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Sorptive Interactions Evaluation of Benomyl Metabolites Mecarzole with the Varyingly Selected Minerals

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Abstract: Soil and soil minerals are the primary recipients of different contaminates coming in immediate contact. Agricultural practices which are dominated by use of different agrochemicals have further aggravated the soil quality. Fungicides, aimed at the extermination, inhibition and growth retardation of fungal species in agricultural crops have been used frequently. Among such fungicides, Benzimidazole based fungicides are of prime significance due to their comparatively improved annihilatory activity. Despite such frequent utilization, the reports on the reception and consequent sorption of Benzimidazole fungicides are scarce. Current work has, for the first time, investigated the interaction of Benzimidazole based fungicide, Mecarzole (metabolite of Benomyl fungicide and also known as Carbendazim) in the selected minerals i.e. corundum (alumina), silica, muscovite and montmorillonite. The interaction was studied via standard equilibration method established in batches. Adsorption and desorption of Mecarzole in the selected minerals was evaluated by multilayer Linear and Freundlich model for different parameters i.e. K_d, K_f, K_{fdes} and K_{des}. Linearity was exhibited by the minerals for attachment of Mecarzole. The highest values of K_d (6.93 mL. μg^{-1}) and K_f (7.99 mL. μg^{-1}) obtained for muscovite are indicative of the higher affinity of muscovite for Mecarzole in comparison to other three minerals. Excellent adsorption of Mecarzole in muscovite is suggestive of the fact that Mecarzole interacting with muscovite is not a threat towards lower soil profiles since there is a stronger bonding. In contrast to muscovite, Mecarzole poorly adsorbed in alumina represents a threat to soils due to possible percolation of poorly adsorbed Mecarzole molecules.

Keywords: Mecarzole, soil minerals, soil quality, physicochemical characteristics, sorption, sorption modelling.

Introduction

Soil pollution caused due to the indiscriminate use of different varieties of pesticides has been quite pronounced since last few decades. Such enhanced pesticide utilization trend can be attributed to the need of fulfillment of larger population and to cause an augmentation in the crop yields in a quicker duration. However, this trend has given rise to the increasing deterioration of environmental resources particularly soil and soil forming minerals. Thus, comprehensive efforts are needed to understand interaction between pesticides and soil components in order to carry out successful abatement. For this purpose, the comprehension of sorption pattern of pesticides in the soil is an integral part (Ahmad, 2018; Ahmad, 2018a, b). Such knowledge exhibits the distribution of pesticides in a controlled or uncontrolled manner (Ahmad, 2018c, d). However, the sorption interaction of different pesticides in soils and soil components i.e. minerals is decided by the physical and chemical aspects of both the soils and the pesticides (Vischetti et al., 2010).

Clay minerals represent a class of minerals known for their commendable adsorptive potential. For such aspects, these minerals have often been used in a commercialized way for the immobilization of different contaminants. Thus, higher proportion presence of such clay minerals in soils signifies the minimum leaching of different pesticides in the lower soil zones and thus reducing the toxicity to lower soil profiles (Ahmad, 2019; Ahmad, 2019b). The consequent desorption of different pesticides once they are adsorbed on minerals is dominated by the clay material nature and other aspects i.e. density of charge, surficial area etc. Such aspects influence the sorptive pattern of the chemical contaminants and hinder their movement in soil profiles and thus causing stabilization against desorption. The clay minerals used in the current research are alumina, silica, muscovite and montmorillonite. The relevant physical and chemical properties of these clay minerals have been shown in Table 1.

By virtue of favorable soils, climatic patterns and water availability, Pakistani landscape represents primarily agriculture-based economy. Pakistani soils have been known for the production of export quality crops inclusive of cereals, fruits, vegetable etc. At the same time, these lands are also vulnerable to the attack by pests. The control of such pests has been done by using different agrochemicals, although efforts have been done to avoid the environmentally damaging pesticides by replacing such pesticides with nano-pesticides (Jaffri and Ahmad, 2017, Jaffri and Ahmad, 2018a- d). Nevertheless, the use of pesticides becomes inevitable since the research domain of nano-pesticides is still an emerging field. Various economically significant crops are protected from different fungal pests by using fungicides. Mecarzole, a Benzimidazole family derivative and daughter product of Benomyl has been frequently used for the management of fungal pests attacking different crops e.g. cauliflower, pears, cotton, apples etc (Fig. 1).

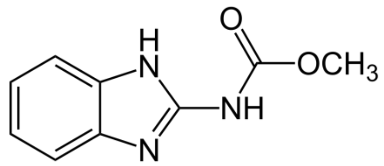

Fig. 1 Chemical structure of Mecarzole

Mecarzole represents the most utilized fungicide in the Asian countries but the negative impacts of Mecarzole on environment and human health cannot be overlooked. It shows a considerable hepatic and renal toxicity in addition to mutagenic effects. Despite such considerable deleteriousness, no researches have been found on the interaction of Mecarzole with soil minerals. Thus, current work has been undertaken to comprehend the role of Mecarzole in soil quality disturbance by means of sorption phenomenon.

Table 1 Relevant physiochemical properties of minerals to be treated with Mecarzole.

Minerals	Formula	pH	AEC (cmol. kg-1)	CEC (cmol. kg-1)	d- spacing (A°)	Specific Surface Area (m2g-1)	Lattice Type
Silica	SiO2	2	0.4	3	0	524	n-a
Montmorillonite	Mx(Al, Fe, Mg4) Si8O20 (OH4)	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	KAl2 (AlSi3O 10) (OH2)	n-a	n-a	3.1	10	70	2:1

Materials and Methods

Materials and Solvents

For investigation of the Mecarzole sorption in the selected minerals, the experimentation was conducted in the laboratory under the simulated conditions. All the experiments were done with analytical grade reagents and with distilled water (DW). Sodium chloride, hydrochloric acid, sodium hydroxide, calcium carbonate and methanol have been purchased from Merck, Germany. Analytical grade Mecarzole was also purchased from Merck, Germany. Minerals i.e. alumina was purchased from BDH, England), silica and muscovite were purchased from Alfa Aesar, Germany. While, montmorillonite was purchased from Sigma Aldrich, Germany. The obtained minerals were utilized without further purification. All the experimental apparatus was sterilized prior to use and the experimentation was done in isothermal conditions of 25 $\pm$ 1. All the experiments were done in triplicates and the average results were shown as the representative results. The data analysis was done by using different parameters of linear and Freundlich models by following Ahmad et al., (2018a-d).

Clay Minerals-Mecarzole Adsorptive Interactions:

Adsorptive interactions were studied by using standard batch equilibrium method. Mecarzole stock solution has been prepared using the analytical grade methanol by dissolving 0.1 g of Mecarzole in 100 mL of methanol. Total six dilutions were extracted from the Mecarzole stock solution i.e. 0.25, 0.5, 0.75, 1.0, 2.5 and 5.0 ppm and the level was raised by DW followed by storage at 10. Properly labelled test tubes were filled with 0.5 g of the selected minerals and added with the 10 ml from each dilution of the Mecarzole stock solution. The filled tubes containing minerals and Mecarzole solution were centrifuged at 5000 rpm for 5 min at ambient temperature 25 for attainment of equilibrium. After that the reaction mixtures were shaken for 24 h. It was followed by analysis of the reaction mixtures via UV-Visible spectrophotometer (BMS, 1602) at 282 lambda maximum.

Clay Minerals-Mecarzole Desorptive Interactions:

For conducting desorption experiment of Mecarzole in the selected soil minerals, batch equilibration experiment was conducted. After the spectrophotometric analysis of adsorbed reaction mixtures, the tubes were decanted and weighed. The settled soil at the bottom was added with 9 mL of the $CaCl_2$ (0.01 M) which was prepared freshly. The added reaction tubes were agitated for 24 hours followed by spectrophotometric evaluation at 282 lambda maximum. The obtained values of UV-Vis for Mecarzole were utilized for plotting of the isotherms of the models employed.

Results and Discussion

Increasing development in the agrarian arena is associated with the contamination of the environmental compartments especially the hydrospheric and pedospheric regions. Major portion of the pesticides reaches the nontarget regions in the ecological setting either through spray drifting, run off and percolation (Singh and Cameotra, 2013). Pesticides' adsorptive and persistence characteristics often determine their distribution in the environmental compartments (Yue et al., 2017; Rubio-Bellido et al., 2016). Soils have been characterized with severe pollution problems especially due to agrochemicals use in the agricultural regions. The responsiveness of soil particles to different contaminants decides the fate of pesticides in different soil profiles. Agricultural pests have been managed by many chemico-biological means (Ahmad and Jaffri, 2018a, b) but the use of chemical fungicides has been augmenting with the passage of time causing soil pollution. However, both characteristics of soils and nature of pesticides particularly nonionic pesticides are known to exert significant impacts on the adsorption of a pesticide in soils. The pesticides adsorbed in the soils are destined to desorb with different rates. In some cases, the detachment of a particular pesticide from soil structure is completely irreversible due to many factors e.g. development of chemical interactions between soils and pesticides, lacking the potential to achieve equilibrium at the time of desorption. Furthermore this reversibility is due to the pesticide loss in case of biologically driven deterioration, precipitation and volatilization (Sánchez et al., 2011). Different studies describe the adsorptive mechanisms of different pollutants in soil matrix (Gevao et al., 2000), or particularly in different clay minerals (Thiebault et al., 2016). However, there exists a disagreement in the results obtained for different soil minerals based studies (Kulik, 2009). Different soil based constituents, e.g. clays and clay-composites are used as an efficacious adsorbent having lower costs for pollutant removal (Bhattacharyya and Gupta, 2008; Auta and Hameed, 2014; Marco-Brown et al., 2018). In the present study, the adsorption and desorption behavior of Benzimidazole derivative, Mecarzole has been evaluated in a concentration dependent manner.

Table 2 Adsorption coefficients of Mecarzole studied in different clay minerals.

Mineral	K_d (mL. μg^{-1})	Slope	R^2	K_f	Slope	R^2	n_f
Alumina	5.22	1.47	0.98	7.38	0.10	0.98	1.2434
Silica	5.27	2.27	0.96	7.12	0.24	0.95	1.2953
Montmorillonite	5.27	2.12	0.84	4.49	0.17	0.99	0.2682
Muscovite	6.93	1.90	0.99	7.99	0.68	0.71	1.2376

Table 3 Desorption coefficients of Mecarzole studied in different clay minerals.

Mineral	K_{des}	Slope	R^2	K_{fdes}	Slope	R^2	n_{des}	H
	(mL.μg^{-1})							
Alumina	17.15	0.19	0.99	17.16	0.036	0.99	0.998	0.802
Silica	15.02	0.39	0.98	15.05	0.068	0.97	1.021	0.788
Montm orillonite	21.08	0.073	0.96	20.96	0.014	0.96	0.982	0.749
Muscovite	16.13	0.43	0.99	16.49	0.1328	0.97	0.928	3.662

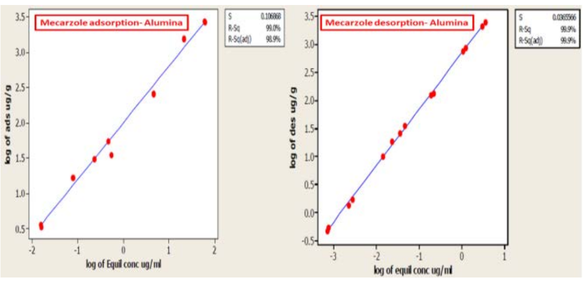

Fig. 2 Freundlich isotherm of adsorption desorption of Mecarzole studied in alumina.

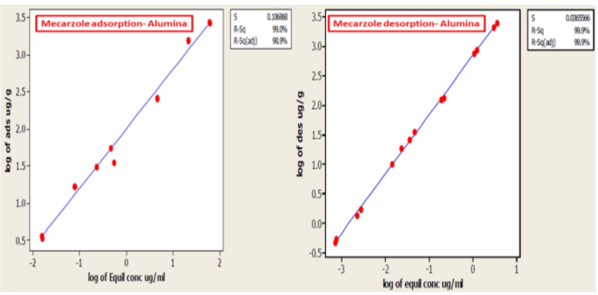

Fig. 3 Freundlich isotherm of adsorption desorption of Mecarzole studied in silica.

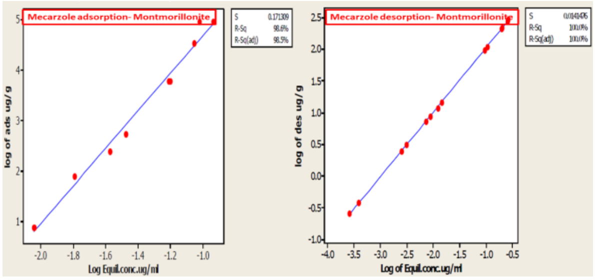

Fig. 4 Freundlich isotherm of adsorption desorption of Mecarzole studied in montmorillonite

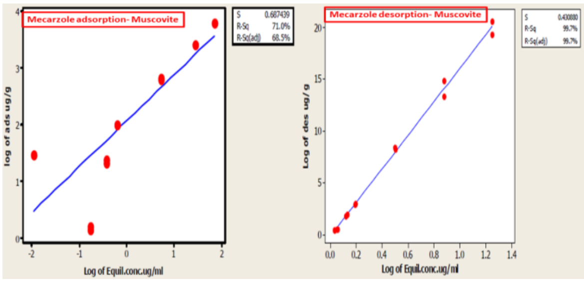

Fig. 5 Freundlich isotherm of adsorption desorption Mecarzole studied in muscovite.

Figures 2-5 show the sorption pattern of Mecarzole in different clay minerals. The comparison for the potential of different minerals in adsorbing the Mecarzole was done by determination of the linear and Freundlich adsorption coefficient. It was done by using the straight line equations in addition to the determination of slopes. Table 2 and Figures 2-5 depict a general nonlinear trend of Mecarzole sorption in the selected clay minerals. Linear and Freundlich adsorption-desorption coefficients i.e. K_d and K_f were calculated by plotting the clay minerals concentration ($\mu g.\ g^{-1}$) against the equilibrium concentration of the Mecarzole ($\mu g.$ mL). However, they express a C-Type isotherm showing perfect fitting with the Freundlich model for having the regression coefficient (R^2) > 0.9 while it expressed a good fit with the linear model for having $R^2 > 0.8$. C-type isotherm shown by all minerals for Mecarzole sorption is expressive of the hydrophobicity of Mecarzole molecules due to their organic genesis and thus they are capable of distributing themselves in a uniform way between the organic content and inorganic mineral solution (Sanchez-Martin et al., 2006). The values of n_f in Table 2 are indicative of the different sorption capacities influenced by varying concentrations. Maximum adsorption of Mecarzole was observed in muscovite, which is indicative of the fact that larger proportion of Mecarzole is trapped by the muscovite particles in a firm manner and thus, the leaching down of Mecarzole molecules is a challenging task. This reflects the positive aspect in one way that the lower soil profiles will be saved from Mecarzole contamination but it also poses a threat that Mecarzole molecules will remain attached to the muscovite particles unless any remediation technique is employed. The adsorptive trend for K_d varied in the following manner.

Muscovite (6.93 mL. µg^{-1}) > Montmorillonite= Silica (5.27 mL. µg^{-1}) > Alumina (5.22 mL. µg^{-1})

The selected minerals were also evaluated for their behavior towards the detachment of Mecarzole molecules followed by adsorption experiment (Table 3). This behavior was analyzed by using linear and Freundlich models by plotting the the clay minerals concentration (µg. g^{-1}) against the log of the equilibrium concentration of the Mecarzole (µg. mL). Since desorption is an opposite process of the adsorption, thus, the minerals good at adsorption expressed poor desorption of Mecarzole. The higher desorption coefficients express the potential of Mecarzole molecules in reaching the lower soil profiles. Desorption isotherms also expressed the C-type isothermal behavior and reflected the perfect fitting with both linear and Freundlich model for yielding $R^2 > 0.9$ in both cases. Sorptive characteristics obtained in current research are in conformity with the variety of pesticides sorbed on different clay minerals e.g. linuron on palygorskite (Belaroui et al 2018), Chlorsulfuron on geothite and bentonite (Ahmad et al., 2016), metalaxyl and fludioxonil on natural clays (Rodríguez-Liébana et al., 2016), and metalaxyl and tricyclazole on natural clays (Azarkan et al., 2016). Furthermore, the hysterical nature of the selected clay minerals towards Mecarzole fungicide was also determined. The value of hysteresis coefficient H was found less than 1 for alumina, silica and montmorillonite but was greater than 1 for muscovite. Value of $H < 1$ refers to the reversibility of adsorption-desorption process. Since the muscovite developed commendable adsorptive interactions with Mecarzole molecules, thus, they are bound irreversibly and consequently showing value more than one for 1.

Conclusion

Pedospheric compartment comprising of different soils and soil minerals have been known for their receptive role in terms of pollutant and contaminant uptake and transferal. Current research has for the first time analyzed the behavior of Mecarzole fungicide in the selected soil minerals i.e. corundum (alumina), silica, muscovite and montmorillonite. The experimentation was done via standard batch equilibrium method. All soil minerals expressed variable affinity towards the Mecarzole adsorption and desorption as a function of the minerals' physicochemical characteristics. Results were indicative of the excellence of muscovite in having highest adsorptive affinity towards Mecarzole and thus, exhibiting lower threat of Mecarzole in leaching towards ground water reservoirs if it comes in contact with Muscovite.

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