Pedospheric Sorption Investigation of Sulfonyl Urea Herbicide Triasulfuron *via* Regression Correlation Analysis in Selected Soils

Khuram Shahzad Ahmad*

Department of Environmental Sciences, Fatima Jinnah Women University, The Mall, Rawalpindi, 46000, Pakistan.

ABSTRACT

Assessing pesticide fate in agricultural soils requires a detailed understanding of their interaction the with decomposing soil component in the environment. Sulfonyl urea herbicide, Triasulfuron, has been evaluated for its sorption behaviour in selected soils *via* batch equilibration method run in duplicate involving UV spectrophotometry. Selected soils possessed a variable degree of physicochemical make-up. Sorption of Triasulfuron fitted well with linear and Freundlich models, yielding C-type isotherms. K_d span over a range of 4.2–11.9 μg mL^{-1}. Correlation and regression analysis proved that pH, organic matter, total organic content and textural properties of soils govern the adsorption and leaching of Triasulfuron. pH and sand expressed negative correlation with K_d (r = –0.997 and r = –0.987) while organic matter, organic content and clay positively impacted K_d (r = 0.987, r = 0.987 and r = 0.980). Negative values of ΔG vividly proved physical and exothermic adsorption processes. Lower values of $\Delta G \le$ –40 kJ mol^{-1} exhibited physiosorption of Triasulfuron in selected soils *via* weak Van der Waal's forces or hydrogen bonding. However, all kinetic values were dependent on the soil physicochemical parameters and demonstrated less adsorption of Triasulfuron for selected soils. Results have been statistically evaluated by ANOVA and the accuracy of fit has been calculated by plotting residual graphs in Minitab. Present study can be further extended to investigation of degradation patterns of Triasulfuron.

1. Introduction

Weed control is an imperative factor for an effective crop production and therefore the prevention of weed-crop competition at an early stage plays a very paramount role.[1] Sulfonylurea (SU) herbicides are a group of herbicides, recently manufactured and the preeminent qualities of these weedicides include their rather immensely active nature and very low application rates.[2] Long-term application of sulfonylurea herbicides often cause curtailment in crop yield annually as well as emergence of resistant weed species to herbicide applications.[3,4]

Triasulfuron (TS) is readily applied to eradicate broad-leafed weeds in wheat and maize crops.[5,6,7,8] Apart from controlling weeds, Sulfonylurea herbicides may even adversely affect the chemical content of crops.[9] Triasulfuron was found to completely reduce the growth of fennel with tissue damage.[10] Triasulfuron (TS) (1-[2-(2-chloroethoxy)phenyl]sulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea) is a member of the group sulfonylurea herbicides which were initially introduced in 1982. TS herbicides are generally used in many countries for its higher specificity for weed control, lower mammalian toxicity and low application rate.[11] Oat, barley, wheat and rye are the main crops which are being protected from weeds by applying TS. Triasulfuron blocks the biosynthetic pathways and halt the synthesis of amino acid pathway, i.e. valine, leucine and isoleucine. At the low rate of about 10–30 g TS 10 000 m^{-2}, TS is efficient enough to remove weeds on a large scale. TS being a weak acid readily dissolves in water and is eventually more mobile in soil and hydrolyze in acidic medium.[12,13] TS degrades in soil with half-life of 5.8–6 days. This dissipation rate may be longer in soil laboratory conditions. Degradation of TS may be enhanced by lowering pH and increased microbial activity resulting in biodegradation.[14] According to Fenoll *et al.*, TS dissipated entirely even before 120 minutes of photodegradation experiment.[15] Ohkawa and Inui have devised yeast gene expression systems in plants that enhance phytoremediation as well as tolerance to chemical residues in the environment.[16] Biotically, TS was found to be degraded by bacteria, *Ochrobactrum* sp.[17]

The fate of Triasulfuron in the environment was revealed by its adsorption and desorption behaviour in geographically distinct soils samples.[18] Despite higher application rates, Triasulfuron has not been studied comprehensively in an agricultural country like Pakistan. Environmental state of Pakistan is already in chaos due to the use of various agrochemicals and lack of sufficient knowledge for proper use and disposal. Thus the present study investigates Triasulfuron sorption behaviour in selected soils and draws a clear environmental trend depicting the dependence of sorption on soils' physicochemical characteristics.

2. Experimental

2.1. Reagents

Analytical grade acetone and methanol with 99.9 % purity were used supplied by Fluka Company. Anhydrous powder of sodium chloride and calcium chloride with analytical

* E-mail: chemist.phd33@yahoo.com / chemist.phd33@fjwu.edu.pk

grade Triasulfuron herbicide of Fluka Company was used.

Adsorption and desorption of Triasulfuron with selected agricultural soils were studied employing standard batch equilibrium method. All experiments were done in replicates. Pesticides solutions of known volume at known concentrations in 0.1 M NaCl for adsorption and 0.1 M CaCl$_2$ for desorption were added to prepared tested soils of known weight. Soil pesticide mixture was then agitated, centrifuged and filtered. Finally, filtered aqueous phase was analyzed by analytical techniques.[19,20,21,22]

2.2. Soil Sampling

Four soil samples of 4 kg were collected from four geographically discrete areas of Pakistan; Sialkot (Punjab) (32.4925°N, 74.5310°E), Ormara (Punjab) (25.2666°N, 64.6096°E), Gilgit (Gilgit Baltistan) (35.9202°N, 74.3080°E) and Karachi (Sindh) (24.8615°N, 67.0099°E). Samples were collected from agricultural field in each district with no or zero use of any pesticide through random sampling at a depth of 0–6 cm, and were stored in clean polythene bags and transferred to lab for further experimentation and analysis. These were air-dried and mixed thoroughly to attain uniformity. Samples were disintegrated by using mortar and pestle and then preserved in sealed labelled Petri dishes for experiment. All the physicochemical parameters including soil texture, pH, soil organic matter (OM), total organic carbon (TOC), cation exchange capacity (CEC), total soil nitrogen (N) and potassium (K) were checked.

2.3. Sorption Experiment

Adsorption and desorption of experiments was carried out at laboratory isothermal and ambient conditions (temperature (25 ± 1 °C) employing batch equilibrium method following *OECD Guideline for the Testing of Chemicals*.[19,20,21]

2.3.1. Adsorption Experiment

All experiments were done under isothermal conditions at ambient room temperature. All samples were run in duplicates for the experiment. Pesticide solutions were prepared in distilled water and stored at 4 °C, whereas Triasulfuron herbicide of different concentrations of 0.25, 0.5, 0.75, 1.0, 2.5, 5.0 and 7.5 ppm were prepared. Pesticide and soil ratio was kept at 1:20. Depending on the selected herbicide concentration, 10 mL of 0.1 M NaCl was added as background electrolyte in each concentration. Each sample consisted of 0.5 g of soil mixed with 10 mL of pesticide solution in 1:10 soil and solution ratio, placed in a 15 mL capped centrifuge tubes. The tubes were continuously shaken on an orbital shaker at 90 rpm overnight at room temperature (25 °C).[23] In order to achieve equilibrium, the adsorption process was done in replicates for each concentration. A blank sample containing only dissolved herbicide and 0.1 M sodium chloride background electrolyte without soil was prepared and treated in parallel with each set of batch experiment in order to calculate the losses and possible deterioration during the experiment. The equilibrated solution was centrifuged at 3000 rpm for 25 min at 25 °C. The supernatants were filtered through 0.2 μm nucleopore syringe filter and filtered aliquots were taken for investigation of the pesticides using a spectrophotometer. The wavelength was taken at λ_{max} 395 nm .

2.3.2. Desorption Experiment

Once the adsorption was done, the remainder of the supernatant was discarded and immediately replaced by 9 mL freshly prepared 0.01M calcium chloride solution. The samples were left overnight on a shaker at 90 rpm. The tubes containing the samples were centrifuged, the sample was filtered and analyzed for desorbed herbicide by UV spectrophotometer. Desorption studies were performed in duplicate.

The analytical method used for analysis of the pesticide sorption in the present research was UV-Visible spectrophotometry using BMS 1602 UV-Visible spectrophotometer (Biotechnology Medical Services K. Group, U.S.A). Adsorption and desorption behaviour of Triasulfuron in 16 concentrations including duplicates was studied by UV-Visible spectrophotometer. UV spectra of Triasulfuron was recorded at 230 nm . To obtain the peak for Triasulfuron, the pesticide solution was run at a wavelength range of 200 to 300 nm .

2.4. Data Analysis

The amount of the Triasulfuron herbicide adsorbed (μg g^{-1} of soil) was calculated by using Equation 1.

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

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 linear type of isotherm Equation 2.

$$K_{d(ads)} = C_s/C_e \tag{2}$$

where $K_{d(ads)}$ is linear or sorption equilibrium distribution coefficient in (mL μg^{-1}). C_e is the concentration (μg mL^{-1}) at the equilibrium concentration. Desorption is expressed as micrograms adsorbed per gram of soil (μg g^{-1} soil) and was calculated from the difference of solution remaining in the soil after the supernatant was poured off. The sorption equilibrium distribution coefficient $K_{d(des)}$ in (mL μg^{-1}) was calculated by Equation 3.

$$K_{d(des)} = C_s/C_e \tag{3}$$

The adsorption isotherms of pesticides in all the soils fitted to the Freundlich adsorption relationship, Equation 4.

$$C_s = K_f C_e^{1/n} \tag{4}$$

where C_s is the amount of adsorbed (μg g^{-1}), C_e is the equilibrium concentration (μg mL^{-1}) and K_f and n are constants. The Freundlich constant normalized to organic carbon (K_{foc}) was calculated by using Equation 5.

$$K_{oc} = \frac{K_d}{\%C}.100 \tag{5}$$

where K_{foc} and K_f are related by Equation 6.

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

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

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

$$K_{Oc} = \frac{K_f}{\%Oc}.100 \tag{8}$$

3. Results and Discussion

In the present research estimation of adsorption and desorption behaviour of Triasulfuron on selected soils was done to gain sorption values or sorption coefficients. The adsorption and desorption coefficients (distribution coefficient (K_d), Freundlich constant (K_f), standard deviation (S), Regression coefficients (R^2), Gibbs free energy (ΔG) and hysteresis (H) of Triasulfuron on different soils were determined as a function of

characteristics of soils like SOM, CEC, pH, soil texture etc. Therefore various soil types of different characteristics were investigated in the present study in order to understand and predict extensive interactions of Triasulfuron with naturally occurring soils.

3.1. Characteristics of Soil Samples

To study adsorption and desorption behaviour of Triasulfuron four agricultural regions of Pakistan were selected for soil collection including Sialkot, Ormara, Gilgit and Karachi. The selection of sampling areas was based on the use of selected pesticides. Soil sampling was done by using the composites and random sampling while soil preparation was done by standard method. The soil physiochemical properties that are considered to be most important for sorption studies of pesticide are texture, organic matter (SOM), organic carbon (TOC), and pH. Other soil characteristics which may have influence on the sorption studies of a pesticide are the cation exchange capacity (CEC) and total nitrogen content (TN).[19,24,25] These physical and chemical properties of four soils were determined and illustrated in Table 1.

The highest values of EC were obtained for sample 4 while lowest was observed for sample 1 (Table 1). This implies that though sample 4 showed more salinity as compare to rest of soil samples yet overall salinity is in medium ranges for all studied samples.

Sample 3 was characterized as acidic soil as compared to other three studied soils which were identified as alkaline (sample 2 and sample 4) and neutral soils (sample 1) by their pH analysis. However, all four soil samples are neither highly acidic nor highly alkaline.

OM is the most influential soil property especially in the present study. As depicted in Table 1, comparatively highest value of OM was found for forest soil 3 and least values of organic matter was found for coastal sample 4. Sample 2 has shown more potential to hold the positively charged ions as depicted by the CEC values. Sample 2 have comparatively more negatively charged situates on the surface which consequently adsorb and hold more cations by electrostatic forces as compare to other soil samples.[26]

Texture analysis of the soil samples depicts highest values of clay, silt and sand in Table 1. Highest value of sand content were found for sample 1 and highest value of clay content were found for sample 3 and *vice versa*.

In present study values of clay content varied among 13 % to 49.1 % whereas values of sand were ranging from 15 % to 77 % and values of silt follow the range from 6 % to 25 % thus demonstrating diverse range of characteristics. Sorption behaviour is highly evaluated on the bases of clay and sand content.

3.2. Adsorption Isotherms

In order to check the sorption behaviour of Triasulfuron in selected soils, the adsorbed and desorbed Triasulfuron concentration (μg mL^{-1}) was plotted against equilibrium concentration of the Triasulfuron in each soil sample (Figs. 1 & 2). The experiments were run in duplicates in order to achieve the values for linear and Freundlich adsorption graphs. Linear and Freundlich adsorption parameters have been shown in Table 2 for selected soils. All soils exhibited C-type isotherm for adsorption of Triasulfuron with values of R^2 approximating 1. C-type isotherm depicted that Triasulfuron was highly hydrophobic and thus it was remarkably distributed in soils posing challenges of environmental mitigation. Isotherms were further used for derivation of parameters like K_d, K_f, R^2, ΔG and hysteresis (H).

3.2.1. *Linear Adsorption Coefficient*

K_d is the most important parameter of linear isotherm also known as partition/distribution coeffcient. Linear adsorption coefficient K_d was different in all soils and ranged in 4.2–11.9 μg mL^{-1} with soil 3 showing maximum adsorption of Triasulfuron and soil 4 was marked with lowest adsorption potential. K_d is considered as a fundamental parameter to enumerate risk and transport potential of pesticide. Besides $K_{d(ads)}$ and movement of pesticide in soil are inversely correlated. Higher $K_{d(ads)}$ value indicates strong affnity (less movement) of a pesticide for a soil while lower values of K_d specifies less affinity and increased possibility of pesticide movement through soils.[22] Highest $K_{d(ads)}$ was found for sample 3 while lowest adsorption K_d was found for sample 4 (Table 2). This indicates strong affinity of Triasulfuron for sample 3 which has resulted in highest adsorption. Whereas sample 4 has more risks of movement of Triasulfuron that has been evidenced by its $K_{d(ads)}$ values. Decreasing order of $K_{d(ads)}$ of Triasulfuron for all soils is as follows:

Soil 3 > soil 1 > soil 2 > soil 4

Strong adsorption of Triasulfuron can be attributed to its highest organic matter (matter (3.5 %), total organic carbon (2.03 %) and lowest pH (6.2) in addition to highest clay content (61 %).[27] While lowest value of $K_{d(ads)}$ was shown by soil 4 which is 4.2 μg mL^{-1} owing to low SOM and clay which could act as medium for enhanced adsorption. Pusino and coworkers studied the sorption behaviour of Triasulfuron in Italian soils. Their results were in accordance with the results of the current study indicating pH to be the most important factor governing the rate of adsorption.[28] More studies are focused towards adsorption of Triasulfuron in neutral to acidic soils but Sarmah *et al.* have studied adsorption in alkaline soils of Australian origin. Their results clearly depicted the inverse relation of high pH soils with adsorption.[29]

3.2.2. *Freundlich Adsorption Coefficients*

Freundlich adsorption model was applied to study adsorption kinetics on the heterogeneous soil surface. K_f for Triasulfuron on selected soil samples are presented in Table 2 and all the four soil samples for Freundlich coeffient K_f were ranging from 2.1 μg mL^{-1} to 8.8 μg mL^{-1}. Soil sample 3 expressed highest adsorption of 8.8 μg mL^{-1}. The Freundlich constant K_f is an

Table 1 Physicochemical properties of selected soil samples.

Sample no.	Regions	EC* /μS cm^{-1}	OM* %	TOC* %	pH	K* /mg kg^{-1}	TN* %	CEC* /Meq 100 g^{-1}	Texture	Sand %	Silt %	Clay %
1	Sialkot	189	2.2	1.3	7.3	80	0.08	7.3	Silty loam	53	6	41
2	Ormara	272	0.7	0.4	8.0	90	0.09	7.7	Silt Loam	76	11	11
3	Gilgit	272	3.5	2.0	6.2	120	0.13	7.4	Clay	15	25	61
4	Karachi	280	0.6	0.4	8.3	100	0.10	7.3	Sandy Loam	77	10	13

*EC= electrical conductivity, OM= organic matter, TOC= total organic carbon, K= soil potassium, TN= total nitrogen and CEC= cation exchange capacity.
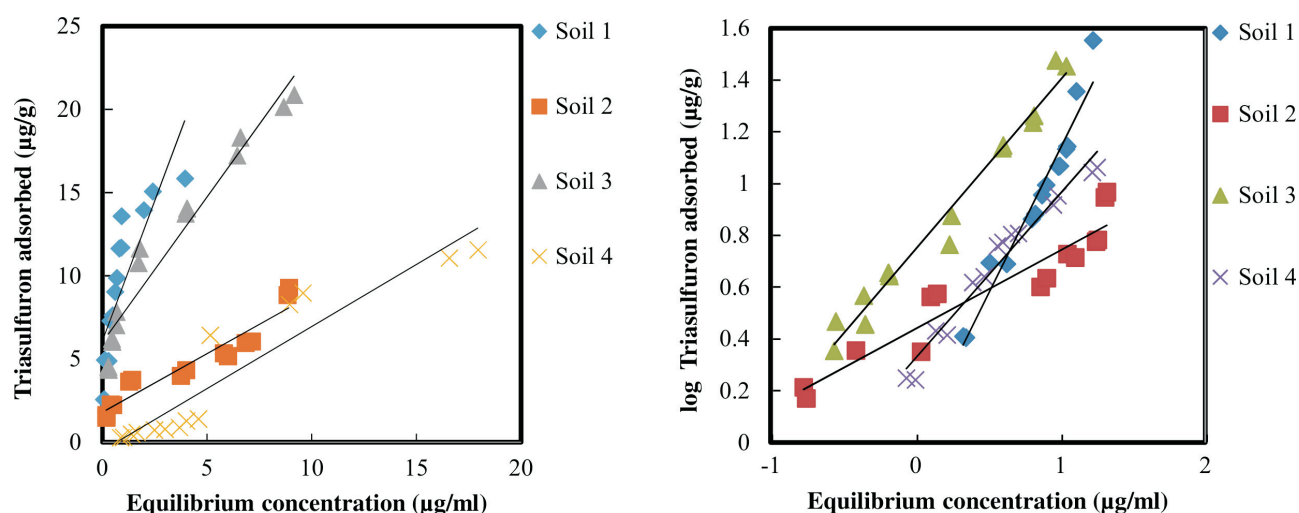
Figure 1 Comparative linear and Freundlich adsorption of Triasulfuron in selected soils.
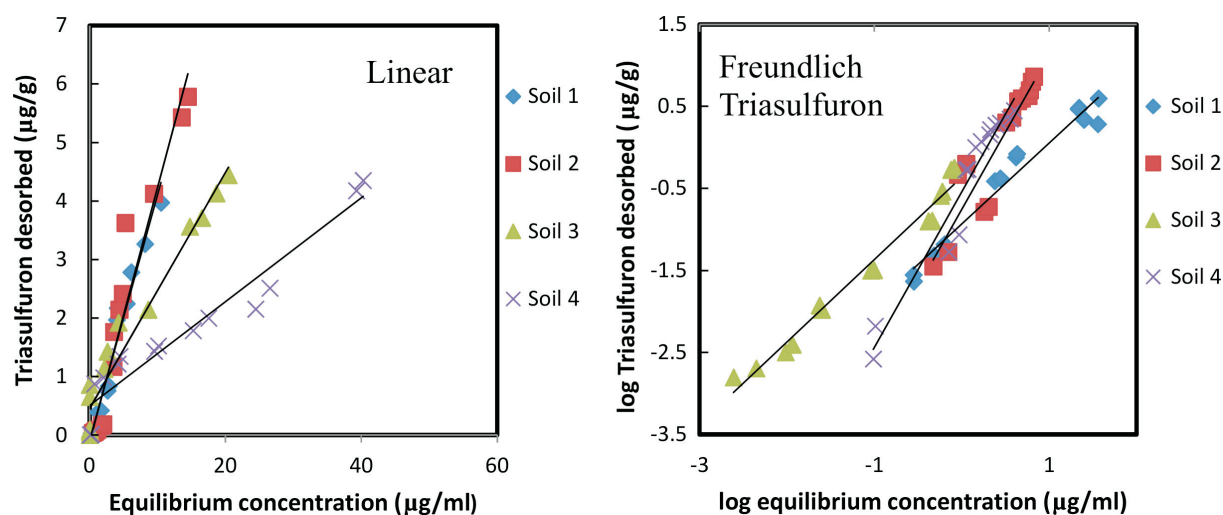

Figure 2 Comparative linear and Freundlich desorption of Triasulfuron in selected soils.

estimated indicator of capacity of pesticides adsorption. As K_f increases adsorption of pesticide also increases while desorption decreases. Desorption of pesticide increases with decreasing $K_{f(ads)}$. This is because high value of K_f depicts least movement of pesticides through soil while lower K_f is indicator of least affinity of pesticides with soils.[30] This elevation in K_f is because of higher soil organic matter (SOM) of soil sample which was 3.5 % as there is positive correlation between SOM and K_d. Another factor justifying the greater adsorption of Triasulfuron in soil 3 is the n_a value. Value of n_a is inversely proportion to the adsorption capability of soil. When n is equal to 1 the partition between the phases is not dependent on the concentration.[31] It can be seen for

soil 3 where n_a value is approximately equal to 1 (0.9). Lower values of n are indicative of higher adsorption and lower desorption while higher values of n are indicative of the low adsorption and enhanced desorption thus n is demonstrating inverse correlation with adsorption of pesticides.[31] In present study n_{ads} range from 0.9 to 3.3. Similarly the n_d values are used to check the intensity of desorption occurring in the soil samples.

3.2.3. Gibbs Free Energy Change (ΔG)

The free energy change ΔG for adsorption of the Triasulfuron on the soil samples is shown in Table 2. The values of ΔG were in the range –11 to –16 kJ mol^{-1}. The negative value of ΔG indicated

Table 2 Linear and Freundlich adesorption parameters of Triasulfuron in selected soils.

Soil sample	K_d /μg mL^{-1}	R^2	K_{OM} /μg mL^{-1}	ΔG /kJ mol^{-1}	S	K_{OC} /μg mL^{-1}	R^2	S	K_f /μg mL^{-1}	K_{FOC} /μg mL^{-1}	n_a	1/n
1	10.8	0.9	287	–14	1.7	678	0.9	0.06	7.8	494	1.5	0.6
2	5.6	0.8	148	–12	0.8	524	0.8	0.08	2.7	254	2.2	0.4
3	11.9	0.9	529	–16	0.5	1232	0.9	0.03	8.8	909	0.9	1.1
4	4.2	0.9	103	–11	1.0	352	0.9	0.05	2.1	177	3.3	0.3

*K_d= distribution coefficient, K_{om} and K_{oc}= leachability index, ΔG= Gibbs free energy, K_f= distribution coefficient for Freumdlich model, K_{foc}= leachability index for Freumdlich model, n_a= linearity factor or adsorption intensity.

that the interaction of Triasulfuron on the selected soils was spontaneous and exothermic behaviour of the interaction.[20] Moreover it is reported ΔG showed efficiency of reaction i.e. if pesticide sorption studies specify the absolute value of ΔG ≤ 40 kj mol^{-1}, then it would depict physical adsorption of that pesticide with the particular soil otherwise it would indicate negative adsorption.[32] In present research the ΔG values of Triasulfuron were proposing the physical adsorption of Triasulfuron with the soils involve weak Van der Waal's forces. Hence it is the weakest category of adsorption.[31]

3.2.4. *Leachibility Index*

The predicted capacity for Triasulfuron retention normalized to the OC content (i.e. K_{oc}) distinguished expressively in studied soils as shown in Table 2. K_{oc} and K_{om} are called Leachibility Index. Weaker adsorption as already depicted by lower negative values for ΔG was governing factor for higher mobility of Triasulfuron in tested soils. Higher K_{oc} values were marked by strong affinity of pesticides towards soils and hence their revulsion towards movement.[33] The strength of adsorption was directly dependent upon K_{oc} values, thus soils having higher K_{oc} values were not prone to fast leaching of Triasulfuron particularly soil 3 (1232 μg mL^{-1}) restricting the faster mobity of Triasulfuron. While for the poor adsorbent soil 4, K_{oc} value is lowest (352 μg mL^{-1}) hence providing suitable conditions for Triasulfuron leaching to lower pedospheric compartments and thus posing ecological challenges with higher costs for mitigation. K_{oc} and K_{foc} determined the transportation and motile nature of Triasulfuron in different soil layers. As the attachment of Triasulfuron was on soil organic matter of soil textural class thus soil organic matter governed the Triasulfuron mobility in selected soils.[34] Thus by augmenting the organic matter, total organic content, clay and by plummeting pH, adsorptive interactions can be enhanced resulting in decreased mobilities. Similarly the Fruendlich model organic coefficient also played decicive role in prediction of pesticide movement in soils. If K_{foc} values are greater than 1000 μg mL^{-1}, pesticides show higher movement in soil and K_{foc} values lying between 150 μg mL^{-1} and 500 μg mL^{-1} are moderately mobile in soil and when more than 500 μg mL^{-1} so mobility is slow. Mobility in soil sample 3 was very slow as K_{foc} is 909 μg mL^{-1} and sample 1, 2 and 4 show moderate movement as their values are less than 500 μg mL^{-1}. K_{foc} values ranged from 177 to 909 μg mL^{-1} with highest value allocated to soil 3.

3.3. Desorption Isotherms

All soils yielded C-type desorption isotherms for Triasulfuron for desorption studies as well. In order to achieve desorption graphs the samples were run in duplicates to ensure correctness. Desorption is reverse of adsorption so in alkaline soils more desorption occurs and in low pH soils desorption process takes place slowly. $K_{d(des)}$ values varied between 5.4 to 14.0 μg mL^{-1}. Soil

4 exhibited higher desorption $K_{d(des)} = 14.0\ \mu$g mL^{-1} for possessing all physicochemical parameters that enhances the escape of poorly adsorbed Triasulfuron molecules. Soils 1 and 3 had higher OM, higher clay content, higher CEC, good texture and low pH which developed durable adsorptive interaction with Triasulfuron due to which they were not desorbed readily. Soil 10 showed higest desorption values because of higher sand content which enhanced desorption. Moreover desorption values increased with increasing pH in the following order:

Soil 3 < soil 1 < soil 2 < soil 4

3.3.1. *Hysteresis Phenomena*

The ratio between $n_{(des)}$ and $n_{(ads)}$ measures the extent of irreversibility of adsorption process, the ratio called the apparent hysteresis indicated greater or lesser irreversibility of adsorption in all soil samples. Largely binding by physical sorption is reversible whereas binding by chemisorption is irreversible. Furthermore chemisorbed chemicals can be incompletely desorbed depending upon desorption methodology or the nature of chemical bond.[21] In present study desorption hysteresis coefficient, H was calculated (Table 3). The values of H were around unity indicating quick sorption in soil. The highest hysteresis was observed in Sialkot with 2.2 % organic matter. Although the occurrence of hysteresis indicates that the adsorption isotherms are slightly different from the desorption isotherms, however value of H close to 1 means that desorption process took place almost as quickly as adsorption did. The high value of $K_{d(ads)}$ as compared $K_{d(des)}$ shows that adsorption is irreversible. Desorption hysteresis can be related to the immobilization of pesticicdes in soil resulting from the irreversible chemical binding.[35] Desorption hysteresis coefficient (H) in tested four soils ranged from 0.4 to 1.1.

3.3.2. *Fitness of Sorption Models*

The lower standard errors (S.E.) and higher values of coefficients, r^2 are used to measure the goodness of fit or best fitting isotherm to the experimental data.[36] R^2 was obtained by fitting experimental data into the linear model in Tables 2 and 3. Linear model is found to be best fitted model for adsorption and desorption studies of Triasulfuron because of its higher values of R square (0.8 to 0.9 for adsorption and 0.8 to 0.9 for desorption) with lower S.E. (0.5 to 1.7 of adsorption and 0.07 to 0.2 for desorption).

Freundlich adsorption model was applied to study adsorption kinetics on the heterogeneous soil surface. The data presented in Table 3 fitted the empirical Equation 3 proposed by Freundlich model. The S.E and r^2 of the each soil for Triasulfuron were presenting best-fitting Freundlich isotherm to the experimental data as illustrated in Tables 2 and 3. R^2 of Freundlich adsorption isotherm were in the range from 0.9 (90 %) to 0.8 (80 %) and related S.E was varied from 0.03 to 0.08. The values of desorption r^2 follow the range of 0.8 to 0.9 with S.E. 0.06 to 0.27. However,

Table 3 Linear and Freundlich desorption parameters of Triasulfuron in selected soils.

Soil sample	$K_{d(des)}$ /μg mL^{-1}	R^2	S	H	$K_{f(des)}$ /μg mL^{-1}	R^2	S	n_d	n_a
1	6.2	0.8	0.07	0.6	4.5	0.9	0.14	2.3	1.5
2	7.7	0.9	0.6	0.4	5.3	0.8	0.30	1.5	2.1
3	5.4	0.9	0.2	1.8	2.4	0.9	0.06	1.6	0.9
4	14	0.9	0.2	1.1	10	0.9	0.27	1.0	3.3

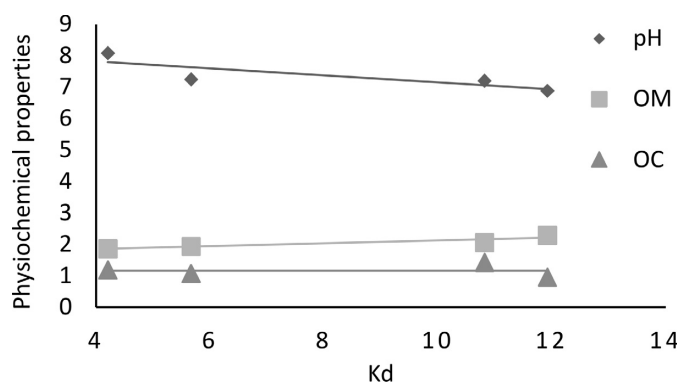*$Kd_{(des)}$= distribution coefficient for desorption, S=standard error, H= hysteresis.

Figure 3 Correlation of physiochemical properties of soil with K_d.

Figure 4 Correlation of different soil textures with K_d of selected soils.

Table 4 Linear regression correlation analysis for sorption properties of selected soils.

Sorption coefficient	Property /x	Correlation coefficient /r	Probability level /p	Intercept (a)	Slope (b)
K_d	pH	–0.997	0.05	35.5	–3.6
	OM	0.987	0.04	3.3	2.6
	TOC	0.987	0.04	3.2	0.001
	Sand	–0.987	0.02	14.5	–0.1
	Silt	0.990	0.05	5.2	0.2
	Clay	0.980	0.04	3.2	0.1

lower values of r^2 and higher values of S.E. illustrate the worst fitted model while present study verified linear and Freundlich good fitted models for pesticides adsorption and desorption studies.[36]

3.4. Statistical Analysis

Further statistical investigations were done regarding the relationship between $K_{d(ads)}$ and the physiochemical properties of soil including OM, TOC and pH and between $K_{d(ads)}$ and soil textures (Table 4) (Figs. 3 & 4). Linear regression analysis was performed to analyze the effect on K_d of the physiochemical properties (Table 4). The analysis provided with the knowledge that pH is negatively correlated (r = –0.997) to $K_{d(ads)}$ while OM and TOC were seen to be positively correlated (r = 0.987 and r = 0.987, respectively). Textural composition of soils also affected Triasulfuron. K_d and clay were found positively correlated (r = 0.980) while presence of sand negatively impacted the Triasulfuron adsorption (r=–0.987). According to Fig. 3 the lowering pH augments the adsorption of Triasulfuron in soils. In a nutshell, soil pH values are accountable for the dissociation or protonation processes of both the Triasulfuron and the adsorbent surfaces (soils), whereas an increase in adsorption was observed with the increasing percentage of OM and TOC. The results also showed that the soil 3, having highest $K_{d(ads)}$ value (11.9 µg g⁻¹), contains relatively high percentage of soil OM (3.5 %), proving the fact that soil OM is directly proportional with the rate of adsorption occurring in that particular soil. Also the CEC values indicate that comparatively higher CEC values

Table 5 Univariate ANOVA analysis of soil samples and K_d values.

Source of variation	SS	d.f.	MS	F	P-value	F crit.
Between soil samples	15.1	3	5.0	0.2	0.8	6.5
Within soil samples	96.3	4	24.0	–	–	–

usually enhance adsorption either by ion exchange or surface precipitation.

In order to compare means of soil samples and adsorption distribution coefficient K_d a univariate ANOVA test was performed on all four soil samples along with their K_d values. In the one way ANOVA sum of squares (SS), mean square (MS), F statistics (F), P-value and F critical values (F crit) were compared within the same groups and between groups (Table 5). For above test we assume that all observations are originating from normal distributions and all the four groups of soils have equal variances. In this case, the P-value (0.8) is greater than the alpha value (α) (0.05) so we do not reject our null hypothesis (H⁰) i.e, the assumption we made earlier. Also it can be observed from the table the F critical value (F crit) (6.5). This is the number given to us such that any number greater than the F crit value would cause us to reject our null hypothesis (H₀). In this experiment the F statistics value (0.2) falls much lower than the F crit value hence it does not lie in the rejection region.

The effect of pH, OM and TOC on K_d was further studied in Minitab 17. Several residual graphs were plotted which determine the goodness of fit in ANOVA. From the residual plots we determine that the ordinary least square assumptions are being met. Satisfying these assumptions indicates, the ordinary least squares regression will produce unbiased coefficient estimates with the minimum variance. Normal probability plots of residuals, residuals *versus* fits and residuals *versus* order of data were plotted in Minitab (Fig. 5). Normal probability plot of residuals shows that our data are distributed normally. The residuals *versus* fits plot determine that our data has a constant variance.

4. Conclusion

Sorption of sulfonylurea herbicide, Triasulfuron (1-[2-(2-chloroethoxy)phenyl]sulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea) was performed with four different soil samples using Batch equilibrium method. The data obtained fitted well with linear and Freundlich models generating C-type isotherms in all cases. It was observed that adsorption tendency of Triasulfuron was highly dependent upon physiochemical make-up of soil samples, including pH, organic matter and texture. Adsorption was measured to be increasing with high values of soil organic matter and clay content and decreasing with increased pH. Statistical tools including ANOVA and regression were utilized to statistically evaluate the experimental results. Results of Gibbs free energy (ΔG) confirmed physical adsorption of Triasulfuron in soils. Triasulfuron exhibit lower to medium mobility with in selected soil samples. Desorption experiments showed inverse relation of herbicide with soil physiochemical properties than adsorption.
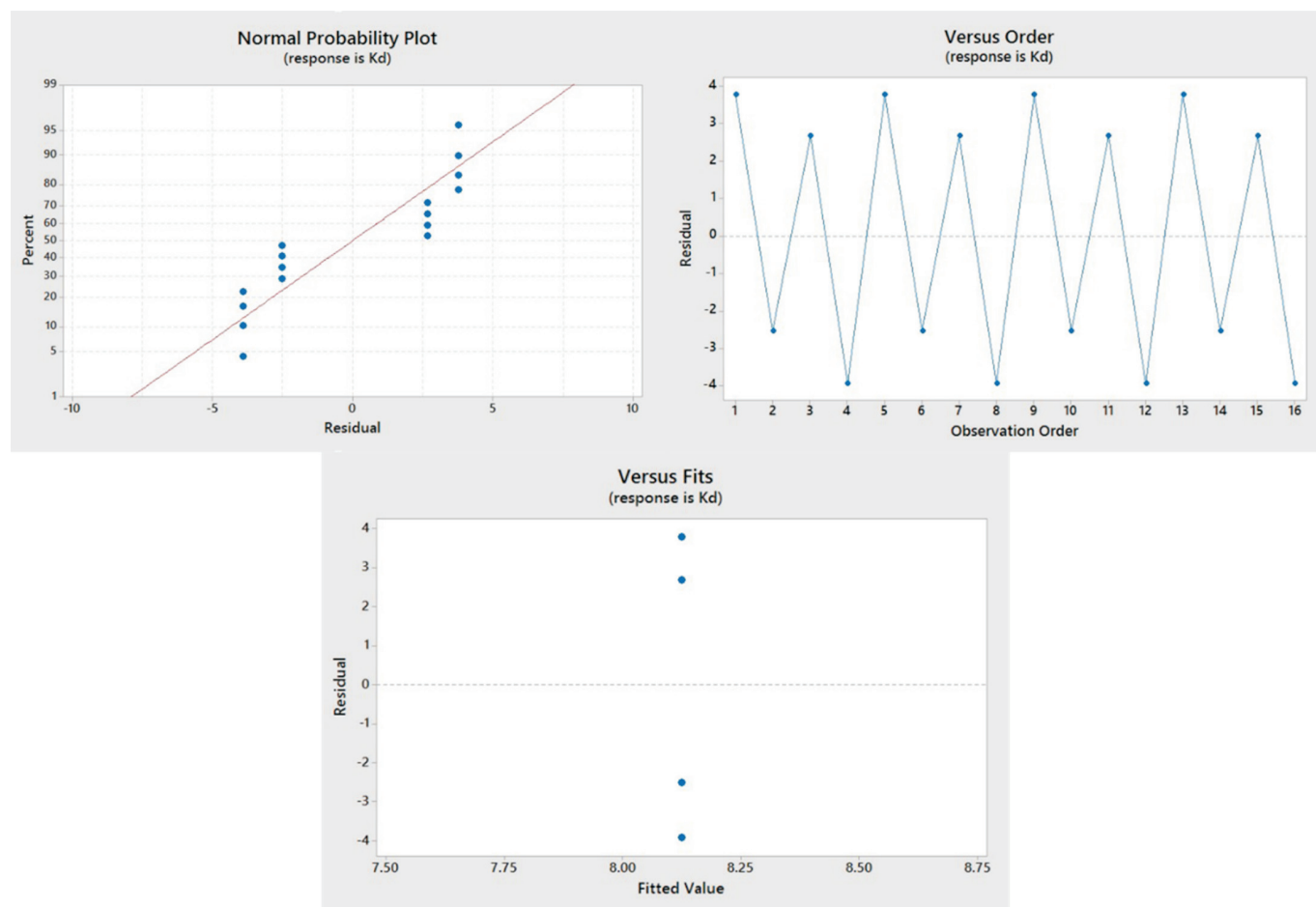
Figure 5 ANOVA Histogram, Versus Order and Versus Fit Residual plots of soil samples with physiochemical properties pH, TOC and OM while the response is K_d.

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