# The Adsorption of Herbicides and Pesticides on Clay Minerals and Soils. Part 2. Atrazine *

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## Abstract

The adsorption of atrazine and two model compounds, 2-chloropyrimidine and 3-chloropyridine on clay minerals (bentonite, montmorillonite and kaolinite), organic matter (humic acid) and soil (with and without organic matter) has been studied using FT-infrared spectroscopy (IR), thermogravimetric analysis (TGA), high pressure liquid chromatography (HPLC) and X-ray diffraction (XRD). 3-Chloropyridine, 2-chloropyrimidine and atrazine were adsorbed through hydrogen bonding on bentonite, montmorillonite, humic acid and soil. In addition to hydrogen bonding, protonation of 3-chloropyridine and atrazine was also observed. In the adsorption of 2-chloropyrimidine on bentonite and montmorillonite an ion exchange mechanism also occurred. No adsorption of 3-chloropyridine or 2-chloropyrimidine was observed on the kaolinite clay mineral. Both the clay minerals and organic matter of soil contribute to the adsorption of organic compounds on soil but the clay minerals bentonite and montmorillonite play a major role in their adsorption on soil.

## Introduction

The past few decades have seen increasing use of a wide range of organic herbicides and pesticides in agriculture which ultimately find their way directly or indirectly into soils. The risk of these compounds finding their way into the human food chain via drinking water has given rise to a need for extensive research into the fate and behaviour of pesticides and other organic molecules. The latter are not classified as pesticides but they are found as degradation products of pesticides and can also act as model compounds in soil. The fate and behaviour of the pesticides in soil environments is governed by various retention, transportation and transformation processes. These processes determine both the efficacy of pesticides in controlling target organisms and their potential for environmental hazards. Transportation and transformation processes of pesticides in soils depend strongly on their retention by the solid organomineral phase. Although retention includes all the processes that prevent or retard movement of pesticides in soils, the primary means of retention is adsorption of pesticides on soil constituents. The most important soil constituents for adsorption are clay minerals and organic matter [2–4].

Atrazine was chosen for study because of its widespread use in agriculture [5] and it has been widely detected in ground water [6] as well as in urban streams [7]. To pre-

vent water contamination it is necessary to understand the mechanism by which atrazine is retained on soil.

The adsorption and desorption of atrazine by soil and its constituents with respect to the influence of the physical factors has been studied extensively and is well documented [8, 9]. Despite extensive work available on the adsorption and desorption of atrazine, little is known at a molecular level regarding the chemistry of its interaction with the soil constituents or any of the transporting agents that may carry it from a soil profile to the groundwater. These interactions ultimately determine its soil adsorption parameters as well as its degradation in soil.

It has been shown that atrazine adsorption is associated with clay minerals and organic matter contained in soil [10–12]. The formation of hydroxyatrazine by surface proton catalysis has been observed in several studies of atrazine interaction with soils, clay minerals and humic substances [13–15].

Atrazine is primarily retained on silicate clays by physical adsorption but both physical adsorption and chemisorption contribute to the retention of atrazine by soil organic matter [12]. Hydrogen bonding (or proton-transfer) and hydrophobic bonding were proposed to interpret the results of studies of the interaction of atrazine with a podzolized soil and its extracted humic compounds [16]. IR spectroscopy was used to study atrazine and humic substance interactions, and either hydrogen bond formation or proton transfer between atrazine and the carboxyl and phenolic groups of humic substances were suggested as likely reaction mech-
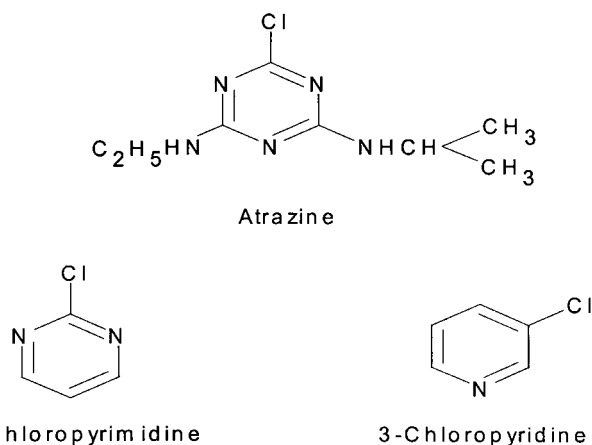
*Figure 1.* Structures of atrazine (AT), 2-chloropyrimidine (CPM) and 3-chloropyridine (CPY).

anisms [17]. Weak adsorption of atrazine by humic acid, involving hydrogen bonding, proton transfer (at low pH), and possibly hydrophobic bonding have also been proposed [5]. The authors suggested that this relatively weak interaction mechanism of atrazine with soil humic acid and the low pH favours the abiotic degradation of atrazine to its hydroxy derivative which is much more persistent in the environments and its potential hazard to groundwater.

The objectives of this study are to provide a better understanding of the interaction mechanisms involved in the adsorption of atrazine (Figure 1) on soil and its constituents using clay minerals (bentonite and kaolinite, together with an acid treated montmorillonite, K10), humic acid, air-dried soil, and soil with and without organic matter. The organic compounds 2-chloropyrimidine and 3-chloropyridine were also used as model compounds (Figure 1). The complementary techniques used were:

(i) Fourier transform-infrared spectroscopy (FT-IR) to identify the interacting moieties,
(ii) thermogravimetric analysis (TGA) to provide quantitative information about the complexes formed,
(iii) X-ray diffraction (XRD) to confirm formation of intercalation complexes,
(iv) high pressure liquid chromatography (HPLC) to provide information on the desorption of the organic component.

## Experimental

### Chemicals

All the chemicals were research grade, (solids having 98% purity and liquids 99%). 2-Chloropyrimidine (CPM) and 3-chloropyridine (CPY) were obtained from Lancaster Synthesis Ltd. Atrazine (AT) was supplied by Ciba Agriculture. BDH Hipersolve UV grade acetonitrile, Hipersolve methanol and chloroform were used throughout this study. The organic free distilled water was prepared by using milli pore Milli-RO and Milli-Q purification systems.

The other materials and methods were as described in the previous paper [1] apart from:

## Adsorption experiments

### Adsorption on clays and soil samples

1 g of each clay and soil sample was immersed in 10 mL methanol solution of CPM, 15 mL chloroform solution of AT or in 5 mL of CPY in a 50 mL conical flask. These were kept on a magnetic stirrer for about 24 hours at room temperature. The solutions were filtered at the pump without washing and dried over silica gel for a minimum of 24 hours.

### Adsorption on humic acid

These samples were prepared by immersing 1 g of humic acid in 10 mL methanol solution of CPM, 15 mL chloroform solution of AT or in 5 mL of CPY in a 50 mL conical flask. These were kept on a magnetic stirrer for 24 hours at room temperature and then transferred to 50 mL propylene centrifuge tubes and centrifuged for about 30 minutes at 3500 rpm. The supernatant solutions were decanted in the pyrex bottles and stored in a refrigerator while the remnant was dried over silica gel for at least 24 hours.

### Desorption experiments

0.1 g of model compound treated samples were mixed separately in 2.5 mL of 80% methanol and 20% water solution, (60/40 methanol/water for the AT treated sample) in 50 mL propylene centrifuge tubes on a rotary shaker for 24 hours. The tubes were centrifuged at 4000 rpm for 30 minutes and then the supernatant solutions were decanted in pyrex bottles and stored in a refrigerator. Solutions were diluted and filtered through Nalgene 0.22 $\mu$m cellulose acetate filters prior to HPLC analysis.

## Results and discussion

### 3-Chloropyridine (CPY)

Although the adsorption of pyridine on clay minerals has been studied extensively in order to obtain information on the adsorption sites [18], no information is available on the mechanism of adsorption of halogenated pyridine derivatives on clay or organic matter in soil.

### IR Studies

Table 1 summarises the positions of the IR bands of 3-chloropyridine (CPY) after adsorption by the various supports. The vibrational frequencies are assigned by following Green *et al.* [19]. No changes were observed with CPY treated kaolinite indicating no adsorption as kaolinite is a non-expandable clay.

The ring stretching modes observed in the 1400–1600 cm$^{-1}$ region are very sensitive to the interaction with the adsorbing sites. The $\nu_{8a}$ ring stretching, which lies at 1572 cm$^{-1}$ in liquid CPY, is displaced to higher wavenumber values in all cases. A similar displacement occurs when the pyridine molecule is coordinated to a metal ion [20] or

*Table 1.* IR band positions (cm$^{-1}$) of 3-chloropyridine in the liquid phase and adsorbed on different media

|  | $\nu_{8a}$ | $\nu_{8b}$ | $\nu_{19a}$ | $\nu_{19b}$ |
|---|---|---|---|---|
| Liquid | 1572 | 1566 | 1467 | 1415 |
| Bentonite | 1588 | 1567 | 1472 | 1421 |
| Montmorillonite | 1586 | 1566 | 1471 | 1421 |
| Humic acid | 1583 | 1566 | 1466 | 1416 |
| Air dried soil | 1596 | 1568 | 1470 | 1417 |
| CSS[a] | 1594 | 1564 | 1484 | 1418 |
| OMS[b] | 1591 | 1564 | 1483 | 1415 |

[a]Carbonate and soluble salt free soil.
[b]Organic matter free soil.

involved in hydrogen-bonding [21]. The $\nu_{8b}$ ring stretching mode shows only a small change on adsorption.

The $\nu_{19a}$ and $\nu_{19b}$ ring vibrations show similar increases. These ring stretching vibrations show an increase in frequency upon coordination of the lone pair on the nitrogen atom to exchangeable cations or upon formation of H-bonds through the nitrogen lone pair to the surface OH groups [22].

The changes observed in the spectra of the supports in the OH stretching region and the changes in the CPY spectra suggest the following interactions between the two components:

- As a result of adsorption of CPY on bentonite the H$_2$O stretching frequencies of bentonite undergo some changes. The OH band at 3636 cm$^{-1}$ shows a decrease in intensity indicating a decrease in the free OH groups. A broad band appears around the 3060 cm$^{-1}$ region suggesting interaction of the OH group. CPY is adsorbed on both bentonite and montmorillonite by hydrogen bonding of the lone pair of the nitrogen atom through a water molecule with the exchangeable cation. The presence of a band at 1624 cm$^{-1}$ in the CPY/montmorillonite system may indicate the protonation of CPY, as the presence of a band at 1635 cm$^{-1}$ in the pyridine-montmorillonite complex has been attributed to the protonation of pyridine [16, 18]. This protonation is due to the presence of protons in this acid treated material.

- The major changes observed in the spectrum of CPY treated humic acid is the increase in the $\nu_{8a}$ ring vibration of the adsorbed CPY and the decrease in the intensity of the band at 1713 cm$^{-1}$ due to the carbonyl group. These results suggest that CPY is adsorbed on humic acid by interaction of the nitrogen atom with the COOH group of humic acid.

- The $\nu_{8a}$, $\nu_{19a}$ and $\nu_{19b}$ ring vibrations of CPY show an increase on adsorption on all the soil samples. The band at 1635 cm$^{-1}$, characteristic of protonation of CPY, is also observed in all the CPY treated soil samples. These results suggest that CPY is adsorbed on the soil samples by the protonation of CPY and hydrogen bonding of the nitrogen atom with the adsorbent sites of the soil.
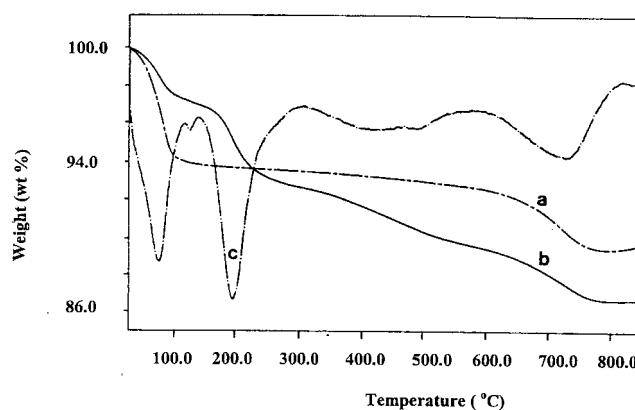


*Figure 2.* Thermogravimetric analysis of (a) bentonite, (b) atrazine treated bentonite, (c) derivative thermogram for atrazine treated bentonite.

*Table 2.* Comparison of guest desorption % weight loss values obtained using thermal and solution desorption

| Adsorbent | CPY desorption | | CPM desorption | | AT desorption | |
|---|---|---|---|---|---|---|
|  | TGA | HPLC | TGA | HPLC | TGA | HPLC |
| Bentonite | 6.0 | 6.1 | 11.0 | 6.3 | 6.0 | 3.7 |
| Montmorillonite | 9.0 | 9.7 | 9.0 | 8.7 | 8.0 | 5.0 |
| Kaolinite | na | na | na | na | 2.0 | 1.0 |
| Humic acid | nd | 4.2 | nd | 19.0 | nd | 1.8 |
| AS | 4.0 | 4.6 | 6.0 | 1.5 | 3.0 | 2.4 |
| CSS | 3.0 | 3.8 | 5.0 | 2.1 | 2.5 | 2.0 |
| OMS | 6.5 | 6.7 | 5.0 | 4.2 | 2.0 | 1.9 |

n.a. - No adsorption.
n.d. - Not determined.

### TGA studies

The TGA curves obtained for the clay-CPY systems are similar to those shown in Figure 2 with three weight loss regions. The three weight losses represent desorption of physically adsorbed water (100 °C region), loss of the CPY (130 °C region) and dehydroxylation of the aluminosilicate layer (700 °C region) [18]. It is difficult to determine accurate weight losses for CPY in the bentonite and montmorillonite complexes due to the close proximity of the water and CPY desorption temperatures. The desorption of CPY from the soil samples gave rise to weight losses of 4% (AS), 3% (CSS) and 6.5% (OMS).

The amount of CPY desorbed from the adsorbents determined by HPLC analysis and that observed by the TGA analysis are given in Table 2. The montmorillonite clay mineral, which is acid treated, shows a greater adsorption of CPY than bentonite. The humic acid has low affinity towards the adsorption of CPY as compared to the clay minerals.

The organic matter free soil sample (OMS) shows greater adsorption of CPY as compared to the air dried soil (AS) and carbonate and soluble salts free soil (CSS). This indicates that the clay minerals play a major role in the adsorption of CPY and removal of the organic matter from the soil increases the adsorption capacity of the soil used in the present study.

*Table 3.* Basal spacings (Å) for clay minerals, after treatment with CPY, CPM and AT

| | Untreated ($d_c$) | CPY treated ($d_o$) | CPM treated ($d_o$) | AT treated ($d_o$) |
|---|---|---|---|---|
| Bentonite | 12.26 | 13.8 | 12.9 | 13.3 |
| Montmorillonite | 12.15 | 14.7 | 13.7 | 13.5 |
| Kaolinite | 7.26 | a | a | a |

[a] Values as for kaolinite.

### XRD studies

Intercalation of CPY into clay minerals would lead to an expansion of the basal spacing. Table 3 summarises the XRD results. An increase was observed with CPY treated bentonite and montmorillonite, but no increase was observed with kaolinite confirming the conclusion of the IR study of no adsorption.

It has been suggested that a 13.8 Å spacing indicates the tilting of the aromatic ring of the pyridine [23], while a 14.7 Å spacing shows a perpendicular arrangement of the intercalated pyridine [24] with respect to the surface of the silicate layers. Therefore, it can be suggested that in the case of bentonite the ring of the 3-chloropyridine molecules is tilted and in montmorillonite it has a perpendicular arrangement with respect to the surface of the silicate layers. The higher amount of adsorption of 3-chloropyridine on montmorillonite as compared to bentonite also supports the perpendicular arrangement of the ring of the 3-chloropyridine molecule.

## 2-Chloropyrimidine (CPM)

The adsorption of pyrimidine on montmorillonite [25] and on illite [26] has been studied with respect to the effect of the physical properties of the clay minerals. The adsorption of naturally occurring pyrimidines and their derivatives on humic acid has also been studied [27]. No work so far is available on the mechanism of adsorption of pyrimidine.

### IR studies

Table 4 compares the positions of the IR bands of 2-chloropyrimidine (CPM) in the liquid and solution phases and after contact with the various supports. The major band vibrations are assigned by following Foglizzo and Novak [28]. No changes were observed with CPM treated kaolinite indicating no adsorption.

The ring stretching modes observed in the 1400–1600 cm$^{-1}$ region are very sensitive to the interaction with the adsorbing sites. The $\nu_{8a}$ ring stretching, which lies at 1594 cm$^{-1}$ in solid CPM, is displaced to higher wavenumber values in all cases. A similar displacement occurs when the pyridine molecule is coordinated to a metal ion [20] or involved in hydrogen-bonding [21]. The $\nu_{8b}$ ring stretching mode shows a shift averaging 10 cm$^{-1}$ on adsorption on

*Table 4.* IR band positions (cm$^{-1}$) of 2-chloropyrimidine in the crystalline and solution phases and adsorbed on different media

| | $\nu_{8a}$ | $\nu_{8b}$ | $\nu_{19a}$ | $\nu_{19b}$ |
|---|---|---|---|---|
| Crystalline | 1594 | 1563 | 1537 | 1433 |
| CH$_3$OH solution | 1604 | n.o. | n.o. | 1450 |
| Bentonite | 1612 | 1576 | 1564 | 1443 |
| Montmorillonite | 1610 | 1570 | 1538 | 1439 |
| Humic acid | 1599 | 1560 | n.o. | 1437 |
| Air dried soil | 1608 | 1561 | n.o. | 1440 |
| CSS[a] | 1607 | 1562 | n.o. | 1440 |
| OMS[b] | 1606 | 1566 | n.o. | 1439 |

[a] Carbonate and soluble salt free soil.
[b] Organic matter free soil.
n.o. Not observed due to overlap with methanol or soil band.

bentonite and montmorillonite but much smaller shifts on adsorption on humic acid and the soil samples.

The $\nu_{19a}$ and $\nu_{19b}$ ring vibrations show similar increases. These ring stretching vibrations show an increase in frequency upon coordination of the lone pair on the nitrogen atom to exchangeable cations or upon formation of H-bonds through the nitrogen lone pair to the surface OH groups [22].

Comparison of the spectra of the supports before and after treatment with CPM suggests the following interactions between the two components:

- The broad shoulder in the 1630 cm$^{-1}$ region in 2-chloropyrimidine treated bentonite may indicate the presence of some pyrimidinium ion [29]. The changes which are observed in the spectra of bentonite on adsorption of 2-chloropyrimidine are a decrease in the intensity and frequency of the band at 3636 cm$^{-1}$ region and an increase in the intensity of bands in the (OH) bonded region. This indicates the hydrogen bonding of 2-chloropyrimidine through a water molecule. Considering all of the above changes it can be suggested that the 2-chloropyrimidine is adsorbed on bentonite through hydrogen bonding, through coordination with exchangeable cations and due to the formation of the 2-chloropyrimidinium ion.

- The changes observed in the spectra of 2-chloropyrimidine treated montmorillonite suggest that the adsorption on montmorillonite involves hydrogen bonding and the formation of pyrimidinium ion.

- The humic acid spectrum shows a slight decrease in the intensity of the OH band on adsorption of 2-chloropyrimidine but no other pronounced change is observed in the spectrum of humic acid. Considering all these changes it can be suggested that the 2-chloropyrimidine may be adsorbed on humic acid by weak hydrogen bonding or by van der Waals bonding.

- The changes in the ring vibrations suggests that 2-chloropyrimidine is adsorbed on soil samples by hydrogen bonding with the active sites in the soil samples.

## TGA studies

The TGA curves obtained for the clay-CPM systems are similar to those shown in Figure 2 with three weight loss regions. For the CPM bentonite system a weight loss of 4% in the temperature range of 150–220 °C indicates the desorption of hydrogen bonded 2-chloropyrimidine. A further weight loss of 7% in the 220–550 °C region is assigned to desorption of the pyrimidinium ion, the different temperatures indicating a greater interaction in the case of the ion.

For the CPM montmorillonite system the corresponding weight losses and temperatures for CPM and the protonated species are 4% (120–340 °C) and 5% (340–580 °C) respectively. The higher temperature range required for desorption of the protonated species compared with bentonite is again a consequence of the acid treatment of the montmorillonite.

The weight losses occurring as a result of the desorption of 2-chloropyrimidine from AS, CSS and OMS samples are similar, being 6%, 5% and 5% respectively.

Desorption of CPM from the solid samples into a methanol/water mixture was also studied using HPLC and compared with the thermal desorption values (Table 2). The amount of 2-chloropyrimidine observed by the HPLC analysis is much lower than the TGA for the air dried soil (AS) and soluble salts free soil (CSS) samples.

## XRD studies

An increase was observed in the basal spacing with CPM treated bentonite and montmorillonite, indicating the formation of intercalates, but no increase was observed with kaolinite (Table 3).

The values obtained for the d(001) basal plane of 2-chloropyrimidine treated bentonite and montmorillonite are 12.9 Å and 13.7 Å respectively. No literature is available on the expansion of clay minerals by the adsorption of pyrimidine. Nevertheless, on comparison of these data with those of the complexes with other heterocyclic aromatic rings it can be suggested that the 12.9 Å basal spacing indicates the parallel arrangement of the pyrimidine ring in the interlayer space of the bentonite. The value of 13.7 Å suggests an inclined arrangement of the pyrimidine ring in montmorillonite. Serratosa [23] suggested that the 12.5 Å value of pyridine treated montmorillonite indicates the parallel arrangement of the pyridine ring and Farmer and Mortland [24] suggested the 13.8 Å spacing for the tilted pyridine ring within the basal spacing of montmorillonite.

## Atrazine (AT)

### IR studies

- The spectra of atrazine treated bentonite shows changes in the 1500–1600 cm$^{-1}$ region as compared to crystalline atrazine. Similar changes were observed in the spectra of atrazine treated soil clay [30] and in atrazine treated montmorillonite [31] and were suggested to be due to the protonation of atrazine. A band at 1740 cm$^{-1}$ observed in the spectrum of atrazine adsorbed on H-montmorillonite from an aqueous solution of atrazine adjusted to pH 3.5 was assigned to the stretching of the carbonyl group of hydroxy atrazine which was formed as a result of protonation of atrazine followed by hydrolysis on the clay surface [32]. No such band is observed in the present study of adsorption of atrazine on bentonite. The other obvious change observed in the spectrum of atrazine as a result of hydrolysis was the decrease in the frequency of the CH wagging band from 800 cm$^{-1}$ to 760 cm$^{-1}$ [5, 32]. No change in the frequency of the band at 800 cm$^{-1}$ is observed in the spectra of atrazine treated bentonite. On the basis of these observations it is suggested that atrazine is adsorbed on the bentonite by protonation and/or hydrogen bonding with exchangeable cations but no degradation to hydroxyatrazine is observed.

- The infrared spectra of atrazine treated montmorillonite shows similar changes in the 1500–1600 cm$^{-1}$ region as were observed in the spectrum of the atrazine-bentonite complex. The shoulder at about 1667 cm$^{-1}$ is more obvious as compared to the spectrum of atrazine treated bentonite. There is no sign of hydrolysis of the adsorbed atrazine because no band is observed in the 1740 cm$^{-1}$ position and a band at 800 cm$^{-1}$ is present. Therefore it can be suggested that atrazine is adsorbed on montmorillonite by protonation and/or hydrogen bonding.

- The striking feature observed in the spectrum of atrazine treated kaolinite is the presence of a weak band at 1740 cm$^{-1}$ and a broad band at 3308 cm$^{-1}$. The presence of these bands indicates that the adsorption of atrazine on kaolinite involves the hydrolysis of atrazine [32].

- The obvious changes observed in the spectra of atrazine treated humic acid are the relatively broadened and increased intensity of the 1617 cm$^{-1}$ band and a decrease in the intensity and frequency of the OH bands from 3426 cm$^{-1}$ in the original humic acid to 3402 cm$^{-1}$ in the atrazine treated humic acid. A band at 800 cm$^{-1}$ is observed in the atrazine-humic acid complex spectrum which suggests that atrazine is not hydrolyzed. These changes suggest that atrazine is adsorbed on humic acid by interacting with the C=O and OH groups by hydrogen bonding and/or by protonation.

- The infrared spectra of air dried soil (AS), carbonate and soluble salts free soil (CSS) and organic matter free soil (OMS) and their atrazine treated samples are illustrated in Figure 3. The spectra of atrazine treated soil samples show changes in band positions in the region of 1500–1600 cm$^{-1}$ as compared to the bands observed in the crystalline atrazine. No band is observed in the 1740 cm$^{-1}$ region and no change occurred in the CH waging 800 cm$^{-1}$ band position on adsorption of atrazine on these soil samples. These results are similar to those observed by Brown and White [30] on adsorption of atrazine on soil clay. The changes in the 1500–1600 cm$^{-1}$ region in the atrazine treated soil
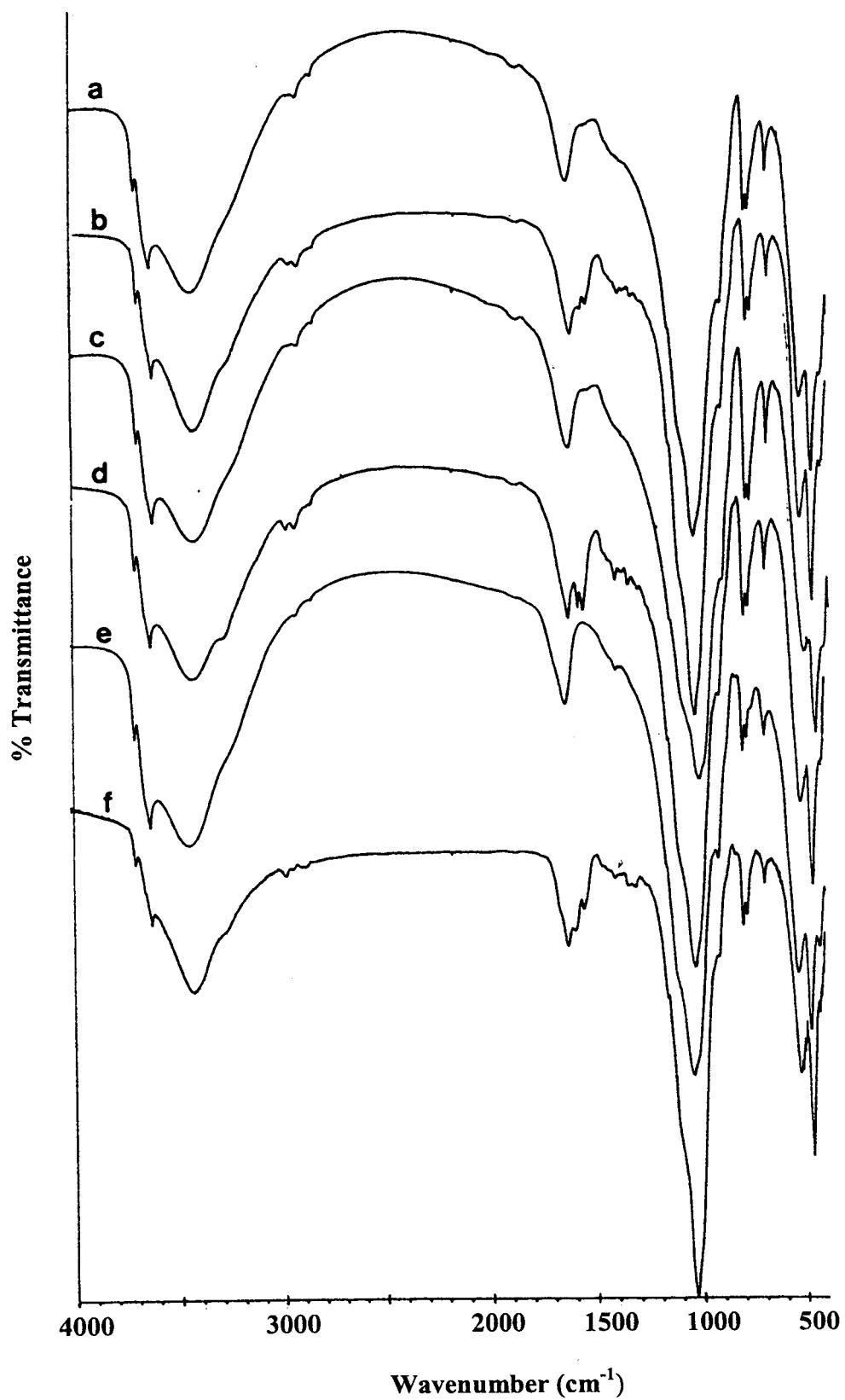
*Figure 3.* Infrared spectra of (a) AS, (b) atrazine treated AS, (c) CSS, (d) atrazine treated CSS, (e) OMS, (f) atrazine treated OMS.

samples suggests that atrazine is adsorbed on the soil by protonation or hydrogen bonding.

*TGA studies*

The TGA curves obtained for the atrazine bentonite system are shown in Figure 2 with three weight loss regions. The weight losses in the AT desorption region were 6%, 8%, 2%, 3%, 2.5% and 2% for bentonite, montmorillonite, kaolinite, AS, CSS and OMS respectively.

The amount of atrazine desorbed from the clay minerals bentonite and montmorillonite obtained from HPLC analysis is smaller as compared to the amount obtained by TGA analysis (Table 2) which suggests that during the desorption experiment atrazine was not totally desorbed due to the presence of the strongly adsorbed protonated atrazine. No marked difference was observed in the adsorption of atrazine on different soil samples. This suggests that all the soil constituents contribute to the total adsorption of the atrazine and the clay minerals play a major role in the adsorption of atrazine on this type of soil.

*XRD studies*

Increases in the basal spacings were observed for bentonite and montmorillonite but not for kaolinite (Table 3), indicating that the IR and TGA observations are due to surface adsorption on kaolinite.

The values observed for the d(001) basal plane spacing of the atrazine treated bentonite and montmorillonite are 13.3 Å and 13.5 Å respectively. Cruz *et al.* [31] observed similar values for the d(001) plane due to the intercalation of hydroxypropazine into the layers of montmorillonite.

Considering the d(001) plane values observed in the case of 3-chloropyridine and 2-chloropyrimidine it can be suggested that the atrazine ring is oriented parallel to the surface of the silicate layers of both bentonite and montmorillonite.

## Conclusions

3-Chloropyridine was adsorbed on the clay minerals, bentonite and montmorillonite, and on soil due to the protonation of 3-chloropyridine and by hydrogen bonding through water molecules with the exchangeable cations. No interaction with kaolinite was observed. 3-Chloropyridine interacted with the COOH group of humic acid through hydrogen bonding. Adsorption was stronger on clay minerals as compared to the organic matter.

2-Chloropyrimidine interacted through hydrogen bonding and ion exchange mechanisms with bentonite and montmorillonite. Interaction with humic acid is either due to very weak hydrogen bonding or van der Waals forces. Adsorption on soil occurred due to hydrogen bonding.

Atrazine was adsorbed on bentonite, montmorillonite, humic acid and soil by protonation and through hydrogen bonding. Hydrolysis of atrazine occurred on the surface of kaolinite. Clay minerals in soil play a major role in the adsorption of atrazine.

All the model compounds and the pesticide were intercalated into the layers of bentonite and montmorillonite.

Comparison of the above results with those reported previously for isoproturon adsorption [1] indicates the following differences:

The infrared spectroscopic data for adsorption of isoproturon on bentonite and montmorillonite indicated weak interaction mainly due to hydrogen bonding. The adsorption of atrazine included a hydrogen bonding mechanism as well as protonation. However, both of these pesticides were not completely desorbed. This was due to their intercalation into the interlayers of bentonite and montmorillonite as shown by the X-ray diffraction study.

Isoproturon was bonded with the kaolinite surface through hydrogen bonding while adsorption of atrazine was mainly due to an ion exchange mechanism. Therefore, desorption of isoproturon was higher than the desorption of atrazine.

Adsorption of both the pesticides on AS, CSS and OMS soil samples was due to hydrogen bonding. The amount of adsorption and desorption of isoproturon and atrazine on AS and CSS soil samples is almost the same but is greater for isoproturon on the OMS soil sample.

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