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Modelling and spectroscopic investigation of 2,4-D adsorption in soil amended with pine sawdust, paunch grass and sewage sludge biochars

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Abstract

2,4-Dichlorophenoxyacetic acid (2,4-D) is a widely used herbicide possessing high herbicidal activity; however, it is potentially toxic to humans and quite persistent in the environment. We investigated the adsorption of 2,4-D in two pasture soils amended with pine sawdust (PSD), paunch grass (PG) and sewage sludge (SS) biochars using batch studies. The results showed that PSD biochar produced at 700 °C exhibited the highest adsorption capacity for 2,4-D among the waste-derived biochars tested, which is 200-fold greater than the control and other biochar-amended soils. In general, the sorption affinity of 2,4-D for biochar amended soils followed an order: PSD > PG > SS. The high adsorption capacity of the PSD may be attributed to its significantly higher specific surface area of 795 m²·g⁻¹ as compared to other soils and biochars. Moreover, the results of the physicochemical characterization showed no difference in surface oxygen functional groups among the PSD, PG and SS. These findings indicate that oxygen-containing surface functional groups have a negligible role in 2,4-D adsorption, as evident from the spectroscopic investigation, thus emphasizing the role of surface area in the 2,4-D adsorption. Lastly, pore intrusion/filling, hydrogen bonding and π - π EDA interactions are postulated to be the plausible adsorption mechanisms for 2,4-D onto biochar amended soils.

Keywords: Soil, biochar, 2, 4-D, adsorption, functional groups, remediation



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INTRODUCTION

Environmental contamination due to the wide application of pesticides in agriculture has become a matter of global concern because of the toxicity and persistence of these organic chemicals in soil and aquatic environment^[1]. Although their occurrence in the environment has been reported for decades, some of their potential negative impacts on human health, animals, and ecosystems were recently recognized, which qualify some of the pesticides as emerging contaminants^[2]. Among the herbicides, 2, 4-Dichlorophenoxyacetic acid (2,4-D, $\text{Cl}_2\text{C}_6\text{H}_3\text{OCH}_2\text{COOH}$) is widely used for plantation crops such as sugarcane, cocoa, and rubber^[3]. It is less toxic to common grasses and can be manufactured at a low cost^[4]. Due to its effectiveness and low cost, 2,4-D has been one of the most widely and frequently detected organic chemicals in the environment, including as an endocrine-disrupting compound^[5-7]. 2,4-D is an ionizable (pK_a at 25 °C = 3.4) chemical having high water solubility of 900 $\text{mg}\cdot\text{L}^{-1}$ ^[8] and a low octanol/water partition coefficient (pH 7, 20 °C) of 0.015^[9]. Therefore, the compound readily dissolves in rainwater and could potentially become highly mobile and transported into the soil environment during conditions conducive to leaching (i.e., heavy rainfall and storm events).

According to the World Health Organisation, 2,4-D is characterized as moderately toxic (class II) and potentially carcinogenic^[10] to human beings and animals and has a drinking water limit of 70 $\mu\text{g}/\text{L}$ ^[11]. 2,4-D has been extensively used in the cereal-growing regions of New Zealand (NZ) and comprised 40% of the total herbicide use in 1998 and a concentration level of 0.09 $\mu\text{g}/\text{L}$ has been detected in groundwater of the Waikato region^[12]. Since 2,4-D is openly sprayed, its residues can easily find their way into nearby water bodies, thus contaminating the media. It is to be noted that in NZ, the maximum allowable value for 2,4-D in water is set at 100 $\mu\text{g}/\text{L}$, and therefore no routine monitoring is conducted at present. However, prolonged exposure to low concentrations over an extended period could result in potential toxic effects on non-target organisms and human health. Past research has shown that the adsorption process dictates the mobility and bioavailability of organic compounds in a soil environment^[13]; thus, the adsorption affinity of a 2,4-D compound is considered a governing process influencing its environmental fate.

Biochar, a carbon-rich solid product produced through the heating of organic biomass in an oxygen-limiting environment (pyrolysis), could be used as an engineered sorbent, mitigating the transport of these chemicals in-situ^[14]. Biochar has been demonstrated to be effective in adsorbing various organic and inorganic compounds in aquatic and soil environments^[15,16]. These past studies indicate that biochar addition to soil could potentially mitigate the movement of chemicals through the soil profile, thereby reducing their environmental risk to the receiving environment.

The sorptive ability of biochar is dependent on the feedstock source and pyrolysis conditions such as temperature, duration, *etc.*^[15]. The physical and chemical properties that also play an important role in the adsorption process include specific surface area (SSA), pH , cation exchange capacity (CEC), surface heterogeneity, and chemical composition of the char^[16,17]. Often, significant variations in the sorptive capacity have been observed between different biochars, suggesting that the adsorption affinity measured is unique to the biochar and could be attributed to the feedstock used. Plant-based biomass (hardwood, softwood, rice husks, seeds, and nuts) is the most common feedstock source used for producing biochar^[18].

Studies have been conducted converting various waste products such as pine sawdust and sewage sludge, poultry litter, broiler litter, and dissolved flotation sludge from the chicken factory into biochars^[19]. Additionally, several studies have been conducted to determine the adsorption affinity of biochars to various organic contaminants^[20,21]. For herbicides, some authors used hardwood biochar, which could have

other economic value than being used as a feedstock for biochar^[22-24]. There is a lack of studies on the sorptive potential of biochar produced from other waste feedstocks such as pine sawdust, corncob, poultry litter, paunch grass (undigested grass from cow's stomach), and sewage sludge for 2,4-D or related compounds. Though pine sawdust is regarded as a biomass source of stationary energy, it has lignocellulosic properties, which could be valuable in developing adsorbents. Paunch grass from the abattoir and sewage sludge production in wastewater treatment plants has a high cost associated with their disposal.

In a study by Jin *et al.* (2016), who investigated the adsorption potential of different biochar amended soils for pesticides, biochar application to soils was as high as 5% to 20% of soil weight^[25]. This rate of biochar addition to soils seems to be unrealistic and unsustainable. For example, assuming a soil bulk density of 1,600 kg·m⁻³ and 0.1 m incorporation of biochar into topsoil, biochar application rate at 1% w/w basis would be 10-15 t·ha⁻¹, so biochar amendment at 5% to 20% is not realistically feasible simply because a huge amount of biochar would be required. Also, for their adsorption experiments, the authors chose very high initial pesticide concentrations. Since partition coefficients are concentration-dependent, the K_d values reported in this study cannot be extrapolated to environmental concentrations that are often in the ng·kg⁻¹ range. On the contrary, at 0.1% w/w basis, the pine needles pyrolyzed at 400 °C dominated the overall adsorption of naphthalene^[26]. There have been a few instances where the authors used various carbon-based adsorbents to remediate the 2,4-D, such as ZnCl₂ modified activated carbon^[27] and red mud-carbon composite^[28]. However, most of the adsorbents were chemically or physically modified to increase adsorption efficiency. Given the complexities associated with the large-scale production of adsorbents, no chemical modifications have been attempted to produce biochar for use in the study.

Therefore, the study investigated the key factors responsible for adsorption of pesticides onto biochar. Specifically, the study aims to: (1) determine the effects of feedstock on biochar production and on 2,4-D adsorption; and (2) elucidate the adsorption mechanisms of biochar amended soil for 2,4-D using a range of spectroscopic investigations. To achieve these objectives, we set out to explore the retention ability of two representative dairy farm soil amended with biochar produced from three diverse feedstock in the form of pine sawdust, paunch grass and sewage sludge using 2,4-D and employing laboratory batch adsorption studies. The central hypothesis was that biochar amended soils would enable the immobilization of 2,4-D and adsorption affinity for the compound would be dependent on types of biochar feedstock and the biochar's inherent properties.

MATERIALS AND METHODS

Soils

Two topsoils (0-5 cm), Matawhero loam (Latitude: 38° 38' 53" S; Longitude: 177° 56' 24" E) and Te Kowhai silt loam (latitude: 37° 43' 41" S; Longitude: 175° 9' 0" E), regions of Hawke's Bay and Hamilton, Waikato region of the North Island of New Zealand, were collected as representative samples of pasture growing. The samples were then dried in ambient conditions and sieved (< 2 mm). Properties of soils used in the study are listed in [Table 1](#). The details of the soil and methods used to determine the physicochemical properties were based on the study of Srivnivasan *et al.*^[19].

Biochar

This study used biochars prepared from paunch grass (PG), sewage sludge (SS) and pinus radiata sawdust (PSD) and were produced by slow pyrolysis (residence time of 40 min) at 700 °C at Lakeland Steel Limited, Rotorua, NZ. The physicochemical properties of biochar used in this study are summarised in [Table 2](#).

Table 1. Selected properties of soils used in the adsorption study (Srinivasan et al.^[19])

Soils	pH1:2 H ₂ O	OC (%)	CEC (cmol _c ·kg ⁻¹)	Sand %	Silt %	Clay %	SSA (m ² ·g ⁻¹)	Exchangeable cations (cmol _c ·kg ⁻¹)						Clay mineralogy %	
								Na	Mg	Al	K	Ca	Fe		Si ^a
Matawhero	6.1	2.1	15.4	11	62	27	60	2.5	38.7	110.4	4.8	43.6	16.6	25.8	q (5); f (3); 17 (i); mm (44); v (31)
Te Kowhai	6.7	5.0	22.3	9	54	37	32.5	0.6	4.0	205.2	0.7	8.7	27.0	38.8	vg (50); ha (35); k (10); cr (4); f (1)

Exchangeable cations were measured using ICPMS by strong acid extraction. aWt% of Si was obtained from energy dispersive x-ray analysis (EDX) of the soils. Cr: Cristobalite; f: feldspar; ha: halloysite; i: illite; mm: montmorillonite; q: quartz; v: vermiculite; vg: volcanic glass.

Table 2. Chemical properties of biochar (produced at 700 °C) used in adsorption studies

Biochar	pH	Total C	Total H	Total N	Total O	O/C	H/C	(O+N)/C	EC	Exchangeable cations [*]			Ash	SSA ^{**}	
	(water)	(%)	(%)	(%)	(%)				(mS·cm ⁻¹)	Ca	Mg	K	Na (%)	(m ² ·g ⁻¹)	
Pine sawdust	9.7	90.9	1.31	0.11	6.1	0.07	0.01	0.07	1.57	26.9	18.2	25.47	1.35	1.58	795
Paunch Grass	8.8	64.79	2.28	1.8	12.4	0.19	0.035	0.22	8.61	1.06	0.12	0.39	0.29	28.73	1.96
Sewage sludge	7.9	77.98	2.10	0.5	19.33	0.25	0.025	0.25	2.30	0.30	0.07	0.12	0.15	12.61	4.45

^{*}Measured by ICPMS; ^{**}measured by BET N₂ adsorption; SSA: specific surface area.

Biochar characterization

The biochars were ground to < 2 mm before soil amendment and pH of the biochars was measured using the standard pH meter (PHM62). In-House[®] conductance meter with a cell constant K = 0.69 cm⁻¹ was used to measure the electrical conductivity (EC) of biochar samples. Briefly, a 1:10 ratio of biochar and water was shaken for 24 h using a rotary drum shaker. To determine the pH and EC, the mixture of biochar and water was centrifuged, and the supernatant was analyzed. Using proximate analysis, the elemental composition (C, H, N, S, O) and ash content of biochars were sent for analysis using a CHN analyzer to Campbell Microanalytical Laboratory (Dunedin, New Zealand). The inductively coupled plasma mass spectrometry (ICPMS) was used to determine the exchangeable cations of biochars, while Brunauer, Emmett and Teller (BET) using N₂ adsorption isotherm method was used to measure the specific surface area (SSA) of biochars. The biochars were characterized by a range of properties, such as heavy metal content. The surface morphology was characterized using Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX), while the surface functional groups were determined using Fourier Transform Infrared Spectroscopy (FTIR). Additionally, Solid-state ¹³C Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron Spectroscopy (XPS) were given as important scope in this characterization. The details of these NMR and XPS characterizations of the biochar were described by Srinivasan et al.^[19].

Batch adsorption studies

The batch adsorption studies followed the experimental protocol developed earlier by Srinivasan *et al.*^[19]. Briefly, a soil sample of 2 g was added to 35 mL-glass centrifuge tubes. The samples of soil and biochar (mass ratio: 2:35) in the centrifuge tubes sealed by screw caps lined with Teflon were vortexed for 30 s to homogenize the mixture. Soils were amended with the different types of biochars (sieved to < 2 mm) at 1.0% of soil weight based on biochar application rates of 10 t·ha⁻¹, with assumed soil bulk density.

A 1000 mg·L⁻¹ stock solution of 2,4-D (98% purity, Sigma Aldrich) was prepared in methanol. To prevent the photodegradation of 2,4-D, the bottle of stock solution was covered with aluminum foil and stored at 4 °C. The stock solution was used to prepare 30 mL of 2,4-D with initial concentrations of 0.5, 1, 2.5, 5, 10, and 15 mg·L⁻¹ in 0.01 M CaCl₂ (Unilab; 94% purity) background electrolyte solution. The centrifuge tubes containing 2,4-D solution and biochar amended soils were wrapped in aluminium foil and rotated in an end-over-end shaker for 18 h in the dark. In the preliminary investigation, 18 h was sufficient to reach apparent equilibrium. All runs were done in duplicates.

Extraction and analysis

After equilibration, for all biochar amended soils (except PSD), centrifugation at centrifuged at 1,750 × g for 10 min was done. Then, the supernatant was filtered using 0.45 µm syringe filters. The filtered samples were placed in amber glass vials for HPLC analysis. For the PSD biochar amended soil with high adsorption capacity, the final aqueous concentrations for some samples were below the detection limit of the instrument. Thus, the solvent extraction method was developed. Pure solvents, namely methanol, acetonitrile (≥ 99.8% purity), deionized water (HPLC grade), hexane, ethyl acetate (≥ 99.8% purity) and dichloromethane (DCM), were used as extraction solvents. The use of ethyl acetate instead of other solvents resulted in higher recoveries > 92% for the chemical. Twenty millilitres of supernatant was extracted with 10 mL ethyl acetate. Then, 1 mL of the extracted ethyl acetate was placed into an HPLC vial and evaporated for dryness under N₂ gas. The remaining contents were reconstituted in 0.5 mL methanol and were immediately analyzed using HPLC.

Analysis of the adsorption affinity of 2,4-D herbicide to biochar amended soils was performed on a Dionex HPLC system comprising an automated sampler, a pump and a UV detector (240 nm wavelength). Chromatography was performed on a 150mm × 4.6 mm Luna (5 µm packing) RP-C18 column. The mobile phase consisted of acetonitrile and water at a ratio of 60:40. A flow rate of 0.8 mL/min and an injection volume of 20 µL were used for 2,4-D analysis with a retention time of 4.5 min.

All samples were analyzed at a wavelength of 240 nm. Using a signal-to-noise ratio of 3 to 1, the limits of detection (LOD) were determined. The LOD and limits of quantification (LOQ) for 2,4-D were 0.05 µg·mL⁻¹ and 0.025 µg·mL⁻¹, respectively. Calibration standards were developed simultaneously with experimental runs, and an R² value of 0.99 was obtained. Blank matrix runs and mobile phase runs were regularly conducted for quality assurance. Soil blank runs carried out indicated no interference from co-eluting peaks, which indicated that the extraction steps performed in this study were sufficiently robust.

The following equation was used to determine the sorbed amount C_s [mg·kg⁻¹]:

$$C_s = (C_i - C_w) \frac{V}{M_s} \quad (1)$$

where C_i ($\text{mg}\cdot\text{L}^{-1}$) is the initial solute concentration, C_w ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of solute at equilibrium, V (L) is the volume of solution, and M_s (kg) is the mass of soil, respectively.

Adsorption modelling

Adsorption of organic compounds in soil organic matter (SOM) rich soils generally follows the typical Freundlich isotherm^[29]. This is also based on the assumption that Freundlich data assumes cations and anions are adsorbed onto the surface simultaneously. The model is further transformed by assuming $N = 1$ and termed as linear Freundlich model, and this is based on the assumption that adsorption occurs exclusively to the organic matter component of the soil^[29].

Adsorption isotherms were modelled using the Freundlich model as below:

$$C_S = K_F C_w^N \quad (2)$$

$$\text{Log } C_S = \text{Log } K_F + N \text{Log } C_w \quad (3)$$

where C_s ($\text{mg}\cdot\text{kg}^{-1}$) is the sorbed concentration equilibrium; C_w ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of aqueous phase; N is the empirical constant related to the adsorption intensity to the heterogeneity of the material; K_f ($\text{mg}^{1-N}\cdot\text{L}^N\cdot\text{kg}^{-1}$) is the Freundlich adsorption constant.

The amount of herbicide sorbed per unit of soil organic carbon, K_{oc} , was calculated using the equation $K_{oc} = K_f/OC\%$, where OC is the organic carbon content of the soil and K_{oc} is defined as the soil organic carbon normalized partition coefficient ($\text{L}\cdot\text{kg}^{-1}$). To compare adsorption across different treatments, the concentration-dependent effective distribution coefficient ($K_d^{eff} = K_f C_w^{N-1}$) was calculated where a concentration of $0.5 \text{ mg}\cdot\text{L}^{-1}$ was used. Similarly, the K_{oc} for each biochar amended soil was calculated for 2,4-D at $0.5 \text{ mg}\cdot\text{L}^{-1}$ using the non-linear equation $K_{oc} = K_f C_w^{N-1}/f_{oc}$, where f_{oc} is the fraction of soil organic carbon.

RESULTS AND DISCUSSION

Biochar and soil characterization

The chemical properties of biochars including elemental analysis, pH, surface area, and exchangeable ions, were summarized in [Table 1](#), while soil's physical and chemical properties were presented in [Table 2](#). The PSD biochar was found to be having the highest carbon percentage of 90.9%, while PG biochar has the lowest of 64.79% fixed carbon. Moreover, PSD has the lowest H/C ratio (0.01) among the biochars, which indicates it is highly aromatized. On the contrary, PG has the highest H/C ratio (0.035), which indicates it has the lowest degree of carbonization and aromaticity. PSD biochar had the highest SSA value of $795 \text{ m}^2\cdot\text{g}^{-1}$ as compared with other biochars. The exchangeable cation capacity for the biochars in terms of Ca^{2+} , Mg^{2+} , K^+ and Na^+ were presented in [Table 2](#). The PSD biochar exhibited the highest exchangeable cation capacity, followed by PG and SS biochars. The trend in the increasing cation exchange capacity can be indicative of the number of exchangeable ions between adsorbent and adsorbate, which is further discussed in the mechanism section. The metal concentrations present in the biochar were analyzed by ICPMS and presented in [Supplementary Table 1](#) along with threshold limits for soil amendment given by the International Biochar Initiative^[30]. The results indicate that all the metal concentrations (Hg, Cu, Pb, Co, Cu, As) were below the range except for Zn^{2+} concentrations which were above the threshold limits

(416 mg·kg⁻¹).

Surface morphology by SEM-EDX

SEM micrographs presented in [Figure 1](#) show that the PSD, PG and SS biochars maintain the surface morphology of their biomass precursor. The results were expected as the biochar structure is a function of feedstock material. The morphology of the PSD from the SEM shows that the material has a smooth, glassy, elongated appearance and a non-porous surface. At the same time, porous structures were evident for the other biochars from the SEM imaging. The EDX point scans were analyzed; compositions are also presented in [Figure 1](#). The EDX results were consistent with the elemental analysis findings, with the highest carbon of 93.5% found in PSD.

Surface functional groups by FTIR analysis

The surface functional groups present on the biochars were investigated by FTIR analysis, and corresponding spectrum as a function of wavenumber are presented in [Figure 2](#). Overall, very similar functional groups were present on all biochars. A plausible explanation for this could be due to the production of the biochars at the same temperature. The results also indicate that the biochars were highly aromatized. Various functional groups of the biochar can affect a number of processes during the biochar-complex media (such as soil) interaction. The FTIR spectra corresponding to 3,440 cm⁻¹ could be ascribed to the vibration of O–H stretching. The peaks at 2,920 and 2,850 cm⁻¹ corresponded to symmetric and asymmetric C–H stretching vibrations. The peaks at 1,730 cm⁻¹ are attributed to the stretching vibration of the C=O bond, while the peaks at 1,620 cm⁻¹ can be correlated with C=O and C=C stretching vibrations from ketones and aldehydes groups^[31]. Overall, oxygen-containing functional groups were a major part and could play a role in the adsorption process.

X-ray Photoelectron Spectroscopy analysis

[Table 3](#) presents the C1s and O1s bonding state and its relative percentage on the surface of the biochar, while [Figure 3](#) shows the peak deconvolution for the C1s and O1s region scan. Additionally, chemical composition was found and presented in

[Table 2](#). The results were consistent with CHN and EDX analyses. At higher resolution, the XPS spectrum of the C1s peaks shows the main peak at 284.8 eV. This could be attributed to the aromatic carbon (C–C), while the presence of other peaks could be associated with oxygen-containing functional groups, namely carbonyl (C–O at 285.7 eV) and carboxylic and/or ester (O–C=O in at 289.2 eV). For all biochars, O1s region scan was deconvoluted into a single peak with a binding energy of 533.4 eV, which is associated with O=C–O.

Nuclear magnetic resonance analysis

The NMR spectra for the biochar are shown in [Figure 4](#), and the corresponding properties are presented in [Table 4](#). The spectra of all biochars were dominated by the aromatic C resonance centred at ~130 ppm, which is a characteristic of aromatic carbon. The shoulder peak in the 165–185 ppm range may be contributed by carboxylic acid (COOH) and esters (COOR)^[32]. The signals at ~55 ppm can be attributed to carbohydrates^[33], while the peaks at ~15 and ~35 ppm could be attributed to alkyl. The PSD, PG and SS biochars were predominantly aromatic, with the presence of alkyl C at a small amount. The negative chemical shift ($\Delta\delta$), which denotes the degree of aromatic condensations of the biochars, is shown in [Table 4](#). Although all biochars were produced at the same temperature, PSD biochar (-9.1) had the highest degree of aromatic condensation, followed by SS and PG. This trend is consistent with the amount of carbon present in the biochar found in the elemental analysis. The PSD biochar has low CP observability

Table 3. C1s and O1s bonding state and its relative atomic percentage on biochar surfaces

Binding energy (eV)	Structure	PSD	PG	SS
284.8	C–C	62.4	27.2	78.6
~ 286.0	C–O	37.6	68.7	21.4
~ 288.0	COOH	-	-	-
289.2	C–O	-	4.1	-
~ 532.5-533	C=O	100	100	100

PG: Paunch grass; PSD: pine sawdust; SS: sewage sludge.

Table 4. NMR observabilities for biochars determined from spin-counting and aromatic condensation ($\Delta\delta$)

Biochar	C(obs) (%)	$\delta^{13}\text{C}$ -benzene-CP (ppm)	$\Delta\delta$ -CP (ppm)
PSD	3.0	119.6	-9.1
PG	18.2	125.8	-2.9
SS	7.8	124.9	-3.8

PG: Paunch grass; PSD: pine sawdust; SS: sewage sludge.

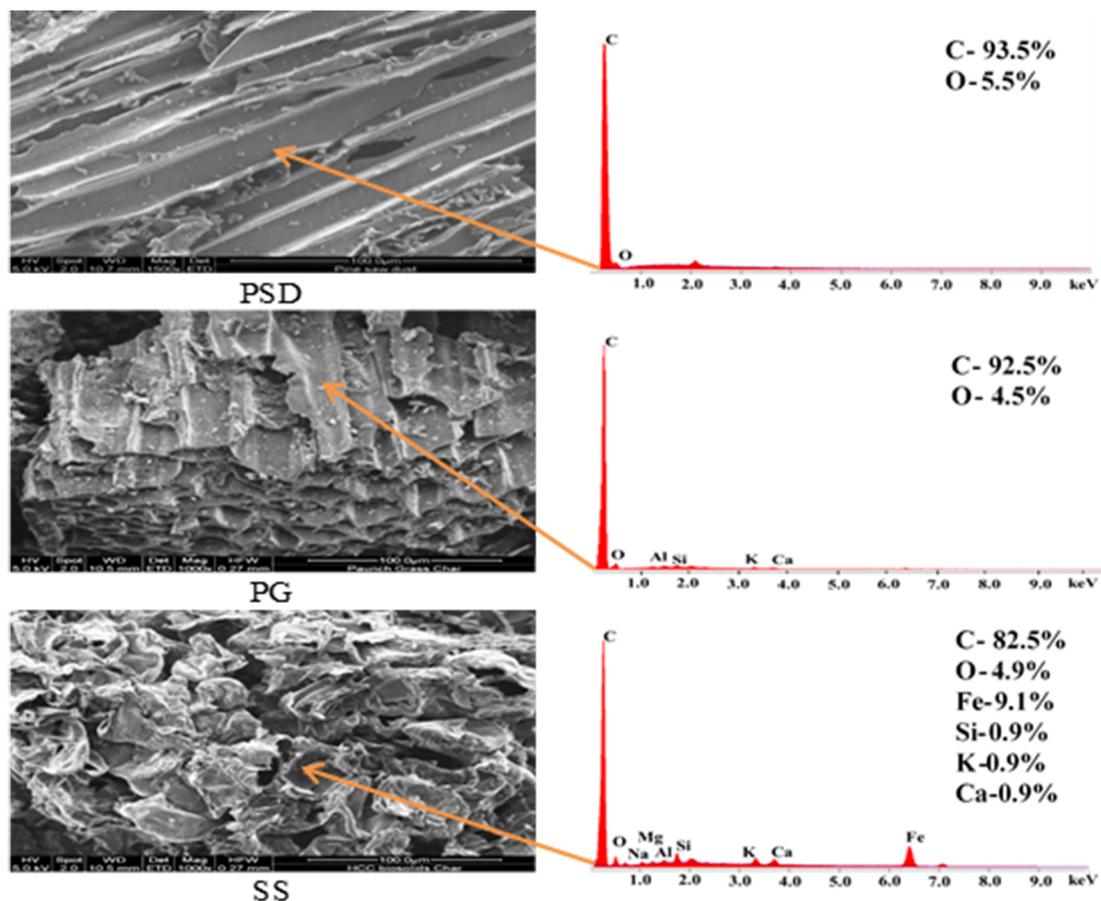


Figure 1. SEM-EDX of biochars used in this study. SEM-EDX: Scanning electron microscope and energy dispersive X-ray spectroscopy.

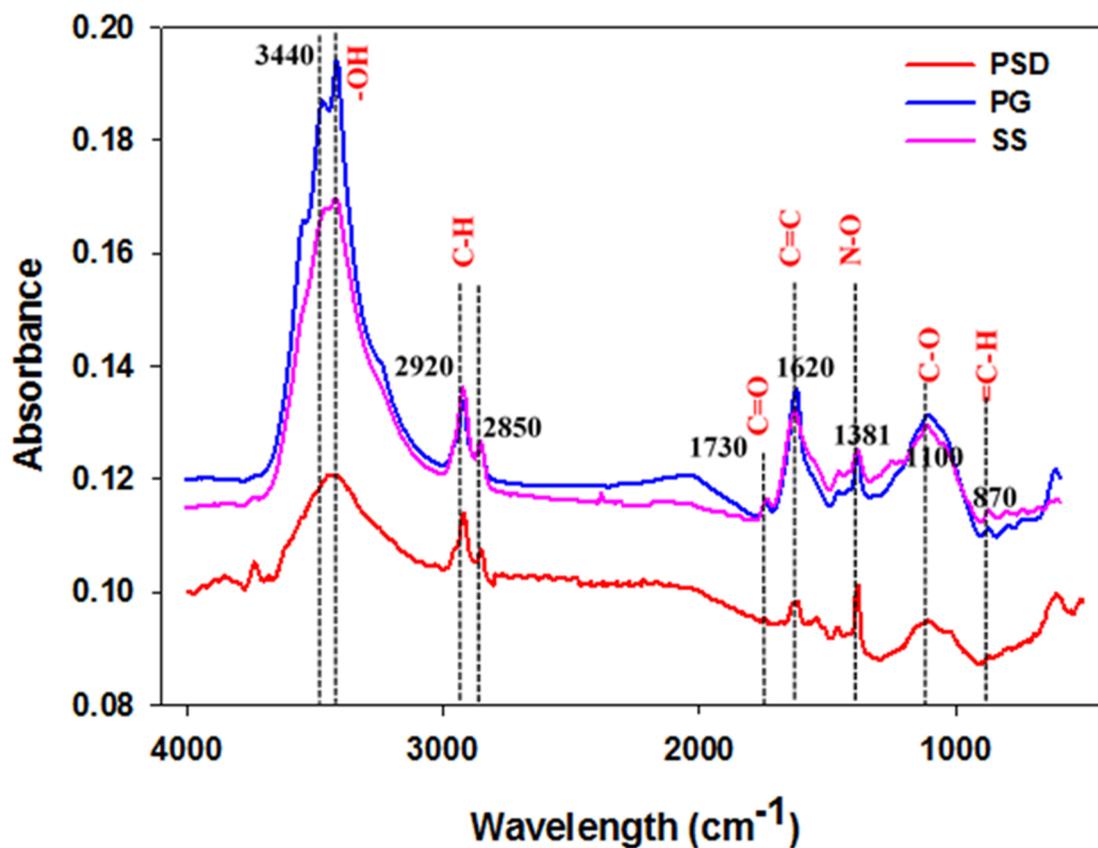


Figure 2. FTIR analysis of biochars. FTIR: Fourier transform infrared spectroscopy.

[Table 4], and this is evident in the poor spectrum of PSD with an evident poor signal-to-noise ratio [Figure 4].

Adsorption isotherms

Adsorption isotherms (linear adsorption model and Freundlich model) for 2,4-D in the different biochar amended soils (Te Kowhai and Matawhero) are shown in Figure 5. The Freundlich isotherm adsorption parameters, K_d and K_d^{eff} were obtained and presented in Table 5. Higher linear determination coefficients (R^2) values (0.90-0.99) suggested that Freundlich isotherms showed a better fitting to adsorption data of all adsorbents compared to linear isotherm indicating 2,4-D adsorption occurs on a heterogeneous surface with the multilayered adsorption^[34].

Overall, PSD biochar amended soils exhibited higher adsorption of 2,4-D than control and other biochar amended soils. There is minimal effect on the adsorption capacity of the soils amended with SS and PG. The K_d values for PSD amended soils were 530 and 315 L·kg⁻¹, which is significantly higher than the remaining soils, with the second highest of 1.59 L·kg⁻¹ for PG biochar amended Matawhero soils. The adsorption capacity, as represented by Freundlich adsorption coefficient (K_F), followed an order: PSD > PG > SS for the Te Kowhai soils and PSD > SS > PG for the Matawhero soils. For Te Kowhai soils, the addition of biochar decreased the linearity based on N values that range from 0.52 to 0.83. In contrast, its addition to Matawhero soil increased its linearity with N values ranging from 0.37 to 1.06 [Table 5]. The K_d^{eff} values for

Table 5. The isotherm parameters for 2, 4-D on Matawhero and Te Kowhai Soil amended with biochars

Treatment		K_d $L \cdot kg^{-1}$	R^2	K_f $mg^1 N \cdot LN \cdot kg^{-1}$	N	R^2	K_d,eff $L \cdot kg^{-1}$	$Log K_{oc}$
Te Kowhai	Control	1.27	0.94	2.06	0.83	0.98	2.32	1.67
	PSD	530.35	0.82	566.11	0.83	0.95	638.23	4.11
	PG	1.13	0.67	3.65	0.52	0.98	5.10	2.01
	SS	1.40	0.85	2.75	0.74	0.98	3.28	1.82
Matawhero	Control	0.44	0.44	1.93	0.37	0.99	2.98	2.15
	PSD	314.87	0.61	360.58	0.61	0.95	474.01	4.35
	PG	1.59	0.98	1.70	0.94	0.98	1.77	1.93
	SS	1.46	0.95	2.06	1.06	0.90	2.43	2.06

PG: Paunch grass; PSD: pine sawdust; SS: sewage sludge.

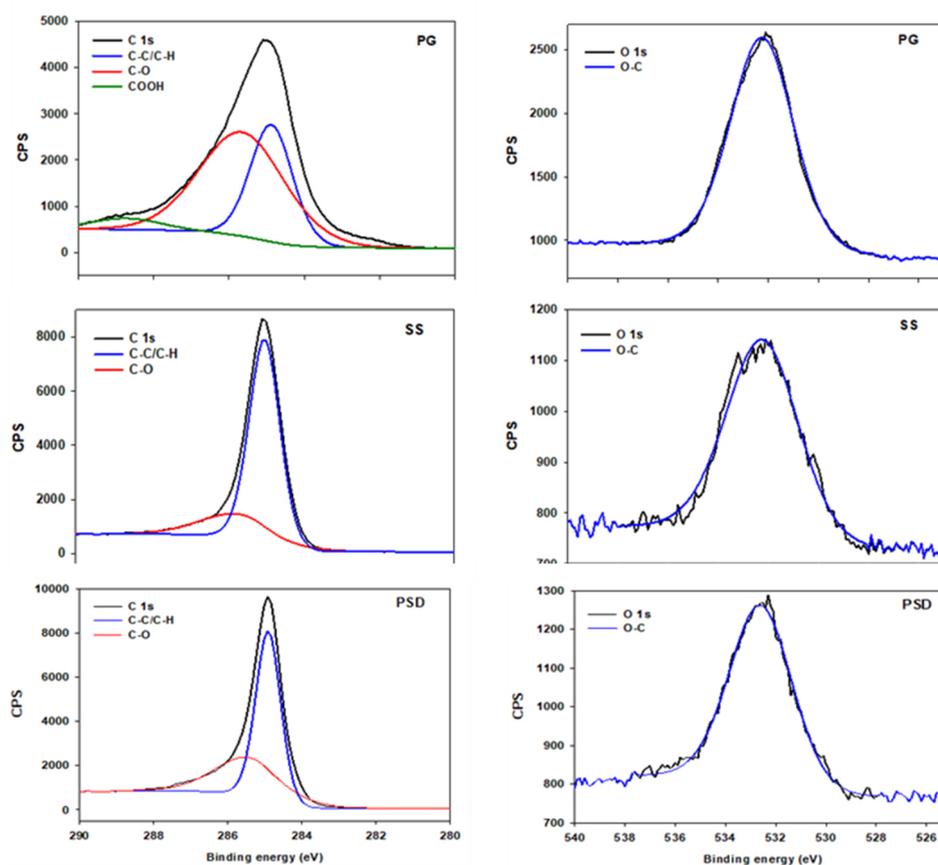


Figure 3. XPS analysis of biochars. XPS: X-ray photoelectron spectroscopy.

2,4-D at the lowest equilibrium concentration ($C_w = 0.5 \text{ mg} \cdot L^{-1}$) ranged from 2.32 to 638 $L \cdot kg^{-1}$ in biochar amended soils. PSD-amended soils showed 20-30 times greater adsorption potential than the control soil.

Comparative data showing the various adsorption parameters such as K_d , K_f and dominant adsorption mechanisms for removal of 2,4-D are shown in Table 6 under carbon-based and soil-based adsorbents. The K_d and K_f values for the PSD amended with soil were higher than most of the recent literature-reported data. The high K_d value in our case for PSD biochar amended soil could be attributed to its extremely high SSA of

Table 6. Comparative adsorption parameters for the carbon-based and soil sorbents from the recent literature

Author	Adsorbent	Max Capacity	K_d	K_f	Mechanism
Zhu et al., 2018 ^[35]	Amino activated corn stalk Biochar	22.84 mg·g ⁻¹	-	0.919	π - π interaction, chemisorption and hydrogen bonding
Essandoh et al., 2017 ^[36]	Switchgrass biochar	134 mg·g ⁻¹	-	2.675 mg·g ⁻¹	van der Waals, dipole-dipole, and π - π interactions and hydrogen bonding
Doczekalska et al., 2018 ^[37]	Flax, hemp shives and miscanthus based activates carbon	2.682 m.mol·g ⁻¹	-	2.41	Dipole-dipole, H-bonding, covalent bonding
Binh & Nguyen, 2020 ^[38]	Corn cob biochar	37.40 mg·g ⁻¹	-	13.8 (mg·g ⁻¹)(mg·L ⁻¹) ⁻¹	Pore-filling, electrostatic, H- bonding, hydrophobic bonding, and π - π EDA interactions
Li et al., 2018 ^[31]	Nitric Acid Modified Activated Carbon Fiber	555 mg·g ⁻¹	-	235.017 (mg·g ⁻¹)(mg·L ⁻¹) ⁻¹	Surface/Physical adsorption
Alikhani et al., 2021 ^[8]	TiO ₂ /BiOBr/Bi ₂ S ₃ nanostructure stabilized on the activated carbon	87.61 mg·g ⁻¹	-	23.3 L/g	-
Salomón et al., 2021 ^[39]	Activated carbon derived from Queen palm fruit	367 mg·g ⁻¹	-		Hydrogen bond, π - π , or electrostatic interactions
Soil systems					
Meftaul et al., 2020 ^[34]	Loam, sandy loam, silt loam, sand, loamy sand, and clay- Australian soils	92 mg·kg ⁻¹	4.68 L·Kg ⁻¹		Surface sorption and partition
Fernandez et al., 2021 ^[40]	Soil and wheat stubble mixture	155.7 mg·kg ⁻¹	-	0.64 (mg·kg ⁻¹)(L·mg ⁻¹) ⁻¹	Electrostatic interactions and non-polar interactions
Cotillas et al., 2018 ^[41]	Clay soil washing and adsorption onto activated carbon	216 mg·g ⁻¹	-	9.01	-
Buerge et al., 2020 ^[42]	Agriculture/railway track		-	K_f -0.83 mL·g ⁻¹	Sorption to organic matter
Ololade et al., 2015 ^[43]	soil without soil organic matter	333 mg·g ⁻¹	Oxic-1.40 Anoxic-1L·kg ⁻¹	1.148	Electrostatic interaction
Ozbay et al., 2018 ^[44]	Calcareous soil	-	0.66 L·kg ⁻¹	2.37	Soil organic matter
Mon et al., 2009 ^[45]	Volcanic ash soil	-	41.1 L·kg ⁻¹	52.5	Soil organic matter
Werner et al., 2013 ^[46]	Below mentioned soils/sorbents			1.44 L·kg ⁻¹	
This study	PSD amended soils	224.12 mg·kg ⁻¹	530.3 L·kg ⁻¹	566 (mg/Kg)/(mg·L)	Hydrogen bond, π - π EDA, and pore intrusion

795 m²·g⁻¹ and aromatic carbon structure. The high log K_{oc} values of soil with PSD also further demonstrate the ability of PSD biochar to immobilize the 2,4-D herbicide due to the strong affinity of 2,4-D to PSD biochar.

Plausible adsorption mechanisms

Adsorption of 2, 4-D onto soil

Between the two soil controls, the adsorption of 2,4-D was higher onto Te Kowhai soil ($K_f = 2.06$) than Matawhero soils ($K_f = 1.93$). The Te Kowhai and Matwhero soils possessed organic carbon content of 5% and 2%, respectively, and have been earlier attributed to the high adsorption of 2,4-D onto soils^[43]. Additionally, electrostatic attraction interaction of positive Fe and Al ions present in the soil with the 2,4-D anions can likely enhance the adsorption of 2,4-D (Ololade et al., 2015)^[43]. The high clay percentage in the Te Kowhai soils could also be an explanation for the higher adsorption than the Matawhero soils. Overall, surface hydroxyls derived from metal hydroxides and metal-SOM complexes and clay mineralogy were postulated to be the plausible adsorption mechanisms^[47].

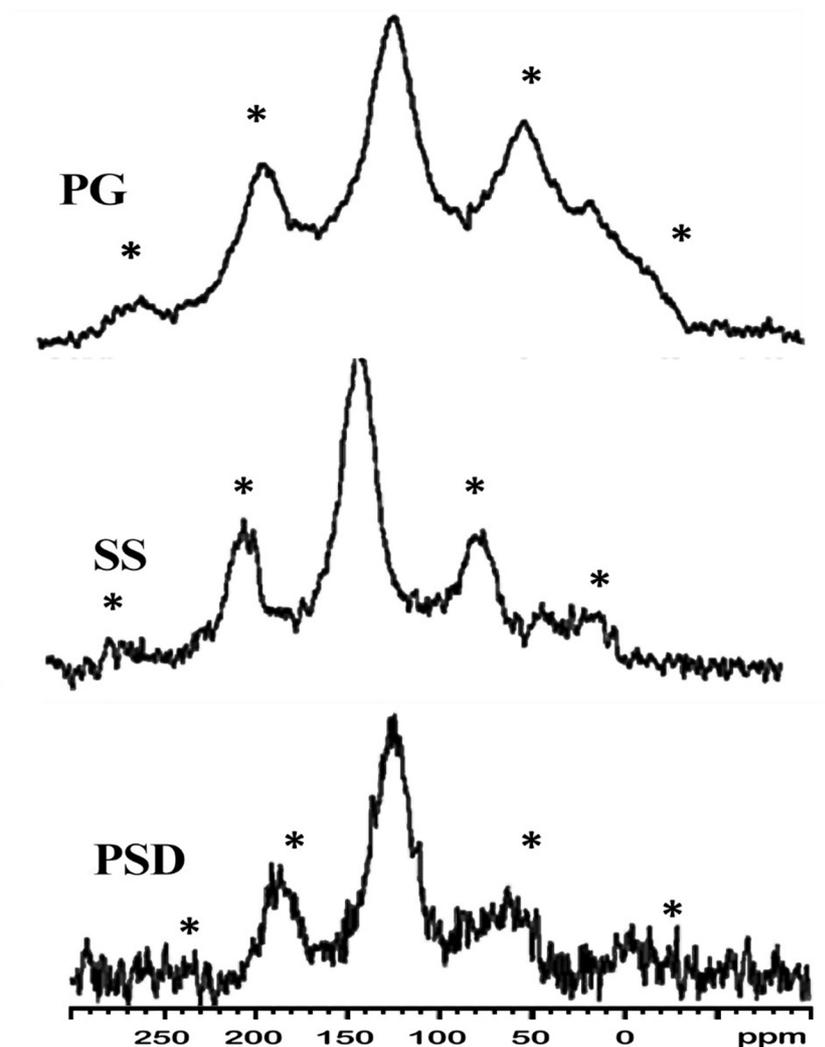


Figure 4. The NMR spectra of paunch grass, sewage sludge and pine sawdust biochar. NMR: Nuclear magnetic resonance.

Adsorption of 2,4-D onto biochar amended soils

The plausible adsorption mechanism of 2,4-D onto biochar amended soils is represented in [Figure 6](#), and it can be broadly explained by three different mechanisms: (i) pore intrusion/filling; (ii) hydrogen bonding; and (iii) π - π EDA interactions. The size of 2,4-D molecular structure is around $1.54 \text{ nm} \times 0.56 \text{ nm} \times 0.22 \text{ nm}$, and SSA for the biochars used as summarized in [Table 2](#) reveals some interesting observations. By comparing the adsorption of 2,4-D onto different adsorbents, it can be surmised that SSA is directly related to the removal of 2,4-D. For instance, PSD has the highest SSA of $795 \text{ m}^2 \cdot \text{g}^{-1}$ and the highest K_f values of 530 and 315 for the two soils. However, the remaining biochar's SSA values were found to be in the range of approximately 2.0 - $8.0 \text{ m}^2 \cdot \text{g}^{-1}$ and showed a similar level of adsorption with K_f values of 1.7-3.65. In addition, the biochar particles' pore size was in the range of micro- and meso-size [[Figure 1](#)], which is greater than the nano size of the 2,4-D, implying the possibility of pore intrusion mechanisms.

Hydrogen bonding as the adsorption mechanism can be explained in two ways: (i) interaction of H^+ ions in the 2,4-D (alcoholic group) with oxygen ions from the functional groups such as hydroxyl, phenolic, present on the biochar; (ii) oxygen ions from the ketonic group or hydroxyl group present in the biochar to the

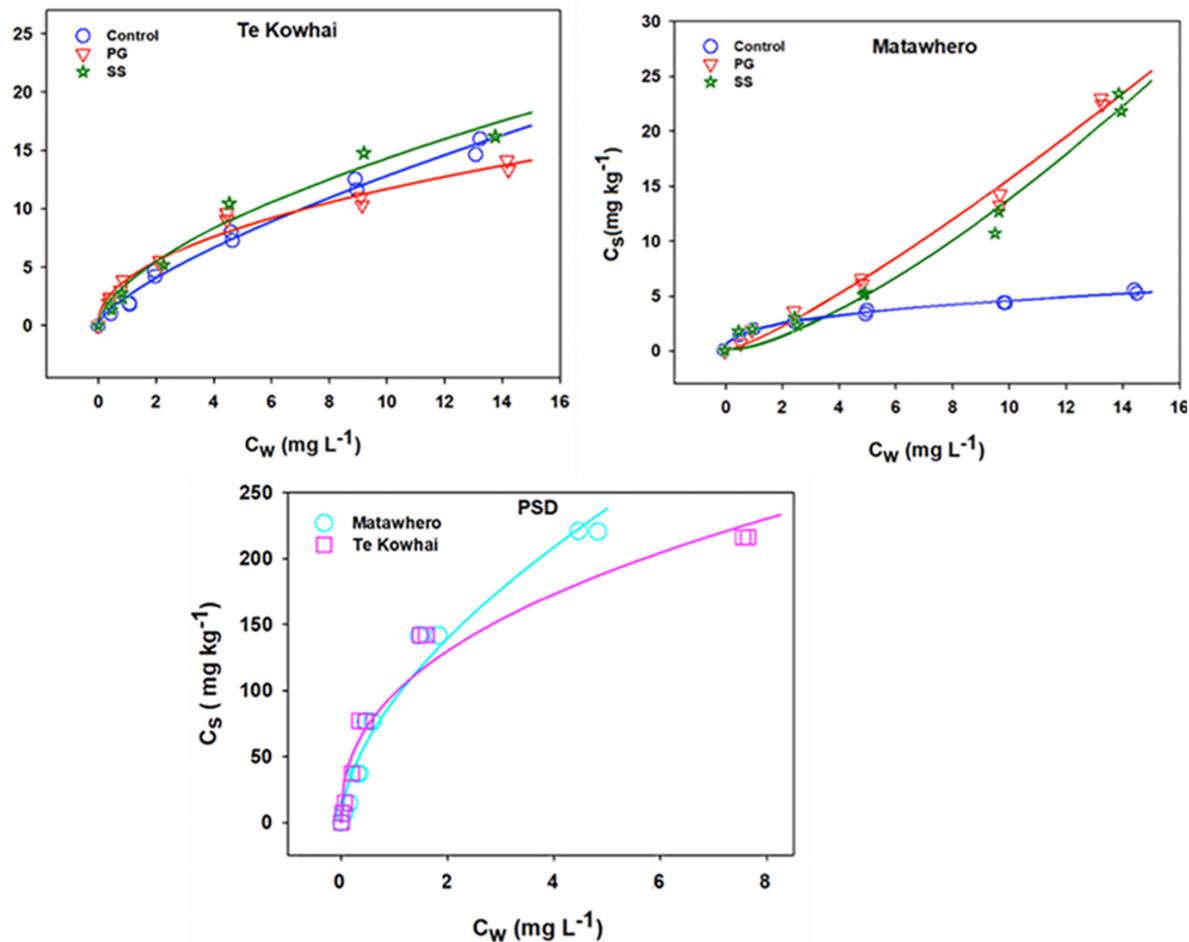


Figure 5. Freundlich isotherm plots for control soil and biochar amended soils. The measured data were represented by symbols, while the model fits were in solid lines.

hydrogen ion from the 2,4-D. Based on the FTIR and NMR analysis, the biochar has functional groups: OH- stretching, C=O stretching, COOR, and carboxylic (-COOH). The presence of hydrogen and oxygen ions in the functional groups and 2,4-D can interact to form potential hydrogen bonds and result in the adsorption of 2,4-D onto biochar. An example of such possible hydrogen bonding is schematized in [Figure 6A](#), where the hydroxylic group is present in the biochar, forming potential hydrogen bonding with 2,4-D.

The third possible adsorption mechanism presented in [Figure 6B](#) could be associated with the π electrons in the aromatic rings of 2,4-D and biochar^[38]. The biochar is highly aromatic (confirmed by NMR and elemental analysis) and contains functional groups such as -OH, C=C, C-H and C=O. The O-H group acts as an electron donor and creates a π - in the cyclic ring of biochar. Then, the halogen (Cl) group in the 2,4-D can withdraw electrons, thus forming π^+ density in the nucleus of 2,4-D^[38]. This resulting interaction could potentially enable 2,4-D adsorption onto biochar. On comparing different biochars, given that the PSD has a high carbon percentage (90.9%) and H/C = 0.01, it is conceivable that it has a high degree of aromaticity and indeed demonstrated a higher adsorption behaviour than the other biochar due to potential dominating effect of π - π EDA mechanisms.

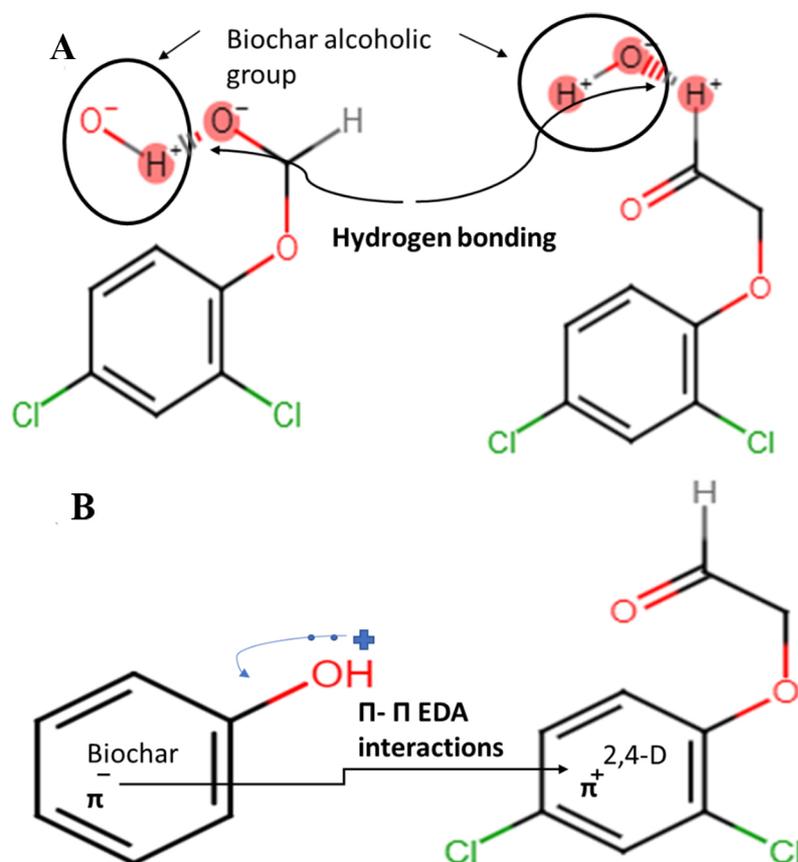


Figure 6. Plausible adsorption mechanisms between PSD biochar and 2,4-D: (A) hydrogen bonding; (B) π - π EDA interactions. PSD: pine sawdust.

ENVIRONMENTAL SIGNIFICANCE

We investigated the utilization of waste-derived biochars (PSD, PG and SS) as an effective adsorbent for a widely used herbicide, 2,4-D, also termed as an emerging contaminant in soil systems. The findings from the study demonstrated that waste-derived biochars have the potential not only to retain and/or reduce the mobility of the compound that can potentially contaminate the surface water and groundwater, but could further decrease the ecological and human health risks. Due to the use of waste as feedstocks to produce biochar, there is no commercial value and competition with other potential uses of these feedstocks, thus demonstrating the potential of minimization or conversion of waste to adsorbent or as soil enhancer that can be beneficial for agricultural sectors. Therefore, the two main environmental significance of this study can be: (i) the retention of herbicide to reduce its mobility and contamination of aquatic environment; and (ii) waste minimization or management of such organic waste stream.

CONCLUSIONS

The following conclusions are drawn from the study.

Amending soil with biochar may increase adsorption capacity for 2,4-D; however, it is dependent on the characteristics of the biochar. The adsorption affinity for biochar amended soils followed an order: PSD >> PG > SS.

PSD biochar ammended soil resulted in increased 2,4-D uptake, suggesting that the mobility potential for the herbicide was decreased. Thus, this could potentially lead to reduction of toxicity and less availability to soil organisms such as microbes, plants and invertebrates. However, caution is required as high adsorption could also lead non-availability of nutrients for the plants.

PSD biochar exhibited a very high adsorption affinity for 2,4 D compared to other biochars due to its significantly higher degree of aromaticity and SSA.

The adsorption affinity of 2,4-D for biochar was not affected by surface functional groups.

Based on the findings, biochars produced from biomass of lignocellulosic origin could potentially be an excellent adsorbent to remediate soils contaminated with similar organic compounds.

DECLARATIONS

Authors' contributions

Review, editing, revision of the manuscript: Reguyal F

Review, editing, plotting, revision of the manuscript: Praneeth S

Conceptualisation, writing original draft, data analysis, modelling, revision, correspondence: Sarmah AK

Availability of data and materials

Data and materials used in this manuscript are confidential.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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