SORPTION OF ORGANIC COMPOUNDS BY Al AND Zr-HYDROXY-INTERCALATED AND PILLARED BENTONITE

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Abstract—Owing to their large and chemically active surface, hydroxy-intercalated and pillared clays can be potent sorbents for organic compounds. The sorption behavior of Al and Zr-hydroxy-intercalated bentonite (HAl-, HZr-MX80), Al and Zr-pillared bentonite (Al-MX80, Zr-MX80), and a commercial Al-pillared bentonite (EXM 534) for 3-chloroaniline (3-CA), atrazine (AT), and 3-chlorophenol (3-CP) was investigated. The results were compared with the sorption behavior of the untreated Na-rich bentonite (MX80) and granulated activated carbon (GAC). Also the influence of the salinity of the sorbate and the age of the sorbents was studied.

Al and Zr-hydroxy-intercalated and pillared bentonites sorbed higher amounts of 3-CA, AT, and 3-CP than the untreated bentonite. The quantities sorbed related to the electron-donating properties of the sorbate and the acidity of the sorbents. Sorbed quantities increased from the hydroxy-intercalated to the pillared species, and from the Al to the Zr forms. The organic bases, 3-CA and AT, were sorbed in higher quantities than the organic acid 3-CP. For AT, the sorbents exhibited a high affinity. Aging of the samples and a high ionic strength of the sorbate reduced the sorption of 3-CA, whereas the sorption of AT was not affected greatly. The sorption capacity of GAC for organic bases was generally higher than that of the hydroxy-intercalated and pillared bentonites.

The data suggest that at initial concentrations at a ppm level, 3-CA and AT can be entirely removed from aqueous solutions by Al and Zr-hydroxy-intercalated and pillared bentonites. These materials, especially Zr-pillared bentonites, represent potent alternative sorbents for atrazine, chloroanilines, and probably a wide range of other organic bases.

Key Words—Activated Carbon, Al-Pillared Montmorillonite, Atrazine, 3-Chloroaniline, 3-Chlorophenol, Sorption, Zr-Pillared Montmorillonite.

INTRODUCTION

The contamination of soils and surface and ground water with non-volatile organic pollutants of anthropogenic origin creates physiological hazards to ecosystems and humans. Owing to their extensive use, these compounds readily enter ecosystems, for example, by industrial and municipal waste water, by leachates emerging from waste deposits, or by agricultural runoff of pesticides. Many of these substances can be detected in surface and ground water, *e.g.*, herbicides such as atrazine, chloroanilines which form during the production of pigments, pharmaceuticals and pesticides, and chlorophenols as constituents of pigments and disinfectants. Even at low concentrations of few parts per billion (ppb) these compounds may be hazardous to plants, animals, and humans for long durations (Rick, 1993; Mueller *et al.*, 1996; Rippen, 1995; Sheldon and Hites, 1978). Owing to their slow degradation, phenols, anilines, and triazines represent a major threat to ecosystems (Johnson and Fuhrmann, 1990; Wolfe, 1980; Agertved *et al.*, 1992; Gaynor and Volk, 1981; Janicke and Hilge, 1977; Kuhn and Suflita 1989; Kondo *et al.*, 1988; Rheinheimer *et al.*, 1990).

Because clay minerals strongly influence the migration, immobilization, and chemical transformation of organic compounds in soils, clay-mineral interaction with organic pollutants has been studied intensely.

Haderlein and Schwarzenbach (1993) suggested that nitroaromatic compounds can sorb specifically to the negatively charged siloxane surfaces of kaolinite. Nonionic organic bases and weak-base pesticides are sorbed by smectites by physical sorption (van der Waals and dipole-dipole interactions) and by hydrogen-bonding with H_2O molecules coordinated to interlayer cations (Swoboda and Kunze, 1968; Yariv *et al.*, 1969; Feldkamp and White, 1979; Cloos *et al.*, 1979; Voudrias and Reinhard, 1986; Barriuso *et al.*, 1994; Sawhney and Singh, 1997). Also, the surface-charge density of the sorbent influences the sorption process (Laird *et al.*, 1992). In summary, the affinity of clay minerals for organic bases seems to increase with increasing polarizing power of the interlayer cations, increasing surface area, and decreasing surface-charge density.

Pillared clays and their uncalcined hydroxy-intercalated precursors possess most of these properties, *i.e.*, interlayer cations of high polarizing power, a high surface area, and a low cation-exchange capacity (CEC). Therefore, these modified clays are expected to show higher sorption capacities for organic compounds than common clay minerals.

Pillared clays were first described by Vaughan *et al.* (1979) and Lahav *et al.* (1978). By intercalation of inorganic polyhydroxo cations in the interlayers of ex-

Table 1. Physiochemical properties of the sorbents (in brackets: aged samples).

	MX80	HAl-MX80		Al-MX80		EXM 534		HZr-MX80		Zr-MX80		GAC[1]
$d(001)$ values (Å)	11.6	18.8	(15.0)	18.2	(16.9)	18.1	(17.3)	19.0	(15.5)	18.5	(16.5)	—
CEC (meq 100 g^{-1}; pH 6.9)	76	52	(52)	45	(50)	40	(51)	55	(53)	45	(47)	n.d.
BET Surface Area (m^2 g^{-1})	22	216	(89)	187	(116)	150	(134)	219	(151)	218	(177)	1000
External Surface Area (m^2 g^{-1})	20	53	(36)	77	(39)	63	(47)	61	(69)	78	(74)	n.d.
Total Pore Volume (μL g^{-1})	105	150	(95)	168	(100)	169	(117)	153	(140)	165	(155)	770
Micropore Volume (μL g^{-1})	1	73	(24)	49	(35)	39	(39)	71	(37)	63	(46)	n.d.

[1] Data from Fluka Chemie AG, Switzerland.

pandable 2:1 clay minerals, hydroxy-intercalated clays are formed. These clays exhibit a $d(001)$ value to 20 Å, depending on the size of the polyhydroxo cation, high surface areas (mostly 200–300 m^2 g^{-1}) owing to the formation of micropores between the intercalated complexes, and Brønstedt and Lewis-type acidity. By calcination of the hydroxy-intercalated clays at temperatures between 300–500°C, pillared clays are formed. The resulting dehydrated and dehydroxylated cations form rigid oxidic pillars of predominantly Lewis-type acidity (Vaughan, 1988). By varying the starting 2:1 clay mineral and the intercalated polyhydroxo cation, pillared clays with different physicochemical properties are formed (Vaughan, 1988; Kloprogge, 1998).

The intercalated Al-polyhydroxo cations are similar to the Keggin molecule $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, also referred to as Al_{13} (Vaughan and Lussier, 1980). Zr-hydroxy intercalated montmorillonites contain planar Zr-tetramers $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (Yamanaka and Brindley, 1979) or larger polymers (Burch and Warburton, 1986).

This paper is part of a broader study concerning the sorption behavior of Al and Zr hydroxy-intercalated and pillared clays for inorganic and organic compounds to develop novel applications for these materials. In this context, the possibility of sorbents in the purification of contaminated water, *e.g.*, for *in situ* leachate treatment in waste-disposal containment systems, should be investigated. For some compounds, such as chlorophenols, it was shown that hydroxy-intercalated and pillared bentonites may be better sorbents than untreated bentonites owing to their high surface acidity and surface area (Zielke and Pinnavaia, 1989).

In this study, Al and Zr-hydroxy-intercalated and pillared bentonites were used as sorbents because they exhibit a high thermal stability (Vaughan, 1988; Bartley, 1988) and are easy to produce. The untreated bentonite and granulated activated carbon as general sorbants for organic compounds served as references. The organic bases 3-chloroaniline (3-CA) and atrazine (AT), and the organic acid 3-chlorophenol (3-CP) were chosen as sorbates based on their environmental relevance and toxicity. Because of the applied nature of

our study, the sorption of 3-CA, AT, and 3-CP was studied both in ultrapure water and in an artificial leachate.

For practical applications apart from sorption behavior, the long-term stability of pillared clays is important also. Singh and Kodama (1990) reported structural changes of Al-pillared montmorillonite with time of aging at room temperature and at different humidities. This observation was also confirmed by our own investigations. Therefore, the effect of aging and the influence of structural changes on the sorption capacity of the hydroxy-intercalated and pillared materials were clarified. These effects may occur under field conditions, such as in a basal barrier of a waste-disposal site.
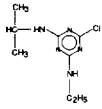
MATERIALS AND METHODS

As starting material, the Wyoming bentonite MX80 (Bentonit International GmbH, Duisburg-Meiderich, Germany) was used. It contained 75 wt. % Na-rich montmorillonite with the formula $Na_{0.3}(Si_{3.96}Al_{0.04})$ $(Al_{1.55}Fe^{3+}_{0.20}Fe^{2+}_{0.01}Mg_{0.24})O_{10}(OH)_2$, quartz, feldspar, and traces (≤ 2 wt. %; Mueller-Vonmoos and Kahr, 1983) of illite, carbonate, kaolinite, pyrite, and organic carbon. The physicochemical properties of MX80 are listed in Table 1. A detailed characterization of MX80 was given by Madsen (1998). No fractionation or pretreatment was done because in industrial production of pillared clays, the raw clay is commonly used without purification.

Al and Zr-pillared bentonite (referred to as Al-MX80 and Zr-MX80) and their hydroxy-intercalated precursors (referred to as HAl-MX80 and HZr-MX80) were used as sorbents. For comparison, we also studied a commercial Al-pillared bentonite, EXM 534, and granulated activated carbon (GAC), which are general sorbents for organic compounds (Table 1). The GAC (trade name D 47/4; particle size 4–8 mm) was supplied by FLUKA Chemie AG (Buchs, Switzerland).

The preparation of the hydroxy-intercalated and pillared bentonites as derived from EXM 534, as well as the analytical methods for the measurement of the properties of the sorbents (Table 1), are given in Matthes *et al.* (1999). The experimental conditions during aging of the hydroxy-intercalated and pillared benton-

Table 2. Physico-chemical properties of the sorbates 3-CP, 3-CA, and AT (pK_1 first hydrolysis constant).

	[1]3-CP	[1]3-CA	[2]AT
Chemical Name	3-chlorophenol	3-chloraniline	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
Formula	C_6H_5ClO	C_6H_6ClN	$C_8H_{14}ClN_5$
Structural Formula			
Molar Weight (g mol^{-1})	128.56	127.57	215.7
pK_1	9.02	3.34 (3-Chloroanilinium-Ion)	1.68
Solubility in Water (25°C; mg L^{-1})	260	n.d.	31 (pH 3); 35 (pH 7)[20°C]

[1] Dean (1973).
[2] Ayele et al. (1996).

ites were chosen according to possible conditions in a basal barrier of a waste-disposal site. The sorbents were aged for 4 mo in a swelling-pressure apparatus at 60°C and at a constant uniaxial pressure of 0.6 MPa in the presence of artificial leachate. The chemical composition of the leachate, based on leachate analyses from the waste-disposal site at Koelliken, Switzerland, is 1.094 g L^{-1} $(NH_4)_2SO_4$, 1.270 g L^{-1} K_2SO_4, 0.610 g L^{-1} NH_4Cl, 0.965 g L^{-1} $CaCl_2$, 10.168 g L^{-1} NaCl, and 3.810 g L^{-1} KCl. The ionic strength was 0.31 and the conductivity was 30 mS cm^{-1}. The pH was adjusted with NH_3 to 6.9.

The sorption tests were performed as batch experiments. The initial concentration of 3-CA was 0.04 × 10^{-3} to 7.84 × 10^{-3} M and for 3-CP the concentration was 0.04 × 10^{-3} to 0.23 × 10^{-3} M. The solutions were obtained by dilution from stock solutions with a concentration of 1000 mg 3-CA or 3-CP per liter ultrapure water Milli-Q (Micropore SA) or artificial leachate. The AT stock solution with a concentration of 32.3 mg L^{-1} was obtained by dissolution of solid AT. Owing to the restricted solubility of AT in water (Table 2), the initial concentration varied from 0.005 × 10^{-3} to 0.15 × 10^{-3} M. To avoid an effect on sorption, no buffer was added.

The sorbents weighed 200 mg after drying at 110°C. The samples were weighed in glass vessels and equilibrated with 10 mL of the sorbate overnight in a tumbler at 120 oscillations min^{-1} at 22 ± 1°C. Afterwards, the solid was separated from the solution by centrifugation (60 min, 2250g). To exclude an effect of the pH on the detection wavelength of 3-CA and 3-CP owing to hydrolysis, the supernatants were separated from the solid. Prior to analysis, the pH was adjusted with a combined buffer of KH_2PO_4 and Na_2HPO_4 (Ernoe, 1987) to 7.0 (3-CA) and 4.5 (3-CP). 3-CA, 3-CP, and AT were measured in the liquid state with a CA-DAS 100 UV-vis-Spectrophotometer (Dr Bruno Lange GmbH, Berlin, Germany) at λ = 222 (AT), 236 (3-CA), and 274 (3-CP) nm. All sorption experiments

were performed at least in duplicate. Reference solutions without any sorbent served as control samples. The percent standard deviations, calculated from replications, were 6.9 (3-CP), 3.4 (3-CA), and 4.0% (AT).

Sorption isotherms were calculated using the empirically determined model of Freundlich (1923): q = $K_F c^{1/n}$ where q is the sorbed quantity, c is the equilibrium concentration in solution, and K_F and 1/n are the Freundlich constants. The parameters K_F and 1/n are obtained by linear regression of the equation: log q = log K_F + 1/n log c. K_F is a measure of the affinity of the sorption sites for the sorbate, and 1/n describes the curvature of the isotherm.

The maximum sorption capacity of Al and Zr-pillared bentonites and activated carbon for AT was determined from batch experiments with initial concentrations between 75–750 μmol g^{-1} sorbent. The sorption isotherms were calculated using one-site Langmuir isotherms (Langmuir, 1918). The Langmuir constants were obtained by linear regression using the reciprocally transformed Langmuir equation (Dowd and Riggs, 1965): $c_{AT}/q_{AT} = 1/(K_L × q_{AT,max}) + c_{AT}/q_{AT,max}$ where q_{AT} is the sorbed quantity of AT, c_{AT} is the equilibrium concentration of AT in solution, K_L is the affinity constant, and $q_{AT,max}$ is the sorption maximum.

RESULTS

Properties of MX80, Al, and Zr-hyroxy-intercalated and pillared bentonites before and after aging

The characteristics of the freshly prepared Al and Zr-hydroxy-intercalated and pillared bentonites and EXM 534 are given in Table 1. Aging at 60°C and 0.6 MPa in contact with artificial leachate resulted in a decrease of the d(001) values, BET surface areas, and micropore volumes owing to a partial collapse of the intercalated polyhydroxo cations and pillars (Table 1). The CEC of the sorbents was not significantly influenced by aging. Also the chemical compositions of the

Table 3. Chemical composition of MX80, Al and Zr-pillared MX80 (in wt. %).

	[1]MX80	[1]Al-MX80	[2]Al-MX80	[1]Zr-MX80	[2]Zr-MX80
SiO_2	63.01	56.89	56.97	55.15	54.14
TiO_2	0.16	0.14	0.14	0.13	0.12
Al_2O_3	20.24	26.36	27.21	17.81	17.64
Fe_2O_3	3.9	3.47	3.54	2.87	3.04
MgO	2.35	1.91	1.82	1.79	1.85
CaO	1.42	0.23	0.33	0.33	0.20
Na_2O	2.20	0.31	0.34	0.31	0.31
K_2O	0.6	0.50	0.86	0.38	0.55
P_2O_5	0.06	0.05	0.05	<0.03	<0.03
H_2O^+	6.07	10.14	8.64	8.04	7.33
ZrO_2	<1	<1	<1	13.2	14.5

[1] Before aging.
[2] After aging.

sorbents remained essentially the same (Table 3) except for increases in the K, Ca, and Na contents owing to cation exchange with the artificial leachate in the range from 1.5 (HZr-MX80) to 17.6 (HAl-MX80) meq per 100 g.

Sorption of 3-CA

The sorption isotherms in Figure 1 show that the minimum amount of 3-CA was sorbed by the untreated bentonite. At initial concentrations between 2.0–9.7 μmol g^{-1}, the removal of 3-CA by MX80 was ≤6% (Table 4). Greater quantities of 3-CA were sorbed by Al and Zr-hydroxy-intercalated and pillared bentonites. At initial concentrations between 2.0–9.7 μmol g^{-1}, Al and Zr-MX80 removed 86–100% and 90–100% of 3-CA, respectively. The removal by the hydroxy-intercalated HAl and HZr-MX80 was between 21–43% and 41–71%, respectively (Table 4). Proceeding from the pH values of the suspensions of 4.4–9.5 (Table 4), 3-CA was sorbed as a neutral molecule.

The sorption of 3-CA was described with Freundlich isotherms (Figure 1; Table 5). The K_F constant of 0.0008 (Table 5) indicates the existence of low-

affinity sites at the surface of the untreated bentonite MX80. HAl and HZr-MX80 exhibit medium-affinity sites (K_F 0.16 and 0.12), and Al and Zr-pillared MX80 high-affinity sites (K_F 3.5 and 1.6).

The aging of Al and Zr-pillared MX80 and EXM 534 at elevated temperature and pressure caused a shift of the sorption isotherms towards those of fresh HAl and HZr-MX80 (Figure 1). The reduction in sorption capacity was accompanied by a decrease of the K_F constants from 3.50 to 0.02 and 1.61 to 0.14, respectively (Table 5), which indicates a change from high- to medium-affinity sites. Also, the sorption of 3-CA by HAl- and HZr-MX80 and, correspondingly, their affinity constants K_F were smaller after aging (Figure 1; Table 5). The pH of the suspension of the aged sorbents was ~1 pH value higher than those of the suspensions of the fresh sorbents (Table 4). Thus, a loss of surface acidity by aging is indicated.

In artificial leachate, smaller quantities of 3-CA were sorbed by Al and Zr-MX80 than in ultrapure water (Figure 2). The K_F values of 0.05 and 0.11, respectively, indicate a change from high- to medium-affinity sites (Table 5). The pH values of the suspensions were lower than in ultrapure water. This result was probably related to the substitution of exchangeable Al and Zr cations and protons of the polyhydroxo cations and pillars by alkali and alkaline-earth cations of the leachate. This is indicated by an increase of the K and/or Na content of Al and Zr-pillared bentonites after aging in contact with artificial leachate (Table 3).

The pH of the clay suspensions ranged from 4.4 to 7.9. Consequently, 3-CA (pK₁ 3.34) was sorbed as a neutral molecule. Only the suspension of Zr-MX80 with a pH of 3.6–3.7 contained both neutral 3-CA molecules and 3-chloroanilinium cations. However it is unclear whether the presence of 3-chloroanilinium cations affected the sorption of 3-CA by Zr-MX80 in artificial leachate.

Within the entire concentration range, 99–100% of 3-CA was removed by activated carbon from ultrapure
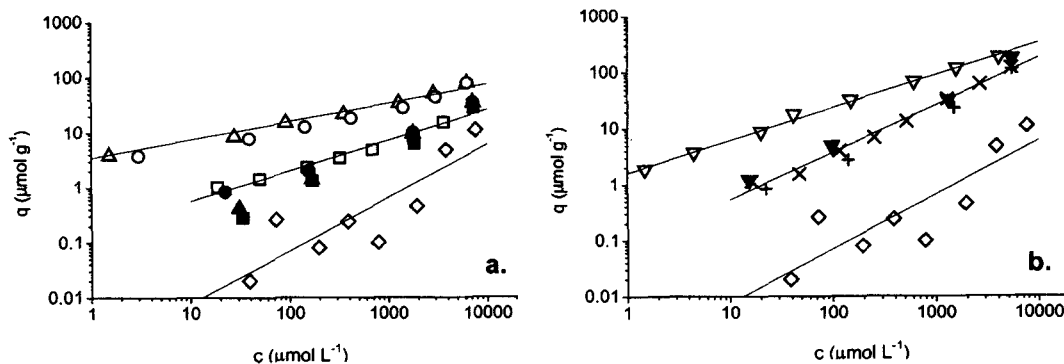

Figure 1. Sorption of 3-CA by fresh and aged samples (a) MX80 (◇), HAl-MX80 (fresh □, aged ■), Al-MX80 (fresh △, aged ▲), and EXM 534 (fresh ○, aged ●); and (b) HZr-MX80 (fresh ×, aged +), and Zr-MX80 (fresh ▽, aged ▼) (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the calculated isotherms.

Table 4. Influence of ionic strength and aging on the removal of AT (initial concentrations 0.25–7.5 μmol g⁻¹) and 3-CA (initial concentrations 2.0–9.7 μmol g⁻¹, or as indicated) by MX80, HAl, Al, HZr, Zr-MX80, EXM 534, and GAG from ultrapure water (UW) and artificial leachate (L).

Material	Aging	Solution	AT		3-CA	
			pH	Removal %	pH	Removal %
MX80	—	UW	9.6–9.7	52–19	9.3–9.5	<6
HAl-MX80	—	UW	5.7–5.8	100–90	5.6–5.7	53–24
Al-MX80	—	UW	5.2–5.4	100–97	4.9–5.0	100–86
EXM 534	—	UW	5.2–5.4	100–97	4.8–4.9	100–80
HZr-MX80	—	UW	4.8–4.9	100–97	5.1–5.3	71–41
Zr-MX80	—	UW	4.3–4.4	100	4.4–4.5	100–90
GAC	—	UW	7.2–7.3	100	7.5–7.9	100
MX80	—	L	7.7–7.8	29–47	7.7–7.9	<5
Al-MX80	—	L	4.3–4.4	99–92	4.4–4.5	32–14[1]
Zr-MX80	—	L	3.5–3.6	100	3.6–3.7	54–32[1]
GAC	—	L	8.1–8.2	100	8.1–8.3	100[1]
HAl-MX80	+	UW	6.2–6.3	98–94	6.3–6.5	18–14
Al-MX80	+	UW	6.0–6.3	97–95	6.3–6.5	21–14
EXM 534	+	UW	6.0–6.1	100–93	6.3–6.4	43–20
HZr-MX80	+	UW	5.3–5.5	100–99	5.6–5.7	43–28
Zr-MX80	+	UW	5.3–5.5	100–99	5.6–5.7	61–50

[1] 2.0–19.4 μmol g⁻¹.

water and artificial leachate. Therefore, no Freundlich constants can be calculated. The pH between 7.5–8.3 indicates that 3-CA was sorbed as neutral molecules.

Sorption of AT

Owing to the nearly complete removal of AT from ultrapure water by Al and Zr- hydroxy-intercalated and pillared bentonites, Freundlich isotherms can only be calculated for MX80 and HAl-MX80 (Figure 3, Table 5). The K_F values of 0.07 and 1.96 indicate the dominance of medium-affinity sites at the surface of MX80 and high-affinity sites at the surface of HAl-MX80. At initial concentrations to 7.5 μmol g⁻¹, the nearly complete removal of AT by Al-MX80, Zr-MX80, and GAC was not significantly affected by the salinity of the sorbate (Table 4), whereas the sorption of AT by MX80 slightly increased in artificial leachate. Similar

to the sorption of 3-CA, the pH of the artificial leachate suspensions was lower than in ultrapure water. Owing to its low pK_1 value at 1.68, AT occurred in ultrapure water and leachate suspensions (pH of 3.6–9.6) as neutral molecules.

In contrast to the sorption of 3-CA, aging of the hydroxy-intercalated and pillared bentonites did not (HZr-MX80, Zr-MX80) or only slightly (HAl-MX80, Al-MX80, EXM 534) influence the sorption of AT (Table 4). Al and Zr-pillared bentonite sorbed higher quantities of AT than their uncalcined precursors, and sorption increased from the Al to the Zr species. Similar to the sorption of 3-CA, the pH of the suspensions of aged sorbents was higher than the pH of the suspensions of fresh sorbents.

The maximum sorption capacities of Zr-MX80 and GAC in ultrapure water were nearly identical (Figure

Table 5. Freundlich constants, K_F [(μmol g⁻¹)/(μmol L⁻¹)$^{1/n}$] and $1/n$, and correlation coefficients R^2 for the sorption of 3-CA, AT, and 3-CP in ultrapure water (UW) and artificial leachate (L).

|	3-CA			AT			3-CP		
	1/n	K_F	R^2	1/n	K_F	R^2	1/n	K_F	R^2
MX80, UW	0.97	0.0008	0.745	0.64	0.07	0.993		n.d.	
MX80, L		n.d.		0.45	0.28	1.000		n.d.	
HAl-MX80, UW	0.55	0.16	0.973	0.42	1.96	0.987	0.56	0.04	0.966
HAl-MX80, aged	0.83	0.02	0.992	0.63	1.82	0.994		n.d.	
Al-MX80, UW	0.33	3.50	0.987		n.d.		0.79	0.02	0.952
Al-MX80, aged	0.81	0.02	0.998		n.d.			n.d.	
Al-MX80, L	0.77	0.05	0.992		n.d.			n.d.	
EXM 534, UW	0.38	2.08	0.974		n.d.		0.91	0.01	0.967
EXM 534, aged	0.64	0.09	0.984		n.d.			n.d	
HZr-MX8, UW	0.78	0.12	0.962		n.d.		0.79	0.02	0.933
HZr-MX80, aged	0.89	0.04	0.986		n.d.			n.d	
Zr-MX80, UW	0.58	1.61	0.996		n.d.		0.89	0.02	0.883
Zr-MX80, L	0.75	0.11	0.980		n.d.			n.d.	
Zr-MX80, aged	0.77	0.14	0.998		n.d.			n.d.	
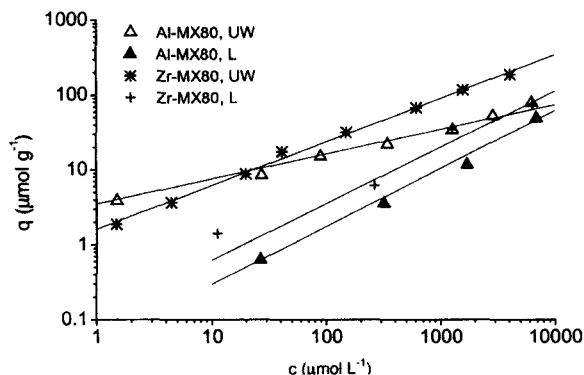
Figure 2.   Sorption of 3-CA by Al and Zr-pillared MX80 in ultrapure water (UW) and artificial leachate (L) (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the calculated isotherms.
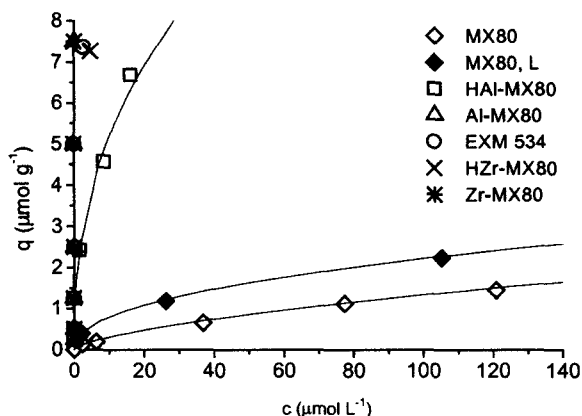

Figure 3.   Sorption of AT by MX80, HAl, Al, HZr, Zr-MX80, and EXM 534 in ultrapure water and artificial leachate (L) (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the calculated isotherms.

4a). Also, the Langmuir constants q_{max} of Zr-MX80 and GAC were close at 117.6 and 129.9 μmol g^{-1} (Table 6), respectively. Al-MX80 exhibited a lower maximum sorption capacity (67.1 μmol g^{-1}). The affinity constants K_L of Al-MX80, Zr-MX80, and GAC were similar (Table 6). In artificial leachate, the maximum sorption capacity of Zr-MX80 decreased to 35.3 μmol g^{-1} and was close to that of Al-MX80 (32.9 μmol g^{-1}; Figure 4b; Table 6). The maximum sorption capacity of GAC was not affected significantly.

Sorption of 3-CP

Sorption of 3-CP by Al and Zr-hydroxy-intercalated and pillared bentonites was described with Freundlich isotherms (Figure 5). The sorption increased in the following order: HAl-MX80 < Al-MX80 ≈ EXM 534 ≈ HZr-MX80 < Zr-MX80. Compared with the sorption of 3-CA and AT, the quantities of 3-CP removed from aqueous solutions by Al and Zr-hydroxy-intercalated and pillared bentonites were lower (Figure 6). At initial concentrations between 0.04 × 10^{-3} to 0.23 × 10^{-3}

M, ~10–30% of the 3-CP was removed from the solution. The K_F values between 0.01–0.04 (Table 5) indicate the existence of sorption sites of medium affinity. The pH values of the suspensions were 5.6–5.9 (HAl-MX80), 4.8–4.9 (Al-MX80 and EXM 534), 4.9–5.0 (HZr-MX80), and 4.0–4.1 (Zr-MX80). Owing to its pK_1 of 9.02, 3-CP was sorbed as neutral molecule.

No sorption of 3-CP was detected for MX80. The pH of the suspensions was between 8.6–8.7 and indicated that apart from a majority of neutral 3-CP molecules, the sorbate also contained chlorophenolate anions. However, none of these species was seemingly sorbed by MX80 in detectable quantities.

DISCUSSION

Sorption of 3-CA

Al and Zr-hydroxy-intercalated and pillared bentonites sorbed higher quantities of 3-CA than the untreated material. Consequently, sorption on basal and edge
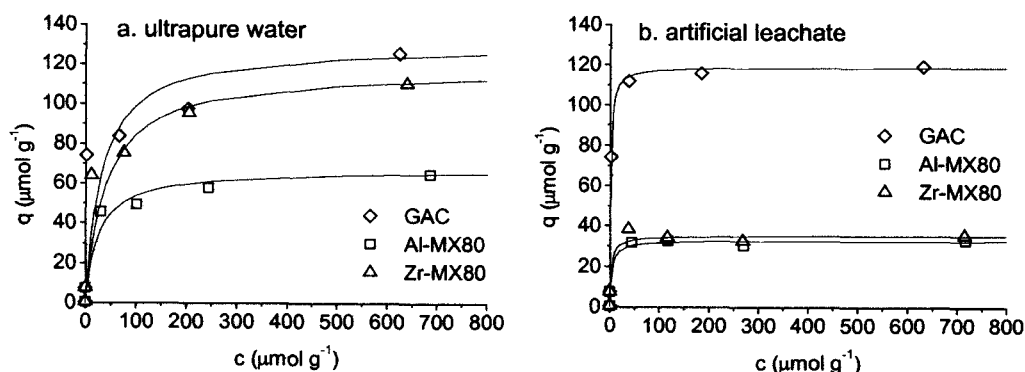

Figure 4.   Determination of the maximum sorption capacity of Al and Zr-pillared MX80 for AT (a) in ultrapure water and (b) in artificial leachate (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the calculated isotherms.
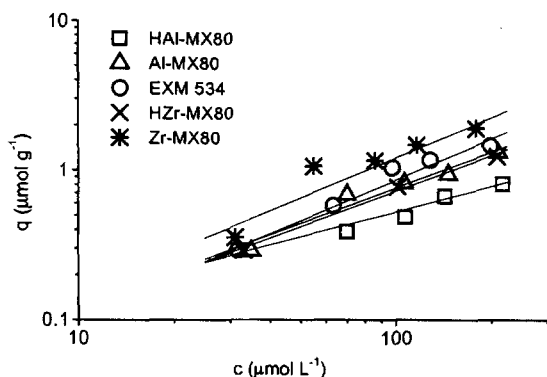
Figure 5. Sorption of 3-CP by HAl, Al, Zr-MX80, and EXM 534 (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the the calculated isotherms.
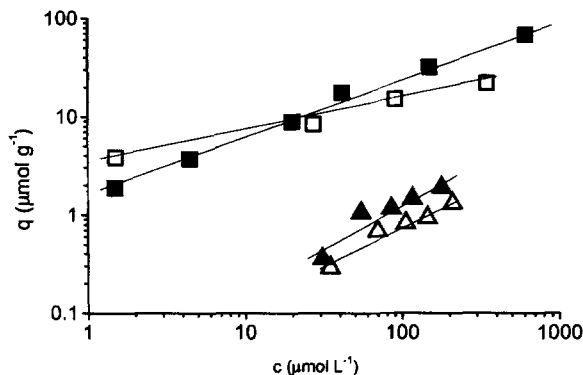

Figure 6. Sorption of 3-CA ($\square$) and 3-CP($\triangle$) by Al-MX80 (open symbols) and Zr-MX80 (solid symbols) (q: sorbed quantity, c: equilibrium concentration in solution). The solid lines represent the calculated isotherms.

surfaces of the montmorillonite is not the governing mechanism. Clearly, sorption was enhanced by the higher surface area of the hydroxy-intercalated and pillared bentonites. However, the order of increasing sorption HAl-MX80 < Al-MX80 ≈ EXM 534 < HZr-MX80 < Zr-MX80 also indicates influences of the acidity and polarizing power of the interlayer cations.

Heller and Yariv (1969) concluded from infrared (IR) spectroscopic measurements that 3-CA coordinates with interlayer cations either directly (type I) or via H_2O molecules (type II). For aniline derivatives, Heller and Yariv suggested that two type-II structures may occur, where one structure may act as proton acceptor and the other as proton donor. The ability to act as a proton donor increases with the polarizing power of the interlayer cation. Also protonated montmorillonites interact with bases forming type-II structures (Yariv et al., 1969). Accordingly, Moreale and Van Bladel (1979) and Cloos et al. (1979) reported strong interactions between acidic sorbents such as H- and Al-containing montmorillonite and chloroaniline molecules with the clay acting as proton donor. This is consistent with our data, i.e., the increasing sorption of 3-CA from the hydroxy-intercalated to the pillared species. The high surface acidity of pillared clays is caused by the release of protons by dehydroxylation of the polyhydroxo cations during calcination. Little is known about the location of these protons in the intercalate, but they contribute to the Brønstedt acidity of the pillared clays (Pinnavaia, 1983).

In artificial leachate, the Al and Zr-hydroxy-intercalated and pillared bentonites exhibited a smaller affinity for 3-CA than in ultrapure water (Table 4). This result may be related to a loss of acidic sorption sites owing to the partial exchange of protons and exchangeable Al and Zr ions (i.e., high ionic potential: Al^{3+}: 13.3 e^2 Å^{-1}, Zr^{4+}: 18.6 e^2 Å^{-1}; Huheey et al., 1995) by Na, K, and Ca ions of the leachate (i.e., low ionic potential: Na^+: 0.86 e^2 Å^{-1}, K^+: 0.66 e^2 Å^{-1},

Ca^{2+}: 3.51 e^2 Å^{-1}; Huheey et al., 1995). This assumption is supported by the low pH of the leachate suspensions compared with the pH in ultrapure water (Table 6).

The pH of most leachate suspensions indicates that 3-CA was sorbed as a neutral molecule. However, the pH (3.7) of the leachate suspension of the most acidic sorbent Zr-MX80 was close to the pK$_1$ value of the 3-chloroanilinium cation (3.34). Apart from a majority of neutral 3-CA molecules, 3-chloroanilinium cations were also present in the solution. The evaluation of the effect of the cationic species on the sorption of 3-CA requires further investigation.

The reduction in sorption capacity of aged hydroxy-intercalated and pillared bentonites for 3-CA is attributed to structural changes, which are accompanied by a loss in surface acidity during aging. Measurements of d values, micropore volumes, and surface areas (Table 1) indicated a partial collapse of the polyhydroxo cations and pillars. The increase of the Na, K, and Ca contents of Al and Zr-hydroxy-intercalated and pillared bentonites after aging in the presence of artificial leachate confirms the uptake of alkali and alkaline-earth cations from the leachate, which results in a loss of surface acidity.

Granulated activated carbon removed 99–100% of the 3-CA from ultrapure water and artificial leachate over the entire concentration range (maximum initial

Table 6. Langmuir constants q_{max} and K for the sorption of AT by Al-MX80, Zr-MX80, and GAC in ultrapure water (UW) and artificial leachate (L).

	UW		L	
	q_{max}	$logK_L$	q_{max}	$logK_L$
Al-MX80	67.1	4.6	32.9	5.4
Zr-MX80	117.6	4.4	35.3	5.5
GAC	129.9	4.5	119.0	5.8

concentration 392 $\mu L \ g^{-1}$). This result is attributed to the high porosity and the large and reactive surface of GAC (770 $\mu L \ g^{-1}$ and 1000 $m^2 \ g^{-1}$, Table 2).

We did not observe any formation of colored complexes owing to charge-transfer reactions and polymerization of aniline at the clay surface. According to Moreale and Van Bladel (1979) and Moreale *et al.* (1985), such color changes only occur in the presence of transition metal cations such as Fe^{3+} and Cu^{2+}.

Sorption of AT

At initial concentrations to 7.5 $\mu mol \ g^{-1}$, between 91–100% of AT was removed from ultrapure water by Al and Zr-hydroxy-intercalated and pillared bentonites. The pH of the ultrapure water and artificial leachate suspensions (≥ 3.5) indicates that AT ($pK_1 = 1.68$) was sorbed as a neutral molecule. Unlike 3-CA, the salinity of the sorbate and aging of the sorbents to an initial concentration of ~ 10 $\mu mol \ g^{-1}$ only slightly influenced the sorption of AT. Consequently, the sorption of organic bases is determined not only by the physico-chemical properties of the sorbent, but also by those of the sorbate.

Organic pesticides in their neutral and protonated form are sorbed by montmorillonites as interlayer complexes (Russell *et al.*, 1968; Ainsworth *et al.*, 1987; Barriuso *et al.*, 1994). According to Welhouse and Bleam (1993a, 1993b), AT molecules exhibit an intermediate reactivity towards donating and accepting hydrogen bonds with complexing agents acting as donors of hydrogen bonds when bound to OH- and H_2O-ligands and as acceptors of hydrogen bonds when bound to surface-oxygen atoms. Laird *et al.* (1994) reported physical sorption of AT molecules to soil clays, whereas Barriuso *et al.* (1994) observed a decrease of the affinity of smectites for atrazine with increasing CEC and surface-charge density and concluded that neutral AT molecules are retained mainly by physical sorption and/or by hydrogen bonding. Sawhney and Singh (1997) observed an increase in AT sorption by smectites with growing polarizing power of the interlayer cation. They suggested that strong hydrogen bonds occur between the AT molecule and the more polarized H_2O molecules coordinated with interlayer cations of high ionic potential.

This suggestion is consistent with our data showing an increase of the sorption of AT with augmenting polarizing power of the interlayered cations and acidity of the sorbents. Accordingly, the enhanced sorption of AT by the starting bentonite MX80 in artificial leachate can be attributed to the exchange of sodium ions by alkali earth cations from the leachate of higher ionic potential.

Compared with 3-CA, AT was sorbed in higher quantities from ultrapure water and artificial leachate suspensions. The higher molecular weight of AT probably favors van der Waals interactions and the higher

nitrogen content of the molecules (Table 2) enhances the formation of hydrogen bonds with Brønstedt-acid sites of the sorbent.

In ultrapure water, the maximum sorption capacity of the most acidic sorbent, Zr-MX80, was similar to that of GAC. Whereas at lower initial concentrations the salinity of the sorbate slightly affected the sorption of AT, at initial concentrations above 10 $\mu mol \ g^{-1}$, the sorption was reduced owing to a decrease of surface acidity of the pillared bentonite. Thus, in artificial leachate suspension, the maximum sorption capacity of Zr-MX80 was below that of GAC. The sorption of GAC was only slightly reduced in artificial leachate owing to competition between the herbicide and the dissolved species. Similar results were obtained by Gicquel *et al.* (1997).

Our results show that AT can be removed by Zr-pillared bentonite from pure and saline aqueous solutions at concentrations to 32 mg L^{-1}. For comparison, the German tolerance values for AT in groundwater range from 0.5 to 2 $\mu g \ L^{-1}$ (Rippen, 1995) and concentrations of 18 $\mu g \ L^{-1}$ are considered hazardous (Rick, 1993). In saline solutions, activated carbon exhibits a higher sorption capacity than Zr-MX80, but pillared clays may be still advantageous. In every recycling, *i.e.*, desorption process of activated carbon, some of the material is lost to oxidation. In contrast, pillared clays can withstand oxidizing conditions during recycling to 500°C as reported by Michot and Pinnavaia (1991) for surfactant-modified Al-pillared montmorillonite.

Sorption of 3-CP

Because no sorption of 3-CP was detected for the untreated bentonite MX80, the enhanced sorption by Al and Zr-hydroxy-intercalated and pillared bentonites is attributed to the intercalated polyhydroxo cations and pillars. Also Zielke and Pinnavaia (1989) did not detect sorption of chlorophenols by montmorillonite, and concluded that the contribution of physical sorption by surface and edge groups of the silicate layers is negligible.

The quantities of 3-CP sorbed by the Al and Zr-hydroxy-intercalated and pillared bentonites were considerably smaller than those of 3-CA and AT. 3-CP ($pK_1 = 9.02$) was sorbed as a neutral molecule. According to Zielke and Pinnavaia (1989), neutral chlorophenol molecules are preferred by Al-pillared montmorillonite over the phenolate forms.

The principle types of surface interactions of neutral organic acids with clay surfaces are similar to those of organic bases, *i.e.*, van der Waals interactions, direct coordination to exchangeable cations, and bridging to coordinated H_2O molecules (Mortland, 1970; Lagaly, 1984; Koskinen and Harper, 1990; Johnston, 1996). Consequently, the sorption of organic acids is affected also by the intercalated species, which is consistent

with our observation of increased sorption of 3-CP from the Al to the Zr-hydroxy-intercalated and pillared bentonites.

Zielke and Pinnavaia (1989) reported that the sorption of chlorophenols by Al and Cr-pillared montmorillonite was influenced by pore structure, composition, and surface area of the sorbents and suggested chemisorption as the dominating sorption mechanism. Kummert and Stumm (1980) described chemisorption of organic acids by γ-Al$_2$O$_3$ through exchange of surface OH groups with anions of the organic acid, which was confirmed by Kung and McBride (1991) who investigated the sorption of 3-CP by hydrous aluminum oxides. Kung and McBride also observed an increasing chemisorption of chlorophenols with increasing structural disorder of the hydrous aluminum oxides. Proceeding from these results, the sorption of 3-CP to the oxidic surfaces of Al and Zr-polyhydroxo cations and pillars could occur also via deprotonation of the 3-CP-molecules and direct coordination to the interlayer metal cations, but a confirmation of this assumption requires further investigation.

Based on IR spectroscopic measurements, Isaacson and Sawhney (1983) and Sawhney (1985) described the polymerization of methylphenols at montmorillonite surfaces which, depending on the interlayer cation, can be accompanied by color changes. However, in our experiments, no color changes were observed.

CONCLUSIONS

Zr and, to a lesser extent, Al-pillared montmorillonites are potent sorbents for 3-chloroaniline and atrazine in aqueous solutions. The increasing sorption capacities for 3-CA and AT from the starting bentonite to the hydroxy-intercalated and pillared bentonite and from the Al to the Zr species indicate a relation between the sorption of organic bases and the acidity of the sorbent. We suggest that pillared clays of high acidity are potent sorbents also for other organic bases than those used in this study.

The results of this study suggest new applications for pillared bentonites as sorbents for the removal of organic compounds from contaminated water or leachate and also as carrier materials, e.g., for pesticides in agricultural practices.

ACKNOWLEDGMENTS

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