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Research Article

Enhancing herbicides sorption in sodic soils through biochar amendment : A promising approach for sustainable agriculture

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Abstract

This study is essential for assessing the binding capacity of Prosopis wood biochar to commonly used herbicides, Pretilachlor and Pendimethalin. Understanding their sorption dynamics at varying biochar application rates and exposure times is crucial for sustainable and effective herbicide management in intensively farming agricultural fields and for reducing environmental contamination. The Prosopis wood biochar was produced in an earthen kiln at 300-350°C. The batch experiment was conducted to study the sorption potential of biochar additions at rates of 0, 5, and 10 t ha-1. The herbicides were added to the homogenized soil-biochar mixes at zero, whole, twice, and four times the recommended dose. The sorption of the herbicides by soil biochar mixture was studied for 12 and 24 hours. The result showed that Pendimethalin sorption increased with biochar application rate, requiring 24 hours for 95% sorption at 4X dose without biochar (77.95 mg/kg soil) and 12 hours with 10 t/ha biochar (75.82 mg/kg soil). The Kd value increased with biochar application (0.57-77.95 mg/kg soil) and decreased with pendimethalin application (77.95-3.04 mg/kg soil). Maximum sorption (95%) was attained within 12 hours for 1X and 2X rates and 24 hours for 4X rates when biochar was added. This demonstrated that although pendimethalin residue in the soil can be immobilized by adding biochar within 8 hours at lower rates, more than 24 hours were required when pendimethalin was applied at higher rates or repeatedly. Biochar can be used to reduce pendimethalin leaching in agricultural fields, especially sodic soils, at higher application rates.

Keywords: Biochar, Herbicide, Pretilachlor, Pendimethalin, Sorption

INTRODUCTION

Intensive agriculture has led to the indiscriminate use of agrochemicals, including herbicides, insecticides, fungicides, and fertilizers, resulting in pollution of the environment, particularly in developing countries where agriculture is the major occupation (Vonk and Kraak, 2020). The use of herbicides has increased extensively recently due to intensive agricultural practices. Herbicide application occurs most frequently in row-crop farming, where they are applied before or during planting to maximize crop productivity by minimizing other vegetation. They also may be applied to crops in the fall to improve harvesting (Sharma *et al.,* 2019). The indiscriminate use of herbicides in intensive agriculture has led to groundwater pollution, causing serious harm to aquatic and terrestrial ecosystems (Ozkara *et al.,* 2016). Pesticides can contaminate groundwater, which is a subject of national importance because groundwater is used for drinking (Pathak *et al.,* 2022). Herbicides enter human tissues through biomagnification of the food chain, causing serious health hazards besides polluting the environment. The retention of applied herbicide in soil takes place through the process of sorption, which directly affects transport through leaching, surface runoff, and volatilization, besides its bioavailability (Mendes *et al.,* 2019).

The inactivation of residual herbicides due to uncontrolled soil application needs serious attention. Agronomic management practices are essential for addressing the residual problems of herbicides in cultivated lands. One feasible method is the use of organic amendments that have the capacity to adsorb these organic pesticide molecules. Biochar, a lignocellulosic carbonaceous byproduct of the pyrolysis process, has attracted widespread attention for its potential to enhance soil absorptivity for nutrients and organic compounds such as pesticides (Singha *et al.,* 2019). Biochar has a high sorption ability, which allows it to sorb and retain nutrients and organic compounds such as herbicides and insecticides (Cara *et al.,* 2022). This can reduce the accumulation of herbicides in agricultural lands and reduce crop uptake due to indiscriminate use. However, the high sorption ability of biochar may also reduce herbicidal efficacy.

Studies have shown that biochar amendments can increase the sorption of herbicides in agricultural soil. This is because biochars that contain a high specific surface area contribute to the increase of soil sorption of herbicides. Biochar amendment can also alter soil properties, such as the ability to adsorb and degrade different chemicals. However, the efficacy of herbicides in biochar-amended soils can be affected by their chemistry and mode of action (Gaffar *et al.,* 2021). The use of biochar as a soil amendment can be a promising strategy for reducing the negative effects of residual herbicides and insecticides in agriculture (Liu *et al.,* 2018). It is important to note that the high sorption ability of biochar may also reduce herbicidal efficacy. Additionally, the efficacy of herbicides in biochar-amended soils can be affected by their chemistry and mode of action.The present study aimed to understand the fate of the two herbicides, Pretilachlor and Pendimethalin,in soil; and the potential of biochar to reduce their negative impacts.

MATERIALS AND METHODS

Soil sample collection and biochar preparation

Surface soil samples (0-15cm) were collected from AnbilDharmalingamAgricultural College& Research Institute (ADAC&RI) farm, Trichyfor the adsorption experiment conducted in the laboratory between August 2019 and 2020.*Prosopis julilora* plant biomass was used for biochar preparation. The biochar was synthesized in the traditional earth mound kiln method at approximately 300-350˚Cfor 48 h. The charred biomass was then homogenized in a Wiley mill to a size < 0.5mm. The air-dried biochar was then stored in airtight containers before the experiment. The 2mm sieved soil samples were mixed with three biochar rates (Control, 5t/ha, 10t/ha) and homogenised thoroughly (Tables 1 and 2).

Analysis of soil and biochar

The processed soil and biochar samples were characterised before the commencement of the experiment for physicochemical properties following standard analytical procedures (Jackson, 1973). The pH was measured by using a pH meter, electrical conductivity (EC) was measured with a conductivity meter (Laboratory testing procedure for soil sample analysis ISO 9001: 2000) (CM-183, ELICO) and soil organic carbon (SOC) was analysed by Walkley and Black (1934) wet digestion method. The micronutrients viz., Cu, Mn, Zn and Fe were determined using atomic absorption spectrophotometer (Shimadzu AA-6300, Japan), and Ca and Mg were measured by using EDTA (Versenate) titration method (Jackson, 1973).The Na and K concentrations were determined using Flame photometer (Toth and Prince, 1949).Soil texture was determined by the Robinson International pipette method (Piper, 1966). Soil porosity (%), particle density (Mgm^{-3}) and bulk density (Mgm^{-3}) were calculated by Cylinder method (Piper, 1966).

Proximate and elemental analysis of biochar

The ash content, sesquioxides and organic carbon content were determined as per standard procedures (Jackson, 1973). Chemical composition of biochar for elemental carbon, nitrogen, hydrogen and sulphur was analysed using CHNS analyzer at Central Electro Chemical Research Institute (CECRI), Karaikudi and the micronutrients viz., Cu, Mn, Zn and Fe were determined using Atomic absorption spectrophotometer (Shimadzu AA-6300, Japan). The soil and biochar analysis results are furnished in Tables 1 and 2.Biochar samples were subjected to Fourier Transformer Infra Red (FTIR) and scanning electron microscopic analysis.

Adsorption study

The soil sample without any treatment (control – no biochar, no herbicide) was collected, dried and sieved by passing through 2-mm sieve. The processed (2mm sieved) soil sample mixed with biochar at the rate of 5t/ha and 10t/hawas fortified by spiking the soil biochar mixture with dilute solutions of herbicides. The added biochar was thoroughly mixed with soil and was placed in centrifuge tubes to which different concentrations (0, x, 2x, and 4x where x is the recommended dose) of the two herbicides, viz., pretilachlor and pendimethalin were added and the experiment was duplicated. After the addition of dilute herbicide solution to soil + biochar mixture, it was allowed for one hour reaction time. To the soil + biochar + herbicide mixture, solvent (0.05 M $CaCl_2$ was added in the ratio of 1:5 and was shaken at 12 and 24 hrs on an end-over-end shaker to attain equilibrium. After equilibration, the soil water suspension was centrifuged at 200 rpm for 15 minutes and the herbicide concentrationwas measured in the supernatant. The amount of herbicide sorbed was calculated from the difference between the initial and final solution concentrations. The herbicides concentration was determined using HPLC-DAD (Gámiz*et al.,* 2019).

FTIR Assay

Fig. 3 shows the FTIR spectra of the biochars obtained from *P. juliflora* by pyrolysis. The band located between 3200 and 2800 cm^{-1} is assigned to asymmetrical and symmetrical stretch vibrations of the C−H bond (e.g., methyl and methylene groups); these groups appearedas a result of tarry remains that partially volatilized, but these could be present in the initial structure of biochar. The bands located between 1600 and 1400 cm^{-1} are assigned to carbon−carbon stretching vibrations in the aromatic ring alkene groups. The bands located between 1200 and 1000 cm^{-1}were assigned to the stretching vibration of the C−O bond (e.g., carboxylic acids in the cellulose and hemicellulose) (Pawar and Panwar, 2022). Finally, the bands located between 800 and 700 cm^{-1}were assigned to the bending vibration of the C−H bond. In the pyrolysis process, temperature affects the final functional groups present on the biochar surface. As the pyrolysis temperature increases from 300-350°C, intense bands increasedue to the aromatization and degradation of lignocellulosic components, such as dehydrogenation reactions.

RESULTS AND DISCUSSION

Effect of biochar on pretilachlor sorption in sodic soil

The results of the pretilachlor sorption in sodic soil through batch equilibrium are presented in Table 3.The findings revealed that pretilachlor required 24 hours for complete sorption when administered at doses of X and 2X without biochar. Regardless of equilibrium time, the sorption of pretilachlor increases as the rate of biochar application is increased. This confirmed several researchers'findings that herbicidessorption increased with biochar application (Zhelezova*et al*., 2017; Penn *et al*., 2018; Tao *et al*., 2019; Sakulthaew*et al*., 2021).Enhanced diuron sorption with an increasing rate of biochar added to soil was reported by Yu *et al.* (2006)due to the presence of organic carbon materials. Similar results for the sorption of pyrimethanil in soil amended with biocharswere observed by Yu *et al.* (2010) and also they observed that biochar with higher surface area and microporosity showed a stronger effect on the reversibility of sorption of the pesticide. When biochar was applied in sodic soil at a rate of 10 t/ha, its complete sorption occurred after 8 hours (Fig. 2). The adsorption properties of biochar (carbon content and surface area of biochar) substantially influence the eventual efficacy of an applied herbicide. It may not be possible to compensate for the reduction in herbicide phyto availability

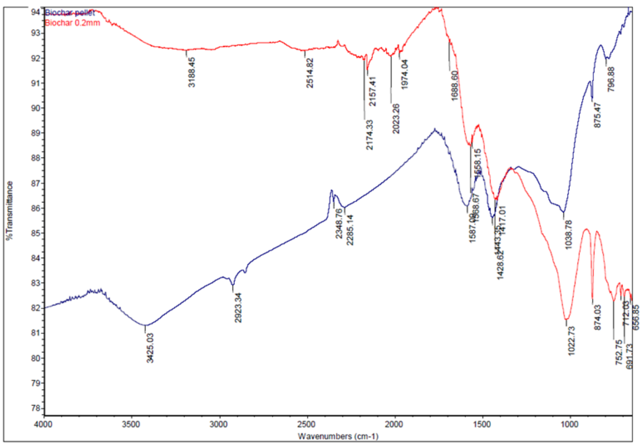

Fig. 1. *Biochar spectra obtained from FTIR*

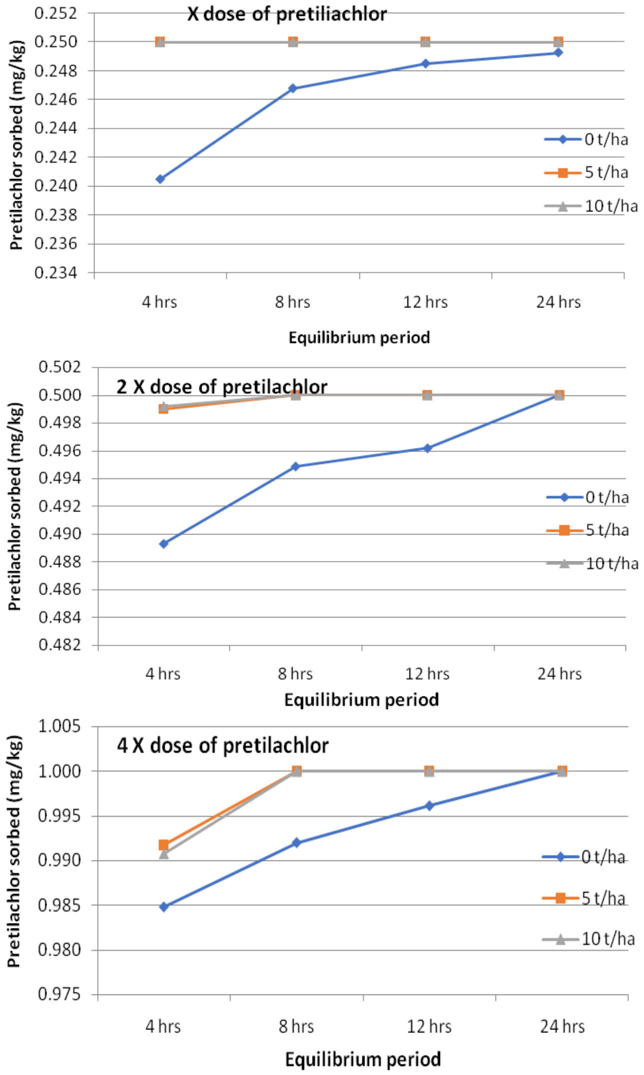

Fig. 2. *Pretilachlor adsorption in sodic soil under batch equilibrium experiment*

caused by adsorption on strongly adsorbing biochar, even with a significantly increased herbicide dose.The effectiveness of an applied herbicide is significantly influenced by the biochar's adsorption properties (Sakulthaew *et al*., 2021).

When pretilachlor rates were raised, the Kd (Distribution coefficient) values ranged from 37 to 640 mg/kg soil (Table 4). Kd values increased as the rate of applied biochar was increased. When the pretilachlor rate was very high (4X), both 5 and 10 t/ha of biochar displayed low Kd values (4X).

The pretilachlor sorption data obtained from lab experiments at different time intervals of equilibrium was fit into Freundlich equation (Fig. 3) and a linear fit was obtained. The Freundlich parameter (n) values, a measure of sorption intensity which reflects the degree to which sorption is the function of herbicide concentration, was equal to 1 (Fig. 3 and 4). This revealed a strong affinity between soil solids and pretilachlor and increased availability of adsorption sites with increased liquid concentration. The determination coefficient (R^2) values for pretilachlor sorption were 0.917, 0.926 and 0.983 at 4, 8 and 12 hrs, respectively, in

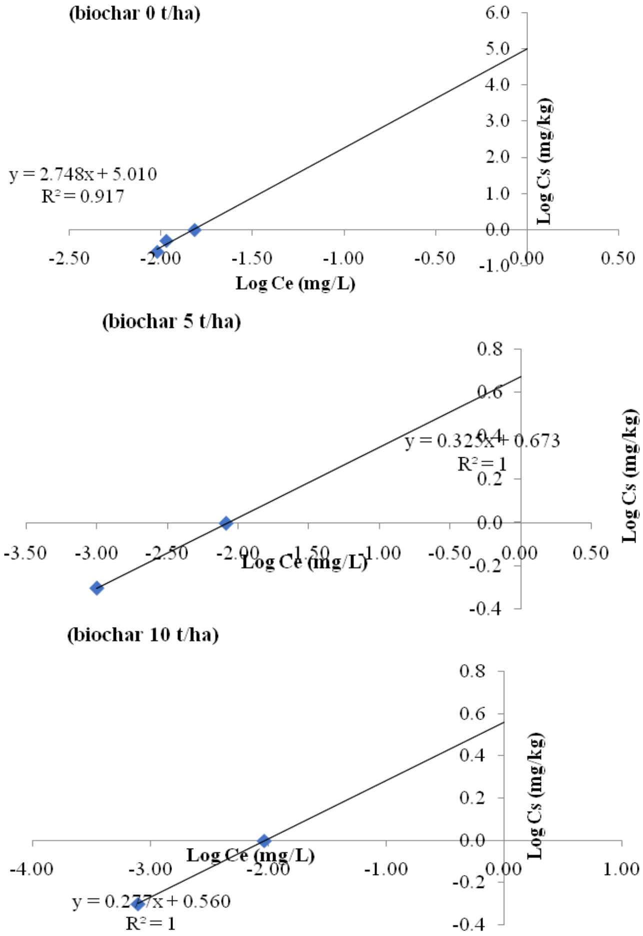

Fig. 3. *Linear plots of Freundlich isotherm for pretilachlor sorption in soil after 4 hrs of equilibrium*

the soil without biochar addition and showed that the most stable time of pretilachlor sorption in sodic soil is 12 hrs without biochar addition. However, with biochar addition as an amendment, complete sorption was reached within 8 hours and was sufficient to immobilize pretilachlor residue in soil (Fig. 4).

Effect of biochar on pendimethalin sorption in soil

The impact of biochar on pendimethalin sorption behaviour of sodic soil treated with biochar at three rates of 0, 5, 10 t/ha, and the doses of pendimethalin were X (750 g/ha), 2X (1500 g/ha) and 4X(3000 g/ha) at various time intervals as 4, 8, 12, 24 hours were evaluated and presented in Table 5.

The findings showed that pendimethalin sorption increased with increasing biochar application rate regardless of equilibrium time. Pendimethalin required 24 hours for complete sorption when applied at 4X dose without biochar. When biochar was applied at the rate of 10 t/ha, complete sorption of pendimethalin occurred after 12 hours when applied at 4X rate (Fig. 5). The pendimethalin sorption coefficient, Kd [L kg1], was determined for linear sorption isotherms using the formula Kd=Cs/Ce, where Ce is the herbicide concentration of the soil solution at equilibrium and Cs is the quantity of herbicide sorbed by the soil [mg kg^{-1}]. The slope of the linear plots of sorbed vs aque-

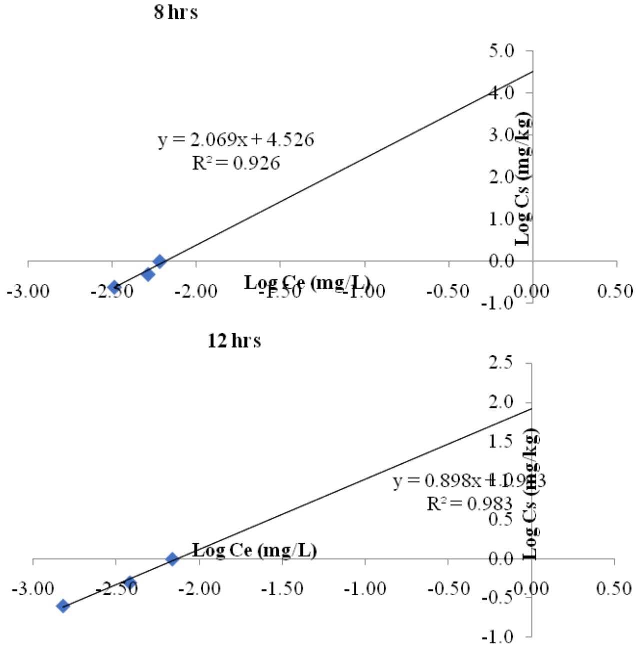

Fig.4. *Linear plots of Freundlich isotherm for pretilachlor sorption in soil at 8 and 12 hrs of equilibrium without biochar addition*

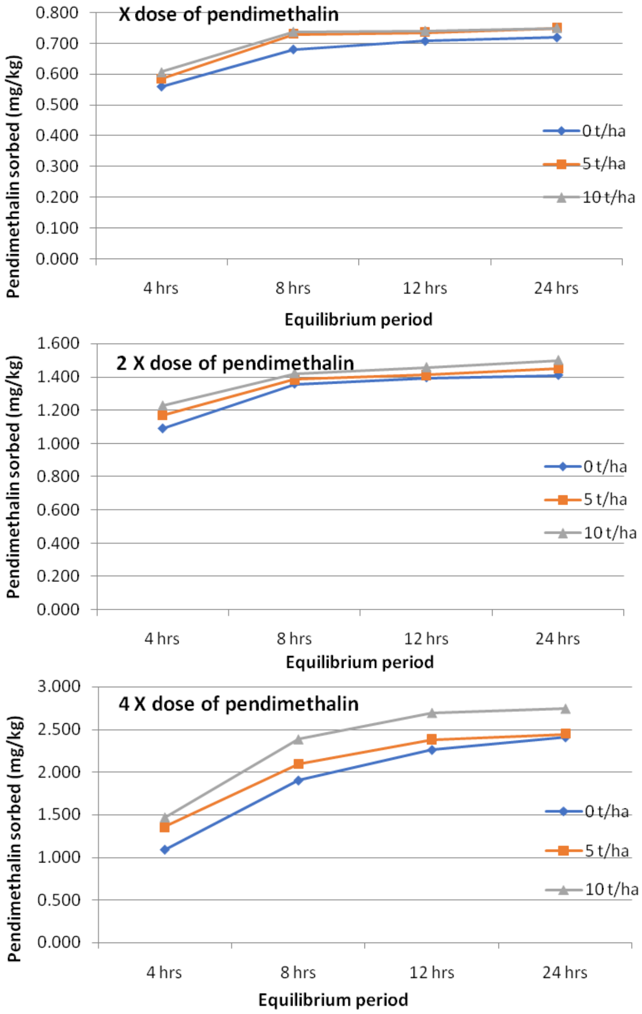

Fig. 5. *Pendimethalin adsorption in sodic soil under batch equilibrium experiment*

Table 1. Initial soil characteristics of sodic soil

Characteristics	Values	Characteristics	Values
pH (1: 2.5)	8.97	Organic carbon (%)	0.74
EC (dS m^{-1}) (1: 2.5)	2.54	Av. Nitrogen (kg ha^{-1})	209
Bulk density (Mgm^{-3})	1.61	Av. Phosphorus (kg ha^{-1})	62.7
Particle density (Mgm^{-3})	2.40	Av. Potassium (kg ha^{-1}	740
% Pore space	32.92	CEC (cmol (p+)/kg)	33.8
Texture	Sandy clay loam		

Table 2. Biochar characteristics

C* %	H* %	N* %	S* %	Ash %	pH	EC dS m^{-1}	OC %	BD Mgm^{-3}	PD Mgm^{-3}	SA $m^2 g^{-1}$
50.52	2.08	1.22	0.143	12.22	7.3	0.41	3.25	0.77	1.29	20.888

Table 3. Pretilachlor sorption (mg/kg) in sodic soil at various application rates as affected by the equilibrium time

Pretilachlor concentration added (g/ha)	Biochar concentration (t/ha)		
	0	5	10
4 hrs			
X	0.240	0.250	0.250
2X	0.493	0.499	0.499
4 X	0.988	0.992	0.991
8 hrs			
X	0.242	0.250	0.250
2X	0.495	0.500	0.500
4 X	0.992	1.000	1.000
12 hrs			
X	0.243	0.250	0.250
2X	0.496	0.500	0.500
4 X	0.996	1.000	1.000
24 hrs			
X	0.246	0.250	0.250
2X	0.500	0.500	0.500
4 X	1.000	1.000	1.000

Table 4. Kd values of pretilachlor as influenced by the biochar and its rate in sodic soil after 4 hrs of batch equilibrium experiment

Dose of pretilachlor	0 t/ha	5 t/ha	10 t/ha	Mean
X	25	0	0	8
2X	73	497	640	403
4X	80	119	107	102
	59	205	249	

ous pendimethalin concentrations was used to calculate the value of Kd. The Kd (distribution coefficient) values after 4, 8, and 12 hours of equilibrium were 0.57-4.52, 1.7256.60, and 3.04-77.95 mg/kg soil, respectively.While the Kd of pendimethalin increased as biochar application increased. It decreased as pendimethalin application rates increased (Table 6).

The Freundlich equation (Fig. 6) used to fit the pendimethalin sorption data from the lab experiment at various equilibrium times showed a linear fit . Regardless of the addition of biochar, the Freundlich parameter (n) values, a measure of sorption strength and a reflection of the extent to which sorption is a function of herbicide concentration, were inferior at 4 hours of equilibrium and nearly equal to 1 at 8 hours of equilibrium (Fig. 6 and 7).

This exhibited "L" type of pendimethalin sorption in the experimental soil, indicating a moderate affinity between soil solids and pendimethalin as well as a reduced availability of adsorption sites with an increase in liquid concentration in the absence of biochar. Penn*et al*. (2018) found that biochar amendment increased the sorption of atrazine in different soils. Gaffar *et al*. (2021) investigated the sorption of atrazine in an organic soil amended with biochar and found that higher pyrolysis temperature increased specific surface area and microporosity, which enhanced the sorption of atrazine. In another study, an activated biochar was synthesized from corn straw and applied to atrazine adsorption. The results showed high affinity and

Table 5. Sorption of pendimethalin (mg/kg) in sodic soil at different rates of application as influenced by the equilibrium time

Pendimethalin concentration added (g/ha)	Biochar concentration (t/ha)		
	0	5	10
4 hrs			
X	0.559	0.585	0.607
2X	1.092	1.171	1.228
4 X	1.088	1.355	1.469
8 hrs			
X	0.680	0.730	0.737
2X	1.359	1.385	1.422
4 X	1.899	2.095	2.381
12 hrs			
X	0.707	0.750	0.750
2X	1.396	1.413	1.458
4 X	2.258	2.379	2.691
24 hrs			
X	0.719	0.750	0.750
2X	1.410	1.451	1.500
4 X	2.406	2.446	2.750

Table 6. Kd values of pendimethalin as influenced by the biochar and its rate in sodic soil at different time intervals of equilibrium

Dose of pendimethalin	0 t/ha	5 t/ha	10 t/ha	Mean
4 hrs				
X	2.93	3.56	4.25	3.58
2X	2.68	3.56	4.52	3.58
4X	0.57	0.82	0.96	0.78
Mean	2.06	2.65	3.24	
8 hrs				
X	9.69	36.21	56.60	34.17
2X	9.61	12.09	18.13	13.28
4X	1.72	2.32	3.85	2.63
Mean	7.01	16.87	26.19	
12 hrs				
X	16.53	54.97	77.95	49.82
2X	13.43	16.18	34.38	21.33
4X	3.04	4.75	8.70	5.50
Mean	11.00	25.30	40.34	

adsorption capacity of the activated biochar for atrazine (do Nascimento *et al.,* 2022).

Maximum sorption was attained within 12 hours for X and 2X rates and 24 hours for 4X rates when biochar is added (Fig. 8). This demonstrated that although pendimethalin residue in the soil can be immobilised by adding biochar within 8 hours at lower rates, more than 24 hours were

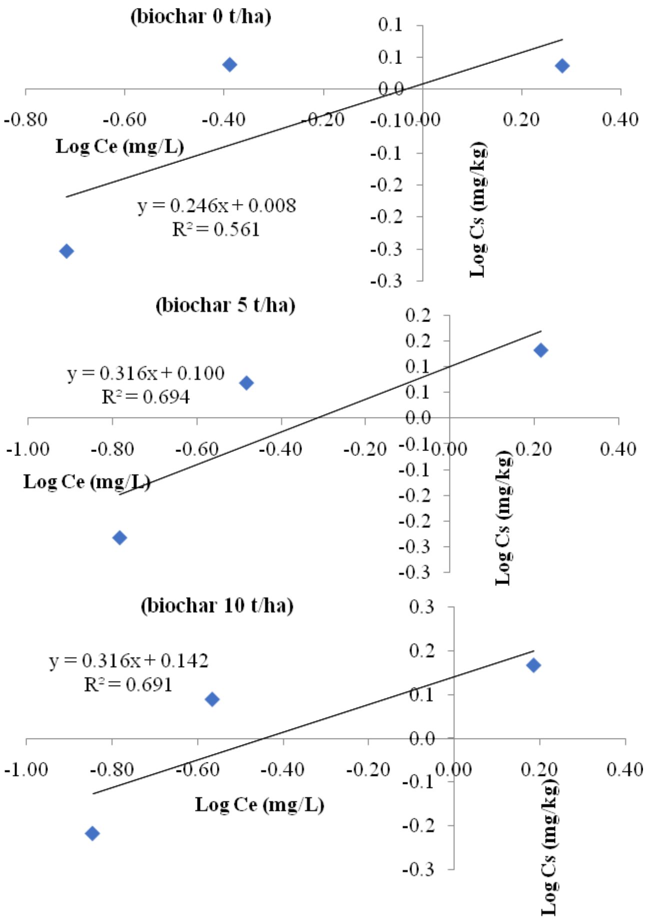

Fig. 6. *Linear plots of Freundlich isotherm for pendimethalin sorption in soil after 4 hrs of equilibrium*

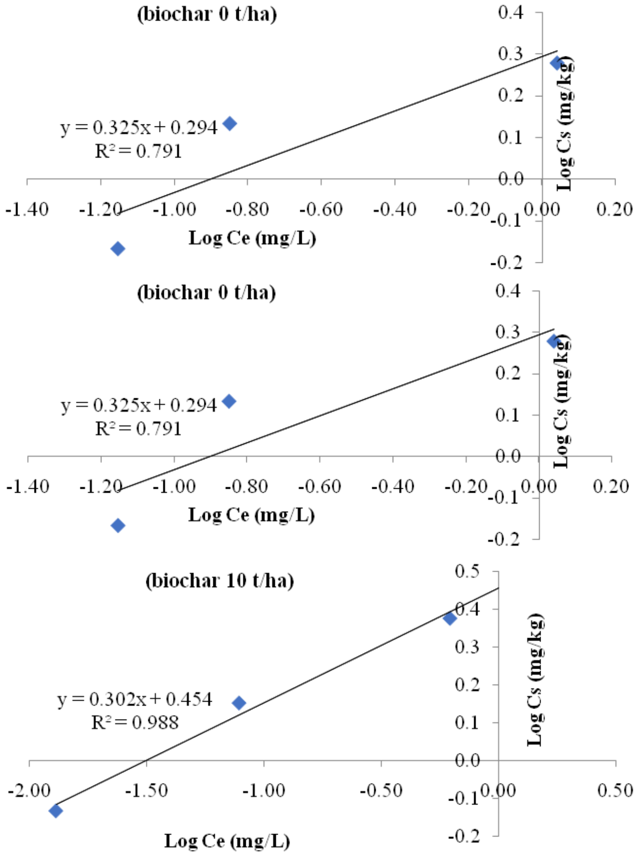

Fig. 7. *Linear plots of Freundlich isotherm for pendimethalin sorption in soil after 8 hrs of equilibrium*

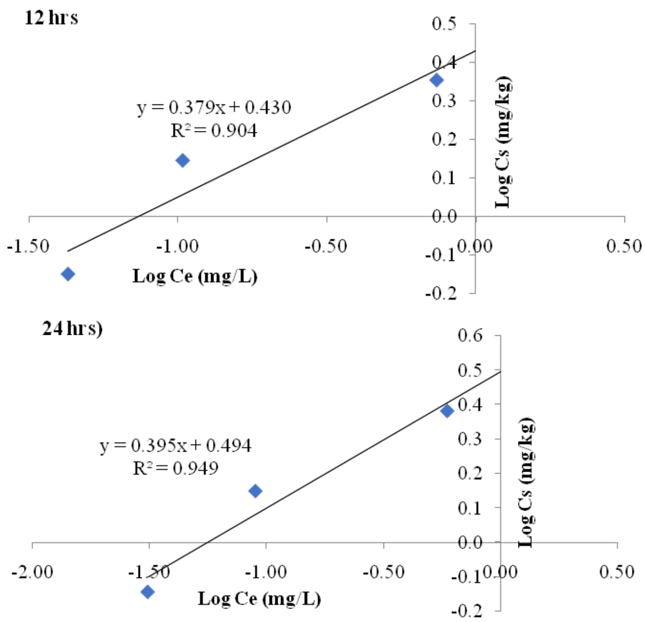

Fig. 8. *Linear plots of Freundlich isotherm for pretilachlor sorption in soil at 12 and 24 hrs of equilibrium without biochar addition*

required when pendimethalin was applied at higher rates or repeatedly or judiciously.Previous studies have reported the beneficial effect of biochar on various soil properties (Khorram *et al.*, 2016; Liu *et al.*, 2018; Ogura *et al.*, 2021).The use of biochar may help improve the sorption of pesticides on soil, reduce their mobility, and lower the risk of contamination of surface and ground waters.

Conclusion

The present study concluded that pretilachlor sorption in sodic soil was higher than pendimethalin and their sorption increased with an increase in biochar application rate. As a result, biochar can be used as an amendment to immobilise pretilachlor/pendimethalin residues without toxic effectson subsequent crops. Pendimethalin, however, required more time to sorb and to immobilise than pretilachlor, and is attributed to the nature of the molecule. As these two herbicides are largely used in rice belts of the Cauvery delta zone(South Tamil Nadu, India), there is every likelihood of residual toxicity/persistence in soil and its accumulation in rice grains due to an overdose / repeated usage in rice fields. Hence, biochar can alleviate the problem of herbicide persistence /toxicity and ensure the efficacy of applied herbicide in controlling weeds.

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Conflict of interest

The authors declare that have no conflict of interest.

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