

Evaluating Chitosan-Modified Banana Peel Biochar (CMBC) for Removing Heavy Metals from Landfill Leachate

(Menilai Biochar Kulit Pisang Terubah Suai Kitosan (CMBC) untuk Menyingkirkan Logam Berat daripada Larut Lesap Tapak Pelupusan)

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ABSTRACT

Heavy metals in landfill leachate are persistent contaminants that can threaten aquatic ecosystems and human health. This study evaluated chitosan-modified banana peel biochar (CMBC) for the removal of heavy metals from actual landfill leachate collected from the Pulau Burung Sanitary Landfill, Malaysia. Banana peel biochar was produced by hydrothermal carbonization and modified with chitosan at biochar-to-chitosan ratios of 10:0, 8:2, 6:4, 4:6, 2:8, and 0:10. The effects of composition and contact time on metal removal were assessed, while SEM and FTIR were used to examine surface morphology and functional groups. The 8:2 formulation (S2-CMBC) gave the highest removal after 120 min, achieving 100% Zn, 66.2% Fe, 45.8% Pb, and 33.9% Ni removal. For Pb, nonlinear kinetic fitting indicated that the pseudo-first-order model provided a better empirical fit ($R^2 = 0.933$; $RMSE = 1.64 \times 10^{-4} \text{ mg g}^{-1}$) than the pseudo-second-order model ($R^2 = 0.870$; $RMSE = 2.28 \times 10^{-4} \text{ mg g}^{-1}$), although the limited number of sampling times warrants cautious interpretation. Treated leachate met the Malaysian discharge limits for Cu, Fe, Ni, Pb, and Zn under the tested conditions, whereas As and Cr remained above the permissible limits. These findings demonstrate the potential of CMBC as an agricultural-waste-derived adsorbent for landfill leachate treatment while indicating that an additional polishing step is required for complete regulatory compliance.

Keywords: Banana peel; biochar; chitosan; heavy metals; landfill leachate

ABSTRAK

Logam berat dalam larut lesap tapak pelupusan merupakan bahan pencemar tegar yang boleh menjejaskan ekosistem akuatik dan kesihatan manusia. Kajian ini menilai biochar kulit pisang terubah suai kitosan (CMBC) untuk penyingkiran logam berat daripada larut lesap sebenar yang diperolehi daripada Tapak Pelupusan Sanitari Pulau Burung, Malaysia. Biochar kulit pisang dihasilkan melalui pengkarbonan hidrotermal dan diubah suai dengan kitosan pada nisbah biochar:kitosan 10:0, 8:2, 6:4, 4:6, 2:8 dan 0:10. Kesan komposisi dan masa sentuhan terhadap penyingkiran logam dinilai, manakala SEM dan FTIR digunakan untuk meneliti morfologi permukaan dan kumpulan berfungsi. Formulasi 8:2 (S2-CMBC) memberikan penyingkiran tertinggi selepas 120 min, iaitu 100% bagi Zn, 66.2% bagi Fe, 45.8% bagi Pb dan 33.9% bagi Ni. Bagi Pb, pemadanan kinetik tak linear menunjukkan bahawa model pseudo-tertib-pertama memberikan padanan empirikal yang lebih baik ($R^2 = 0.933$; $RMSE = 1.64 \times 10^{-4} \text{ mg g}^{-1}$) berbanding model pseudo-tertib-kedua ($R^2 = 0.870$; $RMSE = 2.28 \times 10^{-4} \text{ mg g}^{-1}$), namun bilangan masa pensampelan yang terhad memerlukan tafsiran berhati-hati. Larut lesap terawat memenuhi had pelepasan Malaysia bagi Cu, Fe, Ni, Pb dan Zn di bawah keadaan kajian, manakala As dan Cr masih melebihi had yang dibenarkan. Keputusan ini menunjukkan potensi CMBC sebagai bahan penjerap berasaskan sisa pertanian untuk rawatan larut lesap tapak pelupusan dengan keperluan langkah penggilapan tambahan bagi mencapai pematuhan peraturan sepenuhnya.

Kata kunci: Biochar; kitosan; kulit pisang; larut lesap tapak pelupusan; logam berat

INTRODUCTION

Lead, nickel, zinc, and iron are among the heavy metals commonly detected in municipal landfill leachate. Once released, these contaminants can migrate into surrounding

soil, surface water, and groundwater, where their persistence and potential for bioaccumulation may pose ecological and human-health risks (Dwanga et al. 2024; Izady et al. 2026). Inadequate landfill operation and leachate management

can further increase the risk of contaminant release (Beinabaj et al. 2023). Consequently, considerable attention has been directed toward low-cost and sustainable materials capable of removing metals from complex aqueous matrices.

Biochar is widely recognized as a cost-effective alternative to activated carbon due to its large surface area, porous structure, high carbon content, variety of functional groups, and excellent adsorption capacity (Dinh, Hou & Dao 2022; Liu et al. 2022). Extensive evidence shows it can effectively remove heavy metals (Panwar & Panwar 2022; Xu et al. 2022). Functional groups such as hydroxyls and carboxylic acids promote metal ion adsorption on the surface of biochar (Abd-Talib et al. 2020; Oladipo, Ahaka & Gazi 2019; Zhao et al. 2020). Biochar produced from banana is especially attractive due to its abundance and specific physicochemical properties, which may enhance its adsorption capacity (Tsaoria, Gareso & Tahir 2026).

According to Muhaidin et al. (2024), unmodified biochar generally lacks enough active functional groups to efficiently chelate metals. To address this issue, many researchers have explored enhancing biochar with biopolymers and modifying its surface characteristics. Chitosan, a biopolymer, has been shown to enhance the material's chelation capacity and adsorption efficiency (Phiri et al. 2024; Roy et al. 2022). Because of its superior chelating properties compared with many other adsorbents, chitosan is often used in environmental remediation (Manubolu, Pathakoti & Leszczynski 2024). This substance, a main component of arthropod exoskeletons, is a biopolymer produced by deacetylating chitin (Yu et al. 2023). The degree of deacetylation and the arrangement of acetyl groups along the polymer chain strongly influence chitosan properties. The hydroxyl (-OH) and amino (-NH₂) groups in chitosan serve as active sites, allowing them to form bonds readily with heavy metal ions, as reported by Singh, Smiatek and Moerschbacher (2023) and Skwarczynska-Wojas et al. (2022). Furthermore, numerous studies have demonstrated that chitosan-modified biochar significantly improves adsorption efficiency (Fan et al. 2023; Zhang, Li & Wang 2025). A recent study also indicates that the removal efficiency of chitosan-enhanced biochar made from Chinese herbal waste is strongly affected by contact time (Wang et al. 2024). They also emphasize the importance of physicochemical characteristics and other parameters, such as pH, in heavy-metal removal. Similarly, Perera et al. (2023) state that the amine and hydroxyl groups in chitosan are vital for improving Cr(VI) removal.

Despite growing interest in modified biochars, important uncertainties remain regarding how surface morphology and functional groups influence adsorption performance, particularly in complex multi-metal matrices. SEM and FTIR are useful complementary techniques for

examining surface morphology and identifying functional groups potentially involved in metal binding; however, such characterization should be interpreted as supporting evidence rather than direct proof of a specific adsorption mechanism (Danya et al. 2024). In addition, many published studies employ single-metal solutions or synthetic wastewater, which may not reflect competitive interactions in actual landfill leachate. Therefore, this study evaluates chitosan-modified banana peel biochar (CMBC) for simultaneous heavy-metal removal from actual Malaysian landfill leachate by determining the effects of biochar-to-chitosan ratio and contact time, characterizing the adsorbent using SEM and FTIR, evaluating Pb adsorption kinetics using nonlinear pseudo-first-order and pseudo-second-order models, and comparing treated leachate concentrations with Malaysian regulatory discharge limits.

MATERIALS AND METHODS

LEACHATE COLLECTION AND CHARACTERISATION

Leachate samples were collected from the Pulau Burung Sanitary Landfill (PBSL), Penang, Malaysia, using 20 L acid-washed polyethylene bottles. Samples were transported in iceboxes and stored at 4 °C prior to analysis. For metal quantification, samples were filtered through 0.45 µm syringe filters, acidified to pH 2 with nitric acid, and analyzed for Fe, Ni, Pb, and Zn concentrations using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Avio 200).

PREPARATION OF BANANA PEEL BIOCHAR (BPB)

Cavendish banana peels were washed, oven-dried at 105 °C for 24 h, and ground into a powder. A 1.5 g sample was soaked in 30 mL of 20% H₃PO₄ for 2 h, then hydrothermally carbonized at 230 °C for 2 h in a Teflon-lined autoclave. The resulting solid was rinsed with distilled water and oven-dried at 80 °C overnight to produce the BPB.

SYNTHESIS OF CHITOSAN-MODIFIED BIOCHAR (CMBC)

Chitosan (degree of deacetylation: 85-90%; molecular weight: 9000-10000 g mol⁻¹) was obtained from Chitosan Vietnam. CMBC formulations were prepared at BPB:chitosan weight ratios of 10:0 (S1), 8:2 (S2), 6:4 (S3), 4:6 (S4), 2:8 (S5), and 0:10 (S6), using a total solid mass of 4 g for each formulation. S1 (100% biochar) and S6 (100% chitosan) served as material controls. Each mixture was dispersed in 180 mL of 2% (v/v) acetic acid and stirred for 30 min before being added dropwise to 900 mL of 1.2% NaOH solution. After 12 h, the precipitated material was filtered, washed with deionized water, and dried at 70 °C for 24 h.

CHARACTERISATION OF BIOCHAR, CHITOSAN AND CHITOSAN-MODIFIED BIOCHAR

A Scanning Electron Microscope (SEM, Zeiss EVO MA 10, Germany) operated at an accelerating voltage of 10 kV and a magnification of approximately 1000× was used to examine the surface morphology of the samples. This allowed for a detailed examination of the pore structure and surface characteristics of both unmodified and chitosan-modified biochar, following methods outlined in similar research (Perera et al. 2023). Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu IRTracer-100, Japan) was used to identify functional groups on the biochar surface. Spectra were obtained over 4000–500 cm⁻¹, capturing the primary absorption bands linked to hydroxyl, amino, and carboxyl groups involved in metal binding (Bak, Thomas & Kołodyńska 2022; Wang et al. 2020). The physicochemical properties of biochar, such as pH, electrical conductivity (EC), moisture, and ash content, were evaluated in accordance with ASTM D1762-84 standards (ASTM 2021).

BATCH ADSORPTION EXPERIMENT

In the batch adsorption experiments, 0.2 g of CMBC was added to 20 mL of raw leachate in 100 mL conical flasks. The mixtures were stirred at 120 rpm at room temperature for 10, 60, and 120 min. These contact times represented short, intermediate, and longer adsorption intervals and were selected with reference to previous kinetic studies of chitosan-modified biochar (Wang et al. 2024). Initial and residual concentrations of Fe, Ni, Pb, and Zn were measured by ICP-OES after filtration. Removal efficiency (R, %) was calculated using Equation (1):

$$R (\%) = [(C_0 - C_e) / C_0] \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium metal concentrations (mg L⁻¹), respectively.

STATISTICAL ANALYSIS

All adsorption experiments were conducted in triplicate. For comparison of the two experimental factors, triplicate measurements for each ratio–time combination were summarized as mean values and analysed using two-factor ANOVA without replication. The analysis assessed the main effects of (i) CMBC ratio and (ii) contact time on removal efficiency for each metal. Because each ratio–time combination was represented by a single mean value in the ANOVA, the ratio × time interaction could not be estimated. The analysis was therefore used as a preliminary assessment of the individual main effects rather than as a test of interaction. Statistical significance was evaluated at $p < 0.05$.

KINETIC MODELLING (PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER)

Adsorption kinetics of Pb by the optimized adsorbent (S2-CMBC; biochar:chitosan = 8:2) were evaluated at contact times of 10, 60, and 120 min under the batch conditions described earlier. The adsorption capacity at time t , q_t (mg g⁻¹), was calculated from concentration measurements using Equation (2), where C_0 is the initial Pb concentration (mg L⁻¹), C_t is the Pb concentration at time t (mg L⁻¹), V is the leachate volume (L), and m is the adsorbent mass (g). The experimental q_t data were fitted to the nonlinear pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models given in Equations (3) and (4), respectively. In these models, q_e is the equilibrium adsorption capacity (mg g⁻¹), k_1 is the PFO rate constant (min⁻¹), and k_2 is the PSO rate constant (g mg⁻¹ min⁻¹). Nonlinear least-squares regression was performed in Microsoft Excel Solver using the Generalized Reduced Gradient (GRG) Nonlinear algorithm. The parameters (q_e , k_1) for PFO and (q_e , k_2) for PSO were estimated by minimizing the sum of squared errors between experimental and model-predicted q_t values, subject to non-negativity constraints. Model performance was evaluated using the coefficient of determination (R^2) and root mean square error (RMSE), defined in Equations (5) and (6). A better empirical fit was indicated by R^2 closer to 1 and lower RMSE. The fitted curves in Figure 4 were generated from the estimated parameters using the respective nonlinear kinetic equations and visualized using Python (Matplotlib).

$$q_t = [(C_0 - C_t)V] / m \quad (2)$$

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (3)$$

$$q_t = (k_2 q_e^2 t) / (1 + k_2 q_e t) \quad (4)$$

$$R^2 = 1 - [\sum_{i=1}^n (q_{t,\text{exp},i} - q_{t,\text{pred},i})^2 / \sum_{i=1}^n (q_{t,\text{exp},i} - \bar{q}_{t,\text{exp}})^2] \quad (5)$$

$$\text{RMSE} = \sqrt{\{(1/n) \sum_{i=1}^n (q_{t,\text{exp},i} - q_{t,\text{pred},i})^2\}} \quad (6)$$

where $q_{t,\text{exp},i}$ and $q_{t,\text{pred},i}$ are the experimental and model-predicted adsorption capacities at the i th time point, respectively; $\bar{q}_{t,\text{exp}}$ is the mean experimental adsorption capacity; and n is the number of kinetic observations.

RESULTS AND DISCUSSION

PHYSICOCHEMICAL CHARACTERISTICS OF BANANA PEEL BIOCHAR (BPB)

Table 1 presents the properties of BPB, including biochar yield, pH, ash content, moisture content, and electrical conductivity (EC). It also summarizes the physicochemical properties of banana peel biochar

(BPB). The biochar yield was 36%, indicating the fraction of dry feedstock retained after hydrothermal carbonization and subsequent processing. BPB had an acidic pH of 4.54, low ash content (1.1%), moisture content of 6.0%, and an electrical conductivity of 0.610 dS m⁻¹. The acidic pH is consistent with the presence of oxygen-containing surface functionalities, whereas the low ash content indicates a relatively small inorganic fraction. These properties provide baseline information for interpreting the adsorption behaviour of BPB and its chitosan-modified composites; however, adsorption performance also depends strongly on solution chemistry and the accessibility of surface binding sites. The pH value reported here refers to the prepared BPB and should not be interpreted as the pH of the raw leachate. Because leachate pH was not systematically monitored at each contact time in the present experimental design, the observed differences in metal removal cannot be attributed specifically to pH variation. Future studies should monitor initial and final solution pH and include controlled pH experiments to evaluate the effects of metal speciation, proton competition, and adsorbent surface charge.

STRUCTURAL ANALYSIS BY SCANNING ELECTRON MICROSCOPY (SEM)

Figure 1 shows the surface morphologies of BPB, chitosan (CS), and S2-CMBC. BPB exhibited a porous and heterogeneous surface, whereas CS showed an irregular, rough morphology. Following modification, S2-CMBC displayed a visibly rougher and more heterogeneous surface than BPB, with material deposited across and within portions of the porous structure. The altered morphology is consistent with the incorporation of chitosan onto the BPB surface. Some pore narrowing or partial blockage is also apparent, suggesting that excessive chitosan loading could reduce access to the native biochar pore network. These SEM observations provide morphological evidence of surface modification but do not, by themselves, establish the chemical nature of biochar–chitosan interactions.

STRUCTURAL ANALYSIS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The FTIR spectra are shown in Figure 2. BPB after metal adsorption exhibited a broad –OH band at approximately 3331.7 cm⁻¹ and C–H stretching bands at 2925.02 and 2853.1 cm⁻¹. Additional bands were observed in the fingerprint region, including features near 1598.21, 1299.9, 1232.1, and 1083.1 cm⁻¹, consistent with oxygen-containing functional groups. The CS spectrum showed the characteristic broad –OH/–NH stretching region near 3315.54 cm⁻¹, a –CH₂ band at 2880.03 cm⁻¹, and bands associated with amide and C–O/C–O–C functionalities. For S2-CMBC after treatment, the broad band near 3300.1 cm⁻¹ and bands at 2920.8 and 2862.2 cm⁻¹ were retained, while changes were observed in the amide- and oxygen-containing functional-group regions. The shifts and changes in band intensity are consistent with modification of the chemical environment of –NH₂, –OH, amide, and C–O-containing groups during exposure to the multi-metal leachate. Together with the SEM observations, the FTIR results support the involvement of oxygen- and nitrogen-containing surface functionalities in metal uptake, although they do not identify a single exclusive adsorption mechanism. Differences in removal among Zn, Fe, Pb, and Ni may reflect a combination of metal speciation, hydration behaviour, competition among co-existing ions, and differing affinities for available binding sites in the CMBC matrix.

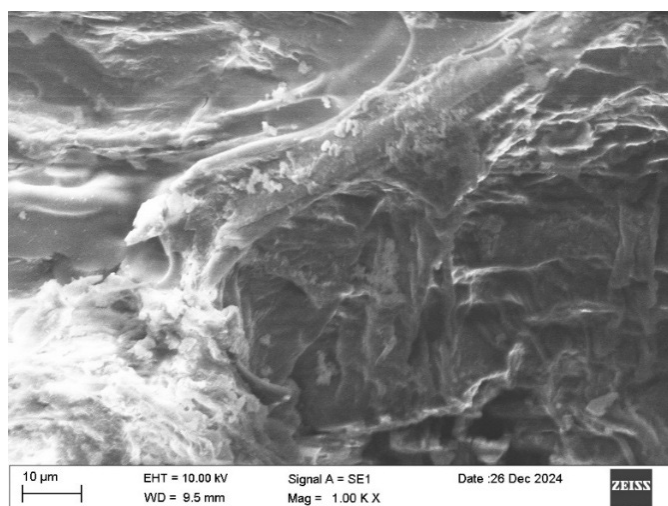
EFFECT OF BIOCHAR-TO-CHITOSAN RATIO AND CONTACT TIME ON HEAVY METAL REMOVAL

The removal efficiencies of Fe, Ni, Pb, and Zn varied with BPB:chitosan ratio and contact time (Figure 3). Overall, S2-CMBC (8:2) gave the highest removal for all four target metals, particularly at 120 min. This result suggests that the 8:2 formulation provided a favourable balance between the native porous structure of BPB and the additional oxygen- and nitrogen-containing functionalities introduced by chitosan.

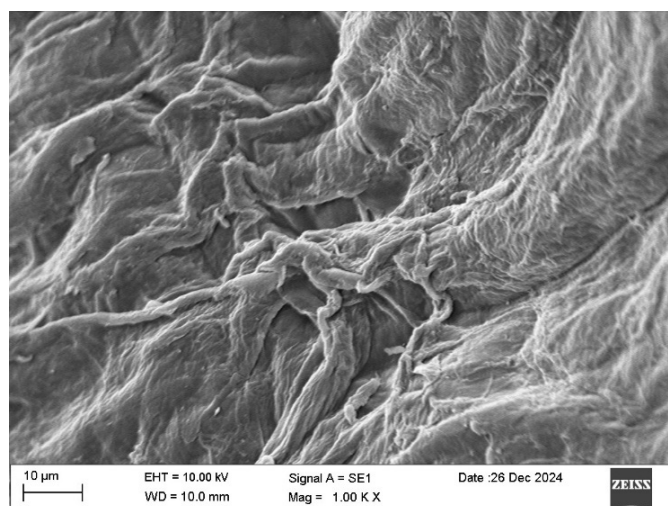
Zn removal increased with contact time and reached 100% for S2 after 120 min. Fe removal reached 66.2%,

TABLE 1. Properties of banana peel biochar (BPB)

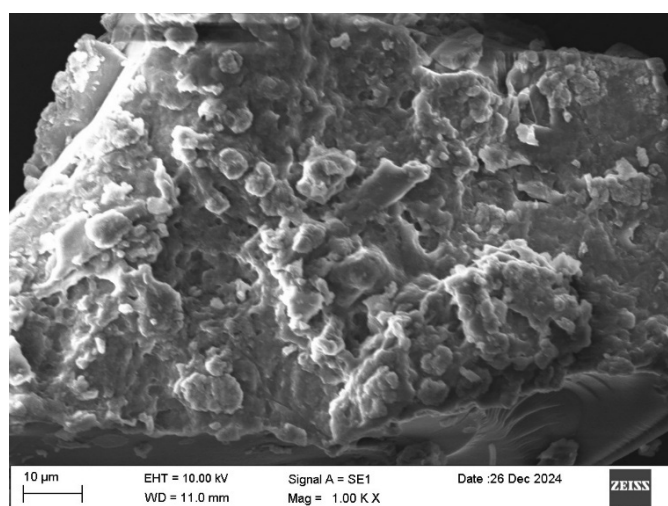
Properties	Values
Biochar yield (%)	36
pH	4.54
Ash content (%)	1.1
Moisture content (%)	6.0
Electrical conductivity (EC), dS/m	0.610



(a)



(b)



(c)

FIGURE 1. SEM micrographs at 1000 $\times$ magnification of (a) banana peel biochar (BPB), (b) chitosan (CS), and (c) chitosan-modified banana peel biochar (S2-CMBC)

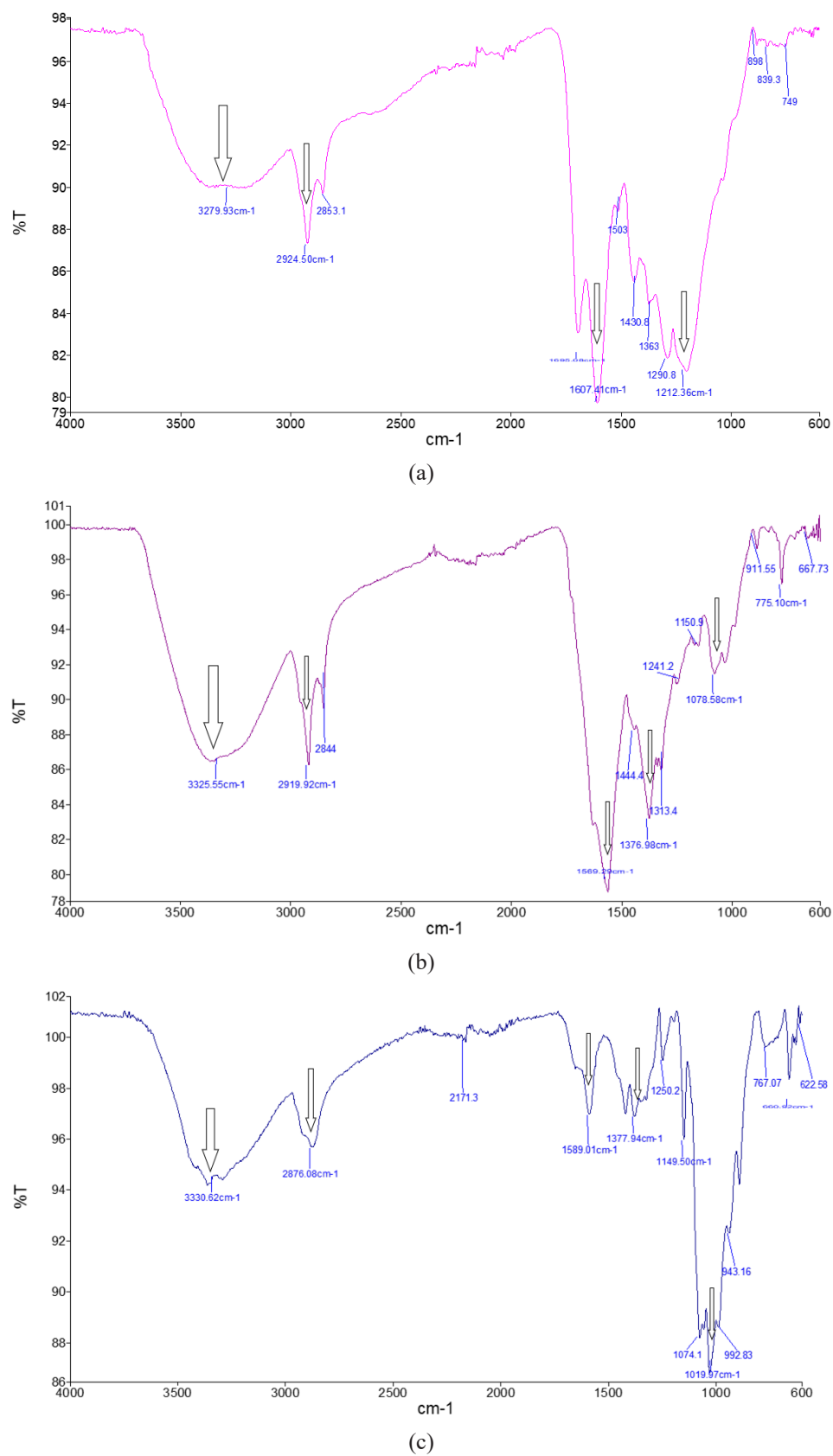


FIGURE 2. FTIR spectra of (a) BPB, (b) CS, and (c) S2-CMBC (8:2) after treatment with landfill leachate

Pb 45.8%, and Ni 33.9% under the same conditions. The lower removal of Pb and Ni relative to Zn and Fe may be associated with differences in aqueous speciation, hydration, competition among co-existing ions, and affinity for the available surface ligands in the real leachate matrix (Negroiu et al. 2021; Song et al. 2021). Formulations containing higher proportions of chitosan showed lower removal, which is consistent with the SEM observation that excessive polymer deposition may partially block the biochar pore network and limit access to adsorption sites. The 8:2 formulation therefore appears to provide a suitable balance between surface functionalization and retention of accessible porosity.

The material controls, S1 (100% biochar) and S6 (100% chitosan), showed lower removal than S2 for the target metals, supporting the benefit of combining the two materials. Pure biochar provides a porous carbonaceous matrix but fewer chitosan-derived amino functionalities, whereas excessive chitosan can coat or obstruct portions of the pore structure. The performance of S2 is therefore interpreted as a composite effect of accessible biochar porosity and chitosan-derived functional groups rather than evidence for a single adsorption pathway.

Figure 3 summarizes the removal efficiencies of Pb, Ni, Zn, and Fe across the six BPB:chitosan formulations and three contact times. Removal generally increased with longer contact time, indicating that extended exposure allowed greater interaction between dissolved metal species and available adsorption sites. S2-CMBC achieved the highest removal after 120 min: Zn (100%), Fe (66.2%), Pb (45.8%), and Ni (33.9%). The observed time dependence is consistent with adsorption progressing toward apparent equilibrium over the tested interval, although the present dataset is not sufficient to establish a specific diffusion-controlled rate mechanism.

The main effects of biochar:chitosan ratio and contact time on Fe, Ni, Pb, and Zn removal were statistically significant ($p < 0.05$). S2-CMBC (8:2) consistently produced the highest removal, reaching 100% for Zn, 66.2% for Fe, 45.8% for Pb, and 33.9% for Ni after 120 min. S1 (10:0) and S6 (0:10) showed lower removal, indicating that the combined biochar–chitosan formulation performed better than either material alone under the tested conditions. Because the ANOVA used mean values from triplicate measurements and was conducted without replication, the analysis was limited to the main effects of ratio and contact time; their interaction could not be evaluated. These statistical results should therefore be interpreted as a preliminary assessment of the individual factors.

Longer contact time generally increased removal efficiency, consistent with progressive occupation of available surface sites over the experimental period. SEM showed substantial changes in surface morphology after chitosan modification, while FTIR indicated the

presence of $-OH$, $-NH_2$, amide, and oxygen-containing groups that may participate in metal uptake. These observations support the interpretation that both the porous biochar matrix and chitosan-derived functional groups contribute to CMBC performance, particularly at the 8:2 ratio where functionalization was achieved without the more extensive pore coverage associated with higher chitosan contents (Perera et al. 2023).

Table 2 compares the performance of S2-CMBC with previously reported chitosan-modified biochars. Under the present conditions, S2-CMBC (8:2) removed 100% of Zn, 66.2% of Fe, 45.8% of Pb, and 33.9% of Ni within 2 h. The Pb removal was lower than values reported for chitosan-modified potato-peel biochar (54.3% at 4 h) (Hussain, Maitra & Khan 2017), sludge-based biochar/chitosan composite (94.3%) (Song et al. 2021), and banana-waste-derived adsorbent (99.8%) (Negroiu et al. 2021). These percentages should not be compared as intrinsic material performance because the studies differ in initial metal concentration, adsorbent dosage, solution pH, contact time, feedstock properties, surface modification, and matrix composition. Importantly, the present work used raw landfill leachate, in which Pb competes with co-existing metals and other dissolved constituents for available adsorption sites, whereas several comparison studies used synthetic or more controlled matrices. Such competitive interactions and differences in solution chemistry may contribute to the lower Pb removal observed here. For Zn, the complete removal obtained in this study compares favourably with the 94.1% reported by Negroiu et al. (2021). Overall, the results indicate that CMBC can provide useful multi-metal removal in a complex real-leachate matrix, although direct cross-study comparison requires careful consideration of operating conditions.

HEAVY METAL CONCENTRATION IN LEACHATE AFTER ADSORPTION

Table 3 compares the concentrations of metals in landfill leachate after treatment with S2-CMBC (8:2) against the permissible discharge limits specified in Malaysia's Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 (DOE 2009). The treatment achieved concentrations below the specified discharge limits for Cu (0.171 mg L^{-1}), Fe (1.455 mg L^{-1}), Ni (0.116 mg L^{-1}), Pb (0.064 mg L^{-1}), and Zn (not detected). These results indicate that S2-CMBC was effective in reducing several regulated metals to compliant concentrations under the tested batch conditions.

In contrast, As (0.387 mg L^{-1}) and Cr (0.142 mg L^{-1}) remained above their respective permissible limit of 0.05 mg L^{-1} . The treated As concentration was approximately 7.7 times the limit, while Cr was approximately 2.8 times the limit. Thus, although CMBC

improved the overall metal profile of the leachate, the treatment was insufficient as a standalone process to achieve complete regulatory compliance.

For metals reported as not detected (ND), concentrations were below the analytical detection limit and were therefore considered compliant with the corresponding regulatory threshold where one was specified. From a practical treatment perspective, the present CMBC configuration could serve as an adsorption step for reducing Cu, Fe, Ni, Pb, and Zn, but additional treatment or polishing specifically targeting As and Cr would be required before discharge. Potential options should be evaluated in future work using the same real-leachate matrix.

PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODELLING OF Pb ADSORPTION

Pb adsorption kinetics were evaluated for S2-CMBC (biochar:chitosan = 8:2) using the measured uptake profile in raw landfill leachate (Figure 4). Pb was selected as the representative metal because it exhibited a measurable time-dependent uptake profile across the tested contact times, whereas Zn approached complete removal and therefore provided limited curvature for discriminating between kinetic models. The experimental adsorption capacity (q_t) increased from $0.00390 \text{ mg g}^{-1}$ at 10 min to $0.00540 \text{ mg g}^{-1}$ at 60 min and then decreased slightly to $0.00500 \text{ mg g}^{-1}$ at 120 min, indicating rapid initial uptake followed by an apparent near-equilibrium region between 60 and 120 min.

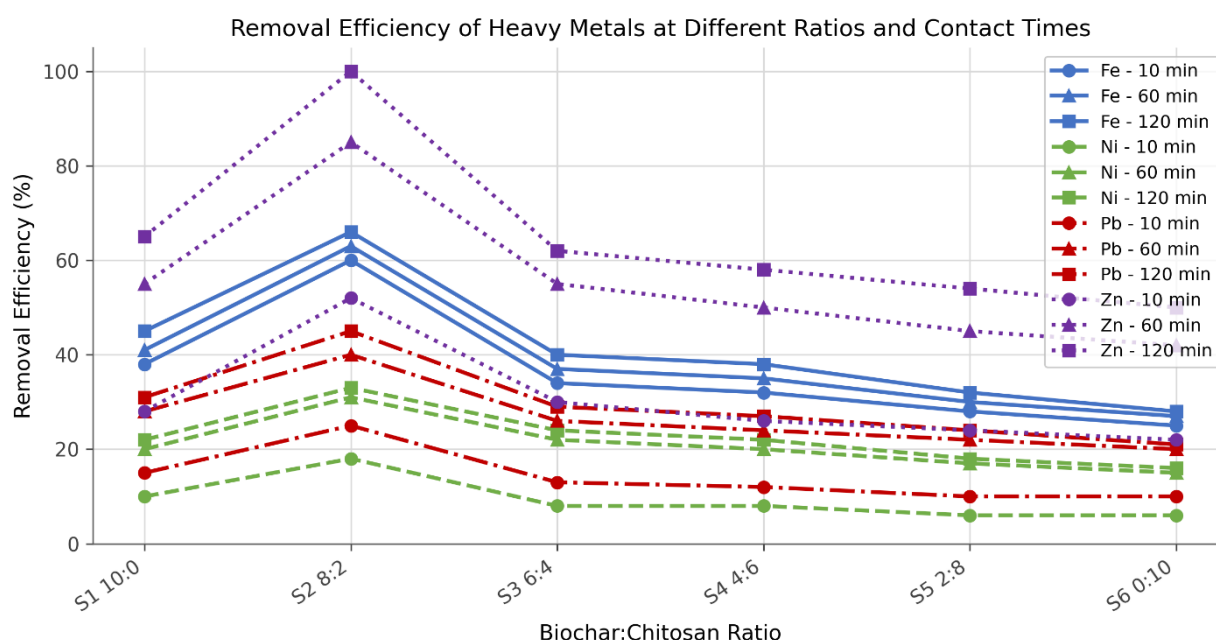


FIGURE 3. Removal efficiencies of Fe, Ni, Pb, and Zn at different biochar:chitosan ratios (S1-S6) and contact times (10, 60, and 120 min)

TABLE 2. Comparison of the findings within this study and those reported in prior scholarly literature

Adsorbents	Chitosan-modified banana peel biochar (8:2 CMBC)	Chitosan-modified potato peel biochar	Chitosan-modified sludge biochar	Chitosan-modified banana waste biochar	Chitosan-modified biochar (ChBC)	Chitosan-modified Chinese herb biochar
Fe	66.2% (2 h)	-	-	57.78	-	-
Ni	33.9% (2 h)	-	-	-	-	-
Pb	45.8% (2 h)	54.3 (4 h)	94.3	-	99.8	99
Zn	100.0% (2 h)	-	-	-	94.1	-
	This study	Hussain, Maitra & Khan (2017)	Song et al. 2021	Negroiu et al. (2021)	Bak, Thomas & Kołodyńska 2022	Wang et al. (2024)

The q_t - t data were fitted to the nonlinear PFO and PSO models. Both models reproduced the overall uptake trend, but the PFO model provided the better empirical fit, with $R^2 = 0.933$ and $RMSE = 1.64 \times 10^{-4} \text{ mg g}^{-1}$, compared with $R^2 = 0.870$ and $RMSE = 2.28 \times 10^{-4} \text{ mg g}^{-1}$ for the PSO model. The lower RMSE for the PFO model indicates a smaller average deviation between the predicted and experimental q_t values for the present dataset. The slight reduction in q_t at 120 min

may reflect variability or matrix effects in raw leachate, including competition among co-existing ions and redistribution between dissolved and particulate phases. Because the kinetic dataset contains only three contact times, these fits should be regarded as indicative empirical comparisons rather than definitive evidence of an adsorption mechanism or rate-limiting step. Future studies should use denser time-point sampling, particularly during the initial uptake period, to improve parameter robustness and mechanistic interpretation.

TABLE 3. Heavy metal concentrations after adsorption compared with permissible discharge limits in Malaysia's Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 (DOE 2009)

Heavy metal element	Average concentration after adsorption (mg/L)	Permissible discharge limit (mg/L)
As	0.387	0.05
Co	ND	NA
Cr	0.142	0.05
Cu	0.171	0.2
Fe	1.455	5.0
Mg	14.67	NA
Ni	0.116	0.2
Pb	0.064	0.1
Zn	ND	2

Note: ND = not detected; NA = not available/not specified in the referenced discharge standard

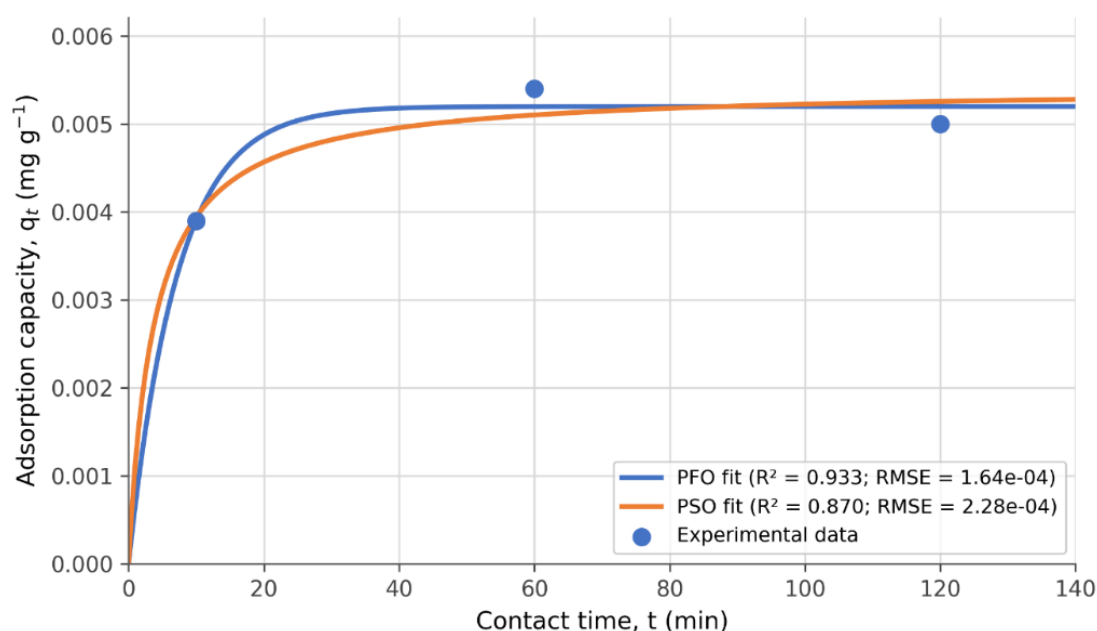


FIGURE 4. Pb adsorption kinetics on S2-CMBC (biochar: chitosan = 8:2) in raw landfill leachate: experimental q_t values at 10, 60, and 120 min with nonlinear pseudo-first-order (PFO) and pseudo-second-order (PSO) model fits. Goodness of fit is indicated by R^2 and RMSE

CONCLUSIONS

This study demonstrates the potential of chitosan-modified banana peel biochar for removing multiple metals from actual landfill leachate. Among the six formulations tested, S2-CMBC (biochar:chitosan = 8:2) provided the best overall performance after 120 min, with removal efficiencies of 100% for Zn, 66.2% for Fe, 45.8% for Pb, and 33.9% for Ni. SEM and FTIR results were consistent with surface modification by chitosan and the presence of oxygen- and nitrogen-containing functional groups that may contribute to metal uptake, although the available characterization does not establish a single adsorption mechanism. For Pb, the nonlinear PFO model provided a better empirical fit than the PSO model; however, the limited number of kinetic sampling points prevents definitive mechanistic discrimination. Under the tested conditions, treated leachate met the Malaysian discharge limits for Cu, Fe, Ni, Pb, and Zn, whereas As and Cr remained above their permissible limits. CMBC therefore shows promise as a low-cost adsorbent derived from agricultural waste, but an additional polishing step would be required to achieve complete regulatory compliance. Future work should include denser kinetic sampling, controlled pH studies, quantitative pore characterization, adsorption-capacity evaluation over a wider concentration range, and treatment optimization for As and Cr. Regeneration studies should also evaluate suitable desorption agents, such as dilute HCl or EDTA, and determine metal recovery, adsorbent stability, regeneration efficiency, and removal performance over repeated adsorption-desorption cycles.

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