Adsorption of Lead(II), Manganese(II), and Copper(II) onto biochar in landfill leachate: implication of non-linear regression analysis

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Abstract
The feasibility of using wood-derived biochar (BC) to remove Pb, Mn, and Cu from landfill leachate was investigated and modeled in this study. The effect of contact time, biochar dosage and particle size on adsorption of the heavy metals onto BC was examined. BC was used in two form i.e. pulverized (PWB) and crushed (CWB) to evaluate the effect of BC particle size on adsorption characteristics. Biochar was produced under the pyrolytic temperature of 740 °C. The kinetics of Pb, Mn, and Cu adsorption onto PWB and CWB were assessed using the pseudo second-order and Elovich models, where both applied models could well describe the adsorption kinetics. Equilibrium adsorption capacity of the heavy metals onto BC in leachate system was evaluated using the Langmuir, non-linearized Freundlich, linearized Freundlich, and Temkin isotherms and found to have the following order for PWB: Non-linearized Freundlich>Temkin>Langmuir>Linearized Freundlich. The Langmuir and linearized Freundlich models could not adequately represent adsorption of the heavy metals onto biochar, especially for CWB. Using the non-linearized Freundlich isotherm significantly reduced adsorption prediction error. The adsorption affinity of PWB for Pb, Mn, and Cu was greater than CWB in all treatments. Wood-derived biochar is suggested to be used for the removal of heavy metals from landfill leachate as an economical adsorbent.

1. Introduction
Effective removal of heavy metals from landfill leachate is of great concern due to the fact that toxic metals can seriously threaten soil and water resources, and therefore the human health even at low concentrations. Landfill leachate may contain a wide range of contaminants at levels enough to raise serious environmental and human health concerns. The majority of published research has focused on removal of ammonia-nitrogen and organic fraction of landfill leachates, such as using biological reactors [1], oxidation processes [2] and membrane separation [3]. Heavy metals content of landfill leachates are known as a serious environmental threat. Various heavy metals may occur in landfill leachates due to the diverse nature of buried wastes. Concentrations of heavy metals in fresh landfill leachate, characterized by lower pH, are usually higher than those in aged leachate [4]. Frequent occurrence of high concentrations of heavy metals in landfill leachate was reported in the literature
Adsorption of heavy metals on carbonaceous materials has recently received considerable attention to remove toxic metals from contaminated aqueous solutions. Salam (2013) investigated the removal of heavy metals from synthetic aqueous solution by adsorption onto carbon nanotubes through a set of batch experiments which showed effective removal of heavy metals [5]. Activated carbon (AC) is a well known strong adsorbent which has been employed to remove heavy metals from different media principally because of its large surface area and high porosity [6-8]. Palm shell activated carbon was successfully used to remove Cu from aqueous solution [9]; but high production expenses of AC may limit its use as adsorbent [10]. Application of economical alternatives to AC has therefore drawn remarkable attention in recent years. For instance, in a study by Soco and Kalemkiewicz (2013), coal fly ash was successfully used for the removal of nickel and copper from a synthetically contaminated aqueous solution [11].

Using of biochar as a novel economical approach in wastewater treatment has attracted considerable attention recently [12]. De Caprariis et al. (2017) employed biochar to remove total organic carbon (TOC) from wastewater, and a very high sorption capacity of biochar was achieved (840 mg/g) [13]. In another study, biochar derived from sewage sludge eliminated Cr from water significantly by 89%, whereas As removal did not exceed 53% [14]. Many studies have focused on the immobilization and mitigation of contaminants, respectively, in soil and effluents [15, 16]; however, investigation on the removal of heavy metals from landfill leachate by biochar has remained limited. This research aimed to investigate the adsorption of Pb(II), Mn(II), and Cu(II) onto wood-derived biochar in fresh landfill leachate. The effects of contact time, adsorbent dosage and particle size on adsorption process were examined. Adsorption kinetics and isotherms of heavy metal ions onto biochar in landfill leachate were specifically investigated in this research.

2. Materials And Methods
2.1. Site description and leachate sampling
Kahrizak landfill which is also known as Aradkooh waste disposal and processing complex is main disposal site of the capital city of Tehran, located at a 25 km distance from the southern part of the
capital city of Tehran having longitude of 51°19′18″E and latitude of 35°27′52″N. Daily more than 8000 tones of wastes are transferred to this landfill. Leachate generated in Kahrizak landfill has long been a serious environmental concern; firstly because of entering all types of municipal wastes, including hazardous household wastes, with poor source separation program, and secondly due to the lack of effective leachate collection and management system. High clay content and therefore low permeability of the land around the landfill caused infiltration of the landfill leachate to be minimal. Therefore, freshly generated leachate at Kahrizak landfill, which is now estimated to be about 637 cubic meters per day [17], flows gravitationally towards the low land next to the burial site creating a leachate lake with a depth of ca. 10 m, with seasonal variations. In this study, the leachate samples were directly collected from the generated leachate stream at the bottom of the waste discharge place at Kahrizak landfill and used for the adsorption experiments. Collected leachate can be classified as relatively fresh leachate based on the low pH values (5.11). Leachate samples were immediately transported to the laboratory. Samples were kept refrigerated at 4 °C without exposure to the ambient air for not more than three days before conducting relevant analysis to prevent potential chemical and biological changes.

2.2. Leachate analysis
Leachate samples characterized according to the Standard Method for the Examination of Water and Wastewater [18]. Raw samples filtered using Whatman Paper Filter No. 1 (pore size: 11 µm) prior to acid digestion in order to remove large particles while retaining suspended solids up to 11 µm in the leachate samples in order to measure the recoverable heavy metals in different phases. Leachate samples were digested with nitric acid, then the digestate passed through MILEXHA 0.45 µm diameter filter followed by the US EPA 3005A method [19]. Partially filtered samples containing suspended particles (up to 11 µm) were analyzed for heavy metal content to imitate close to real conditions, like when landfill leachate is analyzed to control compliance with permissible limits as also suggested by Modin et al. (2011). Samples were digested in triplicate and analyzed for the concentrations of Cd in the final solution using an atomic absorption spectrometer (Perkin Elmer 700). Organic load of the leachate produced at this landfill is markedly higher than that of leachate generated in many other
countries [20, 21]; due to the high content of organics such as food wastes. Received MSW at Kahrizak landfill is characterized by putrifiable fraction of ca. 68% and moisture content of 65%-70% that significantly contribute to high organic load of produced leachate. Elevated ratio of BOD$_5$/COD for landfill leachate as observed in this study indicates the high concentration of biodegradable organic compounds in leachate, and hence a good potential to be biologically degraded. Some characteristics of the leachate are as follow: COD (71245 mg L$^{-1}$); BOD$_5$ (32187 mg L$^{-1}$); BOD$_5$/COD (0.452); TSS (19800 mg L$^{-1}$), TDS (11480 mg L$^{-1}$), N-NO$_3$ (70.34 mg L$^{-1}$), SO$_4$ (1698.12 mg L$^{-1}$); EC (28.86 mS cm$^{-1}$); pH (5.11) and Pb (1.90 mg L$^{-1}$), Mn (7.78 mg L$^{-1}$) and Cu (2.52 mg L$^{-1}$).

2.3. Biochar Preparation

Fresh urban yard trimmings with no pollution background was initially chopped into wood chips of 5-10 cm length and then oven-dried for 48 h. Yard trimmings can be found abundantly in most places and often used for composting or find their way into urban waste stream. Dried wood chips were placed in open crucibles, then weighted, and covered thoroughly with aluminum foil in order to provide an oxygen-limited environment. Biochar derived from the wood chips was produced under the pyrolytic temperature of up to 740 °C with a temperature gradient of ca. 10 °C/min until the desired temperature of 740 ± 5 °C was reached in the muffle furnace under the atmospheric pressure with residence time of 42 min. At the end, samples were kept in the furnace overnight to let them cool down to the room temperature. The produced biochar chips were air-dried over a week, ground using a ceramic mortar and pestle and sieved to 1-2 mm diameter, and mixed thoroughly to gain homogenous crushed wood-derived biochar (CWB). Moreover, some biochar chips were further ground and sieved to 63-75 µm diameter to yield fine-graded biochar to be used as pulverized wood-derived biochar (PWB) in the adsorption experiments. Some physico-chemical properties of the produced biochar are as follow: C (81.5%), H (3.3%), N (0.5%), Ash (3.4%), bulk density (1.5 g/cm$^3$), and pH (9.1).

2.4. Adsorption experiment

The adsorption process of Pb(II), Mn(II) and Cu(II) was conducted under the adjusted pH of 5.1 in order
to eliminate the possibility of formation of metal hydroxide precipitates. Precipitation of heavy metal hydroxides under the pH values of 6.5-7 was reported for heavy metals [22]. Adsorption of heavy metals onto PWB and CWB was carried out versus time at specified intervals up to 24 h. Actual concentrations of Pb(II), Mn(II) and Cu(II) ions in leachate samples were considered as the initial concentration, to simulate real conditions. Each adsorption experiment was conducted in triplicate and the mean values were reported. The percentage removal of heavy metals in the solution was calculated using the following equation

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

Where, \(C_0\) and \(C_e\) are, respectively, the initial and final concentrations of Pb(II), Mn(II) and Cu(II) in leachate samples (mg L\(^{-1}\)). Kinetic solutions were stirred on a shaker at constant rate of 120 rpm at room temperature of 24 ± 2 °C to provide effective interaction of sorbate with sorbent material. At the end of the specified agitation period, obtained mixtures were centrifuged for 15 min at 6000 rpm to separate liquid and solid phases, filtered by Whatman Paper Filter No. 1 (11 µm pore size) and the filtrates were then analyzed for the heavy metals concentrations. The adsorption isotherms were studied in actual leachate system for Pb(II), Mn(II) and Cu(II). Certain quantities of PWB and CWB (0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 5 g) were separately weighted and added to a 100 mL fresh landfill leachate at initial pH of 5.1. The pseudo first-order, pseudo second-order and Elovich models were used to study the kinetics of adsorption of Pb(II), Mn(II) and Cu(II) onto BC in landfill leachate and the Langmuir, non-linearized and linearized Freundlich, and Temkin isotherm models were applied to fit the measured data.

2.5. Error analysis for the kinetic and isotherm models

Non-linear regression as a more general technique to estimate parameters of adsorption models can be used even if the model cannot be linearized. However, isotherm and kinetic models are mainly applied in linear form because less difficult calculations are required to find model parameters. It should be noticed that modifying and linearization of the original model might violate the theories and assumptions behind the development of a given model that means when parameters are estimated
based on linear transformation of a given model it does not necessarily yield best fitting parameters for the nonlinear original model [23]. Error structure of experimental data has been found to be altered when adsorption isotherms transformed into linearized forms. Non-linear regression usually minimizes the error distribution between the experimental and predicted data, unlike linear regression [24]. Therefore linear determination coefficient ($R^2$) should be used to measure the matching degree between experimental and predicted data when linear form of a given adsorption kinetic or isotherm model is applied. Beside linear determination coefficient which is an indicator of the fit between experimental and theoretical data based on used models, the applicability of the applied models can also be verified through error analysis techniques such as sum of error squares (SSE). The Sum of Error Squares SSE is said to be among the widespread used error functions. It can be written as:

$$SSE(\%) = \frac{\sqrt{\sum (q_{e(\text{Experimental})} - q_{e(\text{Calculated})})^2}}{N}$$ (2)

Where, $q_{e(\text{Experimental})}$ is the adsorption capacity at equilibrium condition obtained from adsorption experiments, $q_{e(\text{Calculated})}$ is the calculated value of adsorption capacity at equilibrium state, and $N$ is the number of data points [25].

3. Results And Discussion
3.1. Effect of contact time on the adsorption of Pb, Mn, and Cu onto BC in the leachate

The effect of contact time on the adsorption of Pb, Mn, and Cu in landfill leachate is shown in Figs. 1a and 1b. The adsorbent dosage was fixed at 1 g/100 mL (10 g L$^{-1}$) and the pH value of the fresh leachate was 5.1. The removal rate of the heavy metals experienced a drastic initial increase followed by a gradual rise to reach a plateau, which indicates equilibrium condition. Instant adsorption rate of heavy metals onto BC gradually declined to zero with the equilibrium point of adsorption lay between 150–200 min and 100–150 min for, respectively, PWB and CWB, suggesting that the contact time of 200 min and 150 min is sufficient to establish dynamic balance. The importance of contact time to provide sufficient contact between adsorbates and adsorbent surface has been emphasized by
several authors [24, 26]. It can be inferred from Figs. 1a and 1b that the removal of Pb, Mn, and Cu was greater when PWB was used as adsorbent, compared to CWB. Moreover, longer period of contact time was required for the equilibrium state to be established when biochar with smaller particle size i.e. PWB was used, implying slower occupation of adsorption sites on the surface of PWB due to the greater specific surface provided by PWB relative to CWB. The highest removal rate of 87.96% by PWB was obtained for Pb.

As reaction time prolonged, repulsive forces between the metal ions adsorbed to biochar and those in the aqueous phase might be increased. In addition, unoccupied adsorption sites and therefore adsorption rate will be quickly declined until the establishment of dynamic balance in the system. The same observation was found for Ni uptake from aqueous solution by AC derived from sugar bagasse [26]. From the adsorption diffusion viewpoint, two distinct adsorption stages could be distinguished for the uptake of Pb, Mn, and Cu onto BC in landfill leachate; surface diffusion during which the mass transfer is rapid and physical processes control the adsorption, followed by intra-particle diffusion that is characterized by slow adsorption. Greater adsorption rate for heavy metals was observed for all the applied dosages of BC at initial stages of the experiment, that may be attributed to the higher availability of adsorption sites on BC surface which are rapidly occupied by the solutes in the leachate. When equilibrium is reached mass transfer from the leachate to the surface of BC was significantly restricted (Figs. 1a and 1b), which is consistent with those reported in the literature [21].

3.2. Effect of BC dosage on the adsorption of heavy metals in landfill leachate

BC dosage varied from 0.05 to 5 g/100 ml (0.5 to 50 g L\(^{-1}\)) at initial pH of 5.1, with the reaction times of 200 min and 150 min, respectively, for PWB and CWB. Results indicated that the removal rate of the heavy metals was significantly raised by 1.2, 1.4, and 1.6 times, respectively, for Pb, Mn, and Cu, when PWB content of the leachate increased from 0.5 to 5 g L\(^{-1}\). Obtained results are consistent with the findings of Krishnan et al. (2011), where removal of Ni from aqueous phase increased by AC dosage [26]. The removal rate of Pb, Mn, and Cu did not change significantly as BC content exceeded 2 g/100 mL in leachate, suggesting the optimal dosage of 20 g L\(^{-1}\) for both PWB and CWB to achieve the highest economical adsorption capacity for the heavy metals. Unsaturated adsorption sites may
increase as BC dosage exceeds the optimum amount. The highest removal rate was obtained for Pb followed by Mn and Cu due to addition of PWB (Fig. 1c) and CWB (Fig. 1d).

Removal rate of Mn and Cu was comparable, with slightly higher elimination for Mn. Amount of Pb, Mn, and Cu adsorbed to each gram of BC reduced with rising adsorbent dosage, likely due to the availability of more adsorption sites on the surface of both PWB and CWB. Optimum AC dosage of 7 g/100 mL was found to effectively adsorb COD and NH$_3$-N from landfill leachate [21], which is markedly higher than the optimum dosage of biochar obtained in this study. It might be attributed to the higher levels of COD and NH$_3$-N in leachate compared to those of heavy metals in this study.

Biochar dosage may also induce pH variation, which in turn affects adsorption of adsorbates in aqueous systems by changing the adsorbent surface charge and degree of ionization of adsorbates. Addition of high levels of BC to fresh leachate may increase pH and promote the formation of metal hydroxides. However, adverse effect of low pH on adsorption of Ni onto AC has been reported due to competence with hydrogen ions [27]. The influence of pH on adsorption of heavy metals on various adsorbents has been well documented [28].

### 3.3. Adsorption Kinetics

Batch kinetic experiments were carried out for the adsorption of Pb, Mn, and Cu onto PWB and CWB in landfill leachate. The kinetics for adsorption of heavy metals onto BC was simulated using two kinetic models: pseudo second-order and Elovich kinetic models. The experimental effectiveness is controlled by the adsorption kinetics. Adsorption kinetic models are typically used to investigate the adsorption mechanism and the potential rate of the processes such as mass transfer and chemical reactions [21].

#### 3.3.1. Pseudo second-order kinetic model

The non-linear form of pseudo second-order model is represented as follow:

$$q_t = \frac{k_{2p}q_e^2 t}{1 + k_{2p} q_e t}$$

Where $k_{2p}$ is the second-order adsorption constant (g mg$^{-1}$ min$^{-1}$), $q_e$ is the amount of heavy metals
adsorbed onto biochar when dynamic balance researched (mg g\(^{-1}\)), and \(q_t\) is the amount of adsorbate adsorbed onto biochar at any time, \(t\). In order to gain the linear form of the pseudo second-order kinetic model the following equation should be solved through integration:

\[
\frac{dq_t}{dt} = k_{2p}(q_e - q_t)^2
\]

(4)

If the boundary conditions of \(q_t = 0\) to \(q_t = q_e\) and \(t = 0\) to \(t = t\) is applied, the model can be written as follows:

\[
\frac{t}{q_t} = \frac{1}{k_{2p} q_e^2} + \frac{1}{q_e} t
\]

(5)

Plots of \(t/q_t\) versus \(t\) for adsorption of Pb onto PWB and CWB are illustrated in Fig. 2. Similar graphs could be constructed using the obtained data for Mn and Cu, with the same trend as Pb. Figures 2a and 2b clearly illustrates higher adsorption capacity of PWB compared to CWB for the heavy metals. The pseudo second-order kinetic constants and the theoretical \(q_e\) values using the pseudo second-order expression are given in Tables 1 for all the studied metals. Very high values of \(R^2\) (\(\geq 0.999\)) were found for the pseudo second-order kinetic model in all applied levels of PWB and CWB indicating an excellent linearity. Results showed an excellent agreement between the experimental data and the calculated adsorption capacity by the pseudo second-order kinetic model which is consistent with the literature, where heavy metals in an aqueous solution were removed by carbon nanotubes [5]. Error analysis indicated that deviation occurred by application of the pseudo second-order kinetic model is very small for all levels of BC, regardless of the biochar particle size. This supports the chemisorptions theory behind the pseudo second-order kinetic model for the heavy metals/BC system; however, evaluation of variation of adsorption energy using appropriate isotherms such as Temkin model could provide deeper insight into the nature of metal adsorption onto BC. It can be inferred from Table 1 that the adsorption equilibrium rate for the studied heavy metals, regardless of the BC size, has the following order: Pb > Cu > Mn. The applicability of pseudo second-order model to fit the experimental
kinetics data was also reported for adsorption of heavy metals onto sewage sludge [14]. Predicted adsorption capacity decreased by increasing dosage of PWB and CWB. The adsorption process is mainly a surface phenomenon and increase in adsorption sites on the surface of an adsorbent at a constant adsorbate level could result in alleviated adsorption intensity.

3.3.2. Elovich kinetic model

The Elovich adsorption kinetic equation which was initially developed to describe chemisorption kinetics of gas onto solids [29], has recently gained increasing attention to describe kinetics of adsorption of adsorbates in aqueous phase onto adsorbents. The elovich kinetic model is expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$$

(6)

Where $\alpha$ is the initial adsorption rate (mg g$^{-1}$ min$^{-1}$) and $\beta$ is defined as desorption constant (g mg$^{-1}$) during any experiment [25]. Elovich differential equation can be solved assuming $\alpha \beta t > > 1$ and by applying the boundary conditions of $q_t=0$ at $t = 0$ and $q_t= q_t$ at $t = t$ [29]. Therefore, the linear form of the elovich equation can be presented as follows:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$$

(7)

In order to study the adsorption kinetics using Elovich model a straight line of $q_t$ versus ln $t$ should be plotted to be able to calculate the model constants of $\alpha$ and $\beta$ from the slope and the intercept of the plot. For instance, Pb adsorption capacity of BC predicted by the Elovich kinetic model is shown in Fig. 3. Parameters of the Elovich kinetic model for adsorption of Pb, Mn and Cu onto PWB and CWB are presented in Table 2. Pretty high $R^2$ and low SSE values obtained for the Elovich kinetic model suggesting that adsorption kinetics of the heavy metals onto BC in landfill leachate can be adequately represented by the Elovich kinetic model. However, higher values of $R^2$ and lower values of SSE found for the pseudo second-order kinetic model compared to the Elovich kinetic expression in this study.
Comparison of the kinetic data obtained in this study suggests pseudo second-order kinetic expression is the optimum kinetic expression to represent adsorption of Pb, Mn, and Cu onto BC in landfill leachate.

3.4. Modeling of adsorption isotherms

The equilibrium data were modeled using the Langmuir, non-linearized Freundlich, linearized Freundlich and Temkin isotherms in this study to predict adsorption capacity of PWB and CWB for heavy metals in landfill leachate. Experimental data versus the predicted adsorption of Pb, Mn and Cu onto BC in the leachate using different adsorption isotherms are shown in Fig. 4. Experimental results indicated that Pb could be adsorbed on BC to a higher degree than Mn and Cu. Adsorption of Mn on BC was comparable with that of Cu with slightly higher adsorption for Mn.

3.4.1. Langmuir isotherm

The Langmuir model which is an empirical isotherm assumes uniform energies of adsorption onto the adsorbent surface with no interaction between adsorbate molecules on adjacent sites. All adsorption is also assumed to occur through the same mechanism to form a layer with a thickness of one molecule on solid surface [15]. Once a site is occupied, no further adsorption can proceed at that site based on the Langmuir isotherm representing the surface saturation condition. Langmuir isotherm has been extensively used to evaluate adsorption capacity of a wide range of contaminants such as heavy metals, organic pollutants and dyes [30]. Langmuir model describes a homogeneous adsorption assuming that all the adsorption sites on the surface of a given adsorbent have equal solute affinity. It is also assumed that adsorption of solute at one site does not affect the adsorption at an adjacent site [31]. Therefore, the maximum adsorption capacity obtained by using the Langmuir isotherm is based on complete monolayer coverage of the surface of adsorbent. All adsorption is assumed to occur through the same mechanism. The non-linear expression of Langmuir isotherm model can be illustrated as follows:

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  

where, \( b \) is adsorption equilibrium constant (L mg\(^{-1}\)) which is related to the apparent energy of
adsorption, $q_m$ is the quantity of adsorbate required to form a single monolayer on unit mass of a given adsorbent (mg g$^{-1}$) and $q_e$ is the quantity of adsorbate adsorbed on unit mass of the adsorbent (mg g$^{-1}$) when the equilibrium concentration is $C_e$ (mg L$^{-1}$). Langmuir model equation can be linearized to five different linear types. Details of the various linearized Langmuir expressions and the corresponding plots to determine Langmuir constants i.e. $q_m$ and $b$ were presented in Table 3. Values of the constants for different types of linearized Langmuir isotherm are presented in Table 4 for the adsorption of Pb, Mn and Cu onto BC. Results showed the best fitting parameters for the linearized Langmuir types 1 and 5 for PWB with the highest $R^2$ among the applied linearized forms. Among the five different linearized forms of Langmuir isotherm equations, types 1 and 2 have been used more frequently in the literature [32]. Langmuir isotherm can be further analyzed and the favorable nature of adsorption of adsorbate onto adsorbent can be expressed through determination of the separation factor, $R_L$, which is a dimensionless equilibrium parameter defined by the following equation:

$$R_L = \frac{1}{1 + bC_0}$$

Where $C_0$ is the initial concentration of adsorbate in the bulk solution (mg L$^{-1}$) and $b$ is the Langmuir model constant related to the free energy of adsorption (L mg$^{-1}$). The separation factor, $R_L$, indicates the shape of the isotherm. Values of $0 < R_L < 1$ indicates favorable adsorption, whereas $R_L > 1$ represents an unfavorable adsorption. In addition, $R_L = 0$ represents irreversible adsorption, while the adsorption is linear if $R_L = 1$ [33, 34]. The dimensionless separation factors calculated for adsorption of the heavy metals onto PWB were between zero to one that shows favorable adsorption, while the corresponding values for CWB were greater than 1 indicating an unfavorable adsorption (Table 4). The values of $R^2$ and $R_L$ obtained from Langmuir-1 expression indicate positive evidence that the
adsorption of Pb, Mn, and Cu onto PWB follows the Langmuir isotherm. The fit of the measured data to the Langmuir model reveals the possibility of sorption of the heavy metals onto PWB through chemisorptions [35]. Negative values obtained for maximum adsorption capacity of CWB reveals that adsorption of Pb, Mn and Cu onto CWB in the leachate does not follow Langmuir isotherm, suggesting that heavy metals do not follow the monolayer adsorption on the surface of CWB. In another study, negative values for adsorption capacity of dyes onto AC was obtained [24], which is practically and experimentally impossible. The highest value of the Langmuir constant $b$, 3.22 L mg$^{-1}$, was obtained for Pb adsorption onto PWB (Table 4) exhibiting greater affinity of Pb to the surface of PWB compared to Mn and Cu in landfill leachate.

Maximum adsorption capacities determined using different forms of Langmuir expressions are slightly higher than the experimental adsorbed amounts of Pb onto PWB. The same trend was found for Mn and Cu, to a higher degree compared with Pb. It seems that the monolayer adsorption capacity of Pb onto PWB provided a better fit to the experimental data compared to Mn and Cu. Table 4 indicates that the Langmuir constants obtained from different linear expressions are divergent, implying that transformation of non-linear model to linear forms may alter the error structure of a given isotherm. Smaller values of determination coefficients were gained in types 3 and 4.

Lower values of the SSE were obtained for Langmuir-4 and Langmuir-1 expressions, while Langmuir-5 expression give the highest SSE in most cases. Overally, the lowest value of the SSE will be generated for the Langmuir-1 expression compared to other linear forms, if the BC dosage of 0.05 mg g$^{-1}$ is overlooked. For instance, that 83% of the calculated SSE was attributed to the deviation occurred at dose of 0.05 mg g$^{-1}$, when the experimental adsorption of Cu onto CWB were modeled using the Langmuir-1 expression. Experimental results showed that adsorbed amounts of the heavy metals on BC was clearly increased with rising adsorbent dosage. Figure 4 compares the simulated isotherm curves and measured data for adsorption of Pb, Mn and Cu onto BC based on Langmuir-Type 1 expression. Results indicated that Langmuir isotherm is unable to describe the equilibrium data perfectly in most cases; however, Langmuir-1 expression could better simulate equilibrium data for
adsorption of heavy metals on PWB in the leachate, compared to the other linearized forms of Langmuir model. The error structure varied upon linearization of non-linear Langmuir isotherm equation. Results indicated that the values of $R^2$, $R_L$ and SSE are required to reliably determine the most appropriate form of the linearized type of the Langmuir model to fit the experimental adsorption data.

3.4.2. Linearized and non-linearized Freundlich isotherms

The Freundlich isotherm has been widely applied to characterize the adsorption of organic and inorganic pollutants using various adsorbents [36]. Freundlich isotherm constants found through plotting $\ln q_e$ vs $\ln C_e$ are given in Table 5. The ratio of the amount of adsorbate adsorbed onto a given mass of adsorbent to the adsorbate concentration in the solution using the Freundlich model is represented by the following equation:

\[ q_e = K_f C_e^\frac{1}{n} \]  

where, $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ is the amount adsorbed to solid phase (mg g$^{-1}$), $K_f$ is the Freundlich constant representing the relative adsorption intensity of the adsorbent related to the bonding energy, and $n$ is the heterogeneity factor indicating the deviation from linearity of adsorption which is commonly known as Freundlich coefficient. Linearized form of the Freundlich isotherm can be used to evaluate the adsorption data and determine the Freundlich model constants as follows:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  

The corresponding coefficients of correlation for Freundlich model were found to be high for adsorption of Pb, Mn, and Cu onto PWB and CWB ($\geq 0.99$) indicating a good linearity; however, the values of Freundlich coefficient, $n$, did not fall within the favorable range for CWB. Favorability of the Freundlich isotherm is generally indicated by the magnitude of the exponent $n$. The values of $n$ ranging from 2 to 10 is stated to represent a good fit, values ranging from 1 to 2 indicates relatively
difficult adsorption, and less than 1 shows poor adsorption characteristics [37]. Acceptable adsorption characterized by values of $n$ between 1 and 10 has also been reported in the literature [33, 38]. The highest value of the Freundlich coefficient was obtained for adsorption of Pb onto PWB ($n = 1.992$) (Table 5). Higher values of $K_F$ were found for adsorption of the heavy metals onto PWB indicating the greater relative adsorption capacity of PWB compared to CWB to eliminate Pb, Mn, and Cu from the landfill leachate. Results show that linearized Freundlich and Langmuir models could not adequately describe adsorption of Pb, Mn, and Cu onto CWB in landfill leachate. In order to find the Freundlich maximum adsorption capacity, $q_m$, it is necessary to keep the initial concentration of adsorbate constant and use the variable dosage of adsorbent; that means $ln q_m$ is the extrapolated value of $ln q$ for $C = C_0$. Thus, the Freundlich maximum adsorption capacity can be described as follows:

$$q_m = K_F (C_0)^{\frac{1}{n}}$$

(12)

Where, $q_m$ is the Freundlich maximum adsorption capacity (mg g$^{-1}$), $K_F$ is the Freundlich constant, and $C_0$ is the initial concentration of adsorbate in the bulk solution (mg L$^{-1}$). The calculated maximum adsorption capacity of PWB for Pb, Mn, and Cu using the Freundlich isotherm were greater than the corresponding values for CWB, respectively, by a factor of 2.3, 5.3, and 1.4. Comparing the maximum adsorption capacity produced by application of the Freundlich and Langmuir-1 models reveals that predicted $q_{max}$ using the Freundlich isotherm is markedly lower than the corresponding values obtained by the Langmuir-1 expression for PWB.

It can be inferred from the Figs. 5a, 5b and 5c that the predicted adsorption capacity of PWB and CWB using the linearized Freundlich isotherm is drastically underestimated for Pb, Mn and Cu. Error analysis also indicates high values of SSE for linearized Freundlich isotherm. The SSE values found for the Freundlich model are significantly higher than the obtained values for the Langmuir model.

Overall, results indicated no adequate agreement between the predicted and measured adsorption data, implying the lack of validity of the linearized Freundlich isotherm to model the adsorption of the heavy metals onto BC in the leachate. Both linear and non-linear fitting of the experimental data to
the Freundlich model yields high coefficients of determination in most cases but the error analysis presented a great difference between linear and non-linear fitting. The value of SSE calculated for non-linear fitting was much lower than that obtained for linear fitting, as it could also be realized by comparing experimental and modeled data presented in Figs. 5d, 5e and 5f. Results indicate that non-linear fitting of the measured data to the Freundlich isotherm could provide significantly more robust prediction compared to the linear fitting. However, the obtained values for the constant $n$ was less than 1 when CWB was used as an adsorbent both for linear and non-linear fitting of data indicating unfavorable adsorption of Pb, Mn, and Cu onto CWB. Results indicated much higher values of $q_m$ when non-linearized regression was applied. In other words, linearization of the Freundlich isotherm caused underestimation of $q_m$, while fitting the measured data to non-linearized form of the Freundlich model depicted greater affinity between the experimental and predicted data. Application of non-linear Freundlich isotherm produced more valid data with significantly higher values of determination coefficient as well as much smaller SSE. Overally, results indicated that linearization of the Freundlich isotherm to fit the experimental data may generate higher errors and significantly deviate the predicted adsorption capacity of a given adsorbent from the experimental data.

3.4.3. Temkin Isotherm

The Temkin isotherm is based on the assumption that the heat of adsorption of all the molecules in the layer declines as adsorbent surface coverage increases due to adsorbate-adsorbate repulsions. Fall in the heat of adsorption is considered to be linear for Temkin isotherm rather than logarithmic as implied in the Freundlich isotherm. Adsorption of adsorbate onto adsorbent is also characterized by a unisonous distribution of binding energies up to ca. maximum binding energy [28]. Temkin isotherm equation contains a factor that reflects the adsorbent-adsorbate interactions. The nonlinear form of Tempkin isotherm is represented by the following equation:

$$q_s = \frac{RT}{b} \ln(K TC_s)$$  \hspace{1cm} (13)

Where, $T$ is the absolute temperature in Kelvin (K), $R$ is the universal gas constant, $8.314$ J mol$^{-1}$ K$^{-1}$,
\( b_T \) is the constant related to the heat of adsorption indicating the variation of adsorption energy (J mol\(^{-1}\)), and \( K_T \) is the Temkin equilibrium binding constant (L g\(^{-1}\)) corresponding to the maximum binding energy. The dimensionless term \((RT)/b_T\) can be substituted by \( B_T \), thus Temkin isotherm equation can be linearized as given by the following equation:

\[
q_e = B_T \ln K_T + B_T \ln C_e
\]

(14)

The obtained parameters of Temkin model are given in Table 6. Values of \( R^2 \) found using the linear transformation of the Temkin equation, were comparable were the non-linearized Freundlich model. The variation of adsorption energy, \( b_T \), was positive for all the studied heavy metals implying that the adsorption of Pb, Mn and Cu onto BC is an exothermic reaction (21.73 KJmol\(^{-1}\)). Salam et al. (2013) reported that the physical adsorption is characterized by adsorption energy in the range of 5–40 KJmol\(^{-1}\) [39]. Physiosorption may occur as a result of weak forces of Van der Waals between the adsorbates and adsorbents [30]. Higher amounts of variation of energy obtained using the Temkin isotherm for adsorption of Pb, Mn, and Cu onto PWB relative to those obtained for CWB indicates greater capacity of PWB to adsorb heavy metals in landfill leachate. It should be noticed that the Temkin isotherm does not provide any estimation of the maximum adsorption capacity of a given adsorbent, \( q_m \). In spite of the non-linear Langmuir equation, if the equilibrium concentration is increased, the adsorption capacity of the original Temkin equation, \( q_e \), does not converge to any limiting value. Figure 6 indicates that the predicted equilibrium curves using Temkin model are very close to those obtained experimentally; however, deviation of the predicted adsorption using the Temkin model slightly increased when lower dosage of BC was applied. Error analysis indicates smaller values of the SSE relative to the Langmuir-1 and linear Freundlich isotherms; however, the non-linear Freundlich model exhibited the lowest values of SSE for adsorption of Pb, Mn and Cu onto biochar in this study. Based on the obtained results it seems that Temkin model can adequately describe the adsorption of the heavy metals onto PWB and CWB in the leachate. Adsorption of Pb, Mn
and Cu onto BC in landfill leachate was adequately represented by the applied isotherm models, except the linear Freundlich model implying that adsorption of heavy metals onto BC may be controlled by surface diffusion and pore diffusion simultaneously as well as adsorption at an active preoccupied site. Overall, results indicated promising removal of the heavy metals from landfill leachate using biochar, which could be well described by non-linearized Freundlich and Temkin models.

4. Conclusions
The present study aimed to assess the capability of biochar in removal of Pb, Mn and Cu from landfill leachate and model the adsorption kinetics and isotherms of the heavy metals onto biochar. Results indicated that the wood-derived biochar is an effective adsorbent for the removal of Pb, Mn and Cu from landfill leachate. The adsorption affinity of PWB for Pb, Mn, and Cu was greater than CWB in all treatments. The contact times of 200 min and 150 min were sufficient to reach adsorption equilibrium condition, respectively for PWB and CWB. The removal rate of the heavy metals only slightly enhanced as biochar dosage exceeded 20 g L$^{-1}$ in leachate. PWB showed the highest experimental adsorption intensity of 1.58 mg g$^{-1}$ for the removal of Mn from the landfill leachate. The pseudo second-order kinetic model precisely represented the adsorption kinetic data for BC suggesting the chemisorptions of Cd onto biochar particles. Calculated $q_e$ using the Elovich kinetics model also agreed well with the experimental $q_e$. Two distinct adsorption stages for the adsorption of the heavy metals onto BC in the leachate leachate was clearly observed; first the migration of metals from the leachate system to the external surface of BC during which the mass transfer is very rapid and physical processes control the adsorption, followed by the prolonged intra-particle diffusion characterized by slow adsorption. The non-linear Freundlich isotherm best describes the equilibrium adsorption data, followed by the Temkin isotherm. Linearized Freundlich model could only moderately describe adsorption of the heavy metals onto PWB, while it was not able to represent the adsorption by CWB. Linearization method for the Langmuir isotherm also affects the error structure suggesting that the linearization of non-linear isotherm models may violate the theory behind an isotherm and alter error distribution. It is recommended to use wood-derived biochar as an effective adsorbent to
remove heavy metals from landfill leachate.

Declarations

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Authors’ contributions

Ali Daryabeigi Zand (ADZ) was responsible for developing the theory and idea, carrying out the experiments, performing and verifying the analytic calculations and numerical simulations, and writing the manuscript. Maryam Rabiee Abyaneh (MRA) was responsible for carrying out the experiments, performing the analytic calculations and numerical simulations, and writing the manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included within the article.

Competing interests

The authors declare they have no competing interests.

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Tables

Table 1. Kinetic parameters of the pseudo second-order model for adsorption of heavy metals onto BC in landfill leachate
| Adsorbate | BC Dosage | Pseudo first-order kinetic for PWB | Pseudo first-order kinetic for CWB |
|-----------|-----------|-----------------------------------|-----------------------------------|
|           | $q_e^{(\text{cal.})}$ (mg g$^{-1}$) | $K_{2p}$ | $h$ | $R^2$ | SSE | $q_e^{(\text{cal.})}$ (mg g$^{-1}$) | $K_{2p}$ |
| Pb        | 0.05      | 0.446 | 0.115 | 0.023 | 0.999 | 0.000 | 0.358 | 0.147 |
|           | 0.1       | 0.439 | 0.116 | 0.022 | 0.999 | 0.000 | 0.349 | 0.15 |
|           | 0.25      | 0.341 | 0.15  | 0.017 | 0.999 | 0.000 | 0.272 | 0.197 |
|           | 0.5       | 0.274 | 0.187 | 0.014 | 0.999 | 0.000 | 0.188 | 0.284 |
|           | 0.75      | 0.212 | 0.242 | 0.011 | 0.999 | 0.000 | 0.149 | 0.363 |
|           | 1         | 0.171 | 0.306 | 0.009 | 0.999 | 0.000 | 0.122 | 0.465 |
|           | 1.5       | 0.122 | 0.428 | 0.006 | 0.999 | 0.000 | 0.092 | 0.625 |
|           | 2         | 0.093 | 0.564 | 0.005 | 0.999 | 0.000 | 0.072 | 0.79 |
|           | 3         | 0.065 | 0.807 | 0.003 | 0.999 | 0.000 | 0.052 | 1.104 |
|           | 5         | 0.039 | 1.386 | 0.002 | 0.999 | 0.000 | 0.033 | 1.750 |
| Mn        | 0.05      | 1.616 | 0.031 | 0.082 | 0.999 | 0.001 | 1.404 | 0.037 |
|           | 0.1       | 1.536 | 0.032 | 0.079 | 0.999 | 0.000 | 1.395 | 0.038 |
|           | 0.25      | 1.095 | 0.047 | 0.056 | 0.999 | 0.000 | 0.967 | 0.056 |
|           | 0.5       | 0.85  | 0.061 | 0.044 | 0.999 | 0.000 | 0.729 | 0.074 |
|           | 0.75      | 0.692 | 0.074 | 0.036 | 0.999 | 0.000 | 0.576 | 0.093 |
|           | 1         | 0.561 | 0.094 | 0.031 | 0.999 | 0.000 | 0.473 | 0.121 |
|           | 1.5       | 0.428 | 0.123 | 0.022 | 0.999 | 0.000 | 0.355 | 0.160 |
|           | 2         | 0.34  | 0.154 | 0.018 | 0.999 | 0.000 | 0.282 | 0.201 |
|           | 3         | 0.237 | 0.222 | 0.013 | 0.999 | 0.000 | 0.203 | 0.281 |
|           | 5         | 0.148 | 0.354 | 0.008 | 0.999 | 0.000 | 0.127 | 0.452 |
| Cu        | 0.05      | 0.401 | 0.126 | 0.021 | 0.999 | 0.000 | 0.461 | 0.114 |
|           | 0.1       | 0.392 | 0.131 | 0.021 | 0.999 | 0.000 | 0.425 | 0.123 |
|           | 0.25      | 0.326 | 0.157 | 0.017 | 0.999 | 0.000 | 0.323 | 0.166 |
|           | 0.5       | 0.263 | 0.195 | 0.013 | 0.999 | 0.000 | 0.237 | 0.228 |
|           | 0.75      | 0.216 | 0.237 | 0.011 | 0.999 | 0.000 | 0.184 | 0.293 |
|           | 1         | 0.174 | 0.294 | 0.009 | 0.999 | 0.000 | 0.155 | 0.367 |
|           | 1.5       | 0.133 | 0.384 | 0.007 | 0.999 | 0.000 | 0.117 | 0.491 |
|           | 2         | 0.106 | 0.493 | 0.006 | 0.999 | 0.000 | 0.093 | 0.618 |
|           | 3         | 0.075 | 0.697 | 0.004 | 0.999 | 0.000 | 0.066 | 0.873 |
|           | 5         | 0.048 | 1.094 | 0.003 | 0.999 | 0.000 | 0.042 | 1.378 |
Table 2. Kinetic parameters of the Elovich model for adsorption of heavy metals onto BC in landfill leachate
| Adsorbate | Adsorbent Dosage | Elovich kinetic for PWB | Elovich kinetic |
|-----------|-----------------|-------------------------|----------------|
|           | $q_e$ (cal.) (mg g$^{-1}$) | $\beta$ | $\alpha$ | $R^2$ | SSE | $q_e$ (cal.) (mg g$^{-1}$) | $\beta$ |
| Pb        | 0.05            | 0.487 | 14.493 | 0.056 | 0.953 | 0.002 | 0.388 | 18.18 |
|           | 0.1             | 0.480 | 14.706 | 0.055 | 0.952 | 0.002 | 0.380 | 18.51 |
|           | 0.25            | 0.374 | 18.868 | 0.043 | 0.948 | 0.002 | 0.297 | 23.81 |
|           | 0.5             | 0.297 | 23.810 | 0.034 | 0.948 | 0.001 | 0.205 | 34.48 |
|           | 0.75            | 0.233 | 30.303 | 0.027 | 0.949 | 0.001 | 0.163 | 43.47 |
|           | 1               | 0.184 | 38.462 | 0.021 | 0.937 | 0.000 | 0.134 | 52.62 |
|           | 1.5             | 0.134 | 52.632 | 0.015 | 0.937 | 0.000 | 0.098 | 71.42 |
|           | 2               | 0.098 | 71.429 | 0.011 | 0.937 | 0.000 | 0.078 | 90.90 |
|           | 3               | 0.070 | 100.000 | 0.008 | 0.939 | 0.000 | 0.056 | 125.00 |
|           | 5               | 0.043 | 166.667 | 0.005 | 0.935 | 0.000 | 0.035 | 200.00 |
| Mn        | 0.05            | 1.764 | 4.011 | 0.201 | 0.952 | 0.032 | 1.545 | 4.56 |
|           | 0.1             | 1.708 | 4.132 | 0.195 | 0.952 | 0.031 | 1.530 | 4.60 |
|           | 0.25            | 1.200 | 5.882 | 0.137 | 0.948 | 0.016 | 1.065 | 6.62 |
|           | 0.5             | 0.838 | 8.576 | 0.107 | 0.948 | 0.000 | 0.805 | 8.77 |
|           | 0.75            | 0.755 | 9.346 | 0.086 | 0.948 | 0.006 | 0.634 | 11.11 |
|           | 1               | 0.614 | 11.494 | 0.07  | 0.937 | 0.004 | 0.521 | 13.51 |
|           | 1.5             | 0.465 | 15.152 | 0.053 | 0.937 | 0.002 | 0.377 | 18.8 |
|           | 2               | 0.374 | 18.868 | 0.043 | 0.937 | 0.002 | 0.310 | 22.72 |
|           | 3               | 0.261 | 27.027 | 0.03  | 0.936 | 0.001 | 0.226 | 31.25 |
|           | 5               | 0.163 | 43.478 | 0.019 | 0.936 | 0.000 | 0.141 | 50.00 |
| Cu        | 0.05            | 0.445 | 15.873 | 0.051 | 0.952 | 0.003 | 0.508 | 13.8 |
|           | 0.1             | 0.438 | 16.129 | 0.050 | 0.952 | 0.003 | 0.465 | 15.15 |
|           | 0.25            | 0.352 | 20.000 | 0.041 | 0.948 | 0.001 | 0.352 | 20.00 |
|           | 0.5             | 0.282 | 25.000 | 0.032 | 0.948 | 0.001 | 0.261 | 27.02 |
|           | 0.75            | 0.233 | 30.303 | 0.027 | 0.948 | 0.000 | 0.198 | 35.71 |
|           | 1               | 0.191 | 37.037 | 0.022 | 0.937 | 0.000 | 0.169 | 41.6 |
|           | 1.5             | 0.141 | 50.000 | 0.016 | 0.937 | 0.000 | 0.126 | 55.55 |
|           | 2               | 0.113 | 62.500 | 0.013 | 0.937 | 0.000 | 0.098 | 71.42 |
|           | 3               | 0.078 | 90.909 | 0.009 | 0.936 | 0.000 | 0.070 | 100.00 |
|           | 5               | 0.050 | 142.857 | 0.006 | 0.937 | 0.000 | 0.043 | 166.67 |
Table 3. Langmuir model and its linear and on-linear forms

| Type | Non-linear form | Linear forms | Plot | Parameters |
|------|----------------|--------------|------|------------|
| 1    | \( \frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m} \) | \( \frac{1}{q_e} \) vs. \( \frac{1}{C_e} \) | \( \frac{1}{\text{intercept}} \) | intercept/slope |
| 2    | \( \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b q_m} \) | \( \frac{C_e}{q_e} \) vs. \( C_e \) | \( \frac{1}{\text{slope}} \) | slope/intercept |
| 3    | \( q_e = \frac{q_m b C_e}{1 + b C_e} \) | \( q_e = -\frac{1}{b} \frac{q_e}{C_e} + q_m \) | \( q_e \) vs. \( \frac{q_e}{C_e} \) | Intercept | - \( \frac{1}{\text{slope}} \) |
| 4    | \( \frac{q_e}{C_e} = -b q_e + b q_m \) | \( \frac{q_e}{C_e} \) vs. \( q_e \) | - \( \frac{1}{\text{intercept/slope}} \) | - slope |
| 5    | \( \frac{1}{C_e} = b q_m \frac{1}{q_e} - b \) | \( \frac{1}{C_e} \) vs. \( \frac{1}{q_e} \) | - \( \frac{1}{\text{slope/intercept}} \) | - intercept |

Table 4. Parameters of the five different forms of linearized Langmuir isotherm for the adsorption of Pb, Mn and Cu onto BC in landfill leachate
| Isotherm        | Pb      | Mn      | Cu      |
|----------------|---------|---------|---------|
|                | PWB     | CWB     | PWB     | CWB     | PWB     | CWB     |
| Langmuir-type 1|         |         |         |         |         |         |
| $q_m$ (mg g$^{-1}$) | 0.436   | -0.221  | 5.556   | -0.650  | 5.882   | -0.210  |
| $b$ (L mg$^{-1}$)  | 3.222   | -0.464  | 0.054   | -0.123  | 0.036   | -0.369  |
| $R^2$            | 0.985   | 0.965   | 0.993   | 0.944   | 0.994   | 0.944   |
| $R_L$            | 0.14    | 8.86    | 0.70    | 23.05   | 0.92    | 18.28   |
| SSE              | 0.016   | 0.364   | 0.045   | 9.593   | 0.008   | 0.842   |
| Langmuir-type 2 |         |         |         |         |         |         |
| $q_m$ (mg g$^{-1}$) | 0.477   | -0.407  | 5.682   | -1.103  | 1.605   | -0.351  |
| $b$ (L mg$^{-1}$)  | 3.612   | -0.297  | 0.053   | -0.087  | 0.144   | -0.264  |
| $R^2$            | 0.922   | 0.678   | 0.659   | 0.689   | 0.817   | 0.700   |
| $R_L$            | 0.13    | 2.31    | 0.71    | 3.09    | 0.73    | 3.08    |
| SSE              | 0.018   | 0.009   | 0.065   | 0.179   | 0.003   | 0.017   |
| Langmuir-type 3 |         |         |         |         |         |         |
| $q_m$ (mg g$^{-1}$) | 0.486   | -0.345  | 3.751   | -1.04   | 1.284   | -0.342  |
| $b$ (L mg$^{-1}$)  | 2.632   | -0.337  | 0.087   | -0.091  | 0.187   | -0.270  |
| $R^2$            | 0.890   | 0.829   | 0.587   | 0.880   | 0.712   | 0.886   |
| $R_L$            | 0.17    | 2.81    | 0.60    | 3.41    | 0.68    | 3.24    |
| SSE              | 0.011   | 0.02    | 28.368  | 0.268   | 0.001   | 0.02    |
| Langmuir-type 4 |         |         |         |         |         |         |
| $q_m$ (mg g$^{-1}$) | 0.514   | -0.452  | 5.960   | -1.263  | 1.722   | -0.410  |
| $b$ (L mg$^{-1}$)  | 2.339   | -0.279  | 0.050   | -0.080  | 0.133   | -0.239  |
| $R^2$            | 0.890   | 0.829   | 0.587   | 0.880   | 0.712   | 0.886   |
| $R_L$            | 0.18    | 2.14    | 0.72    | 2.63    | 0.75    | 2.58    |
| SSE              | 0.017   | 0.007   | 0.042   | 0.089   | 0.001   | 0.006   |
| Langmuir-type 5 |         |         |         |         |         |         |
| $q_m$ (mg g$^{-1}$) | 0.444   | -0.196  | 6.000   | -0.556  | 7.536   | -0.180  |
| $b$ (L mg$^{-1}$)  | 3.083   | -0.501  | 0.050   | -0.135  | 0.028   | -0.405  |
| $R^2$            | 0.985   | 0.965   | 0.993   | 0.944   | 0.994   | 0.994   |
| $R_L$            | 0.15    | 23.21   | 0.72    | -21.62  | 0.93    | -27.17  |
| SSE              | 0.015   | 1.001   | 0.042   | 103.066 | 0.009   | 7.146   |

Table 5. Linearized and non-linearized Freundlich isotherm constants for adsorption of Pb, Mn and Cu onto BC
| Isotherm                  | parameters | Pb       | Mn       | Cu       |
|--------------------------|------------|----------|----------|----------|
|                          |            | PWB      | CWB      | PWB      | CWB      | PWB      |
| Linearized               | $K_F$      | 0.086    | 0.021    | 0.056    | 0.003    | 0.024    |
| Freundlich Isotherm      | $n$        | 1.992    | 0.736    | 1.140    | 0.669    | 1.112    |
|                          | $R^2$      | 0.994    | 0.994    | 0.992    | 0.990    | 0.991    |
|                          | $q_{max}$  | 0.119    | 0.051    | 0.337    | 0.064    | 0.056    |
|                          | SSE        | 0.374    | 0.312    | 5.086    | 5.536    | 0.446    |
| Non-linearized           | $K_F$      | 0.343    | 0.189    | 0.275    | 0.906    | 0.201    |
| Freundlich Isotherm      | $n$        | 2.033    | 0.806    | 1.106    | 0.720    | 1.221    |
|                          | $R^2$      | 0.967    | 0.990    | 0.988    | 0.989    | 0.993    |
|                          | $q_{max}$  | 0.472    | 0.422    | 1.751    | 1.650    | 0.434    |
|                          | SSE        | 0.0064   | 0.0012   | 0.0281   | 0.0216   | 0.0009   |

Table 6. Temkin isotherm parameters for adsorption of Pb, Mn and Cu onto BC in the leachate

| Temkin Isotherm Parameters | Pb       | Mn       | Cu       |
|----------------------------|----------|----------|----------|
|                            | PWB      | CWB      | PWB      | CWB      |
| $b_T$                      | 0.114    | 0.191    | 0.538    | 0.824    | 0.154    | 0.266    |
| $K_T$                      | 22.315   | 3.147    | 1.779    | 0.656    | 4.57     | 1.953    |
| $R^2$                      | 0.964    | 0.935    | 0.889    | 0.930    | 0.958    | 0.938    |
| SSE                        | 0.0044   | 0.0080   | 0.262    | 0.131    | 0.0059   | 0.018    |
Figure 1

Effect of contact time and biochar dosage on removal of heavy metals from landfill leachate
Figure 2

Linearized pseudo second-order kinetics for adsorption of Pb onto PWB (a) and CWB (b)

Figure 3

Determined quantities of adsorption capacity of Pb onto PWB (a) and CWB (b) using the Elovich kinetic model
Figure 4

Experimental and predicted adsorption of the heavy metals onto PWB in landfill leachate using Langmuir-1 expression
Figure 5

Experimental and predicted adsorption of the heavy metals in leachate onto PWB and CWB using linearized and non-linearized Freundlich equations.
Figure 6

Experimental and predicted adsorption of the heavy metals in landfill leachate onto PWB and CWB using Temkin equation.