

Selective Modification of Clay Minerals for the Adsorption of Herbicides Widely Used in Olive Groves

RAFAEL CELIS,* CARMEN TRIGO, GRACIA FACENDA,
MARÍA DEL CARMEN HERMOSÍN, AND JUAN CORNEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Avenida Reina Mercedes 10,
Apartado 1052, 41080 Sevilla, Spain

Ground and surface water contamination by herbicides applied to olive groves in Spain and other Mediterranean countries is demanding strategies to prevent and remediate the environmental problems repeatedly caused by such herbicides. In this study, six different organic cations (L-carnitine, spermine, hexadimethrine, tyramine, phenyltrimethylammonium, and hexadecyltrimethylammonium) were incorporated into Na-rich Wyoming montmorillonite (SWy-2) and Ca-rich Arizona montmorillonite (SAz-1) at two different loadings (50% and 100% of the cation exchange capacity of the clays) as a strategy to enhance the affinity of the clay minerals for three herbicides widely used in olive groves: terbutylazine, diuron, and MCPA. The modified montmorillonites were characterized and tested as adsorbents of the herbicides through batch adsorption tests. At the experimental conditions used, some of the modified montmorillonites removed more than 95% of the herbicide initially present in aqueous solution, whereas the unmodified clays removed less than 15%. All three herbicides displayed very strong affinities for SAz-1 exchanged with hexadecyltrimethylammonium cations, particularly when these were incorporated at 100% of the cation exchange capacity of the clay mineral. Terbutylazine and diuron also displayed very strong affinities for SWy-2 exchanged with L-carnitine and spermine, respectively. The chemical characteristics of the organic cation greatly influenced the adsorptive properties of the resultant organoclay. The herbicides were in general reversibly adsorbed by the modified clays. The results indicate that some of the tested modified clays could be suitable for the removal of the assayed herbicides from contaminated water and also as possible supports for the design of slow release formulations of such herbicides to attenuate their environmental impact when used in high-risk scenarios such as olive groves.

KEYWORDS: Adsorption; clay minerals; diuron; MCPA; organoclays; terbutylazine

INTRODUCTION

Ground and surface water contamination by herbicides used in olive groves in Spain and other Mediterranean countries has become a serious issue and has led authorities to prohibit or restrict the application of widely used active ingredients, such as simazine, terbutylazine, and diuron (1, 2). In olive groves, conditions that favor offsite movement of the applied herbicides predominate. Soil texture and pronounced slopes favor herbicide leaching and runoff processes. Climatic conditions of Mediterranean areas, characterized by short but heavy rainfall events, exacerbate the risk of large herbicide transport losses. To compensate for such losses, herbicides need to be applied in

concentrations greatly exceeding those strictly required for weed control, and the excessive quantities added increase the risk of surface and groundwater pollution (3). In this context, there is a need to develop strategies, such as the design of adsorbents with high loading capacities and selectivity, directed to prevent water pollution and restore soil and water contaminated with herbicides applied to olive groves, particularly in high-risk scenarios such as Mediterranean areas.

The use of unaltered and modified clay minerals as adsorbents to prevent and remediate environmental contamination by pesticides has been a subject of great interest in environmental and agricultural chemistry (4–8). The unique features of clays as adsorbent materials are mainly related to their large specific surface area associated with their layered structure, their ubiquitous occurrence in nature, and the possibility of modifying their surfaces to increase their affinity for specific adsorbates (9–11). The mechanism most widely used to increase the affinity of clays for hydrophobic organic compounds, including organic pesticides, consists of replacing the clay's natural inorganic exchange cations with organic cations through ion

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* To whom correspondence should be addressed. Phone: +34 954624711. Fax: +34 954624002. E-mail: rcelis@irnase.csic.es.

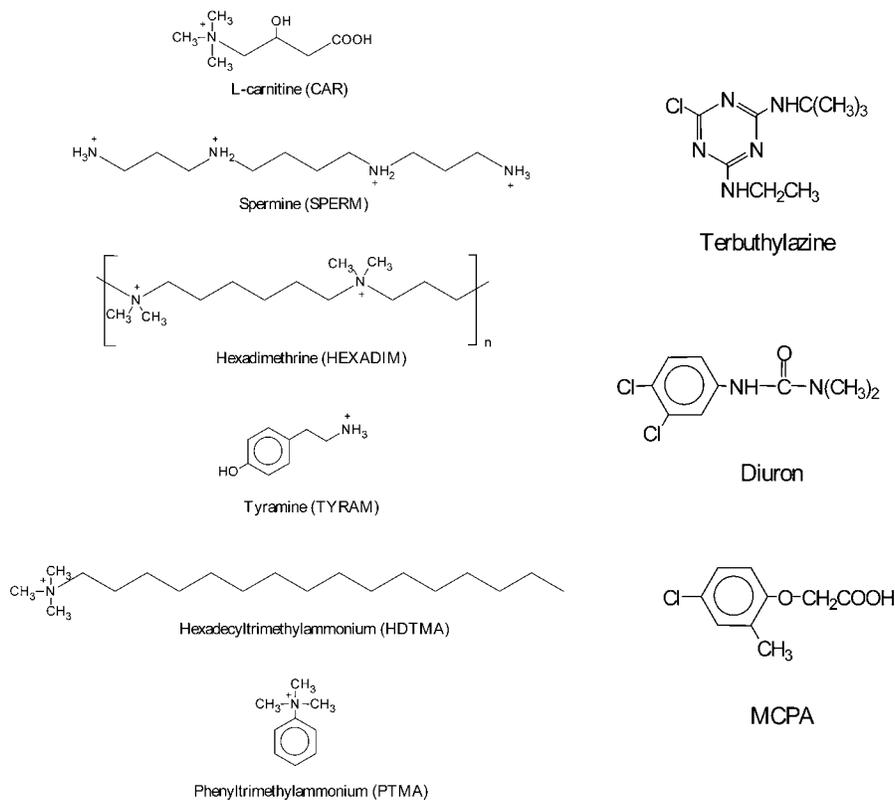


Figure 1. Chemical structures of the modifying cations and herbicides.

exchange reactions. This simple modification changes the nature of the surface from hydrophilic to hydrophobic, increasing its affinity for the pesticide molecule (4, 12–14). The organic cations most commonly used for clay mineral modification are nonfunctionalized quaternary ammonium ions of the general form $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_2\text{NR}_2]^+$, where R is an aromatic or aliphatic hydrocarbon (15, 16).

On the basis that most pesticides contain polar functionalities, it has recently been suggested that organic cations with appropriate functional groups can allow selective modification of clay mineral surfaces to maximize their affinity for selected pesticides. Thus, Cruz-Guzmán et al. (16) studied the ability of three functionalized organic cations, L-carnitine, L-cystine dimethyl ester, and thiamine, to improve the performance of the montmorillonite SWy-2 as an adsorbent of the herbicide simazine. The adsorption of simazine by montmorillonite exchanged with L-carnitine was notably high, which was attributed to the interaction of the weakly basic simazine molecule with the carboxylic functionality of L-carnitine. In a subsequent work, Cruz-Guzmán et al. (17) prepared organoclays by incorporating at different loadings four different natural organic cations into two bentonites differing in their cation exchange capacities and determined the adsorptive behavior of the resultant organoclays for six pesticides. The results revealed that most organobentonites displayed higher affinity for the pesticides than the untreated bentonites, but the improvement in adsorption capacity differed depending on the chemical characteristics of the pesticide and the interlayer organic cation. It was concluded that a suitable selection of the organic cation, on the basis of the presence of certain functional groups, can help improve the performance and selectivity of organoclays as adsorbents of pesticides with regard to the use of nonfunctionalized alkylammonium cations, which in general lack specificity. In addition, the suitability of natural organic cations for clay mineral modification was considered as particularly

interesting to reduce concern about the incorporation of the adsorbent into natural ecosystems for practical applications.

In this work, two montmorillonites (SWy-2 and SAz-1) were modified with organic cations differing in their chemical characteristics, and the modified montmorillonites were characterized and tested as adsorbents of three herbicides widely used in olive groves: terbutylazine, diuron, and MCPA. The aim was to find efficient adsorbents that could be used to remove the assayed herbicides from contaminated water or used as potential supports for the development of slow release formulations of these herbicides to attenuate their environmental impact once applied to soil (8, 18, 19). The organic cations used for the modification of the clay minerals were L-carnitine, spermine, hexadimethrine, tyramine, phenyltrimethylammonium, and hexadecyltrimethylammonium (Figure 1). We paid particular attention to characterizing the montmorillonites treated with spermine, hexadimethrine, and tyramine because these organic cations have not been used before for the modification of SWy-2 or SAz-1. A detailed description of the characteristics of the samples exchanged with L-carnitine, phenyltrimethylammonium, and hexadecyltrimethylammonium can be found elsewhere (8, 16, 17).

MATERIALS AND METHODS

Herbicides and Organic Cations. The chemical structures of the three herbicides, along with those of the organic cations used to modify the clay minerals, are shown in Figure 1. All pesticides and organic cations were supplied by Sigma-Aldrich as high purity compounds (purity >98%).

Preparation of the Adsorbents. SWy-2 Na-rich Wyoming montmorillonite and SAz-1 Ca-rich Arizona montmorillonite from The Clay Minerals Society (Purdue University) were modified with the organic cations through ion exchange reactions. For the synthesis of the montmorillonites exchanged with L-carnitine, spermine, hexadimethrine, and tyramine, the amount of organic cation (chloride or bromide salt) corresponding to 50% or 100% of the cation exchange capacity of

Table 1. Characteristics of Unmodified and Modified Montmorillonite Samples

adsorbent	montmorillonite	modifying cation	C (%)	N (%)	OCtS ^a		d ₀₀₁ ^b (Å)
					expected (%)	actual (%)	
SWy-2 (untreated)	SWy-2	none	0.29 ± 0.01	< 0.05	0	0	n.d. ^c
SWy-2 (blank)	SWy-2	none	0.32 ± 0.01	< 0.05	0	0	15.1
SW-CAR ₁₀₀	SWy-2	L-carnitine	4.10 ± 0.11	0.61 ± 0.01	100	61	14.2
SW-SPERM ₅₀	SWy-2	spermine	1.65 ± 0.02	0.56 ± 0.01	50	53	13.1p
SW-SPERM ₁₀₀	SWy-2	spermine	2.86 ± 0.12	1.01 ± 0.08	100	96	13.0
SW-HEXADIM ₅₀	SWy-2	hexadimethrine	3.22 ± 0.03	0.44 ± 0.02	50	42	14.2p
SW-HEXADIM ₁₀₀	SWy-2	hexadimethrine	5.78 ± 0.06	0.89 ± 0.01	100	88	14.0
SW-TYRAM ₅₀	SWy-2	tyramine	3.00 ± 0.01	0.34 ± 0.01	50	33	14.3
SW-TYRAM ₁₀₀	SWy-2	tyramine	4.42 ± 0.01	0.63 ± 0.01	100	62	14.4
SW-PTMA ₅₀	SWy-2	phenyltrimethylammonium	4.54 ± 0.08	0.52 ± 0.02	50	51	14.4
SW-PTMA ₁₀₀	SWy-2	phenyltrimethylammonium	6.70 ± 0.06	0.82 ± 0.01	100	82	14.6
SW-HDTMA ₅₀	SWy-2	hexadecyltrimethylammonium	9.74 ± 0.04	0.56 ± 0.01	50	58	16.6p
SW-HDTMA ₁₀₀	SWy-2	hexadecyltrimethylammonium	14.84 ± 0.02	0.84 ± 0.01	100	93	18.0
SAz-1 (untreated)	SAz-1	none	< 0.1	< 0.05	0	0	n.d.
SAz-1 (blank)	SAz-1	none	< 0.1	< 0.05	0	0	15.2
SA-CAR ₁₀₀	SAz-1	L-carnitine	4.10 ± 0.01	0.64 ± 0.01	100	41	14.8
SA-SPERM ₅₀	SAz-1	spermine	2.12 ± 0.01	0.87 ± 0.01	50	53	13.1p
SA-SPERM ₁₀₀	SAz-1	spermine	3.78 ± 0.02	1.55 ± 0.01	100	96	13.0
SA-HEXADIM ₅₀	SAz-1	hexadimethrine	4.76 ± 0.12	0.76 ± 0.02	50	47	14.2p
SA-HEXADIM ₁₀₀	SAz-1	hexadimethrine	8.52 ± 0.04	1.36 ± 0.01	100	88	14.2
SA-TYRAM ₅₀	SAz-1	tyramine	3.02 ± 0.10	0.40 ± 0.01	50	25	15.0
SA-TYRAM ₁₀₀	SAz-1	tyramine	5.28 ± 0.12	0.79 ± 0.05	100	50	15.0
SA-PTMA ₅₀	SAz-1	phenyltrimethylammonium	6.85 ± 0.02	0.84 ± 0.01	50	54	15.1
SA-PTMA ₁₀₀	SAz-1	phenyltrimethylammonium	9.58 ± 0.07	1.19 ± 0.01	100	79	15.0
SA-HDTMA ₅₀	SAz-1	hexadecyltrimethylammonium	14.51 ± 0.03	0.85 ± 0.01	50	60	17.3p
SA-HDTMA ₁₀₀	SAz-1	hexadecyltrimethylammonium	22.50 ± 0.01	1.29 ± 0.01	100	101	24.0

^a Organic cation saturation: percentage of the CEC of the montmorillonite occupied by organic cations (calculated from the N content). ^b Basal spacing values for air-dried oriented specimens. (p indicates a poorly defined basal diffraction.) ^c Not determined.

SWy-2 (CEC_{SWy-2} = 764 mmol kg⁻¹) or SAz-1 (CEC_{SAz-1} = 1200 mmol kg⁻¹) was dissolved in 50 mL of 1 mM HNO₃ and added to 1 g of clay mineral. The suspensions were shaken for 24 h, centrifuged, washed 3 times with 100 mL of distilled water, and then freeze-dried. Blank clay samples were also prepared by shaking 1 g of montmorillonite in 50 mL of 1 mM HNO₃ for 24 h, washing three times with 100 mL of distilled water, and then freeze-drying. The HDTMA- and PTMA-montmorillonites were prepared as described in Celis et al. (8).

Characterization of the Adsorbents. Elemental analyses of the unexchanged and exchanged montmorillonite samples were performed using a Perkin-Elmer, model 1106 elemental analyzer (Perkin-Elmer Corp., Norwalk, CT). X-ray diffraction patterns were obtained on oriented specimens using a Siemens D-5000 diffractometer (Siemens, Stuttgart) with CuK_α radiation. The oriented specimens were either air-dried or dried at 200 °C and then cooled down to room temperature before X-ray diffraction measurements. To minimize rehydration of the samples, sample cooling was carried out inside a desiccator, and the time elapsed from heating to recording was as low as 5 min. Fourier-transform infrared (FTIR) spectra were recorded on KBr disks using a Nicolet 5 PC spectrometer (Nicolet Instrument Corp., WI). Thermal analyses were conducted in a Setaram TG-DTA 92 apparatus, model 1618, using a 15 mg sample diluted with 35 mg of Al₂O₃. Differential thermal analyses (DTA) and thermogravimetric analyses (TG) were performed in air between room temperature and 900 °C using a heating rate of 10 °C/min.

Adsorption–Desorption Experiments. The adsorption of terbutylazine, diuron and MCPA by the untreated and modified montmorillonite samples was measured at a single initial concentration C_{ini} = 1 mg L⁻¹ using the batch equilibration procedure. Triplicate 20 mg adsorbent samples were equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of a 1 mg L⁻¹ herbicide solution, prepared in distilled water from a 200 mg L⁻¹ herbicide solution prepared in methanol. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution was removed for analysis. The concentration of herbicide in the supernatant solutions (C_e) was determined by high performance liquid chromatography (HPLC) as described below. Herbicide solutions without adsorbent were also shaken for 24 h and served as controls. The percentage of herbicide adsorbed (%Ads) by

the different adsorbents was calculated by using the following formula: %Ads = [(C_{ini} - C_e)/C_{ini}] × 100.

Adsorption–desorption isotherms of terbutylazine, diuron, and MCPA on selected samples were also obtained. Duplicate 20 mg adsorbent samples were equilibrated with 8 mL of herbicide initial solutions (C_{ini} = 0.1, 0.2, 1, and 2 mg L⁻¹) by shaking mechanically at 20 ± 2 °C for 24 h. After equilibration, the suspensions were centrifuged, and 4 mL of the supernatant solutions was removed for analysis. The herbicide concentration in the supernatant solutions was determined by HPLC. The amount of herbicide adsorbed was calculated from the difference between the initial and the equilibrium solution concentrations. Desorption was measured immediately after adsorption from the highest equilibrium point of the adsorption isotherm, that is, that corresponding to the initial concentration 2 mg L⁻¹. The 4 mL of supernatant removed for the adsorption analysis was replaced with 4 mL of distilled water. After shaking at 20 ± 2 °C for 24 h, the suspensions were centrifuged, and the herbicide concentration was determined in the supernatant. This desorption procedure was repeated three times.

Herbicide Analysis. Terbutylazine, diuron, and MCPA were analyzed by HPLC using a Waters 600E chromatograph coupled to a Waters 996 diode-array detector. The analytical conditions were Novapack C18 column (150 mm length × 3.9 mm i.d.); eluent mixture, 50:50 acetonitrile/water for terbutylazine, 40:60 acetonitrile/water for diuron, and 60:40 methanol/diluted H₃PO₄ (pH 2) for MCPA, at a flow rate of 1 mL min⁻¹; 25 μL injection volume; and UV detection at 220 nm for terbutylazine, 250 nm for diuron, and 230 nm for MCPA. External calibration curves with four standard solutions between 0.1 and 2 mg L⁻¹ were used in the calculations.

RESULTS AND DISCUSSION

Elemental Analysis. The C and N contents of the unexchanged and exchanged montmorillonite samples are given in **Table 1**. The actual percentage of the CEC of SWy-2 and SAz-1 occupied by organic cations (**Table 1**) was calculated from the N content of the samples. The amounts of spermine, hexa-

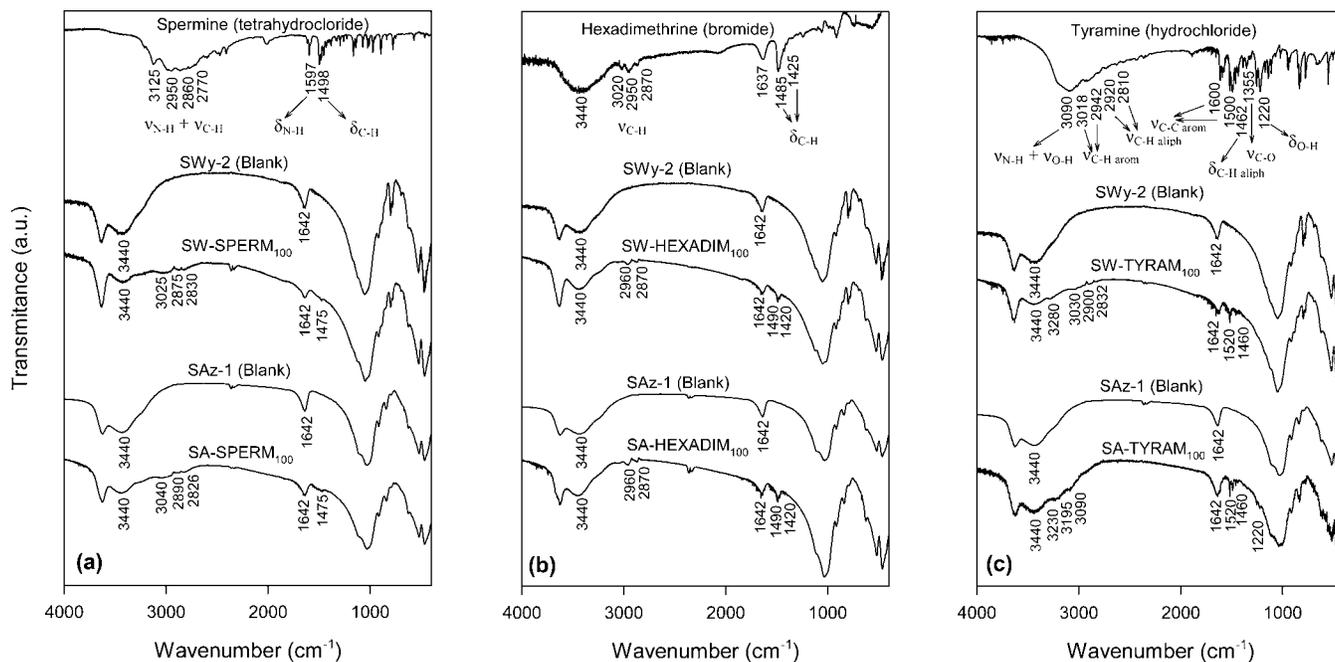


Figure 2. Fourier transform infrared spectra of selected organic cations and unmodified and modified montmorillonite samples.

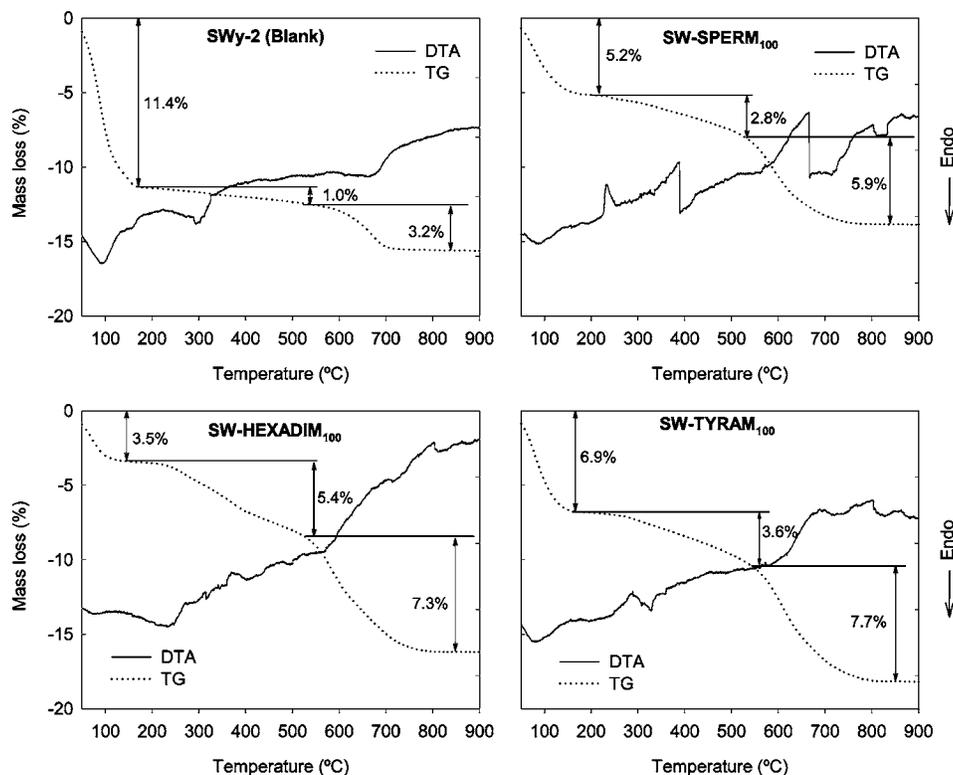


Figure 3. Thermogravimetric (TG) and differential thermal analysis (DTA) of SWy-2 samples modified with spermine, hexadimethrine, and tyramine.

dimethrine, phenyltrimethylammonium, and hexadecyltrimethylammonium present in the samples were close to those added during synthesis. In contrast, carnitine and tyramine displayed some resistance to reacting with SWy-2 and SAz-1, as their amount in the modified clays was considerably lower than that added during synthesis. These results are in accordance with those recently reported by Cruz-Guzmán et al. (16, 17), where small, monovalent polar organic cations were found to display greater resistance to reacting with smectites compared to polyvalent or larger organic cations. Also in accordance with Cruz-Guzmán et al. (17), the results in Table 1 show that the resistance of carnitine and tyramine to reacting with the

montmorillonites is exacerbated for SAz-1 as compared to SWy-2. This is probably due to the presence of Ca^{2+} as the main natural inorganic cation in SAz-1 because Ca^{2+} is more difficult to displace than Na^+ cations in SWy-2 (20).

FTIR Spectroscopy. The FTIR spectra of SWy-2 and SAz-1 treated with spermine, hexadimethrine, and tyramine together with those of the blank clay samples and the pure organic cations are shown in Figure 2. Band assignment was carried out on the basis of Bellamy (21). The appearance of new peaks in the infrared spectra of the exchanged clay samples compared to those present in the spectra of the blank clays provided further evidence for the presence of the organic cations in the modified

clays. In addition, the intensity of the band at about 3440 cm^{-1} , corresponding to the hydration water of montmorillonite, indicated a reduction in hydration water of the clays after treatment with spermine, hexadimethrine, and tyramine cations. This finding is consistent with the fact that organic cations on exchange sites of clay minerals are normally less hydrated than inorganic exchange cations (16).

The group of bands between 3125 and 2770 cm^{-1} in the FT-IR spectrum of pure spermine (Figure 2a) can be assigned to the N–H stretching vibration of the protonated $-\text{NH}_3^+$ and $-\text{NH}_2^+$ groups and to the C–H stretching vibrations of the $-\text{CH}_2-$ groups (Figure 1). The bands close to 1600 and 1500 cm^{-1} can be assigned to N–H and C–H deformation modes, respectively. All these bands were also identified in the FT-IR spectra of SW-SPERM₁₀₀ and SA-SPERM₁₀₀, although those located at about 1600 cm^{-1} were obscured by the deformation vibration of the hydration water of the clay, located at 1642 cm^{-1} . The shift of the N–H and C–H vibration bands upon the interaction of spermine with SWy-2 and SAz-1 reveals some involvement of these groups in the interaction with the clays.

The bands between 3020 and 2870 cm^{-1} in the FT-IR spectrum of pure hexadimethrine (Figure 2b) can be assigned to the C–H stretching vibration of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups, the corresponding C–H deformation modes appearing at 1485 cm^{-1} ($-\text{CH}_2-$) and 1425 cm^{-1} ($-\text{CH}_3$). The bands at 3440 and 1637 cm^{-1} correspond, respectively, to the O–H stretching and O–H deformation vibrations of hydration water and indicate the rapid uptake of water by hexadimethrine bromide in the KBr disk as a result of its highly hygroscopic character. The C–H stretching and deformation vibrations of hexadimethrine were also identified in the FT-IR spectra of SW-HEXADIM₁₀₀ and SA-HEXADIM₁₀₀ at 2960 and 2870 cm^{-1} (C–H stretch) and at 1490 and 1420 cm^{-1} (C–H deformation). They were only slightly shifted compared to their position in the pure compound.

The broad absorption band at about 3090 cm^{-1} in the FT-IR spectrum of tyramine (Figure 2c) can be assigned to the N–H stretching vibration of the $-\text{NH}_3^+$ group and the O–H stretching vibration of the phenolic group, where intermolecular bonding results in shifting of the stretching vibration toward lower wavenumbers compared to typical values for free phenolic groups. Bands corresponding to aromatic C–H stretching vibration modes appeared near 3000 cm^{-1} , whereas those corresponding to aliphatic C–H were identified at 2920 and 2810 cm^{-1} . The bands appearing at about 1600 and 1500 cm^{-1} can be assigned to the aromatic C–C stretching vibrations, although the N–H deformation mode of $-\text{NH}_3^+$ could have contributed to the band located at 1600 cm^{-1} . Bands corresponding to the C–H deformation vibration of $-\text{CH}_2-$ groups (1462 cm^{-1}) and to the C–O stretching (1355 cm^{-1}) and O–H deformation (1220 cm^{-1}) vibrations of the phenolic group were also identified (Figure 2c). Most of these vibration bands of tyramine were identified in the spectra of SW-TYRAM₁₀₀ and SA-TYRAM₁₀₀.

Thermal Analysis. In accordance with the previously reported thermal behavior of organoclay complexes (22, 23), the thermal decomposition of SW-SPERM₁₀₀, SW-HEXADIM₁₀₀, and SW-TYRAM₁₀₀ took place in three steps (Figure 3). A first mass-loss step is observed between room temperature and about $150\text{ }^\circ\text{C}$ and can be attributed to the dehydration of adsorption water associated with the clay and with the interlayer cation. This first mass-loss is considerably greater for the unmodified SWy-2 sample than for the modified clays, probably revealing lower hydration of the organic cations compared to

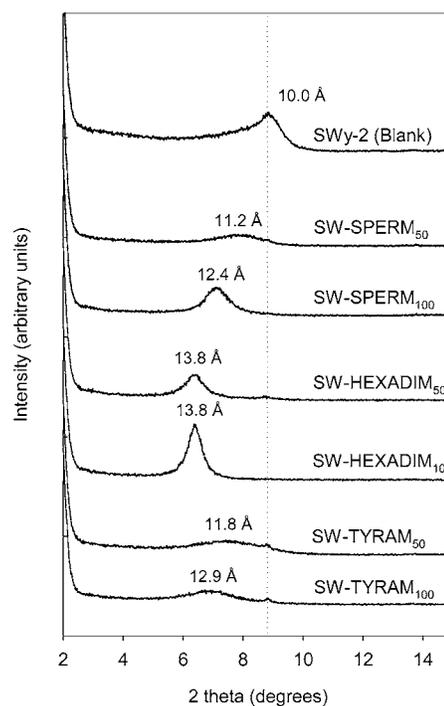


Figure 4. X-ray diffraction patterns of oriented specimens of SWy-2 samples modified with spermine, hexadimethrine, and tyramine dried at $200\text{ }^\circ\text{C}$.

the original Na^+ ions in the unmodified SWy-2 sample. A second mass-loss step is observed over the temperature range 200 – $550\text{ }^\circ\text{C}$ and is assigned to the loss of organic cation. Accordingly, the magnitude of this second mass-loss was directly related to the organic carbon content of the samples: SW-HEXADIM₁₀₀ > SW-TYRAM₁₀₀ > SW-SPERM₁₀₀ > SWy-2 (Blank) (Table 1). The third mass-loss is ascribed to dehydroxylation of the mineral and occurs over the temperature range 550 – $700\text{ }^\circ\text{C}$.

X-ray Diffraction. The basal spacing values, d_{001} , for air-dried oriented specimens of the exchanged montmorillonite samples together with those of the blank SWy-2 and SAz-1 montmorillonites are included in Table 1. The low d_{001} values recorded for the samples modified with carnitine, spermine, hexadimethrine, and tyramine are consistent with the small size of carnitine and tyramine, and strongly suggest the arrangement of spermine and hexadimethrine forming a horizontal monolayer within the clay interlayers (15, 24, 25). The decrease in the basal spacing of SWy-2 and SAz-1 upon treatment with these organic cations (Table 1) can be attributed to the replacement of the inorganic interlayer cation and its hydration water by less hydrated organic cations (9, 16). This observation is consistent with the decrease in the intensity of the IR vibration band corresponding to the hydration water of montmorillonite (3440 cm^{-1}) after treatment with spermine, hexadimethrine, and tyramine (Figure 2), and also with the magnitude of the first mass-loss step observed during thermal decomposition of the samples (Figure 3). After heating at $200\text{ }^\circ\text{C}$ (Figure 4), the blank SWy-2 sample collapsed ($d_{001} \approx 10.0\text{ }^\circ\text{Å}$), whereas the exchanged clays showed some resistance to collapse ($d_{001} > 10.0\text{ }^\circ\text{Å}$), confirming the presence of the organic cations in the clay interlayers (9, 16). Very similar results were obtained for the SAz-1 samples heated at $200\text{ }^\circ\text{C}$, although the basal diffraction of unexchanged SAz-1 dried at $200\text{ }^\circ\text{C}$ was not well defined, presumably because of its high CEC, which may have produced a heterogeneous layer distribution after heating or a partial rehydration of the sample during X-ray diffraction

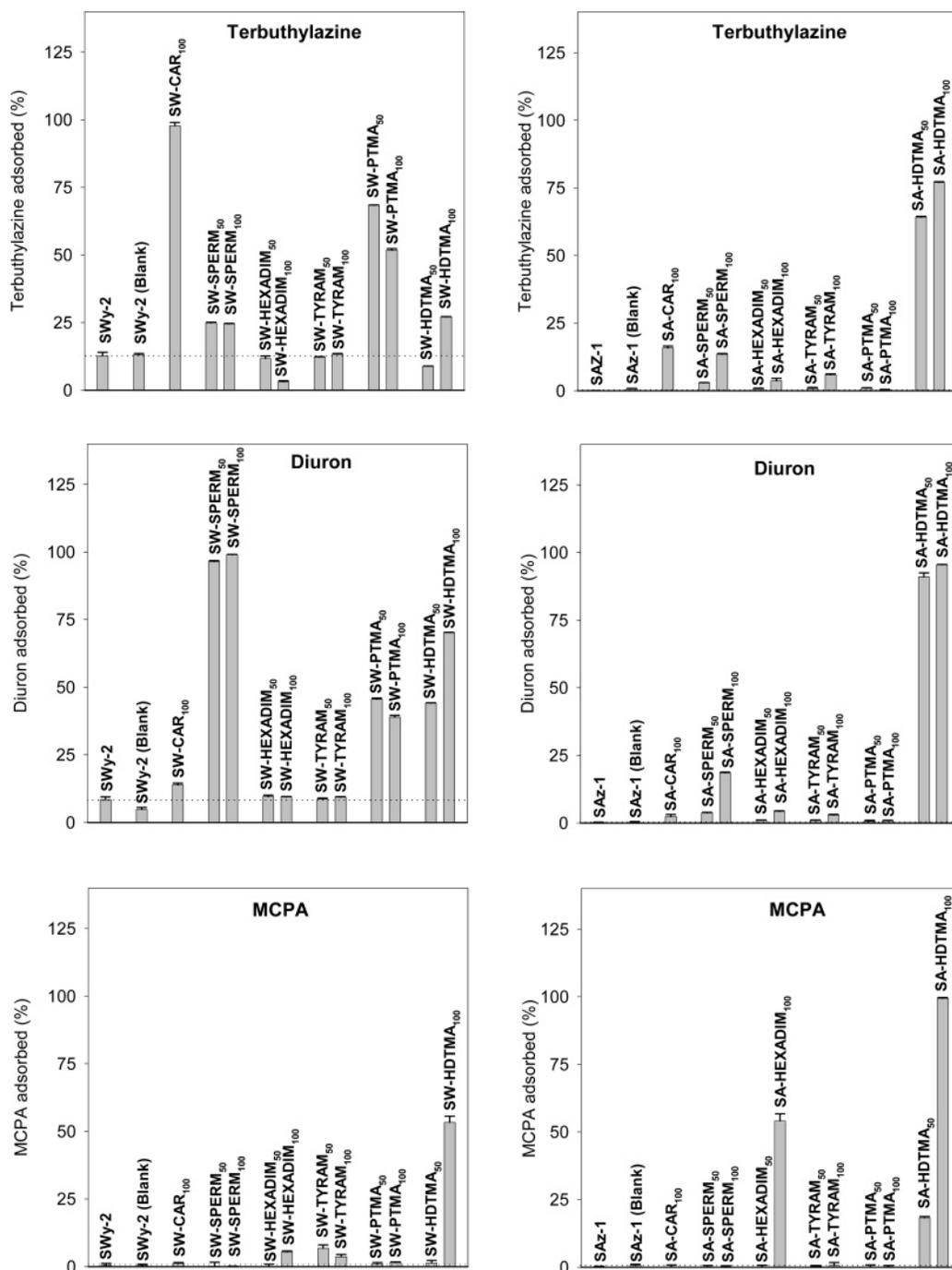


Figure 5. Percentage of terbutylazine, diuron, and MCPA adsorbed by unmodified and modified montmorillonites at an initial herbicide concentration of 1 mg L^{-1} .

analysis (17). The d_{001} values obtained for the montmorillonites exchanged with PTMA and HDTMA (Table 1) are in agreement with previously reported values for these organoclays (15, 25, 26). PTMA exists as discrete species in the interlayers of SWy-2 and SAz-1, resulting in basal spacings of about 14–15 Å. HDTMA forms a bilayer structure ($d_{001} \approx 18 \text{ Å}$) in low-charge montmorillonites such as SWy-2 and a paraffinic structure ($d_{001} \approx 24 \text{ Å}$) in the high-charge montmorillonite SAz-1 (Table 1).

Adsorption–Desorption Experiments. Figure 5 shows the percentage of terbutylazine, diuron, and MCPA adsorbed by the unmodified and modified montmorillonites at a single initial concentration of 1 mg L^{-1} . Adsorption isotherms of the herbicides on selected samples are shown in Figure 6. In all cases, the pH of the equilibrated clay–herbicide suspensions

was greater than 5 so that the molecular forms of terbutylazine ($\text{p}K_{\text{a}} = 2.0$) and diuron and the anionic form of MCPA ($\text{p}K_{\text{a}} = 3.1$) should have predominated during the adsorption experiments. Different degrees of improvement of the adsorbent properties of the modified montmorillonites were observed for all three herbicides, depending on the nature of the organic cation, the type of clay, and the amount of organic cation in the samples.

In general, all three herbicides displayed a great affinity for SAz-1 exchanged with HDTMA and moderate to low affinity for SAz-1 exchanged with the other organic cations (Figures 5 and 6). This can be explained by the paraffinic ($d_{001} > 22 \text{ Å}$) structure resulting from incorporation of HDTMA cations in SAz-1, in particular at high organic cation loadings, which

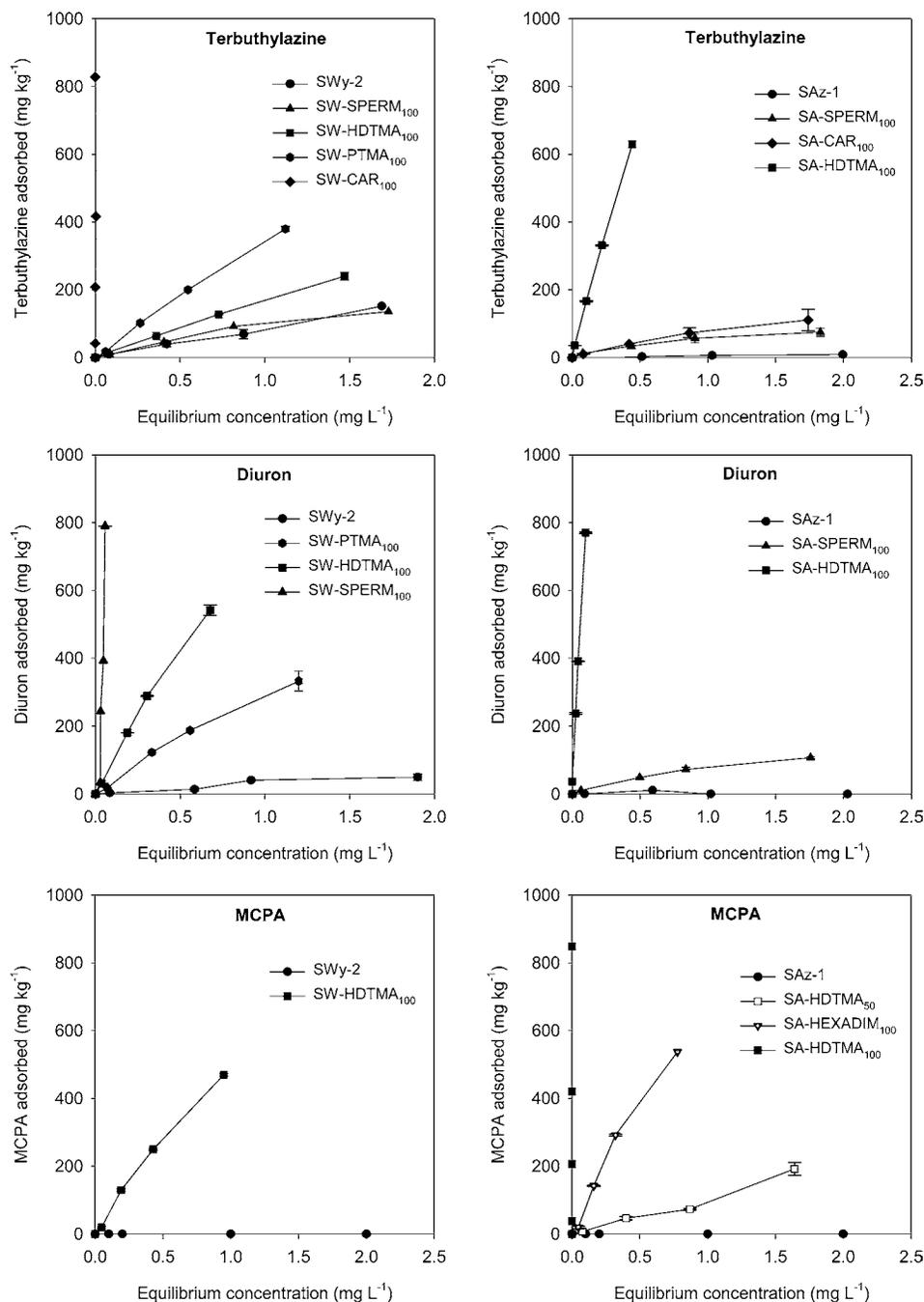


Figure 6. Adsorption isotherms of terbuthylazine, diuron, and MCPA on selected samples.

creates a wide interlayer organic phase with a strong affinity for herbicides. The small basal spacing combined with the proximity of two adjacent cations resulting from the incorporation of the other organic cations in the interlayers of the high-charge montmorillonite SAz-1 results, in general, in little internal space being available for herbicide adsorption (17). Nevertheless, certain organic cations led to some enhancement of the adsorption of terbuthylazine, diuron, and MCPA by SAz-1, mostly at high organic cation loadings (Figure 5). This is presumably due to interactions of the pesticides with the organic cations at external surfaces of the modified clays (17).

For samples prepared from the low-charge montmorillonite SWy-2, modification with carnitine and spermine cations resulted in organoclays with very strong affinities for terbuthylazine and diuron, respectively, whereas modification with the alkylammonium cations, PTMA and HDTMA, resulted in

organoclays with moderate affinity for these herbicides (Figures 5 and 6). The high affinity of terbuthylazine for carnitine-exchanged SWy-2 can be attributed to the weakly basic character of terbuthylazine ($pK_a = 2.0$), which allows an acid–base interaction with the carboxylic group of carnitine. This mechanism has been demonstrated to be responsible for the extensive adsorption of the herbicide simazine by carnitine-treated SWy-2 (16). However, the great affinity of diuron for spermine-exchanged SWy-2 could be a combination of (i) hydrogen bonding between the C=O group of the herbicide and the $-NH_3^+/-NH_2^+$ groups of spermine and (ii) hydrophobic interactions between the herbicide and the alkyl chains of spermine (Figure 1). Polar interactions between C=O groups of pesticides and the protonated amino group of primary amines have been shown to contribute to pesticide adsorption by organoclays (12, 13). However, we believe that the alkyl chains

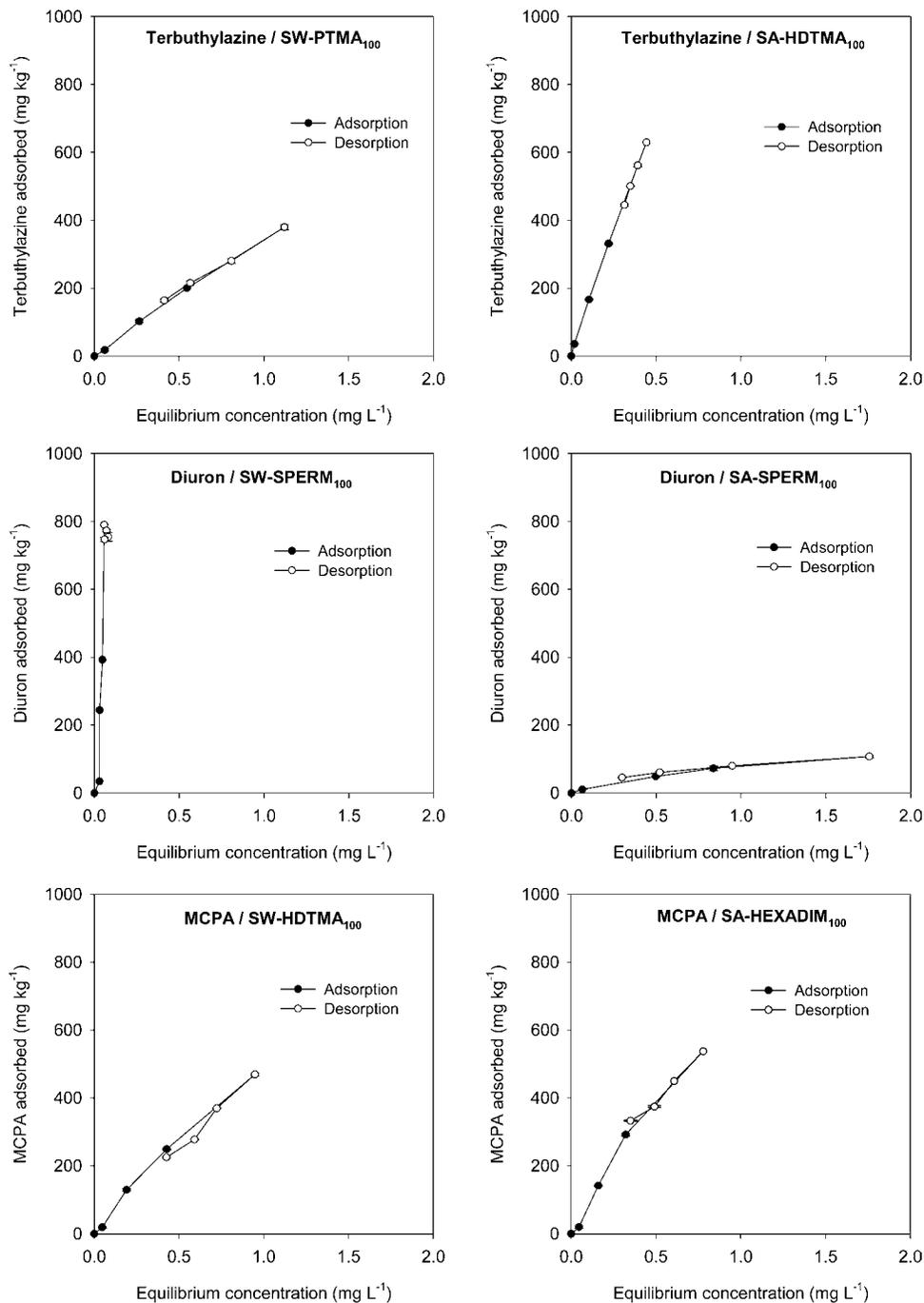


Figure 7. Adsorption-desorption isotherms of terbutylazine, diuron, and MCPA on selected samples.

of spermine probably contributed to stabilize the interaction of diuron with spermine-exchanged SWy-2 because tyramine (also containing an NH_3^+ group) did not provide SWy-2 with such a high affinity for diuron. Independent of the operating mechanism, our results illustrate how the chemical characteristics of the organic cation represent a major factor in determining the performance of organoclays as adsorbents of the assayed herbicides.

The low adsorption of MCPA by most SWy-2 samples (Figure 5) is related to the anionic character of this herbicide at the pH of the equilibrated suspensions ($\text{pH} > 5$). Only HDTMA, when incorporated at 100% of the CEC of the clay mineral, provided SWy-2 with some affinity for MCPA, but this effect was considerably less than that observed after the incorporation of HDTMA cations in the high-charge montmo-

illonite SAz-1 (Figures 5 and 6). This is because the paraffinic structure of SA-HDTMA₁₀₀ provides a better medium for the adsorption of MCPA than the bilayer structure of SW-HDTMA₁₀₀. These results are very similar to those previously reported for the adsorption of other anionic pesticides by SWy-2 and SAz-1 exchanged with HDTMA cations (17, 27, 28).

Desorption isotherms of terbutylazine, diuron, and MCPA on selected adsorbents were obtained, and in general, a reversible behavior was observed (Figure 7). Nevertheless, it should be noted that cases of very high adsorption, such as the adsorption of diuron by SW-SPERM₁₀₀, resulted in ill-defined desorption isotherms because the very low solution concentrations complicated the desorption analysis (29). The observed reversible behavior of most of our systems would be advantageous in terms of recyclability of the adsorbent once used for water decon-

tamination and also from the point of view of using the adsorbents as supports in the design of slow release formulations of the assayed herbicides (13).

In summary, modification of the montmorillonites SWy-2 and SAz-1 with certain organic cations rendered organoclays with excellent affinities for terbutylazine, diuron, and MCPA. For instance, all three herbicides displayed very strong affinities for SAz-1 exchanged with HDTMA cations, particularly when HDTMA was incorporated at 100% of the CEC of the clay mineral. Terbutylazine and diuron also displayed very strong affinities for SWy-2 exchanged with L-carnitine and spermine, respectively. These adsorbents could therefore find application in the removal of the assayed herbicides from contaminated water or as potential supports for the development of slow release formulations of the assayed herbicides, with the purpose of attenuating their environmental impact once applied to soil. The general reversible adsorption-desorption behavior observed for our systems appears to be an interesting property in terms of recyclability of the adsorbents and also from the point of view of the potential use of the adsorbents as supports for the slow release of herbicides.

ABBREVIATIONS USED

MCPA, 4-chloro-2-methylphenoxyacetic acid; FTIR, Fourier-transform infrared; HPLC, high performance liquid chromatography; CAR, L-carnitine; SPERM, spermine; HEXADIM, hexadimethrine, TYRAM, tyramine; PTMA, phenyltrimethylammonium; HDTMA, hexadecyltrimethylammonium; SWy-2, Wyoming montmorillonite; SAz-1, Arizona montmorillonite; CEC, cation exchange capacity.

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LITERATURE CITED

- Albarrán, A.; Celis, R.; Hermosín, M. C.; López-Piñeiro, A.; Ortega-Calvo, J. J.; Cornejo, J. Effects of solid olive-mill waste addition to soil on sorption, degradation and leaching of the herbicide simazine. *Soil Use Manag.* **2003**, *19*, 150–156.
- Santiago-Mora, R.; Martin-Laurent, F.; de Prado, R.; Franco, A. R. Degradation of simazine by microorganisms isolated from soils of Spanish olive fields. *Pest Manag. Sci.* **2005**, *61*, 917–921.
- Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticides into soils from clay-polymer formulations. *J. Agric. Food Chem.* **1998**, *46*, 3797–3802.
- Boyd, S. A.; Shaobai, S.; Lee, J. F.; Mortland, M. M. Pentachlorophenol sorption by organo-clays. *Clays Clay Miner.* **1988**, *36*, 125–130.
- González-Pradas, E.; Villafranca-Sánchez, M.; Gallego-Campo, A.; Ureña-Amate, D.; Fernández-Pérez, M. Removal of atrazine from aqueous solution by natural and activated bentonite. *J. Environ. Qual.* **1997**, *26*, 1288–1291.
- Aguer, J. P.; Hermosín, M. C.; Calderón, M. J.; Cornejo, J. Fenuron sorption by homoionic natural and modified smectites. *J. Environ. Sci. Health, Part B* **2000**, *35*, 279–296.
- Cox, L.; Celis, R.; Hermosín, M. C.; Cornejo, J. Natural soil colloids to retard simazine and 2,4-D leaching in soil. *J. Agric. Food Chem.* **2000**, *48*, 93–99.
- 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.

- Celis, R.; Hermosín, M. C.; Cornejo, J. Heavy metal adsorption by functionalized clays. *Environ. Sci. Technol.* **2000**, *34*, 4593–4599.
- Lagaly, G. Pesticide-clay interactions and formulations. *Appl. Clay Sci.* **2001**, *18*, 205–209.
- Rehab, A.; Akelah, A.; Agag, T.; Shalaby, N. Preparation and characterization of polyurethane-organoclay nanocomposites. *Polym. Compos.* **2007**, *28*, 108–115.
- Hermosín, M. C.; Cornejo, J. Binding mechanism of 2,4-dichlorophenoxyacetic acid by organoclays. *J. Environ. Qual.* **1993**, *22*, 325–331.
- Celis, R.; Koskinen, W. C.; Hermosín, M. C.; Ulibarri, M. A.; Cornejo, J. Triadimefon interactions with organoclays and organohydrotalcites. *Soil Sci. Soc. Am. J.* **2000**, *64*, 36–43.
- Sanchez-Martin, M. J.; Rodriguez-Cruz, M. S.; Andrades, M. S.; Sanchez-Camazano, M. J. Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides: influence of clay type and pesticide hydrophobicity. *Appl. Clay Sci.* **2006**, *31*, 216–228.
- Jaynes, W. F.; Boyd, S. A. Clay mineral type and organic compound sorption by hexadecyltrimethylammonium exchanged clays. *Soil Sci. Soc. Am. J.* **1991**, *55*, 43–48.
- Cruz-Guzmán, M.; Celis, R.; Hermosín, M. C.; Cornejo, J. Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations. *Environ. Sci. Technol.* **2004**, *38*, 180–186.
- Cruz-Guzmán, M.; Celis, R.; Hermosín, M. C.; Koskinen, W. C.; Cornejo, J. Adsorption of pesticides from water by functionalized organobentonites. *J. Agric. Food Chem.* **2005**, *53*, 7502–7511.
- El-Nahhal, Y.; Nir, S.; Serban, C.; Rabinovitch, O.; Rubin, B. Montmorillonite-phenyltrimethylammonium yields environmentally improved formulations of hydrophobic herbicides. *J. Agric. Food Chem.* **2000**, *48*, 4791–4801.
- Hermosín, M. C.; Calderón, M. J.; Aguer, J. P.; Cornejo, J. Organoclays for controlled release of the herbicide fenuron. *Pest Manag. Sci.* **2001**, *57*, 803–809.
- Theng, B. K. G.; Greenland, D. J.; Quirk, J. P. Adsorption of alkylammonium cations by montmorillonite. *Clay Miner.* **1967**, *7*, 1–17.
- Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed; Chapman & Hall: London, 1975; Vol. I.
- Yariv, S. The role of charcoal on DTA curves of organo-clay complexes: an overview. *Appl. Clay Sci.* **2004**, *24*, 225–236.
- Xi, Y.; Ding, Z.; He, H.; Frost, R. L. Structure of organoclays: an X-ray diffraction and thermogravimetric analysis study. *J. Colloid Interface Sci.* **2004**, *277*, 116–120.
- Lagaly, G. Layer charge heterogeneity in vermiculites. *Clays Clay Miner.* **1982**, *30*, 215–222.
- Roberts, M. G.; Li, H.; Teppen, B.; Boyd, S. A. Sorption of nitroaromatics by ammonium- and organic ammonium-exchanged smectite: shifts from adsorption/complexation to a partition-dominated process. *Clays Clay Miner.* **2006**, *54*, 426–434.
- Jaynes, W. F.; Boyd, S. A. Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays Clay Miner.* **1991**, *39*, 428–436.
- Celis, R.; Koskinen, W. C.; Cecchi, A. M.; Bresnahan, G. A.; Carrisoza, M. J.; Ulibarri, M. A.; Pavlovic, I.; Hermosín, M. C. Sorption of the ionisable pesticide imazamox by organo-clays and organohydrotalcites. *J. Environ. Sci. Health, Part B* **1999**, *34*, 929–941.
- Cruz-Guzmán, M. Estudio de Coloides Naturales y Modificados como Adsorbentes para la Reducción de la Contaminación de Suelos y Aguas. Ph.D. Thesis, University of Seville, Spain, 2004.
- Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632–1638.