Journal of Contemporary Research in Chemistry (2017) 2(1): 1-14

Sorption characteristic of Cinosulfuron in Pakistani soils along with two minerals and their statistical evaluation

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Abstract

A Sulfonylurea herbicide, Cinosulfuron was investigated for its adsorption-desorption behavior on two minerals and two Pakistani soils having different geographical conditions. This sulfonylurea herbicide is used in Pakistan against a wide range of leafy weeds and grasses. The sorption experiments were done utilizing batch equilibrium methods. The data obtained showed that adsorption co-efficient isotherm for Cinosulfuron in two tested soils well fitted the Freundlich equation. The isotherm was nonlinear in all cases with slope n<1 resembling the L type curve. Distribution co-efficient ($K_{d)\ parameters}$ were low indicating low adsorption. Low Gibbs free energy values were connoting the phenomena of physisorption in soils. It was observed that Cinosulfuron herbicide showed a relatively greater degree of adsorption on soil samples collected from northern hilly areas of Ayubia, Khyber Pukhtunkhwa (Silt loam) i.e. 25.5% and low adsorption on sandy soil of Multan, Punjab. Soil organic matter (SOM), pH and total carbon content (TOC) were considered to be imperative factors leading to variances in sorption capacity. Their regression and correlation was determined with adsorption distribution coefficient (r=-1, r=1 and r=1 respectively).

Keywords: *Cinosulfuron, sorption, desorption, physicochemical properties, soil organic matter.*

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Introduction

Pesticides are chemicals or mixture of chemicals used to control pernicious organisms (Baxter et al., 2010). Their classification can be done on the basis of either their chemical structure, target compound or their mode of action (Collotta et al., 2013). 48% of total world's food production is destroyed by rodents, birds, weeds, parasites, etc. every year (Pedigo & Rice, 2014). Thus modern agriculture practices rely on wide utilization of pesticides, to control this terrific loss of production (Laurance et al., 2014). Long ago, the pest controlling practices were initiated by employing synthetic methods (Benelli et al., 2015). Neem plant oil is still being used by poultry farmers to eradicate pests without the use of chemical products. Being natural, it has no pernicious effects on the environment thus posing very low risk to mammals (Rovida et al., 2015).
The amount of organic matter in soil, its percentage clay content and pH determine the movement of pesticides from their intended site of application to ground water (Sun et al., 2015). The behavior of pesticides, especially their uncontrolled and/or controlled distribution in soil and sorption behavior, must be well understood to reduce the risk of environmental contamination (Matthews, 2015). The bio-efficacy and persistence of the pesticides is affected by their adsorption and desorption behavior. Moreover, it also effected the uptake of pesticide and its metabolism by any living organism and migratory behavior in the soil and/or ground water (Smaranda & Gavrilescu, 2014). The intermolecular interactions comprising Van der-Waals forces, hydrogen bonding, ligand exchange, charge transfer, chemisorption, dipole-dipole interaction and direct & induced ion-dipole, effect the physicochemical properties such as electronic structure and water solubility for adsorption-desorption studies (Ali & Baugh, 2003).

Sulfonylurea, an exceptional herbicidal group among various commercialized herbicide, mitigate a range of unwanted weeds (Saeki et al., 2016) and grasses for numerous vegetables and crops containing wheat (Kaczyński & Łozowicka, 2017), oats, barley, maize, rice (Mehdizadeh et al., 2016), soyabean, flax, oil seed rap, sugar beets, blueberries, tomatoes, forestry, and potatoes (Ma et al., 2016). Sulfonylurea are popular worldwide because of low mammalian toxicity and exceptional herbicidal activity (Cessna et al., 2015) with 10-40 g/ha application rate in comparison to other herbicides (e.g. for atrazine 2-5 Kg/ha for atrazine) (Gure et al., 2015; Carles et al., 2017). A nexus of relationship of pesticide structure, its mode of action and degradation rate may be able to determine different modifications in the sulfonylurea herbicide rapid degradation (Hua et al., 2016). Sulfonylurea degrades under field condition, primely by chemical hydrolysis and microbial breakdown, faster than conventional herbicides. Hydrolysis is a pH-dependent first order reaction that accelerates at higher temperature (Yueli & Bo, 2011; Lu et al., 2011). Chemical hydrolysis predominates in acidic soils while alkaline soils favors microbial breakdown (Sabadie, 2002). Warm, moist, low pH, light texture soil breakdown relatively faster than cold, high pH and dry heavy texture soils (Mishra & Patel, 2008).

Sulfonyl urea herbicide, Cinosulfuron, 1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-3-[2-(2-6,4-methoxyethoxy)phenylsulfonyl]urea, is used as a post emergent (Loughner et al., 2010) and a pre-emergent herbicide on a number of agricultural crops (Ishaya et al., 2014; Rodenburg & Dermont, 2010). Principally, the breakdown of the urea part of Cinosulfuron occurs at 30ºC (Schneiders et al., 1993). Different microorganisms including bacteria (Ruan et al., 2013) and fungi (Song et al., 2013) have been found capable of degrading Cinosulfuron at a diverse range of pH and temperatures. Sulfonylurea herbicide, trade name Alkanak and Logran used in Pakistan, mitigates a number of weeds in wheat crops (Ukrainczyk & Rashid, 1995). The adsorption behavior of Cinosulfuron, depends on soil pH that possess a negative relationship with adsorption of the herbicide (Khan et al., 2003). The nature and properties of soil and pesticide chemistry influence the mechanisms of binding of nonionic pesticides to the soil components (Chen et al., 2015).

The knowledge of fate of pesticide in terms of persistence and toxicity is limited in spite of their excessive usage that increases its potential to contaminate. The aim of current research is to study how these pesticides effect the environment and soil in Pakistan, along with two minerals. The soil samples were collected from two different agronomic areas of Pakistan. In agro-environment the residue behavior of pesticides is majorly affected by the adsorption processes in soil.

Materials and Methods

Solvents

Methanol and acetone used were from Merck, Germany and 99.9 % pure. Sodium chloride (extra pure) and calcium chloride (anhydrous), sodium chloride from Sigma Aldrich, Germany were used. Cinosulfuron, from ACCU Standard USA, was of analytical standard.

Soil samples

Two soils (0-10cm) were collected from the areas of Punjab and KPK, with no recent history of pesticide application. Soil 1 was taken from Ayubia situated in District of Abbottabad (34.0292° N, 73.4026° E), KPK and soil 2 was from chak no. 136 WB Tehsil Harpa District Multan (30.1984° N, 71.4687° E), Punjab. The two soils possess a considerable difference in level of clay organic matter and pH.

Sample preparation

The samples were mixed thoroughly, dried at r.t (room temperature) then grinded by using mortar and pestle followed by passing through 2 mm screen-sieve, in order to achieve homogeneity, then analyzed for organic matter percentage, pH and moisture content. The weight loss of the sample by heating it to a temperature of 673 K for 24 hours in a Ney Vulcan burnout oven, may oxidize any volatile component thus determined the organic content by elemental analysis (Afyuni et al., 1997). The soil slurry was used to measure the pH using Orion 420 plus pH meter after one-hour contact time (Tang et al., 2009; Zhang et al., 2007). The significant physiochemical properties of soil samples are tabulated in Table 1

Table 1 Physiochemical properties of soils

Sample	Location	Soil Texture	SOM (%)	Clay (%)	Sand (%)	Silt (%)	pH	% C	Primary Crops
Soil 1	Ayubia (KPK)	Silt loam	6.51	44	24	41	7.6	3.79	Maize, French beans
Soil 2	Multan (Punjab)	Loamy & sandy	1.89	12	52	13	8.1	1.10	Wheat, Cotton

Adsorption studies

The experiments were performed following the OECD Guideline for Testing of Chemicals under isothermal conditions at 25±1ºC (OECD, 2005; Shariff, 2012; Doretto et al., 2014). Eight different concentrations of Cinosulfuron 0.25, 0.5, 0.75, 1.0, 2.5, 5.0 and 7.5 ppm were prepared in deionized water, with 1:20 of sorbent/solution ratio, and stored at 4ºC. The ionic strength similar to natural soil was simulated by the addition of background electrolyte, 0.1 M sodium chloride, 10 mL in each concentration, which minimizes the cation exchange and also improves centrifugation. Each sample, consisting 0.5 g soil / mineral, mixed with 10 mL pesticide solution, placed in a 15 mL Pyrex glass- screw cap fitted centrifuge tube and were agitated continuously on a Stuart Orbital Shaker at 90 rpm (25ºC) for 24 hrs in order to achieve equilibrium (Liang et al., 2014). This process was repeated twice for each concentration. The possible degradation during adsorption was also quantified by means of a blank sample in parallel experiment which lacks mineral/ soil and only contains the background electrolyte and dissolved pesticides. The pH of the blank was kept to neutral to avoid any pH related effects. Then the data was evaluated using HPLC and XRD techniques. All experiments were done replicates.

Desorption experiment

After the adsorption experiment, the residue of the supernatant was decanted and 0.01 M $CaCl_2$ freshly prepared solution (9 mL) was added to the soil in the centrifuge tubes (re-weighed) followed by shaking for 24 hrs. Desorption (µg/g' soil) was evaluated from difference, taken into consideration the residual solution in the soil once the supernatant was poured off.

Data analysis

The amount of the Cinosulfuron adsorbed (µg/g of soil) was calculated by using Equation (1).

$$\mathrm{C_s} = \frac{\mathrm{V}}{\mathrm{m}}.(\mathrm{C_b} - \mathrm{C_a})\text{..... (1)}$$

Where, C_s is the amount adsorbed, V is the volume of solution, m is grams of soil taken, C_b is equilibrium concentration of blank and C_a is equilibrium concentration of treatment supernatant. The adsorption values obtained from Equation (1) were used to construct following linear type of isotherm (Equation (2)).

$$\mathrm{K_{d\,(ads)}} = \mathrm{C_s/C_e}\text{..... (2)}$$

Where, $K_{d(ads)}$ is linear or sorption equilibrium distribution co-efficient in (ml/µg). C_e is the concentration (µg/ml) at the equilibrium concentration. Desorption is expressed as micrograms adsorbed/gram of soil (µg/g soil) and was calculated from the difference of solution remaining in the soil after the supernatant was decanted off. The sorption equilibrium distribution co-efficient $K_{d\,(des)}$ in (ml/µg) was calculated by Equation (3).

$$\mathrm{K_{d\,(des)}} = \mathrm{C_s/C_e}\text{...... (3)}$$

The adsorption isotherms of pesticides in all the soils fitted the Freundlich adsorption relationship Equation (4).

$$\mathrm{C_s} = \mathrm{K_f C_e^{1/n}}\text{..... (4)}$$

Where, C_s is the amount of adsorbed (µg/g), C_e is the equilibrium concentration (µg/ml) and K_f and n are constants determined by applying the linearized form of the Freundlich equation. K_{oc} was found by Equation (5) and the Freundlich constant normalized to organic carbon (K_{foc}) was calculated by using Equation (6).

$$\mathrm{K_{oc}} = \frac{\mathrm{K_d}}{\%\mathrm{C}}.100\text{..... (5)}$$

Where K_{foc} and K_f are related as:

$K_{foc} = \frac{K_f}{\%C} . 100$ ..... (6)

The equilibrium organic matter (K_{OM}) by normalizing K_d or by normalizing K_f with the content of was calculated according to equation (7) and equation (8) respectively.

$K_{OM} = \frac{K_d}{\%OM} . 100$..... (7)

$K_{OM} = \frac{K_f}{\%OM} . 100$...... (8)

The hysteresis coefficient (H) for the adsorption isotherm was calculated using the Equation (9)

$H = n_d / n_a$……… (9)

Where n_a and n_d are the Freundlich constants of the adsorption and the desorption isotherms. The standard free energy change of adsorption (ΔG) from the isotherm can be calculated using the following Equation (10) (Nyström et al., 1999).

$\Delta G = -RTlnK_{OM}$..... (10)

The ΔG can be used to judge the adsorption reaction. Its value ≤ -40 $kJmol^{-1}$ indicates physical adsorption of herbicide with the soil.

Results and Discussion

Adsorption isotherm

Comparative linear and Freundlich adsorption was studied for Cinosulfuron on the selected soils and minerals i.e. Bentonite and Geothite (Fig. 1 and Fig. 2 respectively). Freundlich constant (K_f), Distribution coefficient (K_d), standard deviation (S), Hysteresis (H) and Gibbs free energy (ΔG) change of both soil samples and minerals were calculated (Table 2; Table 3). The adsorption reaction is mediated by Gibbs free energy (ΔG) change. The physical adsorption of herbicides on soil is indicated by absolute value of G ≤ 40 kJ/mol. The negative values of Gibbs free energy or ΔG are indicating that at given experimental temperature the interactions of Cinosulfuron on soils were spontaneous. The ΔG values are -10 kJ/mol and -12 kJ/mol. The negative energy of adsorption for partition coefficient is indicating an exothermic binding between soil and pesticide (Shariff, 2012). Values of distribution coefficients K_d adsorption are 27 µg/ml and 5.1 µg/ml signifying the adsorption of Cinosulfuron on both the tested soils. Soil sample 1 with higher organic matter content have high K_d and K_f values. High K_d values are indicative of strong affinity of pesticide for soil (Gebremariam et al., 2012). A correlation of K_f and K_d values was observed with n~1.0. The organic matter content determines the extent of sorption of pesticides in soil. Lower value of $K_{d(ads)}$ for soil 2 signifies limited adsorption sites on soil due to low clay and SOM. The regression coefficient (R2) values were 0.96 and 0.87 with 1 and 1.6 standard error (S). These values are used to obtain the accuracy of fit or the best fitting isotherm for the data (Chen et al., 2015). Values are verifying that the experimental data was well fitted to Freundlich adsorption model.

K_f values were found to be higher than K_d values confirming the strong adsorption of Cinosulfuron. K_f for adsorption of Cinosulfuron were 38µg/ml and 13µg/ml. The highest K_f was observed in soil 1 due to highest organic carbon content. Table 1 shows a significant positive correlation of K_f values with the organic carbon content of the tested soils indicating that organic carbon exerted a strong effect on the sorption of Cinosulfuron in soils. R^2 and S values for Freundlich model of adsorption indicated that the experiment is fitted well to the model. SOM and clay content facilitates adsorption of pesticides by providing more adsorption sites thus soil 1 revealed comparatively higher adsorption. Furthermore, Table 1 shows that the predicted capacity for Cinosulfuron retention normalized to the SOM content (i.e.K_{foc}) differentiated significantly in these two soils. The sorption capacity of these soils was further compared with the K_{oc} values measured. The high K_{oc} values suggest the stronger adsorption capacity in the organic matter of the soils (Pereira et al., 2013). $K_{d(ads)}$ values for Bentonite and Geothite revealed more adsorption on Bentonite mineral as compared to Geothite with value 7.16 µg/ml for Bentonite and 4.07 µg/ml for Geothite. The regression coefficient (R^2) values were 0.49 and 0.18 with 0.1 and 0.1 standard error (S).

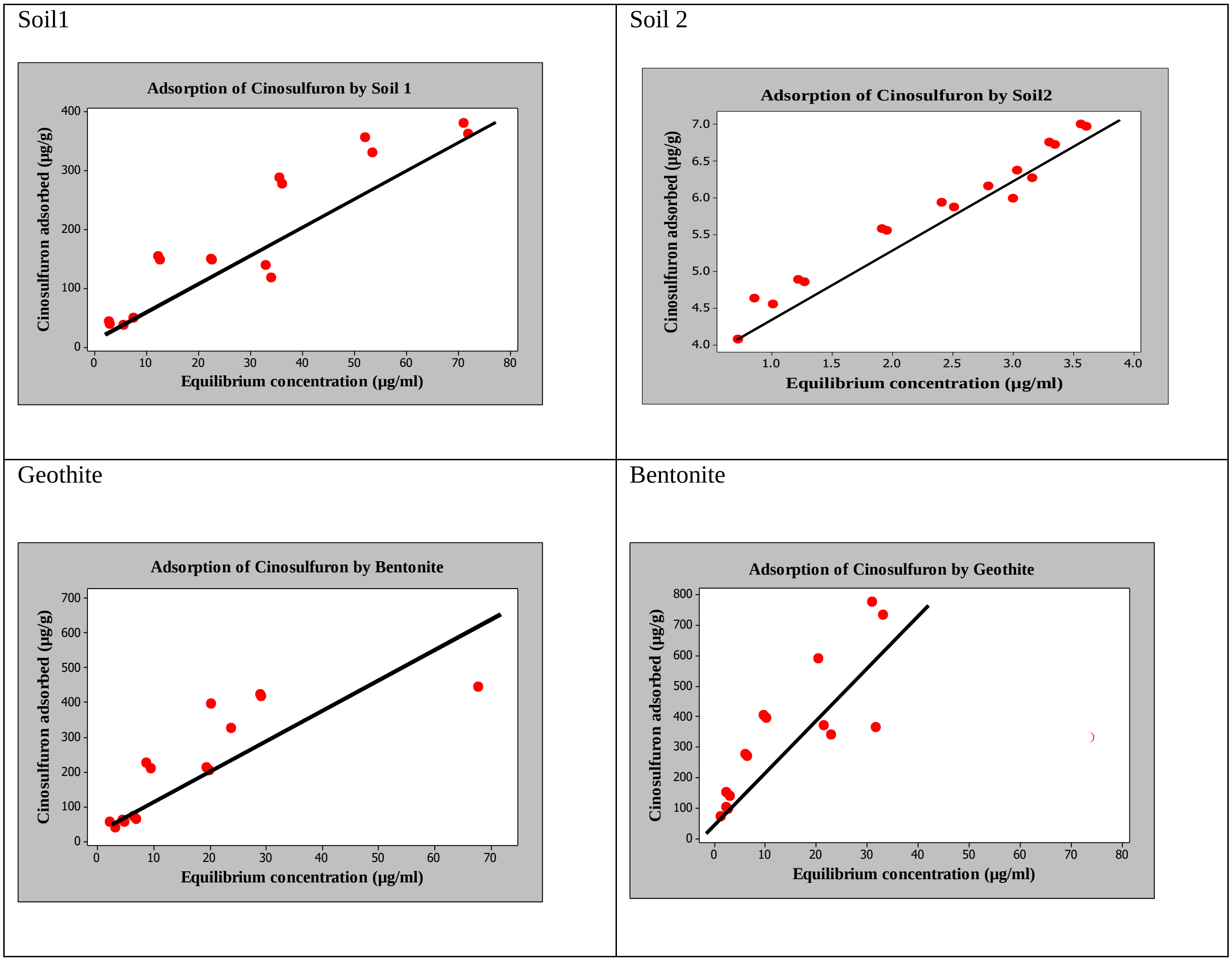


Fig. 1 Comparative adsorption of Cinosulfuronon two soil samples and selected minerals i.e. Geothite and Bentonite

Table 2 Adsorption Coefficients of Cinosulfuron in Selected Soils

Soil	K_d	R^2	K_{oc}	S	K_f	n	R^2		K_{foc}	K_{OM}	G
Soil1	27	0.96	712	1.0	38	1.10	0.97	0.17	1002	56	-10
Soil2	5.1	0.87	463	1.6	13	1.28	0.88	1.80	1181	135	-12

Table 3 Adsorption Coefficients of Cinosulfuron in Selected Minerals

Mineral	K_d	R^2	S	K_f	n	R^2	S
Bentonite	7.16	49.3	1.5	2.97	1.16	82.9	0.4
Geothite	4.07	18.8	1.9	14.4	2.06	82.9	0.4

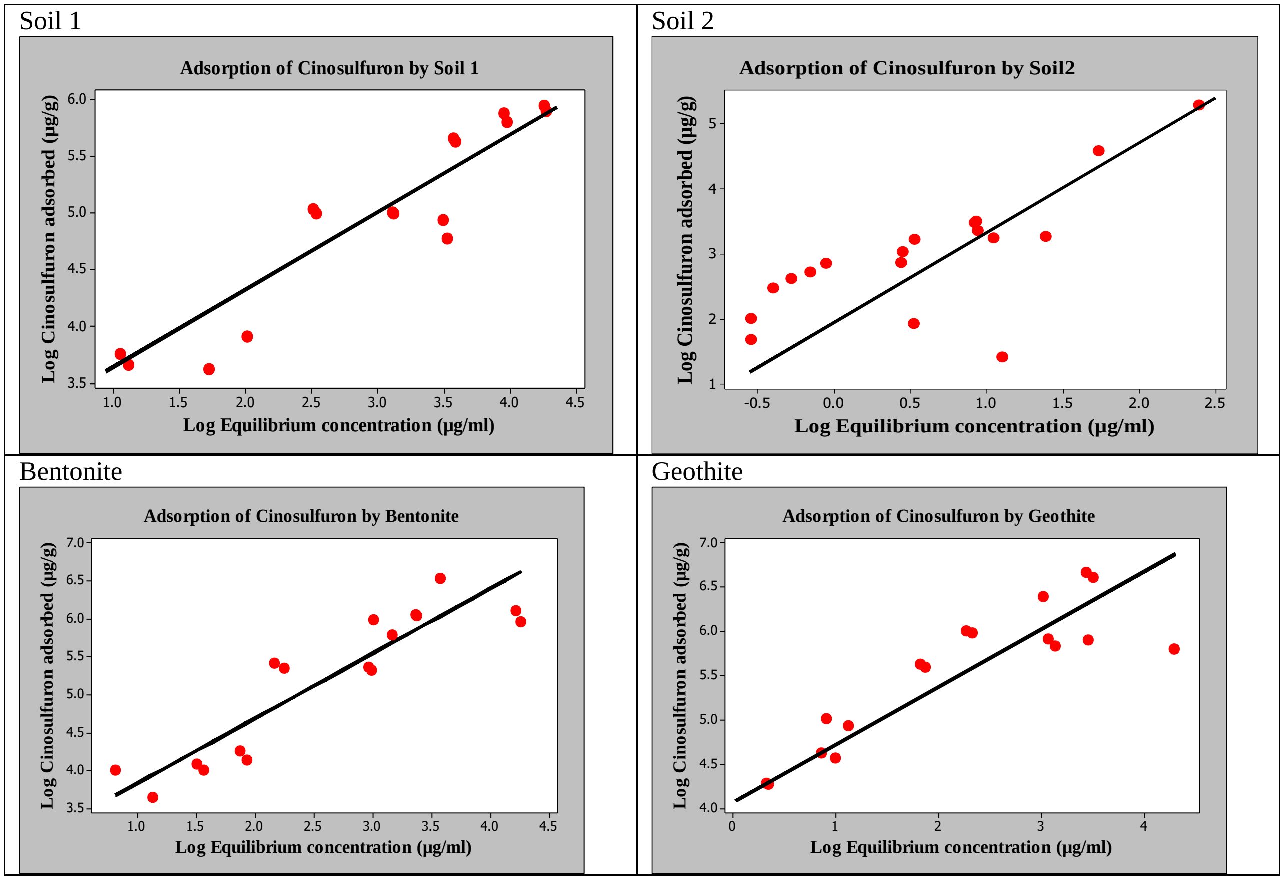


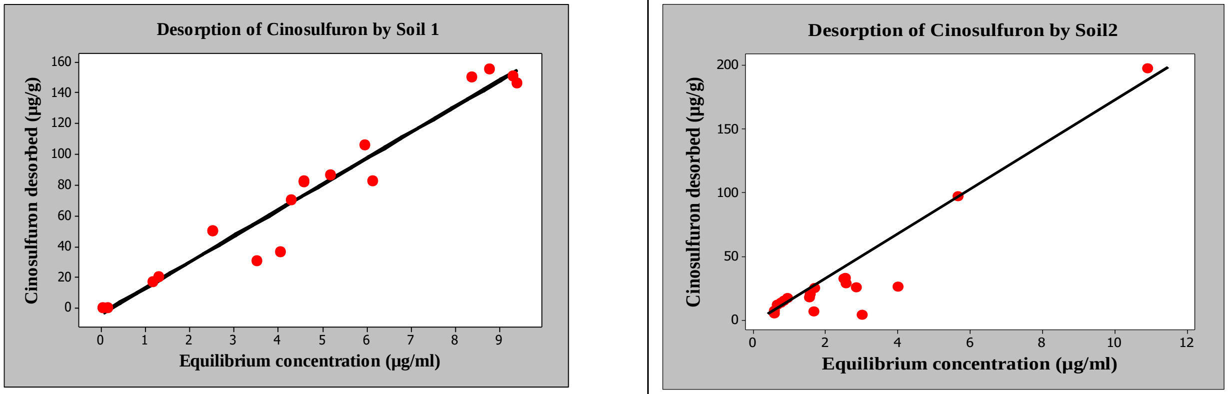
Fig. 2 Comparative Freundlich adsorption of soil samples and minerals; Geothite and Bentonite

Desorption characteristics

Desorption equilibrium distribution co-efficient ($K_{d(des)}$) is calculated by plotting the desorbed pesticide concentration ($C_{s(des)}$) against the equilibrium pesticide concentration ($C_{e(des)}$) and are shown in Fig. 3while Fig. 4 shows Freundlich desorption isotherms. In present study Cinosulfuron pesticide revealed lesser desorption in soil 2 as compared to soil 1. The values of $K_{d(des)}$ were 17.43 µg/ ml and 16.88 µg/ml for desorption (Table 4). Values of K_f were 11.86µg/ml and 13.14 µg/ml. $K_{f(des)}$ values are comparatively lower than $K_{d(des).}$ Low values of $K_{f(ads)}$ indicate an increasing desorption. This is as a consequence of the fact that less K_f values show lower affinity of pesticides and soils (Dada et al., 2012). The R^2 values of Freundlich desorption are 0.76 and 0.96. Variation in hysteresis coefficient values can be seen in Table 4. Hysteresis demonstrated that for soil 1 desorption took place as readily as adsorption because values of hysteresis for Soil 1 (1.05) were very close to 1. The values of $K_{d(des)}$ for minerals Bentonite and Geothite were 13.68 µg/ ml and 13.39µg/ ml (Table 5). The values of $K_{f(des)}$ obtained were 2 µg/ ml and 19.1 µg/ ml.

Soil 1

Soil 2



Bentonite

Geothite

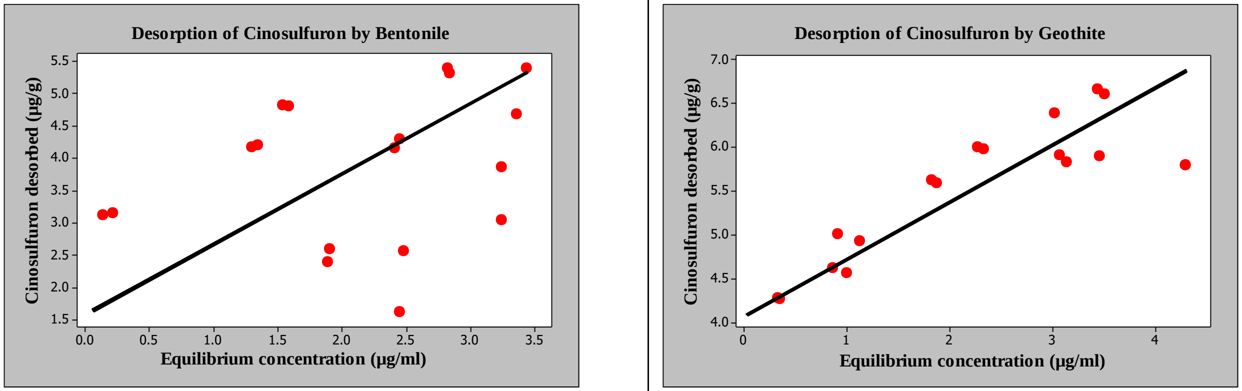


Fig. 3 Comparative desorption of Cinosulfuron on selected soils and minerals

Table 4 Desorption Coefficients of Cinosulfuron in Selected Soils

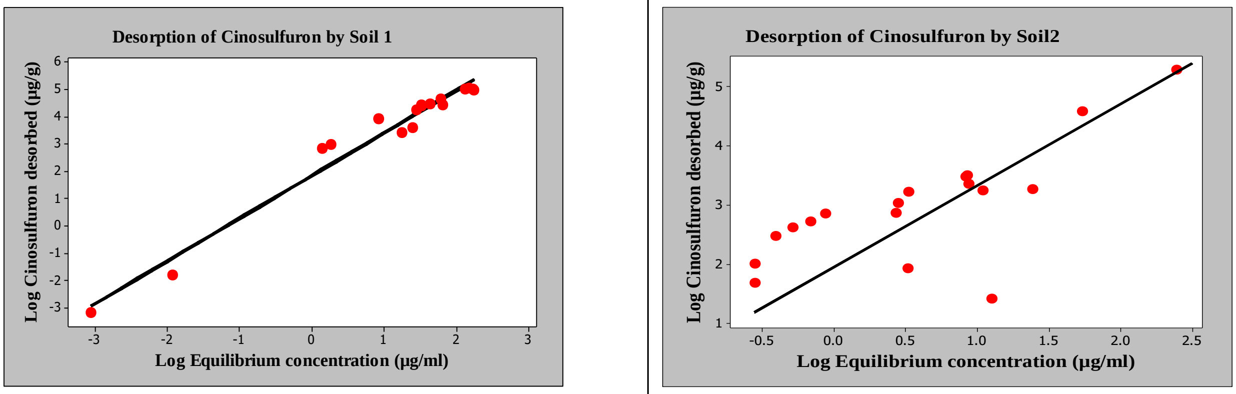
Soil	**$K_{d(des)}$**	**R^2**	**$K_{f(des)}$**	**n**	**R^2**	**H**
Soil1	17.43	0.89	11.86	1.16	0.76	1.05
Soil2	16.88	0.94	13.14	0.89	0.96	0.69

Table 5 Desorption Coefficients of Cinosulfuron in Selected Minerals

Mineral	**$K_{d(des)}$**	**R^2**	**$K_{f(des)}$**	**n**	**R^2**	**H**
Bentonite	13.68	0.71	2.0	0.07	0.99	0.05
Geothite	13.39	0.88	19.1	1.128	1.00	0.54

Soil 1

Soil 2



Bentonite

Geothite

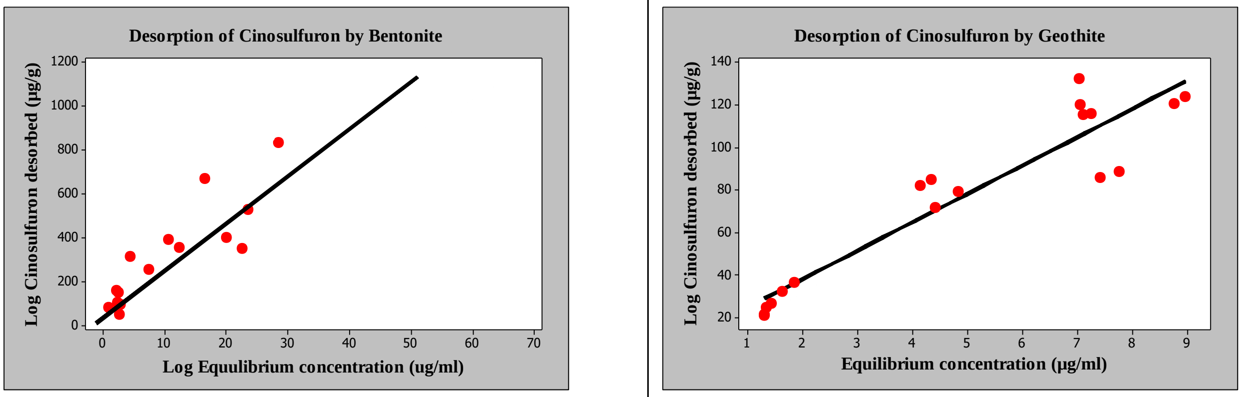


Fig. 4 Freundlich desorption Isotherms of Cinosulfuron on selected soils and minerals

Statistical analysis

Investigations were performed to find the correlation between $K_{d(ads)}$ and the physiochemical properties of soil (pH, OM and TOC) (Table 6; Fig. 5). The data was analyzed for the effect of physiochemical properties on K_d by linear regression analysis. The statistical analysis on $K_{d(ads)}$ revealed that pH is negatively correlated (r=-1) while OM and TOC are positively correlated with $K_{d(ads)}$ (r=1 and r=1 respectively). In accordance with the Fig. 5 the lowering value of pH results in an increase in the process of adsorption. While increasing OM and TOC values result in enhanced adsorption. The results also specified that the Soil 1, having highest $K_{d(ads)}$ value (21 µg/g), contains the high percentage of soil OM (6.51 %) and highest percentage of TOC (3.79 %) proving the fact that Soil OM and TOC is directly proportional with the rate of adsorption occurring in that particular soil. Soil samples, minerals and adsorption distribution coefficient K_d were analysed for means by one-way ANOVA, using BioStat 2009 Professional 5.7.8 statistics tool, on all samples. The calculations by the univariate ANOVA involved different parameters such as sum of squares (SS), mean square (MS), F statistics (F), P value and F critical values (F crit) within the same groups and between groups (Table 7). Prior to this analysis it is assumed that all observations are originating from normal distributions and all the four groups of soils have equal variances. In this scenario, the P value (0.4) was found less than the alpha value (α) (0.05), consequently the null hypothesis ($H_{\circ}$) is excluded in this circumstance i.e, the assumption which was made formerly. It was also observed that the F critical value (F crit) was found to be 18.5. F crit is the value, such that any value of F statistics greater than the F crit value would result in rejection of null hypothesis (H_o). The F statistics value (0.4) in this experiment is less than the F crit value hence it does not lie in the rejection region.

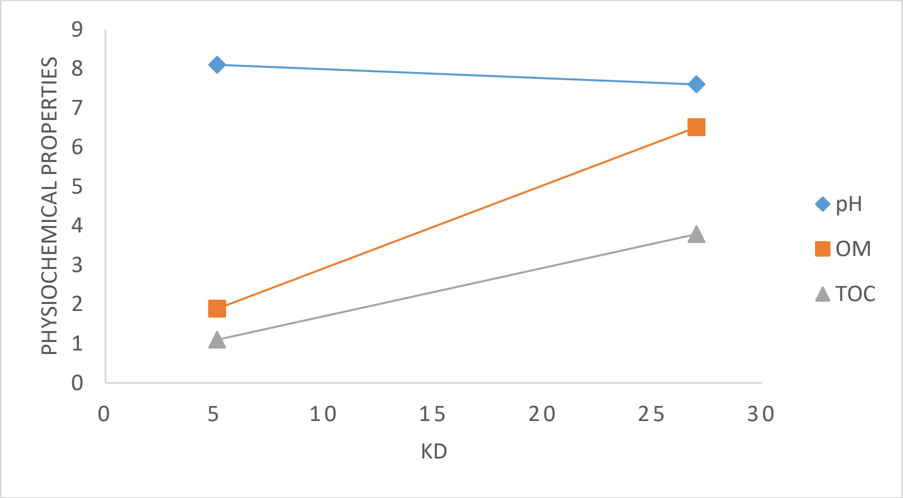


Fig. 5 Correlation of physiochemical properties of soil with K_d

Table 6 Regression and Correlation analysis for sorption properties of selected soils

Sorption Coefficient	**Property (x)**	**Correlation coefficient (r)**	**Intercept (a)**	**Slope (b)**
K_d	pH	-1	8.2	-0.02
	OM	1	0.8	0.21
	TOC	1	0.4	0.12

Table 7 Univariate ANOVA analysis between K_d of soil samples and mineral samples

Source of Variation	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Between Soils and Minerals Samples	109	1	109	0.8	0.4	18.5
Within Soils and Minerals Samples	245	2	122	-	-	-

X – ray powder diffraction (XRD) analysis

XRD studies for soil 1 and soil 2 are shown in Fig.6 and Fig. 7 respectively. The change in basal spacing of soil, measures the adsorption capacity of pesticides, with an expansion from 9.97A° to 13.75A° for soil 1while from 9.99 A° to 10.04 A° for soil 2, with Cinosulfuron (Fig. 6; Table 8). The larger increase in basal spacing of soil is probably because of perpendicular arrangement of Cinosulfuron into the soil inter layer. The parallel arrangement into the interlayer of soil indicated by relative smaller difference. Cinosulfuron can form intercalates by penetrating into interlayer of soil 1. For soil 1, the perpendicular arrangements of the ring into the interlayer may suggested by basal spacing, eqviualent to 13.75A°. The chemical species may form either an outer or inner-sphere complex on reacting with surface. For Geothite and Bentonite XRD results are shown in Fig. 8 and 9 respectively. No major change in the basal spacing was observed for sorption of pesticides with Betonite while for Geothite mineral basal spacing expands from 9.99A° to 12.72A°. Sometimes, sorption is observed even if there is no penetration, indicated by HPLC technique which is due to the surface adsorption.

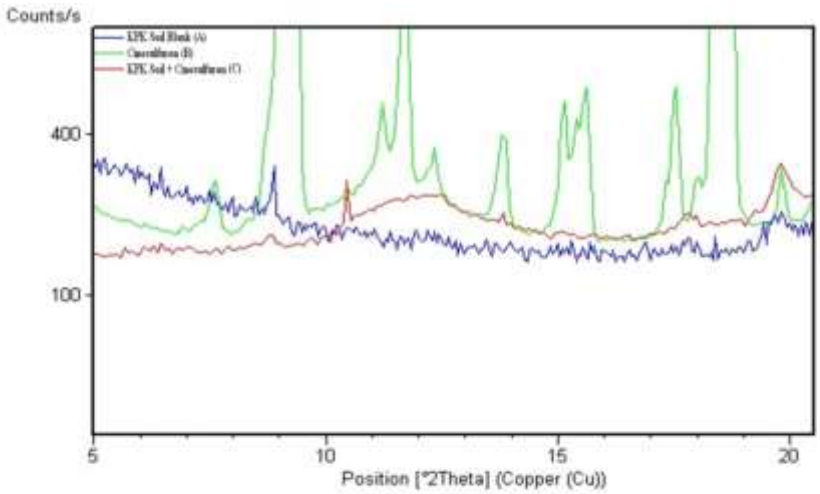


Fig. 6 Soil 1 (KPK)(A) Untreated (B) Cinosulfuron(C) Treated with Cinosulfuron

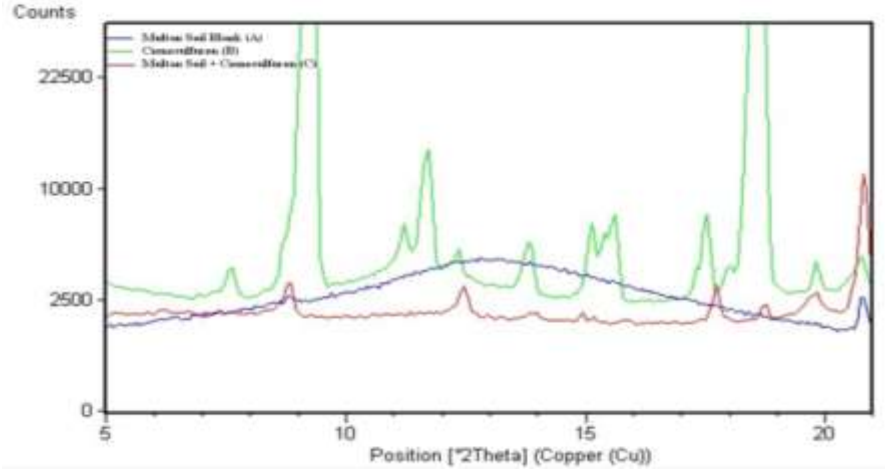


Fig. 7 Soil 2 (Multan) (A) Untreated (B) Cinosulfuron (C) Treated with Cinosulfuron

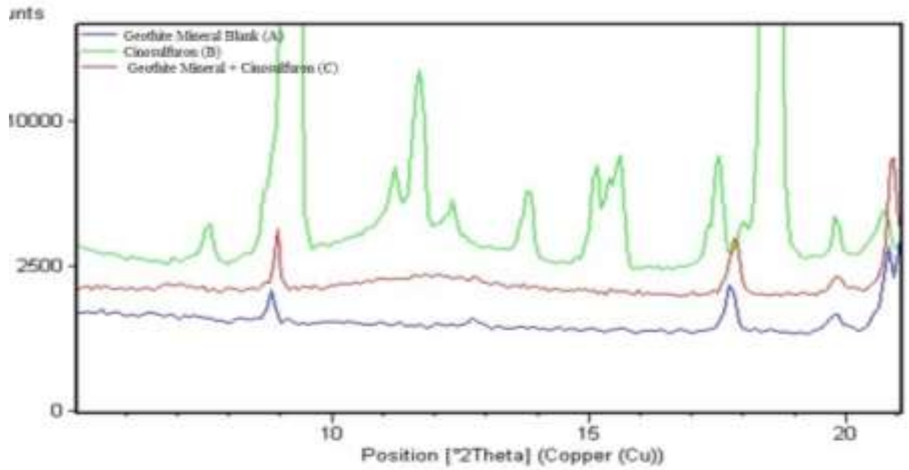


Fig. 8 Geothite mineral (A) Untreated (B) Cinosulfuron (C) Treated with Cinosulfuron

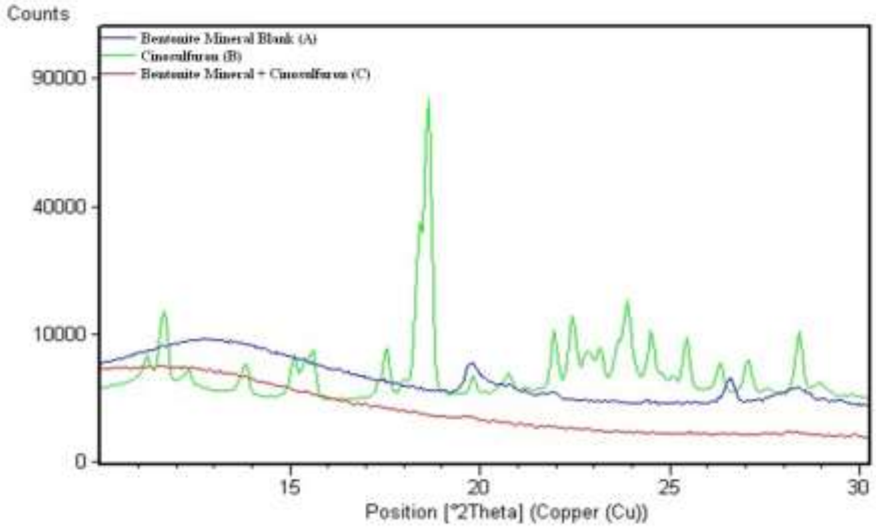


Fig. 9 Bentonite mineral (A) Untreated (B) Cinosulfuron (C) Treated with Cinosulfuron

Table 8 Basal spacing (A°) selected soils treated with Cinosulfuron

	Soil 1	**Soil 2**
Untreated	9.97	9.99
Treated with Cinosulfuron d (001)	13.75	10.04

Table 9 Basal spacing (A°) selected minerals treated with Cinosulfuron

	Geothite	**Bentonite**
Untreated	10.03	12.06
Treated with Cinosulfuron d (001)	12.72	N/A

Conclusion

The current work revealed moderate to weak adsorption capacity of Cinosulfuron in different soil samples that might cause leaching problems. The adsorption-desorption behavior of Cinosulfuron is best-suited with Freundlich isotherm and depends on number of physico-chemical properties of soil like pH value, clay contents, organic carbon and organic matters. The increase in clay content, organic carbon & organic matters and decrease in pH increases the extent of adsorption. In the current work, the desorption hysteresis of Cinosulfuron correlated with the content of organic carbon, soil organic matter and clay significantly and increased from high to low solution concentrations. Both, the solute concentration gradient and the physico-chemical properties controlled the adsorption-desorption behavior of sulfonyl urea. The increase in basal spacing of Goethite mineral and KPK soil signifies the perpendicular arrangement of pesticide into interlayer while for Multan soils sample a relative smaller difference in the basal spacing favors parallel arrangement. In Bentonite there's only surface adsorption as suggested by HPLC technique while XRD results indicates no penetration. The sorption process is reversible in all minerals and these minerals can predict the sorptive behavior of other soils as predicted by hysteresis. Since these minerals are also present in soil. The minerals Bentonite and Geothite release the adsorbed herbicides favorably as suggested by higher desorption values than adsorption.

Author(s) Contribution Statement All the authors carried out the experiments and participated in the design, arrangements and coordination of the study and drafted the manuscript. All authors have read and approved the final manuscript.

Conflict of Interest All the authors have approved the final version of the manuscript being submitted. The article is the authors' original work. The authors declare that they have no conflict of interest.

Acknowledgements The authors acknowledge University of Manchester U.K. Allama Iqbal Open University Islamabad and Higher Education Commission of Pakistan for financial support.

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