MECHANISMS OF INTERACTION BETWEEN MONTMORILLONITE AND 3-AMINOTRIAZOLE

E. MORILLO, J. L. PÉREZ-RODRÍGUEZ* AND C. MAQUEDA

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, Apdo. 1052, 41080 Sevilla, and *Instituto de Ciencia de Materiales, CSIC, Sevilla, Apdo. 1052, 41080 Sevilla, Spain

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ABSTRACT: The adsorption of aminotriazole, at its solution pH, with montmorillonite saturated with different cations has been studied. A pesticide-montmorillonite complex is formed through interlamellar cations which are not displaced. Aminotriazole is situated mostly as a polarized molecule around Mg$^{2+}$ and Zn$^{2+}$ cations, removing a great amount of water. In Na$^{+}$- and Li$^+$-montmorillonite, the pesticide remains as a non-polarized molecule, hydration water being retained in the interlamellar space; the pesticide is coordinated to interlamellar cations through water bridges. For all samples a proportion of cationic aminotriazole is also adsorbed, the amount being greater with increasing polarizing power of the interlamellar cation; consequently, in Fe$^{3+}$-montmorillonite all the aminotriazole adsorbed is in the cationic form.

The adsorption of organic molecules by clay is influenced by the hydration state of the clay and the polarizing power of the interlamellar cations. When interlayer water is present, the cohesion forces of the clay are greatly reduced and, consequently, penetration of the sorbate molecule is facilitated. Thus, molecules compete with water for coordination sites around the cations and, depending on the relative values of the hydration and solvation energies of these, they will (i) replace water and become coordinated to the cations, (ii) occupy sites in a second sphere of coordination around the cations, being bonded to them through bridging water molecules, or (iii) accept a proton from the water of coordination around the cations (Rausell-Colom & Serratosa, 1987).

Studies on the adsorption of 3-aminotriazole by montmorillonite carried out by Russell et al. (1968) showed that the 3-aminotriazole molecule is protonated when adsorbed on montmorillonite surfaces to produce the 3-aminotriazolium cation; protonation is believed to be due to the highly polarized water molecules in direct coordination to the interlamellar cations. This type of reaction also happens for other organic bases, such as pyridine (Farmer & Mortland, 1966; Serratosa, 1966) which, when it is adsorbed on partially dehydrated Mg$^{2+}$-montmorillonite yields the pyridinium ion. In the example of hydrated Mg$^{2+}$-montmorillonite, the pyridine is adsorbed without being protonated; this substance, therefore, can be adsorbed as a cation or as a neutral molecule, according to the condition of the interlamellar space.

In studies carried out in our laboratory on the interaction between several pesticides with clay minerals, some interesting results additional to those of Russell et al. (1968) were obtained for the adsorption of aminotriazole on montmorillonite. The aim of this paper is to investigate further the interaction between montmorillonite and 3-aminotriazole to demonstrate that the adsorption can occur by mechanisms other than cationic exchange, such as ion-dipole and water-bridge interactions.

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MATERIALS AND METHODS

Wyoming montmorillonite saturated with Mg$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Na$^+$ and Li$^+$ was used, saturation being carried out with aqueous solution of the respective chlorides.

The pesticide aminotriazole (3-amino-1,2,4-triazole) is a basic compound that is able to protonate in aqueous solutions depending on the pH, since the pK is 4-14 (Nearpass, 1970). It occurs in two desmotropic forms (I and II); 3-amino-1,2,4-triazole is in the amino (I) form, and its salts in the imino form (III).

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} & \quad \text{(III)} \\
\end{align*}
\]

Solutions of 50 mmol/l of the pesticide, at solution pH (6-3), were added to the samples of montmorillonite saturated with different cations, at a ratio of 2% (w/v). The suspensions were shaken for 24 h at 25°C, and were left to evaporate to dryness at room temperature. The samples obtained were studied by X-ray diffraction (XRD) and infrared (IR) spectroscopy. The basal spacings were determined from several orders of the 00l reflections. The IR absorption spectra of the samples were recorded from 4800 cm$^{-1}$ to 250 cm$^{-1}$ using a Nicolet 5 PC spectrophotometer FT-IR. Samples of montmorillonite saturated with Na$^+$, Li$^+$ and Mg$^{2+}$, before and after treatment with the pesticide, were studied as films, and those saturated with Zn$^{2+}$ and Fe$^{3+}$ were analysed as KBr discs.

Total N was determined using the Kjeldahl method, by digestion of the treated samples with conc. H$_2$SO$_4$ and a catalyst (Se + K$_2$SO$_4$), and displacement of N (as NH$_4^+$) with NaOH (50% w/v) in a vapour stream. The distilled fraction was collected on H$_3$BO$_3$ (4% w/v), and the excess was titrated with 0.02 M HCl.

Interlamellar cations released from the interlamellar space by washing or by treatment were determined by atomic absorption spectrophotometry or flame photometry.

RESULTS AND DISCUSSION

The XRD pattern of Mg$^{2+}$-montmorillonite produced a basal spacing at $\sim$15-2 Å (Fig. 1a), which decreases to 12.98 Å after the treatment with aminotriazole solution (Fig. 1b), although the diffraction at 12-98 Å is not perfectly resolved, showing a shoulder at higher spacings. These data seem to indicate the formation of an aminotriazole-montmorillonite complex which is not homogeneous as the mineral has not reacted completely with the pesticide.

The film yielding a 12.98 Å diffraction peak was washed once with distilled water, and another film prepared with the washed sample produced a basal spacing of 15-2 Å. This basal spacing is that of a Mg$^{2+}$-montmorillonite, indicating that the complex was destroyed by washing with water.

The IR spectrum of the Mg$^{2+}$-montmorillonite film treated with aminotriazole (Fig. 2b) shows absorption bands corresponding to the pesticide; the 1690 cm$^{-1}$ band can be observed which is assigned to the C=N stretching vibration of the exocyclic C=N$^\equiv$H$_2$ group in the imino form (Russell et al., 1968). An absorption band at 1580 cm$^{-1}$ corresponding to the ring C=N stretching vibration is observed, and some bands which can be assigned to an
Montmorillonite-aminotriazole interaction

\[ Q \]

\[ 2.0 \ 53 \ 8.6 \ 11.9 \ 152 \ 185 \ 21.8 \ 25.1 \ 28.1 \ 31.7 \ 35.0 \]

**Fig. 1.** XRD patterns of films of Mg\(^{2+}\)-montmorillonite: (a) untreated; (b) treated with aminotriazole, without washing; (c) washed with distilled water. Cu-K\(\alpha\) radiation.

\( \omega \)-ring vibration are present in the region 1400–1420 cm\(^{-1}\) (Borello & Zecchina, 1963). The spectrum of the sample treated with aminotriazole and washed with water (Fig. 2c), is similar to that of Mg\(^{2+}\)-montmorillonite except that there is a very small band at 1690 cm\(^{-1}\).

The almost complete destruction by washing with water of the complex that yields a diffraction peak at 12.98 Å indicates that a cationic interchange between aminotriazolium cation and interlamellar Mg\(^{2+}\) has been possible only in a very low proportion because, if all the adsorbed aminotriazole is in the cationic form as the saturating cation, this would not be easily released from the interlamellar space. On the other hand, the basal spacing obtained after washing the 12.98 Å film would not again be 15.2 Å, corresponding to Mg\(^{2+}\)-montmorillonite, as the Mg\(^{2+}\) cations would not be in the interlamellar space.

These data indicate that a high proportion of Mg\(^{2+}\) cations remain in the montmorillonite interlamellar space, in spite of aminotriazole, and this was confirmed experimentally by determining the amount of desorbed Mg\(^{2+}\) in the treatment solutions of aminotriazole. The value obtained was 5.47 mEq Mg\(^{2+}\)/100 g (2.59 mEq Mg\(^{2+}\)/100 g is desorbed in distilled water). As the CEC of the montmorillonite is 78.2 mEq/100 g, the release of interlamellar Mg\(^{2+}\) had only taken place to a small extent, and both pesticide and Mg\(^{2+}\) were present in the interlamellar space of the montmorillonite.

If the basal spacing of Mg\(^{2+}\)-montmorillonite decreases from 15.2 Å to 12.98 Å, it must have lost a large proportion of the interlamellar water, which was coordinated to Mg\(^{2+}\) ions, thereby causing the 15.2 Å basal spacing. However, water was not completely displaced.
because the IR spectrum of the complex (Fig. 2b) shows absorption bands at ~1630 and 3340 cm$^{-1}$, due to interlamellar water. The shift of the water stretching band from 3420 cm$^{-1}$ in Mg$^{2+}$-montmorillonite, to 3340 cm$^{-1}$ after aminotriazole treatment, indicates that water molecules are strongly involved in water bridges; probably, the more external hydration shell of Mg$^{2+}$ has been lost, and only water molecules directly coordinated to interlamellar Mg are present. These water molecules form water bridges with aminotriazole.

Some of the aminotriazole molecules may have displaced water to become directly coordinated to the cation, giving rise to modification in the C–N stretching band of the complex, in the C–NH$_2$ exocyclic group, to a higher frequency, 1690 cm$^{-1}$ (the normal frequency of this bond for aminotriazole as a molecule is ~1630 cm$^{-1}$). This is possibly due to the high polarizing strength of the Mg$^{2+}$ cation, which can polarize the aminotriazole molecule in order to reach the (II) form. If aminotriazole acts as dipole, it could displace water molecules on the inner hydration shell of Mg$^{2+}$, and occupy such positions around the interlamellar cation. Similar behaviour is observed in benzonitrile-montmorillonite
Montmorillonite-aminotriazole interaction 273

(Serratosa, 1968), and nitrobenzene-montmorillonite complexes (Yariv et al., 1966). This is the reason that on washing the aminotriazole-montmorillonite complex with water, the pesticide is displaced almost completely from the interlamellar space by water molecules which re-occupy their positions around Mg$^{2+}$, such displacement taking place very quickly.

The behaviour of aminotriazole as a dipolar molecule, leads to a double bond C=N in the exocyclic group, which shows a higher frequency (1690 cm$^{-1}$); because it is an exocyclic C=N bond joined to a five-member ring, there are two N atoms joined to the C atom of the C=N bond, and a positive charge exists on the N atom of such a C=N bond (Bellamy, 1975). That is, the 1690 cm$^{-1}$ band is assigned exactly to the same exocyclic group C=N$^+$/H that Russell et al. (1968) reported. However, considering the XRD data before and after washing the samples, and also the analyses of the treatment and washing solutions, the 1690 cm$^{-1}$ band is considered to be due, in the greatest part, to the group mentioned above, which is also present in the polarized molecule of the pesticide. This is one of the important resonance forms contributing to the true structure of 3-aminotriazole (Russell et al., 1968).

Total N in Mg$^{2+}$-montmorillonite samples treated with aminotriazole and washed with water, has been determined in order to establish the amount of adsorbed pesticide which was not able to be displaced by washing. The value obtained was 16 mEq/100 g, a higher value than that of desorbed Mg$^{2+}$ cations (5-47 mEq/100 g); this may be due to: (i) a part of the adsorbed pesticide is in the neutral form—this is unlikely as the ease of displacement of adsorbed neutral aminotriazole by washing with water has been demonstrated; (ii) Mg$^{2+}$ cations can form complex species, such as [Mg(OH)(H$_{2}$O)$_{x}$]$^{+}$—consequently, some of the negative charges on the silicate layer, which had been compensated by Mg$^{2+}$ cations, can then be compensated by the aminotriazolium cation. The formation of such species can be described by the following equilibrium:

\[ [\text{Mg(H}_2\text{O})x + 1]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Mg(OH)(H}_2\text{O})x]^+ + \text{H}_3\text{O}^+ \]

Equilibrium is more easily displaced to the right if the polarizing power of the cation is higher. The protons which are produced can be taken up by aminotriazole molecules to become cations which remain adsorbed on the mineral surface.

Similar behaviour has been observed for Zn$^{2+}$-montmorillonite (Fig. 3) in which a great part of the initially adsorbed pesticide (Fig. 3b) has been displaced by washing the complex with water (Fig. 3c), with only a small amount remaining adsorbed. Likewise, the XRD data seem to corroborate such displacement, as a decrease in basal spacing from 13.3 Å to 12.8 Å is produced by washing the sample treated with aminotriazole (Table 1).

On the other hand, the amount of desorbed exchange cation (present in the treatment and washing solutions of the Zn$^{2+}$-montmorillonite) is ~2 mEq/100 g, and therefore the adsorption of 3-aminotriazole is not due to a cationic exchange process; this is similar to that observed for Mg$^{2+}$-montmorillonite.

If the treatment with aminotriazole solutions is carried out on Fe$^{3+}$-montmorillonite, the amount of pesticide adsorbed (Fig. 4b) is similar to that remaining adsorbed after washing with water (Fig. 4c), which seems to indicate that almost all the adsorbed aminotriazole is in the cationic form and so cannot be displaced. This is a consequence of the higher polarizing power of the Fe$^{3+}$ cation relative to Mg$^{2+}$ and Zn$^{2+}$ which have similar polarizing powers.
The amount of adsorbed pesticide on the washed samples is higher in Fe$^{3+}$-montmorillonite (34 mEq/100 g) than in Zn$^{2+}$- and Mg$^{2+}$-saturated samples (18 and 16 mEq/100 g, respectively).

The conclusions reached from the data described do not agree with some of the conclusions of Russell et al. (1968) who used similar experimental conditions for aminotriazole-montmorillonite adsorption. They deduced, from a similar IR spectrum of Mg$^{2+}$-montmorillonite after treatment with aminotriazole, that all the aminotriazole adsorbed on montmorillonite (before washing the complex with water) is present as aminotriazolium cation; but if the majority of the pesticide is desorbed by washing with water, this indicates that aminotriazole is adsorbed in the neutral form. Experiments have been carried out treating montmorillonite with aminotriazole at a pH similar to its pK (pH 4) (Fig. 5), in order to study the kind of interaction which can be observed if a part of the pesticide is like the aminotriazolium cation. The adsorbed pesticide is not desorbed at

Table 1. Basal spacings (Å) of Wyoming montmorillonite samples, saturated with several cations, before and after treating with aminotriazole.

<table>
<thead>
<tr>
<th>Saturating cation</th>
<th>Mg$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Fe$^{3+}$</th>
<th>Na$^+$</th>
<th>Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without treatment</td>
<td>15.2</td>
<td>12.6</td>
<td>12.3</td>
<td>12.4</td>
<td>12.8</td>
</tr>
<tr>
<td>Treated with aminotriazole</td>
<td>12.98</td>
<td>13.3</td>
<td>12.6</td>
<td>14.7</td>
<td>14.7</td>
</tr>
<tr>
<td>Treated with aminotriazole and washed</td>
<td>15.2</td>
<td>12.8</td>
<td>12.6</td>
<td>12.4</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Fig. 3. IR spectra of Zn$^{2+}$-montmorillonite: (a) untreated; (b) treated with aminotriazole, without washing; (c) washed with distilled water.
Fig. 4. IR spectra of Fe\(^{3+}\)-montmorillonite: (a) untreated; (b) treated with aminotriazole, without washing; (c) washed with distilled water.

Fig. 5. IR spectrum of film of Mg\(^{2+}\)-montmorillonite treated with aminotriazole at pH 4.

all by washing the complex several times with water, indicating that it is in the cationic form, and the behaviour differs from that described above, with a spectrum exactly the same as the unwashed sample (Fig. 5). Russell et al. (1968) observed that the pesticide adsorbed on the clay is stable to leaching by water, whereas in the complex studied of Mg\(^{2+}\)- and
Zn\(^{2+}\)-montmorillonite, displacement of a great part of the interlamellar aminotriazole takes place with only one washing with distilled water. The amount of pesticide displaced by washing with water is proportional to the polarizing power of the interlamellar cation, being higher if the polarizing power is lower. For this reason, it was considered interesting to study the interaction between aminotriazole and montmorillonite saturated with cations of polarizing power lower than Mg\(^{2+}\) and Zn\(^{2+}\).

The Na\(^{+}\)-montmorillonite film yielded a basal spacing of 12.4 Å (Fig. 6a). After treatment with aminotriazole solution, the basal spacing increased by 2.3 Å to 14.7 Å (Fig. 6b). This increase could indicate the formation of an aminotriazole-montmorillonite complex.

When the film obtained was washed once with distilled water and another film prepared, the basal spacing decreased, adopting again the value of 12.4 Å, corresponding to Na\(^{+}\)-montmorillonite.

The IR absorption spectrum of Na\(^{+}\)-montmorillonite treated with aminotriazole (Fig. 7b) shows an absorption band at ~1630 cm\(^{-1}\), corresponding to the C–N band of the C–NH\(_2\) exocyclic group of the pesticide as neutral molecule, although a small band can be observed at ~1690 cm\(^{-1}\), which would correspond to the C=NH\(_2\) exocyclic group of aminotriazole as a cation or as a polar molecule (as discussed above). Therefore, there are neutral molecules together with cationic species or polarized molecules of aminotriazole in the interlamellar space of montmorillonite. However, the proportion of neutral aminotriazole is much higher than that of the cationic or polarized aminotriazole.
In addition to these bands, another band corresponding to C=N bond in the aromatic ring was observed at 1580 cm⁻¹, and also an absorption band at ~3370 cm⁻¹, corresponding to the stretching of water O–H bonds, which have been displaced towards lower frequencies due to the formation of water-bridges with the pesticide.

Washing the film with water, and preparing another film, results in an IR spectrum (Fig. 7c) in which the majority of the absorption bands present in Fig. 7b have disappeared, except a small one at 1690 cm⁻¹. This seems to indicate that cationic aminotriazole is present in the interlamellar space of montmorillonite, because if there were polarized neutral molecules, they would have been displaced. The rest of the spectrum is similar to that of Na⁺-montmorillonite (Fig. 7a).

It is possible that only aminotriazole cations were in the interlamellar space, and neutral aminotriazole molecules were present over the external surface of the montmorillonite; this is possible as the sample was not washed before preparing the film. However, the basal spacing of the complex (14.7 Å) should remain constant after removing neutral aminotriazole by washing with water, but the basal spacing decreased to 12.4 Å. The
TABLE 2. IR frequencies (cm⁻¹) of some vibrations of pure 3-aminotriazole (AMT), and adsorbed on montmorillonite saturated with several cations.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Non-adsorbed AMT</th>
<th>Adsorbed AMT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mg²⁺, Zn²⁺, Fe³⁺</td>
</tr>
<tr>
<td>C=N stretching (exocyclic C=NH₂)</td>
<td>—</td>
<td>1690 (weak)</td>
</tr>
<tr>
<td>C=N stretching (ring)</td>
<td>1580</td>
<td>1580</td>
</tr>
<tr>
<td>C-N stretching (exocyclic C-NH₂)</td>
<td>1630</td>
<td>1630</td>
</tr>
<tr>
<td>ω-ring vibration</td>
<td>1400–1420</td>
<td>1400–1420</td>
</tr>
</tbody>
</table>

amount of interlamellar Na⁺ desorbed after treating Na⁺-montmorillonite with aminotriazole has been determined, indicating that no appreciable cationic exchange of Na⁺ by aminotriazole had taken place. Therefore, both Na⁺ cations and aminotriazole are present in the interlamellar space of the complex obtained, the pesticide being present almost totally as neutral molecules, but also as a cation to a lesser extent.

These results agree only in part with those obtained by Russell et al. (1968) as these authors observed the presence of a small amount of cationic aminotriazole in the interlamellar space, but they did not mention that neutral molecules of the pesticide also exist in the interlamellar space.

The basal spacing (14.7 Å) of the complex is a consequence of the low polarizing power of Na⁺ cations. Aminotriazole is adsorbed in the interlamellar space of the mineral as a neutral molecule, but not as a polarized molecule, and thus it cannot displace the hydration water molecules of montmorillonite, resulting in an increase in the basal spacing.

Similar results have been observed in the treatment of Li⁺-montmorillonite with aminotriazole, and as for Na⁺-montmorillonite, the initial basal spacing (12.8 Å) increased to 14.7 Å with pesticide treatment, but decreased to 12.8 Å after washing with water. Data from IR spectroscopy are also similar.

Table 2 shows the non adsorbed aminotriazole vibrations and the effect of adsorption on their locations.

CONCLUSIONS

The interaction of aminotriazole, in aqueous solution at pH 6.3, with montmorillonite saturated with various cations varies according to the polarizing power of the cations. For cations with low polarizing power, such as Na⁺ and Li⁺, the pesticide is adsorbed on montmorillonite mostly as the neutral non-polarized molecule, whereas in samples saturated with cations with medium polarizing power, such as Mg²⁺ and Zn²⁺, the aminotriazole is adsorbed, to a very large extent, as the polarized neutral molecule due to the effect of the saturating cations. In both cases, the neutral pesticide, polarized or non-polarized, is desorbed from the interlamellar space of montmorillonite by washing with water. In all the examples described, a part of the adsorbed pesticide is in cationic form, due to the protonation of the aminotriazole molecule as a consequence of the highly polarized water molecules in direct coordination with the cations which are not displaced from their exchange positions.

When montmorillonite saturated with high polarizing power cations, such as Fe³⁺, is
Montmorillonite-aminotriazole interaction

used, all the adsorbed pesticide is in the cationic form, and is impossible to displace from the complex by washing.

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