

## Sorptive Interactions of Fungicidal 2-(4'-Thiazolyl) Benzimidazole with Soils of Divergent Physicochemical Composition

Mehtabidah Ali, Shaan Bibi Jaffri, Khuram Shahzad Ahmad\*, Shahid Iqbal

Environmental Sciences Department, Fatima Jinnah Women University, Rawalpindi, Pakistan

\*Email: [dr.k.s.ahmad@fjwu.edu.pk](mailto:dr.k.s.ahmad@fjwu.edu.pk)

Received: 4 March, 2019

Accepted: 24 April, 2019

**Abstract:** Thiabendazole, 2-(4'-thiazolyl) Benzimidazole fungicide is rampantly used in Pakistan for controlling fungal growth in addition to combating various fungus driven diseases. Thiabendazole leaching and mobility patterns can be easily predicted through investigation of Thiabendazole adsorption and desorption behavior in soils. Present work is carried out by conducting a batch equilibration experiment for evaluation of Thiabendazole adsorption and desorption in soils from four diverse Pakistani climatological regions. Data revealed Thiabendazole had moderate to weak adsorption in selected soils with distribution co-efficient  $K_{d(ads)}$  ranging from 13.33 to 24.04  $\mu\text{g/ml}$  in selected soils. The TBZ adsorption in soils best fitted with Freundlich model ( $R^2 > 0.87$ ). The Freundlich adsorption coefficient ( $K_{f(ads)}$ ) values ranged from 4.51 to 8.90  $\mu\text{g/ml}$ . Thiabendazole adsorption trends in the selected soils were positively influenced by the clay content and soil organic matter while it was negatively influenced by soils' pH. The Freundlich desorption coefficient ( $K_{f(des)}$ ) values spanned over a range of 1.03 to 6.43  $\mu\text{g/ml}$  indicating decreased desorption from soils with creditable affinities for Thiabendazole adsorption. The adsorptive interactions between Thiabendazole and selected soils were primarily physical confirmed through lower values of Gibbs free energy  $\Delta G \leq -40\text{kJ/mol}$ . Thiabendazole desorption was highly hysterical in all soils with profound irreversibility. Thiabendazole possessed medium mobility patterns in selected soils. The lower adsorptive capability of Thiabendazole in selected soils points towards its lower application rates for combating long term environmentally perilous implications.

**Keywords:** Thiabendazole, soil, organic matter, adsorption, Freundlich model, mobility.

### Introduction

Due to economic gains and good agricultural output, the use of pesticides has intensified worldwide.  $2.4 \times 10^6$  tons of large variety of pesticides is applied on  $1.6 \times 10^9$  ha of cultivated region every year throughout the world. Therefore, the global average use of these chemicals is about 1.53 kg/ha annually. Where crop yield improved by pesticides and fertilizers use is an established fact, we also face the dire challenges of food and environmental contamination due to their use. Consequently, this contamination can again become reason for worldwide shortage of agriculture based nutritional goods (Liu et al., 2015). After exploring its potential for agricultural growth, Pakistan has been the major utilizer of agrochemicals including pesticides for controlling pests. Since Pakistani soils are fertile and suitable for growth of many groups but at the same time agriculture activities and soils are exposed to different pests and contaminants. Myriad of approaches have been adopted for the remediation of pesticides and other contaminants, (Iram et al., 2019; Iram et al., 2019a, b; Ifthikhar et al., 2019; Ifthikhar et al., 2018), however, achievement of higher efficiencies remains an issue, due to which minimal use of all pesticides is recommended. In 1954, the agrochemicals were used for the first time and to date this use had elevated to 254 metric tons. There was a transfer of pesticide related matters e.g. manufacturing, sale and distribution of pesticides from public to the private sector in Pakistan. Due to increasing toxicity associated with the pesticides, there might be a shift towards the utilization of novel nano-pesticides aimed at

inhibition of different pathogenic bacterial and fungal strains that destroy export quality crops (Ahmad and Jaffri, 2018 a, b; Jaffri and Ahmad, 2017; Jaffri and Ahmad, 2018a-d). However, currently, the agricultural sector is making use of 30 different types of chemical fungicides and this trend is augmenting with passage of time. Their toxicity is notable for non-target organisms as well and their degradation pathways are complex therefore, they persist in all environmental compartments i.e. lithosphere, hydrosphere, atmosphere and biosphere and exert bio accumulative impacts (El Bakouriet al., 2009; Ghosh et al., 2015).

Benzimidazole based fungicides were used for plant protection and other fungus driven diseases in crops. They were used for the first time in 1960s. In early 1970s, foliar diseases and seed treatments were done with Benzimidazole fungicides. They were treasured for their efficiency in plant protection as compare to other conventional pesticides used at that time. Benzimidazole based fungicides are desirable for use due to their lower application rates, all-encompassing ranges and effectiveness for wiping out infection in advance of incidence causing an escalation in duration of spraying intervals. Thiabendazole, 2-(4'-thiazolyl) Benzimidazole (TBZ) (Figure 1) is member of class of organic chemicals Benzimidazole. As shown in Figure 1, chemical structure of Benzimidazole organic compound consist of aromatic ring joined with an imidazole ring. Like other Benzimidazoles, Thiabendazole can be used for combating post-harvest fungal infections in citrus fruits. Because of its ability of storage on surface tissues

without invading the fleshy inner part, Thiabendazole has been preferred as compare to other fungicides.

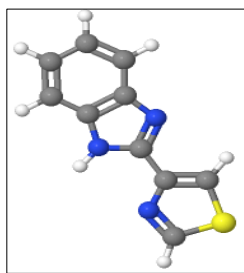


Fig. 1 Three-dimension (3D) structure of Thiabendazole fungicide

Adsorptive interactions between pesticides and soils have profound impact on the pesticide’s environmental fate, degradation and mobility in soil. Therefore, for the accurate estimation of these factors in addition to pesticide’s potential of leaching to the lower lithospheric compartments and groundwater reserves, adsorption and desorption studies are of prime significance. The strong adsorptive interactions between soil and pesticides causes a commendable decrease in degree of pesticide leaching to lower soil compartments and groundwater reserves, rather such adsorbed pesticides are lost with soils by means of erosion. Poor adsorption of pesticides onto the soils enhances the chances of pesticides percolation. Subsequently, the adsorptive interactions between soil and pesticides are the major factor for comprehension of pesticide behavior in soils particularly in terms of mobility (Ismail & Kalithasan, 2004). Sorptive interactions of different pesticides including TBZ is of prime interest for soil scientists, agronomists, nutritionists and environmentalists, since TBZ sprayed on crops for fungicidal activity is not completely received by the crops, rather it also invades the non-target regions, for example the immediate soils beneath those crops. Considering an extensive duration of time, such molecules will slowly and gradually reach the lower soil profiles and underground water reservoirs. The contamination of such lower soil profiles and water reservoirs cannot be remediated like surface soils. Hence, meticulous investigation of TBZ behavior in different soils is an urgent task. Since there is a wide scale application of pesticides but the reliable scientific data in this regard is scant (Ahmad et al., 2015), therefore for gaining an insight into the factors governing mobility of Thiabendazole in soils, this study is designed to achieve quantitative and qualitative extent of Thiabendazole adsorption. To the best of our knowledge, no investigative studies for adsorption and desorption of Thiabendazole have been done in Pakistan

despite its higher application rates. So the present studies are aimed at finding (i) adsorption and desorption of Thiabendazole (TBZ) in selected soils (ii) comprehending the impact of physicochemical parameters’ impact of adsorption and desorption of Thiabendazole in selected soils (iii) estimating the Thiabendazole mobility, physisorption/chemisorption and reversibility of adsorption and desorption process For TBZ sorptive interactions, the batch equilibrium experiment was conducted via UV-Visible spectrophotometer and values were used for isotherm development.

**Experimental**

**Chemicals:** Current study was conducted by utilizing different solvents and chemicals including 99.9% pure analytical grade C<sub>3</sub>H<sub>6</sub>O and CH<sub>4</sub>O. Anhydrous NaCl and CaCl<sub>2</sub> in powder form were also used. Analytical grade Thiabendazole was purchased from Fluka USA.

Table 1. Investigated physicochemical and textural properties of selected soils

Soil parameter	Soil 1	Soil 2	Soil 3	Soil 4
Label	A	B	C	D
pH	6.9	7.7	6.6	7.5
EC (dSm-1)	3.7	3.1	4.2	4
CEC (Meq/100g)	8.6	7.9	8.9	7.6
P (mg/kg)	4.5	5.3	5.2	6.2
K (mg/kg)	120	80	100	120
N (%)	0.0345	0.0265	0.0325	0.0295
OM (%)	7	2.4	3.7	1.3
TOC (%)	2.65	1.89	2.37	1.02
Silt (%)	23	43.19	40.93	27
Sand (%)	9	36.82	38.24	58
Clay (%)	68	19.99	20.83	11
Texture	Clay	Loam	Loam	Sandy loam

[EC: Electrical conductivity, CEC: Cation Exchange capacity, P: Phosphorus, K: Potassium, N: Nitrogen, OM: Organic matter, TOC: Total organic content]

**Soil sampling and preparation:** Soils were selected from four geographical regions with distinct climatological conditions. Soil was sampled at 0 – 6 cm depth in the month of March, April and May, 2017. Special care was taken in collection of samples from those regions where no pesticides have been primarily used, so that the lab based simulated results could only depict the behavior of TBZ without influence of other factors. Soil were obtained by means of an auger. Samples were collected in well sterilized polythene bags following systematic sampling procedure and transported to the laboratory. Soil samples were collected from four contrasting areas in Pakistan. The soil samples were air dried for about 24 hours. For achieving homogeneity, samples were mixed thoroughly. After complete drying, samples were disaggregated

Table 2. Thiabendazole Linear and Freundlich adsorption parameters in selected soils

Soil	K <sub>d(ads)</sub> (µg/ml)	R <sup>2</sup>	K <sub>OM</sub> (µg/m)	ΔG (kJ/mol)	S	K <sub>oc</sub> (µg/ml)	R <sup>2</sup>	S	K <sub>f(ads)</sub> (µg/ml)	K <sub>foc</sub> (µg/ml)	n <sub>a</sub>	1/n
A	24.04	0.86	222	-13.39	3.44	432	0.87	0.13	8.90	336	2.96	0.33
B	15.15	0.97	277	-13.93	1.25	404	0.97	0.52	6.59	349	1.78	0.56
C	17.14	0.90	220	-13.37	2.62	395	0.98	0.05	8.15	344	2.5	0.4
D	13.33	0.85	347	-14.49	0.88	592	0.93	0.06	4.51	442	1.60	0.63

manually, followed by disaggregation in pestle and mortar. Samples were passed through 40 $\mu$ m mesh size. Soil samples after preparation were exposed to the testing for different physical and chemical parameters. The obtained data is detailed in Table 1.

**Sorption studies of Thiabendazole Benzimidazole fungicide:** Sorptive interactions investigation between Thiabendazole and selected soils was done by standard method i.e. batch equilibration assay (OECD, 2000). Experimentation was carried out in the triplicates at the ambient temperature i.e. 25  $\pm$  1  $^{\circ}$ C. Thiabendazole Benzimidazole pesticide solutions were prepared in de-ionized water with 8 different concentration having 0, 0.25, 0.5, 0.75, 1.0, 2.5, 5.0 and 7.5 ppm. The reaction mixtures were added with the NaCl solution, this was done for improvement of centrifugation and minimization of cation-exchange. Centrifuge tubes of 15 ml Pyrex glass along with their caps were weighed. Centrifuge tubes were filled with 0.5 g of soils A, B, C and D and the caps were placed tightly. By keeping ratio at 1:20 for soils/Thiabendazole solution i.e. adsorbent/adsorbate, each centrifuge tube was filled with 10 ml of Thiabendazole standard solution separately from previously labelled volumetric flasks. Centrifuge tubes were placed inside Orbital shaker for 24hours shaking at 90 rpm at temperature (25  $^{\circ}$ C) for uniform mixing of Thiabendazole in four soils. 24 h shaking ensures the equilibrium between adsorbent and adsorbate. The adsorption was equilibrated by preparation of duplicate for each concentration and the blank samples devoid of adsorbent but comprising merely of the dissolved (Thiabendazole) + 0.1 M NaCl. This has been done for compensating for the losses that might have occurred during adsorption of Thiabendazole in soils separately. Centrifuge tubes were inserted in Sigma 2-6E centrifuge for 25 minutes at 25  $^{\circ}$ C and the rotation was set at 3000 rpm.

Decantation of centrifuge tubes was done by using 0.2  $\mu$ m membrane filters for filtration of soil water suspension. Clear aliquots were analyzed by UV-Visible spectrophotometer Bms-1602 at  $\lambda_{max}$  = 254 nm. pH of supernatant was measured in each tube. Since the phenomenon of desorption is reverse of adsorption, therefore same solutions of Thiabendazole were used for desorption analysis. Decantation of supernatant was done for maximum removal of liquid portion from centrifuge tubes. Centrifuge tubes along with the residual soil set at bottom mostly were weighed on weighing machine. The centrifuge tubes were filled with 9ml of freshly prepared 0.1 M CaCl<sub>2</sub> solutions for desorption of Thiabendazole in applied soils separately. Centrifuge tubes were placed inside Orbital shaker for 24hours shaking at 90 rpm at temperature (25  $^{\circ}$ C) for uniform mixing of Thiabendazole in four soils. 24 h shaking ensures the equilibrium between adsorbent and adsorbate. Centrifuge tubes were inserted in Sigma 2-6E centrifuge for 25 min at 25  $^{\circ}$ C and the rotation was set at 3000 rpm. Decantation of centrifuge tubes was done by using 0.2  $\mu$ m membrane filters for filtration of soil water suspension. Concentrations of Thiabendazole were

analyzed with UV-Visible spectrophotometer Bms-1602 at  $\lambda_{max}$  = 254 nm.

### Data analysis

In the current research, the data analysis was done by following the previous researches (Ahmad, 2018a-e) done on for the investigation of sorption behavior of different pesticides.

## Results and Discussion

**Soils' Physicochemical Characterization:** Selected soils exhibited relationship with different textural classes: clay (A), loam (B) (C) and sandy loam (D) with soil A possessing highest clay content of 68%. Soils varied significantly from 1.3 to 7 % in organic matter and pH ranging from 6.6 to 7.45 (Table 1). CEC and EC were positively correlated. While negative correlation was observed for pH and organic matter. Such variation in physicochemical characteristics was obtained due to variation in climatological, mineralogical and altitudinal differences in regions of selected samples. Consequently, such soils become source of generating great diversity of agricultural products of export quality. Investigated soils expressed variable degree of affinity to adsorption by Thiabendazole, 2-(4'-thiazoly) Benzimidazole under laboratory conditions. This variable behavior and affinity of selected soils can be attributed to differences in physicochemical parameters of soil collected from geographically distant biomes having distinct plant and animal communities as well the properties of Thiabendazole are also important while considering its adsorption shown in Table 1. Physicochemical parameters of soil i.e. SOM, OC, texture, CEC, EC, N, P, K etc. exerted overwhelmingly intense impacts on the adsorption of Thiabendazole to the adsorbent surface. Therefore, the adsorption can be explained and confirmed on the basis of these physicochemical characteristics of soils.

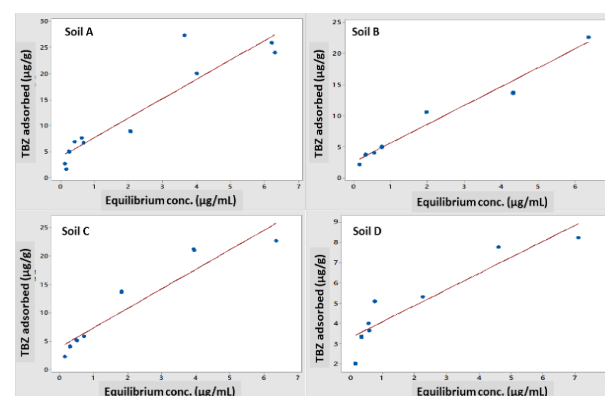


Fig. 2 Linear adsorption isotherms of Thiabendazole release in selected soils

Relevant physicochemical properties of the investigated adsorbents i.e. soils have been shown in Table 1 while the linear and Freundlich adsorption encompassing parameters like  $K_{d(ads)}$ ,  $K_{f(ads)}$ ,  $K_{OM}$ ,  $R^2$ ,  $\Delta G$ ,  $K_{oc}$ ,  $K_{foc}$ ,  $n_a$  and  $1/n$  are shown in Table 2. The isotherms for linear and Freundlich adsorption have been illustrated in Figure

2 and 3. The characterization of adsorption and desorption is done through partition constant K, and usually “d” is written in subscript to express distribution of pesticide in soil. The subscript “d” is replaced by “f” for determination of Freundlich sorption. Adsorption linear equilibrium distribution co-efficient  $K_{d(ads)}$  and adsorption Freundlich equilibrium distribution co-efficient  $K_{f(ads)}$  in ( $\mu\text{g/ml}$ ) estimation was done by means of plotting concentration of the Thiabendazole adsorbed  $C_{s(ads)}$  in ( $\mu\text{g/g soil}$ ) against  $C_{e(ads)}$ , which is the Thiabendazole equilibrium concentration ( $\mu\text{g/ml}$ ).

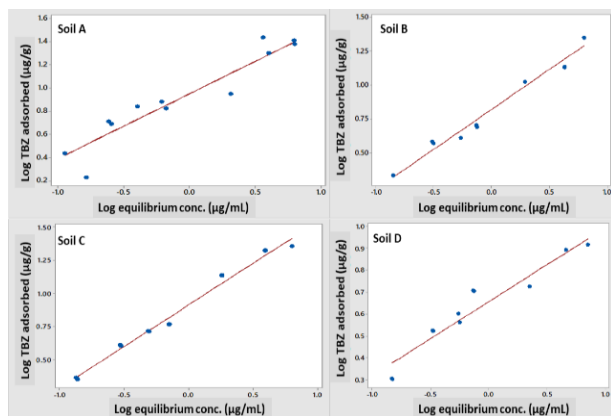


Fig. 3 Freundlich adsorption isotherm of Thiabendazole by selected soils

Adsorption and desorption of Thiabendazole in adsorbent soils in current study is analyzed through linear and Freundlich models due to organic nature of Thiabendazole and also because other models like Langmuir, BET (*Brunauer–Emmett–Teller*) and Gibbs have not been utilized due to their erroneous results in explanation of the aqueous phase sorption. The data sets for selected soils with Thiabendazole application best fitted with Freundlich model ( $R^2 \geq 0.87$ ). The data sheets for Thiabendazole generated the straight line curves similar to C-type isothermal adsorption indicating that adsorption is not limited to specific sites of adsorbent but distributed all over. Adsorption as indicated by C-Type curves shows that the ratio of Thiabendazole to selected soils in solution is variable at different concentrations. Due to the non-uniform surfaces of four soils from diverse geographical areas of Pakistan, the adsorbate was energetically bound to the stronger binding sites first followed by attachment to the rest of mass of adsorbent. C-type curves obtained for Thiabendazole in present study are consistent with Bala Subrahmanyam (1986).

Among all four selected soils applied with Thiabendazole, soil A has the highest  $K_{d(ads)}$  value of

24.04  $\mu\text{g/ml}$ . Soils with greater adsorption affinities will be leached less. Therefore, soil A is less vulnerable to leaching of Thiabendazole ensuring its slow mobility in pedospheric zone. Soil A being the strongest adsorbent of Thiabendazole is also exceeding other samples in having 68% clay content. Clay is a favorable medium for microbial population engaged in nitrogen fixation and derivation of locked carbon content from debris. Consequently, adsorption potential in soil A is enhanced in comparison to other samples. Clay is an important textural factor for elevating the adsorption extent in respective soils. This enhancement in adsorption potential can either be related to the augmented electrostatic interaction between adsorbent surface and charged Thiabendazole species in solution or the other probable cause could be the strong binding of Thiabendazole with the fine 0.002mm thin particles of clay content of soil A. Soil A is followed by soil C in having higher  $K_{d(ads)}$  value of 17.14  $\mu\text{g/ml}$ . Following adsorption trend was observed in current study: Soil A > Soil C > Soil B > Soil D (24.04  $\mu\text{g/ml}$  > 17.14  $\mu\text{g/ml}$  > 15.15  $\mu\text{g/ml}$  > 13.33  $\mu\text{g/ml}$ ).

Soil samples exhibited the strong positive correlation between the  $K_{d(ads)}$ ,  $K_{f(ads)}$  and  $K_{OM}$  values. The highest adsorption in soil A was further confirmed by its highest  $K_{f(ads)}$  value of 8.90  $\mu\text{g/ml}$  followed by soil C with  $K_{f(ads)} = 8.15 \mu\text{g/ml}$ . Lowest values for  $K_{d(ads)}$  and  $K_{f(ads)}$  were seen for the sandy loam soil D i.e. 4.51  $\mu\text{g/ml}$  and 13.33  $\mu\text{g/ml}$  respectively. Thiabendazole adsorption in soil D was minimum due to larger proportion of sand and consequently smaller surface area for Thiabendazole to be adsorbed.  $K_{d(ads)}$  and  $K_{f(ads)}$  were closely related with n approximating 1.0. Due to positive correlation, the soil samples expressed the similar trend for  $K_{f(ads)}$  as in case of  $K_{d(ads)}$ : Soil A > Soil C > Soil B > Soil D (8.90  $\mu\text{g/ml}$  > 8.15  $\mu\text{g/ml}$  > 6.59  $\mu\text{g/ml}$  > 4.51  $\mu\text{g/ml}$ ).

Soil organic matter (SOM) played a decisive role in elevating or alleviating the adsorption between Thiabendazole and investigated soil samples. SOM is directly proportional to the  $K_{OM}$  which is in turn positively correlated with  $K_{d(ads)}$  and  $K_{f(ads)}$ . Adsorption extent is increased due to higher SOM in soil A (Table 2).  $K_{OM}$  in current study ranged from 220 - 347  $\mu\text{g/ml}$ . These findings are consistent with previously done studies by Arias et al., 2008. The landscape of soil A is the recipient of heavy annual rainfalls of 127mm. Therefore, greater moisture content triggers relevant geochemical reactions for formation of soil organic matter. But in this context the region of soil C is recipient of even heavier rainfall than soil A with annual average rainfall of 1239.96 mm. So principally, soil C should have higher SOM due to higher moisture but this

Table 3. Thiabendazole Linear and Freundlich desorption parameters in selected soils

Soil	$K_{d(des)}$ ( $\mu\text{g/ml}$ )	$R^2$	H	S	$K_{f(des)}$ ( $\mu\text{g/ml}$ )	$R^2$	S	$n_d$	$n_a$
A	8.91	0.78	1.99	0.09	1.03	0.42	0.27	2.12	1.78
B	16.40	0.87	1.07	0.54	4.02	0.97	0.64	1.64	1.69
C	13.92	0.92	1.64	0.43	3.80	0.96	0.07	1.50	1.60
D	19.10	0.92	1.01	0.53	6.43	0.93	0.06	1.79	2.96



is not the case. It could be related to the loam texture of soil C, which is not as efficient as clay to allow microbial decomposition activities. Therefore, the agricultural fertility and productivity of soil A is also due to higher content of organic matter because higher  $K_{OM}$  values reflect that SOM act as a medium for receiving sorbate by provision of larger surface area and functional groups. Principle mechanisms through which Thiabendazole binds to the organic matter are hydrogen bonding and charge-transfers after strong complex formation.

Consistent with the previously done investigations with pesticides by Boivin et al., (2008) and Ertli et al., (2004), the results of present study also confirms a strong positive correlation between  $K_{d(ads)}$ ,  $K_{f(ads)}$ ,  $K_{OM}$ ,  $K_{oc}$  and negatively correlated with the adsorbent soil's pH indicating that by increasing soil organic content, soil organic matter and decreasing soil pH cause an increase in adsorption. With the increasing alkalinity in soil, the adsorption was decreased. Soil C had lowest pH of 6.6 and ranked second in adsorption due to its loam texture while clay soil A had a pH of 6.9 but exhibited highest adsorption with Thiabendazole. These finding are consistent with the investigations done by Li et al., (2003). Influence of soils' pH on adsorption of Thiabendazole is due to the enhancement of protonated surface on soil with decreasing pH giving rise to stronger interactions between soil and Thiabendazole. The pH neutralizing property of SOM also protects the soils from larger fluctuations in response to changes in external environment. Thiabendazole had an acid dissociation constant (pKa) of 4.73 and it becomes deprotonated on pH levels higher than 7. Therefore, soil D with highest pH of 7.45 and sandy loam texture behaved as poor adsorbent of Thiabendazole. In addition to texture, SOM and pH; CEC (Table 1) of soils also played significant role in affecting  $K_{d(ads)}$  and  $K_{f(ads)}$  by positively correlating to them. Lombardi et al., 2003 also found that cation exchange takes place with the clay minerals in soils. CEC of the investigated soils varied in following trend: Soil C > Soil A > Soil B > Soil D (8.9 meq/ 100g > 8.6 meq/ 100g > 7.9 meq/ 100g > 7.6 meq/ 100g).

Exchangeability of ions is dependent on soils' SOM. In the present study, the results have deviated minutely from previous studies for soil C with highest CEC of 8.9 meq/ 100g but adsorption lower than soil A with CEC of 8.6 meq/ 100g and highest  $K_{d(ads)}$ . The reason for higher adsorption value of soil A despite lower CEC is the difference in textural classes. Soil C despite its potential for exchanging ions efficiently is loam while for soil A is clay. The same trend was observed in case of pH and EC. Soil C possessing relatively lower pH and higher EC of 4.21 dSm-1 from all other samples couldn't succeed in becoming the best adsorbent for Thiabendazole due to its loam texture.

**Thermodynamic Study:** For detection of physio sorption and chemisorption, value of Gibbs free energy change ( $\Delta G$ ) was determined. For this determination, the value of  $\Delta G \leq 40$  kJ/mol was made the threshold (Carter et al., 1995). Due to the influence of adsorption on the partial

molar Gibbs free energy, the change can be thermodynamically expressed as:

$$\Delta G = -RT \ln K_{OM} \text{ (Osgerby 1970)}$$

where R is the universal gas constant (8.314 kJ.kmol<sup>-1</sup>.K<sup>-1</sup>) and T is temperature in Kelvin (K). This equation shows that higher values of  $\Delta G$  show the improved extent of adsorption. Values of  $\Delta G$  less than 40 kJmol<sup>-1</sup> indicate the weak adsorptive interactions between Thiabendazole and soils. Since the values of  $\Delta G$  ranged from -14.49 kJ/mol to -13.37 kJ/mol (Table 2) in the current study, thus indicating physio sorption for all four investigated soil samples. Thiabendazole adsorption process on adsorbent surface is relatively slow process due to weaker bonds like hydrogen bonding and Van der Waal's interactions.

**Adsorption Strength:** On the basis of  $K_{oc}$  values, adsorption can be categorized into three types: high adsorption in which value of  $K_{oc}$  exceeds 1000  $\mu\text{g/ml}$ , medium adsorption in which the value of  $K_{oc}$  lies between 300 to 1000  $\mu\text{g/ml}$  and low adsorption in which values of  $K_{oc}$  are less than or equal to 300  $\mu\text{g/ml}$ . Relatively slow rates of adsorption are observed due to the fact that at the initiation stage of adsorption between Thiabendazole and soil, larger part of empty surface is accessible for the adsorption. After this phase, due to the large scale capturing of unoccupied sites by Thiabendazole molecules, repulsive forces start operating and cause a delay in adsorption process. This observation is peculiar to all organic pesticides and has been found consist with Krishna & Philip, (2008); Calvet, (1989) and Anil & Swaranjit, (2013).

**Mobility and Leaching pattern of Thiabendazole in selected soils:** Determination of pesticide mobility and fate are significant for removal of pesticide residues and environmental components. On a global scale  $K_{foc}$  and  $K_{oc}$  values are determinants of pesticide mobility and pesticide distribution in soil and water reserves (Suddaby, 2012). McCall et al., (1980) categorization of pesticide mobility were followed for investigating migratory behavior of Thiabendazole. According to McCall et al., 1980 classification pesticides are moderately mobile if their  $K_{oc}$  values range between 150– 500  $\mu\text{g/ml}$  while they have insignificantly low-level mobility if their  $K_{oc}$  value are between 500 – 2000  $\mu\text{g/ml}$ . The  $K_{oc}$  values ranged from 395 - 592  $\mu\text{g/ml}$  while the shown in Table 2. Higher  $K_{oc}$  and  $K_{foc}$  values indicate that Thiabendazole possesses low to medium mobility in all soils. This Thiabendazole mobility in soils is due to higher organic content and mineralogical features of soil. Such mobility patterns of Thiabendazole in selected soils show the degree of Thiabendazole driven pedospheric contamination. By the virtue of insignificant mobility pattern, there are no potential threats associated with the percolation of Thiabendazole in reaching soil deeper profiles or groundwater. This predicted mobility pattern makes Thiabendazole most convenient for not only farmer but also ecosystem. Furthermore, the lower values of  $n_a$  in comparison to  $K_d$

values expresses the higher intensity of adsorption in Thiabendazole – soil systems.

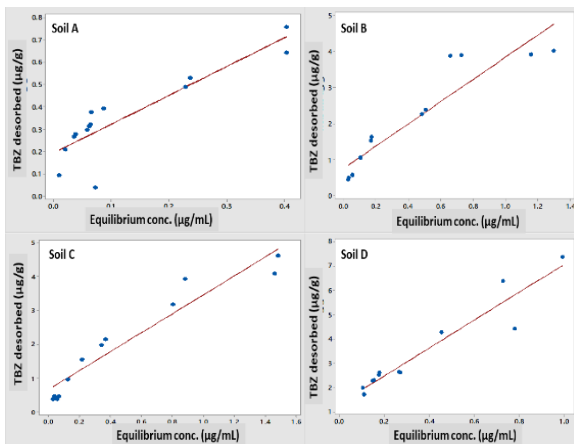


Fig. 4 Linear desorption isotherm of Thiabendazole in selected soil

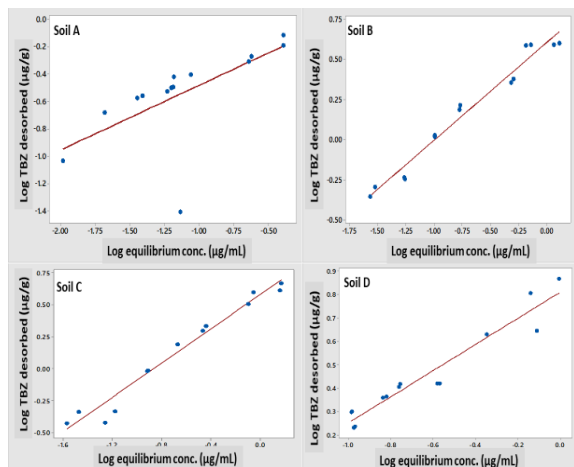


Fig. 5 Freundlich desorption isotherm of Thiabendazole in selected soils

**Desorption of Thiabendazole:** Desorption linear equilibrium distribution co-efficient  $K_{d(des)}$  and desorption Freundlich equilibrium distribution co-efficient  $K_{f(des)}$  in  $\mu\text{g/ml}$  were calculated by plotting concentration of the Thiabendazole desorbed  $C_{s(des)}$  in ( $\mu\text{g/g}$  soil) against  $C_{e(des)}$ , which is the Thiabendazole concentration ( $\mu\text{g/ml}$ ) at the equilibrium concentration for soils shown in Table 3 and Figure 4 and 5. The desorption isotherm obtained for Thiabendazole was also a curve similar to C-type curve indicating that the Thiabendazole was not desorbed uniformly from adsorbent surface. As the process of desorption is opposite of adsorption therefore all the physicochemical factors acting to trigger the adsorption would become limiting factors for desorption. Similarly, the physicochemical factors e.g. high pH, sand content, lower CEC and lower SOM would make soil desorb the pesticide more efficiently. This opposing relation can be explained for soil D having lowest  $K_{d(des)}$  value of  $13.33 \mu\text{g/ml}$  but subsequently highest  $K_{d(des)}$  value of  $19.0 \mu\text{g/ml}$ . The overall desorption trend is as following: Soil D > Soil B > Soil C > Soil A ( $19.10 \mu\text{g/ml} > 16.4 \mu\text{g/ml} > 13.92 \mu\text{g/ml} > 8.91 \mu\text{g/ml}$ ).  $K_{d(des)}$  and  $K_{f(des)}$  are positively correlated shown in Figure 2 respectively and

in Table 3, therefore the similar trend for  $K_{f(des)}$  has also been observed: Soil D > Soil B > Soil C > Soil A ( $6.43 \mu\text{g/ml} > 4.02 \mu\text{g/ml} > 3.08 \mu\text{g/ml} > 1.03 \mu\text{g/ml}$ )

**Hysteresis:** Hysteresis of adsorption and desorption of Thiabendazole in selected soils is the measure of Thiabendazole irreversibility of adsorption desorption and is expressed through the hysteresis coefficient H shown in Table 3. In the present study for four soils, the value of H is in the range of 1.01 to 1.99. Since the values obtained in this study are nearly equal to 1 or are more than 1, therefore hysteresis took place. So, in the present case for selected soils, the reclamation of adsorbed pesticide in adsorbent soils is not possible. This failure in reclamation of Thiabendazole from soil matrix is related to the changes in the mechanistic and structural orientation of Thiabendazole molecules on adsorbent soil surfaces in the adsorption process. The adsorption and desorption processes of Thiabendazole in soils can only be reversible if there are no losses due to degradation. In this case the values of  $K_{d(ads)}$  will be equal to  $K_{d(des)}$  but in current hysteresis is confirmed due to difference in the  $K_{d(ads)}$  and  $K_{d(des)}$  values. The relative high value of  $K_{d(ads)}$  compared with  $K_{d(des)}$  for studies soils shows adsorption is irreversible. Thermodynamically, irreversibility of adsorption and desorption process for Thiabendazole means that there is a sharp difference between the pathways on which both operate. Table 2 and Table 3 shows that soils behaving as good adsorbents have higher values for H e.g. soil A with highest adsorption potential had highest H value of 1.99 showing challenges in irreversibility of reaction. This finding is consistent with Celis et al., 1999.

In addition to the sorption of Thiabendazole from the selected soils, the electro kinetic remediation (EKR) was also carried out by utilization of the electrodes comprising carbon black. EKR was found dependent upon the soils physical and chemical characteristics observed via UV-Vis for alleviation in the absorbance at 300 nm (Figure 6). Therefore, the percentages of removal obtained for each soil is also variable depicted in Figure 6. In the current study, soil sample D expressed highest percentage of removal via EKR, which is attributable to the highest pH of soil D. Current findings for Thiabendazole are consistent with Shahzad, (2017).

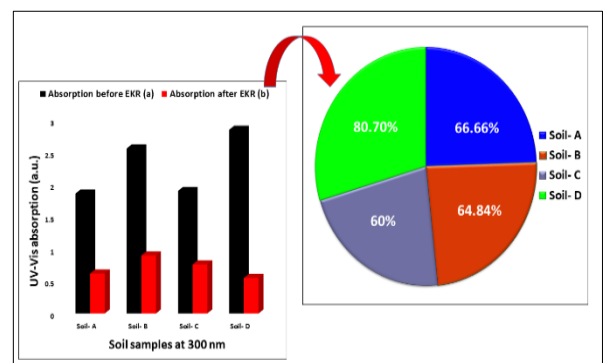


Fig. 6 Electro-kinetic remediation of Thiabendazole exhibiting alleviation in the UV-Vis absorbance at 300nm. The difference of absorbance was used to calculate Thiabendazole removal percentages.

## Conclusion

The current batch equilibration-based investigation found that selected soils exhibited variable extent of affinities for adsorption by Thiabendazole due to their distinct physicochemical characteristics. Soil A and C were best adsorbents of Thiabendazole while soil B and D couldn't efficiently adsorb Thiabendazole and consequently they readily desorbed the Thiabendazole. Adsorption is positively correlated with clay, organic matter and cation exchange capacity. It is concluded that there is a negative correlation between pH and adsorption causing alleviation in adsorption sites with elevation in pH. Mobility and leaching of Thiabendazole is an important factor for exerting ecotoxicological impacts in various compartments of environment, Thiabendazole leached to lesser extent in highly adsorptive soils is readily available to be taken up by plants and transferred to us via food chain. Thiabendazole exhibited low to medium mobility in selected soils. Therefore, more thorough investigations e.g. lysimetric studies and degradation experiments can be conducted for estimation of Thiabendazole leaching into ground water reserves and soils.

## References

- Ahmad, K. S. (2018a). Adsorption Evaluation of Herbicide Iodosulfuron Followed by *Cedrus deodora* Sawdust-Derived Activated Carbon Removal. *Soil Sedi. Contam.*, 2018, 1-16.
- Ahmad, K. S. (2018b). *Arachis hypogaea* activated carbon-assisted removal of 1-(4, 6-dimethoxypyrimidin-2-yl)-3-(3-ethylsulfonylpyridin-2-yl) sulfonylurea herbicide in agriculturally adsorbed soils. *Int. J. Environ. Sci. Technol.*, 2018, 1-12.
- Ahmad, K. S. (2018c). Sorption and *Juglans regia*-derived activated carbon-mediated removal of aniline-based herbicide Alachlor from contaminated soils. *Envir. Earth. Sci.*, 77, 437-445.
- Ahmad, K. S. (2018d). Evaluating the Adsorption Potential of Alachlor and Its Subsequent Removal from Soils via Activated Carbon. *Soil Sedi. Cont.*, 2018, 1-18.
- Ahmad, K. S. (2018e). Exploring the potential of *Juglans regia*-derived activated carbon for the removal of adsorbed fungicide Ethaboxam from soils. *Environ. Monit. Assess.*, 190, 737-744.
- Ahmad, K. S., & Jaffri, S. B. (2018a). Phytosynthetic Ag doped ZnO nanoparticles: Semiconducting green remediators. *Open Chem.*, 16, 556-570.
- Ahmad, K. S., & Jaffri, S. B. (2018b). Carpogenic ZnO nanoparticles: Amplified nanophotocatalytic and antimicrobial action. *IET Nanobiotechnol.*, 2018, 1-15.
- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J. C., & García-Río, L. (2008). The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agric. Eco. Envir.*, 123(4), 247-260.
- Armon, R. H. (2015). Tsunami. In *Environmental Indicators* (pp. 77-88). Springer Netherlands.
- Balasubrahmanyam, S. K. (1986). Environmental dynamics of benomyl and thiabendazole (Doctoral dissertation, Virginia Tech).
- Boivin, A., Cherrier, R., & Schiavon, M. (2005). A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, 61(5), 668-676.
- Calvet, R. (1989). Adsorption of organic chemicals in soils. *Envir. Health Pers.*, 83, 145.
- Carter, M. C., Kilduff, J. E., & Weber, W. J. (1995). Site energy distribution analysis of preloaded adsorbents. *Envir. Sci. Tech.*, 29(7), 1773-1780.
- Celis, R., Koskinen, W. C., Hermosin, M. C., & Cornejo, J. (1999). Sorption and desorption of triadimefon by soils and model soil colloids. *J. Agric. Food Chem.*, 47(2), 776-781.
- El Bakouri, H., Morillo, J., Usero, J., & Ouassini, A. (2009). Natural attenuation of pesticide water contamination by using ecological adsorbents: application for chlorinated pesticides included in European Water Framework Directive. *J. Hydrol.*, 364(1), 175-181.
- Ertli, T., Marton, A., & Földényi, R. (2004). Effect of pH and the role of organic matter in the adsorption of isoproturon on soils. *Chemosphere*, 57(8), 771-779.
- Ghosh, R. K., Ray, D. P., Chakraborty, S., Majumdar, K., & Reddy, D. (2015). Pesticides in environment and their management strategies. *Int. J. Biores. Sci.*, 2(1), 47-54.
- Iftikhar, S., Ahmad, K. S., & Jaffri, S. B. (2018). Myco-driven enhancement and inherent phytoremediation potential exploration of plants for lithospheric remediation. *Sydowia.*, 70, 141-153.
- Iftikhar, S., Saleem, M., Ahmad, K. S., & Jaffri, S. B. (2019). Synergistic mycoflora-natural farming mediated biofertilization and heavy metals decontamination of lithospheric compartment in a sustainable mode via *Helianthus annuus*. *J. Int. Envir. Sci. Tech.*, 1-18.
- Iram, S., Ahmad, K. S., Noureen, S., & Jaffri, S. B. (2019a). Utilization of Wheat (*Triticum aestivum*) and Berseem (*Trifolium alexandrinum*) Dry Biomass for Heavy Metals Biosorption. *Proc. Pak. Acad. Sci.*, 1-10.
- Iram, S., Basri, R., Ahmad, K. S., & Jaffri, S. B. (2019b). Mycological assisted phytoremediation enhancement of bioenergy crops *Zea mays* and *Helianthus annuus* in heavy metal contaminated lithospheric zone. *Soil Sed. Contam.*, 28(4), 411-430.

- Iram, S., Laraib, H., Ahmad, K. S., & Jaffri, S. B. (2019). Sustainable management of *Mangifera indica* pre-and post-harvest diseases mediated by botanical extracts via foliar and fruit application. *J. Plant Dis. Prot.*, 1-6.
- Ismail, B. S., & Kalithasan, K. (2004). Adsorption, desorption, and mobility of permethrin in Malaysian soils. *J. Envir. Sci. Health B.*, 39(3), 419-429.
- Ismail, B. S., Enoma, A. O. S., Cheah, U. B., Lum, K. Y., & Malik, Z. (2002). Adsorption, desorption, and mobility of two insecticides in Malaysian agricultural soils. *J. Envir. Sci. Health B.*, 37(4), 355-364.
- Jaffri, S. B., & Ahmad, K. S. (2017). Augmented photocatalytic, antibacterial and antifungal activity of prunosynthetic silver nanoparticles. *Artif. Cells Nanomed. Biotechnol.*, 2017, 1-11.
- Jaffri, S. B., & Ahmad, K. S. (2018a). *Prunus cerasifera Ehrh.* fabricated ZnO nano falcates and its photocatalytic and dose dependent in vitro bio-activity. *Open Chem.*, 16, 141-154.
- Jaffri, S. B., & Ahmad, K. S. (2018b). Neoteric environmental detoxification of organic pollutants and pathogenic microbes via green synthesized ZnO nanoparticles. *Envir. Tech.*, 2018, 1-12.
- Jaffri, S. B., & Ahmad, K. S. (2018c). Foliar-mediated Ag: ZnO nanophotocatalysts: green synthesis, characterization, pollutants degradation, and in vitro biocidal activity. *Green Proc. Synth.* 2018, 1-10.
- Jaffri, S. B., & Ahmad, K. S. (2018d). Phytofunctionalized silver nanoparticles: green biomaterial for biomedical and environmental applications. *Rev Inorg. Chem.* 38 (3), 127-149.
- Krishna, K. R., & Philip, L. (2008). Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils. *J. Hazard. Mat.*, 160(2), 559-567.
- Liu, Y., Pan, X., & Li, J. (2015). A 1961–2010 record of fertilizer use, pesticide application and cereal yields: a review. *Agr. Sust. Devel.*, 35(1), 83-93.
- Lombardi, B., Baschini, M., & Sánchez, R. T. (2003). Optimization of parameters and adsorption mechanism of thiabendazole fungicide by a montmorillonite of North Patagonia, Argentina. *Appl. Clay Sci.*, 24(1), 43-50.
- Martin, N. A., Beresford, R. M., Harrington, K. C., & New Zealand Plant Protection Society. (2005). Pesticide resistance: Prevention and management strategies 2005. Hastings, N.Z: New Zealand Plant Protection Society Inc.
- OECD (2000) OECD Guidelines for the Testing of Chemicals: Adsorption-Desorption Using a Batch Equilibrium Method. Organisation for Economic Co-operation and Development.
- Osgerby, J. (1970). M. Sorption of un-ionised pesticides by soils. Monograph Series. *Soc. Chem. Indus.*, 37, 63-78.
- Pereira, M. G., Espindula Jr, A., Valladares, G. S., Cunha dos Anjos, L. H., de Melo Benites, V., & Schultz, N. (2006). Comparison of total nitrogen methods applied for histosols and soil horizons with high organic matter content. *Com. Soil Sci. Plant Anal.*, 37(7-8), 939-943.
- Robertson, S. (2009). Re-analysis of the Relationship between Organic Carbon and Loss-on-Ignition in soil. *Com. Soil Sci. Plant Anal.*, 40(17-18), 2712-2720.
- Sarmah, A. K., & Kookana, R. S. (1999). Simultaneous analysis of Triasulfuron, Metsulfuron-methyl and Chlorsulfuron in water and alkaline soils by high-performance liquid chromatography. *J. Envir. Sci. Health b.*, 34(3), 363-380.
- Shahzad Ahmad, K., (2017). Green remediation of Thiabendazole adsorbed soils via mineralization. *Agrochim.*, 61(3), 190-205.
- Shahzad Ahmad, K., Rashid, N., Tazaiyen, S., & Zakria, M. (2014). Sorption-Desorption Characteristics of Benzimidazole Based Fungicide 2-(4-fluorophenyl)-1H-benzimidazole on Physicochemical Properties of Selected Pakistani Soils. *J. Chem. Soc. Pak.*, 36(6), 1189-1195.
- Suddaby, L. (2012). Investigation into irreversible sorption of pesticides to soil.
- Tariq, M. I., S. Afzal, I. Hussain and N. Sultana. (2007). Pesticides exposure in Pakistan: A review. *Environ. Int.*, 33: 1107–1122
- Tatarková V., Hiller E., Halko R. (2014): Retention characteristics of acetochlor in soils collected from different depths in relation to soil properties (Žitnýostrov area, SW Slovakia). *Soil Water Res.*, 9, 58–65.