

# Sorption Behavior of Triazole Fungicides in Indian Soils and Its Correlation with Soil Properties

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Adsorption–desorption of triazole fungicides, hexaconazole [2-(2,4-dichlorophenyl)-1-(1H-1,2,4,-triazol-1-yl) hexan-2-ol], triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butan-2-one], and penconazole[1-(2,4-dichloro- $\beta$ -propyl phenethyl)-1H-1,2,4-triazole] was studied in five Indian soils using batch method. The adsorption isotherms fitted very well to the Freundlich equation. Adsorption of various triazole fungicides increased in this order: triadimefon > hexaconazole > penconazole. The product of the Freundlich adsorption constants,  $K_i(1/n)$ , showed good correlation with the soil organic carbon (OC) content, suggesting that soil OC is the main controlling factor for triazoles adsorption. Clay and silt content of the soil also affected the adsorption constants. Adsorption of hexaconazole and triadimefon was nearly reversible in two low OC soils (soil 3, soil 5) where 90–100% of the sorbed fungicides was released in a single washing step. Otherwise, desorption of triazole fungicides showed hysteresis, and 30–60% of the triazole fungicides were retained by the soil after single washing. IR spectra showed that H-bonds and charge-transfer bonds between humic acid and fungicides probably operated as mechanisms of adsorption.

### KEYWORDS: Hexaconazole; triadimefon; penconazole; adsorption; desorption; organic carbon; humic acid

## INTRODUCTION

Fate of xenobiotics has become a major concern in defining the quality of our environment. Contamination of surface and groundwater by soil applied pesticides occurs through runoff and leaching processes, respectively. Both these processes are greatly affected by the interaction between the pesticide and the soil components, frequently described as adsorption or simply as adsorption (1). Adsorption—desorption properties of soil applied pesticides consequently determine the behavior of the pesticide in the environment. Better understanding of adsorption and factors affecting it make it possible to adjust the pesticide application dose according to soil properties, thus reducing environmental pollution due to pesticide use (2).

Triazole fungicides are widely used on cereals, plant, and ornamental crops (3-6) (**Figure 1**). These fungicides have been reported to have broad spectrum of activity and provide protection in any of the disease situation i.e., have protective, curative, and eradicant action. However, a possible cause of concern is their long persistence in soil (7-12), which may lead to accumulation following repeated application or to leaching to acquifers and drains. Bromilow et al. (11) reported that in a field trial fungicides triademenol, flutriafol, and epoxyconazole were very persistent with  $DT_{50} > 400$  days while propioconazole had  $DT_{50}$  of 200 days. Information on the adsorption behavior of triazole fungicides is very limited. As assessed by Jamet and

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Eudeline (13), using soil thin-layer chromatography of 17 triazole fungicides, these compounds are moderately lipophilic so moderately to strongly sorbed to soil. Generally these fungicides have not been detected in water supply, although triadimefon, when used at very high rates under irrigation, led to triadime fon concentration up to  $616 \,\mu$ g/L in the leachate (14). Bromilow et al. (9) studied adsorption and transport of flutriafol, epoxiconazole, propioconazole, and triadimefon and reported that flutriafol was the least sorbed and leached up to 20 cm depth and others were detected only up to 10 cm depth. Adsorption of triadimefon to thatch and a silty clay loam soil was determined (15). The Freundlich adsorption coefficients normalized to organic carbon (OC) content of soil and thatch were similar; therefore, it was concluded that triadimefon is mainly sorbed on organic matter. Celis et al. (16), who studied adsorption of triadimefon on soils and model soils, suggested that both clay (montmorillonite-type) and organic matter (humic acid) were important for triadimefon adsorption.

In India, of various triazole fungicides, hexaconazole [2-(2,4dichlorophenyl)-1-(1H-1,2,4,-triazol-1-yl) hexan-2-ol], triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butan-2-one], and penconazole[1-(2,4-dichloro- $\beta$ -propyl phenethyl)-1H-1,2,4-triazole] have been registered for crop protection. Earlier, we have shown that hexaconazole is moderately persistent in Indian soils (12), but no information is available on the adsorption behavior of these fungicides under tropical environmental conditions. Therefore, experiments were planned with the following objectives: (a) to determine and compare Hexaconazole







Penconazole

Figure 1. Chemical structures of triazole fungicides.

Table 1. Physicochemical Properties of the Soils Used

classification	soil	рН <sup>а</sup>	organic <sup>b</sup> carbon (%)	clay (%)	silt (%)	sand (%)
Inceptisol	soil 1	8.0	$\begin{array}{c} 0.5 \pm 0.05 \\ 0.6 \pm 0.04 \\ 0.3 \pm 0.07 \\ 0.8 \pm 0.03 \\ 0.4 \pm 0.06 \end{array}$	12	9	78
Alfisol	soil 2	5.9		24	11	65
Vertisol	soil 3	7.8		30	26	44
Vertisol	soil 4	7.7		37	24	39
Inceptisol	soil 5	7.5		13	15	76

<sup>a</sup> Soil pH was determined at 1:1.25 (w/v) soil-to-water ratio. <sup>b</sup> Determined by the Walkley and Black method.

adsorption isotherms of hexaconazole, triadimefon, and penconazole fungicides in five soils with different physicochemical properties and (b) to determine the adsorption mechanism of these fungicides on humic acid.

#### MATERIALS AND METHODS

**Soils.** Five soils from different agro-climatic regions of India were used in the study (**Table 1**). The soils were collected from 0 to 15 cm depth, air-dried and sieved to pass through 2 mm sieve.

**Fungicides.** Compounds were supplied by the manufacturers, hexaconazole (>95% purity) by Rallis India, triadimefon (>99% purity) by Bayer India while penconazole (>96% purity) by Ciba-Geigy.

Adsorption–Desorption Experiment. Adsorption isotherms were obtained by batch method at 1:5 soil:water ratio. To 5 g portions of soil (oven dry weight equivalent) in 50 mL glass centrifuge tubes was added a 25 mL 0.01M CaCl<sub>2</sub> solution of hexaconazole, triadimefon, or penconazole. The CaCl<sub>2</sub> (0.01 M) was used as the background electrolyte. The initial concentration of fungicides ranged between 4 and 16  $\mu$ g/mL for hexaconazole and penconazole and between 4 and 20  $\mu$ g/mL for triadimefon. The concentrations used were below their aqueous solubility at room temperature. The soil–water slurry was shaken for 4 h on a end over shaker. Initial studies had shown that equilibrium was attained after 4 h of shaking. After equilibration soil slurry was centrifuged at 5000 rpm for 10 min, and the concentration

of triazole fungicides was determined in the supernatant. The decrease in the concentration of triazole fungicide in supernatant was taken as the amount of fungicide sorbed by the soil. The mass balance calculations indicated that there is no evidence of loss of triazole fungicide during the period of equilibration. Five different concentrations of each fungicide were used, and each concentration was replicated three times.

Desorption was studied in the same soils as used for adsorption. After adsorption, the supernatant was decanted and was replaced with 25 mL of fresh 0.01 M CaCl<sub>2</sub> solution. Soil-water suspension was again shaken on end over shaker for 4 h and centrifuged, and the supernatant was analyzed for triazole fungicide. The amount of fungicide desorbed was calculated by subtracting the amount of fungicide in the entrapped solution after adsorption experiment from the solution concentration measured after the desorption experiment. Only one desorption was performed on each sample.

Adsorption and desorption data were fit to the linearized Freundlich equation

$$\log x/m = \log K_{\rm f} + 1/n \log C$$

where x/m is the amount adsorbed ( $\mu g/g$ ),  $K_f$  and 1/n are empirical Freundlich constants, and *C* is the equilibrium concentration ( $\mu g/mL$ ).  $K_f$  represents the degree of adsorption, and 1/n takes into account the nonlinearity in the adsorption or desorption isotherm.

The distribution coefficient ( $K_d$ ) was calculated by the linear fit of the adsorption points. The  $K_{oc}$  values were calculated by normalizing adsorption constant  $K_d$  with the OC content of the soil

$$K_{\rm oc} = K_{\rm d} / \% \text{ OC} / 100$$

Simple and multiple correlation were worked out between  $K_{\rm f}(1/n)$  as the adsorption parameter and the characteristics of the soils using statistical graphic system. The significance of the regression equations was judged by *t*-values.

Experiment on Adsorption Mechanism. Adsorption mechanism of triazole fungicides was studied using humic acid (HA) prepared by acid hydrolysis (1N HCl) of sodium salt of humic acid (purchased from Aldrich Chemicals). Fungicide-HA interaction products were obtained (17) by equilibrating 50 mg of HA with 50 mL of 20  $\mu$ g/mL aqueous solution of hexaconazole, triadimefon, and penconazole on mechanical shaker for 24 h at room temperature ( $32 \pm 2$  °C). After centrifugation of fungicide-HA interaction products at 5000 rpm for 10 min, the supernatant was replaced with 50 mL of fresh fungicide solution. Contents of centrifuge tube were further equilibrated for 24 h, and subsequently the fungicide-HA complex was separated by centrifugation. The fungicide-HA interaction product was washed twice with distilled water, dried, and lyophilised. Fungicide, HA, and fungicide-HA interaction products were characterized by FT-IR (Nicolet 400 Spectrometer). FTIR spectra were recorded using KBr pellet obtained by pressing uniformly prepared mixture of 1 mg sample and 100 mg KBr under vacuum.

**Extraction and Analysis of Triazole Fungicides.** For residue analysis, 2 mL of supernatant, each after adsorption and desorption, was extracted with 4 mL of ethyl acetate by vigorously shaking the content in test tube (15 mL capacity) for 1 min. Organic and aqueous layers were allowed to separate, and 1 g of anhydrous sodium sulfate was added to each tube to remove any trace of moisture from ethyl acetate. Residues in the ethyl acetate fraction were quantified by gas–liquid chromatography on a Hewlett-Packard model 3480 GC, equipped with Ni<sup>63</sup> electron capture detector (ECD) and fitted with HP-1 column (10 m × 0.50 mm id × 2.53  $\mu$ m film thickness). The operating conditions were as follows: column 210 °C, injector 250 °C, detector 250 °C, carrier gas (nitrogen) flow rate 45 mL/min. The recovery of this method for all three triazole fungicides was >90%.

#### **RESULTS AND DISCUSSION**

Adsorption Isotherms. Adsorption isotherms for hexaconazole, triadimefon, and penconazole in the soils are presented in Figure 2. All adsorption data fitted very well to Freundlich



Figure 2. Adsorption isotherms of hexaconazole, triadimefon, and penconazole in soils.

<b>Table 2.</b> Freundlich Constants ( $K_{f}$ , $1/n$ , $r$ ), Distribution Constant $K_{d}$ ,
and $K_{oc}$ Values of Hexaconazole, Triadimeton, and Penconazole
Adsorption in Soils

fungicide	soil	K <sub>f</sub>	1/ <i>n</i>	r	K <sub>d</sub>	K <sub>oc</sub>
Hexaconazole	soil 1	1.82(0.01) <sup>a</sup>	0.93(0.02) <sup>a</sup>	0.99	1.70(0.06) <sup>a</sup>	364
	soil 2	1.94(0.02)	1.10(0.04)	0.99	2.46(0.13)	323
	soil 3	1.39(0.03)	0.85(0.06)	0.99	1.18(0.02)	348
	soil 4	1.95(0.02)	1.20(0.04)	0.99	2.48(0.10)	244
	soil 5	1.31(0.02)	1.02(0.03)	0.99	1.38(0.02)	328
Triadimefon	soil 1	1.33(0.04)	0.92(0.07)	0.99	1.31(0.07)	266
	soil 2	1.65(0.03)	0.93(0.05)	0.99	1.42(0.04)	275
	soil 3	1.26(0.02)	0.87(0.05)	0.99	1.04(0.06)	315
	soil 4	1.61(0.03)	0.95(0.06)	0.99	1.41(0.07)	201
	soil 5	0.45(0.06)	1.04(0.10)	0.98	0.53(0.04)	133
Penconazole	soil 1	2.34(0.03)	0.97(0.06)	0.99	2.18(0.16)	468
	soil 2	2.38(0.00)	0.91(0.00)	0.99	2.10(0.02)	397
	soil 3	1.40(0.01)	1.02(0.02)	0.99	1.45(0.03)	350
	soil 4	2.76(0.02)	0.97(0.03)	0.99	2.72(0.13)	345
	soil 5	2.58(0.03)	0.98(0.04)	0.99	2.47(0.10)	645

<sup>a</sup> Figure in parentheses are the respective standard error.

adsorption isotherm, as evident by the very high correlation coefficient values (r > 0.98). The adsorption constants  $K_{f_{ads}}$  and  $1/n_{ads}$  calculated from Freundlich equation are presented in **Table 2**.  $K_{f_{ads}}$ , which represents the amount of fungicide adsorbed at an equilibrium concentration of 1  $\mu$ g/mL, gives an estimate of the extent of adsorption at this concentration, while  $1/n_{ads}$  represents the variation in adsorption with concentration of pesticide.

In general,  $1/n_{ads}$  values for hexaconazole, triadimefon, and penconazole were near 1 or less than 1 except in few cases, indicating the C- or L-type of adsorption isotherms (18). L-type adsorption isotherms are characterized by the strong interaction between adsorbent and adsorbate and adsorption decreases as the aqueous concentration of pesticide increases. However, in a few cases (hexaconazole in soil 2 and soil 4), adsorption isotherms were S-type. These types of isotherms are commonly found in the literature and involve the interaction of the organic compounds having polar groups with the soil and their components. These interactions are characterized by the strong competition between water molecule and the pesticide for the adsorption sites at low pesticide concentration and or molecular interaction between the sorbed species. In the present study, hexaconazole which contains a hydroxyl group shows S-type adsorption isotherm in soils 2 and 4, indicating that the nonlinearity of the adsorption isotherm is probably due to the interaction of hydroxyl group of hexaconazole with the organic or mineral fraction of the soil.

 $K_{f_{ads}}$  values ranged between 1.31 and 1.95 for hexaconazole, 0.45 and 1.65 for triadimefon, and 1.40 and 2.76 for penconazole. The highest  $K_{f_{ads}}$  value for a particular fungicide corresponds to soil containing relatively high OC content (soil 2 and soil 4). However, soil 5 is an exception, which showed high adsorption for penconazole. In general, adsorption values were higher for penconazole, followed by hexaconazole and triadimefon, respectively, indicating that penconazole is the maximum sorbed fungicide while triadimefon is the least sorbed.

To compare  $K_{f_{ads}}$  values of a fungicide in different soil types, the  $1/n_{ads}$  (slope) values should be statistically equivalent otherwise the comparison becomes meaningless. Due to observed variation in the  $1/n_{ads}$  values,  $K_d$  distribution coefficient values were also calculated by linear fit.  $K_d$  values were lower than the corresponding  $K_{f_{ads}}$  value, except for soils where S-type adsorption isotherms were observed.  $K_d$  values followed the same trend as that observed for the  $K_f$  values.

The correlation of adsorption constant  $K_{f_{ads}}$  with soil properties can be used to predict the adsorption of pesticide in different soils or to help in determining the factors responsible for adsorption. But  $1/n_{ads}$  is also an important coefficient for description of adsorption isotherms. Isotherms can change greatly with change of  $1/n_{ads}$ . Therefore, as suggested by earlier workers (17),  $K_{\rm f}(1/n)$  was selected as a parameter of adsorption. The simple and multiple correlation between  $K_{\rm f}(1/n)$  and the soil properties were calculated. A significant positive correlation was observed between soil OC content and the adsorption constants  $K_{\rm f}(1/n)$  for hexaconazole and triadime fon (Table 3). On the basis of a determination coefficient  $(r^2)$  about 86% variation for correlation between OC and adsorption constants of hexaconazole was accounted for by the OC content of the soil. Similarly for triadimefon adsorption, OC alone accounted for 76% variation in the adsorption coefficient. But due to the different behavior of soil 5, correlation between OC and the adsorption constant for penconazole was not significant. When soil 5 was excluded from the correlation analysis, it gave very high correlation between adsorption constants and the OC content, and it alone accounted for the 78% variation for penconazole adsorption. Koc values were calculated by normal-

**Table 3.** Correlation Coefficient of  $K_{\rm f}(1/n)$  with Soil Parameters for Triazole Fungicides

fungicide	рН	OC	clay	silt	clay + silt
Hexaconazole Triadimefon Penconazole	-0.417 -0.342 -0.056	0.930 0.869 0.402 0.886 <sup>a</sup>	0.648 0.683 0.071	0.975 0.047 —0.281	0.974 0.869 –0.091

<sup>a</sup> Soil 5 was excluded from the correlation analysis.

**Table 4.** Multiple Regression Analysis of  $K_1(1/n)$  with Soil Parameters for Triazole Fungicides

		t value		
fungicide	regression equation	00	clay/silt	r <sup>2</sup>
Hexaconazole Triadimefon Penconazole	$\begin{array}{l} 0.747 + 2.539 \ (\text{OC}) - 0.019 \ (\text{silt}) \\ 0.224 + 2.013 \ (\text{OC}) - 0.006 \ (\text{silt}) \\ 0.773 + 3.506 \ (\text{OC}) - 0.025 \ (\text{clay}) \end{array}$	6.17 2.55 7.45	1.88 0.29 3.35	0.950 0.791 0.982

izing the distribution coefficient to OC content of the soil. This normalization assumes that OC content is the primary component of soil controlling adsorption. Compared to  $K_d$ , variation in  $K_{oc}$  values of a particular triazole among different soils is less. In each case 188–268% variation in  $K_d$  was reduced to 136–206% variation in  $K_{oc}$  by referring adsorption to OC. This indicates that soil OC content is mainly responsible for the adsorption of triazole fungicides in soils. However, soil 5 showed very high  $K_d$  and  $K_{oc}$  values for penconazole. The  $K_d$ and  $K_{oc}$  values obtained for triadimefon are in agreement with the values obtained by the earlier workers (11, 13, 16, 19).

Present study indicates that OC content is the single largest parameter, which affects the adsorption of triazole fungicides. However, other soil parameters may have also affected the adsorption of triazole fungicides. Adsorption of all the triazole fungicides was negatively correlated with the soil pH, although the correlation was very poor. Soil clay and silt contents also showed some correlation with the fungicide adsorption constants. The adsorption data were subjected to multiple regression analysis (**Table 4**) by combining two or more variables to understand the relative importance of soil parameters simultaneously. Results indicate that although the soil OC content is

the single largest parameter contributing to the variation in the adsorption of triazole fungicides. However, silt and clay content also affected the adsorption constant. The best fitted regression equations for hexaconazole, triadimefon, and penconazole, along with the corresponding t values, are represented in **Table 4**. In case of penconazole, t values indicate that clay content played an important role in the adsorption of penconazole in the soils. The relative contribution of the OC and clay toward variability in the adsorption are in the ratio of 70:30. The determination coefficient  $(r^2)$  obtained in this case affords a higher variation in adsorption (98%) than the single coefficient obtained when the OC alone was considered. Similarly, silt content contributed significantly toward the adsorption of hexaconazole and triadimefon. OC plus silt content together contributed about 79% and 95% variability in the adsorption of triadimefon and hexaconazole, respectively.

The gradually increasing slope of the multiple regression equations in the order penconazole > hexaconazole > triadimefon also indicates that in a particular soil, penconazole had the highest adsorption, followed by hexaconazole and triadimefon, respectively. Generally, adsorption of pesticides is positively correlated with octanol—water partition coefficient and negatively correlated with their water solubility. Among the triazole fungicides used in the present study, penconazole has maximum water solubility and therefore should be least sorb triazole. On the other hand hexaconazole, which has highest octanol—water partition coefficient, registered intermediate adsorption.

**Desorption Isotherms.** Freundlich constants for desorption of hexaconazole, triadimefon, and penconazole (**Figure 3**) were presented in **Table 5**. Reversibility of adsorption plays an important role in determining the mobility of the compounds in the soil profile. The amount desorbed by the single desorption was quantified and was expressed as the percent of the amount sorbed. Adsorption of hexaconazole was completely reversible in soil 3 and soil 5, and nearly 100% of the sorbed fungicide was desorbed in single washing. On the other hand, only 52–64% of hexaconazole was desorbed from the other three soils. Like hexaconazole, nearly 90% of triadimefon was desorbed from soil 3 and soil 5, while soil 1, soil 2, and soil 5 desorbed 40%, 53%, and 54% of triadimefon, respectively. The amount of penconazole desorbed from different soils varied from 46%



Equilibrium concentration (log µg/ml)

Figure 3. Desorption isotherms of hexaconazole, triadimefon, and penconazole in soils.

 Table 5.
 Freundlich Desorption Constants for Hexaconazole,

 Triadimefon, and Penconazole in Soils

Fungicide	soil	Kf	1/ <i>n</i>	r	1/n <sub>des</sub> /1/n <sub>ads</sub>
Hexaconazole	soil 1	1.76(0.05) <sup>a</sup>	1.10(0.10) <sup>a</sup>	0.997	1.18
	soil 2	3.09(0.07)	1.21(0.14)	0.981	1.10
	soil 4	1.77(0.05)	2.18(0.15)	0.995	1.82
Triadimefon	soil 1	2.89(0.02)	1.42(0.05)	0.986	1.54
	soil 2	2.84(0.03)	0.88(0.06)	0.996	0.95
	soil 3	0.31(0.06)	1.13(0.12)	0.997	1.30
	soil 4	2.50(0.02)	1.03(0.04)	0.987	1.08
	soil 5	0.27(0.17)	1.15(0.36)	0.996	1.11
Penconazole	soil 1	3.74(0.04)	0.92(0.09)	0.996	0.95
	soil 2	1.44(0.07)	1.23(0.17)	0.980	1.35
	soil 3	1.81(0.02)	0.63(0.04)	0.989	0.62
	soil 4	2.21(0.03)	1.60(0.14)	0.999	1.62
	soil 5	1.60(0.02)	1.35(0.05)	0.990	1.38

<sup>1</sup> Figure in parentheses are the respective standard error.

to 70%. There was no significant difference in the amount of hexaconazole, triadimefon, and penconazole desorbed from soil 1, soil 2, and soil 4. However, soil 3 and soil 5 behaved differently, as adsorption was nearly reversible only for hexaconazole and triadimefon while considerable amount of sorbed penconazole was retained in the soil matrix after desorption. It is evident from the soil properties that these two soils have very low OC content. In soils having very low OC content, mineral fraction plays a significant important role.

The Freundlich  $1/n_{des}$  values take into account the nonlinearity in the desorption isotherms and is the index of the intensity of desorption. In the present study, in general,  $1/n_{des}$  values were higher than the  $1/n_{ads}$  values, indicating that the rate of desorption is higher than the rate of adsorption showing hysteresis. The hysteresis (*H*) was quantified using  $(1/n_{des})/((1/n_{ads}))$ ratio is more than 1, while it is positive when the  $(1/n_{des})/((1/n_{ads}))$   $(1/n_{ads})$  ratio is less than one. Generally, desorption for all the fungicides showed negative hysteresis except for penconazole in soil 3, where very strong positive hysteresis was observed (H = 0.62).

Adsorption Mechanism. Humic acid (HA) is one of the main component of the soil organic matter and therefore contributes significantly toward the adsorption of pesticide molecules. Figure 4 represents the FT-IR spectra of pure fungicide, HA, and HA-fungicide interaction complex. Probably due to very small loading of the fungicide in the HA-Fun complex, there is no additional peak in the FT-IR spectra of the interaction complex. The FT-IR spectra of the HA-interaction product and HA are the same in the higher region (>2000  $\text{cm}^{-1}$ ). However, there are few prominent changes in the spectra of HA-fungicide complex over the pure HA in the lower region ( $<2000 \text{ cm}^{-1}$ ). In general, C=O stretching vibration in pure HA at  $1710 \text{ cm}^{-1}$ has broadened and shifted to higher wavenumber in the HAhexaconazole (1723 cm<sup>-1</sup>), HA-triadimefon (1712 cm<sup>-1</sup>), and HA-penconazole 1723 cm<sup>-1</sup>) complexes. This shift in the C=O stretching vibration of carboxyl group of HA indicates that carboxyl group interacts with the suitable moiety in the fungicide molecule. The C=O stretching of carbonyl group in pure triadimefon at 1723 cm<sup>-1</sup> is shifted in the HA-triadimefon complex and merges with the C=O stretching of carboxyl group of HA to give a peak at 1712 cm<sup>-1</sup>. Another important observation in the interaction spectra is the change in the intensity of the peaks. The intensity of the peaks in the region 1450–1350 cm<sup>-1</sup>, corresponding to aromatic C=C stretching, has increased. The peak intensity may have change due to the formation of charge-transfer bonds between the activated electron donor aromatic ring of HA and the deactivated electron acceptor aromatic nucleus of triazole (it is evident from the structure of triazole fungicides that aromatic ring is substituted by electron-withdrawing chloro groups). Similarly, change in



Figure 4. FT-IR spectra of pure triazole (a), pure humic acid (b), and humic acid-triazole (c) interaction product.

Adsorption desorption studies of hexaconazole, triadimefon, and penconazole indicate that the triazole fungicides are moderately sorbed in the low OC content Indian soils. The isotherms fitted the Freundlich equation well. The extent of adsorption followed the order: triadimefon > hexaconazole > penconazole. Linear regression analysis of adsorption constants and soil properties showed that the product of  $K_f(1/n)$  has a good correlation with OC; therefore, OC is the main parameter of soil that dominates the adsorption process. Penconazole, which showed maximum adsorption and minimum desorption, appears to be comparatively safe fungicide than hexaconazole and triadimefon. IR spectra suggested that H-bond and chargetransfer bonds were the main adsorption mechanism of the triazole fungicides with HA.

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