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Equilibrium and kinetic studies in remediation of heavy metals in landfill leachate using wood-derived biochar

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ABSTRACT

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. The adsorption of lead(II), zinc(II), and nickel(II) in fresh landfill leachate onto wood-derived biochar was studied and modeled. The influence of contact time, adsorbent dosage as well as particle size was investigated. Wood-derived biochar produced under the pyrolytic temperature of about 740°C was used in two forms i.e. pulverized (PWB) and crushed (CWB) as adsorbent in this study. The kinetics of Pb, Zn, and Ni adsorption onto PWB and CWB were excellently represented by the pseudo second-order model with very high values of determination coefficient ($R^2 \geq 0.999$) and low sum of error square (SSE). The Langmuir, Freundlich, Elovich and Temkin models were applied to the experimental data to predict the adsorption parameters. Linearization technique for the Langmuir isotherm which can alter the error structure was also studied in the present work. The Temkin isotherm best represents the equilibrium adsorption data for both PWB and CWB. Other used isotherms unable to describe adsorption of Pb, Zn, and Ni onto CWB. PWB was found to uptake the studied heavy metals more effective than CWB in leachate system. Findings of this research demonstrated the applicability of wood-derived biochar as an alternative to activated carbon for the effective adsorption of the heavy metals from landfill leachate system.

Keywords: Adsorption; Landfill leachate; Heavy metals; Biochar; Isotherms; Modeling

1. Introduction

Landfilling of municipal solid wastes (MSW) which is known as the least favorable solution based on integrated solid waste management hierarchy is still a predominant method considered as final disposal option not only in developing countries but also in several highly-developed countries, such as USA and Australia [1,2]. Economic advantages of waste burial in landfills make it an attractive ultimate disposal option for MSW, especially in developing countries such as Iran, where other desirable strategies such as recycling and incineration require extensive planning and investment in infrastructure; and therefore have received less attention.

Leachate generation in most landfill areas is an inevitable phenomenon affected by several factors e.g. waste composition and moisture content, seasonal precipitation, topography of landfill site and cover materials [3]. Landfills are designed to receive high quantities of various wastes to be disposed at economical expenses. Therefore 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 [4], oxidation processes [5], and membrane separation [6]. High variation in quantity and quality of leachate generated in landfill sites makes selection of appropriate treatment approach difficult. Landfill leachate is heterogeneous in nature and may contain a wide range of pollutants including heavy metals

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[7]. 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 [8]. High concentrations of heavy metals in landfill leachate were reported in the literature. Typical concentrations of Cd, Cr, Fe, Mn, Ni, Pb, and Zn in landfill leachate are 0.0001–0.13, 0.0005–1.6, 0.08–2100, 0.01–65, 0.03–3.2, 0.0005–1.5, and 0.00005–120 mg/L, respectively [7,8]. Biodegradation potential of most organic contaminants found in landfill leachate makes their treatment more convenient compared to heavy metals which are not biologically degradable. Moreover, high mobility of heavy metals makes them good candidates to migrate through soil layers in landfill sites posing a threat to soil and groundwater resources. Adverse environmental effects of heavy metals on the environment and human health have been well documented [9,10].

The removal of heavy metals from landfill leachate is of great concern mainly due to their persistence and mobility potential. Although biological treatment is efficient in removal of some organic contaminants from landfill leachate, heavy metals may not be effectively mitigated or contained by such treatment systems. Heavy metals in aqueous solutions are conventionally treated using physic-chemical techniques such as chemical precipitation [11,12], catalytic oxidation [13], membrane technology e.g. reverse osmosis [14], and adsorption on activated carbon [15], but most of them are expensive and require considerable maintenance [16]. The need for safe and economical approaches to remove heavy metals from various contaminated effluents has necessitated research application of adsorbents to eliminate heavy metals from aqueous solutions [17]. Adsorption of heavy metals on carbonaceous materials has gained remarkable attention to remove these toxic metals from contaminated aqueous solutions in recent years. Abdulrazak et al. studied the removal of cadmium, lead, copper, and nickel from synthetic wastewater by adsorption onto activated carbon produced from African palm fruit. Batch experiments were carried out by varying contact time and temperature, which indicated acceptable effectiveness of the activated carbon in removal of heavy metals with the highest removal rate at an optimum contact time of 60 min [18]. Palm shell activated carbon was successfully used as an adsorbent to remove copper from aqueous solutions by Issabayeva et al. [19]. Activated carbon is a well known strong adsorbent which has been employed to remove a wide range of pollutants from different media principally because of its large surface area and high porosity [20–22]; however, high production costs of activated carbons pose a serious drawback for their commercial use as adsorbent [23]. Therefore, researchers continue to seek alternatives to commercial activated carbons, mainly focusing on adsorbents from agricultural and industrial waste materials, in order to produce less expensive adsorbents [24]. For instance, in a study by Soco and Kalembkiewicz coal fly ash was used for the removal of nickel and copper from aqueous solution, which revealed that more than 90% of both cations were removed from the synthetically contaminated solution under equilibrium conditions [25].

Biochar refers to the carbon-rich products produced by heating the biomass in a low/no oxygen environment (pyrolysis) [15]. Application of biochar has expanded during the last decade initially because of its potential to improve soil fertility and long-term soil carbon sequestration, thereby reducing the amount of carbon dioxide emitted to the atmosphere [26]. Biochar can be used to remediate soils contaminated with contaminants, particularly organic compounds, because of its strong affinity to organics. Biochar may also reduce mobilization and release of organic contaminants e.g. PAHs from contaminated soils into groundwater resources [27]. Recently, biochar application as a novel approach in wastewater treatment has attracted considerable attention from researchers [28]. Biochar can be considered as less expensive alternative to activated carbon in adsorption and removal of pollutants for remediation purposes. The utilization of biochar as cost-effective adsorbent to remediate contaminated media has been reported by many researchers [15,27,29]. For instance, De Caprariis et al. employed poplar wood biochar to remove total organic carbon (TOC) from wastewater, and a very high sorption capacity of activated biochar (840 mg/g) was achieved. Adsorption of lead [23] and textile dyes [30] from water has been evaluated using biochar as the adsorbent. Agrafioti et al. studied arsenic and chromium removal from water by biochar derived from sewage sludge, showing that the used biochar has a significant capability for Cr(VI) adsorption (89%), while removal of As(V) did not exceed 53% [15]. The majority of studies focused on the immobilization and mitigation of contaminants, respectively in soil and contaminated effluents [26–28]; however, heavy metals removal from landfill leachate by biochar has rarely been studied.

The main objective of the present paper was to study the feasibility of using wood-derived biochar (WB) for the removal of Pb, Zn, and Ni from freshly collected landfill leachate. To date, no systematic research has been investigated the application of wood-derived biochar for the adsorption of heavy metals in fresh landfill leachate, leaving its capability and controlling conditions unclear. The influence of contact time, adsorbent dose, and biochar particle size on adsorption of the three studied heavy metals in leachate onto biochar was also studied. Adsorption kinetics was evaluated using the pseudo second-order model and the Langmuir, Freundlich, Elovich, and Temkin isotherm models were used to predict equilibrium adsorption parameters.

2. Materials and methods

2.1. Kahrizak landfill characteristics

Aradkooh waste disposal and processing complex which is more commonly called Kahrizak landfill is 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 (Fig. 1). Kahrizak landfill has been receiving all kinds of solid wastes for more than 60 years as the main destination for municipal wastes of Tehran. New trenches have also been constructed in recent years to accommodate collected wastes. Every day ca. 8000 tons of collected urban wastes are transferred to the Kahrizak landfill, which means over 2.9 million tons per year. The landfill is located

Fig. 1. Kahrizak Landfill and waste processing plant.

in an arid area with a mean rainfall of 183 mm/y, evaporation rate of 2370 mm/y, and absolute temperature range of –18–45°C with the average of 17°C. Kahrizak disposal site was used as a dumping site having no leachate and gas collection system, daily and final cover, and runoff drainage system [31].

Waste disposal used to be done initially in natural formations and then in artificial trenches, with no emission control, before focusing on burial of wastes as parallel layers in one section of the landfill in the year 2000. Recently some improvements have been achieved in operation of Kahrizak landfill and processing units and composting facility were added to the complex, but due to the lack of appropriate lining situation, runoff drainage measures, gas collection and leachate management systems, the landfill can be hardly considered as an "engineered landfill" as characterized in the literature [32]. Waste materials are buried in layers of ca. 2–3 m, covered daily with soil and construction wastes, then partially leveled and compacted by the traffic of operating trucks at site. The mountain elevated by waste burial in Kahrizak landfill has hit the height of ca. 60 meters [33]. Leachate generated in Kahrizak landfill has long been a serious environmental concern; firstly because of entering all types of municipal wastes, including hazardous household waste, with no source separation program, and secondly due to the lack of effective leachate collection and management system. Considering the high percentage of biodegradable wastes in Iran's MSW composition, increasing efforts have been made to divert the organic fraction of MSW from open dumping/landfilling mainly through composting. This strategy could reduce the burden on Kahrizak waste disposal site to some extent; however, still the main fraction of collected inorganic wastes found their way into Kahrizak disposal site. Among them, various metallic materials such as used wires, fluorescent lamps, thermometers, batteries, discarded computers, etc. are buried due to the lack of sufficient cultural and technical infrastructure for proper source separation and recycling, which may affect leachate quality at Kahrizak disposal site. High clay content and therefore low permeability of the land caused infiltration of the landfill leachate to be minimal. Therefore, freshly generated leachate at Kahrizak landfill, which is now estimated to be about 637 m^3/d [34], flows gravitationally towards the low land next to the burial site creating a leachate lake with a depth of ca. 10 m as shown in Fig. 1. Area of the lake and volume of the collected leachate undergo seasonal variation.

2.2. Landfill leachate sampling and analysis

Sampling location can affect leachate properties. Generated leachate may absorb various potential contaminants on its way to the leachate lake before mixing with the old leachate, and therefore lose the initial characteristics. Leachate samples were directly taken from the generated leachate stream at the bottom of the waste discharge place at Kahrizak landfill and used throughout the adsorption experiments. Collected leachate can be classified as relatively fresh leachate based on the low pH values (Table 1). 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 possible chemical and biological changes.

Leachate samples characterized according to the Standard Method for the Examination of Water and Wastewater [35]. Lead, zinc, and nickel were selected as target heavy metals for the adsorption experiments in this study and their concentrations in the leachate samples are shown in Table 2. 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, and then the digestate passed through MILEXHA 0.45 μm diameter filter followed by US EPA 3005A method [36]. 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. [37]. Samples were digested in triplicate and analyzed

Table 1
Characteristics of raw leachate collected from Kahrizak landfill

Parameter	Unit	Mean	National Discharge Standards	
			Surface Water	Agricultural Irrigation
COD	Mg L^{-1}	68450	100	200
BOD_5	Mg L^{-1}	30366	50	200
BOD/COD	Mg L^{-1}	0.44	–	–
TSS	Mg L^{-1}	23846	60	100
TDS	Mg L^{-1}	12940	–	–
$N\text{-}NO_3$	Mg L^{-1}	68.33	50	–
SO_4	Mg L^{-1}	1777.67	400	500
EC	mS cm^{-1}	31.10	–	–
pH	–	5.11	6.5–8.5	6.0–8.5

Table 2
Concentration of heavy metals in Kahrizak landfill leachate used in the adsorption studies

Parameter	Unit	Mean ± SD*	National Discharge Standards	
			Surface Water	Agricultural Irrigation
Pb	Mg L^{-1}	1.91	1	1
Zn	Mg L^{-1}	7.75	2	2
Ni	Mg L^{-1}	2.56	2	2

for the concentrations of Pb, Zn, and Ni in the final solution using an atomic absorption spectrometer (AAS).

2.3. Biochar preparation and synthesis

Wood chips used in this research were air-dried and placed in open crucibles, then weighted, and covered thoroughly with aluminum foil in order to provide an oxygen-limited environment. Biochar was produced under the pyrolytic temperature of up to 740°C with a temperature gradient of ca. 10°C/min until the desired pyrolysis 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. Produced biochar chips were originally in granular form having a wide range of particle sizes. The produced biochar chips were air-dried over a week, ground using a ceramic mortar and pestle, sieved to 1–2 mm diameter, and mixed thoroughly to gain homogenous crushed wood-derived biochar (CWB). Moreover, some biochar chips were also milled using a zirconium oxide planet ball mill and sieved to 63–75 µm diameter to yield fine-graded biochar to be used as pulverized wood-derived biochar (PWB) in the adsorption tests. Elemental analyzer was used to determine the elemental composition of C, H, and N in the produced biochar. Suspension of <0.25 mm fraction of the produced biochar and deionized water at a solid to liquid ratio of 1:5 was agitated for 24 h [38]. The slurry was then measured for pH value using a calibrated pH meter (pH 540 GLP).

2.4. Adsorption kinetic and isotherm studies

The adsorption process of Ni(II), Pb(II), and Zn(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 7 and 6.5 was reported for $Ni(OH)_2$ and $Zn(OH)_2$, respectively [39]. Adsorption of heavy metals onto PWB and CWB was carried out versus time at specified intervals up to 24 h. Actual concentrations of Ni(II), Pb(II), and Zn(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 Eq. (1):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are, respectively, the initial and final concentration of heavy metals 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, as described before, for the heavy metals concentrations. The adsorption isotherms were studied in actual leachate system for Ni(II), Pb(II), and Zn(II). Certain quantities of biochar (0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 5 g) in two forms i.e. PWB and CWB were weighted separately and added to a 100 mL fresh landfill leachate at initial pH of 5.1. Pseudo second-order model was used to study the kinetics of adsorption of heavy metals in landfill leachate onto PWB and CWB and the Langmuir, Freundlich, Elovich, and Temkin isotherm models were applied to fit the experimental data.

3. Results and discussion

3.1. Leachate characteristics

Table 1 shows characteristics of fresh leachate generated at Kahrizak Landfill, Iran. Very high concentrations of COD and BOD_5 were detected in the leachate. Organic load of the leachate produced at this landfill is markedly higher than that of leachate generated in most developed countries as reported in the literature [7,40]. Received MSW at Kahrizak landfill is characterized by putrifiable fraction of ca. 68% and moisture content of 65%–70% [41] that significantly contribute to high organic load of produced leachate. The leachate used in this study is classified as fresh according to field observations and pH value of 5.11. Relatively fresh landfill leachates are typically characterized by pH values of as low as 4–6 [31]. Concentrations of Pb, Zn, and Ni in the leachate and their national discharge standards are presented in Table 2.

General characteristics of the leachate used in this study were almost comparable with those of other studies conducted on leachates generated in landfill/dumping sites of Iran; however, concentrations of heavy metals found in this study were slightly higher [41,42]. One explanation could be the age of the leachate and lower pH range of that in the present study. Heavy metals concentration found in Kahrizak landfill leachate is also comparable with those obtained by Shehzad et al. who collected the leachate from Sahom landfill site, Malaysia [40]. In general, fresh leachate which can be characterized by lower pH values contain higher concentrations of heavy metals in dissolved form relative to the old leachate [31]. Variation in buried MSW composition and daily cover content of heavy metals may also contribute to the recorded concentration of heavy metals occurred in landfill leachates. It is necessary to mitigate heavy metal content of leachate generated in landfill sites before discharging to water bodies or reusing that, in order to meet permissible levels and protect the environment and human health.

Theoretically, heavy metal content of landfill leachate produced in Iran is expected to be lower than that of leachate generated in developed countries due to the lower content of metal-containing wastes in MSW stream in Iran; however, Table 2 indicates that detected concentrations of Pb, Zn, and Ni in the leachate used in this study exceed national permissible discharge limits. Efficient source separation programs for generated MSW has not yet established in Iran and a wide range of discarded materials containing hazardous constituents e.g. chemical wastes, batteries, cell phones, and other electronic wastes find their way into the MSW stream. Heavy metals show higher solubility in a fresh leachate than mature or older leachate [31] that means elevated content of them might be expected in fresh leachate in dissolved form. Lower pH values (i.e.4–6) indicate that the leachate is relatively fresh.

3.2. Physico-chemical properties of biochar

Physico-chemical characteristics of the wood-derived biochar are summarized in Table 3. Biochars from various sources were indicated to mainly compose of carbon, hydrogen, nitrogen, and oxygen (> 99% in most cases) [43]. Relatively high carbon content of the biochar (79.5%) could be caused by high pyrolysis temperature applied in this study. Feedstock pyrolyzed at higher temperature has found to have greater carbon content, higher surface area and lower content of nitrogen, hydrogen, and oxygen [43]; nevertheless, carbon content of produced biochar may not show further increase beyond a certain temperature [44]. Ash content of the produced biochar was 3.3% in this study which was pretty high. In general, ash content of biochar increases with pyrolytic temperature and residence time in the furnace. In a study by Okimori et al. increase in pyrolytic temperature from 300°C to 800°C raised ash content of biochar from 0.67% to 1.26% [44]. High pH value of the wood-derived biochar slightly enhanced pH of the landfill leachate when higher dosage of adsorbent mixed with fresh leachate; however, the greatest increase in leachate pH due to addition of 5 g PWB and 5 g CWB were 0.17 (i.e 3.3%) and 0.08 (i.e. 1.6%), respectively. Biochar with smaller particle size i.e. PWB (63–75 μm) enhanced pH of the fresh landfill leachate more than biochar with larger particle size i.e. CWB (1–2 mm) that could be caused by greater contact surface with leachate provided by smaller particles. Solubility of heavy metals are minimized in the pH range of 8–11 [45] which means Pb, Zn, and Ni could also be eliminated from landfill leachate through precipitation; however, biochar addition to the fresh leachate did not increase the pH to that extent in this study.

3.3. Effect of reaction time on the adsorption of heavy metals in leachate

The effect of contact time on the adsorption of Pb, Zn, and Ni in landfill leachate is shown in Fig. 2. 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 by biochar 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 when PWB and CWB were respectively used as adsorbent. The importance of contact time to provide sufficient contact between adsorbates and adsorbent surface has been emphasized by several authors [46,47]. Fig. 2 shows that the adsorption reaction can be divided into three distinct phases; rapid adsorption, slow adsorption reaction, and equilibrium periods. Initially adsorption sites are abundant on the surface of PWB and CWB which could be occupied with adsorbates with high rate. The removal rate of heavy metals gradually decreased with increase in contact time which is consistent with results reported in the literature [48]. 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, during which no net transfer of adsorbates from solution phase to the solid phase is occurred. The same observation was found for Ni uptake from aqueous solution by activated carbon derived from sugar bagasse [47]. It can be inferred from Fig. 2 that the removal of Pb, Zn, and Ni was greater when PWB was used as adsorbent, compared to CWB. Greater removal of Pb

Table 3
Physico-chemical characteristics of the wood-derived biochar

Biochar source	Max. pyrolysis Temp. (°C)	Pyrolysis time (min)	Bulk density (g cm^{-3})	pH	N (%)	H (%)	C (%)	Ash content (%)
Wood chips	740 ± 5	42	1.5	9.2	0.5	3.22	79.5	3.3

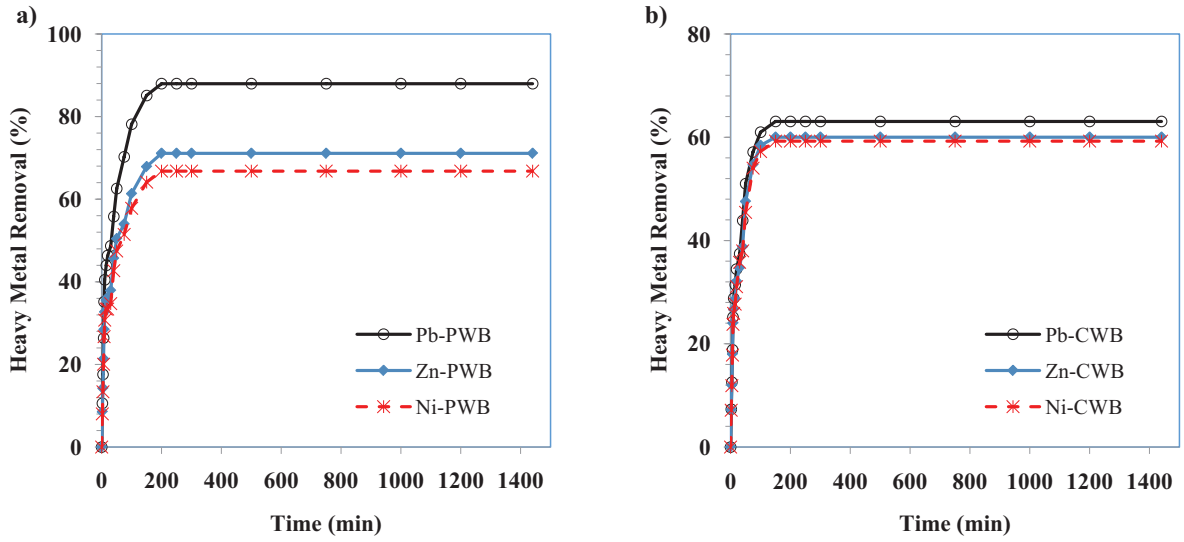

Fig. 2. Effect of contact time on removal of heavy metals from landfill leachate using a) PWB and b) CWB as adsorbent.

than Zn from aqueous solution using carbon-based materials was also reported in the literature [49] (Cu > Pb > Zn > Cd). 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 as adsorbent implying slower occupation of adsorption sites on the surface of PWB due to the greater specific surface provided by smaller particle size biochar i.e. PWB relative to CWB.

3.4. Effect of wood-derived biochar dosage on the adsorption of heavy metals in landfill leachate

The dosage of PWB and CWB was varied from 0.05 to 5 g/100 ml (0.5 to 50 g L^{-1}) in order to study the effect of adsorbent dosage on removal of Pb, Zn, and Ni in fresh landfill leachate at initial pH of 5.1. The reaction time was considered 200 min and 150 min, respectively, for PWB and CWB. It can be inferred from Fig.3 that the removal rate of the selected heavy metals in the landfill leachate was significantly raised by a factor of 1.25, 1.44, and 1.63 for Pb, Zn, and Ni, respectively, as PWB dosage was increased from 0.5 to 5 g L^{-1}. The corresponding increase factor for removal of Pb, Zn, and Ni in presence of CWB in leachate was 1.39, 1.66, and 1.69 when adsorbent dosage varied from 0.5 to 5 g L^{-1} implying the importance of biochar dosage in adsorption effectiveness. Similar findings on adsorption of Ni [47] onto activated carbon and copper onto sewage sludge [39] have been reported. The removal rate of Pb, Zn, and Ni experienced only slight enhancement as adsorbent dosage exceeded 2 g/100 mL in leachate both for PWB and CWB, suggesting the optimal dosage of 20 g/L for both PWB and CWB to achieve the highest economical adsorption capacity for the heavy metals.

Overcrowding of adsorbent particles and therefore overlapping the adsorption sites on the surface of adsorbent is probable at higher adsorbent dosage [50]. In other words, unsaturated adsorption sites may increase as adsorbent dosage exceeded the optimum amount. The highest removal rate was obtained for Pb followed by Zn and Ni due to addition biochar to the leachate (Fig. 3). Removal rate of Zn and Ni was comparable in this study with slightly higher elimination for Zn. Amount of Pb, Zn, and Ni adsorbed to each gram of PWB and CWB reduced with dosage enhancement, likely due to the availability of more adsorption sites on the surface of both PWB and CWB. The adsorbent dosage presents significant impact of prediction of adsorbent cost per unit of remediated pollutants [50]. Optimum activated carbon dosage of 7 g/100 mL leachate was found to effectively adsorb color, COD, and NH_3-N from landfill leachate [40], which is markedly higher than the optimum dosage of biochar obtained in this study. It might be attributed to the much higher levels of color, COD, and NH_3-N in leachate compared to those of heavy metals in this study. Furthermore, removal of Pb, Zn, and Ni from landfill leachate through adsorption onto biochar increased with their atomic mass. Increase in the molecular weight of adsorbates has been reported to elevate adsorption onto surface of a given adsorbent, especially when physical sorption is the dominant adsorption mechanism that is consistent with the findings of this research. Moreover, solubility of the adsorbate which is reversely proportional to the distribution coefficient is an important factor affecting adsorption reaction. In general, the lower the solubility of a given adsorbate (or the higher the distribution coefficient of an adsorbate), the greater would be the adsorption capacity [51]. This is because of the fact that attraction forces between the adsorbate and adsorbent surface can overcome the attraction forces between the adsorbate and the solvent. Distribution coefficient of the heavy metals examined in this work has the following order: Pb > Zn > Ni.

3.5. Effect of biochar particle size on adsorption of heavy metals in landfill leachate

Performance of pulverized biochar in adsorption of Pb, Zn, and Ni from landfill leachate was significantly different from crushed biochar in this study. Removal rate

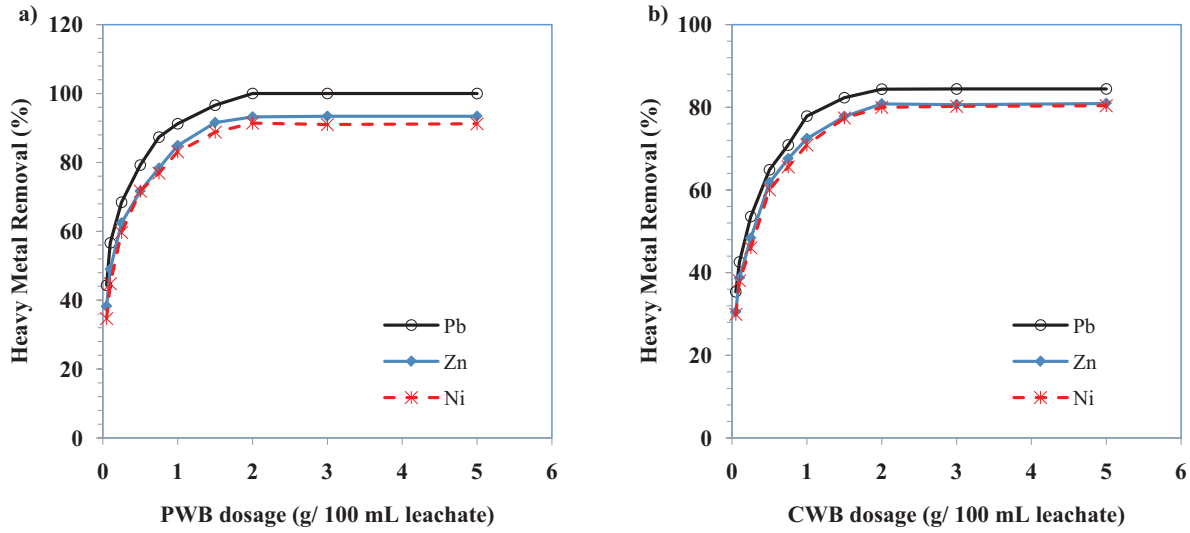

Fig. 3. Effect of a) PWB and b) CWB dosage on removal of heavy metals from landfill leachate.

of the studied heavy metals from leachate system in presence of PWB was significantly higher than that obtained for CWB in all cases at the same condition e.g. at the equal applied dosage of adsorbent. This implies the critical role of biochar particle size in determining the metal adsorption capacity, and hence the fate of heavy metals in landfill leachate. For instance, application of 3 g PWB in 100 ml leachate completely eliminated Pb from the landfill leachate (100% removal), whereas the same amount of CWB could ultimately remove 80.05% of Pb from the same amount of leachate (Fig. 3). Increase in affinity of activated carbon for various pollutants through particle size reduction has been reported in the literature [52]. Activated carbon (2% w/w) has been found to remove up to 64% and 99% of PAHs from aqueous solution using, respectively, granular and powdered activated carbon. In addition, reduction in biochar particle size can normally lead to increase in the number of particles in the system at a certain dosage of biochar providing greater surface area and higher chance of effective contact between adsorbates and the adsorbent surface. Another outcome would be the likelihood of more homogeneous distribution of particles in the system which makes it feasible to better predict adsorption behavior using isotherm models.

Higher adsorption of the heavy metals onto PWB compared to CWB that observed in this study, at the same applied condition, may also be attributed to the mitigation in interference of other compounds in the system by using fine-graded biochar. The interference of the other constituents of landfill leachate on adsorption of the heavy metals on biochar can play an important role due to the fact that other adsorbed molecules may block adsorption sites on the surface of biochar and therefore reducing the heavy metal uptake by biochar. The heavy metals in landfill leachate would have higher chance to attach to unoccupied sites on the surface of biochar if the available adsorption sites are more abundant i.e. when greater surface is provided by smaller biochar particles. This shows the importance of using biochar with smaller particle size distribution as observed for PWB in this study, to provide more adsorption sites for the heavy metals in the landfill leachate to be uptaken and eliminated from the system.

3.6. 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 [53,54]. 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 [46]. 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 squared errors (SSE). The SSE is said to be among the widespread used error functions. It can be written as:

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

where $q_{e(Experimental)}$ is the adsorption capacity at equilibrium condition obtained from adsorption experiments, $q_{e(Calculated)}$ is the calculated value of adsorption capacity at equilibrium state, and N is the number of data points [55].

3.7. Adsorption kinetics

Batch kinetic experiments were carried out for the adsorption of Pb, Zn, and Ni in landfill leachate onto PWB and CWB. The kinetics for adsorption of heavy metals onto wood-derived biochar was simulated using pseudo second-order model three which is widely used to study the adsorption kinetics of various pollutants. 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 [40].

3.7.1. Pseudo second-order kinetic model

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

$$q_t = \frac{k_{2p} q_e^2 t}{1 + k_{2p}\, q_e t} \tag{3}$$

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:

$$\frac{dq_t}{dt} = k_{2p}(q_e - q_t)^2 \tag{4}$$

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_{2p} t \tag{5}$$

Eq. (3) can be linearized and rearranged to other different linear forms as presented in Table 4. The Type 3 of the linearized pseudo second-order model has been reported to yield the highest determination coefficient among the other types of linearized pseudo second-order models and better describe the adsorption of adsorbates onto adsorbents [40,46]. Thus, the following linearized pseudo-second order equation was selected to be applied in this research:

$$\frac{t}{q_t} = \frac{1}{k_{2p}\, q_e^2} + \frac{1}{q_e} t \tag{6}$$

A plot of t/q_t versus t for adsorption of Pb, Zn, and Ni onto PWB and CWB are shown in Figs. 4 and 5, respectively. The values of k_{2p} and q_e can be determined from the intercept and slope of the plots. The kinetic rate constant k_{2p} (g mg^{-1} min^{-1}), initial sorption rate h (mg g^{-1} min^{-1}) and the amount of heavy metals adsorbed at equilibrium condition q_e (mg g^{-1}) at different levels of applied PWB and CWB are, respectively, presented in Table 5.

Very high (≥0.999) values of determination coefficients found for the pseudo second-order kinetic model in all applied levels of PWB and CWB indicating an excellent linearity. Results indicated a very good agreement between the experimental data and the calculated adsorption capacity by the pseudo second-order kinetic model which was also found in the literature for uptake of methylene blue by activated carbon [46] and heavy metals by carbon nanotubes [49]. Additionally, error analysis indicated that deviation occurred by application of the pseudo second-order kinetic model is negligible at all levels of the adsorbents PWB and CWB. Results of the present research show that the pseudo second-order kinetic model is able to well represent the experimental kinetic data of Pb, Zn, and Ni adsorption onto biochar, regardless of the biochar particle size. This supports the chemisorptions theory behind the pseudo second-order kinetic model for the heavy metals/biochar system; however, evaluation of variation of adsorption

Table 4
Different linear forms of Pseudo second-order kinetic equations

Type	Linear equation	Plot	Parameters	
			q_e	k_{2p}
1	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_{2p} t$	$\frac{1}{q_e - q_t}$ *vs.* t	1/intercept	slope
2	$\frac{1}{q_t} = \left(\frac{1}{k_{2p}\, q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{q_t}$ *vs.* $\frac{1}{t}$	1/intercept	intercept^2/slope
3	$\frac{t}{q_t} = \frac{1}{k_{2p}\, q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ *vs.* t	1/slope	slope^2/intercept
4	$\frac{q_t}{t} = k_{2p}\, q_e^2 - \frac{k_{2p}\, q_e^2 q_t}{q_e}$	$\frac{q_t}{t}$ *vs.* q_t	- intercept/slope	slope^2/intercept
5	$\frac{1}{t} = \frac{k_{2p}\, q_e^2}{q_t} - \frac{k_{2p}\, q_e^2}{q_e}$	$\frac{1}{t}$ *vs.* $\frac{1}{q_t}$	- slope/intercept	intercept^2/slope

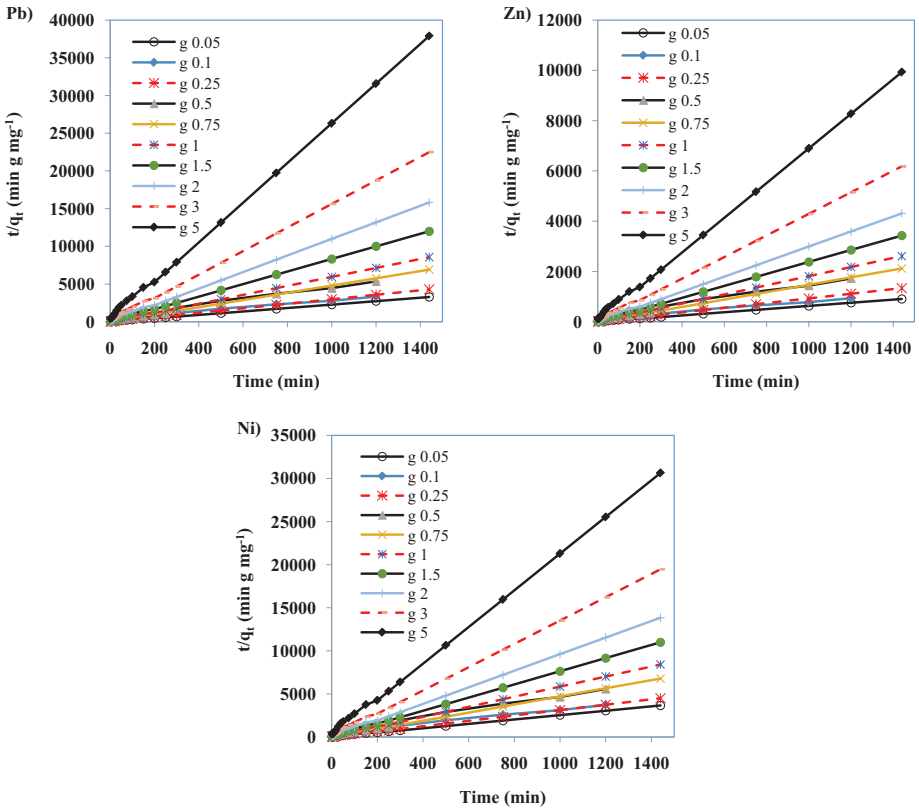

Fig. 4. Linearized pseudo second-order kinetics for adsorption of Pb, Zn, and Ni onto PWB at various levels of the adsorbnet.

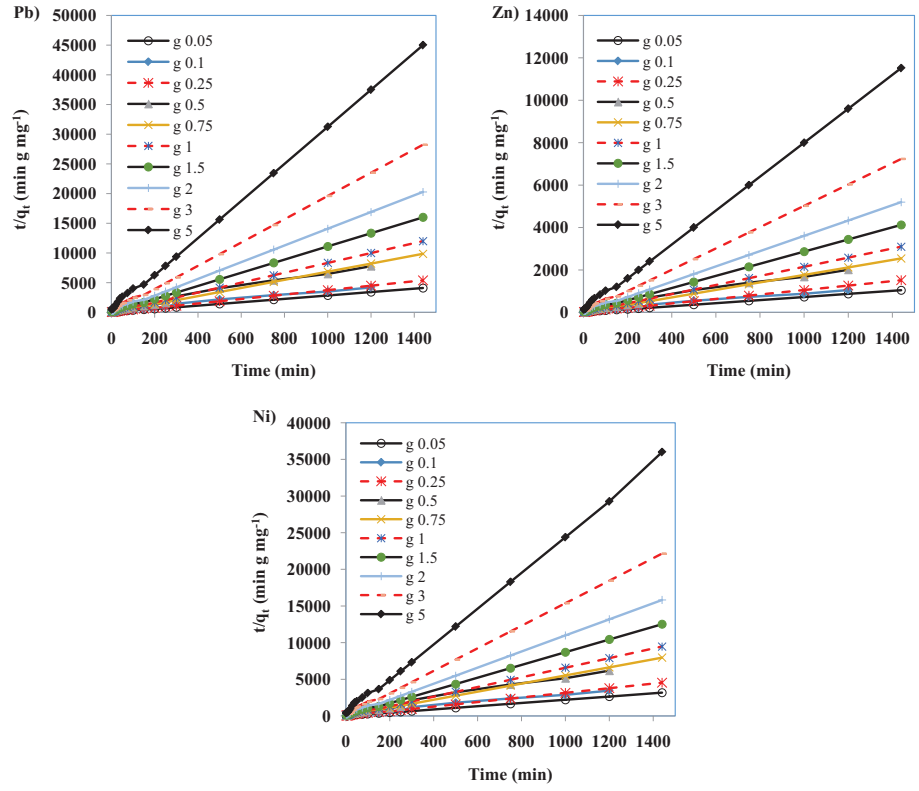

Fig. 5. Linearized pseudo second-order kinetics for adsorption of Pb, Zn, and Ni onto CWB at various levels of the adsorbent.

energy using appropriate isotherms such as Temkin model can provide deeper insight into the nature of adsorption adsorption of heavy metals onto biochar in this study. This suggests that the theory behind the pseudo second-order kinetic model is valid for heavy metals/biochar in leachate system. According to the k_{2p}values (Table 5), it can be noticed that the adsorption equilibrium rate for the studied heavy metals, regardless of the type of the used biochar, is as follows: Pb > Ni > Zn. Studies on adsorption of toxic elements onto other adsorbents such as sewage sludge also confirm the applicability of pseudo second-order model to best fit the experimental data [15]. From Table 5, it was observed that the predicted adsorption capacity decreases with increasing dosage of adsorbents. This is because of the fact that the adsorption process is actually a surface phenomenon in most cases; and increase in adsorption sites on the surface of an adsorbent through increase in mass of the adsorbent, while keeping the initial concentration of adsorbates constant, can lead to a decline in the adsorption intensity which was also observed experimentally in this work.

Table 5
Kinetic parameters of the pseudo second-order model for adsorption of the heavy metals in landfill leachate onto PWB and CWB

Adsorbate	Adsorbent dosage	Pseudo-first-order kinetic for PWB					Pseudo-first-order kinetic for CWB				
		$q_{e(cal.)}$ (mg g^{-1})	K_{2p}	h	R^2	SSE	$q_{e(cal.)}$ (mg g^{-1})	K_{2p}	h	R^2	SSE
Pb	0.05	0.446	0.115	0.023	0.999	0.000	0.358	0.147	0.019	0.999	0.000
	0.1	0.439	0.116	0.022	0.999	0.000	0.349	0.15	0.018	0.999	0.000
	0.25	0.341	0.15	0.017	0.999	0.000	0.272	0.197	0.015	0.999	0.000
	0.5	0.274	0.187	0.014	0.999	0.000	0.188	0.284	0.01	0.999	0.000
	0.75	0.212	0.242	0.011	0.999	0.000	0.149	0.363	0.008	0.999	0.000
	1	0.171	0.306	0.009	0.999	0.000	0.122	0.465	0.007	0.999	0.000
	1.5	0.122	0.428	0.006	0.999	0.000	0.092	0.625	0.005	0.999	0.000
	2	0.093	0.564	0.005	0.999	0.000	0.072	0.79	0.004	0.999	0.000
	3	0.065	0.807	0.003	0.999	0.000	0.052	1.104	0.003	0.999	0.000
	5	0.039	1.386	0.002	0.999	0.000	0.033	1.75	0.002	0.999	0.000
Zn	0.05	1.616	0.031	0.082	0.999	0.001	1.404	0.037	0.074	0.999	0.001
	0.1	1.536	0.032	0.079	0.999	0.000	1.395	0.038	0.073	0.999	0.001
	0.25	1.095	0.047	0.056	0.999	0.000	0.967	0.056	0.052	0.999	0.000
	0.5	0.85	0.06	0.044	0.999	0.000	0.729	0.074	0.039	0.999	0.000
	0.75	0.692	0.074	0.036	0.999	0.000	0.576	0.093	0.031	0.999	0.000
	1	0.561	0.094	0.03	0.999	0.000	0.473	0.12	0.027	0.999	0.000
	1.5	0.428	0.123	0.022	0.999	0.000	0.355	0.16	0.02	0.999	0.000
	2	0.34	0.154	0.018	0.999	0.000	0.282	0.201	0.016	0.999	0.000
	3	0.237	0.222	0.013	0.999	0.000	0.203	0.28	0.011	0.999	0.000
	5	0.148	0.354	0.008	0.999	0.000	0.127	0.452	0.007	0.999	0.000
Ni	0.05	0.4	0.126	0.02	0.999	0.000	0.461	0.114	0.024	0.999	0.000
	0.1	0.392	0.13	0.02	0.999	0.000	0.425	0.123	0.022	0.999	0.000
	0.25	0.326	0.157	0.017	0.999	0.000	0.323	0.166	0.017	0.999	0.000
	0.5	0.263	0.195	0.013	0.999	0.000	0.237	0.228	0.013	0.999	0.000
	0.75	0.216	0.237	0.011	0.999	0.000	0.184	0.293	0.01	0.999	0.000
	1	0.174	0.294	0.009	0.999	0.000	0.155	0.367	0.009	0.999	0.000
	1.5	0.133	0.384	0.007	0.999	0.000	0.117	0.491	0.007	0.999	0.000
	2	0.106	0.493	0.006	0.999	0.000	0.093	0.618	0.005	0.999	0.000
	3	0.075	0.697	0.004	0.999	0.000	0.066	0.873	0.004	0.999	0.000
	5	0.048	1.094	0.003	0.999	0.000	0.042	1.378	0.002	0.999	0.000

3.8. Modeling of adsorption isotherms

Experimental data obtained in adsorption studies can be modeled using various adsorption isotherms. The equilibrium data were modeled using the Freundlich, Langmuir, Elovich and Temkin isotherms in this study. At first, linearized equations were used to determine the appropriate parameters of each model based on the experimental values of q_e and C_e and the nonlinear form of isotherms were then reconstructed using the determined parameters to be able to predict adsorption capacity of PWB and CWB. Linear correlation determination (R^2) can be used to show the fit between the calculated data based on linearized isotherm models and the experimental data whereas the values of SSE was calculated in this study to examine the goodness of fit between the theoretical and experimental values of adsorption capacity used to plot non-linear original isotherm curves.

The experimental adsorption isotherms of Pb, Zn, and Ni in landfill leachate onto PWB and CWB are presented in Fig. 6. Results indicate that Pb is adsorbed on both PWB and CWB better than Zn and Ni. Adsorption of Zn on biochar was comparable with that of Ni with slightly higher adsorption for Zn. Shape of the isotherms can be used as a preliminary tool to describe the nature of a given adsorption reaction before evaluation of adsorption isotherm models and their associated parameters. Adsorption isotherms can be categorized into four main types: L, C, H, and S [53]. From Fig. 6 it seems that the adsorption of the studied heavy metals in landfill leachate onto biochar is more like the L-type and follows this pattern. One probable hypothesis would be that there is no strong competition between the solvent and the adsorbates to occupy the surface sites of adsorbent [48]; however, this needs to be further investigated through determination of isotherm model parameters.

3.8.1. 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 [26]. In other words, the adsorption sites are assumed to be equivalent having unit occupancy potential and at the maximum adsorption, only a monolayer can be formed i.e. adsorbate molecules may only adsorb onto the free surface of a given adsorbent and do not deposit on already adsorbed molecules. The non-linear expression of Langmuir isotherm model can be illustrated as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{7}$$

where C_e is the concentration of adsorbate (heavy metals in this study) in the bulk solution at equilibrium (mg L^{-1}); q_e is the corresponding adsorption capacity i.e. the amount of solute adsorbed per unit weight of adsorbent at equilibrium condition (mg g^{-1}); q_m is the Langmuir model constant indicating the maximum adsorption capacity (mg g^{-1}), and b is another Langmuir model constant which is associated with free energy or net enthalpy of adsorption (L mg^{-1}). Langmuir model equation can be linearized to five different linear types as indicated in Table 6.

The experimental data obtained for adsorption of Pb, Zn, and Ni onto PWB and CWB were treated by a regression analysis to fit different linearized forms of Langmuir isotherm model. Details of the various linearized Langmuir expressions and the corresponding plots to determine Langmuir constants i.e. q_m and b were indicted in Table 7. Values of the constants for different types of linearized Langmuir isotherm are presented in Table 7 for the adsorption of heavy metals in landfill leachate onto PWB and CWB. Results showed best fitting parameters for the linearized Langmuir equation 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 because of the minimization of deviations

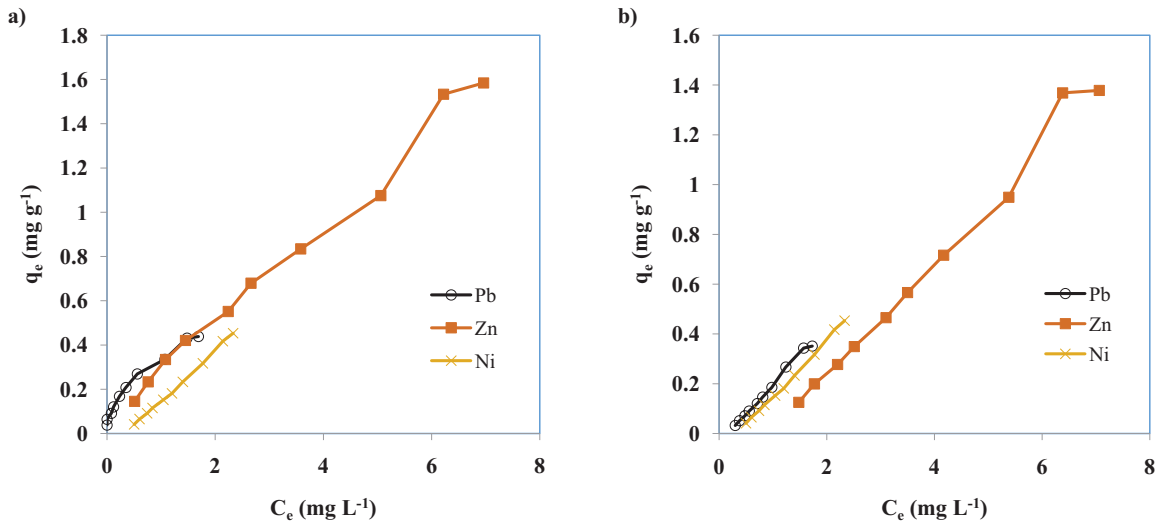

Fig. 6. Experimental isotherms of adsorption of heavy metals in the landfill leachate onto a) PWB and b) CWB.

Table 6
Langmuir model and its linear and on-linear forms

Type	Non-linear form	Linear forms	Plot	Parameters	
				q_m	b
1	$q_e = \frac{q_m b C_e}{1 + bC_e}$	$\frac{1}{q_e} = \frac{1}{bq_m}\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	1/intercept	intercept/slope
2		$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{bq_m}$	$\frac{C_e}{q_e}$ vs. C_e	1/slope	slope/intercept
3		$q_e = -\frac{1}{b}\frac{q_e}{C_e} + q_m$	q_e vs. $\frac{q_e}{C_e}$	Intercept	- 1/slope
4		$\frac{q_e}{C_e} = -bq_e + bq_m$	$\frac{q_e}{C_e}$ vs. q_e	- intercept/slope	- slope
5		$\frac{1}{C_e} = bq_m\frac{1}{q_e} - b$	$\frac{1}{C_e}$ vs. $\frac{1}{q_e}$	- slope/intercept	- intercept

Table 7
Parameters of the five different forms of linearized Langmuir isotherm for the adsorption of heavy metals in landfill leachate onto PWB and CWB

Isotherm	Pb		Zn		Ni	
	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
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
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
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
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

from the fitted model equation giving better error distribution [53].

Longmuir 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:

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

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 $R_L = 1$ [56,57]. The dimensionless separation factors calculated for adsorption of heavy metals onto PWB were less than 1 and greater than zero showing favorable adsorption, while the corresponding values for adsorption of heavy metals onto CWB were greater than 1 in all cases indicating an unfavorable adsorption (Table 7).

The values of the determination coefficient as well as separation factor, R_L, obtained from Langmuir-1 expression indicate positive evidence that the adsorption of Pb, Zn, and Ni in landfil leachate onto PWB follows the Langmuir isotherm. The fit of the measured data to the Langmuir model reveals the possibility of sorption of the studied heavy metals onto PWB through chemisorptions [58]. However, negative values obtained for maximum adsorption capacity of CWB showed that adsorption of the heavy metals in leachate onto CWB did not follow Langmuir isotherm suggesting that heavy metals do not follow the monolayer adsorption on the surface of CWB. The negative values for adsorption capacity have been reported in the literature such as adsorption of dyes onto activated carbon [46], which is practically and experimentally impossible.

Adsorption of Ni onto fly ash was also found to better fit the Langmuir isotherm [59] which is consistent with the results of the present study for PWB; however, adsorption of Ni onto the processed sugarcane leaves in aqueous solution better followed the Freundlich isotherm [60], suggesting that the physicochemical characteristics of a given adsorbent can also play an important role determining the adsorption pattern. The highest value of the Langmuir constant b, 3.22 L mg^{-1}, was obtained for Pb adsorption onto PWB (Table 7) exhibiting greater affinity of this heavy metal to the surface of PWB compared to the other studied heavy metals in landfill leachate.

It can also be inffered from Table 7 that the Langmuir constants obtained from different linear expressions were divergent demonstrating that transformation of non-linear model to linear forms may alter the error structure of a given isotherm model as also reported by other authors [26]. Smaller values of determination coefficient calculated for other linear expressions of Langmuir model, especially types 3 and 4, imply that it is not favourable to apply these types of linearization.

Negative values were also found for separation factor, R_L, when linearized Langmuir isotherm-Type 5 was applied for adsorption of Zn and Ni on CWB. Matematically negative value of separation factor, R_L, could be yield when $b < 0$ and $bC_0 < -1$ that means desorption was occurred instead of adsorption i.e. an unfavorable adsorption condition. Within the context of this work and considering the removal of Ni and Zn from system through addition of CWB to the landfill leachate, negative values of separation factor suggests that linearized Langmuir isotherm-Type 5 should be excluded to fit the calculated data to the measured data. The calculated values for SSE for different types of linearzed Langmuir isotherm are given in Table 8. Lower values of the SSE are obtained when Langmuir-4 and Langmuir-1 expressions are used to fit the experimental adsorption results, while Langmuir-5 expression give the highest SSE in most cases. Therefore, it seems that the values of coefficient of determination as well as separation factor are required to be taken into account, beside the error analysis results to determine the most appropriate form of the linearized type of the Langmuir model to fit the experimental adsorption data. Table 8 indicates that the error structure will get varies upon linearization of non-linear Langmuir isotherm equation and the approach used to linearize the Langmuir isotherm equation may shift the error distribution the better or worse.

Fig. 7 compares the simulated isotherm curves and measured data for adsorption of heavy metals on PWB based on Langmuir-Type 1 expression. Adsorbed amounts of heavy metals on biochar was clearly increased by adsorbent dosage. 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, compared to the other linearized forms of Langmuir model. Table 8 indicates markedly higher errors for adsorption of the heavy metals onto CWB in most cases compared to PWB when different forms of the linearized isotherm was applied. Despite of the high values of determination coefficients in some cases e.g. Langmuir-1 and Langmuir-5 expressions, this isotherm does not describe the obtained equilibrium data perfectly due to the relatively high values of calculated SSE in most cases. In other words, it is more appropriate to apply error analysis beside the determination coefficient of a given linear regression to compare the fitting of experimental and predicted data.

Table 8
The Sum of Error Squares (SSE) for different types of linearzed Langmuir isotherm

Linearized Langmuir Isotherm form	Pb		Zn		Ni	
	PWB	CWB	PWB	CWB	PWB	CWB
Type 1	0.016	0.364	0.045	9.593	0.008	0.842
Type 2	0.018	0.009	0.065	0.179	0.003	0.017
Type 3	0.011	0.02	28.368	0.268	0.001	0.02
Type 4	0.017	0.007	0.042	0.089	0.001	0.006
Type 5	0.015	1.001	0.042	103.066	0.009	7.146

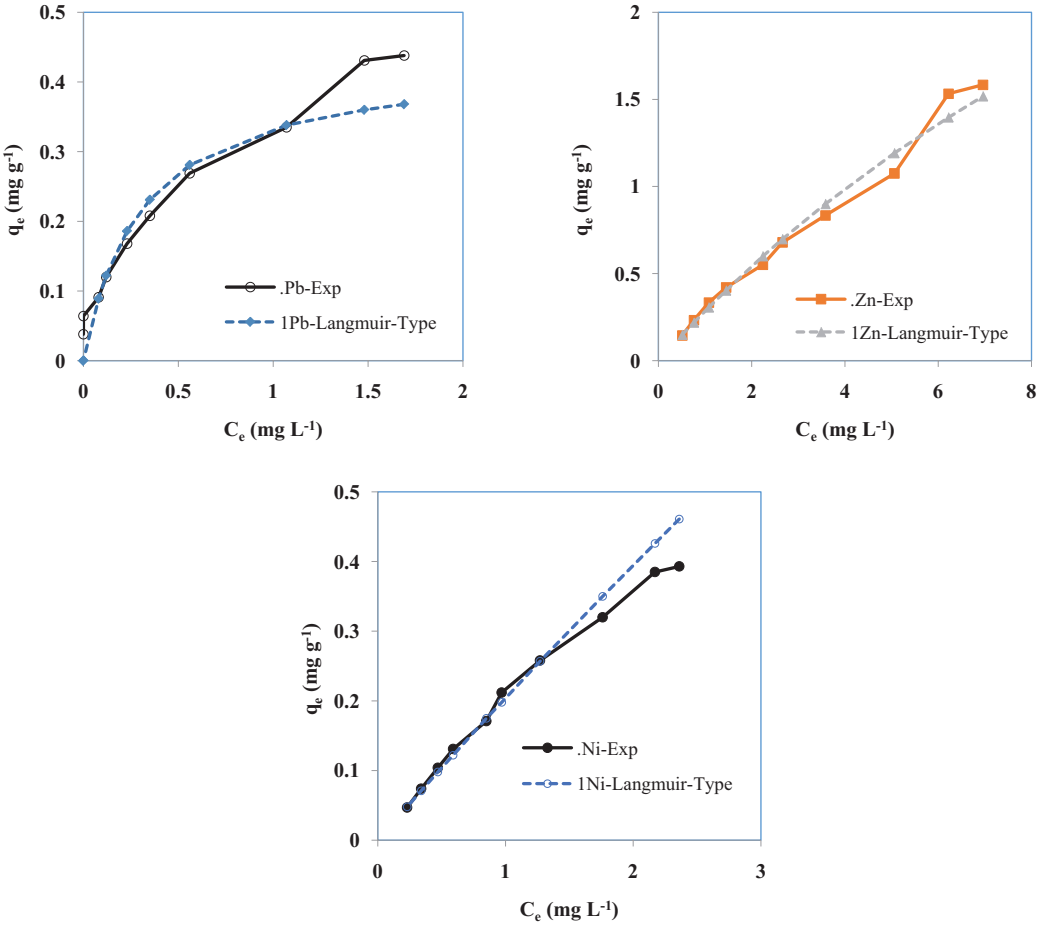

Fig. 7. Experimental and predicted adsorption of the heavy metals in landfill leachate onto PWB using Langmuir-1 expression.

3.8.2. Freundlich isotherm

The obtained equilibrium data were analyzed using the linearized form of Freundlich adsorption model. The Freundlich isotherm has been widely applied to characterize the adsorption of organic and inorganic pollutants using various adsorbents [48,61]. Freundlich isotherm constants found through plotting ln q_e vs ln C_e are given in Table 9.

Freundlich adsorption isotherm, which is conventionally considered to be an empirical isotherm based on adsorption on heterogeneous surface, describes that the adsorption intensity is not constant at different equilibrium concentrations. 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:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{9}$$

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:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{10}$$

The corresponding coefficients of correlation for Freundlich model were found to be high for adsorption of Pb, Zn, and Ni onto PWB as well as CWB (≥ 0.99) indicating a good linearity; however, the values of Freundlich coefficient, n, did not fall within the favorable range for adsorption of the heavy metals in landfill leachate onto CWB to demonstrate a good fit between the predicted and measured adsorption data. 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 [53]. Acceptable adsorption characterized by values of n between 1 and 10 has also been reported in the literature [56]. The highest value of the Freundlich coefficient was obtained for adsorption of Pb onto PWB (n = 1.992) (Table 9) showing the best fit to the Freundlich isotherm in comparison to other experimental adsorption results fitted to the Freundlich isotherm (Fig. 8), though the maximum obtained Freundlich coefficient still did not fall within the favorable range of 2–10 in this study.

Table 9
Linearized Freundlich isotherm constants for adsorption of the heavy metals in landfill leachate on PWB and CWB

Freundlich Isotherm Parameters	Pb		Zn		Ni	
	PWB	CWB	PWB	CWB	PWB	CWB
K_F	0.086	0.021	0.056	0.003	0.024	0.010
n	1.992	0.736	1.140	0.669	1.112	0.669
R^2	0.994	0.994	0.992	0.990	0.991	0.991
q_{max}	0.119	0.051	0.337	0.064	0.056	0.041
SSE	0.374	0.312	5.086	5.536	0.446	0.528

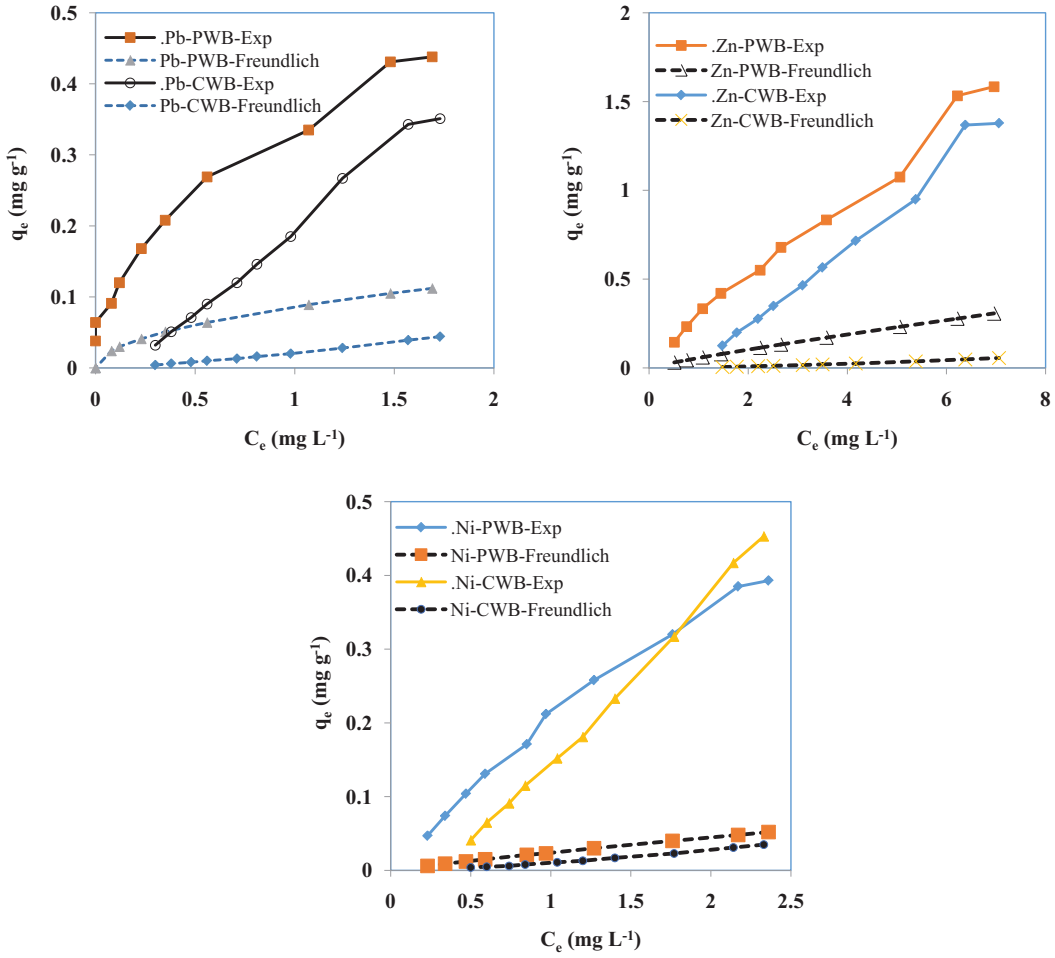

Fig. 8. Experimental and predicted adsorption of the heavy metals in landfill leachate onto PWB and CWB using Freundlich equation.

Greater values of K_f found for adsorption of the heavy metals onto PWB implies the higher relative adsorption capacity of PWB compared to CWB to eliminate Pb, Zn, and Ni from the landfill leachate (Table 9). The higher the K_F value, the greater would be the adsorption intensity. Thus, the pulverized wood-derived biochar was found to be a better adsorbent for Pb, Zn, and Ni in landfill leachate compared to the crushed wood-derived biochar because of more acceptable values of Freundlich coefficient ($1.112 \leq n \leq 1.992$) as well as higher K_f. Beneficial adsorption characterized by values of n between 1 and 10 has been reported in the literature [56]. The values of $1/n$, less than 1 suggests that significant adsorption of solute takes occurs at low concentrations while, the increase in the adsorbed amount is restricted at higher concentrations.

If only the linearized form of Langmuir-Type 1 is used for comparison, Langmuir-1 expression seems to be more suitable than Freundlich model to fit equilibrium data for adsorption of Zn and Ni onto PWB in view of the slightly greater values of determination coefficient. In contrast, when the other linearized forms of Langmuir isotherm is used, the Freundlich isotherm yields more suitable fit for

the measured data in most cases. Results show that none of the Freundlich and Langmuir models could describe adsorption of Pb, Zn, and Ni in landfill leachate onto CWB.

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 [53]; 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:

$$q_m = K_F(C_0)^{\frac{1}{n}} \tag{11}$$

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}) [53]. The calculated maximum adsorption capacity of PWB for Pb, Zn, and Ni using the Freundlich isotherm were, respectively, 2.3, 5.3, 1.4 times greater than the corresponding quantities for CWB. This also indicates PWB could remove Pb, Zn, and Ni from the landfill leachate more effective than CWB. 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. The maximum adsorption capacity calculated using the Langmuir-1 expression were greater than the corresponding values obtained using the Freundlich isotherm by a factor of 3.7, 16.9, and 85.1, respectively, for adsorption of Pb, Zn, and Ni onto PWB.

Fig. 8 shows the experimental and predicted adsorption capacity of biochar in two forms i.e. pulverized and crushed using Freundlich isotherm. It can be inferred from Fig. 5 that the predicted adsorption capacity of both PWB and CWB using the Freundlich isotherm is drastically underestimated for all the studied heavy metals.

Error analysis results are also presented in Table 9 showing high values of the SSE in all cases. It is inferred from Fig. 8 as well as Table 8 that there is not a suitable agreement between the predicted and measured adsorption data, implying the lack of validity of the Freundlich isotherm to model the adsorption of Pb, Zn, and Ni in the landfill leachate onto biochar. The SSE values found for the Freundlich model are higher than the corresponding values for the Langmuir-1 model in most cases.

Greater deviation of the Freundlich model to predict adsorption capacity was observed at higher equilibrium concentrations (Fig. 8) depicting a drawback of the Freundlich isotherm at higher solute concentrations in this study. The quantity of n as an indicator of the distribution of adsorbed ions on the adsorbent surface is found to be less than 2 in all cases suggesting that the Freundlich isotherm is unable to describe the measured equilibrium data adequately especially for the adsorption of Pb, Zn, and Ni in the landfill leachate onto CWB. Nevertheless, the obtained constants for the Freundlich isotherm show more effective removal of the heavy metals from landfill leachate and greater adsorption capacity when PWB was used as adsorbent compared to CWB. The higher the K_F value, the greater would be the adsorption intensity [56]. Therefore, the higher values of K_F obtained for PWB confirms that the adsorption capacity of the PWB is greater than that of CWB for removal of heavy metals from landfill leachate. The Langmuir isotherm was characterized by a slightly better fit to the experimental data than the Freundlich model when PWB was used as adsorbent showing that chemisorption processes are likely of higher importance in adsorption of the heavy metals onto PWB.

3.8.3. Elovich Isotherm

The elovich model is based on a kinetic principle that assumes the adsorption sites on the surface of an adsorbent increase exponentially with adsorption, implying a multilayer adsorption [62]. Elovich isotherm is given by the following equation:

$$\frac{q_e}{q_m} = K_E C_e \exp(-\frac{q_e}{q_m}) \tag{12}$$

where K_E is the Elovich equilibrium constant (L mg^{-1}) and q_m is the Elovich maximum adsorption capacity (mg g^{-1}). The original equation needs to be linearized in order to determine the Elovich parameters. Elovich constant and Elovich maximum adsorption capacity can be calculated from the slope and the intercept of the plot of $\ln(q_e/C_e)$ vs. q_e, if the adsorption follows Elovich equation. Elovich isotherm can be rearranged and linearized as given by the following equation:

$$\ln(\frac{q_e}{C_e}) = \ln(K_E q_m) - \frac{q_e}{q_m} \tag{13}$$

The Elovich isotherm parameters for adsorption of Pb, Zn, and Ni onto biochar were obtained through linearization of the Elovich equation presented in Table 10. The Elovich isotherm exhibited lower coefficients of determination in comparison with the Freundlich and Langmuir isotherms; however, error analysis showed markedly smaller values of the SSE in most cases compared to both Langmuir and Freundlich isotherms. The quantity of Elovich constant, K_E, obtained for adsorption of Pb onto PWB was significantly higher than those obtained for adsorption of Zn and Ni indicating the greater affinity of PWB for Pb compared to Zn and Ni in landfill leachate. Higher value of K_E for adsorption of Pb onto PWB is consistent with the greater removal of Pb from the landfill leachate compared to the other two studied heavy metals. Sum of error squares calculated for the adsorption of heavy metals onto CWB were lower than the corresponding errors found for the Langmuir and Freundlich isotherms; though negative values of Elovich constants were found for adsorption of the heavy metals on CWB (Table 10). This shows that the assumption of the exponential occupation of adsorption sites that implies multilayer adsorption of the heavy metals is not applicable when CWB was used as the adsorbent. Hence, the Elovich isotherm is unable to describe adsorption of Pb, Zn, and Ni in the landfill leachate onto CWB.

Negative values of the Elovich constants are physically not applicable and may be caused due to occurrence of overemphasized data points at low adsorbent dosage as a result of linearization of the isotherm. Although negative values for K_E obtained for CWB is practically not acceptable, but one probable explanation would be that repulsive forces between adsorbed heavy metals may increase at lower lev-

Table 10
Elovich isotherm parameters for adsorption of the heavy metals in the landfill leachate onto PWB and CWB

Elovich Isotherm Parameters	Pb		Zn		Ni	
	PWB	CWB	PWB	CWB	PWB	CWB
K_E	6.516	–0.213	0.057	–0.056	0.165	–0.170
q_{max}	0.238	–0.601	5.208	–1.862	1.41	–0.601
R^2	0.963	0.775	0.58	0.79	0.736	0.790
SSE	0.0093	0.0033	0.0594	0.0443	0.0011	0.0046

els of applied CWB due to the limited surface available to accommodate adsorbed solutes that might shift the adsorption pattern to the multilayer adsorption. Repulsive forces between positively charged adsorbates on adjacent layers is likely to elevated to an extent exceeding the binding forces causing desorption. Therefore, even if the multilayer assumption proposed by the Elovich isotherm is admitted, the quantity of repulsive forces between adjacent layers adsorbing solutes with same electric charge could also play an important role, especially at lower applied dosage of CWB. Furthermore, competitive adsorption of other solutes in the actual landfill leachate containing a wide range of suspended and dissolved compounds can also interfere with the adsorption reaction; particularly when adsorption sites are limited due to the smaller amounts of used adsorbents or the lower specific surface of a given adsorbent. This indicates that the assumption of the exponential occupation of adsorption sites on the surface of CWB that implies multilayer adsorption is not consistent with the findings of this research with the applied condition. Hence, the Elovich isotherm is not able to well describe the adsorption of heavy metals in the landfill leachate onto CWB.

Maximum adsorption capacity of PWB obtained from fitting the measured data to the Elovich isotherm was lower than the corresponding values obtained using Langmuir isotherm; but higher than those obtained for Freundlich model. The values of the maximum adsorption capacity determined using the linear transformation of the Elovich equation for PWB was higher than the corresponding values found for the Freundlich isotherm; but lower than those obtained for the Langmuir-1 expression.

Despite the good determination coefficients, the quantity of maximum adsorption capacity of Pb obtained using the Elovich equation is lower than the measured adsorbed amounts at equilibrium condition corresponding to the adsorption model plateaus. In addition, deviation of the predicted adsorption using the Elovich model raised the equilibrium concentration increased i.e. at lower applied dosage of biochar, particularly for Pb (Fig. 9). Fitting of the heavy metals uptake by PWB to the Elovich isotherm agreed well with previous studies [49]. Results indicates that the adsorption of the heavy metals in landfill leachate can be described using the Elovich isotherm, but the Elovich model is unable to represent their adsorption onto CWB.

3.8.4. 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 [53,63]. Temkin isotherm equation contains a factor that reflects the adsorbent-adsorbate interactions. The nonlinear form of Tempkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \tag{14}$$

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:

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{15}$$

The slope and intercept from a plot of q_e versus ln C_e determines the isotherm constants K_T and b_T. The values of the Temkin parameters are given in Table 11. In addition, b_T, which is the variation of adsorption energy can also be known through determination of the Temkin isotherm constants.

The adsorption data for heavy metals onto PWB and CWB were analyzed using a regression analysis to fit the Temkin isotherm model. The obtained parameters of Temkin model as well as the determination coefficients are presented in Table 11. The SSE were also calculated and given in Table 11. The values of determination of coefficient determined using the linear transformation of the Temkin equation was higher than the Elovich isotherm, but slightly lower than those obtained for the Langmuir-1 and Freundlich models. The high values of the determination coefficients indicate a good linearity. The higher regression values of more than 0.99 for fitting the measured data to the Temkin isotherm may be able to describe the adsorption of the heavy metals in landfill leachate onto PWB and CWB better than the Elovich model. The variation of adsorption energy, b_T, was positive for all the studied heavy metals implying that the adsorption of the studied heavy metals onto biochar is an exothermic reaction that is in agreement with the findings of Hamdaoui and Naffrechoux (2007) where exothermic adsorption of phenolic compounds onto activated carbon was observed [48].

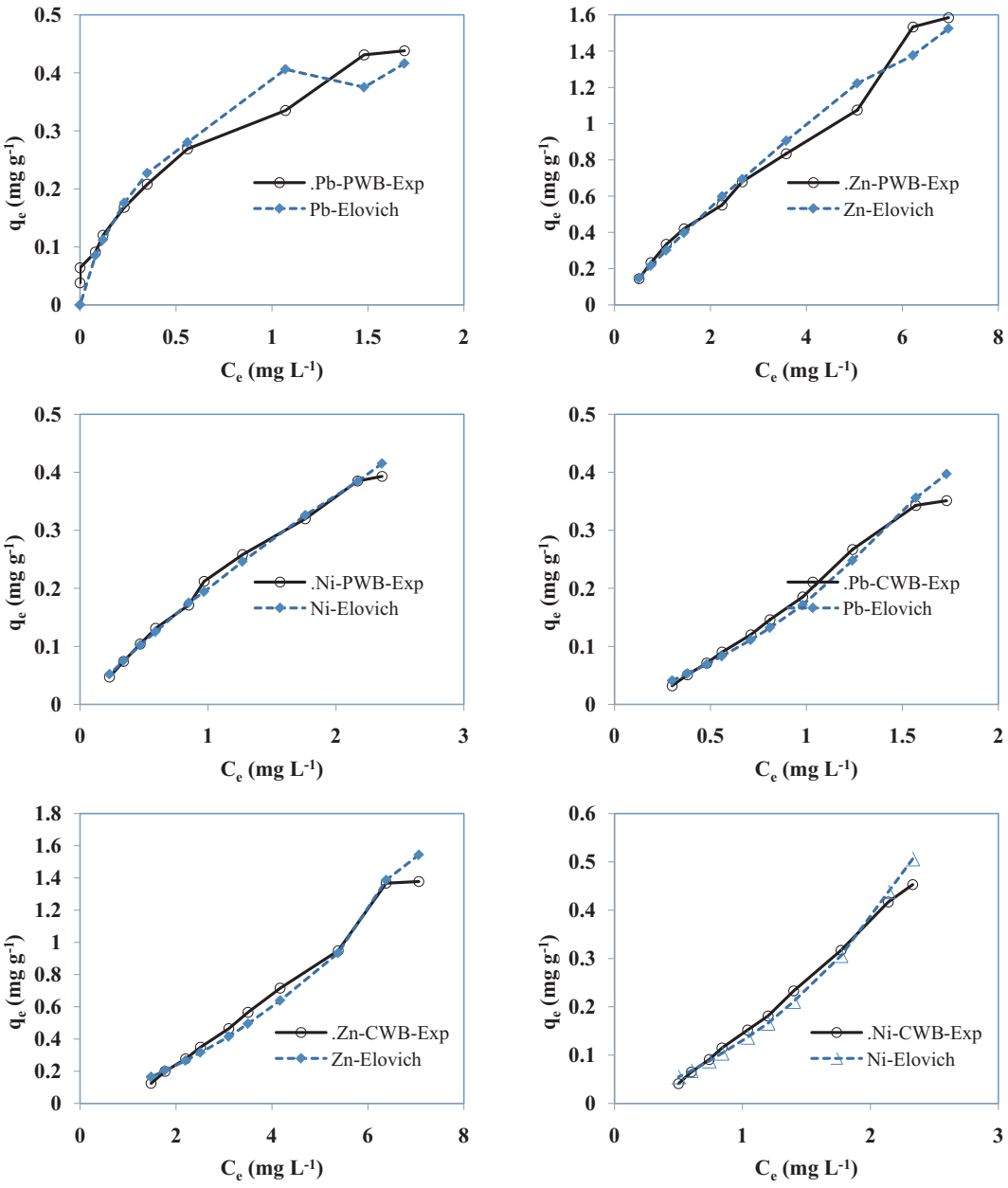

Fig. 9. Experimental and predicted adsorption of the heavy metals in landfill leachate onto PWB and CWB using Elovich equation. .

Table 11
Temkin isotherm parameters for adsorption of the heavy metals in the landfill leachate on PWB and CWB

Temkin Isotherm Parameters	Pb		Zn		Ni	
	PWB	CWB	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
APE	8.55	28.66	31.07	27.87	17.24	26.06
CHI	0.020	0.096	0.527	0.339	0.0538	0.100

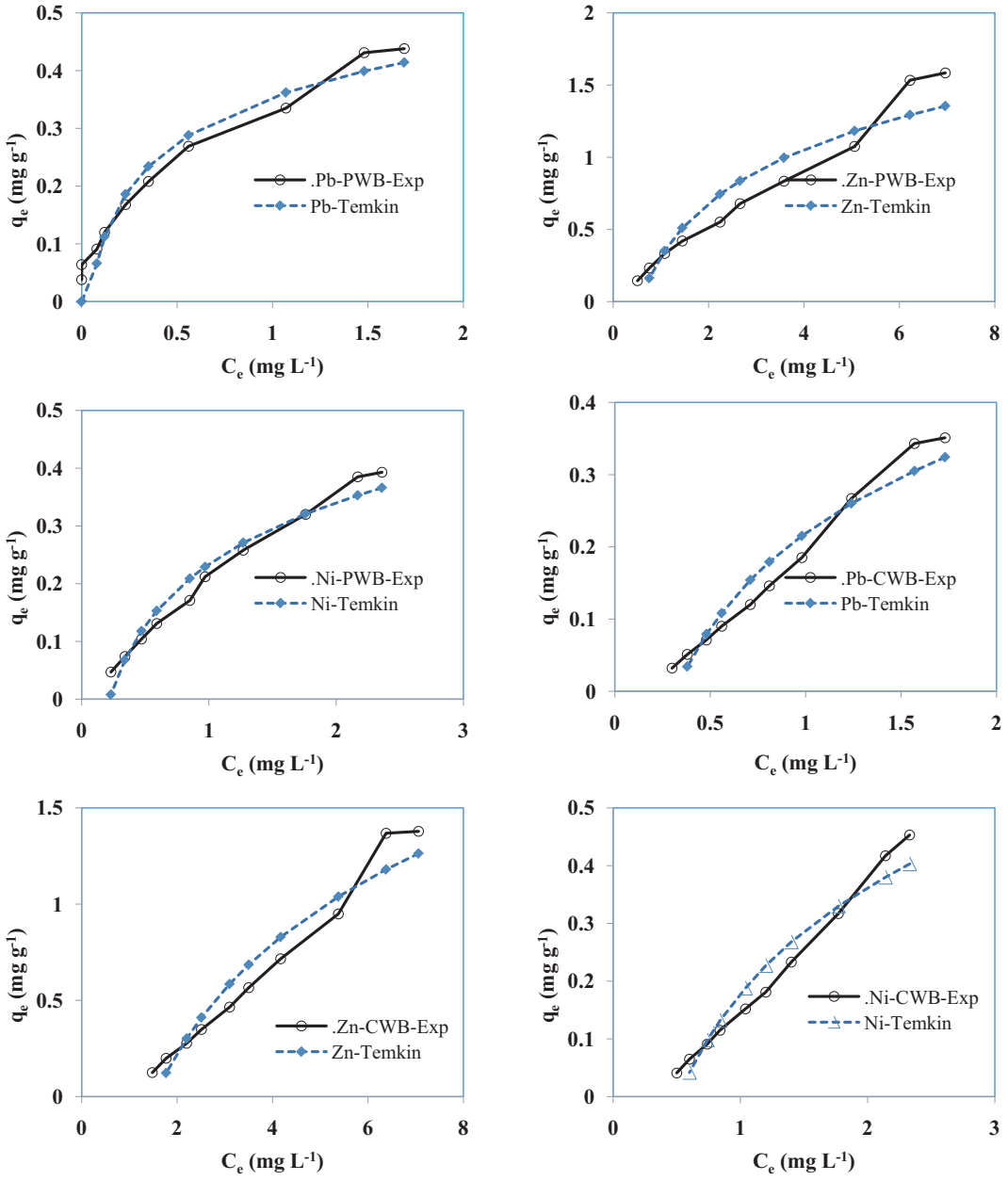

Fig. 10. Experimental and predicted adsorption of the heavy metals in landfill leachate onto PWB and CWB using Temkin equation.

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 Langmir equation, if the equilibrium concentration is increased, the adsorption capacity of the original Temkin equation, q_e, does not converge to any limiting value. The predicted isotherm curves were compared with the corresponding experimental data as shown in Fig. 10 showing 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 biochar was applied that means at higher equilibrium concentrations. Error analysis indicates smaller values of the SSE relative to the Langmuir-1 and Freundlich isotherms in most cases. Based on the obtained results it seems that Temkin model can adequately describe the adsorption of the heavy metals in the landfill leachate onto PWB and CWB because of the high coefficients of determination as well as low values of the obtained SSE.

The variation of adsorption energy, b_T is found to be positive for adsorption of all three studied heavy metals onto PWB and CWB, which indicates that the adsorption reaction is exothermic. The highest value of b_T (21.73 K/mol^{-1}) was obtained for adsorption of Pb in the landfill leachate onto PWB. Released heat of adsorption obtained in this study was lower than 20 KJ/mol^{-1} in all other cases representing the physiosorption of the heavy metals in landfill leachate

onto biochar. Salam et al. (2013) reported that the physical adsorption is characterized by adsorption energy in the range of 5–40 KJ/mol^{-1} [49]. Physisorption may occur as a result of weak forces of Van der Waals between the adsorbates and adsorbents [51]. Higher amounts of variation of energy obtained using the Temkin isotherm for adsorption of Pb, Zn, and Ni onto PWB relative to those obtained for CWB indicates greater capacity of PWB to adsorb heavy metals in landfill leachate.

Adsorption of heavy metals onto PWB was adequately represented using all the applied isotherm models, except the Freundlich model implying that the adsorption onto PWB may be controlled by surface diffusion and pore diffusion simultaneously as well as adsorption at an active preoccupied site i.e. multilayer adsorption is also likely to occur according to the isotherm fitting results.

4. Conclusion

The adsorption of Pb, Zn, and Ni in landfill leachate onto pulverized and crushed biochar particles were investigated in this study. The adsorption experiments showed high effectiveness of biochar for the removal of Pb, Zn, and Ni from the fresh landfill leachate. The adsorption of all three studied heavy metals onto biochar was influenced by contact time, adsorbent dose, and biochar particle size. Equilibrium adsorption was achieved in about 200 min and 150 min for PWB and CWB, respectively. The optimum adsorbent dosage was found to be 2 g/100 ml (20 g L^{-1}) both for PWB and CWB. PWB exhibited significantly higher adsorption capacity toward the heavy metals in landfill leachate in all cases, regardless of the heavy metal species and the adsorbent dosage suggesting the significance of biochar particle size in adsorption experiments. The highest removal rate was obtained for Pb implying greater affinity of PWB and CWB for lead in landfill leachate. Adsorption of Zn and Ni from the landfill leachate using PWB and CWB was comparable with slightly higher removal rate for Zn.

The pseudo second-order kinetic model precisely represented the adsorption kinetic data, both for PWB and CWB. The Temkin isotherm best represents the equilibrium adsorption data for PWB and CWB. Adsorption of heavy metals onto PWB was adequately represented using all the applied isotherm models implying that the adsorption onto PWB may be controlled by surface diffusion and pore diffusion simultaneously as well as adsorption at an active preoccupied site i.e. multilayer adsorption is also likely to occur according to the isotherm fitting results. However, the Elovich, Langmuir, and Freundlich isotherm could only describe the equilibrium adsorption of the heavy metals onto PWB with the following order: Elovich > Langmuir > Freundlich.

Deviation of the predicted data from the experimental data using the Elovich isotherm was lower than those obtained by the Langmuir isotherm at lower levels of applied adsorbents in most cases suggesting a multilayer adsorption of the heavy metals in landfill leachate on biochar rather than a monolayer adsorption when smaller amounts of biochar is used. The mode of linearization of the Langmuir isotherm influences the estimation of model parameters. The type 1 Langmuir expression was found to be the best linearized form among the five examined linearization methods for predicting the optimum parameters for the Langmuir model representing the lowest SSE. PWB showed the highest theoretical adsorption intensity of 5.71 mg g^{-1} for the removal of Zn from the landfill leachate attained using the Langmuir model. Slightly higher deviation of the Langmuir, Freundlich and Elovich models to predict adsorption capacity was observed at higher equilibrium concentrations. The Elovich and Temkin models showed the lowest values of SSE to fit the experimental data, whereas the Freundlich isotherm presented the greatest error values in most cases. The Temkin isotherm provided an estimation of the variation of adsorption energy showing that the adsorption of heavy metals onto biochar is exotherimc, that is charcterized by physiosorption reaction due to the low amount of variation in adsorption energy found in this study. The greatest energy release was found for the adsorption of Pb in landfill leachate onto PWB. Varying the heavy metal concentration in landfill leachate through dilution or thickening to investigate the kinetics and isotherms for adsorption of the heavy metals with different initial concentrations in landfill leachate onto biochar particles is suggested to be evaluated. Finally, biochar in both pulverized and crushed forms demonstrated that it is a promising cost-effective adsorbent for the elimination of heavy metals from landfill leachate system.

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