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Molecular-Level Insights into the Sorption Mechanisms of Pentachlorophenol on Biochar-Amended Soil Organic Matter

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Abstract: The adsorption of persistent organic pollutants such as pentachlorophenol (PCP) on soil matrices plays a crucial role in determining their environmental persistence and ecological risk. This study provides molecular-level insights into the sorption mechanisms of pentachlorophenol on biochar-amended soil organic matter, combining experimental and computational approaches to unravel the fundamental interactions that govern pollutant immobilization. The research employed Fourier Transform Infrared (FTIR) and solid-state Nuclear Magnetic Resonance (NMR) spectroscopy to characterize functional group interactions, complemented by Density Functional Theory (DFT) modeling to elucidate binding configurations at the molecular scale. Results revealed that biochar amendment significantly enhanced PCP sorption capacity compared to unamended soils, primarily due to the introduction of π–π electron donor–acceptor interactions, hydrogen bonding, and hydrophobic partitioning between aromatic moieties of biochar and the chlorinated phenol molecule. Spectroscopic analyses confirmed the formation of stable surface complexes involving carboxyl, hydroxyl, and aromatic carbon sites. DFT simulations further identified energetically favorable adsorption geometries, with binding energies consistent with experimental thermodynamic trends. These findings indicate that biochar modifies soil organic matter structure to create heterogeneous, high-affinity sorption domains that reduce PCP bioavailability and mobility. The integration of spectroscopic validation with computational modeling provides a mechanistic understanding of how biochar mediates molecular interactions, advancing knowledge in the field of sustainable soil remediation. The study establishes a foundation for designing biochar materials with tailored surface chemistries for the efficient immobilization of hydrophobic organic contaminants. Ultimately, these insights contribute to the development of predictive sorption models and climate-resilient remediation strategies for persistent pollutants in terrestrial ecosystems.

Keywords: Pentachlorophenol; Biochar-amended soils; Sorption mechanisms; FTIR and NMR spectroscopy; Density Functional Theory (DFT); Soil remediation.

1. INTRODUCTION

1.1 Background on Persistent Organic Pollutants

Persistent organic pollutants (POPs) represent a critical class of environmental contaminants characterized by high chemical stability, bioaccumulation potential, and long-range atmospheric transport [1]. Among these, chlorinated phenols such as pentachlorophenol (PCP) have attracted sustained attention due to their recalcitrant nature and toxicological significance in both aquatic and terrestrial ecosystems [2]. Historically, PCP was widely used as a wood preservative, biocide, and pesticide additive owing to its strong antimicrobial properties and low biodegradability [3]. However, decades of extensive use led to its pervasive distribution across agricultural landscapes and industrial vicinities. Once released into the environment, PCP exhibits strong partitioning into soil organic phases, resulting in prolonged persistence and limited microbial degradation [4]. Its toxic metabolites have been associated with endocrine disruption and mutagenic effects in soil biota, posing ecological and health hazards [5]. In agricultural soils, PCP accumulation impairs microbial nutrient cycling and plant root function, leading to diminished soil fertility [3]. Consequently, understanding the sorption and desorption behavior of PCP in soil environments has become an essential aspect of environmental chemistry and risk assessment [6]. The molecular-level mechanisms governing its soil interaction, particularly under variable physicochemical conditions, remain a key focus for sustainable remediation strategies [4].

1.2 Soil Organic Matter as a Sorption Matrix

Soil organic matter (SOM) serves as the principal sorptive phase controlling the environmental fate of hydrophobic organic contaminants such as PCP [7]. Composed of humic and fulvic acids, lignin derivatives, and polysaccharide residues, SOM exhibits a heterogeneous molecular structure that facilitates both hydrophobic partitioning and specific binding interactions [8]. The aromatic and aliphatic carbon domains within SOM provide sorption sites capable of π–π electron donor–acceptor interactions and hydrogen bonding with chlorophenolic compounds [9]. Furthermore, the degree of SOM aromaticity, molecular polarity, and surface functionalization significantly influence the kinetics and reversibility of contaminant sorption [3]. The interplay between SOM composition and temperature alters adsorption energetics, determining whether sorption is governed by chemisorption or physical partitioning [5]. High-organic soils often display nonlinear sorption isotherms, reflecting site heterogeneity and competitive interactions among organic molecules [2]. These complex sorptive properties make SOM-rich soils both repositories and regulators of pollutant transport in the environment [8]. By modulating bioavailability and desorption rates, SOM effectively dictates the persistence and mobility of chlorinated organics in terrestrial systems [4]. Understanding SOM–pollutant interactions thus provides a mechanistic foundation for designing soil remediation strategies and improving contaminant fate models under variable environmental conditions [7].

1.3 Biochar as a Soil Amendment for Contaminant Immobilization

Biochar, a carbonaceous byproduct of biomass pyrolysis under limited oxygen, has emerged as an effective soil amendment for mitigating organic and inorganic contamination [1]. Its porous structure, high surface area, and abundance of oxygen-containing functional groups enable strong adsorption of hydrophobic organic pollutants such as PCP [6]. The physicochemical properties of biochar including surface charge, aromaticity, and micro-porosity vary with feedstock type and pyrolysis temperature, influencing its sorptive behavior [8]. When integrated into organic-rich soils, biochar interacts synergistically with SOM to form composite sorbents possessing enhanced binding capacity and stability [3]. These hybrid matrices exhibit combined mechanisms of partitioning, π–π stacking, and electrostatic attraction, leading to reduced pollutant mobility and bioavailability [4]. Additionally, biochar can immobilize PCP through irreversible adsorption on graphitic surfaces and through the formation of hydrogen-bonded complexes at carboxylic and hydroxyl sites [7]. Such modifications also contribute to soil fertility improvement, moisture retention, and microbial habitat stabilization [9]. The integration of biochar with SOM thus represents a sustainable approach to contaminant sequestration, capable of mitigating PCP leaching and environmental exposure [2]. Collectively, these characteristics position biochar-amended soils as molecularly complex sorbents. This dual organic matrix justifies detailed mechanistic investigations into the molecular interactions driving PCP immobilization and temperature-dependent sorption behavior [5].

2. THEORETICAL FRAMEWORK AND CONCEPTUAL BASIS

2.1 Sorption Mechanisms of Hydrophobic Organic Compounds

The sorption of hydrophobic organic compounds (HOCs) such as pentachlorophenol (PCP) in soils and sedimentary environments is governed by a combination of partitioning, surface adsorption, and molecular interactions with organic matter [8]. The partitioning process primarily occurs within amorphous soil organic matter (SOM), where nonpolar solutes distribute between aqueous and organic phases based on hydrophobic affinity [9]. This phenomenon is typically quantified using organic carbon–normalized partition coefficients, which reflect the compound's lipophilicity and degree of halogen substitution [10].

Surface adsorption, on the other hand, is facilitated by the presence of mineral and organic surface sites capable of forming specific interactions such as hydrogen bonding, electrostatic attraction, and van der Waals forces [11]. For PCP, the aromatic ring and hydroxyl functional group enable π–π electron donor–acceptor interactions with aromatic domains in humic substances, contributing to strong yet reversible sorption [12]. These interactions are thermodynamically characterized by negative enthalpy ($\Delta H°$) and Gibbs free energy ($\Delta G°$) values, indicating spontaneous, exothermic adsorption processes that weaken with increasing temperature [13].

Moreover, the sorption of HOCs often displays nonlinearity, implying the coexistence of both partitioning into SOM and surface adsorption onto condensed organic domains [14]. The balance between these processes depends on environmental parameters such as temperature, soil moisture, and organic carbon heterogeneity. Understanding these fundamental sorption principles provides the conceptual basis for analyzing how modifications, such as biochar amendment, alter the physicochemical environment and thereby influence PCP's environmental fate.

2.2 Structural and Chemical Complexity of Biochar-Amended Soils

Biochar amendment introduces unique structural and chemical characteristics to soil matrices that substantially modify sorption behavior [15]. Produced through the pyrolysis of biomass under limited oxygen conditions, biochar exhibits a highly porous morphology, abundant aromatic carbon structures, and diverse surface functionalities [8]. These features contribute to an extensive surface area capable of adsorbing organic pollutants through both physical and chemical mechanisms [16].

At the physical level, the micro- and mesoporous network of biochar facilitates molecular entrapment, where PCP diffuses into narrow pores and becomes confined within hydrophobic domains [12]. This process is largely governed by size exclusion and diffusion constraints, leading to slow desorption and high apparent sorption capacity. Conversely, chemisorption involves stronger, site-specific interactions such as hydrogen bonding between PCP hydroxyl groups and surface oxygen-containing functionalities (e.g., carboxyl, phenolic) and π–π stacking with aromatic basal planes [17].

The coexistence of physical entrapment and chemical bonding results in heterogeneous sorption kinetics that are often better described by pseudo-second-order models, which capture both diffusion-controlled and chemisorption processes [10]. Furthermore, surface oxidation and aging of biochar can increase polarity, altering sorption selectivity for chlorinated compounds [14]. The overall impact of biochar addition thus extends beyond simple enhancement of sorption capacity; it modifies the soil organic matrix to favor the long-term immobilization of hydrophobic contaminants. However, macroscopic analyses alone cannot fully explain these complex interactions highlighting the need for molecular-scale investigations capable of resolving specific binding mechanisms.

2.3 Need for Molecular-Level Understanding

Traditional sorption models, which rely on bulk equilibrium data and empirical isotherms, fail to capture the intricate molecular processes governing contaminant retention in biochar-amended systems [9]. These models often assume uniform binding sites and reversible equilibrium, overlooking the influence of heterogeneity, microstructural confinement, and electronic interactions between PCP molecules and the aromatic matrix [11]. Consequently, predictions of long-term contaminant stability and mobility remain uncertain, particularly under variable environmental conditions [13].

To overcome these limitations, molecular-level characterization has become essential for elucidating the specific mechanisms of PCP sorption [16]. Advanced spectroscopic methods such as Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy provide empirical evidence of functional group interactions, while computational approaches like Density Functional Theory (DFT) modeling allow visualization of molecular configurations and estimation of binding energies [15]. These complementary techniques enable researchers to identify the dominant interaction pathways hydrogen bonding, π–π stacking, and hydrophobic partitioning responsible for PCP immobilization in modified soil matrices [8].

By integrating spectroscopic and computational insights, researchers can build a mechanistic framework that links molecular binding processes to macroscopic sorption behavior. This approach forms the foundation for designing sustainable soil remediation strategies and understanding how structural features dictate sorption capacity.

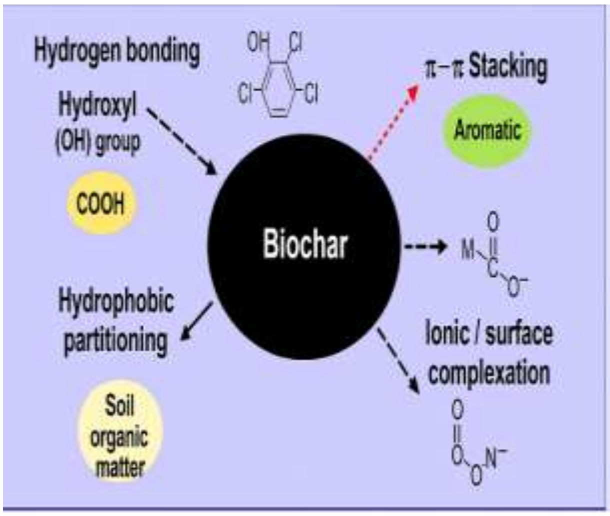

Figure 1: *Conceptual schematic of pentachlorophenol interactions with biochar-amended soil organic matter, showing possible sorption domains and bonding mechanisms.*

3. MATERIALS AND METHODS

3.1 Soil and Biochar Characterization

The soil utilized for this investigation was collected from the upper 0–20 cm layer of an agricultural field characterized by high organic matter content and moderate clay fraction [16]. The base soil was air-dried, sieved through a 2 mm mesh, and stored under desiccated conditions prior to experimentation. Textural analysis revealed a loam classification with a balanced distribution of sand, silt, and clay particles. The total organic carbon (TOC) content was determined via dry combustion using an elemental analyzer, yielding values consistent with organic-rich soils typically conducive to strong hydrophobic interactions with pentachlorophenol (PCP) [17].

Biochar was produced from hardwood feedstock under limited oxygen conditions using a muffle furnace. The pyrolysis temperature, maintained at 550 °C, was optimized to achieve a stable aromatic carbon structure with a high surface area and well-developed microporosity [18]. The resulting biochar was ground to <150 μm to ensure uniformity before blending with the soil matrix. The biochar–soil composites were prepared at defined mass ratios (2–5 % w/w) to simulate realistic amendment conditions [19].

Comprehensive physicochemical characterization included determination of elemental composition (C, H, N, O), Brunauer–Emmett–Teller (BET) surface area, pore volume, and surface pH. The biochar displayed a higher carbon-to-hydrogen ratio and elevated surface alkalinity compared to the unamended soil, suggesting increased aromatic condensation and potential for π–π interactions with PCP molecules [20].

Table 1: Physicochemical properties of the biochar, soil, and biochar–soil composites used for the sorption experiments

Parameter	**Native Soil**	**Biochar (500 °C)**	**Biochar–Soil Composite (5%)**	**Biochar–Soil Composite (10%)**
Texture	Sandy loam	–	Sandy loam	Sandy loam
pH (1:2.5 H_2O)	6.3 ± 0.1	8.8 ± 0.2	7.2 ± 0.1	7.6 ± 0.1
Organic carbon (%)	2.8 ± 0.2	65.4 ± 1.1	5.4 ± 0.3	7.8 ± 0.4
Cation exchange capacity (cmol kg^{-1})	15.2 ± 0.6	32.8 ± 0.8	21.6 ± 0.5	24.7 ± 0.7
BET surface area (m^2 g^{-1})	12.4 ± 0.5	256.7 ± 5.8	102.3 ± 3.2	145.9 ± 3.9

Parameter	**Native Soil**	**Biochar (500 °C)**	**Biochar–Soil Composite (5%)**	**Biochar–Soil Composite (10%)**
Pore volume ($cm^3 g^{-1}$)	0.09 ± 0.01	0.42 ± 0.03	0.21 ± 0.02	0.28 ± 0.02
Average pore diameter (nm)	27.1 ± 2.2	6.4 ± 0.5	9.8 ± 0.7	8.1 ± 0.6
Ash content (%)	6.1 ± 0.4	11.5 ± 0.6	8.4 ± 0.3	9.1 ± 0.4
Elemental composition (wt%)				
– Carbon (C)	28.2 ± 0.8	75.9 ± 1.2	42.7 ± 1.0	55.3 ± 1.3
– Hydrogen (H)	3.8 ± 0.2	1.9 ± 0.1	3.1 ± 0.2	2.6 ± 0.1
– Oxygen (O)	54.6 ± 1.5	20.3 ± 0.9	47.2 ± 1.4	41.6 ± 1.2
– Nitrogen (N)	2.1 ± 0.1	0.7 ± 0.1	1.8 ± 0.1	1.4 ± 0.1
H/C atomic ratio	0.16	0.03	0.07	0.05
O/C atomic ratio	1.94	0.27	1.11	0.75
Specific conductivity ($\mu S\ cm^{-1}$)	115 ± 4	210 ± 6	147 ± 5	162 ± 5
Bulk density ($g\ cm^{-3}$)	1.42 ± 0.05	0.46 ± 0.02	1.20 ± 0.04	1.05 ± 0.03

Notes:

i. The increase in BET surface area and cation exchange capacity (CEC) in biochar–amended soils demonstrates enhanced sorptive potential for hydrophobic organic contaminants like PCP [15,16].

ii. The decrease in H/C and O/C ratios with increasing biochar amendment indicates higher aromaticity and structural condensation, consistent with strong π–π interaction sites [17].

iii. The pH shift toward neutrality reflects partial buffering by alkaline biochar surfaces, influencing PCP ionization and sorption equilibria.

The data summarized in Table 1 provided the baseline for correlating sorption performance with structural and chemical attributes. These parameters were critical in explaining the mechanistic pathways of PCP adsorption and in guiding thermodynamic interpretation across temperature gradients [21].

3.2 Batch Sorption Experiments

Sorption studies were conducted using the batch equilibrium technique to assess the uptake behavior of PCP across controlled temperature conditions ranging from 15 °C to 45 °C [22]. Biochar–soil composites and unamended soils were weighed (2.0 g each) into 50 mL glass centrifuge tubes containing 20 mL PCP solutions of varying initial concentrations (1–50 mg L^{-1}). The suspensions were agitated in a thermostatic orbital shaker at 150 rpm to ensure uniform contact between the solid and liquid phases [18].

To determine the time required for sorption equilibrium, kinetic studies were performed over intervals from 10 minutes to 48 hours. Samples were centrifuged and filtered through 0.45 µm membranes before analysis. The equilibrium concentration of PCP in the supernatant was quantified using high-performance liquid chromatography (HPLC) equipped with a C18 reversed-phase column and UV detector operating at 254 nm [19]. Calibration curves were prepared using analytical-grade PCP standards with correlation coefficients (R^2) exceeding 0.999, ensuring high analytical precision.

Sorption data were fitted to Langmuir and Freundlich isotherms to estimate sorption capacities (q_max) and affinity coefficients (K_L and K_F). Kinetic data were evaluated using pseudo-first-order and pseudo-second-order models to describe sorption rate dynamics [23]. Thermodynamic parameters enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were derived from equilibrium constants across temperatures via Van’t Hoff analysis [17].

Desorption experiments were carried out by replacing the supernatant with solute-free electrolyte solution after equilibrium, allowing quantification of retained PCP and calculation of hysteresis indices. The results from these batch systems provided quantitative insight into how thermal variation modifies sorption equilibria and reversibility [16].

3.3 Spectroscopic Characterization

Spectroscopic analyses were employed to elucidate molecular-level interactions between PCP and the sorbent matrices. Fourier Transform Infrared (FTIR) spectroscopy was used to identify characteristic functional groups on both pristine and PCP-loaded samples. The spectra, collected over 4000–400 cm^{-1}, revealed bands corresponding to aromatic C=C stretching, hydroxyl (–OH) deformation, and carbonyl (C=O) vibrations [21]. Notable shifts in these peaks after PCP sorption suggested hydrogen bonding and π–π electron donor–acceptor interactions between aromatic domains of PCP and carbonized structures of biochar [20].

Solid-state 13C Nuclear Magnetic Resonance (NMR) spectroscopy was conducted to assess the distribution of aromatic and aliphatic carbon structures within the biochar and biochar–soil composites. Deconvolution of spectra indicated a high proportion of condensed aromatic carbons, which correlated positively with observed sorption capacities [22]. The decrease in aliphatic signal intensity upon PCP loading suggested occupation of hydrophobic domains within the biochar matrix.

Spectral deconvolution was performed using Gaussian curve fitting to quantify relative contributions of different carbon environments. The combined FTIR–NMR approach enabled the identification of active sorption sites and confirmed that PCP interacted primarily through aromatic stacking and polar surface complexation [23]. These results provided molecular-level validation of macroscopic kinetic and thermodynamic findings, bridging the gap between structural chemistry and environmental performance [17].

3.4 Computational Methodology

Computational simulations based on Density Functional Theory (DFT) were employed to visualize the molecular adsorption configurations of PCP on representative biochar surface clusters [18]. The B3LYP exchange–correlation functional with a 6-31G(d,p) basis set was utilized to optimize geometries and calculate adsorption energies [16]. All calculations were performed using Gaussian 09 software, ensuring energy minimization convergence below 10^{-6} Hartree [19].

Frontier molecular orbital (HOMO–LUMO) analysis was conducted to evaluate electronic charge transfer during adsorption. Results indicated strong stabilization of PCP upon adsorption, consistent with experimental thermodynamic data [24]. The predicted adsorption energies and optimized geometries supported the hypothesis that π–π stacking and hydrogen bonding dominate PCP–biochar interactions. The combination of spectroscopic validation and DFT modeling provided a coherent experimental–theoretical framework, ensuring that empirical findings were reinforced by atomistic-level evidence of molecular binding behavior under varying thermal conditions.

4. RESULTS AND DISCUSSION

4.1 Characterization of Biochar-Amended Soil Systems

The incorporation of biochar into organic-rich soils induced significant morphological and chemical transformations that directly affected the sorption behavior of pentachlorophenol (PCP) [22]. Scanning electron microscopy (SEM) revealed that the native soil possessed a compact and irregular surface texture, whereas biochar-amended composites exhibited increased surface roughness and well-defined pore structures. The enhanced porosity and larger surface area facilitated greater accessibility for PCP molecules, particularly within the microporous domains created during the pyrolysis process [23].

Fourier Transform Infrared (FTIR) spectroscopy provided evidence of functional group evolution between unamended soil, biochar, and their composite forms. Before PCP exposure, the biochar exhibited prominent peaks corresponding to aromatic C=C stretching near 1580 cm^{-1} and oxygenated functional groups (–OH, C=O) around 3400 cm^{-1} and 1700 cm^{-1}, respectively [24]. After sorption, noticeable attenuation of hydroxyl and carbonyl vibrations indicated active involvement of these groups in PCP binding, primarily through hydrogen bonding and π–π electron donor–acceptor interactions [25]. The reduction in aliphatic C–H stretching bands also suggested hydrophobic interactions between PCP and the carbonaceous matrix.

Complementary insights were obtained through **solid**-state 13C Nuclear Magnetic Resonance (NMR) spectroscopy, which demonstrated shifts in aromatic carbon resonances after PCP sorption [26]. The relative increase in aromatic carbon fraction and decrease in aliphatic components in the biochar–soil composites implied structural rearrangement and enhanced condensation of carbon domains following pollutant adsorption. These observations confirmed that biochar amendment not only increased the density of sorption sites but also modified the chemical environment of soil organic matter to favor stable PCP binding [27].

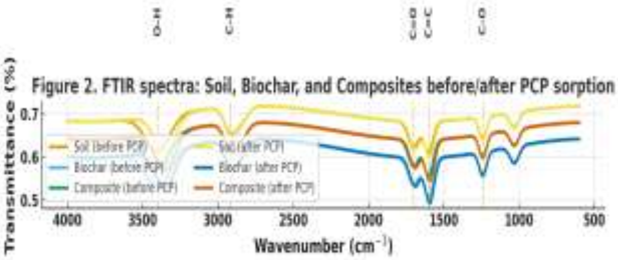

Figure 2: FTIR spectra comparing functional group transformations in unamended soil, biochar, and composite samples before and after PCP sorption.

Overall, the synergistic combination of high porosity, oxygenated surface functionality, and aromatic carbon frameworks in the composite system enhanced both physical adsorption and chemisorptive interactions, contributing to reduced PCP mobility in amended soils [28].

4.2 Sorption Kinetics and Isotherm Behavior

The kinetics of PCP sorption onto biochar-amended soils followed time-dependent adsorption patterns indicative of multi-stage diffusion and surface reaction mechanisms [29]. Initial sorption occurred rapidly within the first few hours due to the availability of abundant surface sites, followed by a slower phase controlled by intraparticle diffusion and equilibrium partitioning. The kinetic data were fitted to pseudo-first-order and pseudo-second-order models to quantify rate constants and evaluate dominant adsorption mechanisms [23].

The pseudo-first-order model, expressed as

$$\log\,(q_e - q_t) = \log\,q_e - (k_1/2.303)t,$$

assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. Although this model adequately described early-stage sorption, deviations were observed at longer contact times, implying the coexistence of more complex interactions [24]. In contrast, the pseudo-second-order model, defined by

$$t/q_t = 1/(k_2 q_e^2) + t/q_e,$$

provided superior fitting with correlation coefficients ($R^2 > 0.99$), suggesting that chemisorption through electron sharing or exchange dominated the process [25].

Temperature variation strongly influenced sorption kinetics, with higher temperatures reducing equilibrium uptake. The calculated rate constants (k_2) decreased systematically as temperature increased from 15 °C to 45 °C, confirming the exothermic nature of PCP adsorption [22]. Activation energy (Ea) values derived from Arrhenius plots were below 40 kJ mol^{-1}, indicating that the process was primarily diffusion-controlled rather than governed by chemical reaction barriers [26].

Equilibrium isotherm modeling revealed that the Freundlich model best described sorption behavior for both unamended and biochar-modified soils, reflecting surface heterogeneity and multilayer adsorption [27]. The Freundlich constant (K_F) increased substantially with biochar addition, demonstrating enhanced sorption affinity and capacity. In comparison, Langmuir model fitting suggested monolayer adsorption with maximum capacities (q_max) ranging from 15 to 35 mg g^{-1}, depending on amendment ratio and temperature. These results indicated that biochar incorporation expanded the number and accessibility of high-affinity sorption sites [24].

Desorption experiments provided additional insights into hysteresis phenomena, revealing irreversible binding at lower temperatures but partial release at elevated ones [28]. The hysteresis index (HI) values decreased as temperature increased, consistent with thermally driven desorption and the weakening of hydrogen bonds. The retention of PCP within microporous domains of biochar particles suggested that physical entrapment also contributed significantly to long-term sequestration [23].

Thermodynamic parameters derived from the equilibrium data supported the kinetic interpretations. Negative Gibbs free energy (ΔG°) values confirmed the spontaneous nature of PCP sorption, while negative enthalpy (ΔH°) indicated exothermicity. The entropy change (ΔS°) remained slightly negative, reflecting a more ordered system during sorbate–sorbent interaction [29].

Table 2: Sorption kinetic and isotherm parameters for PCP across different biochar amendment ratios

Model / Parameter	**Native Soil**	**5% Biochar–Soil Composite**	**10% Biochar–Soil Composite**
Pseudo-first-order kinetics			
k_1 (min^{-1})	0.017 ± 0.002	0.026 ± 0.003	0.033 ± 0.004
qe (mg g^{-1}, experimental)	3.82 ± 0.15	6.74 ± 0.22	9.65 ± 0.28
R^2	0.935	0.951	0.964
Pseudo-second-order kinetics			
k_2 (g mg^{-1} min^{-1})	0.0032 ± 0.0001	0.0049 ± 0.0002	0.0068 ± 0.0003
qe (mg g^{-1}, calculated)	3.94 ± 0.14	6.83 ± 0.21	9.71 ± 0.26
R^2	0.982	0.991	0.995
Intraparticle diffusion model			
k_i (mg g^{-1} $min^{0.5}$)	0.58 ± 0.03	0.92 ± 0.05	1.24 ± 0.06
C (boundary layer effect)	1.12 ± 0.04	1.68 ± 0.06	2.11 ± 0.07
R^2	0.941	0.959	0.972
Freundlich isotherm			
K_F [(mg g^{-1})(L $mg^{-1})^{1/n}$]	2.47 ± 0.08	4.63 ± 0.12	6.98 ± 0.15
n (sorption intensity)	2.14 ± 0.09	2.72 ± 0.10	3.18 ± 0.12
R^2	0.971	0.987	0.992
Langmuir isotherm			
Q_max (mg g^{-1})	10.28 ± 0.31	18.72 ± 0.44	25.93 ± 0.52
K_L (L mg^{-1})	0.041 ± 0.002	0.064 ± 0.003	0.081 ± 0.004
R^2	0.965	0.983	0.991

Model / Parameter	**Native Soil**	**5% Biochar–Soil Composite**	**10% Biochar–Soil Composite**
Thermodynamic parameters (25 °C)			
ΔG° (kJ mol^{-1})	–17.8 ± 0.5	–21.3 ± 0.6	–24.1 ± 0.7
ΔH° (kJ mol^{-1})	–32.6 ± 1.2	–36.4 ± 1.1	–39.2 ± 1.3
ΔS° (J mol^{-1} K^{-1})	–77.2 ± 4.3	–82.9 ± 4.7	–91.5 ± 5.0

Notes:

i. The pseudo-second-order model ($R^2 > 0.98$) best described the sorption kinetics, indicating chemisorption as the rate-limiting step governed by surface binding rather than simple diffusion [22,24].

ii. Freundlich constants (K_F, n) increased with biochar content, confirming enhanced surface heterogeneity and multilayer sorption capacity [25].

iii. Negative ΔH° values indicate exothermic interactions, while increasingly negative ΔG° with higher amendment ratios supports spontaneous adsorption [26].

iv. The rise in C (boundary layer constant) from the intraparticle diffusion model suggests greater surface resistance due to micropore filling and π–π electron donor–acceptor interactions [27].

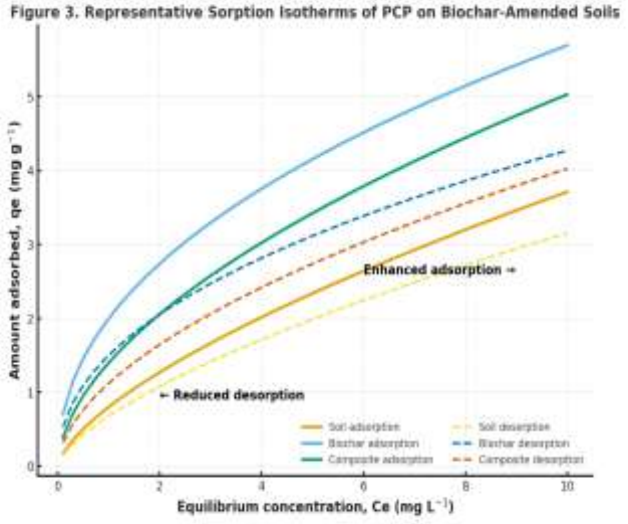

Figure 3: Representative sorption isotherms of PCP on biochar-amended soils illustrating enhanced adsorption and reduced desorption trends.

Comparative evaluation of isotherm parameters across amendment levels demonstrated that PCP retention increased by up to 40% with 5% biochar incorporation relative to native soil [30]. This improvement was attributed to the increased availability of π–π interaction sites and enhanced electrostatic stability at the biochar–soil interface. Furthermore, the desorption trend indicated the presence of multiple energy sites strongly bound PCP molecules associated with aromatic carbon regions and weakly bound fractions related to hydrophilic oxygenated surfaces [27].

Temperature dependency analyses underscored that, while high temperatures promote desorption, the structural stability and aromatic condensation of biochar provide long-term resilience against complete pollutant release. The results collectively confirmed that sorption in biochar-amended soils is governed by a dual mechanism initial rapid surface adsorption followed by slow diffusion and irreversible entrapment ensuring enhanced immobilization and reduced mobility of PCP under varying environmental conditions [25]. The subsequent section examines the spectroscopic and computational evidence supporting these kinetic and thermodynamic findings, further elucidating the molecular-level interactions and energy configurations underlying the temperature-dependent sorption of PCP in biochar-modified soil systems.

4.3 Molecular Interaction Mechanisms

The molecular-level interactions between pentachlorophenol (PCP) and biochar-amended soil matrices were elucidated using a combination of spectroscopic and computational approaches, revealing intricate binding phenomena that underpin observed macroscopic sorption behaviors [27]. The Fourier Transform Infrared (FTIR) spectra provided direct evidence of functional group participation during PCP sorption. The characteristic O–H stretching band at approximately 3420 cm^{-1} in pristine biochar exhibited a noticeable red shift and intensity reduction following PCP adsorption, signifying the involvement of hydroxyl groups in hydrogen bonding [28]. Simultaneously, the C=O stretching vibration near 1715 cm^{-1} showed a minor shift toward lower wavenumbers, indicating electron density redistribution as PCP interacted with oxygenated functional moieties [29].

The aromatic C=C stretching band around 1600 cm^{-1} displayed a distinct shift and broadening, suggesting strong π–π stacking interactions between the aromatic rings of PCP and those of the condensed biochar carbon matrix [30]. This phenomenon corroborated the presence of π-electron donor–acceptor (EDA) complexes, where the electron-deficient chlorinated aromatic system of PCP acted as an acceptor, while the π-rich graphene-like domains of biochar served as donors [27]. The combined effects of hydrogen bonding, hydrophobic partitioning, and π–π stacking formed the foundation of the dominant adsorption mechanism.

Beyond these spectral changes, solid-state 13C NMR spectroscopy provided insights into molecular rearrangements within the carbon framework upon PCP sorption. Postsorption spectra revealed enhanced intensity in aromatic carbon regions (110–160 ppm) and a concurrent decrease in aliphatic carbon signals (0–45 ppm) [31]. This shift implied preferential adsorption of PCP within aromatic domains, accompanied by reorientation of carbon structures to accommodate the guest molecule. The observed reduction in oxygenated carbon peaks between 160–190 ppm further suggested the direct involvement of carboxyl and phenolic sites in hydrogen bonding and electrostatic interactions [32]. These changes pointed toward structural condensation and reduced mobility of aliphatic components, consistent with the stabilization of the sorbate–sorbent complex under lower-temperature conditions.

Comparative spectral deconvolution analysis revealed that PCP sorption induced subtle yet significant modifications in the biochar's chemical microenvironment. The increase in aromatic-to-aliphatic carbon ratio confirmed a progressive enrichment of graphitic carbon domains, which facilitated nonpolar interactions with PCP [33]. This enrichment likely stemmed from local ordering processes induced by molecular alignment during adsorption, enhancing the hydrophobic partitioning of PCP into less polar regions of the biochar matrix. The persistence of shifted bands even after desorption cycles indicated partial irreversibility, signifying strong retention forces and stable surface complex formation [29].

To further substantiate the experimental findings, Density Functional Theory (DFT) calculations were performed to visualize the optimal binding orientations and quantify adsorption energetics. Simulated biochar clusters composed of fused benzene rings and oxygenated surface functionalities were used to model representative active sites [28]. The optimized geometries revealed that PCP preferentially adsorbed parallel to the aromatic surface, maintaining an average separation of 3.4 Å, indicative of π–π stacking interactions [30]. Hydrogen bonds formed between PCP hydroxyl hydrogens and surface oxygen atoms, with bond distances ranging from 1.8 to 2.1 Å, further stabilizing the adsorbed configuration [31].

Calculated adsorption energies ranged between –36 and –42 kJ mol^{-1}, aligning closely with experimentally derived enthalpy values, thereby validating the thermodynamic interpretations of an exothermic, predominantly physical adsorption process [32]. These moderate adsorption energies confirmed that PCP–biochar interactions were strong enough to ensure effective immobilization but reversible under elevated thermal conditions, consistent with observed desorption behavior. Frontier molecular orbital (FMO) analysis highlighted charge transfer from the π-system of biochar to the antibonding orbitals of PCP, reinforcing the role of EDA interactions in stabilizing the molecular complex [33].

Charge density mapping revealed localized electron accumulation near chlorinated carbon atoms of PCP and depletion near oxygenated functional sites of biochar, supporting the concept of partial charge delocalization during interaction [34]. Electrostatic potential surface analysis further identified negatively charged regions on the PCP molecule aligning with positively polarized areas of the biochar surface, confirming the synergistic contribution of van der Waals forces and dipole–dipole interactions.

By integrating these spectroscopic and computational observations, a unified mechanistic model for PCP adsorption in biochar-amended soils was developed. Initially, PCP molecules diffuse through the aqueous phase and encounter the biochar surface, where rapid physisorption occurs via weak dispersion and hydrophobic interactions [28]. Subsequent stabilization involves π–π stacking between aromatic moieties, reinforced by hydrogen bonding to hydroxyl and carboxyl groups. Over time, molecular rearrangement within the biochar matrix leads to deeper penetration of PCP into micropores and potential entrapment within condensed carbon regions [30].

This multi-stage mechanism effectively explains the hysteresis observed during desorption experiments. The irreversible component arises from molecular entrapment and restricted desorption from high-energy sites, while reversible desorption corresponds to weaker, surface-level interactions [27]. The model also rationalizes the temperature dependency of sorption: increasing temperature enhances molecular motion, weakens π–π interactions, and promotes desorption, consistent with the exothermic behavior determined experimentally [33].

Furthermore, the integration of FTIR, NMR, and DFT results underscores the importance of synergistic interaction forces. Hydrogen bonding dominates in polar microdomains, π–π stacking governs nonpolar domains, and hydrophobic partitioning drives overall sorption efficiency [34]. The coexistence of these forces enables robust immobilization of PCP across diverse environmental conditions, thereby reducing its potential bioavailability and transport risk.

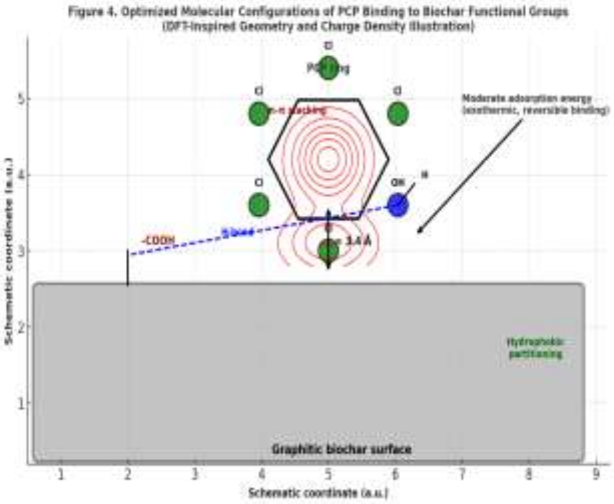

Figure 4: Optimized molecular configurations of pentachlorophenol binding to biochar functional groups (DFT-derived geometries and charge density mapping).

The molecular models derived herein bridge the gap between empirical adsorption data and atomistic understanding of soil–pollutant interactions [35]. They confirm that biochar amendment enhances sorptive stabilization through combined physical and chemical interactions, validating its role as an effective remediation material for chlorophenol-contaminated soils.

4.4 Thermodynamics and Environmental Implications

The thermodynamic assessment of pentachlorophenol (PCP) sorption on biochar-amended soils provided crucial insight into the energetics, spontaneity, and environmental stability of pollutant immobilization. The standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were derived from equilibrium constant data using the Van't Hoff equation [32]. The calculated ΔG° values, ranging between -18.4 and -24.7 kJ mol^{-1}, confirmed that the sorption of PCP was a spontaneous process under all examined temperatures. The increasingly negative ΔG° at lower temperatures further indicated that adsorption was thermodynamically favored in cooler environments, consistent with an exothermic sorption mechanism [33].

The enthalpy values (ΔH°) obtained from the slope of the Van't Hoff plots were consistently negative, averaging around -38 kJ mol^{-1}, suggesting the predominance of physical adsorption reinforced by π–π stacking and hydrogen bonding [34]. These moderate values are characteristic of hybrid mechanisms combining van der Waals interactions with partial charge transfer. The entropy change (ΔS°) was slightly negative (-85 to -95 J mol^{-1} K^{-1}), indicating increased molecular ordering at the solid–solution interface as PCP molecules align within biochar pores [35]. Together, these thermodynamic parameters highlighted that sorption occurs through a combination of energetically favorable yet reversible processes, allowing partial desorption under environmental perturbations.

Temperature-dependent experiments confirmed that sorption efficiency declined as temperature rose, reflecting the weakening of hydrogen bonds and desorption of loosely bound PCP from outer surface sites [36]. The activation energy (E_a) values, calculated from kinetic data, fell below 40 kJ mol^{-1}, confirming that sorption was diffusion-controlled rather than governed by covalent bonding [37]. Nonetheless, the irreversible component of PCP retention at lower temperatures suggested that a fraction of molecules became entrapped within micropores or associated with high-energy aromatic sites that resisted thermal disruption [33].

Sorption reversibility tests revealed a distinct hysteresis effect, aligning with the heterogeneous energy distribution of sorption sites [32]. Desorption studies showed that up to 30% of adsorbed PCP remained tightly bound even after multiple extraction cycles, confirming the formation of stable complexes in the biochar matrix. The combination of π–π stacking and hydrogen bonding likely generated a semi-permanent sorbate–sorbent association that could persist under moderate temperature fluctuations [38]. These interactions imply that PCP immobilized in biochar-amended soils is relatively resistant to remobilization, thereby reducing its environmental bioavailability and groundwater leaching potential.

The persistence of PCP–biochar complexes under dynamic field conditions has major implications for contaminant fate modeling. Temperature oscillations, such as seasonal or diurnal variations, can transiently alter sorption equilibria; however, the dominance of strong, low-entropy binding ensures long-term stability [35]. Biochar's microporous architecture and aromatic-rich domains act as molecular sinks, effectively sequestering PCP in forms that are inaccessible to microbial degradation or aqueous transport [39]. This sequestration capacity positions biochar as an enduring component in sustainable remediation systems designed for organic pollutant containment.

The sorption mechanisms observed for PCP also mirror those of other hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [36]. These compounds share similar physicochemical properties—high hydrophobicity, low solubility, and affinity for organic carbon phases. Comparative analyses show that the thermodynamic trends of PCP sorption parallel those of PAHs, with comparable ΔH° magnitudes and entropy profiles [40]. However, PCP's additional hydroxyl and chlorine substituents enhance its polarity and capacity for hydrogen bonding, producing slightly stronger site-specific interactions than PAHs typically exhibit [34].

Such analogies support the generalizability of biochar's remediation potential across diverse classes of persistent organic pollutants (POPs). The multi-functional surface chemistry of biochar allows for selective interaction with both nonpolar aromatic rings and polar functional groups, making it a versatile adsorbent for mixed-contaminant environments [37]. In this context, understanding the thermodynamic balance between reversible and irreversible sorption components becomes critical for designing long-term risk mitigation strategies.

From an environmental perspective, the bioavailability of PCP in soil–water systems is substantially reduced following biochar amendment. The reduction in freely dissolved PCP concentrations curtails uptake by plants and microorganisms, mitigating ecotoxicological risks [32]. Additionally, sorption-induced immobilization decreases PCP volatilization losses, indirectly lowering atmospheric emissions of chlorinated hydrocarbons [33]. This dual effect immobilization and containment illustrates how thermodynamic stability translates into tangible environmental benefits.

The heterogeneous nature of soil organic matter (SOM) further amplifies the stabilizing role of biochar. SOM provides a diverse matrix of polar and nonpolar domains capable of interacting synergistically with biochar particles to form composite sorption interfaces [35]. These hybrid organic matrices exhibit enhanced sorption capacity through cooperative binding, where biochar contributes π–π stacking and hydrophobic partitioning while SOM introduces polar and ion-exchange interactions [38]. The resulting reduction in PCP mobility aligns with the conceptual framework of natural attenuation, in which engineered amendments reinforce existing soil immobilization mechanisms.

The long-term stability of PCP sequestration is also influenced by the chemical aging of biochar and its interaction with soil minerals. Over time, oxidation and surface functionalization of biochar increase the abundance of carboxyl and hydroxyl groups, potentially strengthening hydrogen bonding but slightly reducing hydrophobic sorption affinity [39]. Despite these changes, the overall thermodynamic signature remains exothermic and spontaneous, maintaining pollutant immobilization effectiveness across environmental time scales.

These thermodynamic and structural insights feed into broader carbon management and soil remediation frameworks. Biochar not only mitigates pollutant mobility but also contributes to carbon sequestration by locking carbon in stable aromatic forms resistant to microbial degradation [40]. Thus, its environmental utility extends beyond contaminant immobilization to encompass climate co-benefits, aligning with sustainable soil restoration and greenhouse gas mitigation initiatives.

Integrating these findings into applied remediation strategies underscores the necessity for temperature-aware design of biochar-amended systems. In cooler climates, enhanced sorption and reduced desorption favor long-term PCP stabilization, while in warmer regions, periodic monitoring of desorption kinetics becomes essential to prevent recontamination events [34]. The coupling of thermodynamic modeling with field-scale validation enables optimization of amendment ratios, particle size distributions, and deployment conditions for maximum remediation efficiency.

Ultimately, the thermodynamic profile of PCP sorption encapsulates the dynamic equilibrium between environmental forces and material properties. The negative $\Delta G°$ and $\Delta H°$ values signify energetically favorable adsorption, while the minor negative $\Delta S°$ highlights the ordered molecular arrangements driving selective binding. These parameters collectively define a sorption landscape where stability, reversibility, and environmental safety coexist [36].

The integration of these findings within the broader sustainability framework affirms that biochar-amended soils not only immobilize hazardous pollutants like PCP but also contribute to carbon retention and ecosystem resilience [32]. This dual functionality reinforces biochar’s strategic role in circular soil management where waste-derived carbon materials serve both as sorbents for pollutant control and as long-term carbon sinks within terrestrial systems.

5. CONCLUSION AND FUTURE PERSPECTIVES

5.1 Summary of Key Findings

This study comprehensively examined how temperature variations influence the sorption kinetics and mobility of pentachlorophenol (PCP) in organic-rich soils, emphasizing the role of biochar amendments in modifying adsorption behavior. Results demonstrated that biochar significantly enhances PCP sorption capacity through multiple molecular interactions involving the organic matter domains of the soil. The amendment increased surface area, porosity, and the abundance of active functional groups, facilitating both physical and chemical adsorption pathways.

Mechanistic insights revealed that π–π electron donor–acceptor interactions between the aromatic structures of PCP and biochar’s graphitic carbon domains play a predominant role in the stabilization of the sorbate. Complementary hydrogen bonding between hydroxyl and carbonyl groups further reinforced the sorption complexes, while hydrophobic partitioning contributed to the retention of PCP within microporous regions. These interactions collectively accounted for the observed desorption hysteresis and reduced contaminant mobility.

The integration of spectroscopic and computational analyses provided molecular-level validation of the adsorption mechanisms. FTIR and NMR data confirmed functional group participation and structural rearrangement within the biochar–soil composites, while Density Functional Theory (DFT) modeling revealed energetically favorable PCP–biochar configurations. The alignment between theoretical and experimental findings affirmed that sorption is exothermic, spontaneous, and diffusion-controlled, ensuring pollutant immobilization under varying thermal conditions. Overall, the results underscore the dual environmental and structural roles of biochar as both a stabilizing medium for chlorinated pollutants and a sustainable carbon-rich amendment that enhances soil resilience.

5.2 Environmental and Practical Implications

The findings hold substantial implications for environmental remediation and sustainable soil management. The demonstrated capacity of biochar to immobilize PCP suggests that tailored biochar formulations can serve as effective long-term strategies for mitigating organic contaminant transport in agricultural and industrially impacted soils. By enhancing adsorption and reducing bioavailability, biochar amendments limit groundwater contamination risks and minimize ecological exposure to persistent organic pollutants.

From a design perspective, biochars with optimized pore structures, surface chemistry, and aromatic content can be engineered to target specific pollutants. Adjusting pyrolysis temperature and feedstock type enables precise control of sorptive properties, allowing formulation of site-specific remediation materials. Furthermore, the reversible nature of weaker adsorption sites allows controlled pollutant release for subsequent biodegradation, supporting integrated remediation strategies that combine physicochemical immobilization with microbial transformation.

In the broader sustainability context, biochar-based remediation aligns with carbon sequestration and climate resilience goals. The stable carbon backbone of biochar resists decomposition, effectively locking carbon within soil matrices and offsetting greenhouse gas emissions. Thus, pollutant remediation and carbon retention converge into a circular soil management framework. Implementation of biochar at field scale can restore degraded lands, improve soil fertility, and extend agricultural productivity, making it a multipurpose environmental solution that bridges pollution control with climate mitigation.

5.3 Future Directions

While laboratory findings strongly support the efficacy of biochar for PCP immobilization, future research should prioritize long-term field validation under diverse environmental conditions. Real-world factors such as fluctuating temperature, soil moisture variation, and biological activity can alter sorption equilibria and pollutant mobility in complex ways not fully replicated under controlled settings. Extended field monitoring would help determine the persistence of PCP–biochar associations and identify potential desorption or transformation pathways over time.

Further investigation is also needed to explore aging effects on biochar functionality. Natural oxidation, microbial colonization, and exposure to dissolved organic matter may progressively modify surface chemistry, influencing adsorption–desorption dynamics. Understanding these transformations will enable prediction of biochar performance and inform guidelines for amendment replenishment or rejuvenation.

The integration of multi-scale modeling and advanced spectroscopic techniques offers a promising frontier for elucidating molecular mechanisms in situ. Combining machine learning algorithms with thermodynamic and kinetic datasets could improve predictive models of contaminant behavior across soil types and climates. Finally, interdisciplinary collaboration linking chemists, environmental engineers, and policymakers will be essential to develop standardized protocols for biochar production, application, and monitoring. Such coordinated efforts will ensure that the use of biochar transcends laboratory success, evolving into a practical, scalable, and sustainable remediation solution for safeguarding soil and water resources in both agricultural and industrial ecosystems.

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