Adsorption of Pesticides from Water by Functionalized Organobentonites

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Replacement of natural inorganic cations of clay minerals with organic cations has been proposed as a strategy to improve the adsorptive capacity of clay minerals for organic compounds, including pesticides. The organic cations most commonly used for this purpose have been quaternary ammonium ions containing alkyl or aryl chains without specific functional groups. In this work, we evaluated the ability of two bentonites (SWy-2 and SAz-1) exchanged with four natural organic cations containing diverse functional groups (L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, and thiamine) as adsorbents of pesticides varying in their chemical structures (simazine, hexazinone, triadimefon, alachlor, carbaryl, and imazethapyr). For comparison purposes, the adsorptive properties of two "classical" organobentonites, hexadecyltrimethylammonium- and phenyltrimethylammonium-exchanged bentonites, were also determined. Most organobentonites displayed higher affinity for the pesticides than the untreated bentonites, but the improvement in adsorption capacity varied depending on the characteristics of the pesticide and the interlayer organic cation. Triadimefon, carbaryl, and imazethapyr displayed the highest affinity for carnitine (K_f = 229–2377)-, thiamine (K_f = 83–354)-, and cystine (K_f = 96–100)-treated bentonites, respectively, whereas alachlor was adsorbed similarly by all organobentonites. In general, pesticide adsorption–desorption hysteresis was greater for adsorbents with the highest adsorption capacities. The results demonstrate that selective modification of smectitic clay minerals with natural organic cations containing appropriate functional groups can be a useful strategy to improve their performance for the removal of specific pesticides from the environment.

KEYWORDS: Bentonites; organoclays; adsorption; pesticides

INTRODUCTION

There has been much interest in the use of organoclays as adsorbents to prevent and remediate environmental contamination by pesticides and other organic pollutants (*1–6*). The replacement of the original inorganic exchange cations of clay minerals with organic cations through ion exchange reactions has been shown to yield organoclays with organophilic properties; hence, this simple modification has been proposed for the improvement of the adsorptive capacity of clay minerals for nonionic organic compounds, including hydrophobic pesticides (*2*, *7*, *8*). The organic cations most commonly used for this purpose are quaternary ammonium ions of the general form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$, where R is an aromatic or aliphatic hydrocarbon (*9*). With these alkylammonium type cations, the major factor determining the adsorptive properties

of these organoclays has been the organic cation arrangement in the clay mineral interlayers, which is a function of the size of the hydrocarbon chains of the alkylammonium cation, the surface charge of the clay mineral, and the amount of organic cation in the interlayer (*4*, *5*, *9*, *10*).

Because most pesticides contain polar groups, it can be hypothesized that organic cations with appropriate functional groups could allow selective modification of clay mineral surfaces to maximize its affinity for selected pesticides. For instance, Cruz-Guzmán et al. (*11*) studied the ability of three polar organic cations, L-carnitine, L-cystine dimethyl ester, and thiamine, to improve the performance of the bentonite SWy-2 as an adsorbent of the herbicide simazine. They pointed out the importance of the structural complementarity between the pesticide molecule and the cation preadsorbed on the bentonite in determining the performance of organobentonites as adsorbents of simazine. Therefore, a suitable selection of the chemical characteristics of the organic cation might help improve the adsorbent properties of organoclays with regard to the use of alkylammonium organic cations without specificity

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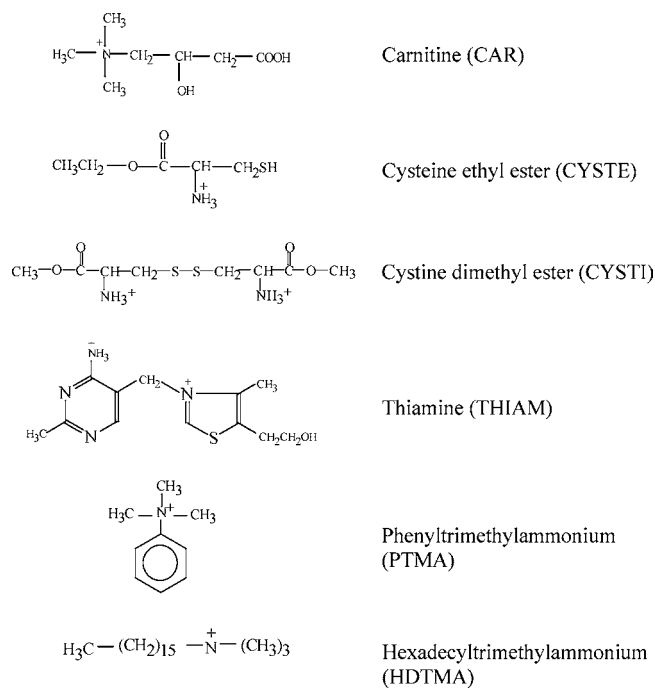*J. Agric. Food Chem.*, Vol. 53, No. 19, 2005 **7503**

Figure 1. Chemical structures of L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, thiamine, phenyltrimethylammonium, and hexadecyltrimethylammonium cations.

(*11*). Li et al. (*12*) observed the influence of diverse functional groups of organic matter on the clay adsorbent behavior for two different pesticides. Groisman et al. (*13*) studied the adsorption of two organophosphate pesticides by a bifunctional organoclay. The organoclay was able to selectively adsorb organophosphate pesticides and to catalyze their hydrolysis and thereby detoxify them.

In this work, we hypothesize that the presence of functional polar groups in the organic cation structure influences the capacity and selectivity of the adsorption behavior of organoclays for pesticides, since most pesticides have functional polar groups in their structure. For the organoclay preparation, we have selected two bentonites with different cation exchange capacities, SWy-2 and SAz-1, and four organic cations, L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, and thiamine (**Figure 1**), which were incorporated in the bentonites at different saturation rates by exchange reactions. The organic cations were selected on the basis of (i) their natural origin, which should reduce concern about the incorporation of these materials into soil and aquatic environments, and (ii) the presence of diverse functional groups in their structures, with the aim to establish specific relationships between the pesticide adsorption and the structural characteristics of the organic
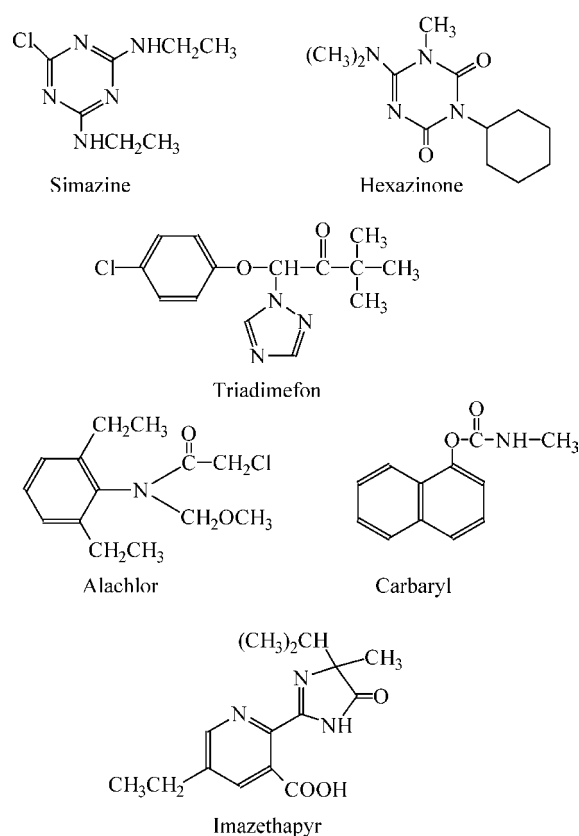

Figure 2. Chemical structures of pesticides simazine, hexazinone, triadimefon, alachlor, carbaryl, and imazethapyr.

cations. The objective of this research was to determine the ability of these organobentonites as adsorbents of six pesticides with different chemical natures. For comparison purposes, the adsorptive properties of two "classical" organobentonites, hexadecyltrimethylammonium- and phenyltrimethylammonium-exchanged bentonites, were also determined.

MATERIALS AND METHODS

Organic Cations. The four natural organic cations, L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, and thiamine, and the synthetic alkylammonium organic cations, phenyltrimethylammonium and hexadecyltrimethylammonium, were purchased as high purity chloride salts (purity > 98%) from Sigma (Germany).

Pesticides. Chemical structures of the used pesticides are shown in **Figure 2**, and some of their chemical characteristics are given in **Table 1** (*14*, *15*). The unlabeled pesticides had a purity >99% and were purchased from Riedel-de Haën. The ^{14}C-labeled pesticides used in this work (i.e., triadimefon, alachlor, carbaryl, and imazethapyr) had a radiochemical purity >97% and a specific activity >200 kBq μmol^{-1}

Table 1. Chemical Characteristics of the Pesticides

	chemical name (IUPAC)	water solubility (mg L^{-1})	charge characteristics
simazine	6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine	5	weakly basic (pK_a = 1.7)
hexazinone	3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H, 3H)-dione	33000	weakly basic[a]
triadimefon	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butanone	260	weakly basic[a]
alachlor	2-chloro-2′,6′-diethyl-N-methoxymethylacetanilide	242	neutral
carbaryl	1-naphthyl methylcarbamate	40	neutral
imazethapyr	(RS)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid	1400	amphoteric (pK_{a1} = 2.1, pK_{a2} = 3.9)

[a] pK_a not available.

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Table 2. Elemental Analysis Results of Unexchanged and Exchanged Bentonites

sample	%C	%S	organic cation content (mmol kg^{-1})	OCtS^a (%)
SWy-2 (untreated)	0.31 ± 0.01^b	—^{c}	0	0
SWy-2 (blank)	0.30 ± 0.01	—	0	0
SW–CAR$_{50}$	0.38 ± 0.04	—	8	<5
SW–CAR$_{100}$	3.09 ± 0.02	—	330	43
SW–CAR$_{150}$	5.21 ± 0.03	—	554	72
SW–CYSTE$_{50}$	2.60 ± 0.03	1.20 ± 0.01	382	50
SW–CYSTE$_{100}$	4.14 ± 0.04	2.08 ± 0.01	637	83
SW–CYSTI$_{50}$	1.84 ± 0.02	1.00 ± 0.01	159	42
SW–CYSTI$_{100}$	3.74 ± 0.04	2.26 ± 0.02	357	93
SW-THIAM$_{50}$	2.93 ± 0.12	0.54 ± 0.06	183	48
SW-THIAM$_{100}$	5.69 ± 0.08	1.19 ± 0.05	374	98
SAz-1 (untreated)	—	—	0	0
SAz-1 (blank)	—	—	0	0
SA-CAR$_{50}$	2.36 ± 0.08	—	281	23
SA-CAR$_{100}$	3.90 ± 0.15	—	464	39
SA-CAR$_{150}$	4.83 ± 0.04	—	575	48
SA-CYSTE$_{50}$	1.57 ± 0.07	0.75 ± 0.04	262	22
SA-CYSTE$_{100}$	2.33 ± 0.09	1.55 ± 0.03	389	32
SA-CYSTI$_{50}$	3.14 ± 0.05	2.00 ± 0.01	327	54
SA-CYSTI$_{100}$	4.45 ± 0.13	2.88 ± 0.04	464	77
SA-THIAM$_{50}$	4.28 ± 0.01	0.91 ± 0.08	297	50
SA-THIAM$_{100}$	7.24 ± 0.07	1.42 ± 0.07	502	84

^{a} Organic cation saturation: percentage of the CEC compensated by the organic cations (calculated from the organic carbon content). ^{b} Mean ± standard error. ^{c} Not detected.

and were supplied by Sigma. All ^{14}C-labeled pesticides were uniformly labeled in the aromatic ring.

Synthesis of the Organobentonites. SWy-2 Wyoming bentonite and SAz-1 Arizona bentonite from The Clay Minerals Society (Purdue University) were prepared with the four natural organic cations through ion exchange reactions. For the synthesis, the amount of L-carnitine, L-cysteine ethyl ester, L-cystine dimethyl ester, or thiamine (chloride salts) corresponding to 50, 100, or 150% of the cation exchange capacity of SWy-2 (CEC$_{SWy-2}$ = 764 mmol kg^{-1}) and SAz-1 (CEC$_{SAz-1}$ = 1200 mmol kg^{-1}) was dissolved in 50 mL of 1 mM HNO$_3$ and added to 1 g of SWy-2 or SAz-1. The suspensions were shaken for 24 h,

centrifuged, washed three times with 100 mL of distilled water, and then freeze-dried. Blank bentonite samples were also prepared by shaking 1 g of bentonite in 50 mL of 1 mM HNO$_3$ for 24 h, washing three times with 100 mL of distilled water, and then freeze drying. The alkylammonium-exchanged bentonites used as reference materials in the adsorption−desorption experiments were hexadecyltrimethyl-ammonium- and phenyltrimethylammonium-bentonite, containing an amount of alkylammonium cation equal to 50 and 100% of the CEC of SWy-2 or SAz-1. The preparation and characteristics of these samples have been reported elsewhere (*15*).

Characterization of the Organobentonites. Elemental analyses (C, N, S) of the unexchanged and exchanged bentonite samples were performed using a Perkin-Elmer, model 1106, elemental analyzer (Perkin-Elmer Corp., Norwalk, CT). All samples were also characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction, and specific surface area measurements. FT-IR spectra were obtained on KBr disks in a Nicolet 5 PC spectrometer (Nicolet Instr. Corp., Madison, WI). Basal spacing values (d_{001}) were obtained by X-ray diffraction on oriented specimens using a Siemens D-5000 diffrac-tometer (Siemens, Stuttgart) with Cu Kα radiation. Specific surface areas were obtained by N$_2$ adsorption at 77 K using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan). The samples were outgassed at 80 °C and equilibrated under vacuum for 4 h before measuring the N$_2$ adsorption isotherm.

Pesticide Adsorption−Desorption Experiments. Pesticide adsorption−desorption isotherms were obtained using the batch equilibration procedure. Duplicate 20 mg adsorbent samples were equilibrated by shaking for 24 h at 20 ± 2 °C with 8 mL of pesticide solutions, prepared in distilled water, with concentrations ranging from 1 to 40 μmol L^{-1}, except for hexazinone, whose concentrations ranged from 0.1 to 1.6 mmol L^{-1}. The pH of the equilibrated suspensions ranged between 6 and 7 for the bentonites exchanged with thiamine, cysteine, and cystine and between 5 and 6 for the bentonites exchanged with carnitine. After equilibration, the suspensions were centrifuged and 4 mL of the supernatant solution was removed for analysis. For simazine and hexazinone, the concentration of pesticide in the supernatant solutions was determined by high-performance liquid chromatography (HPLC) using a Waters 600E chromatograph coupled to a Waters 996 diode array detector and following the methods described by Cruz-Guzmán et al. (*11*) and Celis et al. (*15*), respectively. For triadimefon, alachlor, carbaryl, and imazethapyr, the concentration of pesticide in the supernatant solutions was determined by liquid scintillation counting,

Table 3. Freundlich Coefficients for Simazine, Hexazinone, and Triadimefon Adsorption by Unexchanged and Exchanged Bentonites

sample	simazine		hexazinone		triadimefon	
	K_f	N_f	K_f	N_f	K_f	N_f
			SWy-2			
SWy-2	28 (24–33)^a	0.79 (0.71–0.87)	12 (7–20)	0.45 (0.13–0.77)	88 (81–95)	1.65 (1.58–1.72)
SW-CAR$_{100}$	50 × 10^3 (1 × 10^3–28 × 10^4)	1.15 (0.52–1.58)	82 (78–86)	0.59 (0.56–0.62)	2317 (1905–2820)	0.73 (0.61–0.84)
SW-CAR$_{150}$	12 × 10^4 (58 × 10^3–25 × 10^4)	1.76 (1.44–2.08)	105 (89–124)	0.73 (0.64–0.82)	2377 (2043–2765)	0.81 (0.71–0.91)
SW-CYSTI$_{50}$	400 (331–485)	0.85 (0.69–0.73)	18 (14–22)	0.49 (0.35–0.63)	705 (663–749)	1.23 (1.18–1.27)
SW-CYSTI$_{100}$	753 (733–775)	0.67 (0.65–0.69)	40 (39–41)	0.52 (0.51–0.53)	429 (344–533)	1.42 (1.26–1.59)
SW-CYSTE$_{50}$	211 (161–276)	0.58 (0.44–0.72)	ND^b	ND	ND	ND
SW-CYSTE$_{100}$	170 (142–204)	0.66 (0.56–0.75)	ND	ND	ND	ND
SW-THIAM$_{50}$	138 (137–140)	0.75 (0.74–0.76)	31 (26–37)	0.47 (0.37–0.57)	644 (621–669)	1.02 (1.00–1.05)
SW-THIAM$_{100}$	100 (83–121)	1.07 (0.97–1.17)	21 (19–24)	0.71 (0.58–0.84)	1076 (1007–1151)	0.79 (0.75–0.83)
SW-HDTMA$_{50}$	ND	ND	11 (6–20)	1.49 (0.88–2.11)	445 (443–447)	0.95 (0.94–0.95)
SW-HDTMA$_{100}$	ND	ND	23 (19–27)	0.69 (0.59–0.79)	1021 (829–1258)	0.67 (0.55–0.79)
SW-PTMA$_{50}$	188 (179–198)	0.69 (0.66–0.71)	75 (58–97)	0.62 (0.48–0.76)	4018 (3634–4442)	0.91 (0.84–0.97)
SW-PTMA$_{100}$	96 (95–98)	0.87 (0.75–0.98)	63 (58–69)	0.45 (0.41–0.49)	4656 (4162–5208)	0.86 (0.80–0.93)
			SAz-1^c			
SAz-1	0^d	-	0	-	0	-
SA-CAR$_{50}$	240 (219–262)	0.59 (0.55–0.64)	ND	ND	ND	ND
SA-CAR$_{100}$	305 (284–327)	0.58 (0.54–0.62)	9 (7–12)	1.67 (1.18–2.15)	229 (206–255)	0.82 (0.77–0.88)
SA-CAR$_{150}$	391 (386-395)	0.55 (0.55–0.56)	10 (8–11)	1.35 (1.13–1.57)	273 (247–302)	0.79 (0.74–0.85)
SA-HDTMA$_{50}$	112 (111–113)	0.90 (0.85–0.96)	102 (94–110)	0.76 (0.71–0.80)	2547 (2251–2881)	0.89 (0.81–0.98)
SA-HDTMA$_{100}$	160 (159–161)	0.96 (0.92–1.00)	165 (143–190)	0.82 (0.74–0.89)	3981 (3288–4820)	0.97 (0.84–1.10)

^{a} Standard error of the coefficients. ^{b} ND, not determined. ^{c} Very low or negligible adsorption on SAz-1 organobentonites do not appear in the table. ^{d} Adsorption < 2%.

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Table 4. Freundlich Coefficients for Alachlor and Carbaryl Adsorption by Unexchanged and Exchanged Bentonites

	alachlor		carbaryl	
sample	K_f	N_f	K_f	N_f
		SWy-2[d]		
SWy-2	0[a]		739 (647–845)	0.88 (0.80–0.95)
SW-CAR$_{100}$	82 (77–88)[b]	1.46 (1.43–1.50)	ND[c]	ND
SW-CYSTI$_{100}$	86 (81–91)	1.17 (1.14–1.20)	ND	ND
SW-CYSTE$_{100}$	37 (30–45)	1.07 (0.97–1.17)	ND	ND
SW-THIAM$_{50}$	ND	ND	354 (273–459)	1.32 (1.17–1.47)
SW-THIAM$_{100}$	67 (64–69)	1.24 (1.22–1.25)	133 (113–157)	1.39 (1.31–1.47)
SW-HDTMA$_{50}$	185 (181–190)	1.01 (1.00–1.02)	499 (476–523)	0.99 (0.97–1.01)
SW-HDTMA$_{100}$	394 (379–410)	0.94 (0.91–0.96)	1151 (948–1397)	0.85 (0.74–0.96)
SW-PTMA$_{50}$	424 (408–440)	1.53 (1.50–1.55)	43 (38–49)	4.32 (4.18–4.46)
SW-PTMA$_{100}$	617 (605–628)	1.27 (1.26–1.28)	301 (181–499)	2.61 (2.09–3.13)
		SAz-1[d]		
SAz-1	0		0	
SA-THIAM$_{100}$	8 (8–8)	0.74 (0.74–0.74)	83 (81–84)	0.99 (0.98–1.00)
SA-HDTMA$_{50}$	948 (882–1020)	0.92 (0.88–0.97)	2148 (2118–2178)	1.04 (1.03–1.05)
SA-HDTMA$_{100}$	1205 (1082–1342)	0.95 (0.88–1.03)	3436 (3340–3534)	1.03 (1.01–1.05)
SA-PTMA$_{50}$	17 (13–22)	1.07 (0.95–1.18)	56 (53–59)	1.23 (1.20–1.26)
SA-PTMA$_{100}$	49 (41–57)	0.88 (0.81–0.95)	197 (181–213)	0.99 (0.95–1.03)

[a] Adsorption < 2%. [b] Standard error of the coefficients. [c] ND, not determined. [d] Very low or negligible adsorptions for SWy-2 and SAz-1 organobentonites do not appear in the table.

using a Packard Tri-Carb 2100TR liquid scintillation analyzer. For this purpose, the initial solutions of these pesticides were prepared by mixing labeled and nonlabeled pesticide to give a ^{14}C activity of about 70 Bq mL^{-1}. In all cases, the amount of pesticide adsorbed was calculated by the difference between the initial and the final solution concentrations. Pesticide solutions without adsorbent were also shaken for 24 h and served as controls.

Desorption was measured immediately after adsorption from the highest initial concentration point of the adsorption isotherms. 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 pesticide concentration was determined in the supernatant. This desorption procedure was repeated three times. All adsorption and desorption studies were conducted in duplicate.

Pesticide adsorption−desorption isotherms were fitted to the Freundlich equation: $C_s = K_f C_e^{N_f}$, where C_s is the amount of pesticide adsorbed at the equilibrium concentration C_e and K_f and N_f are the empirical Freundlich constants, which can be calculated from the linear plot of log C_s vs log C_e. Hysteresis coefficients, H, were calculated according to $H = N_{fd}/N_f$, where N_f and N_{fd} are the Freundlich N constants obtained from the adsorption and desorption isotherms, respectively (*16, 17*).

RESULTS AND DISCUSSION

Elemental Analysis. Results of the elemental analysis of unexchanged and exchanged bentonite samples are summarized in **Table 2**. Data corresponding to SWy-2 organobentonites were previously presented in Cruz-Guzmán et al. (*11*). The actual percentage of the CEC of SWy-2 and SAz-1 occupied by organic cations (**Table 2**) was calculated assuming that carnitine and cysteine occupied one cation exchange position, whereas cystine and thiamine occupied two cation exchange positions.

Carnitine and cysteine were the organic cations displaying the highest resistance to react with SAz-1, as the amounts of these organic cations in SA-CAR and SA-CYSTE samples were considerably lower than those added during the synthesis (**Table 2**). For carnitine, this is possibly due to the combination of the presence of an ionizable carboxylic group in the cation structure and its monovalent nature, according to the behavior observed for SWy-2 (*11*). For cysteine, the organic cation saturation was dependent on the type of bentonite. The lower saturation degree

Table 5. Freundlich Coefficients for Imazethapyr Adsorption by Unexchanged and Exchanged Bentonites

	imazethapyr	
sample	K_f	N_f
	SWy-2[d]	
SWy-2	0[a]	
SW-CAR$_{100}$	76 (71–81)[b]	1.01 (0.98–1.05)
SW-CAR$_{150}$	94 (84–106)	0.93 (0.88–0.99)
SW-CYSTI$_{50}$	100 (89–112)	0.94 (0.88–1.00)
SW-CYSTI$_{100}$	96 (85–108)	0.99 (0.93–1.05)
SW-THIAM$_{100}$	76 (66–88)	0.89 (0.82–0.96)
SW-HDTMA$_{100}$	ND[c]	ND
	SAz-1[d]	
SAz-1	0	
SA-HDTMA$_{100}$	659 (616–705)	0.90 (0.86–0.94)

[a] Adsorption < 2%. [b] Standard error of the coefficients. [c] ND, not determined. [d] Very low or negligible adsorptions for SWy-2 and SAz-1 organobentonites do not appear in the table.

for SAz-1 as compared to SWy-2 is possibly due to the presence of Ca^{2+} as the main natural inorganic cation in SAz-1, since Ca^{2+} is more difficult to remove than Na$^+$ cations in SWy-2. Cystine and thiamine are divalent cations, producing a negligible difference between both types of bentonites.

FT-IR Spectroscopy, X-ray Diffraction, and Specific Surface Area Measurements. Specific surface area measurements, basal spacing values from X-ray diffraction studies, and FT-IR spectra of the modified SAz-1 bentonite samples together with those of the SAz-1 blank bentonite and the pure organic cations (data not shown) are very similar to data for SWy-2 exchanged samples, which are presented in Cruz-Guzmán et al. (*11*). It is important to note that (i) when cations with different sizes are introduced in montmorillonite, they produce different basal spaces depending on the surface charge of the clay mineral (*4, 5, 9*) and (ii) X-ray diffraction peaks of SAz-1 samples heated at 200 °C were not well-defined presumably due to the high CEC of SAz-1, which produces an heterogeneous layer distribution after heating or a partial rehydration of the samples during the X-ray diffraction analysis.
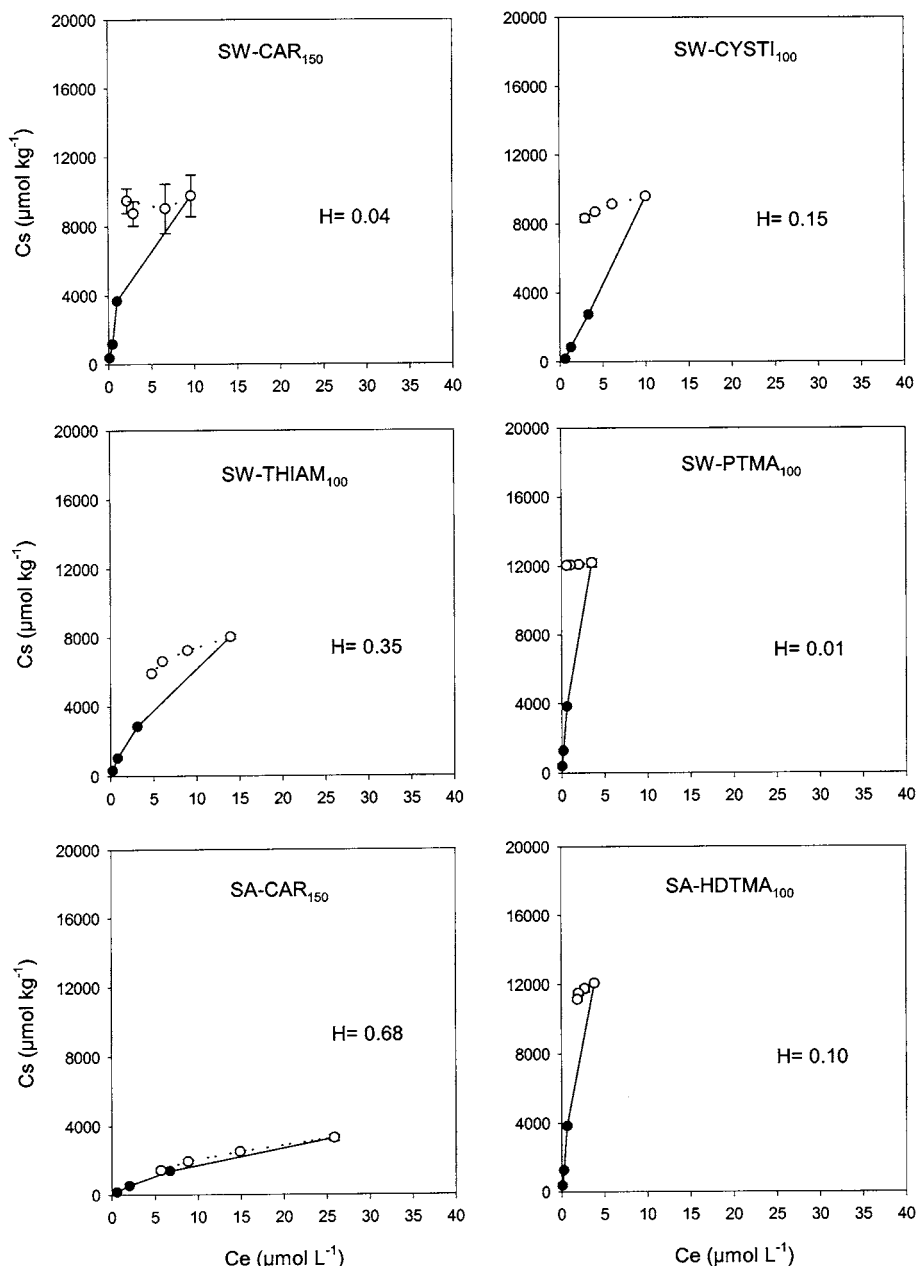
Figure 3. Triadimefon adsorption–desorption isotherms on organobentonites.

Adsorption−Desorption Studies. Tables 3−5 show the Freundlich coefficients (K_f and N_f) for isotherms. The adsorption coefficients for blanks are not shown because they are very similar to the values for untreated samples. All adsorption isotherms, except those of simazine on SW-CAR samples (*11*), fitted the Freundlich equation with $R^2 > 0.93$ (data not shown). The improvement of the adsorptive properties of the bentonites after treatment with the used organic cations is evidenced by the higher Freundlich K_f values of the exchanged bentonites as compared to unexchanged ones (**Tables 3−5**). N_f values were, in general, <1, showing specific interactions between the pesticides and the organobentonites (*18*). Only some cases, such as hexazinone on SA-CAR samples, triadimefon on SWy-2 and SW-CYSTI, alachlor on SW-CAR, and carbaryl on SW-THIAM, had N_f values > 1, indicating S-isotherms (*19*). These isotherms probably resulted from competition between pesticides and water molecules for the adsorption sites in the adsorbents or from the presence of intermolecular interactions between the adsorbed pesticide molecules (*18−20*). Simazine adsorption

isotherms on SW-CAR samples, which were reported in a previous study (*11*), were found to be H type, reflecting the high affinity of this pesticide for those organobentonites.

K_f values (**Tables 3−5**) show that, in general, the organic modification of SWy-2 and SAz-1 produced an increase in the adsorption properties of these bentonites for the selected pesticides. This effect can be attributed to the incorporation of organic cations in montmorillonite, which changes the nature of the surface of the mineral from hydrophilic to hydrophobic, increasing its affinity for the organic molecules of pesticides (*1, 2, 5, 7, 10*). K_f values for hexazinone are not directly comparable with the other pesticide K_f values, due to the higher range of concentration used for hexazinone isotherms than for the other pesticides.

We observed different degrees of improvement of the adsorbent properties of the selected organobentonites for all of the selected pesticides, depending on the type of the bentonite, the degree of organic cation saturation, and the nature of the organic cation.
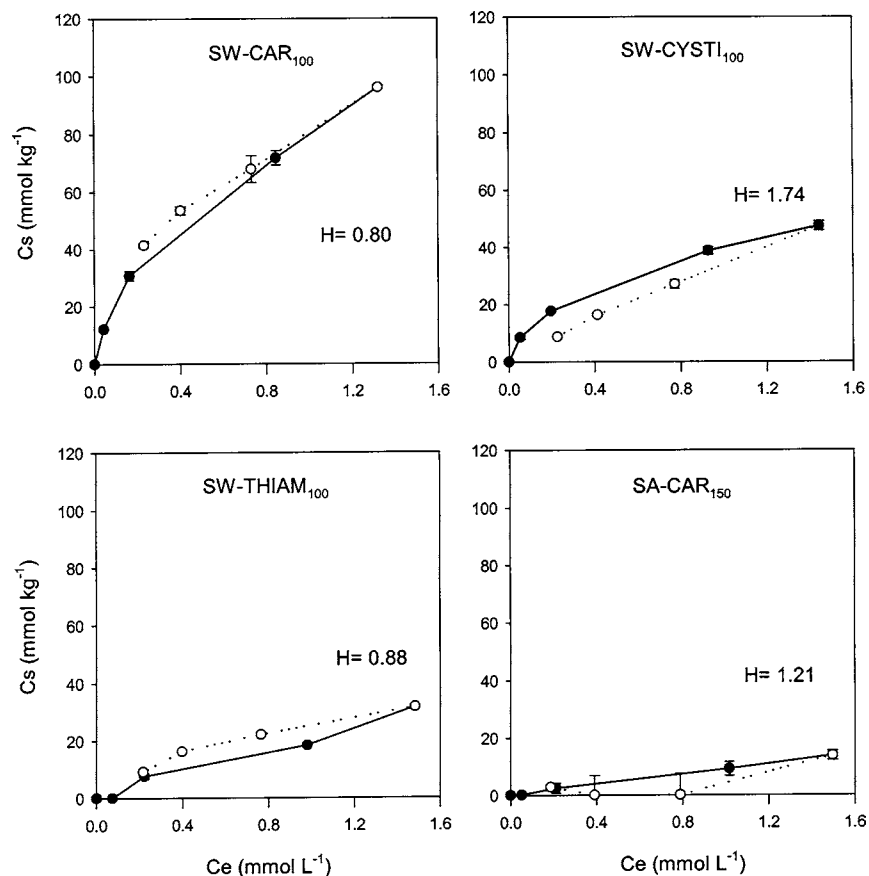
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Figure 4. Hexazinone adsorption–desorption isotherms on organobentonites.

Type of Bentonite and Organic Cation. In general, all of the pesticides had low adsorption on the original (unexchanged) SWy-2 and SAz-1 samples, with the values of K_f lower for SAz-1 than those for SWy-2. Differences in the adsorption capacity of clay minerals with different CEC have been observed previously for diverse pesticides (*21–26*). The high CEC of SAz-1 produces only a few hydrophobic siloxane regions available as adsorption sites for organic molecules as nonionic pesticides (*27, 28*). The presence of the above-mentioned hydrophobic regions in SWy-2 would permit a certain adsorption of the organic molecules (*27, 28*).

In general, adsorption of the pesticides on SWy-2 organo-bentonites was higher than the adsorption on the SAz-1 organobentonites, except in the case of the HDTMA cation, for which an opposite behavior was observed (**Tables 3–5**). These results could be explained by the different structures of the organobentonites depending on their organic cation saturation and the size of this interlaminar organic cation. As all cations used, except HDTMA, are relatively small ones, the obtained organobentonites are called "adsorptive" (*29, 30*). These types of adsorptive organobentonites have higher adsorption capacities if they are SWy-2 types than if they are SAz-1 ones, because SWy-2 organobentonites have organic cations more separated, allowing the entrance of pesticide molecules in the interlaminar spaces of montmorillonite.

The HDTMA-SA organobentonites have higher adsorption capacities than the HDTMA-SW organobentonites. Large organic cations in SAz-1 arrange vertically, due to the proximity of the mineral charges, producing an increase in the basal space of montmorillonite and a paraffinic structure, so that the organic phase has a high affinity for the pesticide (*4, 5, 30*). In SWy-2, large organic cations arrange horizontally, with little space for the entrance of the pesticide (*5*).

Steric factors are also important in the adsorption of pesticides to organoclays. Small organic cations are known to exist as discrete species on low-charge organosmectites, resulting in a considerable amount of noncovered surface, which in turn is available for the adsorption of organic contaminants (*9, 31, 32*).

Amount of Organic Cation. In general, for all selected pesticides, an increase in the amount of organic cation produced an increase in the adsorption coefficients (**Tables 3–5**) (*2, 33*). However, there were some exceptions whereby an increase in the rate of saturation with organic cation of the bentonite produced a decrease in K_f value, i.e., simazine adsorption on SW-THIAM samples, triadimefon adsorption on SW-CYSTI, and carbaryl adsorption on SW-THIAM, possibly due to steric effects during the adsorption at high organic cation saturation of the bentonite (*34, 35*). Consequently, a maximum transformation of the mineral surface from hydrophilic to hydrophobic does not always produce the best interactions between pesticides and bentonites (*36*).

Chemical Nature of the Organic Cation. The chemical nature of the organic cation strongly influences the adsorbent behavior of the organobentonites. CAR produced the greatest increase in the adsorption values as compared to unexchanged bentonites for the weakly basic pesticides, i.e., simazine, hexazinone, and triadimefon. The presence of a carboxylic group in CAR and the basic nature of these pesticides produced an acid–base interaction (*11*). In SW-CAR samples, pesticides had greater access to the adsorption sites than in SA samples, where these acid–base interactions possibly only occur at the edges of the clay mineral particles, as pesticides cannot access the interlaminar space. Other organic cations with important functional groups in the retention of simazine, hexazinone, and triadimefon were CYSTI (with a carbonyl group) and THIAM (with an aromatic ring). Triadimefon (with a benzene ring) had a high
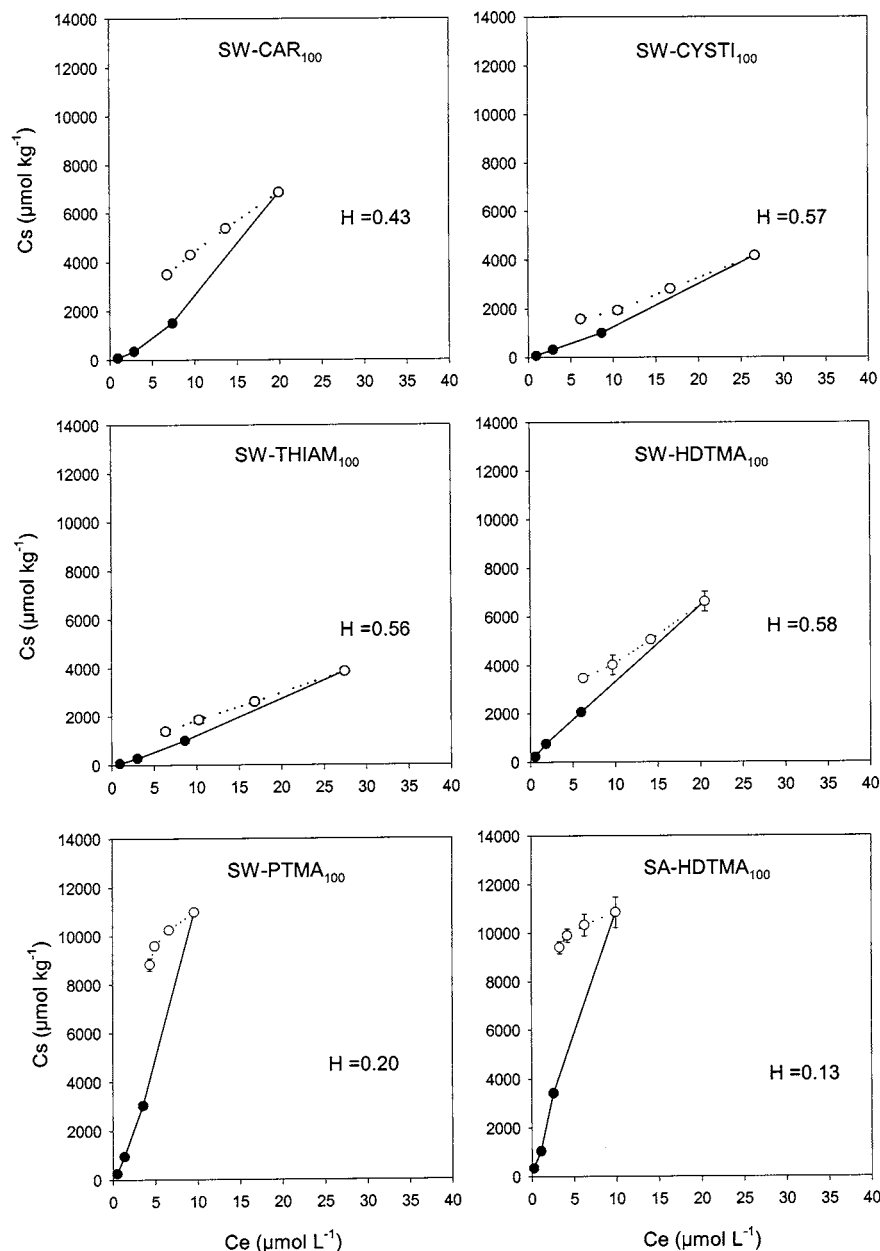
Figure 5. Alachlor adsorption–desorption isotherms on organobentonites.

affinity for SW-PTMA samples, possibly due to interactions between rings of the pesticide and interlaminar cation in the organobentonite (*37*).

In agreement with the behavior previously observed for simazine (*11*), the adsorption–desorption of triadimefon (**Figure 3**) showed greater hysteresis in the adsorbents with the highest adsorption capacities, indicating strong interactions between the pesticide and the adsorbents with the highest affinity for it. Hexazinone showed low or even negative hysteresis in all cases (**Figure 4**). Cases of negative hysteresis (i.e., the desorption curve lies below the adsorption curve) have previously been found in pesticide adsorption–desorption studies and related to experimental artifacts, which are observable only when the pesticide–adsorbent interactions are weak (*17, 28*).

The weak interactions between hexazinone and organobentonite samples could be related to the high water solubility of this pesticide (**Table 1**) and consequently its affinity for the aqueous phase and the high hexazinone concentrations used in our experiments (*18*). For simazine and triadimefon, the presence of polar interactions between pesticides and polar functional

groups of the organic cations could explain the strong interaction of simazine with SW-CAR, SW-CYSTI, and SA-CAR and that of triadimefon with SW-CAR. The main difference in the adsorption–desorption behavior of simazine and triadimefon was that triadimefon adsorption showed high hysteresis in SW-PTMA (**Figure 3**) while simazine adsorption showed low hysteresis for bentonites exchanged with alkylammonium cations (*11*). This presumably is due to the presence of a phenyl ring in triadimefon, which allows relatively strong ring interactions with PTMA cations (**Figure 2**).

For neutral, aromatic pesticides (alachlor and carbaryl), carbaryl had a high affinity for THIAM in the bentonite, possibly due to the interactions between the aromatic rings (*38*). However, the aromatic nature of alachlor and carbaryl also led to high affinity for bentonites exchanged with PTMA and HDTMA. Other authors have noted a similar high adsorption of aromatic pesticides on clay minerals exchanged with alkylammonium cations (*2, 29, 39*). PTMA increases the affinity of the bentonite for these aromatic pesticides due to the $\pi-\pi$ interactions between pesticides and PTMA rings (*36–38*). In
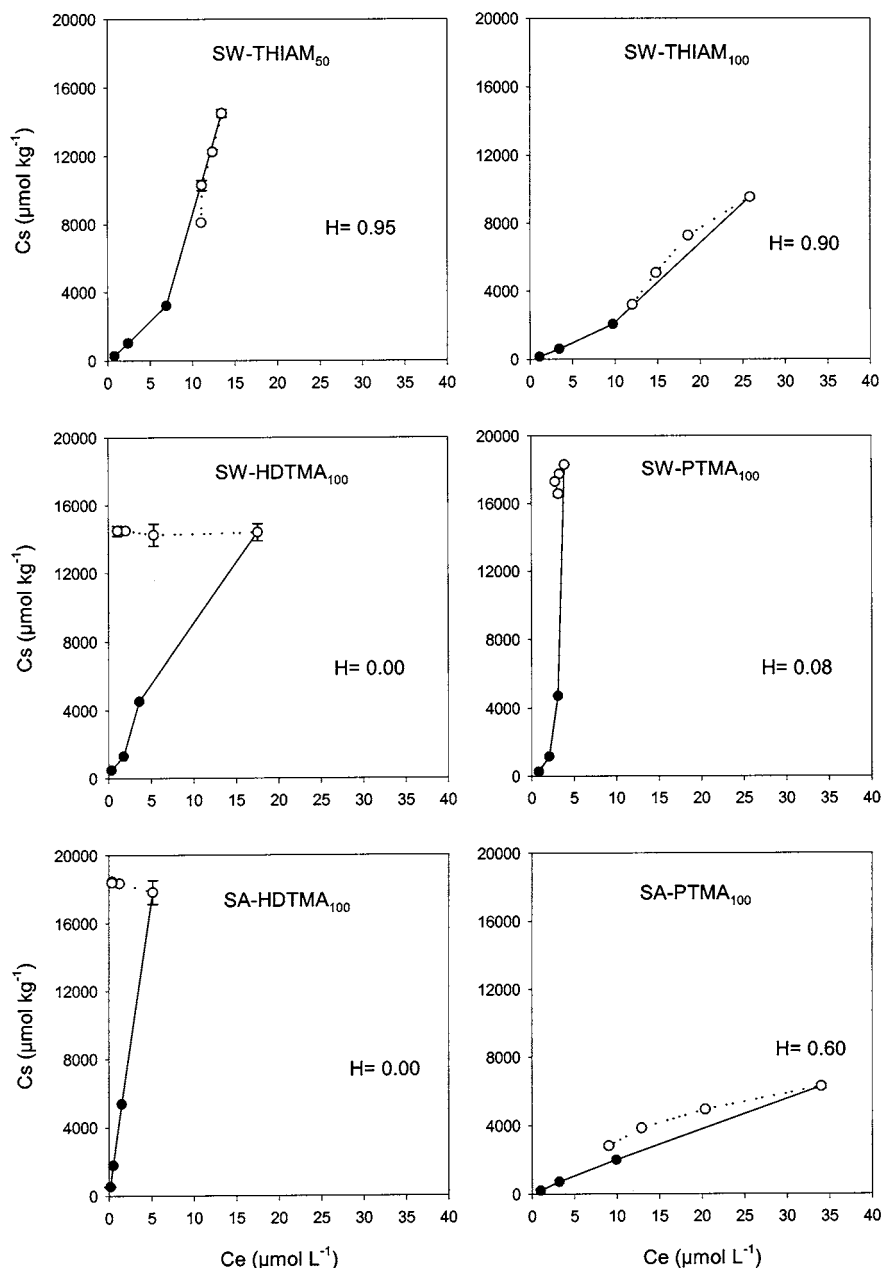
Figure 6. Carbaryl adsorption–desorption isotherms on organobentonites.

our studies, the best adsorbent for alachlor and carbaryl was SA-HDTMA. For both pesticides, the adsorption showed greater hysteresis for the adsorbents with the highest adsorption capacity (SA-HDTMA and SW-PTMA) (**Figures 5** and **6**), indicating strong interactions between the pesticide and the adsorbent with the highest affinity for it.

In our experiments, pH values of equilibrated suspensions were higher than the pK_a value of imazethapyr (pK_{a1} = 2.1, pK_{a2} = 3.9) (*40*); therefore, the predominant imazethapyr species in solution was anionic. Low imazethapyr adsorption on unexchanged bentonites (SWy-2 and SAz-1) (**Table 4**) was possibly due to the anionic character of the pesticide at the pH values of the suspensions (pH > 5) and to repulsion between the anionic species and the negatively charged mineral surfaces (*10, 41*). CYSTI and CAR cations produced an increase in the affinity of the bentonites for imazethapyr, but the best adsorbent for this pesticide was SA-HDTMA. The carboxylic group of CAR could interact with the basic N of imazethapyr, and divalent cations of CYSTI and THIAM presented a higher

affinity for this pesticide than CYSTE, possibly due to the better efficiency of divalent cations for neutralizing the surface negative charge of montmorillonite than that of monovalent cations such as CYSTE. The large cation HDTMA, exchanged at 100% and arranged vertically in SAz-1 bentonite, produced a sufficient separation of the clay mineral layers, resulting in a decrease in the electrostatic repulsion between the imazethapyr and the mineral surfaces.

Imazethapyr showed low hysteresis in all cases (**Figure 7**). The acid nature of imazethapyr possibly produced weak interactions between the pesticide and the organobentonites. According to these results, Celis et al. (*41*) observed low hysteresis for the acid herbicide picloram (anionic pesticide at pH > 6) adsorbed to SA-HDTMA (H = 0.75).

In conclusion, the presence of functional groups in the organic cation influences the adsorption capacity and selectivity of organobentonites for selected pesticides. Consequently, a suitable selection of the chemical characteristics of the organic cation can optimize the adsorbent properties for pesticides of
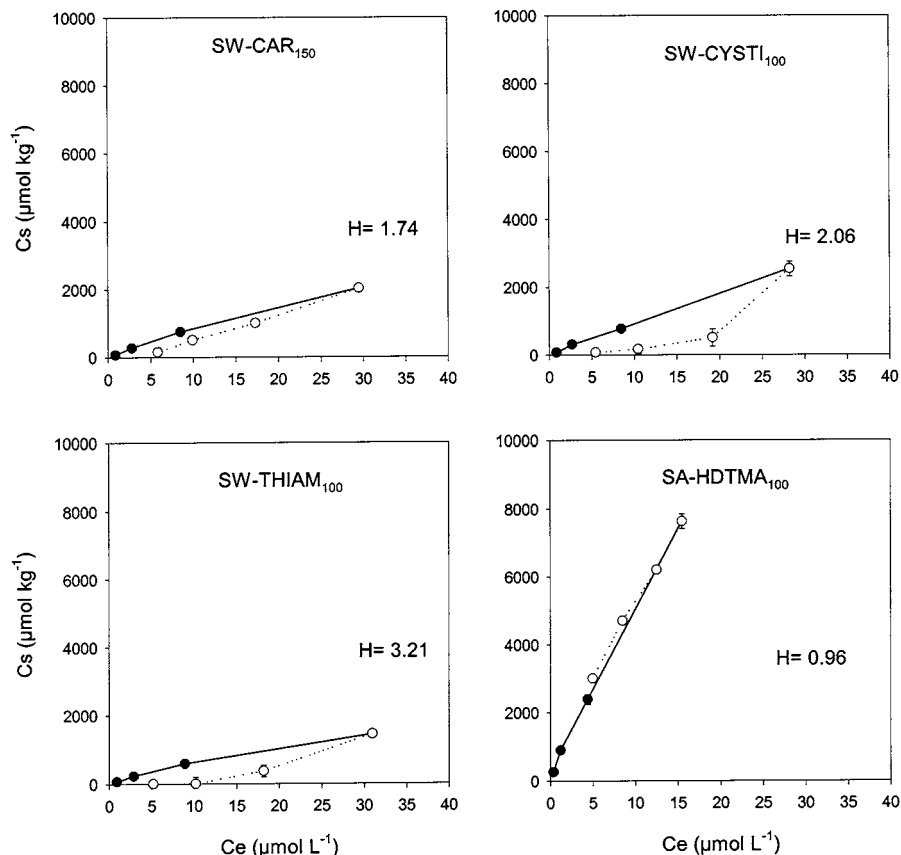
Figure 7. Imazethapyr adsorption–desorption isotherms on organobentonites.

the organobentonites as compared to the use of alkylammonium cations, which lack in general of specificity. In general, organobentonites with high affinity for selected pesticides showed a higher resistance to desorption than organobentonites with less affinity for them. These results reveal that organo-bentonites might be potentially useful as agents to immobilize selectively pesticides in soils or to delay their movement toward underground waters and as supports in formulations of slow release of pesticides. The viability of the use of natural organic functionalized cations to prepare organobentonites is particularly interesting for minimizing the impact of the adsorbent once added to soil or aquifers.

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