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Adsorption-Desorption Mechanism of Synthesized Benzimidazole Based Fungicide 2-(3'-Pyridyl) on Selected Soil Minerals

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Abstract: The adsorption and desorption phenomenon of synthesized Benzimidazole based fungicide, 2-(3'-pyridyl) benzimidazole (PyBlm), was investigated by batch equilibrium method. Four soil minerals were utilized for the sorption studies including; alumina, silica, muscovite and montmorillonite. Highest value of adsorption coefficient ($K_{d(ads)}$), obtained for montmorillonite mineral (Mx (Al, Fe, Mg_4) Si_8O_{20} (OH_4)) was 2779 µg ml^{-1}. Highest rate of adsorption is attributable to its considerably large surface area of 628 m^2g^{-1} and highest inter-lattice d-spacing, 10 Å. Highest desorption ($K_{d(des)}$) was also observed in montmorillonite mineral (21.45 µg ml^{-1}). Montmorillonite thus displayed increased sorption capacity for PyBlm among all tested minerals. Hysteresis coefficient ranged from 0.58 to 3. The results were statistically evaluated by using one-way analysis of variance (ANOVA). Furthermore, statistical evaluation done with the help of Minitab 17 expressed the good fitting of the obtained results, which was shown by means of residual plots. Current research which suggests the variable adsorption and desorption of PyBlm expresses the profound dependence of PyBlm interaction on the physicochemical characteristics of the selected minerals. All minerals except montmorillonite expressing poor adsorption signifying the percolation of PyBlm through them towards the lower soil profiles. Results obtained in the present research show of that montmorillonite in firmly interacting with the PyBlm molecules and thus alleviating the possibility of PyBlm percolation to lower soil profiles.

Keywords: Fungicide, montmorillonite, silica, muscovite, sorption.

Introduction

The population expansion of the previous decades has eventuated an increased use of pesticides for expansion in agricultural production (Koleli et al., 2006). Pests often tend to get resistant against old pesticides used on the same sites repeatedly (Georghiou, 2012). Thus, there is a need to synthesize new pesticides in order to overcome this complication. However, pesticides in any case are accountable for causing serious environmental issues, which raises several potential concerns (Krishna and Philip, 2008). Assessing and evaluating the fate of pesticides in environment is thus highly imperative to predict the magnitude of contamination (Konda et al., 2002). The study of adsorption and desorption phenomena for this impetus is essential. This knowledge thus aids in assessing the repercussion of uncontrolled pesticide use in the environment. The sorption phenomenon thus envisages the mobility of pesticides in the environment, predicting the extent of ground water contamination as well as its uptake by plants and other microorganisms (Singh and Cameotra, 2013). The physicochemical properties of pesticides have a great impact on their sorption mechanism in soils and minerals (Sondhia and Khare, 2014; Hall et al., 2015). The soil components regulating the rate of adsorption-desorption include organic matter content, soil minerals and clay content (Afolabi et al., 2016). The behavior of different pesticides in the soils is dictated by number of factors. Thus, the environmental fate of any pesticide is decided by the way it is volatilized, percolation to deeper layer, run off and deterioration by chemico-biological means. After spraying pesticide on a particular crop, it is evident that by no method, the crop receives 100% of the sprayed pesticide. But instead, the crops receive meagre amount and large quantity goes to the land beneath and consequently gives rise to percolation in soil layers. Such pesticides are in the ionic form and thus readily react with water and lead to the formation of different oxides that possess an ability of intermixing with pedospheric compartment and alleviate the soil's fertility extent (Fenner et al., 2013).

Pakistan is an agronomic country dependent largely on agricultural systems for economic growth. The fertile lands are constantly exposed to the attack of vicious pests negatively affecting different crops and agricultural regions, for which different efforts have been made for remediation (Iram et al., 2019; Iram et al., 2019a, b; Ifthikhar et al., 2019; Ifthikhar et al., 2018). Moreover, environmental compartments are still continuing to be affected by contamination and pests. Different efforts are in emerging phase to control such pests in an effective way, particularly nano-pesticides have been designed for the control of different bacterial and fungal strains (Ahamd and Jaffri, 2018 a, b; Jaffri and Ahmad, 2017; Jaffri and Ahmad, 2018a-d). However, the use of chemical pesticides in present

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era is exceeding the other emerging modes. Pesticides use is thus inevitable. Fungicides are among the most widely used pesticides among which Benzimidazole based pesticides are very common (Aharonson and Kafkai, 1975). Benzimidazole driven pesticides have been known for their specificity in terms of mode of action by causing interference in the meiotic cellular division and consequently leading to the inhibition of the fungal growth of different fungal strains that act as plant pests (Roy, 2002). Fungicides pose great risk to human beings as a huge number of antagonistic effects have been observed (Santana-Rodríguez et al., 2010). Benzimidazole based fungicides are utilized in crops as anthelmintic agents and systemic fungicides to control both pre and post-harvest control (Uclés et al., 2015). Fungicides resistance has been found in several fields thus there is need for manufacturing new fungicides (Panebianco et al., 2015). The current research is aimed at evaluating the sorption behavior of the newly synthesized fungicide, 2-(3'-pyridyl) benzimidazole (PyBlm) in different soil minerals (Fig 1). The adsorption and desorption mechanism of the pesticide in soil minerals will aid in determining the fate and extent of leaching in soil. The results can also be utilized to assess the amount of surface and groundwater contamination it might cause.

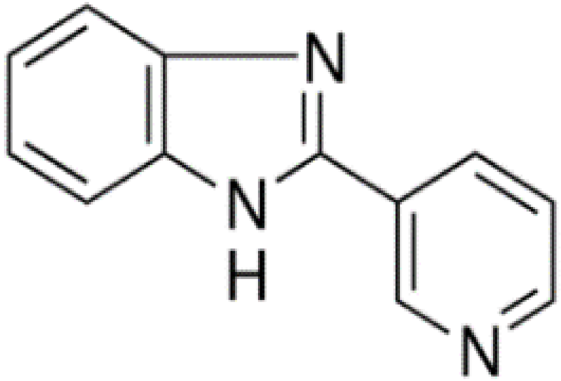

Fig. 1 Chemical structure of 2-(3'-pyridyl) benzimidazole.

Materials and Methods

Chemicals

All the solvents i.e. $(CH_3)_2CO$ and CH_3OH used in the current research were 99% pure and purchased from Merck, Germany. NaCl was utilized for adjusting the ionic aspects and the pesticide stock solution was prepared in distilled water. Four soil minerals were utilized for the adsorption and desorption studies including; alumina, silica, muscovite and montmorillonite.

Table 1 Physiochemical properties of soil minerals.

Minerals	Formula	pH	AEC (cmol kg^{-1})	CEC (cmol kg^{-1})	d-Spacing (A^o)	Surface Area (m^{2}g^{-1})	Lattice type
Silica	SiO_2	2	0.4	3	0	524	N/A
Montmorillonite	Mx (Al, Fe, Mg_4) Si_8O_{20} (OH_4)	2.5	0.3	85	10	628	2:1
Alumina	Al_2O_3	9.1	6.3	0.5	3.1	164	N/A
Muscovite	$KAl_2(AlSi_3O_{10})$ (OH_2)	7.9	N/A	3.1	10	70	2:1

AEC= anion exchange capacity, CEC= cation exchange capacity

Table 2 Adsorption coefficients of PyBlm in selected minerals.

Minerals	K_d (µg/ml)	R^2	S	K_f (µg/ml)	1/n	n_a	R^2	S
Alumina	1.430	0.97	0.57	3.81	0.52	1.92	0.95	0.16
Silica	1.020	0.99	0.35	2.32	0.57	1.74	0.95	0.16
Muscovite	1.250	0.98	0.39	3.45	0.46	2.15	0.89	0.20
Montmorillonite	2779	0.69	30.68	39.73	2.33	0.42	0.37	1.01

Adsorption Experimentation

The adsorption experiments have been performed under normal room temperature (25 ± 1°C). The preparation of 2-(3'-pyridyl) benzimidazole stock solution was carried out by the dissolution of 10 drops of $(CH_3)_2CO$ followed by mixing in 1 L distilled water and stored at 4°C. Eight different dilutions were prepared for PyBlm (0, 0.25, 0.5, 0.75, 1, 2.5, 5 and 7.5 ppm). All the experimentation was done in duplicate. NaCl was used as background electrolyte (0.1 M solution). Mineral sample (0.5 g) was added in each 15 ml centrifuge tube along with 10 ml of pesticide solution. Mineral/solution ratio was kept 1:10. It was followed by the agitation of the reaction mixtures at 90 rpm for 24 h in an orbital shaker at ambient temperature for obtaining equilibrium. A blank sample with only pesticide and no mineral was also run in parallel in each batch equilibrium experimental set (OECD, 2005). 3000 rpm centrifugation was done for each batch for 25 min followed by filtration through a 0.2 µm nylon filter. The clear aliquots were analyzed by a Hitachi U-2800 UV-Visible spectrophotometer at λ_{max} 240 nm.

Desorption Experimentation

The evaluation of desorption was done with the same reaction mixtures used for adsorption experimentation. In a typical desorption experiments, the centrifuge tubes after UV-Vis analysis for discarded of the supernatant and the residual soils were injected with the freshly prepared $CaCl_2$ (9 ml of 0.01 M). Then it was agitated in the same manner as done for adsorption i.e. 90 rpm for 24 h in an orbital shaker at ambient temperature. Finally, the amount of the desorbed pesticide was determined by taking the absorption by UV-Vis.

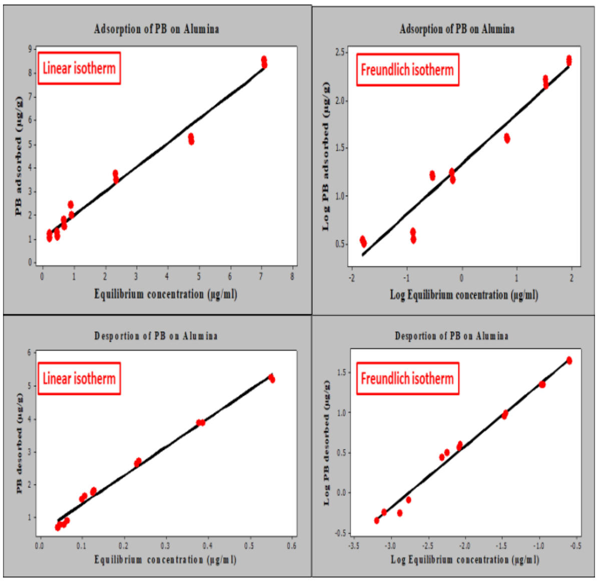

Fig. 2 Linear and Freundlich adsorption and desorption isotherms for PyBlm on alumina

Data Analysis and Statistical Evaluation

Data analysis was done by following the previous researches (Ahmad, 2018a-d). The data were statistically evaluated by applying univariate ANOVA in Excel 2013 (Microsoft, USA). Furthermore, the residual plots were drawn on the in Minitab 17.

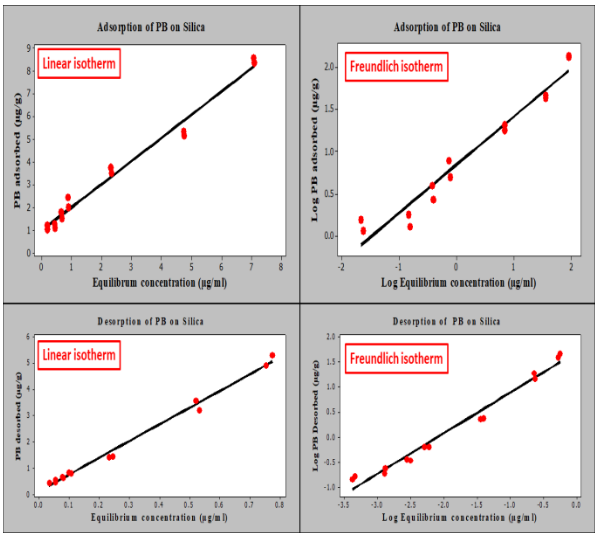

Fig. 3 Linear and Freundlich adsorption and desorption isotherms for PyBlm on silica

Results and Discussion

The physical and chemical properties of the selected soil minerals were determined (Table 1). The soil minerals utilized in the current experiment encompassed silica, montmorillonite, alumina and muscovite. The pH of these minerals ranged from 2-9.1. The anion and cation exchange capacity (AEC and CEC) of minerals were also determined. Mobility of pesticide depends upon AEC and CEC of the minerals in soil. Furthermore, the specific surface area of minerals was also determined. The AEC and CEC are associated with the specific surface area of each mineral (Kabat-Pendias, 2004). These properties were found to be positively correlated with each other. Montmorillonite mineral with highest CEC value 85 cmol kg^{-1} was found to possess the greatest specific surface area 628 m^2 g^{-1}. The inter-planar spacing or the d spacing was also obtained for each soil mineral. Montmorillonite and muscovite were found to possess d spacing equal to 10 Å while alumina comprised of 3.1 Å d spacing (Chin et al., 2001; Magana et al., 2008). The larger the specific surface area of minerals the more d spacing was observed. The d spacing of montmorillonite mineral was reported to be 12 Å in a previous study conducted by Jung et al. (2003).

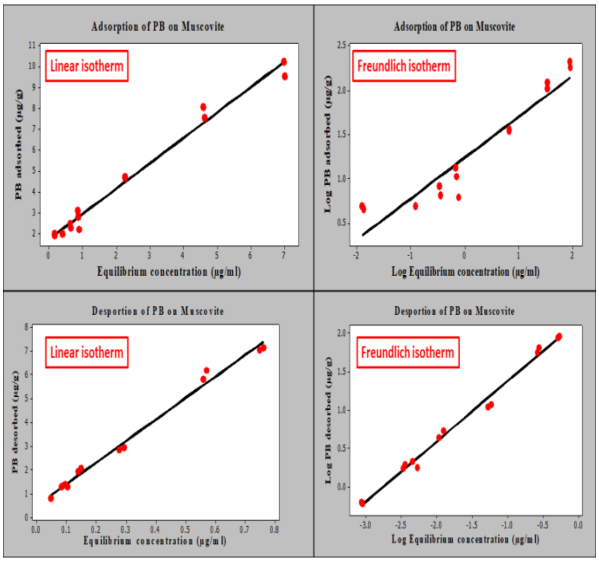

Fig. 4 Linear and Freundlich adsorption and desorption isotherms for PyBlm on muscovite.

Adsorption experiments with pure minerals provided valuable knowledge for the fungicide contamination because such experiment depicted the extent to which this pesticide was adsorbed. PyBlm adsorptive and desorptive phenomena were investigated by UV-Vis. The lambda maximum for PyBlm was obtained at 240 nm. Figures 2-5 represent the linear and Freundlich sorptive isothermal behavior of PyBlm in the selected minerals. For the comprehension of the attachment pattern of PyBlm to the selected minerals as a function of concentration, the amount of minerals was plotted versus PyBlm equilibrium concentration. Different adsorption and desorption parameters were determined and are presented in Table 2,3. Different parameters included adsorption-desorption distribution coefficient (K_d), Freundlich adsorption coefficient (K_f), n_a and hysteresis coefficient.

Table 3 Desorption coefficients of PyBlm in selected minerals.

Minerals	$K_{d(des)}$ (µg/ml)	R^2	S	$K_{f(des)}$ (µg/ml)	1/n	nd	R^2	S	H
Alumina	8.67	0.99	0.16	8.38	0.76	1.29	0.99	0.070	0.67
Silica	6.36	0.99	0.15	3.22	0.18	5.22	0.98	0.140	3.00
Muscovite	9.02	0.99	0.23	8.74	0.78	1.26	0.99	0.070	0.58
Montmorillonite	21.45	1.00	0.01	21.73	1.01	0.98	1.00	0.004	2.30

Table 4 One-way ANOVA for PyBlm adsorption coefficient K_d

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1593928	3	531309	1.4	0.02	3.2
Within Groups	5910674	16	369417			

The adsorption distribution coefficient (K_d) for linear model for soil minerals ranged from 1.02 to 2779 µg/ml. Montmorillonite exhibited the highest adsorption value which can be attributed to its highest d spacing and greatest surface area (10 Å and 628 m^2 g^{-1}). A greater d spacing reveals that the mineral possesses more inter-planar spacing along with high surface area. These mineral attributes can result in attachment of more pesticide molecules to the mineral crystal. The R^2 values of linear adsorption model lay between 0.69-0.99 indicating best fit to this model. The Freundlich distribution coefficient (K_f) values spanned over a range of 2.32 to 39.73 µg/ml. Their R^2 values lay between 0.37-0.95. The extent of irreversibility of adsorption was assessed by the na values ranging from 0.42 to 2.15. The montmorillonite mineral with highest adsorption rate was found to have lowest na value. Montmorillonite minerals have been found to be very good adsorbents for pesticides. Montmorillonite, a clay mineral has isomorphic substitution. It has a lattice of 2:1 layer (Bhattacharyya and Gupta, 2008). Its high cation uptake capacity has also been displayed by Dähn et al.(2002).

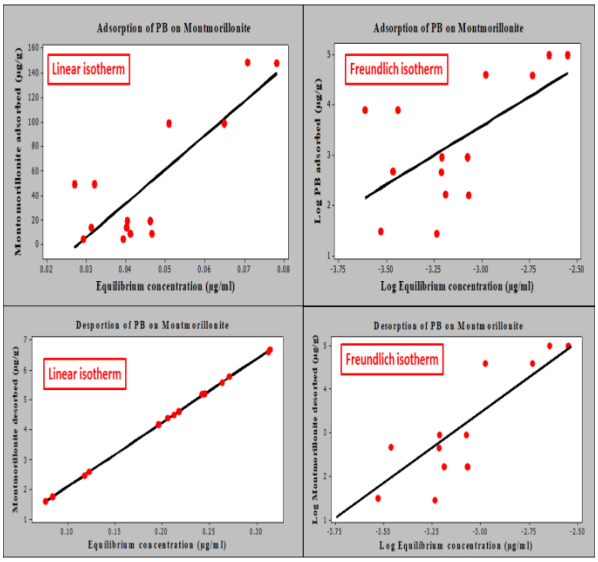

Fig. 5 Linear and Freundlich adsorption and desorption isotherms for PyBlm on montmorillonite.

Furthermore, the adsorption on montmorillonite is also dependent on pH. During the process of adsorption, the montmorillonite structure undergoes interlayer swelling with the exposure to water. This phenomenon is dependent upon atomic radii and valencies of the cations that are exchanged during the process. Adsorption thus occurs at both the edge sites which are more reactive (Hennig et al., 2002). Consequentially two complexes are formed; the inner sphere pesticide complex and the outer sphere pesticide complex (Elzinga and Sparks, 1999). Due to these phenomena a considerable adsorption rate has been observed in montmorillonite among all soil minerals.

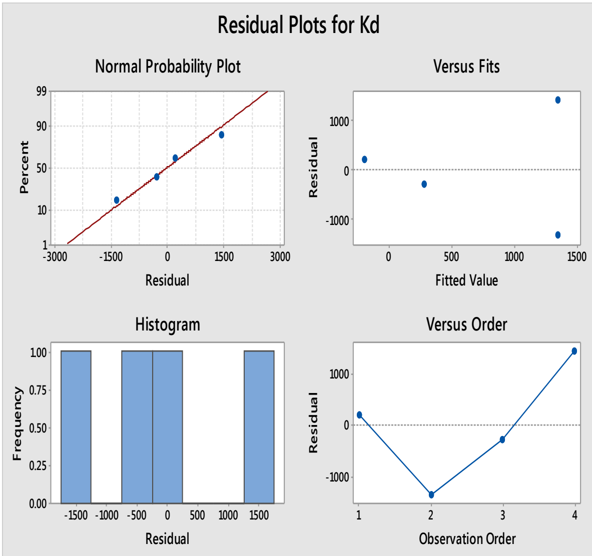

Fig. 6 ANOVA Histogram, Versus Fit, Versus Order and Normal Probability Residual plots of minerals with physiochemical properties pH, CEC, surface area and d spacing while the response is K_d.

The desorption parameters studied on these minerals revealed the linear desorption distribution coefficient ($K_{d\ (des)}$) ranging from 6.36 to 21.45 µg/ml. The R^2 values for this lied from 0.99 to 1.00, thus indicating the best fit to linear desorption model. The Freundlich desorption coefficient constant ($K_{f\ (des)}$) spanned between 3.22 to 21.73 µg/ml. The R^2 values ranged from 0.98 to 1.00. This indicates a good fit to the model. Highest desorption was also observed in montmorillonite. The adsorption and desorption of a fungicide, Penconazole by mineral montmorillonite was also found to be highest among different soil minerals (Sanchez-Martin et al., 2006). The extremely high adsorption value of montmorillonite mineral for PyBlm than the desorption value indicates the ease with which it adsorbs the organic molecules. Penconazole fungicide was the most hydrophobic pesticide that was adsorbed in the interlayer space.

PyBlm might also be mostly adsorbed due its hydrophobicity on montmorillonite mineral. The hysteresis (H) value was found varying in all minerals. The value < 1 indicated that the desorption process occurred as rapidly as adsorption, while >1 depicted that it was slower than adsorption.

The results for the sorption of PyBlm in the selected minerals indicate the reversibility of the PyBlm sorption process since there are no clues of chemisorption or stronger adsorptive interactions shown by the obtained isotherms. For that reason, the adsorption distribution coefficients are much smaller in comparison to the desorption coefficients. However, in case of montmorillonite, there is an augmented surface area and CEC, due to which the sorptive process is irreversible, as expressed by the higher hysteresis coefficient i.e. H = 2.30. In case of other minerals, the value of H < 1 signifies the reversibility in the results.

Such patterns depicted in the current research indicate two factors dominate the fate of PyBlm in the selected minerals. In case of stronger adsorption, the desorption rate is much slower showing the attachment of PyBlm molecules to the clay minerals in a firm way. Thus, percolation of PyBlm is blocked by minerals which exhibit affinity towards it. In this case, lower water profiles are protected from the harmful residues of PyBlm. However, in the reverse situation, if the adsorptive interaction with the molecules of PyBlm are poor, they assist in the percolation of PyBlm and thus challenge the integrity of lower profiles of the soils in addition to the deterioration of the ground water resources. Adsorption model results were statistically evaluated by applying univariate ANOVA between Kd and the physicochemical properties of minerals including; pH, CEC, specific surface area and d spacing (Table 4). The results were further assessed by plotting the residual graphs in Minitab 17. The residual plots depicted the goodness of experimental results (Fig. 6).

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