of the surfactant expressed as the percentage of the CEC of the mineral occupied by the organic cations.

X-ray diffraction (XRD) analysis was performed using a Philips PANalytical X'Pert High Score diffractometer (Almelo, The Netherlands) with CuK_α radiation to assess the intercalation of cationic surfactants in the clay galleries. For this purpose, the Na- and CTMA-minerals were dispersed in the deionized water, dropped on the glass slides and air-dried. XRD patterns were recorded between 2 and 40° (2θ) at a scanning speed of 2°/min.

Fourier transform infrared spectroscopy (FT-IR) was carried out to identify the attached organic cations on the surface of the clays and the functional groups of the organo-minerals surfaces. The Na and CTMA-mineral surfaces were scanned with a JASCO 460 spectrophotometer in KBr pellets (1 wt%) (JASCO International Co., Ltd., Tokyo, Japan).

Herbicide adsorption and desorption experiments

Adsorption isotherms of 2,4-D on the Na- and organo-minerals were obtained by batch equilibration technique using 100 mL centrifuge tubes. Triplicate 0.2 g of each sorbent, were equilibrated with 50 mL of 0.01 M sodium chloride solutions containing 2,4-D with initial concentrations from 0.1 to 1.5 mM in an incubator shaker at 25°C for 24 h. After equilibration, the suspensions were centrifuged and the equilibrium concentrations of the herbicide (C_e) were determined in the supernatants by a 6505 UV-Visible spectrophotometer at wavelength of 282 nm. The amount of herbicide adsorbed was calculated in each instance from the difference between initial (C_i) and final concentration (C_e) in solution.

Desorption of 2,4-D from the organo-minerals was measured immediately after adsorption at the greatest initial concentration using successive dilution method. After shaking of the herbicide-sorbent mixtures at 25 ± 0.5°C for 24 h, the supernatants were separated by centrifugation at

3,500 rpm for 20 min. Then, 25 mL of the supernatant was removed to determine 2,4-D concentration and replaced with 25 mL of the 0.01 M NaCl. This desorption cycle was repeated seven times. Desorption isotherms were prepared by plotting the 2,4-D remained on the organo-minerals after each desorption cycle vs. the corresponding equilibrium 2,4-D concentrations in solution.

Preparation of 2,4-D slow-release formulations

A strong association complex was prepared according to the method described by Hermosin et al.^[4] by adding 10 mL of methanol to 1 g of organo-mineral-herbicide mixture (4% herbicide content), followed by a 24 h shaking and air-drying. The amount of 2,4-D in all formulations corresponded to a 4% content in active ingredient (a.i.). All solids were then thoroughly ground in an agate mortar and stored at 4°C until used.

Herbicide batch release experiments

Release of 2,4-D from the SRFs to water was conducted by suspending triplicate of 5 mg of 2,4-D (a.i.) as free technical product or air-dried powder of the SRFs in 250 mL distilled water in glass bottles lined with screw caps. At selected times after herbicide application (from 0 to 168 h), the bottles were hand-shaken, allowed to settle for 10 min, and then 2 mL of the supernatant solution was removed and centrifuged. The 2,4-D concentration was subsequently determined in the filtrates. The time-dependent 2,4-D release data were then tested to be described by some kinetic models among which the pseudo first-order model (Eq. (1)) showed the best fits:

$$C_t = C_e (1 - e^{-k_1 t}) \quad (1)$$

where C_t and C_e (μM) are the 2,4-D concentration set up by the SRFs at time t and at equilibrium, respectively, and k_1 (min^{-1}) is the pseudo first-order rate constant.

Herbicide leaching experiment

The method described by El-Nahhal et al.^[27] was used for herbicide leaching studies. Columns made of polyethylene tubes (surface area of 113.04 cm^2 , 30 cm height) were filled with <2 mm portion of a soil containing 50.2% clay, 45% silt and 4.8% sand. The soil was sampled from the surface 5 cm of an agricultural field at Isfahan, Iran. The soil surfaces were then sprayed with the field rate (1.40 a.i. kg/ha) of 2,4-D suspension soil either as free technical or SRFs. The columns were carefully irrigated with 500 m^3/ha (50 mm) water, applied in portions during 3–5 h with 20-min intervals and left for 24–48 h for equilibration. Then each column was sliced along its length, forming two pots representing different soil depths and garden cress (*Lepidium sativum*) seeds (0.80 g m^{-2}) were sown uniformly in each pot. Four weeks after sowing, plant shoot dry weight

was determined to estimate herbicide presence at different soil depths in the columns. The experiment was set up in a completely randomized factorial design with four replicates. Data were analyzed using a one-way analysis of variance (ANOVA) and the means were compared using least significant differences (LSD) at $P < 0.05$.^[28]

Bioassay

In order to test the weed controlling efficacy of the 2,4-D SRFs, plant experiments were carried out by sowing white clover (*Trifolium repens*) and ryegrass (*Lolium perenne*) seeds as weed and main plants, respectively, in 0.5 L pots in triplicates. *Lolium perenne* is the most widely used ryegrass for turf purposes and *trifolium repens* is the most common turf weed. Therefore, it is important that the herbicide formulation can kill the weeds without serious injury to the turfgrass.

The pots were filled with the soil and 20 seeds of white clover and 0.5 g seeds of ryegrass were sown at a depth of approximately 0.5 cm. The soils in the pots were sprayed with the free technical and SRFs at a rate of 1.4 kg ha^{-1} a.i. one day after sowing and before germination. In order to achieve homogeneity in such small pots, the herbicide was dissolved in 10 mL of water and the solution was uniformly sprayed on soil surface of each pot. Three pots were left without herbicide addition as control. The fresh and dry weights of both plants were determined 40 days after treatment. The optimal conditions for growth (light, temperature and fertilizer) were made and the plants were irrigated with 30 mL of deionized water daily. The effect of formulations type on plant dry weight were analyzed using a ANOVA and the means were compared using LSD at $P < 0.05$.^[28]

Results and discussion

Surfactant loading of the organo-minerals

The amount of CTMA surfactant loading of the modified minerals was determined from the OC content of the samples. The OC contents of the clays modified with CTMA⁺ in amounts equal to 100% and 200% of the clay CEC were respectively, 10.5% and 16.93% for the organo-bentonites and 2.8% and 4.37% for the organo-zeolites showing the greater surfactant loading of the modified bentonites. Treatment of the bentonite with CTMA⁺ at an initial concentration corresponding to 100% of the CEC resulted in the occupation of 70% the exchange sites by the surfactant. However, regarding the bentonite sample treated with CTMA⁺ at initial concentration equal to 200% of the CEC, the mineral surface was saturated with the organic cation equivalent to 113% of the CEC.

When zeolite treated with CTMA equal to 100% and 200% of the clay CEC, the exchange sites were actually

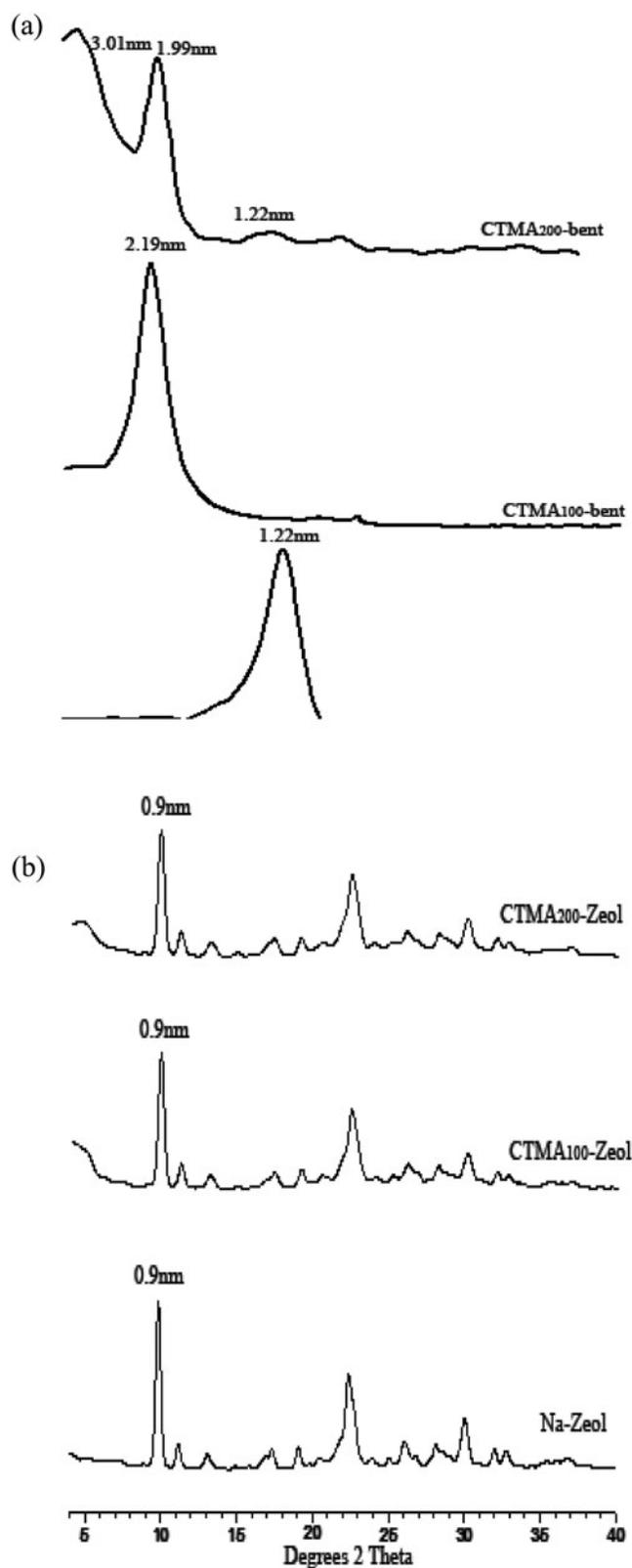


Fig. 1. X-ray diffractograms of: (a) Na-bent and organo-bentonites (CTMA₁₀₀-bent and CTMA₂₀₀-bent), and (b) Na-zeol, and organo-zeolites (CTMA₁₀₀-zeol and CTMA₂₀₀-zeol).

saturated with the organic cation equal to 10.8% and 16.8% of the CEC, respectively. The dimensions of the open channels in zeolite are probably not sufficiently large to accommodate CTMA head groups;^[29] therefore, the sorption of the CTMA cations was only limited to the external surfaces of zeolite resulting in CTMA⁺ loading of zeolite to be much lower than its CEC.

X-ray diffraction patterns

The CTMA cations were intercalated in the interlayer space of the bentonite. The $d(001)$ values of Na-bent was at 12.2 Å, while CTMA₁₀₀-bent showed the main peak at 21.9 Å which may reflect a paraffin-type monomolecular arrangement of surfactant within the clay galleries.^[30] The intercalated surfactants enlarge the clay interlayer spacing to make room for the herbicide to penetrate into the gallery space during the preparation of the SRFs.

Three peaks were observed at 12.2, 19.9 and 30.1 Å in the X-ray diffractogram of CTMA₂₀₀-bent (Fig. 1a). The pseudotrilayer arrangement of CTMA cations can well explain the basal reflection at 19.9 Å and paraffin-type monolayer arrangement is the best for 30.9 Å.^[31] The broadened peaks may suggest that there may be several phases coexisting. Zhu et al.^[31] also observed 19.8 and 30.5 Å peaks when a montmorillonite clay was treated with concentration of CTMA⁺ equal to 2CEC.

The XRD analyses did not show obvious differences between Na-zeol and its CTMA-modified products (Fig. 1b). As expected, modification of zeolite by CTMA did not change the clay structure.

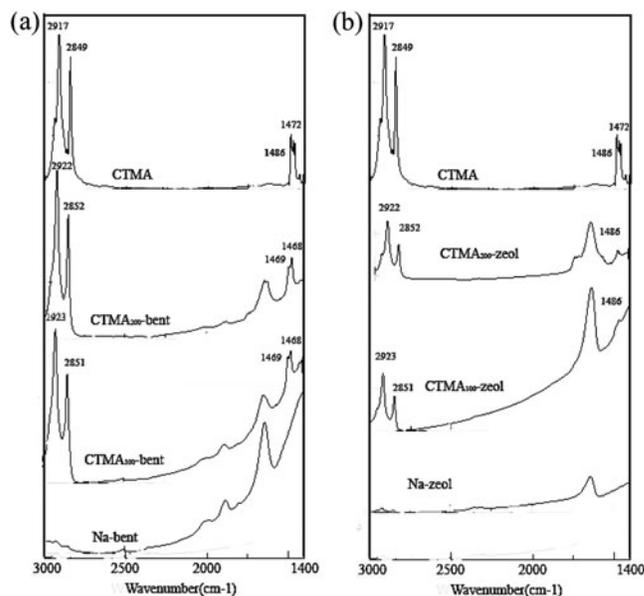


Fig. 2. FT-IR spectra of pure CTMA, Na- and CTMA-modified bentonite (a) and zeolite (b).

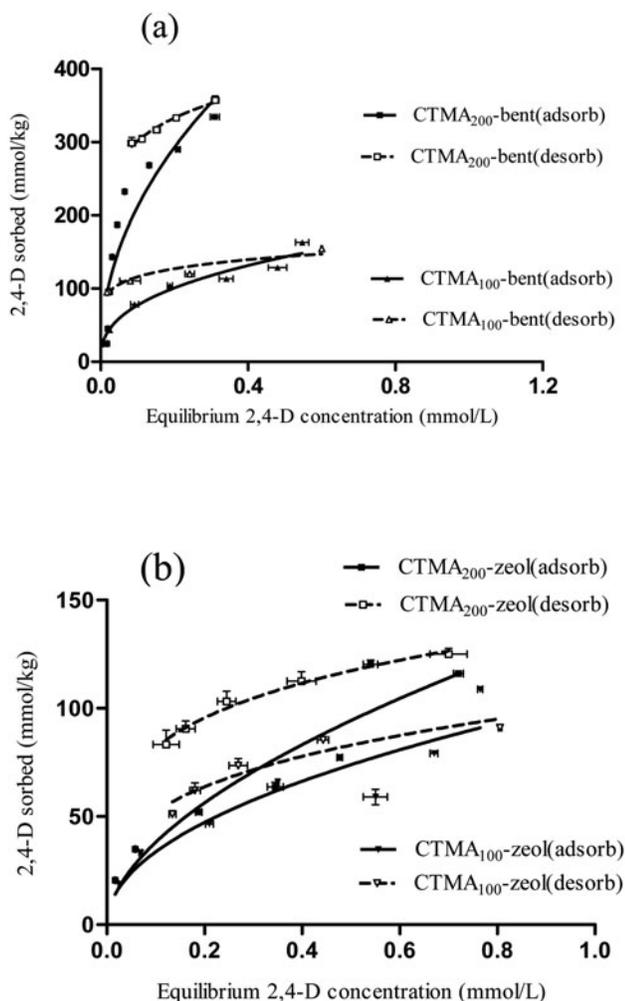


Fig. 3. Adsorption–desorption Freundlich isotherms of 2,4-D on Na- and organo-bentonites (a) and Na- and organo-zeolites (b). Bars represent standard errors of triplicate samples.

FT-IR spectra

Marked changes occurred in the surface properties of the minerals when the Na⁺ was replaced with CTMA⁺ as verified by FT-IR spectra shown in Fig 2. The intense bands in the spectrum of the pure CTMA in the range of

2,800–3,000 cm⁻¹ which is related to asymmetric and symmetric vibration of methylene group (-C-H) of aliphatic carbon chain [32,33] can be observed in the organo-minerals spectra, as well. FT-IR bands of the sorbed CTMA on zeolite, however, slightly shifted toward greater wave number which can be attributed to a crystal-field effect from the clay.[34] The bands centered at 1,472 and 1,486 cm⁻¹ in the pure CTMA spectrum related to scissoring and bending vibrations of methylene groups of CTMA, respectively,[35,36] were also found in CTMA₁₀₀-bent and CTMA₂₀₀-bent spectra at 1,469 and 1,468 cm⁻¹, respectively, showing significant changes in the methyl deformation region (Fig. 2a).[32,37] The surfactant methyl groups have probably lost their free rotation due to adsorption onto the mineral interlayer spaces. From the IR spectral bands related to the surfactant only a band at 1,486 cm⁻¹ was seen for the two modified zeolites which may probably be related to little CTMA⁺ loading on the zeolite (Fig. 2b).

Adsorption/desorption isotherms

Comparative 2,4-D sorption/desorption patterns on/from the organo-clays are shown in Fig 3. Both Langmuir and Freundlich equations adequately ($P < 0.01$) described 2,4-D sorption by CTMA-modified bentonite and zeolite, the latter equation being slightly superior (Table 1).

Only slight amount of 2,4-D was retained by Na-bent, and the herbicide was not adsorbed on Na-zeol at all. This may be due to the repulsion of the 2,4-D anions by the negatively charged hydrated surface of the minerals. The surfactant-modified bentonites and zeolites, however, displayed much greater capacity to retain 2,4-D compared to the unmodified minerals and the capacity of the organo-minerals for 2,4-D sorption increased by increasing the loading of the surfactant on the clay surfaces (Table 1). Based on the Q_{\max} values calculated from the fitted Langmuir equations, the following sequence of sorption capacities were observed for the sorbents:

$$\text{CTMA}_{200} - \text{bent} > \text{CTMA}_{200} - \text{zeol} > \text{CTMA}_{100} - \text{bent} > \text{CTMA}_{100} - \text{zeol} \gg \text{Na} - \text{bent} > \text{Na} - \text{zeol}$$

Table 1. Isothermal constants for 2,4-D sorption onto the sorbents.

	CTMA ₁₀₀ -zeol	CTMA ₂₀₀ -zeol	Na-bent	CTMA ₁₀₀ -bent	CTMA ₂₀₀ -bent
Fitted Langmuir					
Q_{\max}	121 (18.38) ^a	207.5 (51.71)	6.5 (1.26)	164.5 (10.45)	415.8 (26.34)
K_L	3.416 (1.33)	1.726 (0.79)	1.73 (0.75)	10.44 (2.42)	13.56 (2.12)
R^2	0.79**	0.84**	0.75**	0.91**	0.92**
Fitted Freundlich					
K_F	103.7 (5.94)	139.4 (8.55)	4.16 (0.23)	186.9 (6.68)	620.4 (60.55)
N	0.49 (0.06)	0.56 (0.07)	0.54 (0.09)	0.38 (0.26)	0.46 (0.04)
R^2	0.85**	0.89**	0.75**	0.96**	0.84**

^aData in parentheses show standard error of replicates.

**Significant at 0.01 probability level.

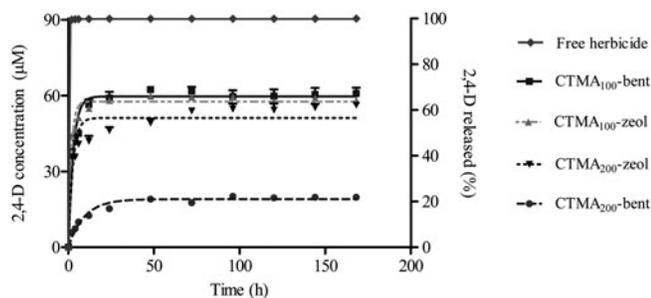


Fig. 4. Kinetics of 2,4-D release from different formulations. Lines represent modeled results using the pseudo-first-order equation and bars represent standard errors of triplicate samples.

The sorption of 2,4-D on the modified minerals is probably due to hydrophobic interactions as well as electrostatic, Van der Waals and H bindings.^[38] Hermosín and Cornejo^[39] also studied binding mechanisms of 2,4-D by decylammonium-modified montmorillonite and vermiculite. They suggested weak lyophilic (ring-tail) bonding on external surfaces of organo-montmorillonite and hydrogen bonding between carbonyl group of 2,4-D and ammonium group of the interlayer organic cations of organo-vermiculite as the main mechanisms involved in the 2,4-D adsorption. Greater adsorption capacity of CTMA₂₀₀-bent suggests that this organo-mineral can be used superiorly for preparing slow release systems of 2,4-D.

The results of desorption experiments showed that a portion of the herbicide was irreversibly retained by all modified minerals within the period of the experiment. As shown in Figure 3, 86 (31%), 59 (37%), 44 (48%) and 54 (45%) mmol 2,4-D kg⁻¹ were desorbed from CTMA₂₀₀-bent, CTMA₁₀₀-bent, CTMA₂₀₀-zeol and CTMA₁₀₀-zeol, respectively, after five cycles of desorption. In other words, desorption of 2,4-D from the sorbents showed hysteresis with different strength, which can be due to strong interactions between 2,4-D anions and the CTMA cations on the mineral surfaces.

Table 2. Pseudo-first-order kinetic parameters for 2,4-D release from different formulations.

Formulation	C_e	k_1	R^2
CTMA ₂₀₀ -bent	19.04	0.10	0.93**
CTMA ₁₀₀ -bent	59.68	0.35	0.94**
CTMA ₂₀₀ -zeol	51.17	0.38	0.87**
CTMA ₁₀₀ -zeol	57.67	0.57	0.97**
Free technical	90.42	2.84	0.99**

^aData in parentheses show standard error of replicates.

**Significant at 0.01 probability level.

Herbicide release kinetics

The release of 2,4-D from different formulations with time is presented in Figure 4. Desorption of 2,4-D from the free technical product was great and fast in the way that almost total active ingredient was released in the first hours. Formulation of 2,4-D with organo-minerals, however, considerably reduced both the quantity and the rate of the herbicide entered the solution phase after the defined times. For instance, at the end of the experiment, i.e. after 168 h, 22%, 60%, 62% and 64% of the adsorbed 2,4-D released from the CTMA₂₀₀-bent, CTMA₁₀₀-bent, CTMA₁₀₀-zeol and CTMA₂₀₀-zeol, respectively (Fig. 4).

Kinetic parameters for 2,4-D release from different formulations are represented in Table 2. The pseudo first-order rate constant (k_1) varied from 0.1 to 2.84 min⁻¹ and the 2,4-D concentration maintained by the SRFs at equilibrium (C_e) was ranged from 19.04 to 90.42 µM. The greatest 2,4-D release kinetic parameters were calculated for the free technical herbicide. Both the extent and rate of 2,4-D release, however, decreased after formulation of the herbicide with the organo-mineral complexes. The lowest C_e and k_1 values were observed for the CTMA₂₀₀-bent. As deduced from the sorption parameters represented in Table 1, CTMA₂₀₀-bent forms the strongest interactions with 2,4-D anions among the organo-minerals studied. This might markedly retard the release of herbicide from this organo-bentonite. Hermosín et al.^[4] also investigated different HDTMA-montmorillonite organo-clays as carriers of 2,4-D and reported that the final release proportion of the retained herbicide after 7 days was from 10% to 75% depending on the methodology used for the preparation of the complexes.

Based on the observed herbicide release pattern, it seems that the organo-modified minerals used in this study are suitable supports for preparing SRFs, because they reduced the amount of herbicide immediately available for rapid transport losses in a given period of time.

Herbicide leaching

In order to find whether the SRFs can diminish herbicide mobility, the column leaching experiment was conducted in a greenhouse. Statistical analysis of the data showed significant differences ($P = 0.05$) among means of shoot dry matter production of garden cress (test plant) at different soil depths in the columns (Fig. 5). 2,4-D applied as the free technical product disappeared from the top soil and accumulated in a deeper soil layers, where it caused germination inhibition of the test plant. The greatest activity of the free herbicide was observed in the 10–25 cm soil depth indicating more leaching of 2,4-D from this formulation. Regarding the SRFs, however, the maximum herbicidal activity were measured in the 0–5 cm soil layer which clearly demonstrate the effectiveness of the organo-mineral complexes in retaining 2,4-D herbicide in the topsoil and

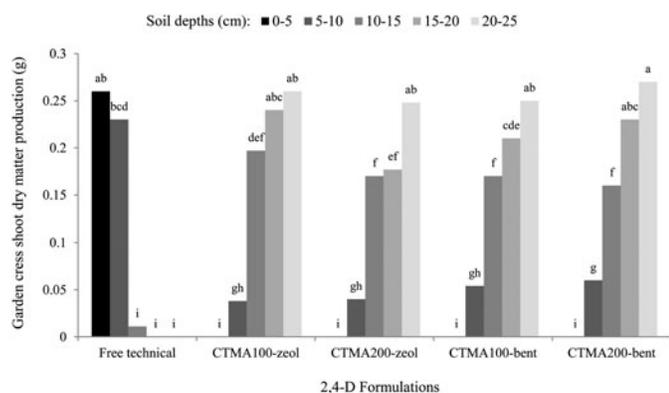


Fig. 5. Leaching of the free technical product and slow-release formulations of 2,4-D applied at 1.40 kg ha^{-1} followed by irrigation of $500 \text{ m}^3 \text{ ha}^{-1}$ using garden cress as a test plant. Means followed by the same letter at a representative depth are not significantly different at 0.05 level.

reducing the herbicide leaching through the soil column. Therefore, all of the organo-mineral complexes synthesized in this study can reduce the downward mobility of 2,4-D in soils. El-Nahhal et al.^[24] also showed that BTMA-clay formulations produced slow release of alachlor to the environment, maintaining the herbicidal activity in the top soil as assessed by a bioassay using green foxtail and wheat as test plants.

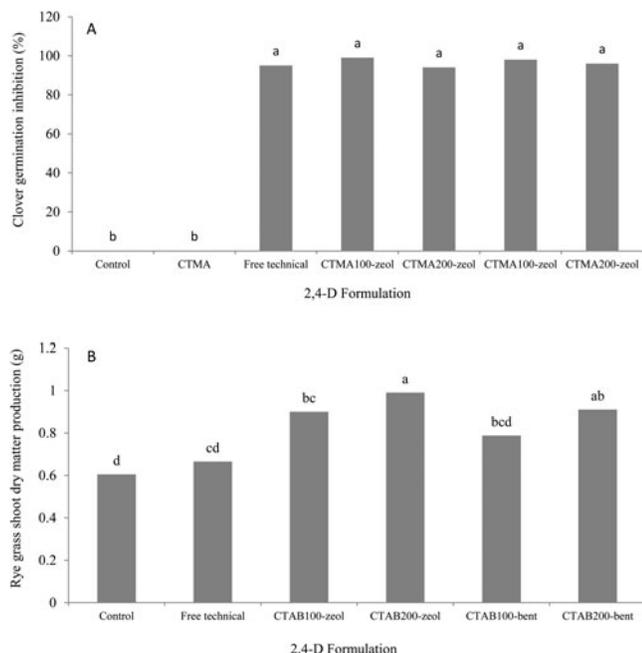


Fig. 6. Germination inhibition of clover (a) and shoot dry matter production of ryegrass (b) grown in soils sprayed with different 2,4-D formulations. Means followed by the same letter are not significantly different at 0.05 probability level.

Weed controlling efficiency of the herbicide formulations

Figure 6a shows the germination inhibition of the weed plant (clover) and shoot dry matter production of the main plant (ryegrass) as a result of 2,4-D application in different formulations. The results showed that all of the organo-mineral formulations applied preemergence were statistically as effective as the free herbicide in controlling of the test plant. The surfactant did not have any inhibitory effect on germination and growth of the plants as can be seen in Figure 6b. Hermosín et al.^[4] also showed that SLFs of 2,4-D developed based on organo-montmorillonite applied postemergence were nearly as efficient as the free herbicide formulation in weed control.

Figure 6b shows shoot dry matter production of ryegrass grown in pots sprayed with different 2,4-D formulations. It can be seen that the addition of 2,4-D not only did not reduce but also improved the ryegrass growth as compared to the control. Enhancement of dry matter production treated with some 2,4-D formulations can be due to plant growth regulatory character of 2,4-D or eliminating the competition of the clover with ryegrass after the herbicide application. Therefore, the synthesized 2,4-D SRFs can be satisfactorily used to control clover weeds in lawns, golf courses, athletic fields and parks without making serious injury to the ryegrass plants.

Conclusions

Sorption-desorption as well as column leaching and bioassay experiments were conducted to understand whether CTMA-modified bentonite and zeolite can be practically used as support for slow release formulation of 2,4-D. The modified clays prominently retain 2,4-D herbicide and gradually release it to the liquid phase. It makes these organo-minerals suitable candidates for SRF of this herbicide. Data from bioassay experiments revealed that the amount of 2,4-D released from all of the formulations is sufficient to kill clover weeds in the early stages of seed germination without harming the ryegrass. Leaching studies revealed that the SRFs reduce the herbicide mobility within the soil columns keeping a great portion of the herbicide active ingredient in the upper soil layer. Therefore, using these slow release formulations can improve weed control efficacy and reduce frequencies of 2,4-D application, which is important from an economical and environmental perspectives.

References

- [1] Miller, G.T. *Sustaining the Earth*, 6th Ed.; Thompson Learning, Inc.: Pacific Grove, CA, 2004.
- [2] Chevillard, A.; Angellier-Coussy, H.; Guillard, V.; Gontard, N.; Gastaldi, E. Controlling pesticide release via structuring agropolymer and nanoclays based materials. *J. Hazard. Mater.* **2012**, *205–206*, 32–39.

- [3] Garabrant, D.H.; Philbert M.A. Review of 2,4-dichlorophenoxyacetic acid (2,4-D) epidemiology and toxicology. *Crit. Rev. Toxicol.* **2002**, *32*, 233–257.
- [4] Hermosín, M.C.; Celis R.; Facenda G.; Carrizosa M.J.; Ortega-Calvo J.J.; Cornejo J. Bioavailability of the herbicide 2,4-D formulated with organoclays. *Soil Boil. Biochem.* **2006**, *38*, 2117–2124.
- [5] World Health Organization (WHO). 2,4-D in Drinking-water; Background document for development of WHO Guidelines for Drinking-water Quality; Author: Geneva, 2003.
- [6] Balinova, A.M.; Mondesky M. Pesticide contamination of ground and surface water in Bulgarian Danube plain. *J. Environ. Sci. Health Part B.* **1999**, *34*, 33–46.
- [7] Wood, J.A.; Anthony D.H.J. Herbicide contamination of prairie springs at ultratrace levels of detection. *J. Environ. Qual.* **1997**, *26*, 1308–1318.
- [8] US Environmental Protection Agency (US EPA). *Basic Information about 2,4-D (2,4-Dichlorophenoxyacetic Acid) in Drinking Water*. US Environmental Protection Agency, Office of Water: Washington, DC, 2012. Available at <http://water.epa.gov/drink/contaminants/basicinformation/2-4-d-2-4-dichlorophenoxyacetic-acid.cfm> (accessed Jan 2012).
- [9] US EPA. *2,4-D; Order Denying NRDC's Petition To Revoke Tolerances*. Federal Register **2012**, *77*, 23135–23158. Available at http://www.epa.gov/oppfead1/cb/csb_page/updates/2012/2-4d-petition.html (accessed Sep 2012).
- [10] Cao, Y.S.; Huang L.; Chen, J.X.; Liang, J.; Long, S.Y.; Lu, Y.T. Development of a controlled release formulation based on a starch matrix system. *Int. J. Pharm.* **2005**, *298*, 108–116.
- [11] Agnihotri, S.A.; Aminabhavi, T.M. Controlled release of clozapine through chitosan microparticles prepared by a novel method. *J. Control Release.* **2004**, *96*, 245–259.
- [12] Pereira, F.M.; Goncalves, A.R.; Ferraz, A.; Silva, F.T.; Oliveira, S.C. Modeling of 2,4-dichlorophenoxyacetic acid controlled-release kinetics from lignin-based formulations. *Appl. Biochem. Biotech.* **2002**, *98*, 101–107.
- [13] Singh, B.; Sharma, D.K.; Gupta, A. A study towards release dynamics of thiram fungicide from starch alginate beads to control environmental and health hazards. *J. Hazard. Mater.* **2009**, *161*, 208–216.
- [14] Sarkar, B.; Xi, Y.; Megharaj, M.; Naidu, R. Orange II adsorption on palygorskites modified with alkyl trimethylammonium and dialkyldimethylammonium bromide: An isothermal and kinetic study. *Appl. Clay Sci.* **2011**, *51*, 370–374.
- [15] Xin, X.; Yang, J.; Feng, R.; Zhao, J.; Chen, G.; Wei, Q.; Du, B. Preparation, characterization and adsorption performance of cetyl Pyridine bromide modified bentonites. *J. Inorg. Org. Poly. Mater.* **2012**, *22*, 42–47.
- [16] Xi, Y.; Mallavarapu, M.; Naidu, R. Adsorption of the herbicide 2,4-D on organo-palygorskite. *Appl. Clay Sci.* **2010**, *49*, 255–261.
- [17] Sarkar, B.; Megharaj, M.; Xi, Y.; Naidu, R. Surface charge characteristics of organo-palygorskites and adsorption of p-nitrophenol in flow-through reactor system. *Chem. Eng. J.* **2011**, *185*, 35–43.
- [18] Zhan, Y.; Lin, J.; Zhu, Z. Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent. *J. Hazard. Mater.* **2011**, *186*, 1972–1978.
- [19] Undabeytia, T.; Nir, S.; Rubin, B. Organo-clay formulations of the hydrophobic herbicide norflurazon yield reduced leaching. *J. Agric. Food Chem.* **2000**, *48*, 4767–4773.
- [20] Undabeytia, T.; Nir, S.; Tel-Or, E.; Rubin, B. Photostabilization of the herbicide norflurazon by using organo-clays. *J. Agric. Food Chem.* **2000**, *48*, 4774–4779.
- [21] El-Nahal, Y.; Nir, S.; Serban, C.; Rabinovitz, O.; Rubin, B. Organo-clay formulations of acetochlor for reduced movement in soil. *J. Agric. Food Chem.* **2001**, *49*, 5364–5371.
- [22] Hermosín, M.C.; Calderon, M.J.; Aguer, J.P.; Cornejo, J. Organoclays for controlled release of the herbicide fenuron. *Pest. Mang. Sci.* **2001**, *57*, 803–809.
- [23] Nennemann, A.; Mishael, Y.; Nir, S.; Rubin, B.; Polubesova, T.; Bergaya, F.; Damme, H.V.; Lagaly, G. Clay-based formulations of metolachlor with reduced leaching. *Appl. Clay Sci.* **2001**, *18*, 265–275.
- [24] Trigo, C.; Celis, R.; Hermosín, M.C.; Cornejo, J. Organoclay-based formulations to reduce the environmental impact of the herbicide diuron in olive groves. *Soil. Sci. Soc. Am. J.* **2009**, *73*, 1652–1657.
- [25] Hamidpour, M.; Kalbasi, M.; Afyuni, M.; Shariatmadari, H. Kinetic and isothermal studies of cadmium sorption onto bentonite and zeolite. *Int. Agrophys.* **2010**, *24*, 253–259.
- [26] Rhoades, J.W. Cation exchange capacity. In *Methods of Soil Analysis*; Page, C.A., Ed.; ASA Press: Madison, WI, 1986; 149–158.
- [27] El-Nahal, Y.; Nir, S.; Polubesova, T.; Margulies, L.; Rubin, B. Leaching, phytotoxicity, and weed control of new formulations of alachlor. *J. Agric. Food Chem.* **1998**, *46*, 3305–3313.
- [28] SAS Institute. SAS/STAT User's Guide, Release 8; SAS Institute: Cary, NC, 2000.
- [29] Ghiaci, M.; Abbaspur, A.; Kia, R.; Seyedeyn-Azad, F. Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. *Separ. Pur. Technol.* **2004**, *40*, 217–229.
- [30] Ray, F.; He, H.; Klopogge, T.; Bostrom, T.; Duong, L.; Yuan, P.; Xi, Y.; Yang, D. Changes in the morphology of organoclays with HDTMA⁺ surfactant loading. *Appl. Clay Sci.* **2006**, *31*, 262–271.
- [31] Zhu, J.; Hongping, H.; Guo, J.; Yang D.; Xie, X. Arrangement models of alkylammoniumcations in the interlayer of HDTMA⁺ pillared montmorillonites. *Chin. Sci. Bull.* **2003**, *48*, 368–372.
- [32] Xi, Y.; Ding, Z.; Hongping, H.; Ray, F.L. Infrared spectroscopy of organoclays synthesized with the surfactant octadecyltrimethylammonium bromide. *Spectrochim. Acta A.* **2005**, *61*, 515–525.
- [33] Zhu, R.; Zhu, L.; Xu, L. Sorption characteristics of CTMA-bentonite complexes as controlled by surfactant packing density. *Colloid. Surface. A.* **2007**, *294*, 221–227.
- [34] Covarrubias, C.; Garcia, R.; Yanez, J.; Arriagada, R. Preparation of CPB-modified FAU zeolite for the removal of tannery wastewater contaminants. *J. Porous. Mater.* **2008**, *15*, 491–498.
- [35] Hongping, H.; Ray, F.L.; Jianxi, Z. Infrared study of HDTMA⁺ intercalated monmorillonite. *Spectrochim. Acta. A.* **2004**, *60*, 2853–2859.
- [36] Li, Z.; Jiang, W.T.; Hong, H. An FTIR investigation of hexadecyltrimethylammonium intercalation into rectorite. *Spectrochim. Acta. A.* **2008**, *71*, 1525–1534.
- [37] Vahedi-Faridi, A.; Guggenheim, S. Crystal structure of tetramethylammonium exchanged-vermiculite. *Clay. Clay Miner.* **1997**, *45*, 859–866.
- [38] Malla, P.B. Vermiculite. In *Soil Mineralogy with Environmental Applications*; Dixon, J.; Schulze, B., Eds.; Soil Science Society of America, Inc.: Madison, WI, 2002; 501–529.
- [39] Hermosín, M.C.; Cornejo, J. Binding mechanism of 2,4-dichlorophenoxyacetic acid by organo-clays. *J. Environ. Qual.* **1993**, *22*, 325–331.
- [40] Celis, R.; Hermosín, M.C.; Carrizosa, M.J.; Cornejo, J. Inorganic and organic clays as carriers for controlled release of the herbicide hexazinone. *J. Agric. Food Chem.* **2002**, *50*, 2324–2330.