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Interaction of aminotriazole with montmorillonite and Mg-vermiculite at pH 4

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ABSTRACT: The interaction of aminotriazole (AMT) at pH 4 on Wyoming montmorillonite (mainly with Na ions) and Mg-vermiculite has been studied by X-ray diffraction and infrared spectroscopy. The AMT is adsorbed on montmorillonite in the cationic form by cation exchange. The amount of pesticide adsorbed was 71 mEq/100 g, which comprises ~91% of the CEC of this sample (78.2 mEq/100 g). Saturation was reached in 24 h, giving rise to a complex with basal spacing 12.5 Å. Vermiculite adsorbs 167 mEq/100 g, almost 20% greater than the CEC (141 mEq/100 g), and the basal spacing was stabilized at 13.68 Å after five weeks of treatment with AMT. A part of the AMT is adsorbed in cationic form, displacing a great part of the exchangeable Mg²⁺ cations. The rest is adsorbed in molecular form by coordination to the Mg²⁺ cations which remain in the interlamellar space, removing a great amount of water, and remaining in the interlamellar space of vermiculite after washing with water, probably because of a steric hindrance from the AMT cations adsorbed.

The transport and evolution of contaminants in the soil environment are governed by a series of processes taking place in the soil which depend mainly on the type of soil, pH, the nature of the soil colloids, moisture content and environmental factors (Sánchez-Camazano & Sánchez-Martín, 1990). The content and nature of the clay fraction is of special interest, mainly due to its high surface area and, for some clay minerals, their large cation exchange capacity (Khünel, 1992; Kowalska *et al.*, 1994). The physico-chemical properties of clays are particularly important in pesticide adsorption in soil. The reversibility of pesticide adsorption on clays is of fundamental importance, inasmuch as irreversible adsorption may produce permanent soil contamination as well as block a part of the soil CEC. For this reason, one aspect of clay-pesticide adsorption that should be considered is the mechanism by which the pesticide is held to the clay minerals (Dios-Cancela *et al.*, 1992).

The chemical properties of some pesticides change depending on the environmental conditions under which they are applied. The pesticide aminotriazole (3-amino-1,2,4-triazole), AMT, is used extensively as a non-selective herbicide which inhibits chlorophyll formation and regrowth from buds. Studies on the adsorption of AMT by montmorillonite at its solution pH, carried out by Russell *et al.* (1968) showed that the AMT molecule is protonated when adsorbed on montmorillonite surfaces to produce the aminotriazolium cation. On the other hand, Nearpass (1970) postulated that adsorption of AMT on montmorillonite was due to proton association and cation exchange, and no molecular adsorption occurred. However, Morillo *et al.* (1991) demonstrated that adsorption of AMT on montmorillonite under these conditions yields a pesticide-clay complex formed through interlamellar cations of montmorillonite which, in general, are not

displaced, AMT being situated mostly as a polarized molecule. So, because of the chemical characteristics of this pesticide, several interaction processes may occur, and for this reason, it was considered worthwhile to study the adsorption behaviour of AMT under acidic conditions, in which a part of the pesticide is in solution as a cation. Two clay minerals, montmorillonite and vermiculite, were chosen because of their high surface area and high CEC, in order to establish the possible differences in relation to interaction with AMT.

MATERIALS AND METHODS

Wyoming montmorillonite (SWy-1) and vermiculite from the Santa Olalla deposit (Huelva, SW Spain) were used. Both clay minerals were used as received, vermiculite having 99% of its CEC compensated by Mg^{2+} cations.

The pesticide AMT is a basic compound that is protonated in aqueous solutions depending on the pH. It occurs in two desmotropic forms (I and II); 3-amino-1,2,4-triazole is in the amino form (I), and its salts are in the imino form (II) (Fig.1).

The pK is 4.14 (Nearpass, 1970), so the pH of the aqueous solutions was held to 4 in order to obtain a part of the pesticide in its cationic form (III). The interaction of montmorillonite and vermiculite with AMT was carried out using 0.1 M pesticide aqueous solutions. Samples of 0.15 g were treated with 20 ml of AMT solutions at pH 4, in 50 ml polypropylene centrifuge tubes. The suspensions were shaken continuously at 25°C. Montmorillonite samples reached saturation in 24 h. With vermiculite, the pesticide solutions were

changed every day for five weeks, before saturation was reached.

After reaction, the samples were washed with distilled water before small amounts of the dispersions were air dried on glass slides, at room temperature and humidity, and examined as oriented films by X-ray diffraction (XRD). The basal spacings were determined from several orders of the 00 l reflections.

The samples were also studied by infrared (IR) spectroscopy (prepared as KBr discs) in the range 4800 to 250 cm^{-1} using a Nicolet 5PC FT-IR spectrophotometer.

Total interlamellar N was determined by the Kjeldahl method (digestion of the samples with concentrated H_2SO_4 and a catalyst (Se + K_2SO_4) and displacement of N as NH_3 with NaOH (50% w/v) in a vapour stream; the distilled fraction was collected on H_3BO_3 (4% w/v), and the base $H_2BO_3^-$ was titrated with 0.02 M HCl). The results obtained by this technique were also corroborated by N and C analysis using a CNH Perkin-Elmer 240-C elemental analyzer.

The CEC of the clay minerals was determined by saturation in NH_4^+ with 1 N ammonium acetate solution at pH 7, followed by determination of interlamellar N by the Kjeldahl method.

RESULTS AND DISCUSSION

The XRD pattern of Wyoming montmorillonite yielded a basal spacing of 14.9 Å (Fig. 2a) which decreased to 12.5 Å after treatment of the sample with AMT solution at pH 4 (Fig. 2b). Besides the 12.5 Å reflection, several higher-order reflections are observed (6.26, 4.15, 3.12 Å). The decrease in

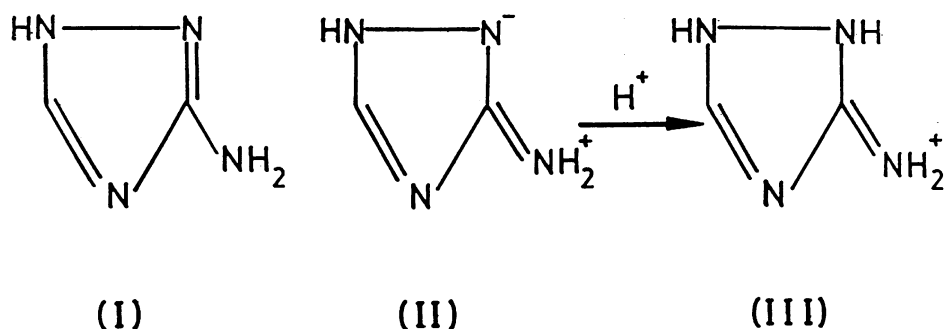


Fig. 1. Amino (I) and imino (II) forms of AMT and the structure after protonation.

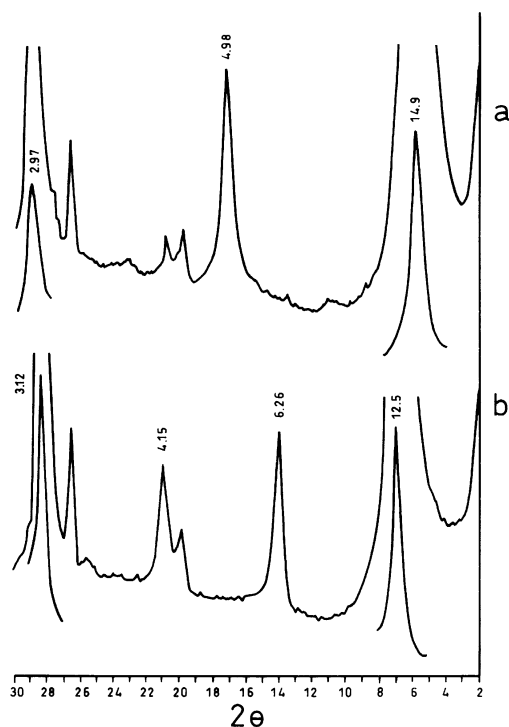


Fig. 2. XRD pattern of montmorillonite: (a) untreated; (b) treated with AMT at pH 4 for 24 h. Spacings in Å; Cu- $K\alpha$ radiation.

the basal spacing from 14.9 to 12.5 Å indicated an important alteration of the montmorillonite interlamellar space. It can be attributed to the formation of the AMT-montmorillonite complex, as confirmed by IR spectroscopy.

The IR spectrum of Wyoming montmorillonite treated with AMT solution (Fig. 3c) showed several absorption bands which are not present in the untreated montmorillonite IR spectrum (Fig. 3b), and which correspond to the aminotriazolium cation. In the absorption spectrum of the AMT-montmorillonite complex (Fig. 3c), there is a band at $\sim 1690\text{ cm}^{-1}$ assigned to the C–N stretching vibration of the exocyclic $\text{C}=\text{NH}_2^+$ group in the imino form (cationic AMT) (Russell *et al.*, 1968). In general, this kind of vibration appears at $\sim 1630\text{ cm}^{-1}$ when it corresponds to the exocyclic C–NH₂ of AMT in the amino form (Fig. 3a), but it can appear at higher frequencies for the following reasons (Bellamy, 1975): to be an exocyclic C–N bond joined to a five member ring; to have two N

atoms joined to the C atom of the C–N bond; or to apply a positive charge to the N atom of the C–N exocyclic bond. These conditions are fulfilled for the AMT cation. The band at $\sim 1580\text{ cm}^{-1}$ is assigned to the ring C–N stretching vibration. It appears at lower frequencies than the typical range of this group ($1665\text{--}1645\text{ cm}^{-1}$) due to the conjugation with the exocyclic C–N bond. Some other bands appear between $3160\text{--}3130\text{ cm}^{-1}$ and belong to stretching vibrations of C–H bonds in the ring, which always appear at higher frequencies in five-member aromatic heterocycles (Bellamy, 1975). The intensity of the absorption bands corresponding to interlamellar water (3420 and 1630 cm^{-1}) was only slightly reduced in the complex compared with the untreated montmorillonite, probably due to the displacement of water molecules as a consequence of AMT cations, which occupy a part of the interlamellar space.

These experimental results indicate that the pesticide AMT is adsorbed at the interlamellar space of montmorillonite as aminotriazolium cation under the experimental conditions previously described, in particular at pH 4. Thus, AMT adsorption proceeds by cation exchange, since the pesticide remains adsorbed after washing the samples with water.

These results are different from those previously reported by Morillo *et al.* (1991) using AMT at a solution pH of approximately 6.3 and montmorillonite saturated with several interlamellar cations. Under such conditions, pesticide-montmorillonite complexes were formed without displacement of interlamellar cations. For cations with low polarizing power, such as Na^+ and Li^+ , the pesticide was adsorbed on montmorillonite mostly as the neutral non-polarized molecule, whereas in samples saturated with medium polarizing power cations, such as Mg^{2+} and Zn^{2+} , polarized neutral AMT molecules were adsorbed. In both cases, the neutral pesticide was desorbed from the interlamellar space by washing with water. When montmorillonite was saturated with high polarizing power cations, such as Fe^{3+} , all the adsorbed pesticide was in the cationic form, and could not be displaced by washing. This is the only case in which the complex was similar to that obtained by treating montmorillonite at pH 4. There are other cases in which coordination strength of a pesticide-clay complex is directly correlated to the polarizing power of the interlamellar cation (Micera *et al.*, 1988; Bosetto *et al.*, 1993).

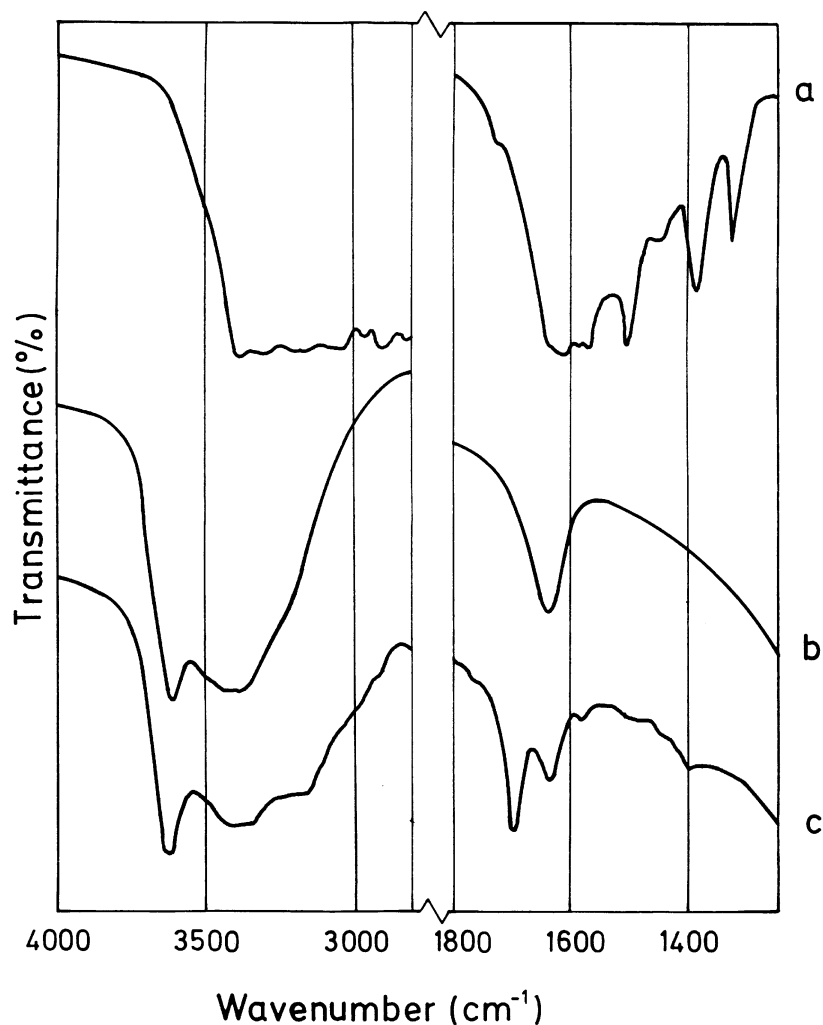


FIG. 3. IR spectra of (a) pure AMT; (b) untreated montmorillonite; (c) montmorillonite treated with AMT at pH 4 for 24 h.

The amount of pesticide adsorbed by montmorillonite was calculated from the interlamellar N and C content to be 71 mEq/100 g, which comprises ~91% of the CEC of this sample (78.2 mEq/100 g).

Taking into account that the basal spacing of the AMT-montmorillonite complex is 12.5 Å, and the distance between the oxygen planes of the montmorillonite layer is 9.6 Å (Grim, 1968), the interlamellar distance is 2.9 Å which can be compared with the size of an AMT molecule ($6.9 \times 3.4 \times 3.9 \text{ \AA}^3$) (Jeffrey *et al.*, 1983). If

AMT is at the interlamellar space in a horizontal position, that is, parallel to montmorillonite layers, the complex basal spacing would be increased by ~3.4 Å to 13 Å. The experimentally lower value of 12.5 Å indicates that coulombic and Van der Waals forces hold the aromatic ring in close contact with the layers (Knight & Tomlinson, 1967). This reduction in the basal spacing could also be caused by the partial introduction of CH and NH groups of the AMT ring into the hexagonal cavities of the silicate crystal structure. This phenomenon should disturb the vibration frequencies of these

groups, but these possible changes are masked by the change in the frequencies of these groups due to the formation of the imino form of AMT.

The basal spacing of the vermiculite before reaction with AMT was 14.33 Å (Fig. 4a); after one week in contact with AMT solution at pH 4 it was 13.83 Å (Fig. 4b). In both cases integral higher orders reflections were observed: 7.17, 4.76, and 3.58 for 14.33 Å; 6.92, 4.61 and 3.45 for 13.83 Å.

The XRD pattern corresponding to vermiculite treated for five weeks with AMT solution (Fig. 4c) showed a basal spacing of 13.68 Å. Higher-order reflections are 6.85, 4.55 and 3.42 Å. This basal

spacing remained unaltered when the period of reaction was further increased.

In vermiculite, the amount of AMT adsorbed was obtained from the C and N content. It was ~167 mEq/100 g clay, which is almost 20% greater than the CEC (141 mEq/100 g) (Justo, 1984). The basal spacing of 13.68 Å was higher than that obtained when the amount of AMT adsorbed was similar to the CEC, and when the cations were situated parallel to the layers, which would be ~12.5 Å, according to the size of an AMT molecule.

A computer program, based on Fourier transform methods (Vila & Ruiz-Amil, 1988), was applied to the results obtained from XRD analysis, in order to establish whether the basal spacing obtained corresponded to an interstratified structure or a pure phase (segregated phase). This program has previously been applied to different systems in which the formation of a clay mineral-organic compound complex was studied (Aragón *et al.*, 1992). The results obtained by the Fourier transform method confirm the formation of a complex corresponding to a pure phase, that is, there is homogeneous distribution of AMT in each inter-layer of vermiculite.

The IR spectra of Mg^{2+} - and AMT-vermiculite are shown in Fig. 5. The spectrum of AMT treated vermiculite (Fig. 5b) shows some absorption bands of AMT.

The amount of AMT adsorbed is greater than the CEC of vermiculite so that not all pesticide adsorbed is bound by cation exchange. This seems to be contrary to the IR results, since the band observed at 1690 cm^{-1} has been ascribed to the C–N stretching vibration of the exocyclic $C=NH_2^+$ of AMT in cationic form, and this kind of vibration should appear at $\sim 1630\text{ cm}^{-1}$ when it corresponds to AMT in the amino form; but this latter band is not observed in the IR spectra (Fig. 5b).

On the other hand, a great part of its water has been lost by vermiculite after complex formation, and this is indicated by the reduction of the water absorption band at $\sim 1630\text{ cm}^{-1}$ which, in AMT-vermiculite, appears only as a shoulder of the 1690 cm^{-1} band of AMT. Also, the water stretching band at 3420 cm^{-1} has been shifted to 3390 cm^{-1} after AMT treatment. This shift could indicate that the few water molecules remaining at the interlamellar space are involved in water bridges with AMT, or they are highly polarized. Some AMT molecules may have displaced water to

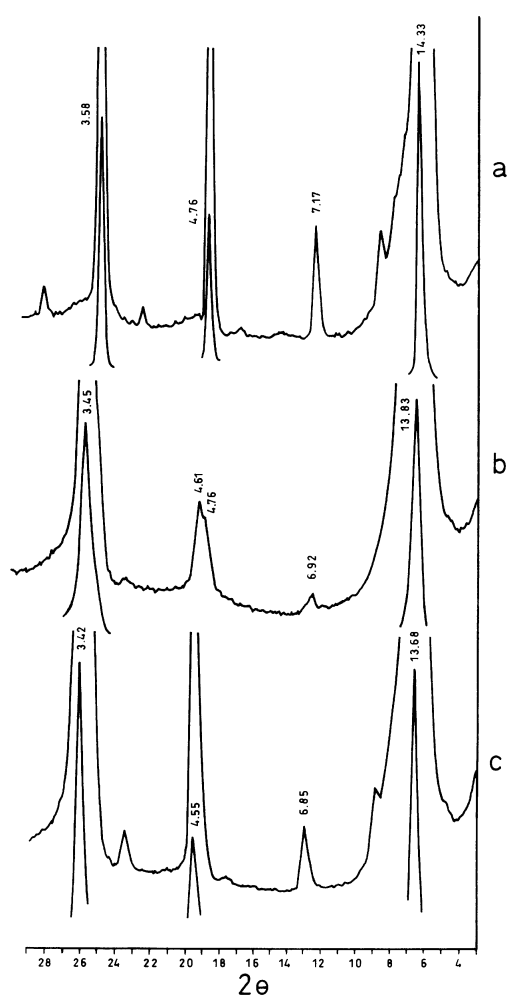


FIG. 4. XRD pattern of vermiculite: (a) untreated; (b) treated with AMT at pH 4 after one week; (c) after five weeks; spacings in Å; Cu- $K\alpha$ radiation.

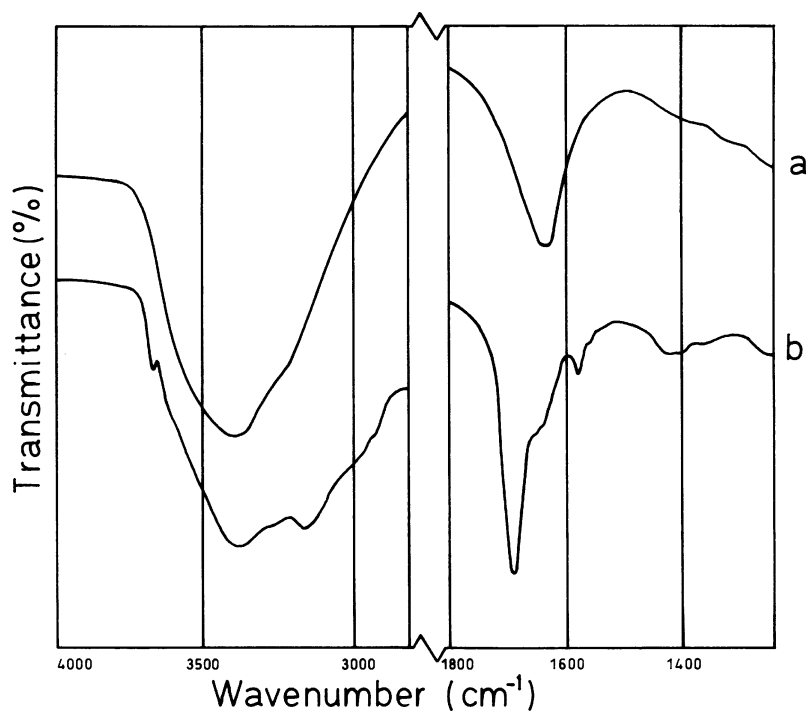


FIG. 5. IR spectra of vermiculite: (a) untreated; (b) treated with AMT at pH 4 after five weeks.

become directly coordinated with the cation, as a consequence of the high polarizing strength of the Mg^{2+} cation. This behaviour has previously been observed in benzonitrile-montmorillonite complexes (Serratos, 1968), nitrobenzene-montmorillonite complexes (Yariv *et al.*, 1966), and also in AMT-montmorillonite complexes (Morillo *et al.*, 1991) when the solution pH was 6.3 and conditions were different from those used in the present study.

In both cases, AMT as a cation and as a dipole contains the exocyclic group $C=NH_2^{2+}$ (Fig. 1, II) which is responsible for the 1690 cm^{-1} band. In fact, the greater part of AMT may be in cationic form and cannot be released from the interlamellar space by washing with water. A portion of Mg^{2+} saturating cations may also remain, being dipoles of AMT around them. These AMT molecules may be released by washing with water, but they remain in the interlamellar space, probably because of a steric hindrance from the adsorbed AMT cations or are held by interaction with them. This is the reason for the 13.68 \AA spacing observed in the complex, instead of 12.5 \AA if the amount of AMT adsorbed was similar to the CEC.

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