

## ENHANCING CHLORPYRIFOS SORPTION POTENTIAL OF AGRICULTURAL SOIL BY BIOCHAR AND COMPOST ADDITION

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Chlorpyrifos (CP) is a toxic and broad-spectrum pesticide. Owing to the extensive soil and crop application of CP to control insects/pests, its significant concentrations have been reported in different crop plants, fruits, vegetables and other food items locally and internationally. The strategies to immobilize pesticide residues in the soil are of great concern to restrict their offsite transport. A batch study was conducted to evaluate the potential of biochar and compost in enhancing CP sorption. Soil samples were supplemented with biochar and compost at two levels, i.e. 0.25% and 0.50% w/w basis. The sorption of CP was assessed at five applied concentrations viz. 5, 10, 50, 100 and 200 mg L<sup>-1</sup>. CP sorption exhibited linear trend and increased with increasing concentration upto 50 mg L<sup>-1</sup> after that it decreased with its increasing levels. Freundlich model well fitted and explained the sorption behavior of CP in un-amended as well as amended soil as indicated by the correlation coefficient (R<sup>2</sup>) values (> 0.90). Both biochar and compost addition significantly increased the sorption potential of the soil. With both amendments sorption capacity increased with increasing level. However, biochar-amended soil showed significantly higher sorption capacities (K<sub>f</sub>, 28.68 and 218.83 mg kg<sup>-1</sup>) for CP compared to compost-amended soils (15.95 and 111.85 mg kg<sup>-1</sup>) at 0.25 and 0.50%, respectively. Conclusively, above organic amendments have potential to effectively sorb CP and could be used to remediate CP polluted areas by immobilizing CP and ultimately decreasing its bioavailability.

**Keywords:** Chlorpyrifos, pollution, remediation, sorption, organic amendments

### INTRODUCTION

The usage of pesticides has aggravated due to rapid development in industrialization and food stress on global agriculture. The pesticides are very helpful in increasing crop production by mitigating the damage caused by insect/pests, pathogens and weeds (Kamboh *et al.*, 2016), but at the same time these have led to many health problems in non-target organisms like humans and animals and have contaminated the environment (Budarz *et al.*, 2017). Pimentel (2004) and Chenseng *et al.* (2006) stated that out of the total pesticides applied the 99.9% contaminate the air, soil, surface and ground water while only 0.1% reaches the target pests. In this way, the pesticides can transfer to the food chain and severely affect the living organisms (Xu *et al.*, 2017). Chlorpyrifos (CP) is a toxic organophosphate insecticide (Rogers *et al.*, 2009). The residual detection of CP in the soil, water, food items and its toxicity hazards in humans and animals (Flaskos *et al.*, 2012; Jack *et al.*, 2012; Lozowicka *et al.*, 2016) have attracted the great attraction of researchers towards evaluating its environmental fate and remediation strategies to tackle its widespread contamination.

In controlling the pesticides translocation to the receiving environment (plants, ground or surface water), the adoption of effective agricultural strategies to mitigate their impact has become imperative (Rojas *et al.*, 2015). According to Arias-Esteves *et al.* (2008) sorption is the leading factor controlling the behavior and distribution of pesticides in the terrestrial and aquatic environment. The soil applied organic amendments can significantly affect the transport of pesticides in soil (Cederlund *et al.*, 2017). Biochar has capacity to restrict the mobility of pesticides and hence their leaching potential through strong sorption (Tatarkova *et al.*, 2013; Cederlund *et al.*, 2017). In case of composted materials containing several major functional groups, such as carboxyl, phenolic, alcohol and carbonyl are responsible for sorption of organic contaminants like CP (Tejada *et al.*, 2011). The information regarding effect of biochar and compost in enhancing CP sorption is limited in the literature. Moreover, their comparative effect on CP sorption dynamics in sandy clay loam soil needs to be elucidated. Therefore, the present study was designed with the hypothesis that compost and biochar amendment to soil may increase the CP sorption capacity of soil and ultimately reduce its bioavailable fraction in solution phase. This study was carried out to evaluate the

impact of two different organic amendments at two dose levels in enhancing sorption of CP.

## MATERIALS AND METHODS

**Chemicals:** Analytical grade CP (99.5%) was purchased from Dr. Ehrenstorfer GmbH (Germany) used as a reference standard. Technical grade (97% pure) CP was obtained from Ali Akbar Enterprises, Pvt. Ltd. Lahore, Pakistan used to spike the sorption experiment samples. The acetone, methylene chloride and n-hexane used were also of high purity and obtained from Merck (Germany). Calcium chloride ( $\text{CaCl}_2$ ) and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were purchased from Sigma-Aldrich (Sydney, Australia).

**Soil and amendments:** The soil was collected randomly from upper (0-30 cm) surface from the farm area of Village No.132/GB in the district of Faisalabad, Pakistan. Soil was dried for a week in the laboratory and passed through 2 mm stainless steel sieve after grinding with the help of wooden roller. The biochar was prepared following the procedure stated by Sanchez *et al.* (2009) through the pyrolysis of wheat straw at 500°C under limited oxygen conditions using a laboratory muffle furnace. The feedstock was kept in a pre-heated furnace for total 80-90 minutes with heating rate of 7-10°C min<sup>-1</sup> and holding at target temperature (500°C) for 20 minutes. The method described by Ahmad *et al.* (2007) was adopted to produce compost through the decomposition of agricultural wastes and plant leaves in aerobic conditions using a locally fabricated composter. The biochar and compost were dried at 70°C in an oven for three days, ground to a fine powder manually with a grinder and roller, passed through 200 µm sieve and stored for use in the experiment.

The selected properties of amendments and soil are given in (Table 1).

**Sorption experiment:** The sorption of CP on amended and un-amended soil was tested using batch equilibrium method. Standard stock solution (1000 ppm) and the working solutions of CP were prepared in acetone. Triplicate soil samples (5 g each) un-amended and amended with 0.25% and 0.50% of both biochar and compost was taken in 50 ml centrifuge tubes. The working solutions were used to spike the soil samples resulting in the final concentrations of 5, 10, 50, 100 and 200 mg L<sup>-1</sup>. After spiking soil with CP solutions, the centrifuge tubes were kept in the fume hood for the evaporation of carrier acetone. When all the carrier solution was evaporated, 20 mL of background solution 0.01 M  $\text{CaCl}_2$  (freshly prepared in ultrapure water) was added in each tube. To test the pesticide degradation during the batch process, a blank with only  $\text{CaCl}_2$  and pesticide solution without adsorbent was used. All the samples were shaken for 24 h at a constant temperature in an orbital shaker. The 24 h period is sufficient enough to achieve equilibrium (Rojas *et al.*, 2013). All the samples were run in triplicate, and the values presented in results were the mean of three replicates.

**Aqueous phase Extraction for chlorpyrifos:** To determine the CP concentration in supernatant the extraction procedure was as follows. After shaking the solid and solution phases were separated by centrifugation for 15 minutes at 2500 revolutions per minute (RPM). The well separation of both phases by centrifugation was guaranteed by (Delgado-Moreno *et al.*, 2010). After centrifugation, the supernatant was removed from the centrifuge tubes through pipetting and taken in glass separatory funnel of 100 mL capacity. The supernatant in separatory funnel was vigorously mixed with

**Table 1. Some selected characteristics of experimental soil and amendments.**

Parameter	Soil	Biochar	Compost
EC <sub>w(1:10)</sub> (dS m <sup>-1</sup> )	3.21 ± 0.08	4.01 ± 0.08	3.10 ± 0.15
TSS (mmol <sub>c</sub> L <sup>-1</sup> )	32 ± 0.2	--	--
pH <sub>w(1:10)</sub>	7.44 ± 0.10	7.89 ± 0.08	6.25 ± 0.09
Texture	Sandy clay loam	--	--
Sand (%)	56.4 ± 1.04	--	--
Silt (%)	18.9 ± 0.98	--	--
Clay (%)	24.7 ± 1.01	--	--
CaCO <sub>3</sub> (free lime) %	4.80 ± 0.06	21 ± 1.91	39 ± 2.54
CEC cmol <sub>c</sub> kg <sup>-1</sup>	5.2 ± 0.87	85 ± 3.94	107.5 ± 4.34
Total nitrogen (mg kg <sup>-1</sup> )	217 ± 19.79	9000 ± 126	12274 ± 165
Total phosphorus (mg kg <sup>-1</sup> )	321 ± 24.49	3400 ± 61	2931 ± 32
Total potassium (mg kg <sup>-1</sup> )	232 ± 21.56	36000 ± 282	1700 ± 12
Total organic carbon (%)	0.87 ± 0.03	43.80 ± 1.65	35.36 ± 1.32
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	--	4.83 ± 0.09	1.37 ± 0.04
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	--	0.0051 ± 0.0001	0.0035 ± 0.0001
Pore width (nm)	--	5.0 ± 0.51	18 ± 0.32

Values are presented as means ± standard error of three replicates, EC: Electrical conductivity, TSS: Total soluble salts, CEC: Cation exchange capacity

equal volume of methylene chloride for one minute. The fraction of methylene chloride was collected after phase separation and filtered with Whatman filter paper No. 41 containing 20 g of anhydrous sodium sulfate in order to remove moisture contents. The remaining aqueous phase in the separatory funnel was extracted two more times with fresh methylene chloride, and after filtration, the filtrate of all three steps was combined and concentrated on a rotary evaporator at 35°C to about 5 mL and taken in 10 mL glass amber vials. The concentrated filtrate was further dried under air nitrogen generator to dryness. The residues were redissolved in 1 mL hexane to run on a gas chromatography mass spectrometry (GC-MS) (Shimadzu QP-2010) for CP determination. The difference between the CP concentration in the supernatant at equilibrium and the initial CP concentration in the solution was taken as the amount of CP sorbed using the following formula.

$$C_s = \frac{(C_i - C_e)}{W} V \quad (1)$$

Where,  $C_i$  = initial concentration of CP spiked ( $\text{mg L}^{-1}$ ),  $C_e$  = equilibrium CP concentration in supernatant ( $\text{mg L}^{-1}$ ),  $C_s$  = amount of CP sorbed ( $\text{mg kg}^{-1}$ ),  $V$  = volume of solution (L),  $W$  = adsorbent mass (g)

The removal percentage of CP was calculated using equation

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

**Distribution coefficient ( $K_d$ ):** The distribution coefficient was calculated by dividing CP sorbed concentration  $C_s$  by CP equilibrium concentration  $C_e$  as reported by Rojas *et al.* (2015).

$$K_d = \frac{C_s}{C_e} \quad (3)$$

**Sorption data Analysis:** The data obtained from the sorption of CP study were fitted to the Freundlich and Langmuir isotherms to obtain sorption parameters. The Langmuir model assumes the sorption of adsorbate as a monolayer on the surface of adsorbent. The sorption energy at each sorption site is same with no interaction between sorbed molecules. While, Freundlich model applies to adsorbents having heterogeneous structure and assumes the multilayer sorption of adsorbate on the surface of adsorbent (Giles *et al.*, 1960; Mesa and Spokas, 2011). According to Freundlich adsorption isotherm,

$$\log C_s = \log K_f + \frac{1}{n} \log C_e \quad (4) \quad \text{OR}$$

$$C_s = K_f (C_e)^{1/n} \quad (5)$$

Where,  $C_s$  = weight of CP adsorbed per unit weight of adsorbent ( $\text{mg kg}^{-1}$ ),  $C_e$  = equilibrium CP concentration in solution ( $\text{mg L}^{-1}$ ),  $1/n$  = empirical constant which indicate sorption intensity or surface heterogeneity,  $K_f$  = Freundlich constant related to sorption capacity ( $\text{mg kg}^{-1}$ ).

The plots between  $\log (C_e)$  vs.  $\log (C_s)$  were constructed for soil, soil + biochar and soil + compost treatments under study.  $1/n$  and  $\log (K_f)$  represent gradient and intercept, respectively while,  $K_f$  indicates Freundlich constant calculated by taking antilog of intercept.

The CP sorption data were also fitted to Langmuir model to obtain equation and Langmuir parameters

$$\frac{1}{C_s} = \frac{1}{Q_m \cdot K} \frac{1}{C_e} + \frac{1}{Q_m} \quad (6)$$

Where,  $C_s$  = weight of CP adsorbed per unit weight of adsorbent ( $\text{mg kg}^{-1}$ ),  $Q_m$  = maximum sorption capacity relative to total surface coverage ( $\text{mg kg}^{-1}$ ),  $C_e$  = equilibrium CP concentration in solution ( $\text{mg L}^{-1}$ ),  $K$  = Langmuir constant indicates affinity between adsorbate and adsorbent

The plots between  $1/C_s$  and  $1/C_e$  were made for soil, soil + biochar and soil + compost under investigation. The Langmuir parameters  $1/Q_m \cdot K$  and  $1/Q_m$  represent the slope and intercept respectively, while Langmuir constant  $K$  was calculated as  $1/\text{slope} \cdot Q_m$ .

**Quality assurance:** All chemicals used in this study were chromatographically pure and National Institute of Standards and Technology (NIST) traceable. All laboratory consumables and centrifuge tubes were dipped in 20% nitric acid solution which was prepared with ultrapure water overnight and then flushed thoroughly with ultrapure water. The quality and reliability of extraction process was assured by conducting a recovery experiment by spiking CP with known concentrations ranging from 1 to 50  $\text{mg kg}^{-1}$  and extracting with same process described earlier. The recovery values obtained between 88-92% indicated good extraction efficiency. Blank samples containing only soil and background solution were run and extracted similarly for quality control. The quantification of CP was done by running standards (99.5%) of CP and constructing calibration curve. The linear plots obtained with  $r^2 > 0.96$ . Experiments were carried out in three replicates and the reported results were the average of three replicated along with the standard deviation.

**Statistical analysis:** The fitness of sorption data for models was assessed by performing regression analysis of statistics (version 8.1). The sorption data were also processed for standard deviation in MS Excel (Microsoft Corporation, Pullman, Washington, USA).

## RESULTS

### *Sorption of chlorpyrifos to amended and un-amended soil:*

The amount of CP sorbed on individual soil and compost and biochar amended soil and percent CP removal is presented in (Table 2). Generally, the CP sorption increased with the increase in the initial concentration of CP in both un-amended and amended soil but the trend was not linear. All amended treatments showed significantly high  $K_d$  values compared to un-amended treatment for CP sorption. In case of un-amended soil, the CP sorption linearly increased up to the initial CP concentration of 50  $\text{mg L}^{-1}$  at which 162.2  $\text{mg kg}^{-1}$  CP was sorbed with maximum CP removal (81%) and  $K_d$  value (17.16  $\text{L kg}^{-1}$ ). After that CP sorption decreased with increasing concentration. In case of compost amended soil at 0.25% level of compost maximum CP removal (89.8%) was recorded at

**Table 2. Comparative effect of compost and biochar on chlorpyrifos sorption and removal.**

Treatment	Initial CP conc. (mg L <sup>-1</sup> )	CP sorbed (mg kg <sup>-1</sup> )	CP Removal (%)	K <sub>d</sub> (L kg <sup>-1</sup> )
CP + soil	5	10.00	50.00	4.00
CP + soil	10	23.40	58.50	5.64
CP + soil	50	162.20	81.10	17.16
CP + soil	100	311.80	77.95	14.14
CP + soil	200	560.96	70.12	9.39
CP + soil + compost 0.25%	5	16.00	80.00	16.00
CP + soil + compost 0.25%	10	29.68	74.20	11.50
CP + soil + compost 0.25%	50	179.60	89.80	35.22
CP + soil + compost 0.25%	100	357.92	89.48	35.54
CP + soil + compost 0.25%	200	676.36	84.55	22.53
CP + soil + compost 0.50%	5	19.68	98.40	246.00
CP + soil + compost 0.50%	10	37.56	93.90	61.57
CP + soil + compost 0.50%	50	195.20	97.60	162.67
CP + soil + compost 0.50%	100	383.88	95.97	96.25
CP + soil + compost 0.50%	200	747.72	93.47	58.13
CP + soil + biochar 0.25%	5	17.40	87.00	26.77
CP + soil + biochar 0.25%	10	32.32	80.80	16.83
CP + soil + biochar 0.25%	50	186.76	93.38	56.42
CP + soil + biochar 0.25%	100	368.08	92.02	47.63
CP + soil + biochar 0.25%	200	692.04	86.51	26.53
CP + soil + biochar 0.50%	5	19.96	99.80	1996.00
CP + soil + biochar 0.50%	10	39.60	99.00	396.00
CP + soil + biochar 0.50%	50	198.00	99.00	396.00
CP + soil + biochar 0.50%	100	388.76	97.19	136.93
CP + soil + biochar 0.50%	200	761.00	95.13	78.87

**Table 3. Isotherm modeling parameters of Freundlich and Langmuir models for chlorpyrifos sorption.**

Treatments	Freundlich <sup>a</sup>			Langmuir <sup>a</sup>		
	1/n <sub>f</sub>	K <sub>f</sub> (L kg <sup>-1</sup> )	R <sup>2</sup>	Q <sub>m</sub> (mg kg <sup>-1</sup> )	K (L kg <sup>-1</sup> )	R <sup>2</sup>
Soil + CP	1.29±0.23	4.34±0.41	0.92**	88.50±6.04	0.043±0.0050	0.96**
Soil + CP + Compost 0.25%	1.18±0.20	15.95±1.01	0.93**	26.46±3.02	0.003±0.0002	0.95**
Soil + CP + Compost 0.50%	0.76±0.03	111.85±6.02	0.92**	1.10±0.09	0.004±0.0003	0.85*
Soil + CP + Biochar 0.25%	1.06±0.10	28.68±3.21	0.91**	28.74±2.29	0.001±0.0001	0.93**
Soil + CP + Biochar 0.50%	0.55±0.01	218.83±9.87	0.97**	0.10±0.01	0.005±0.0002	0.86*

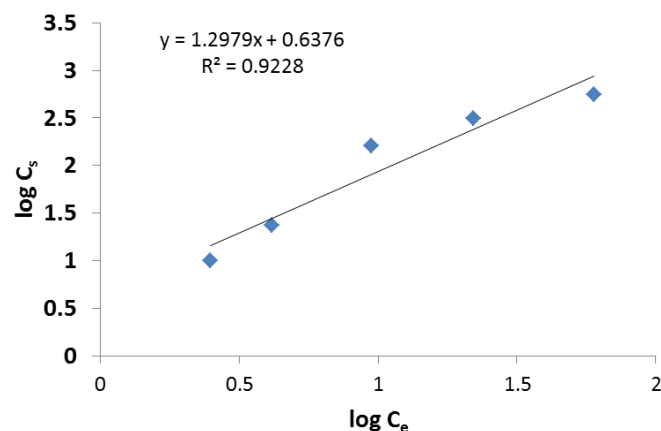
\*correlation is significant at  $p < 0.05$ ; \*\*correlation is significant at  $p < 0.01$ ; <sup>a</sup> model parameter values are presented as mean ± standard error of three replicates.

initial CP concentration of 50 mg L<sup>-1</sup> with K<sub>d</sub> value 35.22 L kg<sup>-1</sup>. While at 0.50% level of compost maximum CP removal (98.4%) with K<sub>d</sub> (246 L kg<sup>-1</sup>) was recorded with initial CP concentration of 5 mg L<sup>-1</sup>. The biochar amended soil showed similar trend up to 50 mg L<sup>-1</sup> and maximum (93.38 and 99.8%) CP removal and K<sub>d</sub> values (56.42 and 1996 L kg<sup>-1</sup>) were recorded at 50 and 5 mg L<sup>-1</sup> initial CP concentration respectively. However, in all biochar-amended treatments more sorption was recorded as evident from significantly high K<sub>d</sub> values at each CP level compared to compost-amended treatments (Table 2).

**Adsorption isotherm modeling:** The values of Freundlich and Langmuir modeling parameters have been shown in Table 3. The correlation coefficient (R<sup>2</sup>) was used to express the

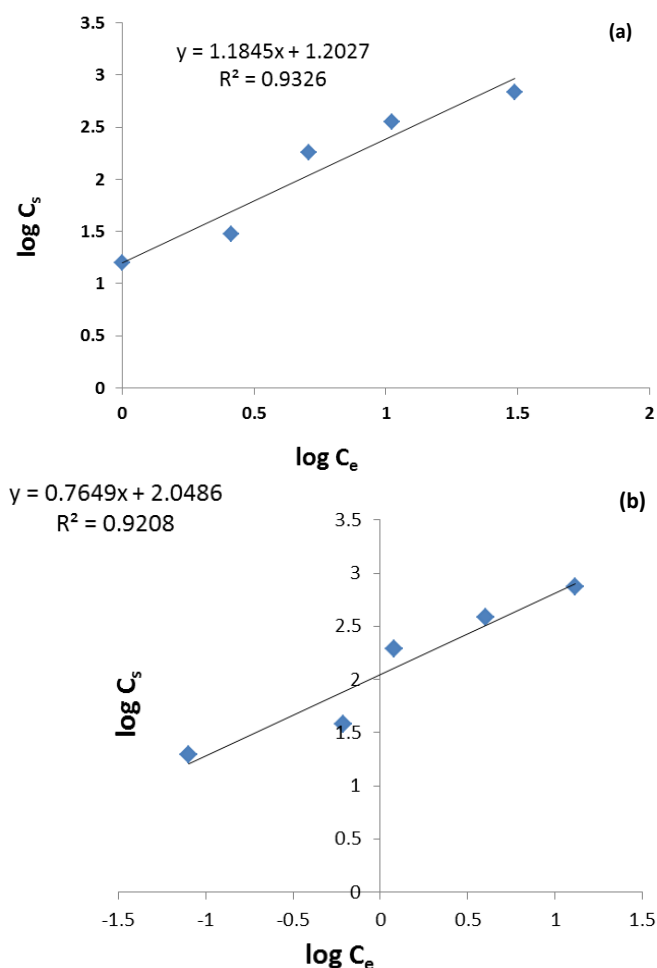
conformity between CP sorption data and the values predicted by models. The relatively high values of R<sup>2</sup> (> 0.90) indicated that the sorption data of CP best fitted to the Freundlich model. In case of Langmuir model parameters, the values of correlation coefficient are less than 0.90 for the CP sorption on soil + compost 0.50%, and soil + biochar 0.50% and the values of Langmuir constants recorded are very low in all cases which is improbable. This indicates the assumed monolayer sorption in this model is not applicable for CP sorption on compost and biochar surfaces in our experiment. So the Langmuir model did not successfully described the CP sorption behavior. For this reason only Freundlich model was chosen for further discussion.

The Freundlich isotherm for the CP sorption on individual soil is shown in Fig. 1. The isotherm was constructed by plotting equilibrium CP concentration versus sorbed CP concentration per unit weight of soil. The linear form of Freundlich equation (4) was used to examine the constructed isotherm and the data showed good fit. This can be proved by looking at the correlation coefficient ( $R^2$ ) value (0.92). From this linear plot, the values of  $1/n$  and  $K_f$  were obtained. The  $1/n$  was obtained from the slope, and  $K_f$  was calculated by taking the antilog of the intercept. The values of  $1/n$  and  $K_f$  were obtained as 1.29 and  $4.34 \text{ mg kg}^{-1}$  respectively.

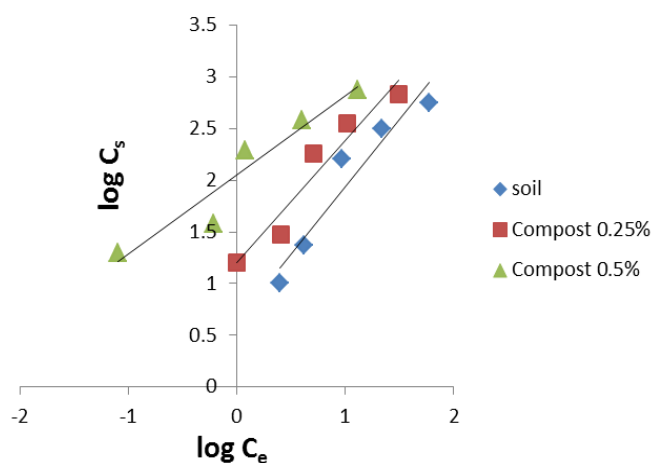


**Figure 1. Freundlich sorption isotherm for chlorpyrifos with individual soil.**

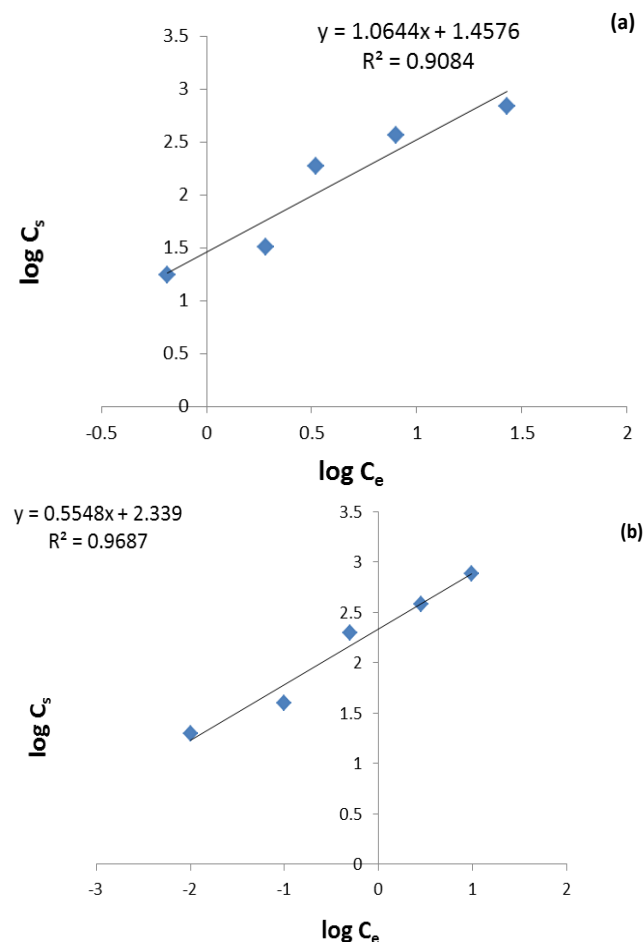
Figs. 2 and 3 show the Freundlich isotherm for CP sorption on soil amended with compost and biochar respectively. The compost-amended soil at 0.25% and 0.50% showed  $R^2$  values 0.93 and 0.92 and  $1/n$  values 1.18 and 0.76 and  $K_f$  values 15.95 and  $111.84 \text{ mg kg}^{-1}$  respectively (a 3.7 and 25.8 fold increase in sorption capacities with respect to un-amended soil. While, the biochar-amended soil showed  $R^2$  (0.91 and 0.97) and  $1/n$  (1.06 and 0.56) values for the CP sorption at 0.25% and 0.50% respectively with 6.6 and 50 fold increase in sorption capacities than unamended soil. However, biochar at 0.25% level showed sorption capacity  $28.68 \text{ mg kg}^{-1}$  (80% increase) and at 0.50% level  $218.83 \text{ mg kg}^{-1}$  (96% increase) compared to compost amended treatments (Table 3). The sorption capacity can also be assessed by the position of the curve on the isotherm. The higher curve indicates high sorption capacity. The compost and biochar amended soils at 0.25% levels showed high curves on the isotherms compared to individual soil, which became higher with increasing compost and biochar levels to 0.50% (Figs. 3. and 5). The sorption capacities for CP were found in the order of soil + biochar 0.50% > soil + compost 0.50% > soil + biochar 0.25% > soil + compost 0.25% > only soil (un-amended).



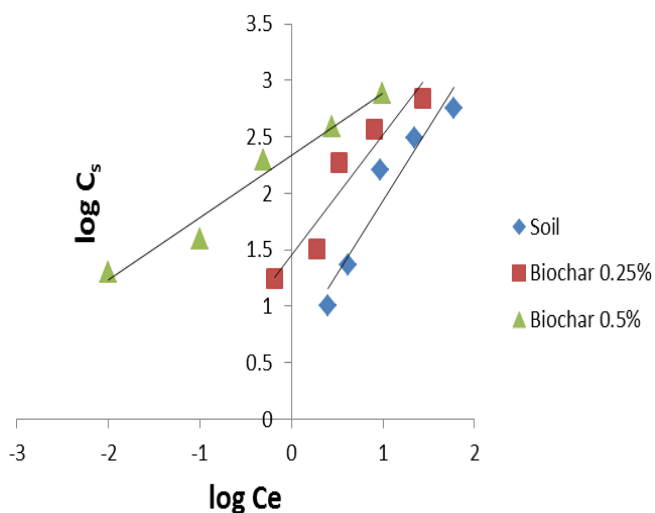
**Figure 2. Freundlich sorption isotherm for chlorpyrifos sorption on (a) soil + compost 0.25% (b) soil + compost 0.50%.**



**Figure 3. Combined sorption isotherm for chlorpyrifos sorption on soil and compost.**



**Figure 4. Freundlich sorption isotherm for chlorpyrifos sorption on (a) soil + biochar 0.25% (b) soil + biochar 0.50%.**



**Figure 5. Combined sorption isotherm for chlorpyrifos sorption on soil and biochar.**

## DISCUSSION

The large-scale application of CP has resulted in the contamination of soil and water environment (Rayu *et al.*, 2017). Therefore, remedial actions are needed to restrict the translocation of CP to the receiving environment (Yang *et al.*, 2010). The sorption is one of the efficient processes affecting the fate of pesticides in the environment. Sorption techniques are friendly regarding being cost-effective, using less energy and using the tools which are easy to use and readily available (El Bakouri *et al.*, 2009; De Wilde *et al.*, 2009a). Organic matter added in soil provides the most important sorbent surfaces for the nonpolar pesticides having low water solubility because phase partitioning is driven by hydrophobic interactions (Hamaker and Thompson, 1972; Moyo *et al.*, 2014). The soil applied organic amendments can affect the adsorption of pesticides in soil and reduce their mobility (Cederlund *et al.*, 2017).

The capacity of two types of organic amendments in increasing the sorption of CP on soil was tested in this study. The sorption data were subjected to Freundlich and Langmuir models. By correlation coefficient values, it was assessed that the Langmuir model was not applicable with the sorption data of this study. Moreover, minimal values were obtained for Langmuir parameters ( $K$  and  $Q_m$ ) which are impracticable (Monkiedje and Spiteller, 2002; De Wilde *et al.*, 2009b). In Langmuir model it is assumed that monolayer sorption occurs on the sorption sites present on the adsorbent surface (Langmuir, 1918). Therefore, monolayer sorption of CP is not valid for this study. The non-applicability of Langmuir model for pesticide sorption has been reported by some researchers. Such as, De Wilde *et al.* (2009b) evaluated the adsorption of various pesticides on organic amendments and concluded that Langmuir model was not applicable for the adsorption of metalaxyl on straw, peat mix, cow manure and coconut chips. These results were later confirmed by Rojas *et al.* (2013) and Rojas *et al.* (2015) for CP sorption on different organic amendments. While, Freundlich model was well fitted with this study sorption data as indicated by the correlation coefficient values ( $> 0.90$ ) in all cases. This indicates that CP sorption on the surface of soil and amendments is a multilayer sorption process (Rojas *et al.*, 2013; Rojas *et al.*, 2015).

The data regarding percent sorption of CP on un-amended and amended soil (Table 2) indicates the non-linearity of sorption. These results are in line with that reported by Spurlock and Biggar (1994) and De Wilde *et al.* (2009b). They stated that the organic amendments and pesticides polar groups interact specifically with each other which results in the non-linearity of sorption. Adjustment of sorption data to the Freundlich model also indicates the non-linearity of sorption (Rojas *et al.*, 2013).

We can classify the sorption isotherm as L, S, C and H type according to nature of slope ( $1/n$ ). L type curves indicate the flat orientation of adsorbate on the surface of adsorbent with

slope value  $< 1$ , while, S type curves shows vertical adsorbate orientation with slope value  $> 1$  (Giles *et al.*, 1960). For the CP sorption on un-amended soil, soil + 0.25% compost and soil + 0.25% biochar the isotherm was of S type ( $1/n > 1$ ) and for CP sorption on soil + 0.50% of both amendments the isotherm was of L type ( $1/n < 1$ ). The  $1/n$  values can be used to determine the strength of the bond between adsorbate and adsorbent, the higher value of  $1/n$  indicates the bond is weak (Ismail *et al.*, 2013). The highest  $1/n$  value was found for un-amended soil while for amended soil lower values were found in all cases in this study indicates the more strength of adsorption.

Sorption mechanisms include electrostatic attractions between pesticide and charged surfaces of biochar. Besides it, diffusion and partitioning into the carbonized and non-carbonized biochar fractions (Ahmad *et al.*, 2014), hydrophobic effect, hydrogen bonding, and pore filling may also contribute (Tan *et al.*, 2015). In case of compost humic substances containing several major functional groups, such as carboxyl, phenolic, alcohol and carbonyl are responsible for sorption of organic contaminants like CP (Tejada *et al.*, 2011). These properties make both biochar and compost as efficient sorbent materials for a variety of organic contaminants for reducing their toxicity. In our study, the Freundlich parameter  $K_f$  values significantly increased in all amended treatments. The increased  $K_f$  values are also indicator of high sorption capacity (Giles *et al.*, 1960). Our results correspond well with the previous findings reported on enhanced insecticide sorption by the addition of biochar (Yu *et al.*, 2006; Spokas *et al.*, 2009; Cederlund *et al.*, 2017; Tang *et al.*, 2017) and by the addition of compost (Kravvariti *et al.*, 2010; Tejada *et al.*, 2011).

The sorption capacity of the pesticide can be assessed by the position of the sorption isotherm on the y-axis. The high curve on the y-axis indicates more sorption capacity of the adsorbents for adsorbate (Rojas *et al.*, 2013). All the amended treatments showed higher sorption isotherm for CP sorption on y-axis compared to un-amended treatment. However, Biochar at both levels performed better compared to compost as indicated by high  $K_f$  values (Table 3). The biochar exhibits microporosity and high specific surface area (Deng *et al.*, 2017). The more CP sorption potential of biochar could be attributed to its high organic carbon contents, specific surface area, greater pore volume and lower pore width compared to compost used in our study (Table 1).

**Conclusion:** The effect of compost and biochar was assessed to enhance the sorption capacity of the soil for CP. The experimental sorption data were validated with Langmuir and Freundlich isotherm models. Freundlich model well fitted and explained the sorption behavior of CP in un-amended as well as amended soil. Although, both compost and biochar significantly enhanced the sorption of CP and the maximum sorption capacity was achieved at the 0.50% level of both

amendments. However, biochar showed high sorption capacity for CP compared to compost. Overall, the sorption capacities obtained were in the order of soil + biochar 0.50%  $>$  soil + compost 0.50%  $>$  soil + biochar 0.25%  $>$  soil + compost 0.25%  $>$  only soil. The results are of practical significance and could be implied for the remediation of CP contaminated soil. The implications are important in areas where CP is potentially handled and spilled as well as extensively used as a soil application to control insect/pests.

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