

## Adsorption of Imidazolinone Herbicides on Smectite–Humic Acid and Smectite–Ferrihydrite Associations

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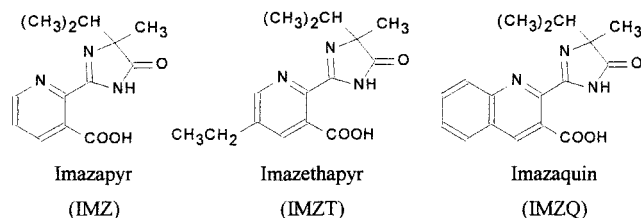
Adsorption of imazapyr (IMZ), imazethapyr (IMZT), and imazaquin (IMZQ) was studied on two smectite–humic acid and two smectite–ferrihydrite binary systems prepared by treating a Wyoming smectite with a humic acid extracted from soil (4 and 8% w/w of the smectite) and with just-precipitated synthetic ferrihydrite (8 and 16% w/w of the smectite). Adsorption of the three herbicides on the smectite was not measurable at pH >4.5, presumably because of negative charges on the surface of the smectite. Adsorption on the smectite–humic acid systems was also not measurable, presumably because of negative charges on the surface, despite the high affinity of the three herbicides for humic acid, the adsorption order of which was IMZ < IMZT ≪ IMZQ. Adsorption decreased in the order IMZ < IMZT < IMZQ on the smectite–ferrihydrite systems and IMZQ < IMZT < IMZ on ferrihydrite, although here the differences were small. These results show that even though pure smectite cannot adsorb herbicides, it modifies the adsorption capacity of ferrihydrite. The mutual interaction of active phases such as humic acid, ferrihydrite, and smectite alters the characteristics of the resulting surface and hence the adsorption process. Investigations of herbicide adsorption have been seen to produce more reliable results if conducted on polyphasic systems rather than on single soil components.

**KEYWORDS:** Imazapyr; imazethapyr; imazaquin; adsorption; binary system; humic acid; ferrihydrite; smectite

### INTRODUCTION

Imazapyr [IMZ; 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid], imazethapyr [IMZT; 5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid], and imazaquin [IMZQ; 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)quinoline-3-carboxylic acid] are widely used imidazolinone herbicides that inhibit nucleic acid synthesis. IMZ is employed in civil and industrial applications, and IMZT and IMZQ are used in agriculture (1). The only difference between them is a substituent on the pyridine ring:

Previous studies (2) have shown a good correlation between IMZ, IMZT, and IMZQ adsorption on soil and the amount of organic carbon and oxides and oxyhydroxides of amorphous or low-crystalline iron. Investigation of their adsorption on a humic acid (HA) (3) and a synthetic ferrihydrite (Fh) (4) has demonstrated their affinity for these surfaces. The herbicide's adsorption on HA is strongly influenced by the nature of the substituent of the pyridinic ring, whereas this is less evident on



Fh. Adsorption studies on the Fh–HA systems (4 and 8% HA) based on those proposed by Celis et al. (5), in the search for a better interpretation of these processes, have shown that when associated with Fh, HA retains its ability to interact with the herbicides, although the extent of adsorption is less dependent on their chemical structure (6).

This paper reports the continuation of these studies through an investigation of herbicide adsorption on smectite–HA and smectite–Fh binary systems to determine the role of the main soil components in the adsorption of imidazolinone herbicides.

### MATERIALS AND METHODS

**Herbicides.** IMZ and IMZQ were certified standards (99% purity) purchased from Riedel de Haën (Seelze, Germany). IMZT (99% purity) was kindly provided by the BASF Co. All of the reagents were of analytical or HPLC purity.

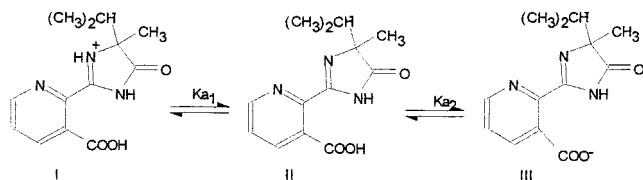
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The water solubility of IMZ is  $11.3 \text{ g L}^{-1}$  at  $25^\circ\text{C}$ , and its  $\text{p}K_{\text{a}}$  values are  $\text{p}K_{\text{a}1} = 1.9$  and  $\text{p}K_{\text{a}2} = 3.6$ . The corresponding values for IMZT are  $1.4 \text{ g L}^{-1}$ ,  $2.1$ , and  $3.9$  (1) and for IMZQ,  $0.06 \text{ g L}^{-1}$ ,  $1.8$ , and  $3.8$  (7).  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  indicate the amphoteric nature of the imidazolinones as shown by the equilibrium for IMZ:



**Sorbents.** The following components were used to prepare the binary systems: Wyoming smectite (SWy), HA, and two-line Fh. The SWy was the  $<2 \mu\text{m}$  fraction of a homoionic smectite ( $\text{Na}^+$ ). It was purchased from the Crook County Co. HA was extracted with  $0.5 \text{ N NaOH}$  from the A ( $0\text{--}15 \text{ cm}$ ) horizon of a histosol according to the IHSS procedures (8), precipitated with  $6 \text{ N HCl}$ , washed with  $0.1 \text{ N HCl}$  and  $0.3 \text{ N HF}$  and then with demineralized water, dialyzed in Spectra/Por membranes (MW cutoff =  $3.5 \text{ kDa}$ ) to a final water conductivity of  $<3 \mu\text{S cm}^{-1}$ , and freeze-dried.

Fh was prepared according to the method of Schwertmann and Cornell (9). To make its preparation consistent with that of binary systems containing Fh and SWy,  $\text{NaOH}$  was used instead of  $\text{KOH}$  to precipitate Fe from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The suspension obtained by precipitation of Fe from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with a solution of  $\text{NaOH}$  was centrifuged, washed, dialyzed for 5 days in Spectra/Por membranes (MW cutoff =  $10 \text{ kDa}$ ) to a final water conductivity of  $<3 \mu\text{S cm}^{-1}$ , and freeze-dried.

**SWy—HA Binary Systems (SWy—HA 4% and SWy—HA 8%).** HA ( $0.4$  and  $0.8 \text{ g}$ ) was suspended in  $400 \text{ mL}$  of  $\text{H}_2\text{O}$ . The suspensions were brought to pH 10 with a  $0.1 \text{ N NaOH}$  solution and then to pH 6.5 with  $0.1 \text{ M HCl}$ . Then,  $10 \text{ g}$  of SWy was added, and the suspensions were shaken at  $25^\circ\text{C}$  for  $16 \text{ h}$  in the dark, dialyzed (MW cutoff =  $10 \text{ kDa}$ ) to a final water conductivity of  $<3 \mu\text{S cm}^{-1}$ , and freeze-dried. The resulting binary systems contained about 4 and 8% HA w/w, respectively. A blank (SWy—HA 0%) was obtained by treating the SWy in the same way without adding the HA.

**SWy—Fh Binary Systems (SWy—Fh 8% and SWy—Fh 16%).** Aqueous solutions ( $15$  and  $30 \text{ mM}$ ) of  $\text{Fe}(\text{NO}_3)_3$  were admixed with  $10 \text{ g}$  of SWy and shaken for  $10 \text{ min}$ , followed by the addition of an  $\text{NaOH}$  solution to pH 7.5. The suspensions were then agitated at  $25^\circ\text{C}$  for  $16 \text{ h}$  in the dark, dialyzed (MW cutoff =  $10 \text{ kDa}$ ), freeze-dried, and stored at room temperature. These binary systems contained about 8 and 16% Fh w/w, respectively. A blank (SWy—Fh 0%) was prepared as follows: An  $\text{HNO}_3$  solution at the same pH (2.5) as the  $\text{Fe}(\text{NO}_3)_3$  solution was admixed with  $10 \text{ g}$  of SWy, shaken for  $10 \text{ min}$ , admixed with an  $\text{NaOH}$  solution to pH 7.5, agitated at  $25^\circ\text{C}$  for  $16 \text{ h}$  in the dark, dialyzed (MW cutoff =  $10 \text{ kDa}$ ) to a final water conductivity of  $<3 \mu\text{S cm}^{-1}$ , and freeze-dried.

**Characterization of the Sorbent Surfaces.** HA was characterized according to a method outlined by Swift (8). Its elementary composition was determined with a LECO model 600 C—H—N analyzer and the O content from the difference.

The total C percent of the systems was determined with a Perkin-Elmer XC total C analyzer (Perkin-Elmer Corp, Norwalk, CT).

The sorbents containing Fe were treated with ammonium oxalate for  $4 \text{ h}$  at  $25^\circ\text{C}$  in the dark and with sodium dithionite—citrate—bicarbonate for  $16 \text{ h}$  at  $25^\circ\text{C}$  according to the method of McKeague and Day (10) to determine their amorphous and total Fe oxide contents. The concentration was determined by atomic adsorption spectrophotometry (AAS).

pH values were measured after equilibration of  $200 \text{ mg}$  of solid with  $10 \text{ mL}$  of a  $0.01 \text{ N CaCl}_2$  solution followed by centrifugation.

Specific surface areas ( $A_{\text{BET}}$ ) were determined by adsorption of  $\text{N}_2$  at  $77 \text{ K}$  using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan, Italy) after degassing at  $80^\circ\text{C}$  and equilibration under vacuum for  $15 \text{ h}$ . Values were obtained by applying the BET method (11) to the adsorption isotherms.

X-ray diffractograms (XRD) were obtained with a Siemens D-5000 diffractometer (Siemens, Stuttgart, Germany), using  $\text{Cu K}\alpha$  radiation from  $3$  to  $80^\circ 2\theta$  in  $0.020^\circ 2\theta$  steps.

Fourier transformed infrared spectrophotometry (FTIR) was carried out with a Perkin-Elmer 2000 instrument on KBr pellets composed of  $0.5 \text{ mg}$  of sample in  $200 \text{ mg}$  of KBr.

The  $^{13}\text{C}$  nuclear magnetic resonance spectrometry (NMR) spectrum of HA in solution was recorded with a JEOL EX-400 sample diluted in NaOD ( $100 \text{ mg}$  of HA in  $2 \text{ mL}$  of NaOD) in the following conditions: free induction decay (FID), magnetic field =  $9.6 \text{ T}$ , amplitude =  $55 \text{ kHz}$ , scans =  $2000$ , and excitation pulse =  $6.25 \mu\text{s}$ .

**Adsorption and Desorption.** Aqueous  $140 \mu\text{M}$  herbicide solutions were diluted to  $20$ ,  $40$ ,  $60$ ,  $80$ ,  $100$ , and  $120 \mu\text{M}$ ;  $0.01 \text{ N CaCl}_2$  was used as the supporting electrolyte to minimize ionic strength variations. Five milliliters (or  $4 \text{ mL} + 1 \text{ mL}$  of  $\text{HCl}$  for adjusting the pH when necessary) of each solution was equilibrated with  $50 \text{ mg}$  of sorbent for  $24 \text{ h}$  at  $25^\circ\text{C}$  in the dark because previous kinetics studies had found that equilibration of the three herbicides is complete after  $24 \text{ h}$  and that no degradation occurs, as shown by blanks without the sorbents prepared under the same conditions. The supernatant was separated by centrifugation at  $25^\circ\text{C}$  at  $1200\text{g}$  for  $30 \text{ min}$ . One milliliter diluted with  $4$  or  $9 \text{ mL}$  of a  $50:50$  (v/v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution acidified to pH 2 with  $\text{H}_3\text{PO}_4$  was analyzed by high-performance liquid chromatography (HPLC) to determine the herbicide concentrations at equilibrium and the amount adsorbed as the difference, using a Spectra System P2000 with a Spectra Series UV 100 detector, a SupelcoSil LC-ABZ column ( $15 \text{ cm}$ ,  $4.6 \text{ mm}$ ,  $5 \mu\text{m}$ ), and a  $20 \mu\text{L}$  loop. The mobile phase was a mixture of  $\text{H}_2\text{O}$  (acidified to pH 2 with  $\text{H}_3\text{PO}_4$ ) (A) and  $\text{CH}_3\text{CN}$  (B): IMZ, 75% A; IMZT, 60% A; and IMZQ, 50% A. In these conditions the retention time was  $2.80 \text{ min}$  for all of the herbicides. The wavelengths were  $240$ ,  $255$ , and  $250 \text{ nm}$  for IMZ, IMZT, and IMZQ, respectively.

Desorption isotherms were obtained on the SWy—Fh 8% system, using the same procedures as for the adsorption isotherms: after equilibration for  $24 \text{ h}$  and centrifugation,  $4 \text{ mL}$  of supernatant was replaced with  $4 \text{ mL}$  of  $0.01 \text{ N CaCl}_2$ , and the suspension was shaken for  $24 \text{ h}$  at  $25^\circ\text{C}$  in the dark and centrifuged; concentration of the herbicides was determined in the supernatant as described above. This desorption procedure was repeated three times.

All of the adsorption and desorption isotherms were determined twice and fitted to the Freundlich equation:

$$x/m = K_f C_e^{1/n}$$

where  $x$  = the amount of herbicide adsorbed in  $\mu\text{mol}$ ,  $m$  = the sorbent mass in  $\text{kg}$ ,  $C_e$  = the equilibrium concentration of herbicide in  $\mu\text{M}$ , and  $K_f$  and  $1/n$  are the Freundlich coefficients.

All of the sorbent and binary system isotherms were obtained at the natural pH value of the sorbents in the presence of the herbicide solutions (final pH). To allow comparison of herbicides' adsorptions on sorbents with different pH values, experiments were also carried out after the pH of the suspensions had been adjusted using  $\text{HCl}$ .

The herbicide-on-HA isotherms were obtained at the natural pH 2.3, whereas those on Fh were obtained at the natural pH 5.7 and also at pH 4.6 following adjustment with  $1 \text{ mL}$  of  $0.015 \text{ N HCl}$ , to allow comparison with the SWy—Fh isotherms. For the same reason adsorption on SWy was investigated at pH 4.6 by adding  $1 \text{ mL}$  of  $0.0010 \text{ N HCl}$  and also at the natural pH 6.9. The SWy—HA and SWy—Fh isotherms were obtained at the natural pH of these two associations:  $5.5$  and  $4.6$ , respectively. Finally, desorption isotherms of the three herbicides on the SWy—Fh 8% system were obtained at the natural pH ( $4.6$ ).

## RESULTS AND DISCUSSION

**Characterization of HA.** Some of the physical and chemical properties of the HA are shown in Table 1. It has also been characterized by  $^{13}\text{C}$  NMR and FTIR as shown in panels a and b, respectively, of Figure 1. The IR spectrum was interpreted according to the guidelines of Stevenson and Goh (12), Bellamy

Table 1. Some Properties of the HA

pH (CaCl <sub>2</sub> )	ash (%)	E4/E6	total acidity (mequiv g <sup>-1</sup> )	-COOH (mequiv g <sup>-1</sup> )	phenolic OH (mequiv g <sup>-1</sup> )	C (%)	H (%)	N (%)	O (%)
2.3	1.4	3.8	8.19	4.44	3.75	51.9	3.7	4.0	40.3

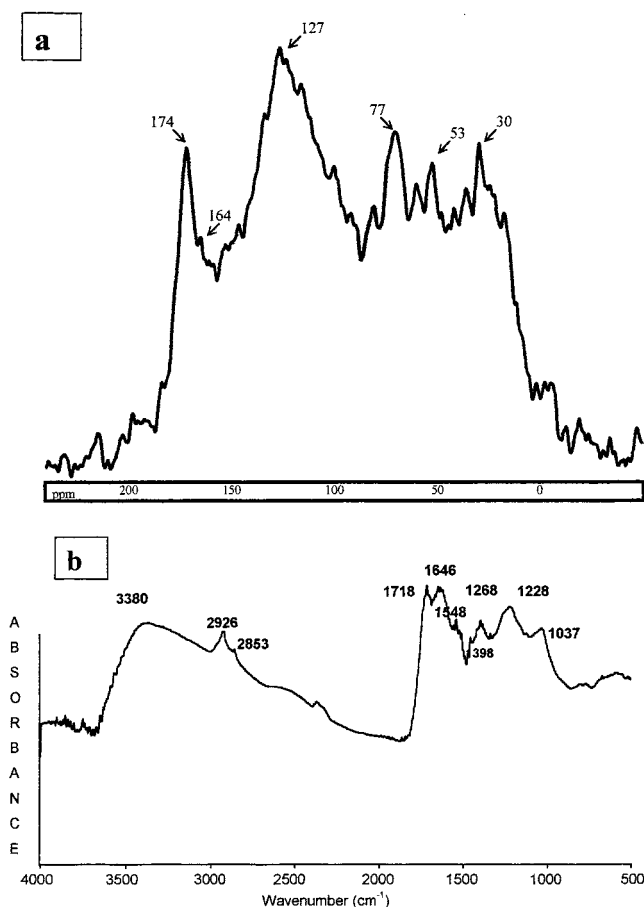


Figure 1. (a) NMR and (b) FTIR spectra of HA.

(13), Lin-Vien et al. (14), and Swift (8); the NMR spectra were interpreted according to the procedures of Preston and Schnitzer (15, 16), Preston and Blackwell (17), Schnitzer and Preston (18), and Swift (8).

The NMR spectrum (high intensity at 127.0 ppm, corresponding to the C resonance of the nonsubstituted aromatic or the alkyl-substituted ring), the bands of its IR spectrum at 1548 cm<sup>-1</sup> (stretching of -C=C- aromatic) and 1646 cm<sup>-1</sup> (stretching of -C=C- aromatic with contribution of COO-), and its low E4/E6 ratio (i.e., a high degree of condensation) all show that the HA is highly aromatic.

The aliphatic region (0–50 ppm) of the NMR spectrum reflects a low presence of nonsubstituted saturated aliphatic carbon. High resonance, on the other hand, is observed in the region of O and N bound to aliphatic C (50–105 ppm). The high resonance at 77 ppm may be attributable to the C of the carbohydrates. The high carboxyl group concentration (titered at 4.44 mequiv g<sup>-1</sup>) of this HA is also corroborated by its high IR absorbance at 1718 cm<sup>-1</sup> (stretching of the CO of COOH), by the band at 1229 cm<sup>-1</sup> (deformation of the O-H of COOH), and by the NMR signal at 174 ppm. The shoulder at 164 ppm may be attributable to resonance of the phenolates as shown by the high phenol group titer (3.75 mequiv g<sup>-1</sup>) and the IR absorbance at 1268 cm<sup>-1</sup>, which is in the region of the stretching and deformation of the phenolic O-H.

Table 2. Some Physicochemical Properties of the Single Inorganic Sorbents and of the SWy-HA and SWy-Fh Binary Systems

sorbent	pH (CaCl <sub>2</sub> )	Fe (%)	C (%)	HA <sup>a</sup> (%)	A <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
single					
Fh	5.8	53.4			346
SWy	7.0				25
SWy-Fh 0%	6.3				25
SWy-HA 0%	6.5				25
binary					
SWy-HA 4%	5.2		2.26	4.35	4
SWy-HA 8%	5.2		3.54	6.82	3
SWy-Fh 8%	4.7	3.9			58
SWy-Fh 16%	4.8	7.3			83

<sup>a</sup> Calculated on the basis of the C content of the HA.

**Characterization of Fh.** Some properties of Fh are shown in Table 2. The ratio between the Fe extractable in ammonium-oxalate and in sodium dithionite-citrate-bicarbonate (Fe<sub>o</sub>/Fe<sub>d</sub>) was very close to 1 (0.99), showing that amorphous or very low crystalline iron oxide was obtained. The surface area measured by N<sub>2</sub> adsorption was in agreement with the data reported in the literature (19).

**Characterization of SWy, SWy-HA 0%, and SWy-Fh 0%.** Some properties of these sorbents are shown in Table 2. The fact that SWy-HA 0% and SWy-Fh 0% exhibit pH values lower than that of SWy is presumably due to the preparation procedure, that is, like the associations, but without the addition of HA and Fh, respectively.

Measurement of A<sub>BET</sub> by means of N<sub>2</sub> adsorption is not representative of the total surface area of SWy because the N<sub>2</sub> molecule is unable to penetrate the interlamellar spaces of the clay (20–23). The A<sub>BET</sub> values of SWy, SWy-HA 0%, and SWy-Fh 0% are the same, as expected.

**Characterization of the SWy-HA Binary Systems.** Some of the properties of these systems are reported in Table 2. The lower pH of the SWy-HA associations compared with SWy-HA 0% is presumably due to HA's carboxyl groups, as observed by Celis et al. (5).

The C content of the associations was close to what had been expected according to amount of added HA.

The drastic drop of the A<sub>BET</sub> of the SWy caused by its association with HA (from 25 to a few m<sup>2</sup> g<sup>-1</sup>) gives an indication of the surface coating of SWy by HA. It is known, indeed, that the specific area of HA is not measurable by N<sub>2</sub> adsorption, because N<sub>2</sub> is unable to penetrate the humic macromolecule (20–23).

The XRD patterns of the SWy-HA systems showed a decrease of the d<sub>001</sub> values, from 15.6 Å at 25 °C to 9.9 Å at 200 °C, in all SWy-HA systems, due to removal of water; the absence of any change in the d<sub>001</sub> values after HA association indicated that, as previously suggested (24, 25), most of the HA is adsorbed on the external surface of the SWy and not in the interlayer space.

Studies of the interaction between humic substances and clays (26–29) have made it clear that because clays usually carry a negative charge, they will hardly form strong bonds when interacting with negatively charged humus, at least for monovalent interlayer cations, such as sodium. In soil, however, humic

**Table 3.** Freundlich Coefficients ( $1/n$ ,  $K_f$ ) of Herbicide Adsorption on HA, on Fh at pH 4.6 and 5.7, and on the SWy–Fh 8% and SWy–Fh 16% Systems and of Herbicide Desorption on the SWy–Fh 8% System

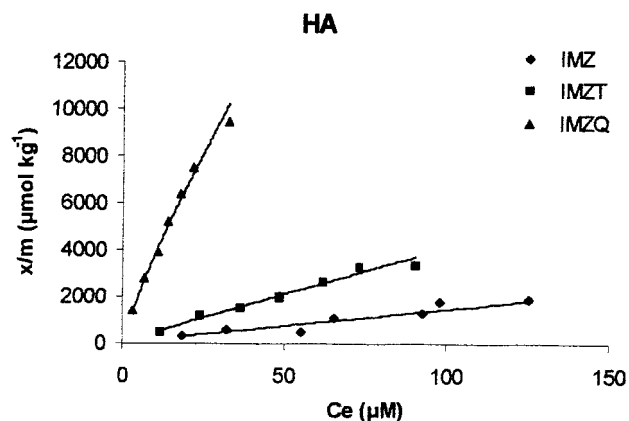
	sorbent		pH <sup>a</sup>	IMZ			IMZT			IMZQ		
				$1/n$	$K_f$	$R^2$	$1/n$	$K_f$	$R^2$	$1/n$	$K_f$	$R^2$
adsorption	single	HA	2.3	0.96	17.6	0.883	0.95	57.1	0.998	0.84	542.9	0.994
		Fh	4.6	0.83	348.2	0.992	0.86	285.2	0.990	1.08	100.3	0.996
		Fh	5.7	0.77	127.5	0.991	0.87	72.19	0.997	1.07	24.9	0.994
	binary	SWy–Fh 8%	4.6	0.90	33.9	0.976	0.74	124.8	0.998	1.31	25.0	0.993
		SWy–Fh 16%	4.6	0.96	48.7	0.984	0.77	139.1	0.995	1.18	37.1	0.987
desorption		SWy–Fh 8%	4.6	0.87	42.8	1.000	0.48	412.2	0.996	1.45	15.5	0.886

<sup>a</sup> pH of the supernatant after 24 h of adsorption.

substances are strongly bound to the mineral matrix, and this bond can only be broken by rather violent treatment. In his paper on the interaction of clay minerals with organic matter, Greenland (27) noted that organic anions interact with such minerals by employing the exchangeable clay anion to form a "cationic bridge" through substitution of water molecules from its hydration shell with the oxygen of an anionic group, such as the carboxylate or phenate of an organic polymer. He also suggested that this coordination is accompanied by other binding forces between organic anions and clay minerals, especially in the presence of rather extensive portions of uncharged humic matter, which is flexible enough to come into intimate contact with the clay particles. The forces that may result in interaction include the hydrogen bond resulting from water adsorption, the London forces, and the Colombian and ion–dipole interactions. Greenland postulated that close contact between clay and a humic substance, marked by multiple short-range interactive forces, is prevented in the presence of large volumes of water, whereas if these are subsequently removed, an appreciable mineral surface will come into close contact with the organic matter. The London forces (corresponding to nonpolar van der Waals forces) become so significant that even though the contribution of each contact point is small, the final adsorption energy may be rather great because there are many points and these forces are additive. If clay and organic matter are simultaneously deprived of water, therefore, as during freeze-drying, these additional adsorption mechanisms may come into operation and the organomineral interaction may occur.

During the preparation of SWy–HA systems, the absorbance measurements (285 nm) of the HA solution before and after its interaction with SWy indicated that part of the HA remained in solution. However, after freeze-drying, the absorbance of the liquid phase when the solid sample was dispersed again in water dropped drastically, indicating that most of the HA was bound to SWy during the freeze-drying process.

**Characterization of the SWy–Fh Binary Systems.** Some of the physical and chemical properties of these systems are shown in Table 2. The total amount of Fe determined by solubilization in sodium dithionite–citrate–bicarbonate was 53% in pure Fh and 3.9 and 7.3% in the SWy–Fh 8% and 16% systems, respectively. Such values were in agreement with the amount of Fe introduced during the preparation of these sorbents. The Fe<sub>o</sub>/Fe<sub>d</sub> ratio was found to be very close to 1 (0.98 for SWy–Fh 8% and 0.93 for SWy–Fh 16%), showing that amorphous or very low crystalline Fe resulted from the preparation. Comparison with the A<sub>BET</sub> values for SWy–Fh 0% shows an increase in surface area as a function of the Fh percentage, as previously observed (30, 31), presumably due to amorphous oxide on the outer layers of the SWy hindering the orientation of its quasi-crystals (5). The decrease in pH in

**Figure 2.** Adsorption isotherms of IMZ, IMZT, and IMZQ on HA at pH 2.3.

these associations compared with SWy and SWy–Fh 0% stems from the presence of iron oxide on the SWy surface. Interaction of SWy with Fh may lead to the release of protons in solution from hydroxyl groups on the Fh surface and thus lower the pH of the suspension.

XRD disclosed a nonsignificant fall in  $d_{001}$  as a function of increased Fe percentage at the same temperature. Thus, a purely surficial SWy–Fh interaction lacking Fh between the SWy layers may be hypothesized (30). As observed for SWy–HA, at 200 °C the  $d_{001}$  values fall from 13.9 to ~10 Å due to the removal of water.

**Adsorption on the Individual Sorbents.** Freundlich's adsorption coefficients for IMZ, IMZT, and IMZQ on the individual sorbents and the binary systems are reported in Table 3. The corresponding isotherms are shown in Figures 2–6.

Results for the adsorption of these three herbicides on HA were already available (3). It was nonetheless decided to determine their adsorption on the HA used to prepare the binary associations at the pH of HA in 0.01 N CaCl<sub>2</sub> (2.3) (Figure 2). The molecular form of the herbicides prevailed at this pH (69.0, 60.4, and 74.2% for IMZ, IMZT, and IMZQ, respectively). Earlier work, however, has shown that the adsorption decreased ~1 order of magnitude at pH 4, at which the anionic form predominates (71.3, 55.4, and 61.2% for IMZ, IMZT, and IMZQ, respectively) (3). Investigation at higher pH values is impossible, due to partial solubilization of the HA. The adsorption order (IMZ < IMZT < IMZQ) was the same as that reported by Gennari et al. (2) and Nègre et al. (3). The extent of adsorption increased as a function of herbicide lipophilicity in agreement with the  $K_{ow}$ , which is thus a good predictor of herbicide affinity for soil organic matter (2).

Results for the adsorption of these three herbicides on Fh were also already available (4). It was nonetheless decided to

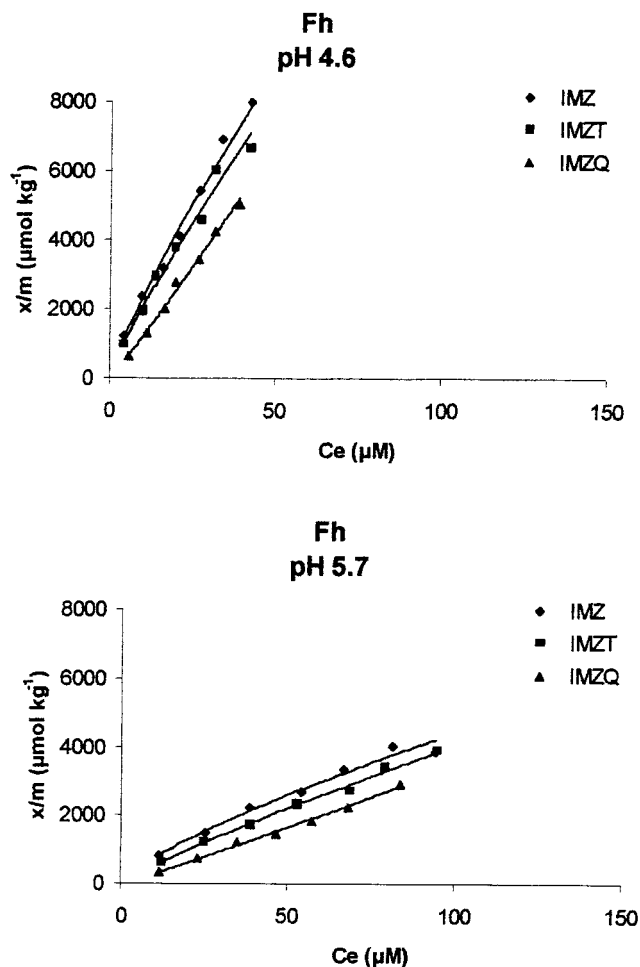


Figure 3. Adsorption isotherms of IMZ, IMZT, and IMZQ on Fh at pH 4.6 and 5.7.

determine their isotherms at the pH values and adsorbate/sorbent ratio used for the binary systems. Comparison of the isotherms at pH 4.6 (conditioned with HCl) and pH 5.7 (natural pH) (Figure 3) showed that the adsorption order was always  $IMZQ < IMZT < IMZ$ , whereas its magnitude increased at the lower pH, most likely due to an increase in the positively charged groups on the Fh surface and hence a greater electrostatic attraction for the dominant anionic form of the herbicides. These findings agree with those reported for Fh (4, 6) and studies of the adsorption of carboxylic acids on iron oxides suggesting that the interaction may be confined to such attraction or else be the result of a ligand exchange that tightly binds the ion to the positively charged iron oxide surfaces (32–34). Comparison of Figures 2 and 3 shows that the between-herbicide adsorption differences are much less marked on Fh than on HA at both pH values, whereas the adsorption order is reversed, as expected, because the typically hydrophilic surface of Fh and the typically hydrophobic surface of HA obviously have a greater affinity for IMZ (the most hydrophilic of the three) and IMZQ (the most hydrophobic), respectively.

Adsorption on SWy was investigated at pH 4.6 and 6.9 and was not measurable presumably because of the reciprocal repulsion of the negative charges on its surface and the anionic form of the herbicides at these pH values. Similar results were obtained for SWy–HA 0% and SWy–Fh 0%.

**Adsorption on the SWy–HA Binary Systems.** Adsorption on the SWy–HA 4% and 8% binary systems was not measurable at pH 5.5 (the natural pH of the sorbents in the presence of  $CaCl_2$  and of the herbicide solution). This suggests that

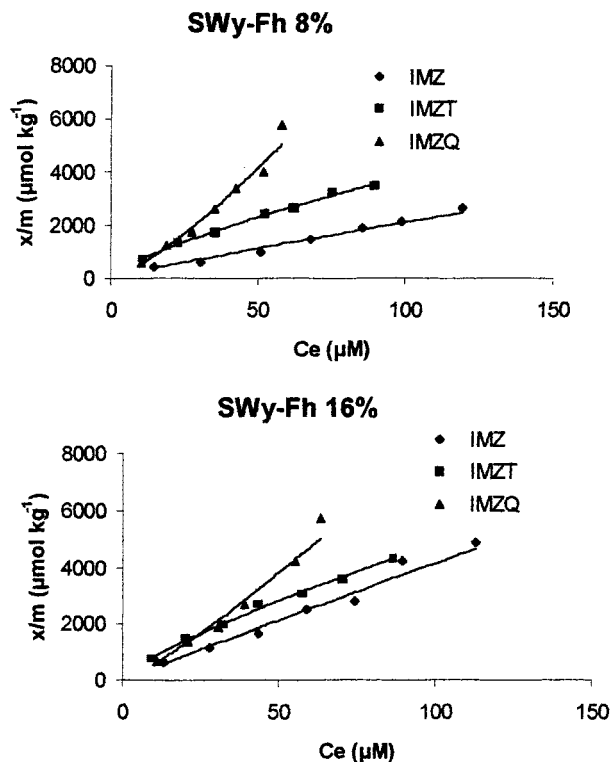


Figure 4. Adsorption isotherms of IMZ, IMZT, and IMZQ on the SWy–Fh systems at pH 4.6.

despite the high affinity of the three herbicides, especially IMZQ, for HA at low pH, as can be seen in Figure 2 and as previously observed (3), at pH 5.5 the presence of negative charges on SWy and of dissociated carboxylic groups on HA resulted in the repulsion of the anionic form of the herbicides and prevented adsorption.

**Adsorption and Desorption on the SWy–Fh Binary Systems.** Comparison of the isotherms of the three herbicides on SWy–Fh 8% and 16% at pH 4.6 (Figure 4) with that of Fh at the same pH (Figure 3) shows that adsorption is less on the binary systems because their formation reduces the amount of Fh available. It is also clear that the adsorption order is reversed and that the differences between herbicides are greater, especially for SWy–Fh 8%, showing that the adsorption is more dependent on their chemical structure when Fh is associated with SWy.

Comparison of the isotherms and of the Freundlich adsorption coefficients (Table 3) shows that isotherms are of type L for IMZ and IMZT and of type S for IMZQ (35). The greater affinity of IMZT for the surfaces compared with IMZ may be due to structural differences between them. IMZT, in fact, has an ethyl group on its pyridine ring. This electrodonor substituent intensifies the negative charge of the acid anion and destabilizes it. One may thus suppose that the destabilized carboxylate group of IMZT is more reactive than that of IMZ and hence that IMZT is more likely to recombine via a ligand exchange. The high number of positive charges on pure Fh presumably promotes a nonspecific electrostatic interaction, whereas a ligand exchange mechanism promoted on the less positive surface of the association favors the adsorption of IMZT rather than IMZ. It can in any event be pointed out that the adsorption order of IMZ and IMZT is the same as that described for soils with different physical and chemical properties by Gennari et al. (2). Pusino et al. (36, 37) have also reported that IMZT is more adsorbed than IMZ as shown by their adsorption on the same soils.

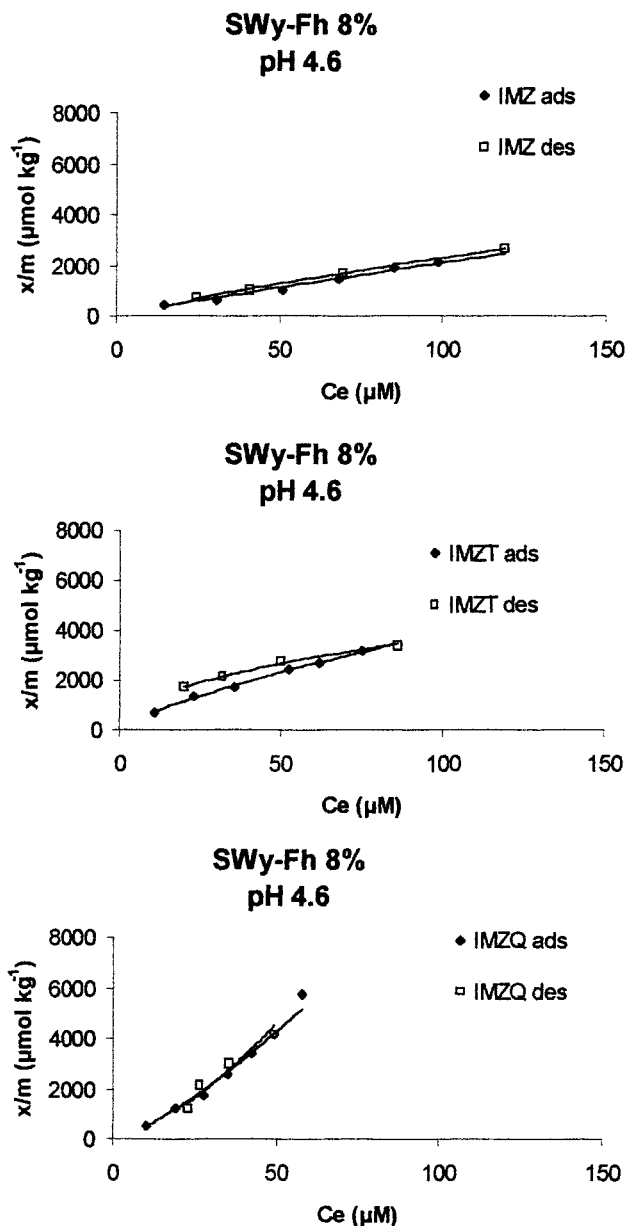


Figure 5. Adsorption-desorption isotherms of IMZ, IMZT, and IMZQ on the SWy-Fh 8% system at pH 4.6.

Isotherms of adsorption of IMZQ on the SWy-Fh systems are of the S type, whereas the isotherm on Fh at the same pH was close to linear. This result confirms that the smectite, although not contributing quantitatively to adsorption, affects the interaction mechanism of this herbicide with the surface. The fact that an S type isotherm occurs only in the case of IMZQ depends probably on its high hydrophobic nature due to its quinolinic group. The S type isotherm shows that adsorption increases as a function of the amount of herbicide adsorbed. In the case of aromatic compounds, this reflects the perpendicular orientation to the surface of the adsorbed molecules (35). Assuming that the interaction between IMZQ and the sorbent surface takes place via its carboxylate group, the quinolinic group should be oriented toward the solution. A perpendicular orientation could be promoted by the interaction through electron transfer mechanisms between the quinolinic groups of two adjacent adsorbed molecules. On the other hand, in previous adsorption studies on Fh, S type isotherms were seen to occur at pH values at which both the anionic and neutral forms of

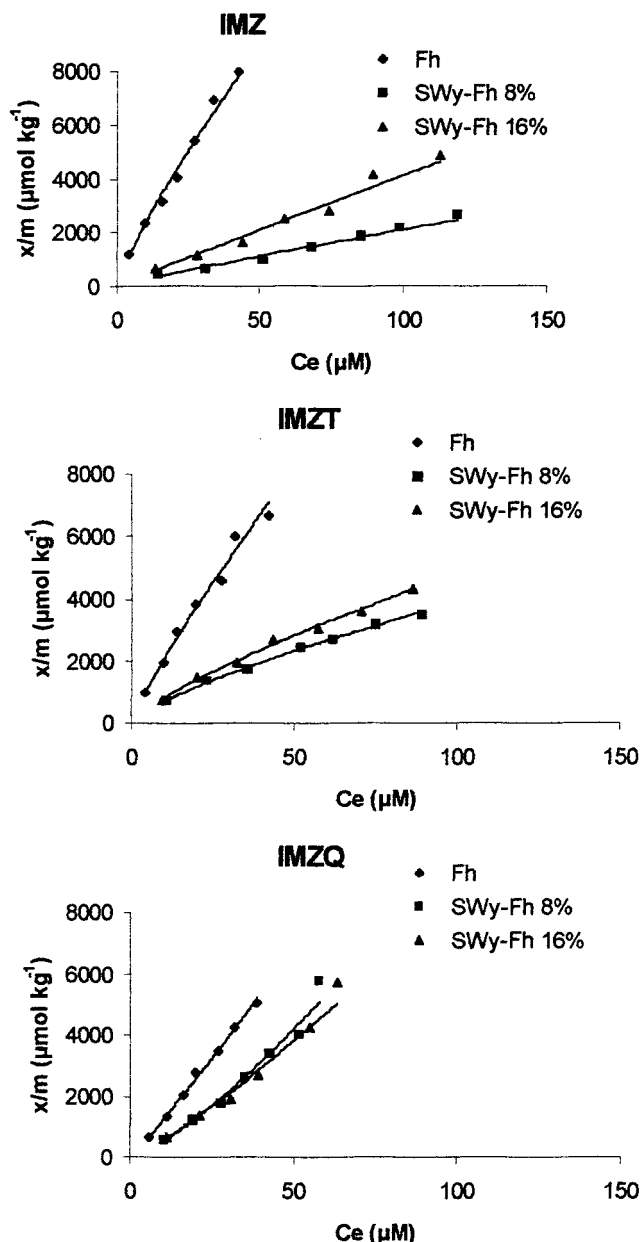


Figure 6. Adsorption isotherms of IMZ, IMZT, and IMZQ on Fh and on the SWy-Fh systems at pH 4.6.

IMZQ were present in relevant amounts. It was supposed that the adsorbed anionic molecules could interact through their lipophilic moiety with the neutral molecules not adsorbed on the polar surface of the adsorbent, leading to an increase of the total adsorbed amount of herbicide. At the pH of the isotherms (4.6), 13.7% of IMZQ is in neutral form and the above mechanism could also take place.

The desorption isotherm (Figure 5) points out that IMZ is completely desorbed without any hysteretical behavior indicating a reversible adsorption mechanism, probably electrostatic attraction, as suggested by the adsorption results. The desorption isotherm of IMZQ (Figure 5) indicates also the complete reversibility of the interaction and reflects the particular behavior of this herbicide as indicated by the  $1/n$  value of desorption  $> 1$ . On the contrary, the adsorption of IMZT (Figure 5) is hysteretical and not completely reversible. The fact that some of the adsorbed molecules are too strongly bound to the surface to be desorbed supports the above-mentioned hypothesis that

IMZT could be adsorbed, besides electrostatic interaction, through a more specific mechanism such as ligand exchange.

The isotherms for IMZ, IMZT, and IMZQ at pH 4.6 on Fh and the two SWy–Fh associations shown by herbicide and not by sorbent in Figure 6 reveal that the differences between the SWy–Fh 8% and 16% systems are negligible for IMZT and IMZQ. In contrast, IMZ is very sensitive to the Fh percentage. This provides further evidence for the dependence of its interaction mechanism on the magnitude of the positive charges on the sorbent surface, which is not surprising if one takes into account that IMZ is the most hydrophilic of the three herbicides and thus has the greatest affinity for the Fh surface (Figure 3).

These results indicate that herbicide adsorption on SWy–Fh associations is presumably attributable to the Fh. SWy, however, is not restricted to a secondary role as the inert support on which Fh is adsorbed, but interacts with it in the formation of the system. This reverses the IMZQ < IMZT < IMZ adsorption order observed on Fh and induces the formation of an S type isotherm in the case of IMZQ. Moreover, one cannot rule out the possibility that the resultant surface of the systems interacts with the herbicides via a specific mechanism, for example, ligand exchange, that is sensitive to the structural differences between the herbicides.

The following conclusions can be drawn from this study:

- SWy is not able to adsorb the herbicides.
- Pure HA at its natural pH (2.3) displays a high affinity for the three herbicides, especially the most hydrophobic (IMZQ), whereas it loses its adsorbing power when associated with SWy, probably because of the higher pH of the systems (5.5).
- Fh displays a high affinity for the three herbicides in relationship to their hydrophilic nature, although there are no marked differences in their adsorptions.
- When Fh is associated with SWy, adsorption occurs but is influenced by the chemical structure of the herbicide. The resulting surface, in fact, displays a greater affinity for IMZT, which is thus more adsorbed than IMZ as observed on soils, and induces the formation of an S type isotherm for IMZQ with a consequent increase in the quantity of herbicide adsorbed as a function of the concentration in solution. Formation of this isotherm was not actually observed in the soils but can reasonably be attributed to the fact that the clay content in the binary associations is much higher than that normally found in soils.

In summary, studies of the adsorption of IMZ, IMZT, and IMZQ on binary associations formed of Fh, HA, and SWy have illustrated the great importance of these fundamental soil components in the adsorption process. It has also been demonstrated that small pH variations have a strong influence on the adsorption of these herbicides on individual sorbents and binary associations and that adsorption itself is encouraged by low pH levels, as observed in soils.

It can thus be reasonably asserted that the mutual interaction of active phases such as humic acid, ferrihydrite, and smectite alters the characteristics of the resulting surface and hence the adsorption process. Therefore, investigation of herbicide adsorption will produce more reliable results if conducted on polyphasic systems rather than single soil components.

#### ABBREVIATIONS USED

IMZ, imazapyr; IMZT, imazethapyr; IMZQ, imazaquin; HA, humic acid; Fh, ferrihydrite; SWy smectite; SWy–HA, smectite–humic acid binary system; SWy–Fh, smectite–ferrihydrite binary system.

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