ADSORPTION OF TWO QUINOLINECARBOXYLIC ACID HERBICIDES ON HOMOIONIC MONTMORILLONITES

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Abstract—The adsorption of the herbicides quinmerac 7-chloro-3-methylquinoline-8-carboxylic acid (QMe) and quinclorac 3,7-dichloroquinoline-8-carboxylic acid (QCl) on homoionic Fe^{3+}-, Al^{3+}-, Cu^{2+}-, Ca^{2+}-, K^+- and Na^+-exchanged montmorillonite was studied in aqueous solution. Adsorption data were fitted to the logarithmic form of the Freundlich equation. Ca- and Na-exchanged montmorillonites were ineffective in the adsorption of QMe. On the other hand, the QMe adsorption on Fe-exchanged montmorillonite was rapid and the equilibrium was attained after 15 min. An H-type isotherm was observed for the QMe adsorption on Fe-clay, indicating a high affinity of the solute for the sorption sites and almost complete adsorption from dilute solution. On the other hand, the adsorption isotherm of QMe on Al- and K-clay was of the S-type. This shape suggests that the solvent molecules may compete for the sorption sites. A Fourier transform infrared (FTIR) study suggested that the adsorption mechanism of QMe on Fe-, Al- and K-clay involves the protonation of QMe molecule due to the acidic water surrounding the saturating cations. The greater acidity of Fe-clay compared with Al- and K-clay explains both the lower QMe adsorption observed on Al and K systems and the lack of adsorption on Na and Ca systems. In contrast, the formation of a Cu complex permitted QMe to be adsorbed to a large extent to Cu-clay as shown by FTIR analysis. The QCl was adsorbed only by Fe-clay and the adsorption isotherm of QCl on Fe clay was of the S-type. This finding is consistent with the lower basic character of the QCl molecule nitrogen. In fact, the replacement of the electron-releasing methyl group in QMe with an electron-withdrawing Cl atom to form QCl makes the nitrogen lone-pair electrons of the quinoline ring unavailable for either protonation or complexation.

Key Words—Adsorption, Herbicides, Infrared Spectroscopy, Montmorillonite, Quinclorac, Quinmerac.

INTRODUCTION

Substituted quinolinecarboxylic acids are a class of highly selective herbicides of which quinmerac and quinclorac are two representative compounds. Quinmerac effectively controls important dicotyledonous weeds in sugar beet, oilseed rape and wheat (Grossmann and Scheltrup, 1997). Quinclorac is principally used in rice crops (Grossmann, 1998). Both are auxin-type herbicides and cause the inhibition of shoot growth accompanied by chlorosis and necrosis (Chism *et al.*, 1991; Grossmann and Scheltrup, 1997; Sunohara and Masumoto, 1977; Grossmann and Scheltrup, 1995). Generally, investigations of the behavior of herbicides in soils and plants have shown that the adsorption processes by soil are of great importance. Several studies have stressed the role of organic matter in the adsorption and inactivation of xenobiotics whereas little attention has been given to inorganic soil colloids. Soil organic matter was found to be the major factor determining QMe adsorption in soil (Deschauer and Kögel-Knabner, 1990). However, the influence of clay minerals and

hydrous oxides could not be taken into account because of the small amounts of these components in the soils investigated. A study showed that the adsorption capacity of iron oxides for QMe increases with decreasing degree of crystallinity (Schwandt *et al.*, 1992). A recent paper confirms that the adsorption of quinmerac onto an iron oxide-rich soil with variable charge is strongly influenced by mineralogy, particularly by iron and aluminum oxides (Vasudevan *et al.*, 2002).

On the other hand, there is little information in the literature concerning the behavior of QCl in soil. Laboratory tests indicate that QCl is persistent in soil (Mabury and Crosby, 1996). In a controlled-moisture lysimeter study, the amount of QCl remaining in the soil varied with soil moisture. Under dry conditions, ~80% of QCl applied remained 1 y after application (Hill *et al.*, 1998). The activity of clay minerals in adsorbing pesticides was widely emphasized in several reviews (Mortland, 1986; Ortego *et al.*, 1991; Kowalska *et al.*, 1994). The contribution of clay to the adsorption of pesticides in soil is particularly important when the soil organic carbon content is small relative to the clay content (Cox *et al.*, 1995).

In this paper, we investigated the adsorption of QMe and QCl from water on a montmorillonite saturated with

different exchange cations. This research was aimed at evaluating the effectiveness of clay minerals and the dependence on the exchangeable cations in removing these herbicides from soil waters. Additionally, a spectroscopic study was carried out to elucidate the mechanisms acting in the retention of QMe and QCl by clays.

MATERIALS AND METHODS

Chemicals and clays

The QMe and QCl (purity 99.4 and 99.8%, respectively) were obtained from BASF AG, Milan, Italy. The purity was checked by high-performance liquid chromatography (HPLC). The structures of QMe and QCl are given in Figure 1. According to the literature (Worthing and Hance, 1991), the solubility in water is 22 and 0.065 mg kg^{-1} for QMe and QCl, respectively. Our experimentally determined values for QMe and QCl solubility were 216 and 49 mg L^{-1}, respectively. The structures of quinmerac and quinclorac are given in Figure 1.

The QMe hydrochloride (QMeHCl) was prepared by bubbling anhydrous HCl into a chloroform solution of QMe. The precipitate was filtered and dried under vacuum. All solvents were of HPLC grade (Carlo Erba Reagenti, Milan, Italy) and were used without further purification.

The Cu^{2+} complex of QMe was prepared by mixing equimolecular aqueous solutions of QMe (1.5×10^{-3} mol) in ~5 mL (pH 6.2) and CuCl$_2$.2H$_2$O (1.5×10^{-3} mol) in ~2 mL. The precipitate was filtered and washed with ethanol (99.5%). After recrystallization from absolute ethanol + chloroform (2 + 1 v/v), the compound was air dried.

Montmorillonite no. 26 (bentonite) from Crook County, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, New York, was used. The <2 µm fraction was obtained by sedimentation. The cation exchange capacity (CEC) of the Na-form, determined by the method of Hendershot and Duquette (1986), was 0.902 eq kg^{-1}. Al^{3+}-, Fe^{3+}-, Cu^{2+}-, Ca^{2+}-, K$^+$- and Na$^+$-exchanged samples were prepared by repeated treatments of the clay with 1 N solutions of the respective metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until free of Cl$^-$, and dried at room temperature.

Adsorption

Batch adsorption isotherms on different cation-saturated montmorillonites were determined at 25±2ºC. Triplicate 50 mg samples of air-dried clay were equilibrated in polyallomer centrifuge tubes with 5 mL of aqueous herbicide solution. The herbicide concentration ranges, 20–970 µM for QMe and 20–237 µM for QCl, were chosen on the basis of solubility. The tubes were stirred using Teflon-coated magnetic stir bars for 14 h. Generally, 95% of adsorption occurred within 15 min on Fe^{3+}-montmorillonite. No adsorption was observed on Ca^{2+}- or Na$^+$-montmorillonite even after 20 d.

The suspension was centrifuged (15,000 g, 15 min) after 14 h, and the supernatant liquid was pipetted off and analyzed immediately by HPLC. The amount adsorbed by montmorillonite was calculated from the difference between the initial and final concentrations of herbicide in solution. The adsorption studies of QMe on Al- and K-clay and of QCl on Cu-montmorillonite were also performed from an organic (CHCl$_3$) solution of herbicide, as described below. After centrifugation, all the adsorption suspensions were tested for metal ions by spectrophotometric methods. No metal release was observed in any case. All the experiments were performed in triplicate.

HPLC analyses

The HPLC analyses were carried out using a Perkin Elmer LC 250 instrument equipped with a µBondapaK C$_{18}$ analytical column (10 µm, 3.9 × 150 mm). A Perkin Elmer LC 130 diode array detector tuned to 240 nm (band width 5 nm) and Perkin Elmer Omega 2 chromatography software were used. Acetonitrile plus water eluant (pH 3) was used at a flow rate of 1 mL min^{-1} using 25% and 35% by volume acetonitrile concentrations, respectively, for the QMe and QCl determinations. Under these analytical conditions, the retention times of QMe and QCl were 3.8 and 4.2 min, respectively. The quantification of QMe and QCl was based on external standards. Calculations were based on the average peak areas of the external standards.

Infrared analysis

The FTIR spectra were recorded using a FTIR Nicolet 205 spectrophotometer over the range 4000–600 cm^{-1}. Spectra of QMe, QCl, QMeHCl and the QMe-Cu complex were obtained on KBr disks.
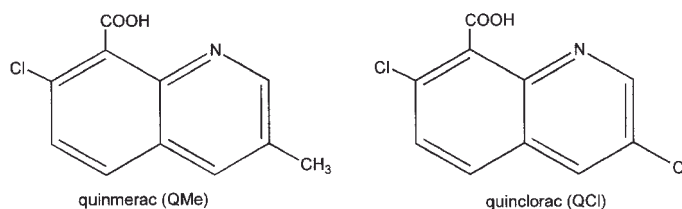

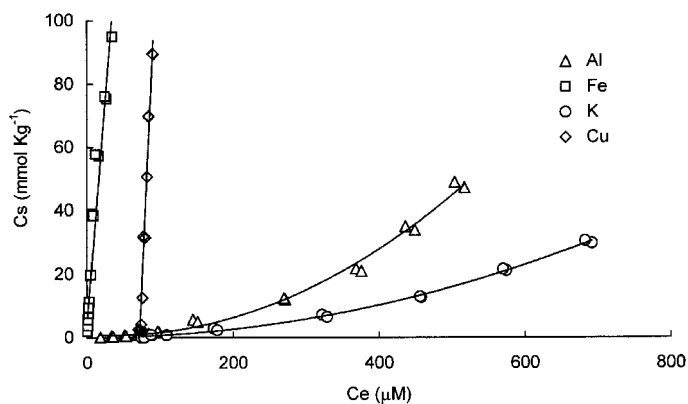Figure 1. Structures of quinmerac (QMe) and quinclorac (QCl).

Figure 2. Adsorption isotherms of QMe on montmorillonite.

Samples (self-supporting films) suitable for the IR analysis of QMe adsorbed on Al^{3+}-, Fe^{3+}-, Cu^{2+}-exchanged montmorillonite were obtained by contacting 50 mg of clay with 5 mL of a 970 μM solution of QMe with stirring for 14 h. After separating the solution, the clay fraction was washed with distilled water, centrifuged, and then re-suspended into distilled water. The slurry was evaporated on a polyethylene sheet at room temperature. Because of the low adsorption level of QMe on Al- and K-clay and of QCl on Cu-montmorillonite from water solution, the study in these cases was carried out from $CHCl_3$ solutions of herbicides. Samples for the latter spectra were prepared by evaporating 5 mL of aqueous clay suspension (1% w/v) on a polyethylene sheet at room temperature. The air-dried films were divided into two portions. One was placed in a 2% herbicide $CHCl_3$ solution for 14 h, then removed and rinsed several times with pure solvent, and finally air dried. The remaining portion was treated, in a similar way, with pure solvent. The IR spectra were recorded immediately after air drying. Differential spectra were obtained for herbicide-montmorillonite complexes by subtracting the spectra of the corresponding blank clay film from those of the clay-organic complexes. Only IR absorptions between 2000 and 1200 cm^{-1} are discussed here because this region is the most appropriate for providing evidence for adsorption mechanisms in clays. Each adsorption experiment was run in duplicate and repeated three times. All the spectra were the mean of at least 64 scans at 4 cm^{-1} resolution and these conditions were sufficient to produce a good signal to noise ratio.

Data analysis

Data were fitted to the logarithmic form of the Freundlich equation, $\log C_s = \log K_f + 1/n \log C_e$, where C_s (in units of mmol Kg^{-1}) is the amount of herbicide adsorbed by clay, C_e (in μM units) is the equilibrium concentration in solution, and $\log K_f$ and $1/n$ are empirical constants representing the intercept and the slope of the isotherm, respectively. Fitting was per-

formed by a least-squares regression analysis program using the Stat View 512 statistical package (Brain Power, Inc., Calabasas, California, USA).

RESULTS

Adsorption from water

The adsorption of QMe on Fe-montmorillonite was rapid and the equilibrium was attained after 15 min. In contrast, Ca- and Na-montmorillonites were unable to adsorb QMe. The adsorption isotherm of QMe on Fe-exchanged clay is shown in Figure 2. The isotherm is of the H-type according to the classification of Giles *et al.* (1960); this shape is characterized by a high affinity of the solute for the adsorbent.

In the presence of Al- and K-montmorillonite, the isotherms are of the S-type, Figure 2. This curve indicates that the adsorption becomes increasingly favored as concentration increases (Giles *et al.,* 1960). This result is usually attributed to strong competition with the solvent molecules for substrate sites. An unusual trend is shown by the adsorption isotherm of QMe on the Cu-montmorillonite. At low equilibrium concentrations, QMe did not show detectable affinity for the Cu-exchanged clay. On the contrary, above a C_e of
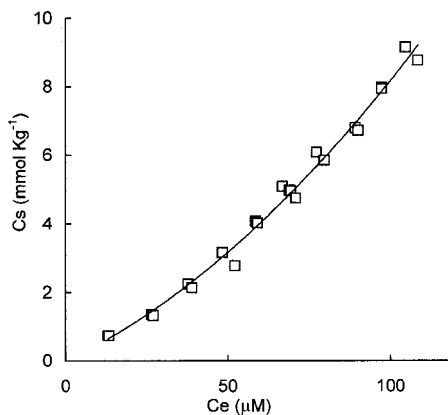

Figure 3. Adsorption isotherms of QCl on Fe-montmorillonite.

~70 μM, the affinity of QMe for the clay became so strong that the herbicide was completely removed from solution. These findings cannot be explained by a single adsorption process. Finally, QCl was adsorbed only by Fe-clay, but in this case the adsorption isotherm of QCl on Fe-clay was of the S-type (Figure 3). The empirical Freundlich relationship was used to evaluate the adsorption data ($r \geqslant 0.99$), except for adsorption of QMe on Cu-montmorillonite ($r = 0.75$). Therefore, in this case, the Freundlich equation was not used. The values of K_f and $1/n$ are given in Table 1. The Fe-clay is more effective in promoting both QMe and QCl adsorption. The results suggest that the exchangeable cation affects the adsorption extent of both herbicides. Evidence for the mechanisms acting in the adsorption of QMe and QCl were obtained by FTIR.

Infrared analyses

The FTIR spectra of QMe, in the free, protonated, and Fe-clay complex form, are compared in Figure 4. The spectra indicate that the herbicide undergoes significant changes upon interacting with montmorillonite surfaces. QMe exhibits an absorption at 1721 cm^{-1} owing to the stretching mode of the carbonyl group. The FTIR spectra of QMe Fe-montmorillonite complex show a weak absorption for the carbonyl group at 1747 cm^{-1}. The displacement to higher wavenumbers suggests an increase in the double-bond character of the C=O group, probably due to the loss of intermolecular hydrogen bonding of the dimeric form of the QMe in the solid state. Further distinguishing features of the QMe Fe-montmorillonite complex are additional absorptions centered at 1537 and 1642 cm^{-1}, respectively, with the latter value typical of the protonated aromatic heterocyclic nitrogen (Cook, 1961; Pouchert, 1975). The above results seem consistent with the QMe form protonated at the quinoline moiety. The spectrum of QMe hydrochloride (Figure 4, trace b) shows bands similar to those observed for the QMe Fe-montmorillonite complex, *e.g.* the absorptions at 1537 and 1642 cm^{-1} of the clay complex are present in the spectrum of protonated QMe centered at 1537 and 1638 cm^{-1}, respectively. The proton sources are probably the acidic water molecules surrounding the saturating Fe ions.

The IR spectrum of the QMe Cu-clay complex was different from the spectrum of QMe in the Fe-clay adsorbed form (Figure 5). No absorption attributable to

un-ionized carboxyl groups was observed in the spectrum of the QMe Cu clay complex (Figure 5, trace b). Bands assignable to the $\nu_{as}(COO)$ and $\nu_{sym}(COO)$ modes of carboxylate groups, the former less intense, appear at 1616 and 1404 cm^{-1}, respectively. Furthermore, the appearance of a strong absorption band at 1540 cm^{-1} suggests that the complexation process may also involve the N atom of the quinoline ring. This binding mode
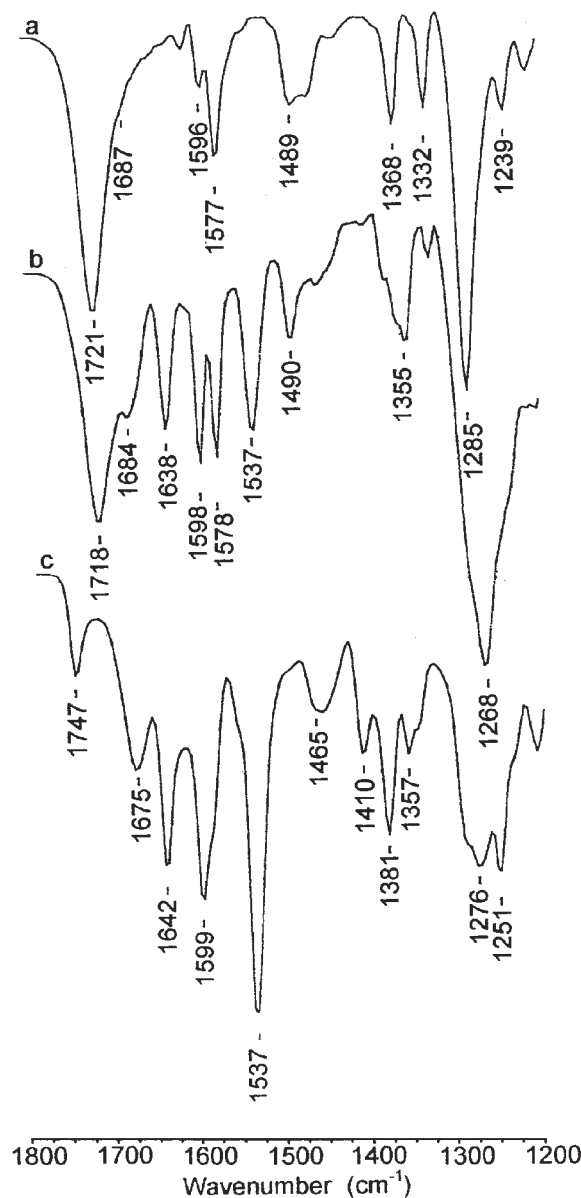

Figure 4. FTIR spectra of: (a) QMe ν (cm^{-1}): 1721 (stretching vibration of carboxylic group); (b) QMe hydrochloride ν (cm^{-1}): 1718 (stretching vibration of carboxylic group), 1638 and 1537 (bending vibrations of protonated quinoline nitrogen); (c) Fe-montmorillonite treated with aqueous solution of QMe ν (cm^{-1}): 1747 (stretching vibration of carboxylic group), 1642 and 1537 (bending vibrations of protonated quinoline nitrogen).

Table 1. Freundlich parameters for the adsorption of QMe and QCl on *M*-exchanged montmorillonite.

Herbicide	M	pHs[a]	K_f	$1/n$	r
QMe	Fe^{3+}	3.9	4536	0.91	0.99
QCl	Fe^{3+}	3.9	26.6	1.23	0.99
QMe	Al^{3+}	4.6	0.80	1.73	0.99
QMe	K^+	6.7	0.24	1.78	0.99

[a] pH of aqueous clay suspension

could afford a 6-membered ring chelation of Cu through the assistance of the N from the quinoline ring and an O from the carboxylic group, respectively, of the QMe molecule. The IR spectrum of the QMe Cu complex is shown in Figure 5a. Despite the similarity of the two spectra, the IR bands of the QMe in the Cu-clay complex are somewhat different from those of the pure complex in the solid state. These changes are expected because of interlayer water molecules and the difference in structure relative to the solid state that is typical for interlayer metal complexes (Pusino *et al.*, 1989; Strinna Erre *et al.*, 1997).

A structural study of the QMe Cu complex formed in the clay interlayer is beyond the scope of this work. However, the findings agree with the particular shape of the adsorption curve. At low QMe concentrations, the lack of QMe adsorption to the Cu-saturated clay reflects the lower polarizing power of Cu compared to Fe and Al (Figure 2). When the QMe concentration is increased, formation of a Cu-QMe complex permits greater QMe adsorption.
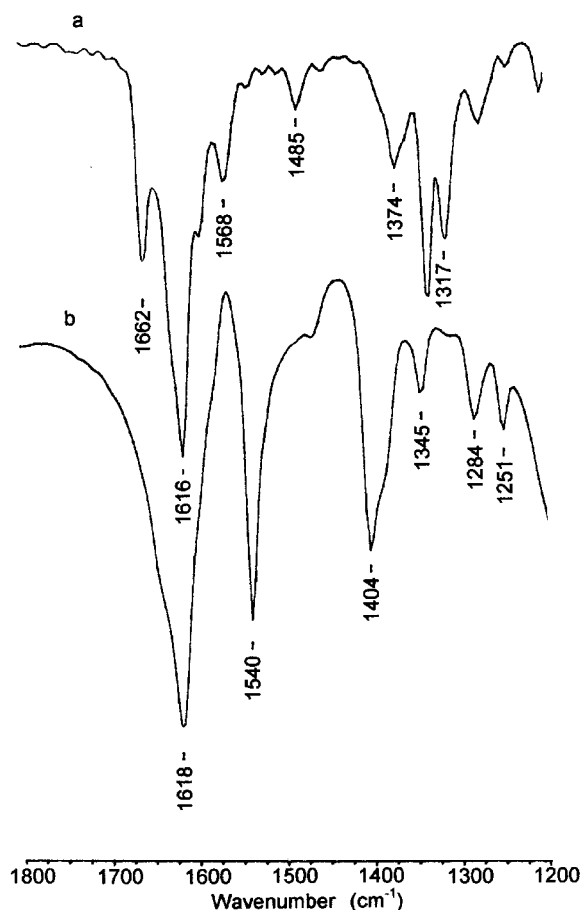
Because of the rather low adsorption levels from a QMe water solution on Al- and K-montmorillonite, no evidence on the adsorption mechanism can be obtained from FTIR spectra. Therefore, the adsorption of QMe on K- and Al-clays was studied from $CHCl_3$. The FTIR spectra of Al- and K-herbicide montmorillonite complexes, obtained from organic solution, were very similar to each other and to that of the QMe Fe-montmorillonite complex. The organic medium increases the acidity of the residual H_2O molecules surrounding the interlayer cations, which may contribute to greater retention of QMe by a protonation mechanism.

Figure 6 shows the FTIR spectra of QCl and the Fe-clay complex from the water solution (traces a and b, respectively). The absorption bands centered at 1522 and 1632 cm^{-1} suggest that herbicide protonation is still the mechanism acting in the retention of QCl on Fe-clay, but this interaction is weaker than for QMe. In fact, the replacement of methyl, an electron-releasing group, with chlorine, an electron-withdrawing atom, in the quinoline ring of the QCl molecule makes the electron lone pair of
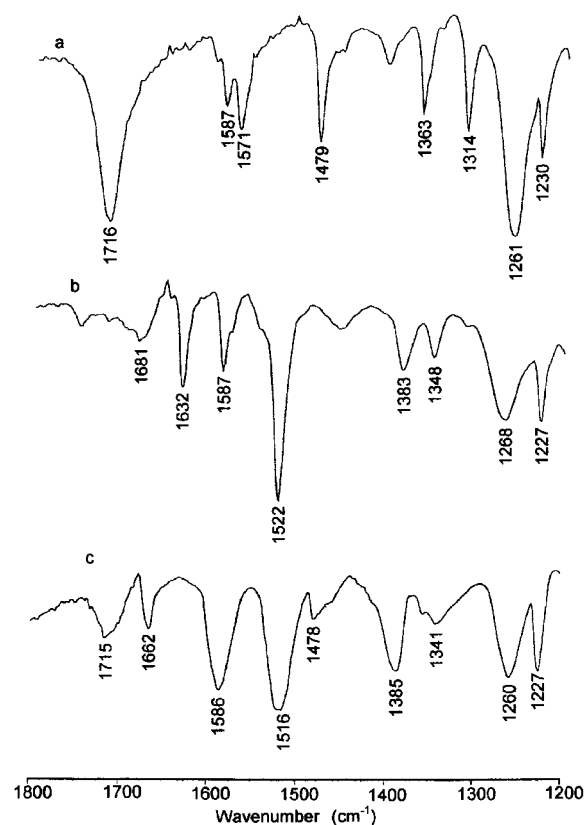

Figure 5. FTIR spectra of: (a) QMe-Cu complex ν (cm^{-1}): 1616 and 1374 (asymmetric and symmetric stretching vibrations of carboxylate group); (b) Cu-montmorillonite treated with aqueous solution of QMe ν (cm^{-1}): 1616 and 1404 (asymmetric and symmetric stretching vibrations of carboxylate group).

Figure 6. FTIR spectra of (a) QCl ν (cm^{-1}): 1716 (stretching vibration of carboxylic group); (b) Fe-montmorillonite treated with aqueous solution of QCl ν (cm^{-1}): 1632 and 1522 (bending vibrations of protonated quinoline nitrogen); (c) Cu-montmorillonite treated with a chloroform solution of QCl ν (cm^{-1}): 1715 (stretching vibration of carboxylic group), 1662 and 1516 (bending vibrations of protonated quinoline nitrogen).

N less prone to protonation. Only the Fe-clay effectively adsorbed QCl from a water solution. The adsorption of QCl to Cu clay was studied from $CHCl_3$ and the relative FTIR spectrum is shown in Figure 6c. In this case, no band attributable to complex formation was detected as in QMe on Cu-clay. In contrast, the appearance of absorption bands centered at 1516 and 1662 cm^{-1} are consistent with the QCl form protonated at the quinoline moiety. Therefore, the increased acidity of the residual interlayer water due to the presence of the organic solvent promoted a weak adsorption through a protonation mechanism, but the weak donor characteristic of the heterocyclic nitrogen of QCl does not permit the complexation of interlayer Cu ions.

DISCUSSION

The adsorption of both QMe and QCl was affected by the type of exchangeable cation on the clay. The results indicate that Ca- and Na-clays are ineffective in adsorbing QMe from water. The pK_a value of QMe is 4.3 (Worthing and Hance, 1991). The pK_a values calculated by QSAR (Hermens, 1989) showed that the QMe herbicide is a diprotic acid with the two protonation sites on the quinoline nitrogen and the carboxylate group. Both these groups are acidic with pK_a values of 5.2 and 2.9, respectively. Thus, depending on pH, QMe can exist in cationic, neutral and anionic forms. At the pHs of the Ca-, K- and Na-montmorillonite suspensions ($pHs_{Ca} = 6.5$; $pHs_K = 6.7$; $pHs_{Na} = 7.1$), the anionic form of the herbicide mostly prevails. This anionic species has a negligible but non-zero affinity for the negative surfaces of the clay. In fact, in the presence of a K-exchanged clay suspension, QMe was weakly adsorbed. However, interlayer water is known to be substantially more acidic than the bulk suspension. The greater effectiveness of K-exchanged clay for pesticide adsorption compared to Ca- and Na-clay has been observed several times (Haderlein and Schwarzenbach, 1993; Haderlein *et al.,* 1996) and attributed to the lower degree of hydration of K^+. This results in a smaller hydration sphere for K^+ so that a larger number of pesticide molecules can be accommodated in K-clay interlayer than in Ca- and Na-clay.

The adsorption of QMe on Fe-, Al- and K-montmorillonite water suspensions follows the Freundlich equation. At the pH value of the Fe-clay suspension ($pHs_{Fe} = 3.9$), QMe is mostly in zwitterionic form and shows a strong affinity for the clay. According to FTIR spectra, adsorption of QMe on Fe-clay involves protonation of the QMe molecule by acidic water surrounding the Fe^{3+} saturating cations to yield cationic QMe with the positive charge present on the quinoline ring nitrogen.

The greater acidity of the Fe-clay compared with the Al-clay ($pHs_{Al} = 4.6$) explains the greater degree of QMe adsorption due to the protonation of the herbicide

molecule. On the other hand, the formation of a chelate complex with the saturating ion permits QMe to be adsorbed to a significant extent onto Cu-clay. This feature is known for Cu ions, and may be ascribed to the greater tendency of this cation to form stable complexes with nitrogenous ligands (Pusino *et al.,* 1988; Duda *et al.,* 1996; Calamai *et al.,* 1997).

The QCl was adsorbed only on Fe-montmorillonite. The acidity constants for QCl are not available in the literature. In an aromatic heterocycle, the kind of substituent may affect the basicity of the ring heteroatom. An electron-withdrawing group in the ring makes the N atom less basic. For example, quinoline (pK_a = 4.90; Lide, 1992) is markedly more basic than 3-Brquinoline (pK_a = 2.09; Lide, 1992). Analogously, it is reasonable to assume that the QCl quinoline ring is less basic than that of QMe. Most likely, at the pHs values of clay suspensions (except for Fe-clay), QCl would exist predominantly in the anionic form, leading to a repulsion interaction with the negatively charged clay surfaces. Furthermore, the unavailable electron lone pair of the QCl molecule N limits adsorption even by complexation.

CONCLUSIONS

Adsorption of the herbicides, QMe and QCl, by clays depends on the herbicide ampholytic characteristics and the exchangeable cation of the clay. Due to the greater basicity of the quinoline ring, QMe is adsorbed on clays by at least two different mechanisms. In Fe-, Al- and K-clays the low pH is sufficient to protonate the quinoline nitrogens, therefore the QMe zwitterionic form of the herbicide exists in solution. The adsorption involves the transfer of a proton from the water surrounding the saturated ions to the carboxylate group of QMe. In the Cu-clay the formation of a metal complex with the herbicide permits the adsorption of QMe to a greater extent. On the other hand, the lower basicity of the QCl molecule, due to the presence of an electron-withdrawing chlorine atom in a QCl quinoline ring, makes the herbicide anionic even in the acidic clay suspensions. Therefore, the repulsion between negative charges hinders QCl adsorption. These data suggest that QCl could be more mobile in subsurface environments than QMe.

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