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GLYPHOSATE-HYDROTALCITE INTERACTION AS INFLUENCED BY pH

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Abstract—Adsorption and the mechanism of adsorption of the herbicide glyphosate [N-(phosphonomethyl) glycine] by hydrotalcite (HT) and by hydrotalcite calcined at 500°C (HT500) was studied. The values of the Freundlich K constant of the adsorption isotherms and the distribution coefficients, Kd, depend on the pH of the adsorption system and vary between 55.54–9603 (K) and 36.82–6252 (Kd) for HT and between 10,106–23,242 (K) and 17,801–26,558 (Kd) for HT500. X-ray diffraction and infrared spectroscopy studies showed that glyphosate is not adsorbed into the interlayer of HT. The adsorption mechanisms are (1) electrostatic attraction between the surface of HT, charged positively below pH 12 according to its point of zero charge and the glyphosate anion, and (2) ligand exchange between the P-OH and/or C=O groups of the herbicide and the Al and Mg atoms of the HT surface. The occurrence of one or both mechanisms depends on the pH of the adsorption system. These adsorption mechanisms and the amphoteric nature of glyphosate account for the variation in K and Kd values with respect to pH. Previous studies on adsorption of different organic anions by HT have only considered the mechanism of anion exchange as important.

Key Words—Adsorption, Adsorption Mechanism, Calcined Hydrotalcite, Glyphosate, Hydrotalcite, pH.

INTRODUCTION

Hydrotalcites are double layer hydroxides, and are often called "anionic clays". The structure consists of brucite-like layers with a positive charge owing to the replacement of Mg by Al. These layers are neutralized by interlayer anions (Miyata, 1980; Cavani *et al.*, 1991). H_2O molecules occupy the remaining interlayer space. The interlayer anions and H_2O molecules can be exchanged by organic or inorganic anions and by polar molecules. At 500–800°C, hydrotalcite decomposes to form oxides of magnesium and aluminum, and the calcined product can be rehydrated with anions in solution to reform hydrotalcite (Miyata and Okada, 1977).

Because of the anionic-exchange capacity, these materials have been examined as adsorbents for anionic organic pollutants in aqueous media (Hermosin *et al.*, 1993, 1996; Ulibarri *et al.*, 1995). Studies have generally focused on determining the capacity of hydrotalcite to adsorb a pollutant by using adsorption isotherms and on detecting the possible intercalation of a pollutant by X-ray diffraction. However, in adsorption studies conducted to date, it has not been taken into account that these materials (as other metal oxides and hydroxides) have a variable surface charge that changes in magnitude and sign as a function of pH in addition to a permanent positive charge. Depending on the point of zero charge of the hydrotalcite (PZC = 12) (Han *et al.*, 1998), the surface is positively charged below pH 12 and negatively charged above this value. Accordingly, below this pH, hydrotalcite may in theory, adsorb any anion by electrostatic attraction (non-specific adsorption). Additionally, the Mg and Al cations at the surface, like corresponding oxides, may adsorb certain anions through ligand exchange (specific adsorption), regardless of the surface charge of the material. Among these anions are phosphates, phosphonates, arsenates, and many carboxylic acids (Hsu, 1977; Parfitt, 1978).

In this work, we study the interaction of glyphosate, an organophosphorus herbicide, with hydrotalcite as a function of pH of the aqueous system. The glyphosate molecule is amphoteric, ranging from a univalent positive charge at pH < 2 to a trivalent negative charge at pH > 10. This herbicide is widely used in agriculture and has been detected in surface and subsurface waters (Mensink and Janssen, 1994).

Related studies include adsorption of glyphosate by soils (Sprankle *et al.*, 1975; Glass, 1987) and by soil components, such as smectites (Shoval and Yariv, 1979), iron and aluminum oxides (McConnell and Hossner, 1985; McBride and Kung, 1989), humic acids (Celano and Piccolo, 1991), and studies on glyphosate-forming complexes and chelates with divalent and trivalent cations in solution (Motekaitis and Martell, 1985; Subramaniam and Hoggard, 1988; McBride, 1991).

MATERIALS AND METHODS

Synthetic hydrotalcite (HT) used in this study was prepared by the co-precipitation method described by Reichle (1986). The HT product has a formula of $Mg_{0.657}Al_{0.342}(OH)_2(CO_3)_{0.171}\cdot 0.87H_2O$ [anion-exchange capacity (AEC) of 4.1 meq g^{-1}]. The magnesium and aluminum oxide has a formula of $Mg_{0.657}Al_{0.342}O_{1.171}$ and was prepared by calcination of the HT at 500°C for 24 h (HT500). ^{14}C-labeled glyphosate was obtained from Amersham International (Buckingham, UK). Non-radioactive herbicide was obtained from Promochem Ltd. (St. Albans, UK). The oxides of aluminum

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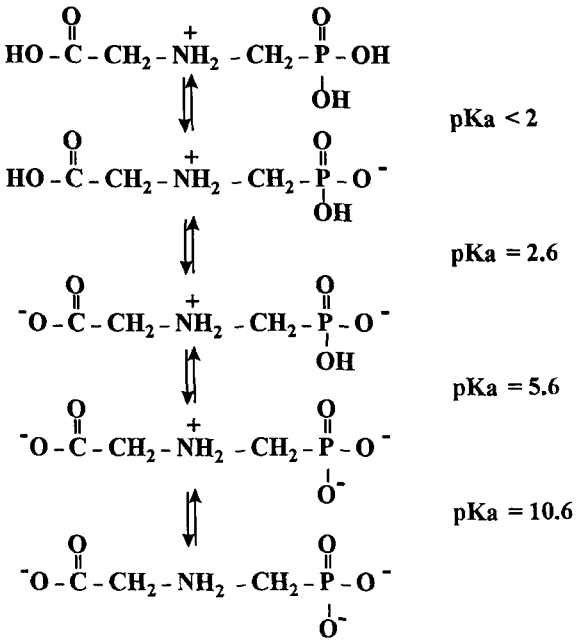


Figure 1. Dissociation species and ionization constants (Sprankle *et al.*, 1975).

(Al_2O_3) and magnesium (MgO) have 99.9% purity, and were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin).

Glyphosate [N-(phosphonomethyl) glycine] is an anionic organophosphorus herbicide that is highly soluble in water (12 g L^{-1}). The dissociation species and related ionization constants as proposed by Sprankle *et al.* (1975) are shown in Figure 1.

Adsorption isotherms were obtained using a batch equilibrium method with ^{14}C-labeled glyphosate. Fifty mg of HT, HT500, or oxides of aluminum and magnesium were mixed with 10 mL of solution containing 5, 10, 15, 20, or 25 μg mL^{-1} of herbicide and a solution activity of 170 Bq mL^{-1}, in 20-mL stoppered centrifuge tubes. The suspensions were maintened at 20°C with intermittent shaking. Previous kinetic research showed that a steady state is reached in <24 h. After a steady state was reached, the suspensions were centrifuged for 30 min at 3000 G. To determine herbicide concentration at equilibrium, a 1.0-mL aliquot of clear supernatant solution was mixed with 4.5 mL of scintillation fluid (Ecoscint A. National Diagnostics, Atlanta, Georgia) and ^{14}C activity (disintegrations per min) was determined on a Beckman LS 1800 Scintillation Counter (Beckman Instruments Inc., Fullerton, California). All experiments were performed in duplicate. The concentration of the equilibrium solute in the solid phase was determined as the difference between the initial pesticide concentration and the equilibrium concentration. Owing to the amphoteric nature of the glyphosate molecule, the adsorption isotherms were obtained in solutions adjusted to pH values of 2, 3.9, 5.5, and 11.5.

The interaction of HT and HT500 with glyphosate was studied by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Samples of both forms of HT were treated with high concentrations of glyphosate until an adsorption greater than the AEC of the samples was reached. XRD patterns were recorded on a Philips 1730 diffractometer using CuKα radiation. IR spectra were recorded on an FT-IR Midac spectrophotomer using the KBr pellet technique.

RESULTS

Figure 2 shows the adsorption isotherms of glyphosate by HT and HT500 obtained at initial pH val-

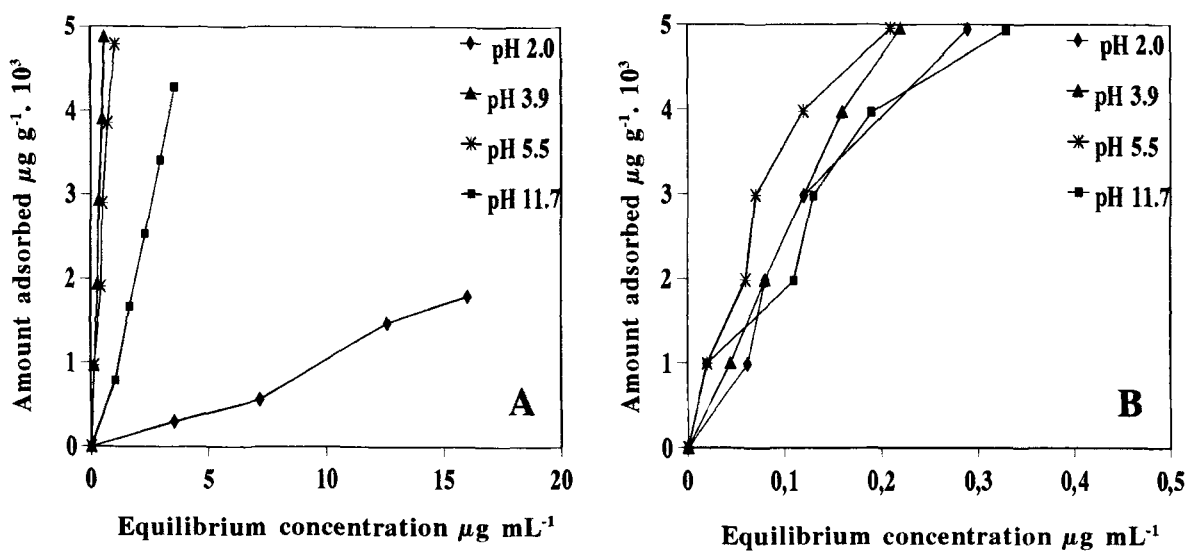


Figure 2. Adsorption isotherms of glyphosate on HT (A) and on HT500 (B) at different pH values.

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Table 1. Freundlich constants (K) and distribution coefficients (Kd) for the adsorption of glyphosate by HT and HT500 at different pH values.

Sorbent	pH		Adsorption constant		
	Initial	Final	K	n	Kd[1]
HT	2.0	5.0	55.54	0.80	36.82
	3.9	7.2	9603	0.79	6252
	5.5	7.2	4724	1.09	5372
	11.5	11.5	762.1	0.72	408.8
HT500	2.0	7.5	17,822	1.06	19,428
	3.9	8.4	23,242	0.99	22,820
	5.5	9.5	19,997	1.22	26,558
	11.5	12.0	10,106	1.54	17,801

[1] Equilibrium concentration Ce = 0.2 μg mL^{-1}.

ues of 2, 3.9, 5.5, and 11.5. In general, the isotherms are C type and sometimes L type, based on Giles *et al.* (1960). Each isotherm is in accord with the Freundlich adsorption equation with r values >0.93. The values of the K and n constants of this equation are given in Table 1. The n values indicate the dependence of adsorption on the concentration of the solution, and the K constant indicates the amount of herbicide adsorbed for an equilibrium concentration equal to unity. The K value was determined by extrapolation when adsorption was very strong, and required a distribution coefficient (Kd) to be determined for an equilibrium concentration of 0.2 μg mL^{-1}. The Kd value and the K value were used to compare the capacity of HT and HT500 to adsorb glyphosate and to study the effect of pH on adsorption.

Figure 3 shows the amount of glyphosate adsorbed by HT and by HT500 and the pH as a function of time, starting from pH values of 3.9 and 5.5. The adsorption of glyphosate by HT is nearly total at both initial pH values whereas the herbicide adsorption by

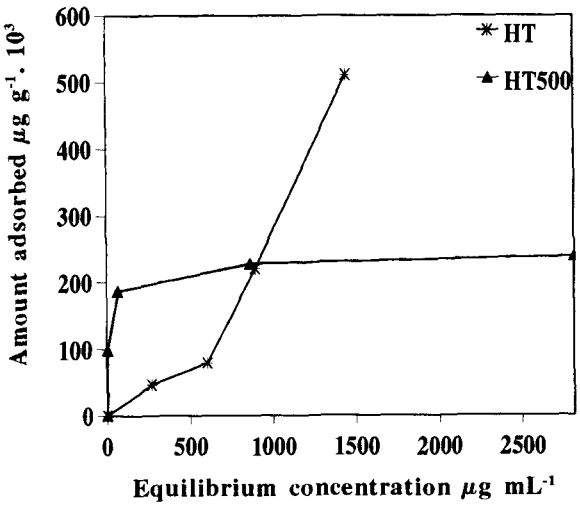


Figure 4. Adsorption isotherms of glyphosate on HT and on HT500 at high concentrations of herbicide.

HT500 is 91% (initial pH value 3.9) and 82% (initial pH value 5.5) of the total amount adsorbed. Because the HT suspension reached a steady state in pH prior to the addition of glyphosate and because nearly all adsorption occurred early in the experiment at near the initial pH, the later increase in pH during the experiment is related to the high buffering capacity of hydrotalcites. Thus, the pH could not be kept constant during the adsorption experiments.

To determine if intercalation of glyphosate occurs, samples of HT and HT500 treated with glyphosate were studied by XRD. Intercalation of organic molecules into HT is generally accompanied by an increase in *d*(001)-value (Kopka *et al.*, 1988; Hermosin *et al.*, 1996). Samples of HT and HT500 with large amounts of adsorbed herbicide are required. Figure 4 show the

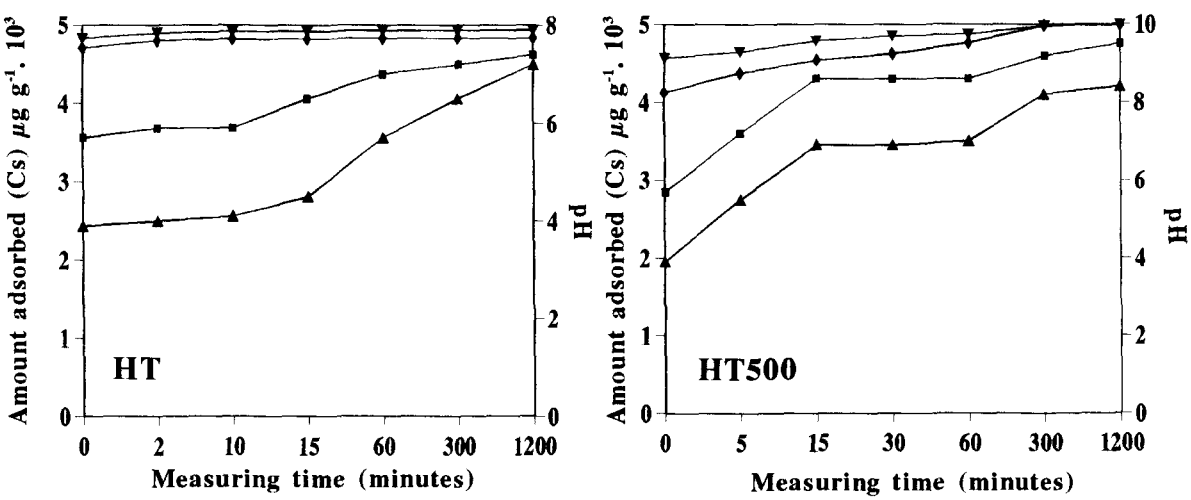


Figure 3. Evolution of the glyphosate amount adsorbed and of pH as a function of time for HT and HT500. (▼) Cs and (▲) pH at pH initial = 3.9; (♦) Cs and (■) pH at pH initial = 5.5.

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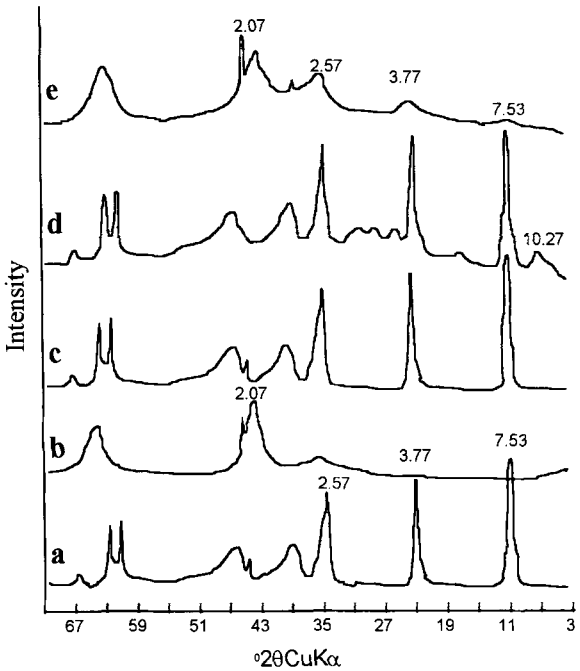


Figure 5. XRD patterns of a) original HT, b) HT500, c) HT500 treated with water and samples of d) HT and e) HT500 treated with solution of glyphosate. The numbers above the peaks correspond to $d(00l)$-values in Å.

adsorption isotherms of glyphosate by HT and HT500 determined using concentrations of herbicide to an amount four-fold greater than necessary to saturate the AEC. The HT isotherm thus obtained is in accord with the Freundlich equation whereas the HT500 isotherm is consistent with the Langmuir equation. In the studied concentration range, saturation for HT was not achieved, whereas saturation was nearly complete for HT500. Nonetheless, in both cases, adsorption was greater than the AEC of the samples. HT with glyphosate adsorbed in amounts greater than the AEC were used for the XRD study.

Figure 5 shows XRD patterns of original HT, HT500, HT500 treated with water, and samples of HT and HT500 treated with solution of glyphosate.

To determine the interaction mechanism involving ligand exchange in the adsorption of glyphosate by HT, the IR spectra of undissociated glyphosate, HT, and HT500 (Figure 6), and the IR spectra of glyphosate, HT-glyphosate, and HT500-glyphosate at pH values of 3.5 (Figure 7), 5.6, and 11.0 were obtained. The spectra showed that the bands attributed to the C=O group of the carboxylate and those of the P-OH and P-O$^-$ groups of the phosphonate in the adsorbed glyphosate were different from those of free glyphosate, whereas the other bands remained unaffected. Table 2 shows the frequencies of these bands in free and adsorbed glyphosate at different pH values.

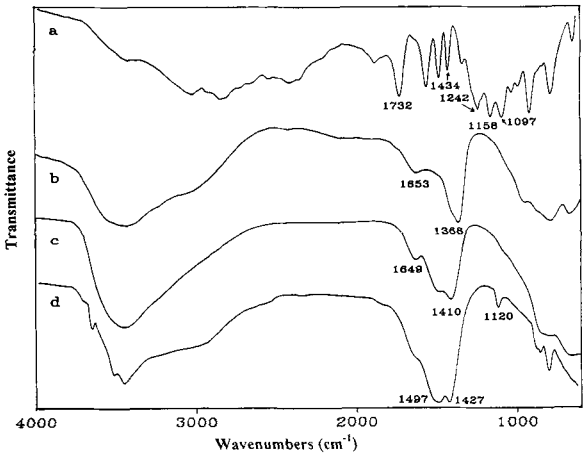


Figure 6. IR spectra of a) undissociated glyphosate, b) original HT, c) HT500, d) magnesium oxide.

In the non-dissociated glyphosate, the C=O bands occur at 1732 and 1434 cm^{-1} (Figure 6, trace a) and in dissociated glyphosate these bands occur at 1634 and 1406 cm^{-1}, suggesting the formation of carboxylate anion. The P-OH and P-O$^-$ bands always occur at 1171 and 1084 cm^{-1}, except in glyphosate at pH 11, in which the glyphosate molecules are dissociated and only the band at 1084 cm^{-1} occurs (Table 2).

In glyphosate adsorbed by HT at pH values of 3.5 and 5.6, the bands attributed to the C=O group are the same as the bands from free glyphosate whereas the bands of the P-OH and P-O$^-$ groups are shifted 27 and 69 cm^{-1} to lower frequencies relative to glyphosate (Figure 7). In the glyphosate adsorbed by HT500 at the same pH values, the C=O bands are shifted 20 and 8 cm^{-1} (pH 3.5) and 34 and 10 cm^{-1} (pH 5.6) to lower frequencies relative to glyphosate. The P-OH and P-O$^-$ bands are also shifted to lower frequencies

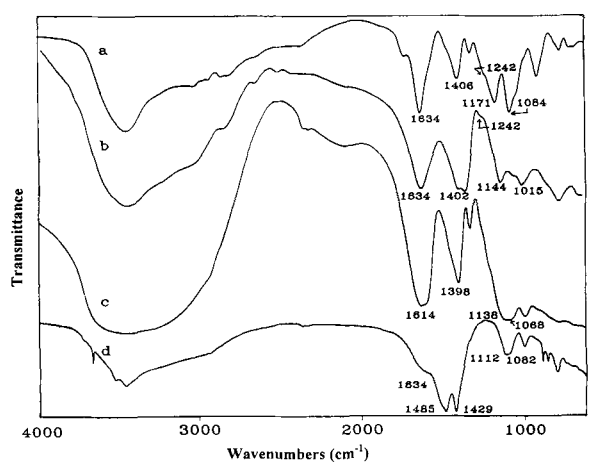


Figure 7. IR spectra of (a) glyphosate at pH 3.5 and of samples of (b) HT, (c) HT500, and (d) magnesium oxide treated with glyphosate at pH 3.5.

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Table 2. IR frequencies (cm^{-1}) of the C=O, P-OH, and $P-O^-$ groups of free glyphosate and of glyphosate adsorbed by HT samples at different pH values.

	Glyphosate			HT-glyphosate			HT500-glyphosate		
pH	νC=O	νP-OH	$\nu P-O^-$	νC=O	νP-OH	$\nu P-O^-$	νC=O	νP-OH	$\nu P-O^-$
3.5	1634 1406	1171	1084	1634 1402	1144	1015	1614 1398	1138–1068[1]	—
5.6	1634 1406	1171	1084	1634 1403	1114	1015	1600 1396	1135–1066[1]	—
11.0	1634 1406	—	1084	1634 1402	—	1087	1610 1370	—	1087

[1] Broad band.

relative to glyphosate and broad bands occur at 1138–1068 cm^{-1} (pH 3.5) and 1135–1066 cm^{-1} (pH 5.6). In the glyphosate adsorbed by HT at pH 11.0, neither the C=O nor the $P-O^-$ bands are affected by adsorption, whereas the former is affected in the glyphosate adsorbed by HT500.

To help in the interpretation of the results, and in view of the chemical composition of HT, it was considered appropriate to study the adsorption of glyphosate by Mg oxide and Al oxide. Figure 8 shows adsorption isotherm of glyphosate by aluminum and magnesium oxides at pH 3.5. The Freundlich K constants obtained from the adsorption isotherms of the herbicide by both oxides were 3724 for MgO and 1129 for Al_2O_3. These results suggest a greater affinity of glyphosate for the Mg ion.

In the IR spectrum of glyphosate adsorbed by Mg oxide (pH 3.5), a shift of the P-OH group band to lower frequencies relative to glyphosate was observed (Figure 6, trace d and Figure 7, trace d); this was similar to the shift observed in the spectrum of the HT500-glyphosate sample relative to glyphosate. The interaction of glyphosate with Al_2O_3 using IR could not be studied because the bands relating to C=O, P-OH, and $P-O^-$ groups are masked by a very broad and intense band.

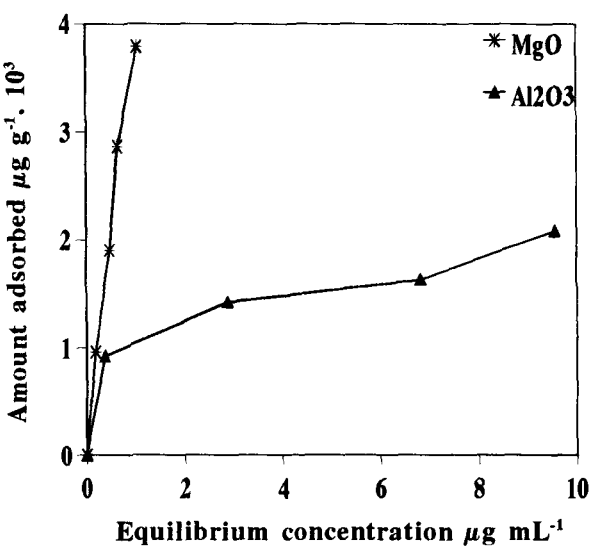


Figure 8. Adsorption isotherm of glyphosate on aluminum and magnesium oxides at pH 3.5.

DISCUSSION

Based on the K and Kd values (Table 1), HT500 has a greater capacity to adsorb glyphosate than HT. In both cases, the lowest K value was obtained for initial pH values of 2 and 11.5 of the glyphosate solution, where the molecule is positively charged or is trivalent negatively charged. The strongest adsorption of glyphosate corresponded to the pH values where the molecule has a net negative charge of one or two. These K values are higher than those of Glass (1987) for the adsorption of glyphosate by clay minerals and those of McConnell and Hossner (1985) for the adsorption of the herbicide by iron and aluminum oxides.

Because of the anionic nature of the molecule of glyphosate and its strong adsorption by hydrotalcite, the molecule may be intercalated into the interlayer of HT through anionic exchange with the CO_3^{2-} anion or by recrystallization of the HT500 in the HT500-glyphosate-water system. These types of intercalation of organic anions were observed by XRD for adsorption of chlorophenols and nitrophenols in anionic form (Hermosin *et al.*, 1993; Ulibarri *et al.*, 1995), in the adsorption of dodecylbenzene sulphonate (Pavlovic *et al.*, 1997), and in the adsorption of benzene-carboxylic acids (Sato and Okuwaki, 1991). However, replacement of the inorganic anion by the organic anion was always incomplete owing to the high bond strength holding CO_3^{2-} within the structure. Additionally, in the adsorption of mono- to pentacarboxylic acids by HT, Sato and Okuwaki (1991) observed that the amount of benzene-carboxylate ions incorporated in the interlayer of hydrotalcite and the selectivity of anion adsorption increased with increasing charge density of the ions.

The XRD pattern of HT showed intense *d*(00*l*) peaks at 7.53, 3.77, and 2.57 Å (Figure 5, trace a). The XRD pattern of HT saturated with glyphosate is similar to that of HT, although a small peak occurs

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also at 10.27 Å (Figure 5, trace d). This latter peak probably corresponds to a small amount of intercalated glyphosate. The thickness of the brucite-like layer is 4.8 Å (Clearfield *et al.,* 1991), the thickness of the remaining interlayer occupied by the intercalated-glyphosate molecules is 5.47 Å. This interlayer is 1.17 Å larger than the size of the molecule (4.3 Å), based on scale models of the molecule. This difference is probably related to the electrostatic attraction of the PO_3^{2-} and COO^- groups exerted by each of the positively-charged brucite-like layers, which required a tilted arrangement of the molecule, as is common with other intercalated-organic anions in HT (Clearfield *et al.,* 1991; Kopka *et al.,* 1988).

The amount of exchange of CO_3^{2-} ions by the glyphosate anion in HT was low and did not correspond to pesticide adsorption greater than the AEC. The XRD pattern of HT500 saturated with glyphosate was similar to that of HT500, but a broad peak at 7.53 Å may indicate slight recrystallization of the original HT (Figure 5, trace e). Thus, recrystallization of hydrotalcite with glyphosate anions in the interlayer does not occur significantly. Furthermore, the mechanism of adsorption of glyphosate by HT500 appears to impede recrystallization of HT that normally occurs spontaneously in aqueous media, since CO_3^{2-} is always present in water and becomes intercalated (Figure 5, trace c).

Therefore, the glyphosate anion is adsorbed onto the external surface of HT and HT500, and two types of interactions are possible. One interaction may occur through electrostatic attraction between the surface of HT, which is positively charged below pH 12, and the glyphosate in anionic form above pH 2. The alternative interaction may occur via ligand exchange through specific functional groups of the glyphosate and the Mg and/or Al atoms of the surface of HT. In fact, glyphosate has two functional groups, carboxylate and phosphonate; these groups may become strongly coordinated to oxides, hydroxides, and metal ions (McBride and Kung, 1989; Subramanian and Hoggard, 1988). The occurrence of either one or both interactions depends on the pH of the system.

The results of the IR study indicate that the adsorption of glyphosate onto the external surface of the HT and HT500 occurs through ligand exchange between Mg and/or Al ions and the P-OH and C=O groups of the glyphosate. In HT500 at pH 3.5 and 5.6, there is a simultaneous interaction of the C=O and P-OH groups with the metal ions, probably forming chelates or bidentate complexes. The IR study of glyphosate adsorption by Mg oxide also shows that a similar interaction mechanism of ligand exchange is involved in the adsorption.

The interaction mechanism of ligand exchange proposed for the adsorption of the glyphosate anion by HT and HT500 was proposed previously from spectroscopic studies in glyphosate adsorption by iron and aluminum oxides and hydroxides (McConnell and Hossner, 1985; McBride and Kung, 1989), and by copper oxide (Glass, 1984), and in the formation of complexes of this herbicide with divalent and trivalent cations, including Mg and Al (Motekaitis and Martell, 1985; Subramaniam and Hoggard, 1988). The ligand exchange mechanism between glyphosate and iron and aluminum oxides of soil is believed responsible for the immobility and inactivation of this herbicide in soils (Sprankle *et al.,* 1975; McConnell and Hossner, 1985).

Alternatively, interaction through ligand exchange was proposed from spectroscopic studies in the adsorption of inorganic phosphates and carboxylic acids by iron and aluminum oxides and hydroxides in the soil (Bolt, 1976; Evanco and Dzombak, 1998), and in the adsorption of the anionic herbicide 2,4-D by goethite (Watson *et al.,* 1973). However, despite that, 2,4-D is largely adsorbed by HT and the molecules of herbicide do not appear to become intercalated, Hermosin *et al.* (1992) do not consider ligand exchange as a possible interaction mechanism.

The two types of interaction proposed and the variation in the charge of HT and of glyphosate as a function of pH of the solution explain the variations in the values of the K constant (Table 1). For HT and HT500, the K values are higher in adsorption at pH 3.9 and 5.5, where more favorable conditions prevail for electrostatic attraction. Also more favorable conditions occur where the molecule has net negative charges of 1 or 2. Moreover, K values are higher at pH 3.9 and 5.5 owing to ligand exchange through the partially dissociated phosphonate group at these pH values. At pH 2, adsorption is lower. At this pH, the surface of the HT and the molecules of glyphosate are positively charged, producing an electrostatic repulsion hindering the ligand-exchange interaction. At pH 11, there is a strong electrostatic attraction between the molecules of glyphosate with a net trivalent negative charge and the surface of HT, which continues to be electrostatically positive at that pH. However, there is no ligand exchange interaction by the phosphonate group because it has become dissociated (absence of the P-OH group). However, this type of interaction could exist via the C=O group of the COO^-.

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