

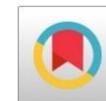


Modelling the heavy metals sorption and adsorption on biochar-treated soil in Egypt

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DOI: [10.21608/ajsws.2025.367401.1023](https://doi.org/10.21608/ajsws.2025.367401.1023)



Article Information

Received: April 11th, 2025

Revised: April 17th, 2025

Accepted: April 22nd 2025

Published: May 5th 2025

ABSTRACT: A laboratory experiment was conducted to investigate and evaluate the sorption-adsorption of heavy metals (cadmium and cobalt) on sandy soil treated with biochar at rates of 0, 1, 2.5, and 5% (w/w). The sorption-adsorption data were fitted on some sorption-adsorption isotherm models using the software Iso-Fit and Excel softwares. The isotherm models were Linear, Freundlich, Langmuir and proposed new models. Measured and simulated data were compared statistically to evaluate model reliability. The result indicated that the sorption-adsorption of heavy metals was more pronounced in sandy soil treated with biochar especially at 5%. The sorption-adsorption percentage was decreased by increasing the initial concentration of heavy metals and also increased with increasing the biochar rates.

The results showed that the average sorption-adsorption percentage were 89.03% for (Cd) and 72.66% for (Co) at 0% biochar. The corresponding values for 5% biochar were 92.15% for (Cd) and 91.12% for (Co).

Also, the experimental data was analyzed to examine the adsorption isotherm models. The distribution coefficients (K_d) obtained from the linear sorption-adsorption isotherm model were 172.77 and 66.56 L/kg for Cd and Co respectively at 0% biochar suggesting a relatively weaker interaction with heavy metals in comparison to sandy soil treated with 5% biochar in which the K_d account as 292.11 and 260.56 L/kg for Cd and Co respectively. The soil treated with biochar demonstrates a greater affinity for heavy metals. Metals can be arranged according to their K_d values, i.e., their affinities for the soil, in the following relative sequence: Cd > Co. This general sequence tends to vary slightly for different soil types. The obtained results are promising and useful in industrial wastewater infiltration into the soil profile and groundwater.

According to the goodness of fit statistical description. We may infer that all of the isotherm models that were employed in this study provide an acceptable explanation of How heavy metals sorb and absorb. The Linear, Freundlich and the novel model (GK2) were more appropriate models than the other isotherm models.

As general, understanding the sorption-adsorption dynamics of heavy metals in soil systems is essential for managing contaminated sites and protecting environmental health. This research recommends future studies to verify the competitive mechanism of heavy metals sorption-adsorption correlated to the soil characteristic parameters.

Keywords: heavy metals, sorption, adsorption, speciation, modeling, sorption isotherm models, biochar .

INTRODUCTION

One important environmental process that affects the mobility and bioavailability of heavy metals is their sorption-adsorption on soil. Numerous intricate processes that are impacted by environmental factors, soil characteristics, and particular interactions between metals and soil constituents control the sorption-adsorption of heavy metals in soils. To effectively manage heavy metal contamination in natural ecosystems and agriculture, it is imperative to comprehend these variables. To improve cleanup efforts, future research should concentrate on developing prediction models for metal transport and retention in soils (Bradl, 2004).

Heavy metal ions and other added compounds can be rendered immobile by soil. The primary cause of xenobiotic immobilization is sorption qualities, which are dictated by the soil's physicochemical characteristics, including its pH, water content, temperature, amount of clay and organic component, and characteristics of the specific metal ion (Hussain *et al.*, 2022).

With processes like adsorption, ion exchange, precipitation, and complexation playing crucial roles in the retention and immobilization of metals including cadmium (Cd), lead (Pb), copper (Cu), and zinc (Zn), biochar is an efficient substance for sorbing heavy metals in polluted soils. According to recent research, biochar effectively lowers metal mobility and bioavailability, minimizing groundwater contamination and enhancing soil health. A promising technique for environmental remediation, biochar's sorption-adsorption ability is greatly influenced by its features, such as its surface area, pyrolysis temperature, and feedstock type (Hussain *et al.*, 2022; Niazi *et al.*, 2020; Ahmed *et al.*, 2021).

Research on the sorption of heavy metals on soils altered with biochar has proven crucial, especially for environmental remediation. Because it can decrease the mobility and bioavailability of heavy metals like cadmium (Cd), lead (Pb), arsenic (As), copper (Cu), and zinc (Zn), biochar is being researched extensively. Adsorption, ion exchange, precipitation, and complexation are the main mechanisms of sorption-adsorption that help immobilize metals in the soil and lower the likelihood that they will leak into groundwater or be absorbed by plants (Xiong *et al.*, 2022).

To comprehend the adsorption and immobilization of metal ions in soils or other environmental media, heavy metal sorption-adsorption models are crucial. These models aid in forecasting how heavy metals would behave in contaminated environments and evaluating the efficacy of remediation-related amendments such as clays, charcoal, or organic materials (Zhou *et al.*, 2021a; Chen *et al.*, 2022).

Isotherm (e.g., Langmuir, Freundlich), kinetic (e.g., pseudo-first-order, pseudo-second-order), and thermodynamic models are the primary models utilized for heavy metal sorption-adsorption. These models aid in the explanation of the connection between sorption capacity and concentration, as well as the impact of temperature, pH, and contact time (Li *et al.*, 2022;

Bolan *et al.*, 2021). To comprehend the efficacy of adsorbents such as biochar for environmental cleanup, heavy metal sorption-adsorption models are essential. Recent research has shed light on the use of a variety of models, including Freundlich, Langmuir, and pseudo-second-order kinetic models, to assess the sorption capabilities of biochar for arsenic, copper, cadmium, and lead. These models aid in evaluating the effects of variables including metal concentration, contact time, and biochar properties on the immobilization of heavy metals in soils. According to the results of these investigations, biochar is still a useful technique for reducing soil heavy metal contamination (Huang *et al.*, 2022; Tao *et al.*, 2021).

The present study focuses on sorption-adsorption of heavy metals on soil treated with biochar at different rates. The resulted data were fit with some sorption-adsorption isotherm models.

2. MATERIALS AND METHODS

II.1. Soil sampling

Sandy and sandy loam soil samples were collected from surface layer (0–30 cm depth) of the farmed area at El-Sadat City, Menofia Governorate, Egypt (30° 25'06" N, and 29° 34'30" E). The air-dried soil samples were sieved using a 2.0 mm and stored for analysis. Physical and chemical properties of the soil samples were determined according to the methods described by Carter and Gregorich (2008) and illustrated in Table (1).

Table (1). physical and chemical analyses of soil samples

Parameters	Value
Particle-size distribution, %	
Sand	96.00
Silt	0.00
Clay	4.00
Textural class	sandy
Soil bulk density, g/cm ³	1.60
Chemical properties	
pH	7.7
EC, dS/m (1:2, water extract)	0.413
OM, %	0.43
CaCO ₃ , %	1.84
Soluble cations, meq/l	
Ca	0.967
Mg	1.352
Na	0.893
K	0.939
Soluble Anions, meq/l	
HCO ₃	0.136
Cl	1.736
SO ₄	2.145
Available nutrients, mg/kg	
N	2.145
P	17.40
K	300.00
Available Heavy metals, mg/kg	
Cd	0.027
Co	0.043
Ni	0.063
Pb	0.201

II.2. Biochar sample

The biochar used in this study was obtained from Amazon.eg (Miegos Biochar). The biochar was produced by pyrolysis at a high temperature (500 °C) under limited oxygen conditions.

The biochar was subjected to chemical analysis, according to Carter and Gregorich (2008). The chemical properties of Biochar are presented in Table (2).

Table (2). Chemical analysis of Biochar

Parameters	Value
EC (1:10, water extract), dS/m	2.52
pH (1:10, water suspension)	8.50
Soil organic carbon, %	70.0
Soluble nutrients, %	
N	0.27
P	0.08
K	0.32
Ca	400
Mg	700
Total Elements, %	
N	1.5
P	7.0
K	2.0
C/N ratio	5:3
H/C ratio	25:9
Heavy metals, mg/kg	
Cd	0.41
Co	0.54
Ni	1.13
Pb	1.82

II.3. Biochar characteristics

The biochar was analyzed with SEM, and the surfaces of BC were imaged with many follow channels in diameters of around 29 and 95 nanometers for soft biochar and from 27 to 89 nm for hard biochar. The structural difference may reflect the specific surface area and the adsorption capacity.

The functional groups identified from the FTIR spectra for the soft and hard biochar samples are reported. The spectra of soft biochar demonstrated many bands such as amides group, aromatic group, carboxyl group, nitro group, thiocarbonyl, and alkyl group

II.4. Soil-Biochar mixture preparation

The rates of biochar being mixed with sandy soil have been at 0, 1, 2.5, and 5% (w/w), and then the mixtures were incubated for 30 days at room temperature (25±2 °C) with the rewetted soil-biochar mixture at field capacity every 7 days. After incubating the soil mixture, it was air dried and passed through a 2.0 mm sieve, which was consequently retained until the analysis.

II.5. Reagents

All chemical reagents used in this study were analytical grade. The reagents were Cd (NO₃)₂·4H₂O and Co (NO₃)₂·6H₂O. The stock solutions of Cd and Co with a concentration of 1000 mg/L were prepared by dissolving a certain amount of the corresponding reagent into a 1000 mL volumetric flask. The stock solutions and the working solutions diluted from the stock solutions were stored at 4°C under HNO₃ (5% w/w) conditions to prevent the heavy metal ions from hydrolysis. Distilled water (DI) was used throughout the experimental steps.

II.6. The batch sorption-adsorption of heavy metals:

The Cd²⁺ and Co²⁺ stock solutions at 1000 mg/l were prepared using the analytical grade chemical. Following this, dilutions of Cd (0.0 to 5.0 mg/l) and Co (0.0 to 5.0 mg/l) were done by appropriately diluting the stock solution by distilled water. Three repetitions of each experiment were used, and the experiments were carried out in a 100 ml flask with 50 ml of a heavy metal solution at varying concentrations and 2.0 g of sandy soil treated with biochar. The mixture was agitated for an hour at 200 rpm in a rotary shaker before being filtered through Whatman filter paper (No.1). The residual concentration of heavy metals (filtrate) kept for analysis. The heavy metals in filtrate were measured using ICP-MS (Ivajlo et al., 2008). Some sorption-adsorption models were used to fit the sorption-adsorption data.

Once equilibrium was reached, the sorbents' capacities were computed using the following formula, the adsorbed metal for each sample was determined based on a mass balance of the metal ion (Vijayaraghavan et al., 2006):

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

(1)

Where:

q_e = amount of sorbate at equilibrium, mg kg⁻¹ (adsorption capacity),

V = the volume of the solution (L),

m = the mass of the soil (g),

C_0 = the initial concentration of metal (mg L⁻¹), and

C_e = Equilibrium concentration of sorbate-adsorption in solution, mg L⁻¹

The following formula was used to calculate the sorption-adsorption percentage of heavy metals in the solution (Sethuraman and Balasubramanian, 2010):

$$\text{sorbed}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100$$

(adsorption capacity)(2)

II.7. Mathematical modelling of the sorption-adsorption process

Using the program IsoFit and Excel software, the sorption-adsorption data were fitted to a few sorption-adsorption isotherms models to examine and contrast the sorption-adsorption of heavy metals on sorbent materials (Matott, 2004; Matott and Rabideau, 2008). The potential of an adsorbent to remove a contaminant down to water resources has been predicted using isotherm sorption models. The amount of pollutant absorbed and the amount still in the solution will balance out once a mass of adsorbent and a waste stream come into contact for a long enough period. The relationship between the solute's equilibrium concentration (C_e) and adsorption capacity (q_e) can be expressed mathematically as a sorption isotherm. It is crucial to model sorption isotherm data to forecast or compare adsorption performances. The sorption-adsorption data should be modelled using one-, two-, three-, or four-parameter isotherm models (Table 3).

Table (3). Isotherm sorption-adsorption models used in the present study

Sorption isotherm models	Equation	
Linear or Henry isotherm (Xue et al., 2001)	$q_e = K_d \times C_e$	(3)
Freundlich isotherm (Freundlich, 1906 and Jain et al., 2003)	$q_e = K_f \times C_e^{1/n}$	(4)
Langmuir isotherm (Langmuir, 1916)	$q_e = \frac{q_m \times b \times C_e}{1 + b \times C_e}$	(5)
New model (GK1)	$q_e = q_m (1 - EXP(-K_{GK1} \times C_e))$	(6)
New model (GK2)	$q_e = \frac{K_{GK2} \times C_e}{b_{GK2} + C_e^n}$	(7)
Freundlich + Linear isotherm	$q_e = K_f \times C_e^{1/n} + K_p \times C_e$	(8)
Langmuir + linear isotherm (Xing et al., 1996)	$q_e = \frac{q_0 \times b \times C_e}{1 + b \times C_e} + K_p \times C_e$	(9)
Fritz III (Fritz and Schluender, 1974)	$q_e = \frac{a_0 \times C_e^{b1}}{a_1 + a_2 \times C_e^{b1}}$	(10)
Fritz II (Fritz and Schluender, 1974)	$q_e = \frac{A \times C_e^{b1}}{1 + B \times C_e^{b2}}$	(11)
New model (GK3)	$q_e = \frac{(K_{GK1} * C_e)}{(1 + K_{GK2} * C_e)} * (1 - EXP(-K_{GK3} * C_e))$	(12)
Redlich-Peterson (Redlich and Peterson, 1959)	$q_e = \frac{A \times C_e}{1 + B \times C_e^g}$	(13)

II.8. Performance evaluation of sorption-adsorption models

To assess the dependability of the model, statistical comparisons were made between simulated and measured data (AgriMetSoft, 2018). The coefficient of determination (R²), the root mean square error (RMSE), the normalized root mean square error (NRMSE) (Jacovides and Kontoyiannis, 1995), and the index of Willmott (d) (Willmott, 1982; Willmott et al., 1985) were used to determine the degree of agreement between the predicted and measured values.

The statistical indices expressed in Equations (13 to 17) as following:

II.8.1. The Average Absolute Error (AAE)

Absolute percentage error between simulated and observed values may be calculated using the following equation (Loague and Green, 1991):

$$AAE = \frac{\sum_{i=1}^n |O_i - S_i|}{n}$$

(13)

II.8.2. Root Mean Square Error (RMSE)

Root means square error (RMSE) is calculated as follows (Loague and Green, 1991):

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (S_i - O_i)^2}{n}}$$

(14)

If RMSE is close to zero, the model performance can be described as acceptable.

II.8.3. Coefficient of Determination (R²)

$$R^2 = 1 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (O_i - O_{av})^2}$$

(15)

A value between 0 and 1 that indicates how well a statistical model predicts a result is called the coefficient of determination (R²).

II.8.4. Index of agreement (d)

The index of agreement (d) was calculated using the Willmott et al. (2012) equation:

$$d = 1 - \frac{\sum_{i=1}^n (S_i - O_i)^2}{\sum_{i=1}^n (|S_i - O_{av}| + |O_i - O_{av}|)^2}$$

(16)

The agreement (d) value index varies between 0 and +1 (Andarzian et al., 2011; Valbuena et al., 2019). According to d values, the closer to one indicates that estimated and observed values are identical.

II.8.5. Correlation coefficient (r)

The correlation coefficient is an indication of the degree of closeness between observed and simulated values. The observed and simulated values are correlated better when the correlation coefficient approaches 1.0. If observed and anticipated values are totally independent, i.e., uncorrelated, then r will be zero. The correlation coefficient was estimated by the following equation:

$$r = \frac{\sum_{i=1}^n (O - O_{av})(S - S_{av})}{\sqrt{\sum_{i=1}^n (O - O_{av})^2 \sum_{i=1}^n (S - S_{av})^2}}$$

(17)

Where:

n = the number of observations,

1/n = exponent in Freundlich isotherm

O_i = the observed value

O_{av} = the mean of the observed value.

qt = amount of sorbate adsorbed at time t, mg kg⁻¹

S_i = the simulated value

S_{av} = the mean of the simulated value

II.8.6. Normalized Root Mean Square Error

The normalized root means square error (NRMSE) (Jacovides and Kontoyiannis, 1995) is calculated as follows:

$$\text{NRMSE}(\%) = \frac{\text{RMSE}}{O_{av}} \times 100$$

(18)

If NRMSE is less than 10%, model simulation can be considered perfect (between 10 and 20%; acceptable, 20 and 30%; fair, greater than 30%; poor) (Valbuena et al., 2019).

II.9. Soil characteristics analysis:

The soil samples were air-dried, passed through a 2 mm sieve and analyzed. Some physical and chemical properties of the collected soil samples were determined according to the recommended procedures as follows:

II.9.1. Physical properties of soils

The bulk density of each soil sample was measured according to the weight of the soil and the volume of the packed column. Particle-size distribution was determined by the hydrometer method (Carter and Gregorich, 2008).

II.9.2. Chemical properties of soils

Total carbonates were estimated volumetrically using a calcimeter and calculated as calcium carbonate percentages according to Richards (1954). The modified Walkley-Blacks titration method determined organic

carbon (OC) (Carter and Gregorich, 2008). The organic matter content (OM) was calculated using the suitable constant ($OM = 1.724 \times OC$).

Electrical conductivity (EC) of soil: water extract, 1:2 (w/v), soluble cations and anions were measured and determined using methods according to Jackson (1973). The concentration of available heavy metals in soil samples was determined by extraction with DTPA extractant (Lindsay and Norvell, 1978) and determined with ICP-MS (Ivajlo et al., 2008).

II.10. Statistical analysis

All obtained data of the present study were, statistically, analyzed according to the design used by the Statistix (2024) computer software program and were tested by analysis of variance. The revised least significant difference test at 0.05 level of probability was used to compare the differences among the means of the various parameter combinations as illustrated by Gomez and Gomez (1984).

3. RESULTS AND DISCUSSION

III.1. Characteristics of Biochar

The Biochar sample (BC) was subjected to analysis by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD). These methods were used to characterize its surface functional groups.

III.1.1. Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEM) images are very useful to obtain accurate details about surface structure of bio-sorbents. The image of biochar might then allow us to understand morphological changes during the carbonization stage. The SEM pictures of biochar used in the present study is given in Photos 1. The surfaces of biochar were imaged with many hollow channels varying in diameters from 13.48 to 22.73 nm. These porous structures of biochar are likely providing a high internal surface area and adsorption ability for heavy metals. The structural difference may reflect the specific surface area and the adsorption capacity as environmental and cost-effective adsorbent for elemental nutrients or metal pollutants.

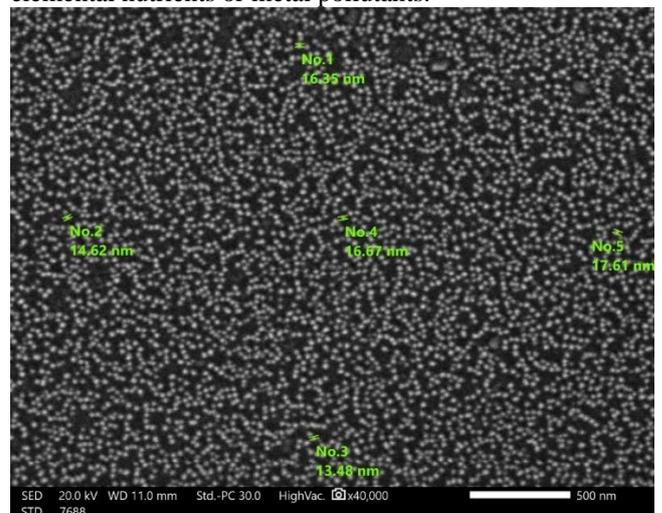


Photo 1. SEM micrograph of Biochar used in the present study

III.1.2. The Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is a laboratory method commonly applied in numerous industrial and research fields. Infrared spectroscopy is based on the measurement of the interaction of infrared radiation with matter. The energy absorbed due to molecule vibrations is reflected as absorption band in the spectrum. By means of the former interrelation the spectrum provides information on the chemical composition of the sample, rather like a chemical “fingerprint”. Initial investigations focused on the applicability of this analytical method in waste management and particularly in organic carbon characterization. FTIR spectroscopy was proven to be

an appropriate method for process monitoring and quality control of final products. Due to the fact that infrared spectroscopic methods deal with small of sample amounts preparation of the laboratory sample is a sensitive issue (Socrates, 2004).

The functional groups identified from the FTIR spectra for the biochar is illustrated in Figures 1. The spectra demonstrated many bands at 1636 cm^{-1} (amides group), 1259 cm^{-1} (aromatic group), and 1150-1040 cm^{-1} (alkyl group) as shown in Figure 1. The spectra of biochar demonstrated many bands at 1676 cm^{-1} (amides and carboxyl groups), 1459 cm^{-1} (amide group), and 549 cm^{-1} (alkyl group), 1200 cm^{-1} ($=\text{C}=\text{S}$ group), 1350 cm^{-1} ($=\text{SO}_2$ group),

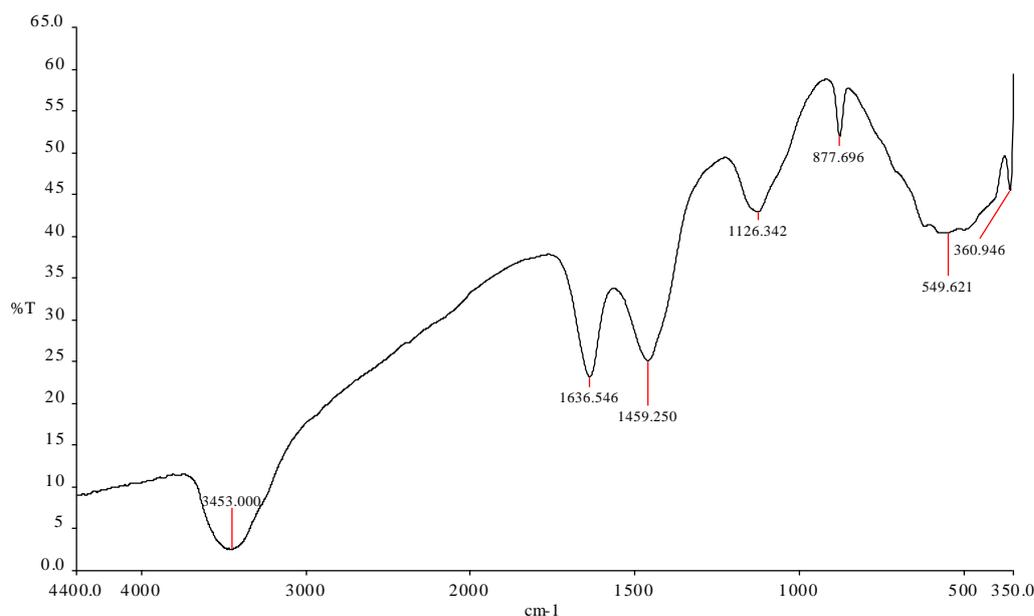


Figure (1). FTIR Spectra of Biochar

III.1.3. The energy-dispersive X-Ray Microanalysis (EDX)

The energy-dispersive X-Ray Microanalysis (EDX) of the biochar are described in Figures (2). For EDX quantification of these features, an accelerating voltage of 10 kV was used since this was enough to generate all elemental peaks of interest (Table 4). To optimize the chemical analysis of elements in biochar present in the samples, the analyzer mode in the INCA software was used to find the optimal choice of accelerating voltage. In Figure (2), the synthesized spectrum for an accelerating voltage of 4 kV is seen. It is clear that with a lower accelerating voltage, the carbon and oxygen peaks are much stronger compared to the other peaks. A lower accelerating voltage is preferred. Table (4) shows the approximate chemical analysis of biochar.

Table (4). The EDX elemental analysis of biochar sample

Elements	Biochar	
	Mass%	Atom%
C	64.22	71.55
O	17.78	15.06
Mg	14.64	12.11
Si	1.19	0.57
P	0.17	0.08
K	1.07	0.37
Ca	0.60	0.20
Fe	0.18	0.05
Cu	0.17	0.04
Total	100.00	100.00

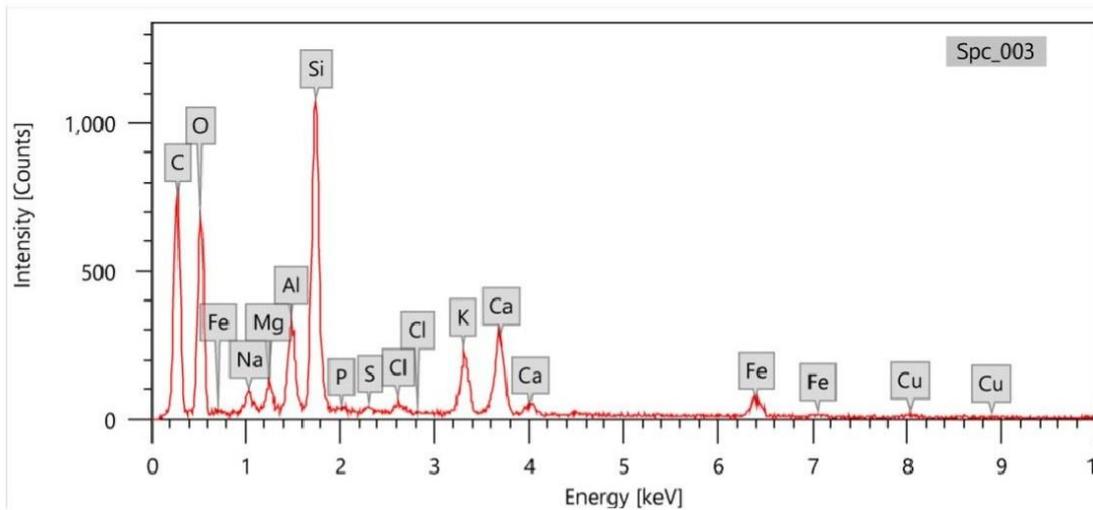


figure (2). EDX spectra of biochar sample

III.2. Sorption-adsorption of heavy metals on biochar-treated soil

The equilibrium sorption-adsorption of heavy metals (Cd and Co) ions on sandy soil treated with biochar are shown in Tables (5 and 6) at 0% biochar.

The adsorption capacity ranged from 10.543 to 101.255 mg/kg for (Cd), 8.346 to 84.475 mg/kg for (Co). The average sorption-adsorption percentage were 89.03% (as Cd), 72.66% (as Co).

Table (5). Equilibrium sorption-adsorption capacity of heavy metals on sandy soil mixed with 0% biochar

Cd^{2+}				Co^{2+}			
C_0 mg/l	C_e mg/l	q_e mg/kg	Sorption %	C_0 mg/l	C_e mg/l	q_e mg/kg	Sorption %
0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.00
0.466	0.044	10.543	90.51	0.466	0.132	8.346	71.66
0.932	0.096	20.908	89.75	0.932	0.251	17.024	73.08
2.330	0.258	51.778	88.91	2.330	0.620	42.738	73.38
4.659	0.609	101.255	86.93	4.659	1.280	84.475	72.53
Average			89.03	Average			72.66

Tables (5) and Figures (3 and 4) show the equilibrium isotherms for each heavy metal (Cd^{+2} and Co^{+2}) onto biochar treated sandy soil (at 0% biochar). The findings demonstrated that soil absorbed the initial concentration of the heavy metal ions from the aqueous solution to a degree of approximately 89.03 and 72.66% of (Cd and Co, respectively) for sandy soil treated with 0% biochar.

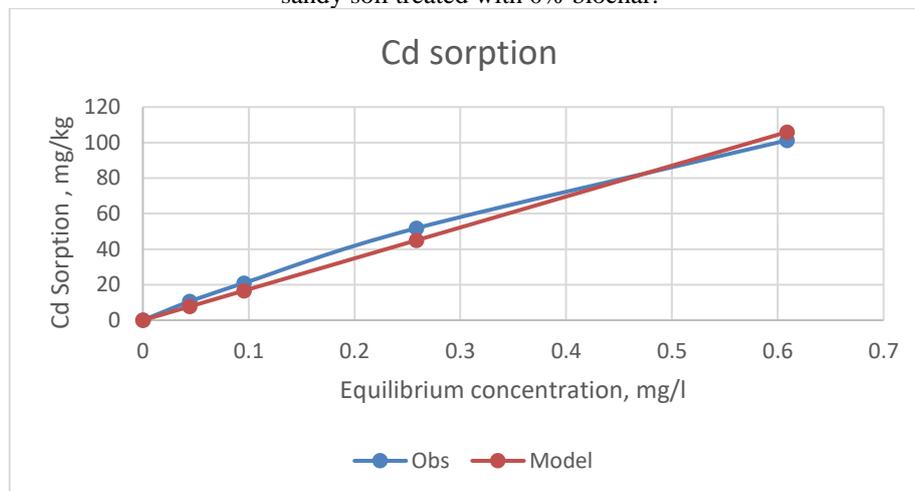


Figure (3). Linear isotherm of Cd on sandy soil treated with 0% biochar

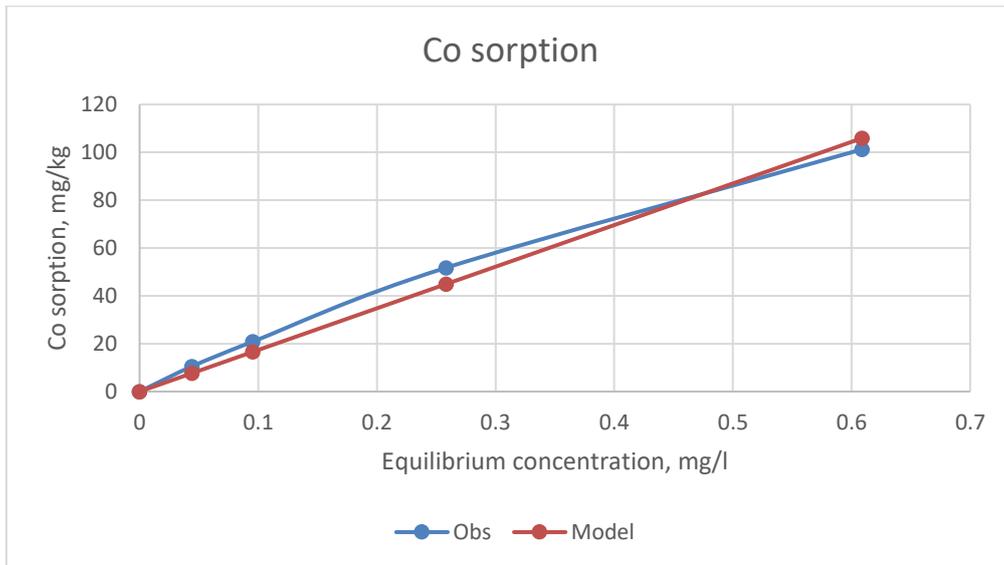


Figure (4). Linear isotherm of Co on sandy soil treated with 0% biochar

The equilibrium sorption-adsorption of heavy metals (Cd and Co) ions on sandy soil treated with biochar at 1% are shown in Table (6). The sorption-adsorption capacity ranged from 10.855 to 103.410 mg/kg (as Cd), 9.745 to 94.025 mg/kg (as Co). The average sorption-adsorption percentage were 90.98% (as Cd), 82.23% (as Co).

Table (6). Equilibrium sorption-adsorption capacity of heavy metals on sandy soil mixed with 1% biochar

Cd^{2+}				Co^{2+}			
C_0 mg/l	C_e mg/l	q_e mg/kg	Sorption %	C_0 mg/l	C_e mg/l	Q_e mg/kg	Sorption %
0.000	0.0000	0.000	0.00	0.000	0.0000	0.000	0.00
0.466	0.0317	10.855	93.20	0.466	0.0761	9.745	83.67
0.932	0.0741	21.443	92.05	0.932	0.1492	19.564	83.98
2.330	0.2350	52.363	89.91	2.330	0.4535	46.900	80.53
4.659	0.5226	103.410	88.78	4.659	0.8980	94.025	80.73
Average			90.38	Average			82.23

The equilibrium sorption-adsorption of heavy metals (Cd and Co) ions on sandy soil treated with biochar at 2.5% are shown in Table (7). The sorption-adsorption capacity ranged from 10.490 to 105.649 mg/kg (as Cd), 10.022 to 100.718 mg/kg (as Co). The average sorption-adsorption percentage were 90.98% (as Cd), 86.36% (as Co).

Table (7). Equilibrium sorption-adsorption capacity of heavy metals on sandy soil mixed with 2.5% biochar

Cd^{2+}				Co^{2+}			
C_0 mg/l	C_e mg/l	q_e mg/kg	Sorption %	C_0 mg/l	C_e mg/l	q_e mg/kg	Sorption %
0.000	0.000	0.000	0.00	0.000	0.0000	0.000	0.00
0.466	0.046	10.490	90.06	0.466	0.0650	10.022	86.04
0.932	0.089	21.080	90.49	0.932	0.1281	20.094	86.26
2.330	0.227	52.575	90.28	2.330	0.3101	50.484	86.69
4.659	0.433	105.649	90.71	4.659	0.6303	100.718	86.47
Average			90.98	Average			86.36

The equilibrium sorption-adsorption of heavy metals (Cd and Co) ions on sandy soil treated with biochar at 5% are shown in Table (8). The sorption-adsorption capacity ranged from 10.793 to 107.374 mg/kg (as Cd), 10.578 to 106.300 mg/kg (as Co). The average sorption-adsorption percentage were 92.15% (as Cd), 91.12% (as Co).

Table (8). Equilibrium sorption-adsorption capacity of heavy metals on sandy soil mixed with 5% biochar

Cd²⁺				Co²⁺			
C₀ mg/l	C_e mg/l	q_e mg/kg	Sorption %	C₀ mg/l	C_e mg/l	q_e mg/kg	Sorption %
0.000	0.000	0.000	0.00	0.000	0.000	0.000	0.00
0.466	0.034	10.793	92.66	0.466	0.043	10.578	90.82
0.932	0.076	21.405	91.89	0.932	0.082	21.245	91.20
2.330	0.190	53.498	91.86	2.330	0.205	53.113	91.20
4.659	0.364	107.374	92.19	4.659	0.407	106.300	91.26
Average			92.15	Average			91.12

Figures (5 and 6) show the equilibrium isotherms for each heavy metal (Cd⁺² and Co⁺²) onto biochar- treated sandy soil (at 5%). The sorption-adsorption capacity was increased as the application rate of biochar increased (Senthilkumar & Prasad, 2020). In addition, BC has porous structure, charged surface, and surface functional groups (such as carboxyl, hydroxyl, phenolic hydroxyl, and carbonyl groups). These properties are the important factors that influence the migration, transformation, and bioavailability of heavy metals in soil (Nartey & Zhao, 2014).

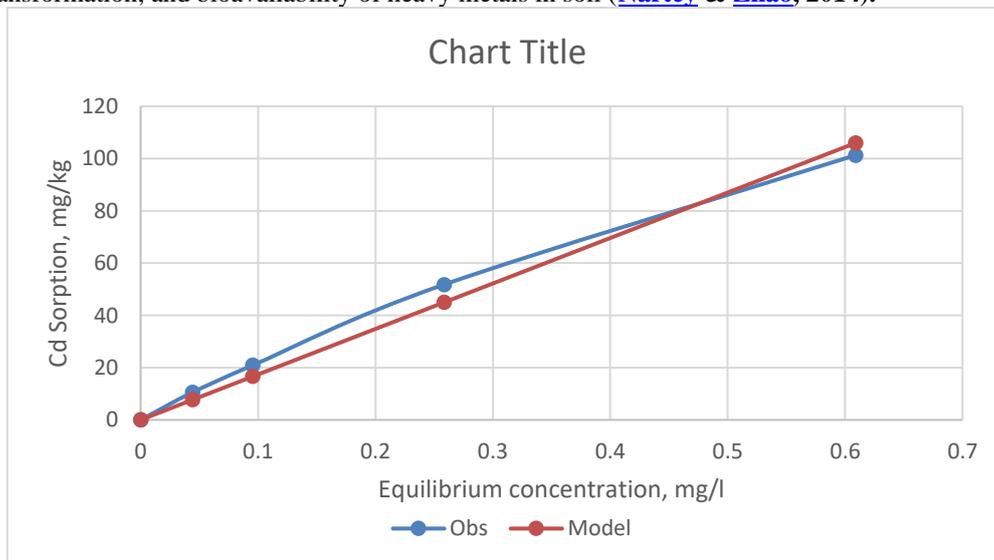


Figure (5). Linear isotherm of Cd on sandy soil treated with 5% biochar

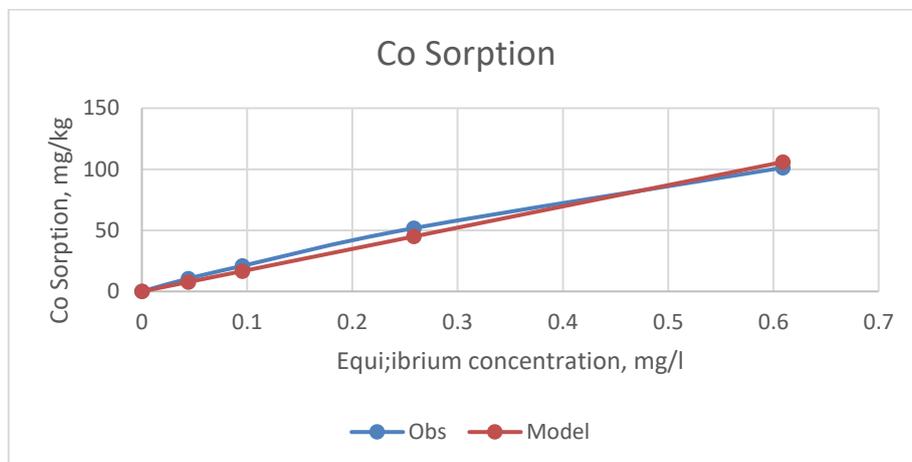


Figure (6). Linear isotherm of Co on sandy soil treated with 5% biochar

The initial concentration of heavy metal ions is a crucial component affecting adsorption since the adsorbent's ability to absorb these ions is restricted to a certain amount. The data in Tables 5 through 8 show that as the initial concentration increases, the percentage of ions adsorbed decreases. The actual number of ions adsorbed per unit mass of the adsorbent, on the other hand, rose in proportion to the initial ion concentration in the test solution, as shown in Tables 5 to 8.

Because there are a lot of surface-active sites compared to the total number of metal ions in the solution, all of the metal ions can interact with the soil at low concentrations and be quickly extracted from the solution. The data in Tables (5 to 8) show that the percentage of ions that were adsorbed decreased as the initial concentration of metal ions rose. The actual number of ions adsorbed per unit mass of the adsorbent, however, likewise rose with increasing beginning ion concentrations in the test solution, as these tables clearly show.

Since all metal ions interact with soil at low concentrations, they are quickly extracted from the solution because of the large proportion of surface-active sites to total metal ions. In contrast, higher concentrations result in a higher adsorption of metal ions per unit weight of the adsorbent, which is represented by the symbol q_e . The experiments by **Karthikeyan et al. (2004)** and **Mohanty et al. (2005)** showed that using larger concentrations of metal ions allowed for the evaluation of the adsorbent's maximal adsorption capability.

The mechanics behind the adsorption of cations onto the surface of adsorbents can be clarified using the

adsorption isotherm, and equilibrium studies are essential for determining the adsorbent's capacity. Several isotherm models, including linear, Freundlich, Langmuir, Langmuir–Freundlich, Generalized Langmuir–Freundlich, and two new models, were used in this study to examine the experimental data in order to provide a thorough analysis of the adsorption isotherm, as shown in Tables (9 to 12).

In this work, adsorption isotherm models were investigated through the analysis of experimental data. According to **Abdulrasaq and Basiru (2010)**, The sorption process is often described using adsorption isotherms like Langmuir and Freundlich models (**Ali et al., 2023; Ola et al., 2025**). These models provide information about the sorption-adsorption capacity and affinity of heavy metals.

In sandy soil treated with 0% biochar, the coarser texture and reduced surface area contribute to less efficient sorption-adsorption processes. This type of soil is particularly susceptible to leaching, resulting in the potential loss of both nutrients and contaminants instead of their retention (Ali et al., 2023). Conversely, sandy soil treated with biochar, characterized by a mixture of finer particles and organic matter, enable more intricate interactions such as ion exchange and surface adsorption, which improve the retention of heavy metals. Additionally, the structural properties of this soil type enhance water retention, thereby increasing the duration of contact between metal ions and soil particles (**Razzaghi et al., 2020**).

Table (9). Sorption-Adsorption isotherm parameters of models for heavy metals sorption-adsorption on sandy soil treated with 0% biochar

Isotherm model	Parameters	Cd	Co
Linear	Kd	172.77	66.56
	R ²	0.9898	0.9995
Freundlich	Kf	153.614	66.653
	1/n	1.2067	1.0259
Langmuir	R ²	0.9993	0.9997
	qm	343.01	1253.65
	b	0.6879	0.0564
New model (GK1)	R ²	1.0000	0.9998
	qm	198.20	774.41
	K	1.1743	0.0904
Langmuir-Partition Isotherm	R ²	1.0000	0.9998
	q0	105.33	21.04
	b	1.5496	0.5181
	Kp	82.2872	59.5297
New model (GK3)	R ²	0.9999	0.9998
	K1	235.775	70.000
	K2	0.686	0.046
	K3	238.891	238.891
	R ²	1.0000	0.9998

Table (10). Sorption-Adsorption isotherm parameters of models for heavy metals sorption-adsorption on sandy soil treated with 1% biochar

Isotherm model	Parameters	Cd	Co
Linear	Kd	203.92	105.12
	R ²	0.9908	0.4797
	Kf	175.716	103.269
Freundlich	1/n	1.2166	1.0674
	R ²	0.9998	0.9985
Langmuir	qm	377.97	1442.46
	b	0.7174	0.0774
	R ²	0.9982	0.9979
GK1	qm	219.48	900.61
	K	1.2145	0.1227
	R ²	0.998	0.9979
GK2	Kb	175.72	200.00
	n	0.1781	0.9503
	R ²	0.9998	0.9395
Langmuir-Partition Isotherm	q0	14.51	26.90
	b	19.1702	1.1469
	Kp	172.59	88.50
	R ²	1.0000	0.9982

Table (11). Sorption-Adsorption isotherm parameters of models for heavy metals sorption-adsorption on sandy soil treated with 2.5% biochar

Isotherm model	Parameters	Cd	Co
Linear	Kd	241.21	160.23
	R ²	0.9993	0.9999
Freundlich	Kf	252.172	160.030
	1/n	0.9589	1.0019
	R ²	0.9998	0.9999
Langmuir	qm	10588.52	2111.59
	b	0.0230	0.0792
	R ²	0.9991	0.9998
GK1	qm	6014.54	1293.20
	K	0.0404	0.1284
	R ²	0.9992	0.9998
GK2	Kb	7117.03	680.48
	n	9.1022	0.0084
	R ²	0.9993	0.9999
Langmuir-Freundlich	qm	2729.99	1862.11
	b	0.0977	0.0921
	n	0.9386	0.9706
	R ²	0.9997	0.9999
Langmuir-Partition Isotherm	q0	137.29	21.25
	b	0.213	0.4078
	Kp	241.2937	153.1367
	R ²	0.9993	0.9999

Table (12). Sorption-Adsorption isotherm parameters of models for heavy metals sorption-adsorption on sandy soil treated with 5% biochar

Isotherm model	Parameters	Cd	Co
Linear	K_d	292.19	260.60
	R^2	0.9994	0.9999
Freundlich	K_f	303.319	263.999
	$1/n$	0.9699	0.9883
Langmuir	R^2	0.9996	1.0000
	q_m	4879.21	2676.13
GK1	b	0.0611	0.1006
	R^2	0.9991	0.9994
GK2	q_m	2873.38	1606.48
	K	0.1032	0.1667
Langmuir-Freundlich	R^2	0.9991	0.9997
	K_b	2247.10	1646.35
Langmuir-Partition Isotherm	n	8.9071	8.1883
	R^2	0.9994	0.9999
Langmuir-Freundlich	q_m	3009.42	2445.19
	b	0.1067	0.1154
Langmuir-Freundlich	n	0.9498	0.9643
	R^2	0.9995	1.0000
Langmuir-Partition Isotherm	q_0	172.91	21.25
	b	0.0001	0.2777
Langmuir-Partition Isotherm	K_p	292.1725	255.1041
	R^2	0.9994	0.9999

Tables (9 to 12) provide the sorption-adsorption isotherm parameters for each model. The findings showed that all evaluated models adequately described the sorption data in cases where the (R^2) was more than 0.99. The sorption-adsorption capacity was in the following order: Cd > Co. Additionally, These characteristics help the soil become more stable and boost its ability to hold nutrients. The sorption-adsorption of heavy metals on soil was better described by the Freundlich, which showed to be more stable and accurate. The distribution coefficients (K_d) for sandy soil treated with biochar are illustrated in Table (13). Metals can be ordered in the following relative sequence: Cd > Co based on their K_d values or soil affinities. The high affinity for heavy metal sorption-adsorption due to its high surface area and negative surface charge density (Ali et al., 2023; Ola et al., 2025). In general, sandy soil treated with biochar exhibited higher sorption-adsorption capacities for heavy metals compared to no addition of biochar. The Cd having the greatest affinity for heavy metals. The results indicated that the K_d was increased as increasing the biochar application rate. When biochar is applied to soil, it can enhance the sorption-adsorption of heavy metals, thereby reducing their bioavailability and potential toxicity. Biochar contains functional groups such as carboxyl, phenolic, and hydroxyl groups that can form complexes with heavy metal ions. These functional groups provide active sites for metal binding. The heavy metals were binding on biochar surface area through the mechanisms of sorption-adsorption, ion

exchange, or surface complexation (Zhou et al., 2021b; Ola et al., 2025).

Sandy soil exhibits a distribution coefficient (K_d) of 172.77 and 66.56 L/kg for Cd, Co respectively (Table 13) suggesting a relatively weaker interaction with heavy metals in comparison to sandy soil treated with biochar in which the K_d account as 292.11 and 260.56 L/kg, respectively at 5% biochar application. The soil treated with biochar demonstrates a greater affinity for heavy metals.

Table (13). Distribution coefficients of heavy metals (K_d value) for sandy soil treated with biochar

Biochar rate %	Cd	Co
0	172.77	66.56
1	203.92	105.12
2.5	241.21	160.22
5	292.11	260.56

The mobility of heavy metals in soil can be described by a distribution coefficient (K_d), which is the ratio of metal concentration in the solid phase to that in the liquid phase at equilibrium (Anderson et al., 1988; Khater, 2007). Distribution coefficients can be computed from the slopes of the adsorption isotherms.

Due to its broad applicability to a variety of adsorption data, linear regression has been used extensively to assess performance and goodness of fit. To bridge the gap between experimental and modeling data, many researchers have also used nonlinear regression analysis extensively. Understanding the importance of both linear and nonlinear regression analysis in different adsorption systems is therefore crucial.

III.2. Performance evaluation of sorption and adsorption models

Tables (9 to 12) illustrate the goodness of fit statistical description. We may infer that all of the isotherm models that were employed in this study provide an acceptable explanation of how heavy metals adsorb. The Linear, Freundlich and the novel model (GK2) were more appropriate than the other isotherm models.

One method for explaining the movement of contaminants in an aqueous medium and the subsequent development of containment strategies is adsorption (Ayawei et al., 2005; Shotoo et al., 2016). Adsorption onto mineral surfaces, precipitation, and ion exchange are the main mechanisms that contribute to the sorption process. The kind of soil and the amount of heavy metals present can affect the precise mechanism (Dube et al., 2001; Sangiunsaak and Punrattanasin, 2014).

The transport and availability of heavy metals to microorganisms and plants are greatly influenced by how long they are retained in the soil. The ecological risks of metals are reduced when they are firmly bonded to soil particles, reducing the possibility that they will leak into groundwater or be absorbed by plants. However, these balances can be upset by changes in environmental conditions, such as greater precipitation or changes in land use, which can lead to more pollutants leaking (Liu et al., 2022).

Understanding adsorption equilibrium is crucial for comprehending the dynamics of the adsorption process. The findings from this study on the adsorption rates of cadmium (Cd), cobalt (Co) across various biochar application rate indicate that the equilibrium state was achieved as predicted by the proposed models. The linear, Freundlich, and new isotherm models effectively characterize the adsorption isotherms observed. Among the soil treated with biochar examined, biochar at 5% exhibited the highest adsorption capacity, while sandy soil without biochar demonstrated the lowest. Furthermore, the adsorption potential across nearly all soil treated with biochar was determined to follow the order of $Cd > Co$, highlighting that the adsorption capacity is significantly influenced by the specific surface area and charge characteristics of the biochar (Gao et al., 2021; Ibrahim et al., 2022).

Future research in this area should focus on using cutting-edge methods, such as nanotechnology, to develop effective sorbents for heavy metals in order to lessen their negative effects on the environment. More predictive models that can anticipate the behavior and ultimate distribution of heavy metals across various soil types, amendment applications, and environmental conditions are also desperately needed. Considering all pertinent variables and parameters, this field of study has yielded important insights into the sorption processes of heavy metals in soils. Additionally, it might encourage the development of fresh, more efficient remediation techniques to address wastewater treatment-related issues. Furthermore, this study indicates that more research is required to examine the competitive mechanisms of heavy metal sorption in relation to the particular soil properties.

The use of soil treated with biochar can greatly enhance the sorption of heavy metals, providing a workable remedy for soil remediation and encouraging the development of healthier soils. Using the treated wastewater for irrigation could also be beneficial. To maximize the use of biochar for particular soil and pollution conditions, more investigation and fieldwork are required. One interesting method for cleaning up contaminated soils or for using the treated wastewater for irrigation is the sorption of heavy metals on soil treated with biochar. It has been demonstrated that biochar can efficiently adsorb heavy metals, lowering their toxicity and bioavailability.

The following are some advantages of using biochar for heavy metal remediation:

1. Economical: Since biochar is frequently made from waste, it is an affordable remediation option.
2. Eco-friendly: Biochar is a naturally occurring, non-toxic, and biodegradable substance that can enhance the fertility and health of soil.
3. Long-term solution: Biochar offers a long-term solution for heavy metal cleanup because it can linger in the environment for generations.

It may draw the conclusion that biochar can enhance soil sustainability and health, but that its use needs to be carefully controlled to prevent adverse environmental effects. They draw attention to the necessity of more study to maximize the production, use, and monitoring of biochar.

In conclusion, managing contaminated sites and protecting the environment depend on an understanding of the sorption-adsorption dynamics of heavy metals in soil treated with biochar. In order to improve predictive models and create efficient remediation plans that are tailored to different soil types and contamination scenarios, ongoing study is necessary. Because of its demonstrated high affinity for heavy metals, biochar holds promise as a remediation method for contaminated water and soil.

CONCLUSION

In conclusion, managing contaminated sites and protecting the environment depend on an understanding of the sorption-adsorption dynamics of heavy metals in soil treated with biochar. In order to improve predictive models and create efficient remediation plans that are tailored to different soil types and contamination scenarios, ongoing study is necessary. Because of its demonstrated high affinity for heavy metals, biochar holds promise as a remediation method for contaminated water and soil, the porous structure of biochar and large surface area make it appropriate to describe by sorption-adsorption than sorption only or adsorption only.

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الملخص العربي

نمذجة امتصاص وامتصاص العناصر الثقيلة على التربة المعاملة بالفحم الحيوي باستخدام واحدة من الأراضي المصرية

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أجريت تجربة معملية لدراسة وتقييم امتصاص العناصر الثقيلة (الكاديوم والكوبالت والنيكل والرصاص) على التربة الرملية المعالجة بالفحم الحيوي بمعدلات 0 و 1 و 2.5 و 5% (وزن/وزن). تم توفير بيانات الامتصاص على بعض نماذج الامتصاص باستخدام برنامج IsoFit وبرنامج Excel كانت نماذج الامتصاص الخطية ونماذج فرويندليتش ولانجموير والنماذج الجديدة المقترحة. تمت مقارنة البيانات المقاسة والمحاكاة إحصائياً لتقييم موثوقية النموذج. وقد لوحظ أن امتصاص العناصر الثقيلة كان أكثر وضوحاً في التربة الرملية المعالجة بالفحم الحيوي، خاصةً عند نسبة 5%. كما انخفضت نسبة الامتصاص بزيادة التركيز الأولي، وزادت أيضاً مع زيادة معدلات الفحم الحيوي. أظهرت النتائج أن متوسط نسبة الامتصاص كان 89.03% في حالة ال Cd و 72.66% في حالة ال Co و 78.46% في حالة ال Ni و 91.49% في حالة ال Pb عند 0% بيوتشار. القيم المقابلة ل 5% بيوتشار كانت 92.15% للكاديوم ، 91.12% للكوبالت ، 85.94% للنيكل و 92.13% للرصاص

كما تم تحليل البيانات التجريبية لفحص نماذج الامتزاز. بلغت معاملات التوزيع (Kd) التي تم الحصول عليها من نموذج الامتصاص الخطي 172.77 و 66.56 و 82.14 و 262.32 لتر/كجم لكل من Cd و Co و Ni و Pb على التوالي عند 0% بيوتشار مما يشير إلى تفاعل أضعف نسبياً مع العناصر الثقيلة مقارنة بالتربة الرملية المعالجة ب 5% بيوتشار، حيث بلغت معاملات Kd 292.11 و 260.56 و 159.34 و 305.76 لتر/كجم على التوالي. تُظهر التربة المعالجة بالفحم الحيوي تقارباً أكبر للعناصر الثقيلة. يمكن ترتيب العناصر وفقاً لقيم Kd الخاصة بها، أي انجذابها للتربة، بالتسلسل النسبي التالي: الرصاص < الكاديوم ، النيكل . الكوبالت. يميل هذا التسلسل العام إلى الاختلاف قليلاً باختلاف أنواع التربة. والنتائج التي تم الحصول عليها واعدة ومفيدة في تسرب مياه الصرف الصناعي إلى التربة والمياه الجوفية.

وفقاً لمدى ملاءمة الوصف الإحصائي. يمكننا أن نستنتج أن جميع نماذج الامتصاص التي تم استخدامها في هذه الدراسة توفر تفسيراً مقبولاً لكيفية امتصاص العناصر الثقيلة. كانت النماذج الخطية ونماذج فرويندليتش والنماذج الجديدة (GK2) أكثر ملاءمة من النماذج الأخرى.

وبصفة عامة، فإن فهم ديناميكيات امتصاص العناصر الثقيلة في أنظمة التربة أمر ضروري لإدارة المواقع الملوثة وحماية الصحة البيئية. يوصي هذا البحث بإجراء دراسات مستقبلية للتحقق من الآلية التنافسية لامتصاص العناصر الثقيلة المرتبطة بمتغيرات خصائص التربة.

وفي الختام، تعتمد إدارة المواقع الملوثة وحماية البيئة على فهم ديناميكيات امتصاص العناصر الثقيلة في التربة المعالجة بالفحم الحيوي. ومن أجل تحسين النماذج التنبؤية ووضع خطط علاجية فعالة تتناسب مع أنواع التربة المختلفة وسيناريوهات التلوث، من الضروري إجراء دراسة مستمرة. ونظراً لما أظهره الفحم الحيوي من تقارب كبير مع العناصر الثقيلة، فإنه يبشر بالخير كوسيلة علاجية للمياه والتربة الملوثة.