Role of Ferrihydrite in Adsorption of Three Imidazolinone Herbicides

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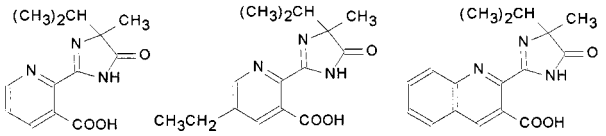
Adsorption of the imidazolinone herbicides imazapyr, imazethapyr, and imazaquin on synthetic ferrihydrites, either freeze-dried or not-freeze-dried, has been studied. The synthetic ferrihydrites were characterized by X-ray diffraction, scanning electron micrographs, and specific area determination. On each ferrihydrite, adsorption was found to be strongly dependent on pH. The highest extent of adsorption took place at pH values close to the pK_a of the carboxylic group of the herbicides. No adsorption was observed at pH > 8. The freeze-drying process reduced the adsorptive capacity of the ferrihydrite by formation of larger aggregates provoking a decrease of the surface area. The chemical differences between the herbicides did not strongly affect the adsorption process of the herbicides. However, imazaquin was more adsorbed than the other two herbicides, in particular at pH close to its pK_a.

Keywords: *Imazapyr; imazethapyr; imazaquin; adsorption; ferrihydrite; freeze-drying*

INTRODUCTION

Imazapyr (IMZ), imazethapyr (IMZT), and imazaquin (IMZQ) are imidazolinone herbicides used primarily to control a wide spectrum of broadleaf and grass weed species. IMZT is used in soybeans and leguminous crops, and IMZ is mainly used in noncrop lands and in forestry because it is particulary active against sedges and woody species (*1*). IMZQ, though less active than the other two, has been commercialized for its very high soybean selectivity (*2*). IMZ, IMZT, and IMZQ have the same structure except for the nicotinic acid substituent:



Imazapyr (IMZ) Imazethapyr (IMZT) Imazaquin (IMZQ)

In our previous paper (*3*) we reported adsorption isotherms of these three herbicides on 10 soils with different physicochemical characteristics. The order of adsorption was IMZ ~ IMZQ < IMZT independent of the soil type. Through evaluation of correlations between the extent of adsorption and the soil characteristics, we also established that the soil components involved in the adsorption process were organic matter, on which adsorption was promoted by low pH, amorphous or poorly ordered iron oxides, and organic-matter-bound iron.

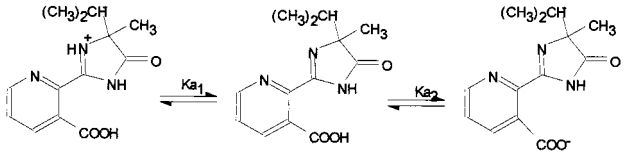
The role of iron oxides in adsorption of some imidazolinone herbicides had also been observed by Pusino et al. (*4*) and Regitano et al. (*5*). In our previous work (*6*) on adsorption of IMZ, IMZT, and IMZQ on hematite, goethite, and ferrihydrite we confirmed that this last sorbent was the most effective. In this work, to better understand the role of amorphous or poorly ordered iron oxides in the adsorption processes, the adsorption of the three molecules on a synthetic ferrihydrite has been studied. The main scope was to study the effect on the adsorption process of the pH of the ferrihydrite–herbicide systems and the influence of the preparation of the ferrihydrite (with and without freeze-drying) and the chemical structures of the herbicides on adsorption.

MATERIALS AND METHODS

Chemicals. IMZ and IMZQ certified standards (99% pure) were purchased from Riedel de Haën, Seelze (Germany). IMZT was a gift from Cyanamid Company. All reagents were analytical or HPLC grade.

The solubility in water of IMZ is 11.3 g L^{-1} at 25 °C, the pK_a values are pK_a1 = 1.9 and pK_a2 = 3.6; for IMZT the solubility at the same conditions is 1.4 g L^{-1}, pK_a1 is 2.1 and pK_a2 is 3.9 (*1*); finally, for IMZQ solubility in water at 25 °C is 0.060 g L^{-1}, pK_a1 is 1.8 and pK_a2 is 3.8 (*7*).

The pK_a1 and pK_a2 indicate the ampholitic character of imidazolinones corresponding to the equilibrium reported for IMZ:



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Sorbents. The synthetic ferrihydrites were prepared according to the method of Schwertmann and Cornell (*8*) by

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dissolving 40 g of $Fe(NO_3)_3 9H_2O$ in 500 mL of distilled water and adding ca. 330 mL of KOH 1 M to bring the pH to 7−8. The last 20 mL was added dropwise with constant checking of the pH. To remove nitrate, ferrihydrite was dialyzed for 5 days (water was changed every 6 h, until water conductivity was < 3 μS cm^{-1}), then a sample was maintained in suspension (not-freeze-dried ferrihydrite) at +10 °C and another sample was freeze-dried (freeze-dried ferrihydrite) and stored at room temperature.

Characterization of Sorbents. Freeze-dried ferrihydrite was step-scanned by X-ray diffractometer (Philips, PW 1729) using Co Kα radiation, from 15° to 80° 2 Å with 0.05° 2 Å step and 30 s counting time.

Surface area of the freeze-dried ferrihydrite was measured by H_2O and N_2 adsorption: H_2O adsorption was performed at $p/p_o = 0.33$ using a saturated solution of $MgCl_2$ and assuming that the water molecule occupies an area of 10.8 $Å^2$ (*9*). N_2 adsorption was obtained using a Carlo Erba Sorptomatic 1900 (Fisons Instr.) equipment. Samples were outgassed at 25 °C under vacuum for 16 h before measuring the N_2 adsorption isotherm. Surface area of the not-freeze-dried ferrihydrite (suspension) was not determinable with the above methods.

Scanning electron micrographs were obtained with SEM Cambridge 360 equipment; a powder sample of freeze-dried ferrihydrite was placed on a stab and Au coated before scanning; a sample of not-freeze-dried ferrihydrite was put on a stab and air-dried (to have a powder sample without freeze-drying), then was Au coated before scanning.

The synthetic ferrihydrites were treated with NH_4-oxalate at pH 3 (*10*) to dissolve amorphous and poorly ordered phases and with dithionite-citrate-bicarbonate (*11*) at 25 °C for 16 h to dissolve both amorphous and any crystalline Fe oxides.

Adsorption at Different pH Levels. The adsorption capacity of the ferrihydrite was characterized by determination of the amount of each herbicide adsorbed at the initial concentration of 140 μM over a range of pH from 2.8 to 5.4 and at pH 8.7 using a batch equilibrium method.

Not-freeze-dried ferrihydrite: 1.5 mL of ferrihydrite suspension containing 33 mg of ferrihydrite was added to 16 mL of IMZ, IMZT, or IMZQ solution at 140 μM. To minimize ionic strength changes 0.01 N $CaCl_2$ was used as background electrolyte. HCl or NaOH (2.5 mL at the suitable concentration) were added in order to obtain the desired final pH.

Freeze-dried ferrihydrite: Powder (33 mg) was dispersed in 1.5 mL of H_2O then added to 16 mL of IMZ, IMZT or IMZQ solution as described above.

The suspensions obtained were shaken for 24 h in the dark at 25 °C. Preliminary studies showed equilibration to be complete within 24 h with no degradation of herbicides occurring in this period. Blank samples (without ferrihydrite) were carried out in the same conditions. The supernatant was separed by centrifugation at 20 000 rpm at 25 °C for 30 min and 1 mL of supernatant was diluted with 4 or 9 mL of H_2O acidified to pH 2 with H_3PO_4/CH_3CN (50% v/v) and analyzed by HPLC for determination of the concentration of the herbicides. The instrument was a liquid chromatograph SpectraSYSTEM P2000 equipped with a SpectraSERIES UV100 UV detector, a SupelcoSil LC-ABZ column (15 cm; 4.6 mm; 5 μm), and a 20-μL loop. The mobile phase was A, H_2O acidified to pH 2 with H_3PO_4, and B, CH_3CN. The composition of the mobile phase and the wavelength of analysis for each herbicide were: IMZ, 75% A, 240 nm; IMZT, 60% A, 255 nm; and IMZQ, 50% A, 250 nm.

Adsorption Isotherms. The adsorption isotherms were determined at pH 2.8 at which the molecular form of the herbicides is predominant; at the nonmodified pH of the ferrihydrite−herbicides suspension (5.4 in the case of the not-freeze-dried ferrihydrite and 5.2 in the case of the freeze-dried one) at which the herbicides are nearly completely ionized; and, for freeze-dried ferrihydrite, at pH 3.8, at which both molecular and ionized forms are present at about the same percentage.

Not-Freeze-Dried Ferrihydrite. Ferrihydrite suspension, 1.5 mL containing 33 mg ferrihydrite, was added with 16 mL of IMZ, IMZT, or IMZQ solution at 20, 40, 60, 80, 100, 120, and 140 μM. $CaCl_2$ (0.01 N) was used as the background electrolyte to minimize ionic strength changes. HCl (2.5 mL 0.025 N) was added in order to obtain the isotherms at pH 2.8. H_2O instead of HCl was added for the isotherms at not-modified pH.

Freeze-Dried Ferrihydrite. Ferrihydrite powder (33 mg) was dispersed in 1.5 mL of H_2O, then added with 16 mL of IMZ, IMZT, or IMZQ $CaCl_2$ solution at the above concentrations and 2.5 mL of 0.025 N HCl or 0.005 N HCl for the isotherms at pH 2.8 and 3.8, respectively. H_2O (2.5 mL) was added for the isotherms at not-modified pH.

Analytical conditions were the same as those used for adsorption at different pH levels.

Adsorption isotherms were described by the Freundlich equation:

$$x/m = K_f\, Ce^{1/n} \quad (1)$$

where x = amount of sorbate adsorbed (μmol), m = unit mass of adsorbent (kg), Ce = equilibrium concentration of sorbate (μM), K_f and $1/n$ are the Freundlich coefficients.

Kd (distribution coefficient) was used to express the amount adsorbed at a single concentration (*Ce*):

$$Kd = x/m/Ce \quad (2)$$

All adsorption studies were conducted in duplicate.

Evaluation of the Possible Complexation of Fe^{3+} by the Imidazolinone Molecules. The possible formation of Fe−imidazolinone molecule complexes involving the iron ions present in the solution could lead to erroneous quantification of the amount of herbicides actually adsorbed. Consequently, we checked, in the experimental conditions used for adsorption experiments, the possible release of Fe^{3+} in solution by ferrihydrite. Fe in solution was measured by flame atomic absorption spectrophotometry, using a Perkin-Elmer 3030 with deuterium background correction. We observed that the amount of Fe^{3+} aq released by the freeze-dried ferrihydrite over the entire considered pH range was less than 0.1 ppm (AAS detection limit for Fe), whereas from the not-freeze-dried ferrihydrite a partial solubilization of Fe^{3+} occurred at pH < 3 (20 μM Fe at pH 2.8).

As studies of Duda et al. (*12*) and Rajamoorthi et al. (*13*) report the formation of complexes between Cu^{2+} and IMZ and IMZT, respectively, we conducted preliminary experiments in order to check for the possible formation of such complexes between Fe^{3+} and the imidazolinone molecules.

Solutions of IMZs in 0.01 M $CaCl_2$ were added with $Fe(NO_3)_3$ (20 μM) in order to obtain final metal-to-ligand ratios of 1:1, 1:2, and 1:3. The pH was adjusted to 2.8 with HCl. Blank samples (without $Fe(NO_3)_3$) were also prepared. These solutions were shaken overnight, centrifuged, diluted, and analyzed in the same conditions as those used for imidazolinone adsorption experiments. The concentrations of the herbicides in the solutions were the same as those in the corresponding blank samples: the presence of insoluble iron−imidazolinone complexes was therefore excluded.

As the formation of soluble metal−imidazolinone complexes may occur as well, and it has been seen to provoke a shift of the absorption maximum of the UV spectra of IMZT (*13*), we performed UV spectra of iron−imidazolinone solutions and of the corresponding blank solutions. UV spectral analyses were performed on a HITACHI V-2000 UV/VIS spectrophotometer. For the three herbicides, at the various studied concentrations, no shift of the absorption maximum was observed; therefore, the presence of iron−imidazolinone complexes in the solutions was also excluded. As an example, the spectra obtained in the case of IMZT are shown in Figure 1.

These preliminary tests allow us to conclude that, even in the presence of a slight solubilization of the not-freeze-dried ferrihydrite, at pH < 3, the small amounts of Fe in solution do not affect the results of the adsorption experiments.

RESULTS AND DISCUSSION

Characteristics of Iron Oxides. Both iron oxides showed a ratio of an Fe extractable in NH_4-oxalate to

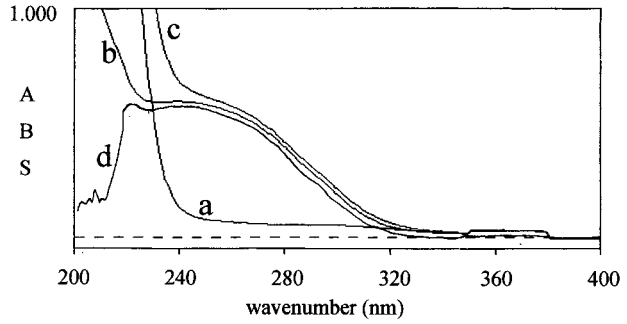

Figure 1. UV spectra: (a) $Fe(NO_3)_3$ solution (0.02 mM); (b) IMZT solution (0.06 mM); (c) IMZT plus $Fe(NO_3)_3$ solution at the above concentrations; and (d) differential spectrum (spectrum (c) minus spectrum (a)).

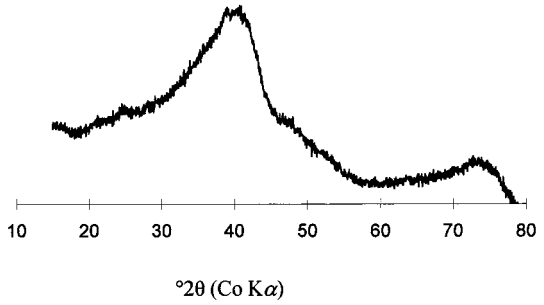

Figure 2. XRD trace of freeze-dried ferrihydrite.

Fe extractable in dithionite-citrate-bicarbonate very close to one (0.98), indicating that they were amorphous or poorly crystalline material.

The freeze-dried ferrihydrite was a pure 2-line ferrihydrite (Figure 2). Its surface area measured by N_2 adsorption and by H_2O adsorption was 277 and 280 m^2 g^{-1}, respectively, in agreement with the data reported in the literature (*14*−*16*). Comparison of the scanning electron micrographs of the not-freeze-dried ferrihydrite (Figure 3a) and of the freeze-dried ferrihydrite (Figure 3b) indicates that the freeze-drying process induces an increase of the aggregation degree of the particles, and formed aggregates are difficult to redisperse (*8*).

Adsorption Studies. Adsorption experiments are illustrated in Figure 4 (adsorption at a single concentration over a large pH range) and Figures 5 to 7 (adsorption isotherms at three pH values).

Effect of pH on Adsorption. The results of the experiments indicate that the extent of adsorption, as judged from the *Kd* parameter, was strongly dependent on pH. The highest Kd values were obtained at about pH 4 for all herbicides and this pH is very close to their pK_a2 (Figure 4a, b). Over the considered pH range the ferrihydrite surfaces are positively charged, and their charge increases as pH decreases. At pH > pK_a2 adsorption is promoted by the predominance of the anionic form of the herbicide which is attracted by the positive charge of the surface. Anionic forms of carboxylic acids have been observed to bind weakly to the positive sites of the oxide surface (*17*, *18*), but some authors report also the formation of strong bonds through a ligand exchange mechanism (*19*−*21*).

The maximum of adsorption of carboxylic acids is usually obtained, as in our cases, near the pK_a of the acids where the increase in surface positive charge is counterbalanced by a decrease in negative charge of the acids (*22*).

The mechanism involved in the adsorption of the molecular forms of carboxylic acids has not been clearly

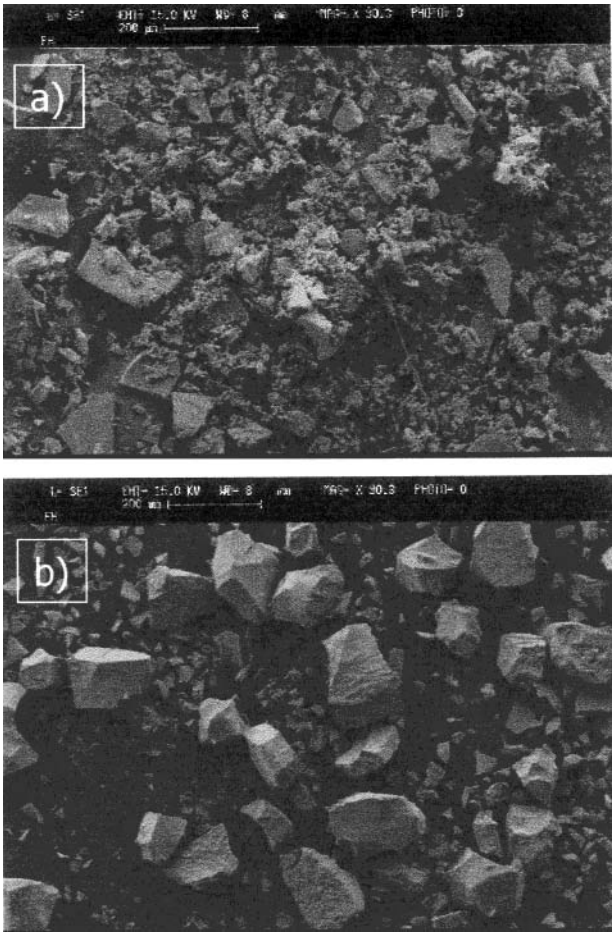

Figure 3. Scanning electron micrographs of not-freeze-dried (a) and freeze-dried (b) ferrihydrite.

elucidated, although it has been observed that the surface OH groups on the iron oxide promotes deprotonation of the carboxyl, inducing the molecule−ferrihydrite interaction (*16*). At low pH values the adsorption decreases probably because (a) the decrease of pH provokes a decrease of the amount of superficial OH groups responsible for the above mechanism; or (b) protonation of the imidazolinone nitrogen (form I of the equilibrium reported in Materials and Methods), although not relevant in the solution according to the pK_a1 (<15% at pH 2.8), could be enhanced by the positive charges of the surface, resulting in repulsion of the herbicides.

At pH 8.7 no adsorption of the herbicides occurs; because at this pH, both the ferrihydrites and the herbicides were negatively charged (form III of the equilibrium reported in Materials and Methods) so they tend to repulse each other.

The effect of pH on adsorption was also pointed out by the adsorption isotherms (Figures 5−7). For each ferrihydrite, adsorption was higher at pH 2.8 than at pH close to 5, confirming the results of Figure 4. On freeze-dried ferrihydrite, adsorption isotherms were also performed at pH close to pK_a2 confirming that the highest extent of adsorption took place at this pH value (Figure 7).

Effect of Ferrihydrite Freeze-Drying. From Figures 4−6, we can deduce that the not-freeze-dried ferrihydrite adsorbs larger amounts of each herbicide than the freeze-dried ferrihydrite. This effect is particularly noticeable at the most acidic pH values. The

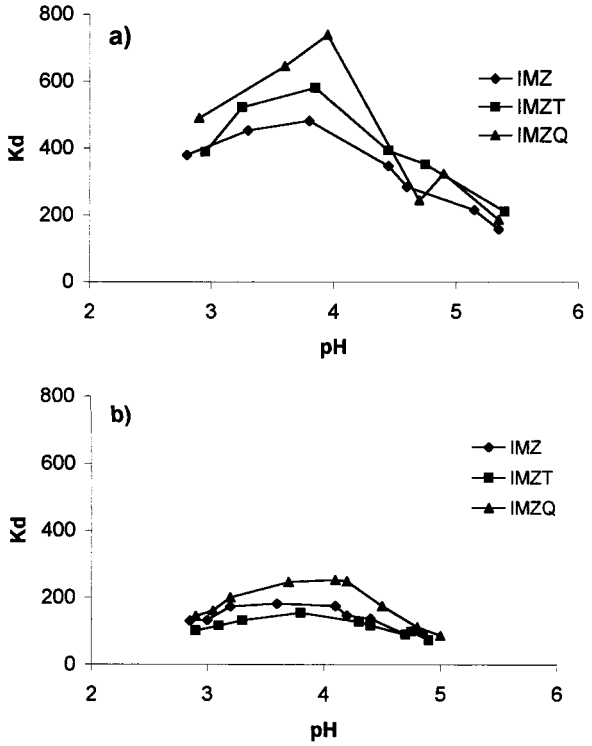

Figure 4. Kd of the adsorption of IMZ, IMZT, and IMZQ on not-freeze-dried (a) and on freeze-dried (b) ferrihydrite at different pH levels.

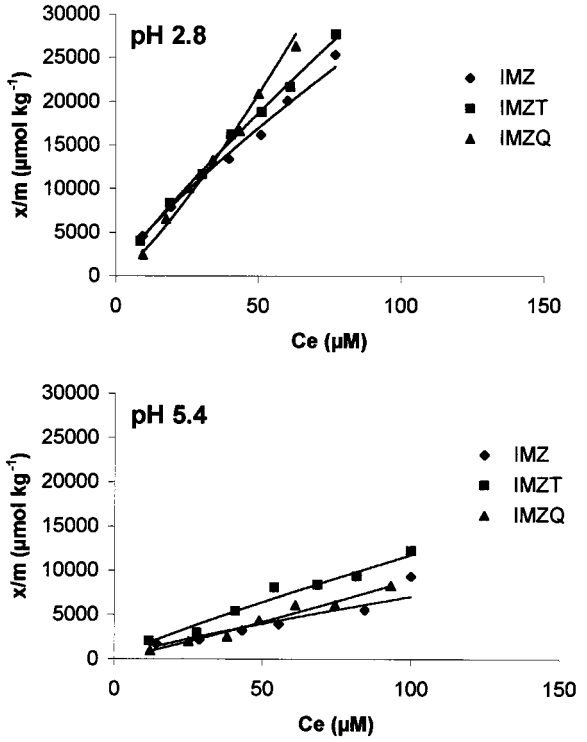

Figure 5. Adsorption isotherms of IMZ, IMZT, and IMZQ on not-freeze-dried ferrihydrite at pH 2.8 and 5.4.

minor adsorptive capacity of the freeze-dried ferrihydrite could be attributed to its probably lower specific surface area induced by the formation of larger aggregates during the freeze-drying process. The formation of larger aggregates in the freeze-dried ferrihydrite determines the reduction of its buffer capacity, as seen by adding H^+ to ferrihydrite−0.01 N $CaCl_2$ suspensions to obtain a given pH of the supernatant (Figure 8). More

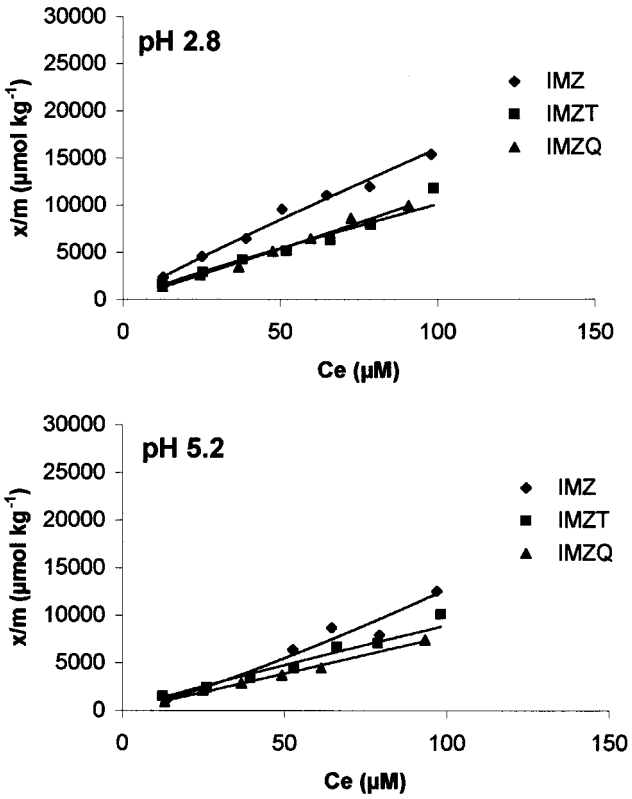

Figure 6. Adsorption isotherms of IMZ, IMZT, and IMZQ on freeze-dried ferrihydrite at pH 2.8 and 5.2.

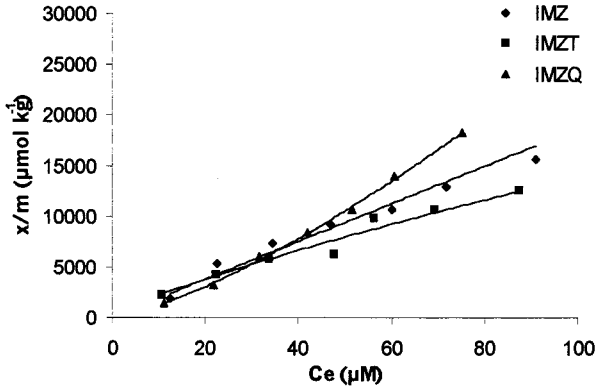

Figure 7. Adsorption isotherms of IMZ, IMZT, and IMZQ on freeze-dried ferrihydrite at pH 3.8.

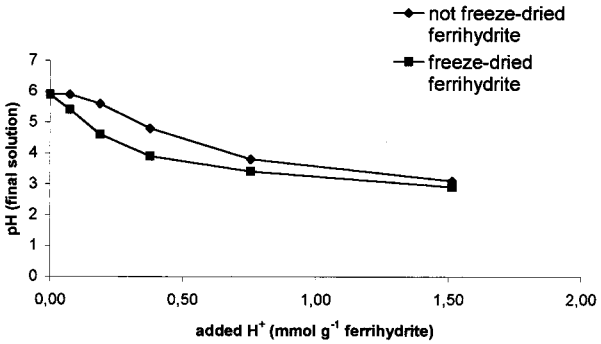

Figure 8. H^+ titration of ferrihydrite.

H^+ is needed to decrease the pH of the not-freeze-dried ferrihydrite suspension than that of the freeze-dried one. Consequently, at a given pH the positive charge of the not-freeze-dried ferrihydrite should be higher than that of the freeze-dried one.

Table 1. Freundlich Coefficients (1/*n*, K_f) of Herbicides Adsorption on Not-Freeze-Dried and on Freeze-Dried Ferrihydrite

		IMZ			IMZT			IMZQ		
sorbent	pH[a]	1/*n*	K_f	R^2	1/*n*	K_f	R^2	1/*n*	K_f	R^2
freeze-dried ferrihydrite	2.8	0.92	231.6	0.992	0.90	160.9	0.981	1.03	95.9	0.990
	5.2	1.22	47.3	0.982	0.91	135.9	0.968	1.02	72.7	0.990
	3.8	1.00	196.2	0.961	0.80	342.5	0.973	1.35	53.7	0.997
not-freeze-dried ferrihydrite	2.8	0.80	727.1	0.995	0.87	611.2	0.998	1.23	167.3	0.989
	5.4	0.82	161.8	0.909	0.86	214.0	0.953	1.10	57.6	0.978

[a] pH of the supernatant after 24 h adsorption.

The higher positive charge and the probably higher surface area of the not-freeze-dried ferrihydrite should be responsible for the higher herbicides adsorption.

We can conclude that the differences in adsorption observed between the freeze-dried and the not-freeze-dried ferrihydrite are related to their aggregation state. Although both the ferrihydrites have been synthesized in the laboratory and are not representative of a real environmental situation, they are both useful for better understanding the adsorption processes in soil. From a methodological point of view, the use of the solid freeze-dried ferrihydrite is easier and quantitatively more reliable than that of the suspended not-freeze-dried ferrihydrite and can be recommended for adsorption studies.

Differences of Adsorption between the Herbicides. From our previous study on adsorption of the same herbicides on different soils, (*3*) we concluded that the nature of the substituent of the pyridinic group affected the adsorption process inducing the adsorption order IMZ ≈ IMZQ < IMZT. In the case of adsorption on humic acids, this order was changed in IMZ < IMZT ≪ IMZQ (*23*). In all the studies on soils and humic acids, 1/*n* Freundlich coefficients were <1 for the three herbicides, whereas in the case of the ferrihydrites, in all the tested conditions, 1/*n* of IMZQ was always ≥1, 1/*n* of IMZT was always <1, and that of IMZ was ≤1 (except adsorption on freeze-dried ferrihydrite at pH 5.2) (Table 1). These results lead to two considerations: (a) the comparison of the K_f as an indication of the extent of adsorption could lead to erroneous conclusions because the K_f unit is dependent on the 1/*n* value (*3, 24*); and (b) the order of adsorption is dependent on the concentration of the herbicides. For example, at pH 3.8 (Figure 7) the order of adsorption on freeze-dried ferrihydrite is IMZQ < IMZ ≈ IMZT at Ce < 30 μM and IMZT < IMZ < IMZQ at Ce > 30 μM.

Consequently, it is not possible to express a representative order of adsorption of the herbicides from the isotherms. However, the differences between the isotherms of the three herbicides at each pH and on each ferrihydrite are less relevant than in the case of soil adsorption and much less relevant than in the case of humic acid adsorption.

The curves of *Kd* versus pH (Figure 4) point out that the three herbicides have similar behavior at the extreme pH but IMZQ is more adsorbed than the other two herbicides at pH values close to the pK_a2. From the isotherms at pH 3.8 (Figure 7) we obtained a 1/*n* value of IMZQ > 1 (1.35) corresponding to an S curve according to the Giles (*25*) classification, whereas the 1/*n* values for IMZ and IMZT were ≤1. An S curve indicates that the more solute there is already adsorbed, the easier it is for additional amounts to became fixed (*25*). The main difference between IMZQ and the other two herbicides is its high lipophilicity due to the presence of the quinoline moiety. If we assume that the anionic form of the molecule is adsorbed through its carboxylate group, its quinoline moiety should form a lipophilic coating on the iron oxide surface. According to its low solubility and its high octanol−water partition coefficient (*3*) the molecular form of IMZQ could be adsorbed on this coating through a partition mechanism provoking an increase of the total adsorbed amount which is particulary noticeable at the highest concentrations. This hypothetical mechanism may explain the S isotherm at pH 3.8 and the different behavior of IMZQ in the pH range in which significant amounts of both neutral and anionic forms are present. At the extreme pH of Figure 4 IMZQ exhibits more or less the same *Kd* as the other two herbicides. At the highest pH the concentration of the molecular form is too low (<5%) to allow the formation of the double layer. At the lowest pH the double layer mechanism could be prevented by the decreasing availability of the anionic form and by the enhanced presence of the protonated form. This adsorption mechanism of IMZQ is obviously a hypothesis which needs to be confirmed by mechanistic studies.

CONCLUSION

This study has confirmed that amorphous or poorly ordered Fe oxides have an important role in the adsorption of IMZ, IMZT, and IMZQ, and it has pointed out the influence of the pH of the system and of the state of aggregation of the Fe oxide.

However, the adsorption data obtained on ferrihydrite and the previous results of adsorption on humic acids (*3, 23*) do not completely explain the order of adsorption observed in soil (IMZ ∼ IMZQ < IMZT), probably because these pure soil components are not representative of the complex adsorption surfaces resulting from their mutual associations. For a more realistic interpretation of the adsorption processes, studies of adsorption on polyphasic systems such as those proposed by Celis et al.(*26*) are needed.

ABBREVIATIONS USED

IMZ, imazapyr; IMZT, imazethapyr; IMZQ, imazaquin.

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