



Removal of Pb(II) from contaminated water using low-temperature pyrolyzed agricultural and forest waste biochars: a comparative study

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ABSTRACT

This paper investigates the use of biochars prepared from abundant agricultural and forestry wastes in the removal of toxic Pb(II) ions from aqueous solutions. The biochars were prepared by the pyrolyzation at 400°C of saw dust, rice straw and rice husk. The efficacy of biochar in Pb(II) removal depends on its grain size, the dose of the biochar, pH and the initial concentration of the metal ion solution. The optimum adsorption was found to be within 1 h at a pH range of 5.0–7.0. Three isotherm models were employed to describe the Pb(II) adsorption on to biochar surfaces. Among these, the Langmuir isotherm model was a better fit for saw dust and rice straw biochar gave the highest regression coefficients of 0.97 and 0.95, respectively. But rice husk obeys the Langmuir model only at low concentrations with a regression coefficients of 0.956. The separation factor (R_L) for saw dust and rice straw biochars were 0.234 and 0.128; this indicates a favourable sorption isotherm for Pb(II). The results of this study showed that 90%–94% removal of Pb(II) ion from aqueous solution could be attained by using saw dust biochar. The Freundlich model fitted well with the experiment data for all three sources of biochars. Only rice husk biochar fitted the Temkin isotherm model. The adsorption capacity of the biochars was in the order of saw dust>rice straw>rice husk. The FTIR spectra of three biomass samples indicated that Pb(II) metal can be adsorbed by the biochars specifically through the formation of surface complexes between Pb(II) and the functional groups on biochars.

Keywords: Agricultural waste; Adsorption; Isotherm models; Pyrolysis of organic waste; Wastewater treatment

1. Introduction

Heavy metals pollutants of surface and groundwater are a concern as they pose serious health threats even at extremely low concentrations [1]. Among many sources of heavy metal pollutions, industrial activities are nowadays significant [2]. Therefore, industrial effluents should be treated properly before being discharged into the natural environment. Chemical precipitations, conventional adsorption [3,4], ion exchange [5], membrane separation methods [6] and electro-remediation methods are used more commonly to treat industrial wastewater. Among these methods, precipitation is the most economical, hence widely used, but

many industries still prefer chemical procedures for the treatment of effluents due to economic factors [7,8]. However, due to complexing agents in wastewater, efficiency of the precipitation process can drastically be decreased [9], and this creates incomplete processing and the production of toxic sludge. Therefore, numerous novel approaches have been investigated to develop cost effective and efficient heavy metal adsorption techniques [10,11].

Lead (Pb) is one of the most commonly found heavy metals in aqueous wastes. It is mainly released to water from industries such as metal plating, tanneries, oil refining and ore mining. It is also very well documented that lead is toxic to humans and wildlife [12]. Acute exposure to Pb in the environment causes health problems such as hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioural changes and learning

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disabilities [13,14]. Chronic exposures to extremely lower levels (<10 µg/L) of Pb could cause anaemia, kidney disease, nervous disorders and even death [15]. Therefore, the efficient and accurate treatment of industrial wastewater containing Pb is extremely important.

Adsorption is considered as a user-friendly and a cost effective-purification and separation method for removal of heavy metals [16]. Therefore, it has been widely used for the treatment of wastewater. Recently hybrid materials or polymers with functionalized groups exhibit more efficient adsorption affinities for heavy-metal ions when they are used as the hybrid adsorbents [17,18]. However, applications are less due to the lack of sufficient theoretical understanding. Inorganic-organic hybrid materials with biochar were effectively used for removal of Pb(II) from waste water [19]. Activated carbon is frequently used as an adsorbent material but only a few milligrams of metal ions can be adsorbed per gram of activated carbon [20,21]. Due to the difficulty in regeneration, activated carbon becomes expensive for treating wastewater, and hence the introductions of low cost alternatives are extremely important [22]. Sorption materials made from agricultural or industrial by-products such as biochars are therefore emerging widely to remove heavy metals from aqueous solutions due to their abundant availability, low cost, and favourable physical, chemical and surface characteristics [23].

Biochars are pyrogenic carbon-rich materials mainly composed of aromatic compounds that could be used as effective adsorbents. These can be produced by thermo-chemical decomposition (pyrolysis) of biomass at temperatures of 200°C–900°C in the presence of little or no oxygen [24,25]. The production temperature and feedstock composition of the materials have a significant influence on the pore structure, surface area and adsorption properties of biochar [26]. Biochars with a large amount of carbon are usually formed at high temperatures by pyrolysis. At high temperatures (400°C–700°C), biochar generally have a lower amount of functional groups on the surface this is due to decarboxylation. Whilst at lower temperatures biochar contain a significant amount of C=O and C-H groups that promote nutrient and water retention [27]. Surface functional groups such as ligno-cellulose sites begin to degrade at approximately 120°C, hemicelluloses at 200°C–260°C, cellulose between 240°C and 350°C and lignin at 280°C–350°C [28]. Many previous studies have pointed out that biochar produced at high temperatures from: wastes of animal, food, forestry, paper mill and crop residues, municipal solid waste, sludge are potential sorbents for treating contaminated water due to the existence of carboxyl, hydroxyl and phenolic functional groups in the surface [29,30]. Biochar has also been extensively used for the removal of pesticide and hydrocarbons pollutants from water and wastewaters [31]. It has a significant potential as a soil modifier due to its slow oxidizing process in the soil environment [32]. This oxidation process has been lead to significant increases of acidic surface oxygenated groups which are essential for improving the nutrient holding capacity, water retention ability and binding capacity of positively charged metal ions to biochar [33].

Agricultural waste materials contains hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch with varieties of functional groups such as acetamido,

alcoholic, carbonyl, phenolic, amido, amino and sulfhydryl groups [34,35]. These groups have the ability to bind to heavy metal ions by the donation of an electron pair to form complexes or chelates with the metal ions in solution [36]. Therefore, agricultural waste materials can be used as an effective, economic and eco-friendly biosorbent to treat water and wastewater. However, most of the early studies used high temperature pyrolyzed materials. Therefore, this study aims to identify a better biochar, obtained from agricultural and forestry waste, which is pyrolyzed at a low temperature that can then be used to remove Pb(II) from an aqueous environment. Biochar made from rice husk, rice straw and saw dust that has been pyrolyzed at 400°C has been investigated. These materials were characterized and investigated under different physico-chemical conditions for the removal of Pb(II) from contaminated wastewater.

2. Materials and methods

Biochar derived from rice husk and rice straw generally showed higher ash content at all temperature ranges [37]. Khodadad et al. [38] also noted that biochar obtained from saw dust, pyrolyzed at low temperature contains a relatively larger amount of aromatic-organic matter that increases the adsorption capacity. Biochar materials for this study were prepared by pyrolyzing rice husks, rice straws, and saw dusts at 400°C for 2 h. The pyrolyzed materials were washed thoroughly with deionized water to remove any remaining dirt. It is then dried at 100°C and mechanically sieved to use for adsorption experiments. Batch sorption studies were conducted under laboratory simulated conditions using known concentrations of Pb(II) solutions. A stock solution (1,000 mg/L) of Pb(II) was prepared by using Pb(NO₃)₂ and diluted to the required concentrations. All adsorption experiments were performed at room temperature (27°C ± 1.0°C). The experimental variables were initial pH of the solution, contact time and particle size of the biochar.

Batch experiments were carried out using the prepared materials to select the suitable size fraction of different biochar materials. Particle size fractions were <0.125, 0.125–250, 0.250–0.50 and >0.50 mm. The various of particle sizes were tested with an initial Pb(II) concentration of 5.0 mg/L. Samples were taken at 30 min intervals and experiments were conducted over a 9-h period. After selecting the most suitable size fraction for optimum Pb(II) adsorption, other experiments were continued using suitable particle size. To find out the optimum equilibrium time for sorption of Pb(II) on saw dust and rice straw, biochar were conducted. All experiments were performed thrice and the average values were used in all calculations. 0.1 g biochar of <0.125 mm mesh sizes was mixed in 100 mL Pb(II) solution. Samples were shaken at 600 rpm and samples were collected at different time intervals. The pH for the experiments were adjusted as the original pH of the test solution was 2.6. After completion of each test, the solution was filtered using 0.45 µm cellulose acetate filters and the residual Pb(II) ion concentration of the solution was determined by Varian 240FS atomic absorption spectrometrically (AAS). To determine the optimum pH range for the adsorption of Pb(II) by different biochar samples, 100 mL of Pb(II) solution was transferred into five 250 mL glass conical flasks containing 0.1 g of the adsorbents separately.

The initial pH of the suspension was adjusted from 3.0 to 9.0 by adding either 1.00 M HNO₃ or 1.00 M NaOH and the mixtures were shaken for 60 min using a mechanical shaker. The equilibrium sorption was carried out at room temperature using a concentration range of 5 to 30 mg/L Pb(II). 0.1 g of each biochar was weighed into 250 mL glass conical flasks and 100 mL of the Pb(II) ion solution were added. The conical flasks were shaken for 60 min at room temperature in a shaker at 600 rpm. The substrates were removed from the mixture by filtration and the concentrations of the residual ion in the solution were determined by AAS. Hach Sension pH meter was used for all pH measurements.

All experiments were performed in triplicate. After selecting the optimum conditions, the amount of Pb(II) removed or adsorbed and the removal percentages (%) of Pb(II) were calculated using the mass balance equations given below:

$$q = \frac{(c_i - c_f)V}{m} \quad (1)$$

$$\text{Removal percentage(\%)} = \frac{(c_i - c_f) * 100}{c_i} \quad (2)$$

where q is the amount mg/g of Pb(II) adsorbed, C_i and C_f are the initial and final concentrations of Pb (II) (mg/L), respectively, V is the volume of solution and m is the weight of the biochar used for the experiment. All materials were characterized by Fourier Transformation Infrared Spectroscopy (FTIR) using a Thermo Scientific Nicolet iS-10 spectrometer between 400 and 4,000 cm⁻¹ in which samples were mounted onto a transparent polyethylene film.

3. Results and discussion

3.1. Sorption experiments

Sorption experiments were carried out to determine a suitable particle size, optimum pH, required time and the initial Pb(II) content of the solution. Five (5.0) mg/L initial Pb(II) concentration was used as previous studies were conducted at the same initial concentration [39,40]. The most suitable particle size biochar for the optimum adsorption was found to be <0.125 mm. This was possibly due to the biochars having a large surface area and therefore higher number of metal binding sites hence further experiments were performed using this size fraction (Fig. 1).

The initial pH of the solutions was set between 3 and 9 for Pb (II) sorption while initial concentration was maintained as 5 mg/L. The percent removal of Pb(II) at initial pH of 3.0, 4.0, 5.0, 7.0 and 9.0 on rice husk biochar were 34%, 59%, 69%, 74%, 82%, respectively, whereas for rice straw biochar, it was 51%, 82%, 83%, 83%, 83% and for saw dust it was 6.5%, 54%, 90%, 89%, 94%. The adsorption of Pb(II) was 90% at pH 5.0 for saw dust biochar. Previous studies indicated that almost 92% of Pb(II) adsorption was obtained with the same type of biochar at this pH [41]. As indicated in their study Pb(II) adsorption was followed by a pseudo-second order kinetics in which adsorbent dosage was 5 g/L with the equilibrium time of 1 h. When the pH was increased to 9, the maximum Pb(II) adsorption was achieved by the saw dust biochar (94%), whereas rice straw biochar reached its maximum adsorption of Pb(II) as 83%. Rice husk biochar also was recorded as 82% adsorption at pH 9. The zero point charge (pH_{ZPC}) of saw dust, rice straw and rice husk biochar was 6.68, 7.8 and 8.5, respectively [41,42]; hence, the pH was below the pH_{ZPC}, the biochar surfaces are negatively charged so that they can attract positively charged ions. Sreejalekshmi et al. [43] indicated that the maximum adsorption percentage for Pb(II) ions at the pH 6 was 97% and was achieved in 120 min of contact time between the saw dust and the solution. At low pHs with higher hydronium concentrations, these may protonate the sorption sites in biochar and reduces the binding of Pb(II). In addition, at low pH, most of the functional groups are protonated [44]. This will reduce the number of binding sites available for the adsorption of metal ions. As the pH increases, the binding sites become negatively charged due to the presence of the hydroxyl group and Pb(II) ions can be precipitated as insoluble hydroxide.

The adsorption of heavy metals from biochar obtained from pig and cow manure showed that with increasing pH, the adsorption efficiency of Pb(II) increases since the competition of metal ions and protons to bind to these sites were decreased [45]. It is clearly shown that low pH is not economically viable for the removal of Pb(II) ions using selected biomass biochar since the removal is less than 45% (Fig. 2a). However, near 90% of Pb(II) were removed at neutral pH levels from saw dust while 70%–80% of the Pb(II) adsorption were observed for rice straw and rice husk biochars at a neutral pH.

The influence of contact time for the adsorption of Pb(II) on the biochars was investigated by successively increasing

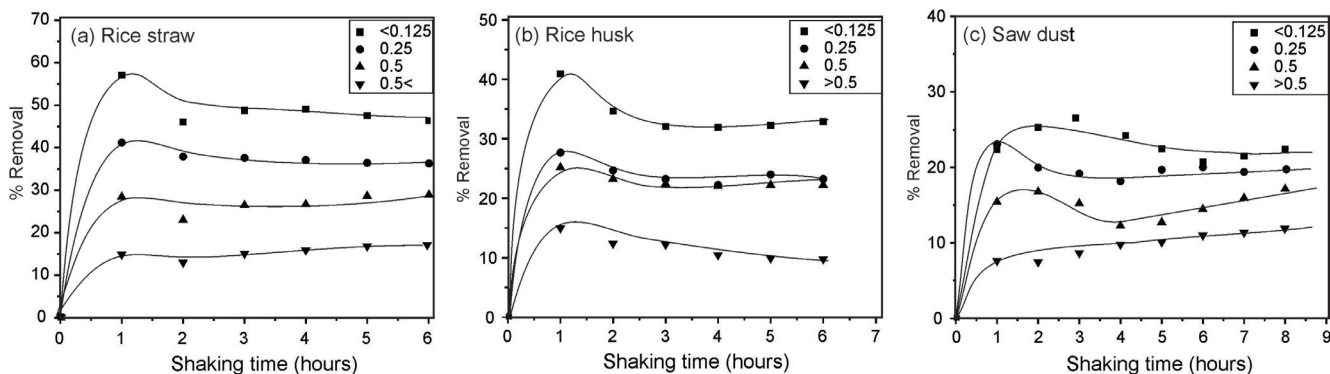


Fig. 1. Adsorption of Pb(II) on to different size fractions of (a) rice straw, (b) rice husk and (c) saw dust biochars with the shaking time.

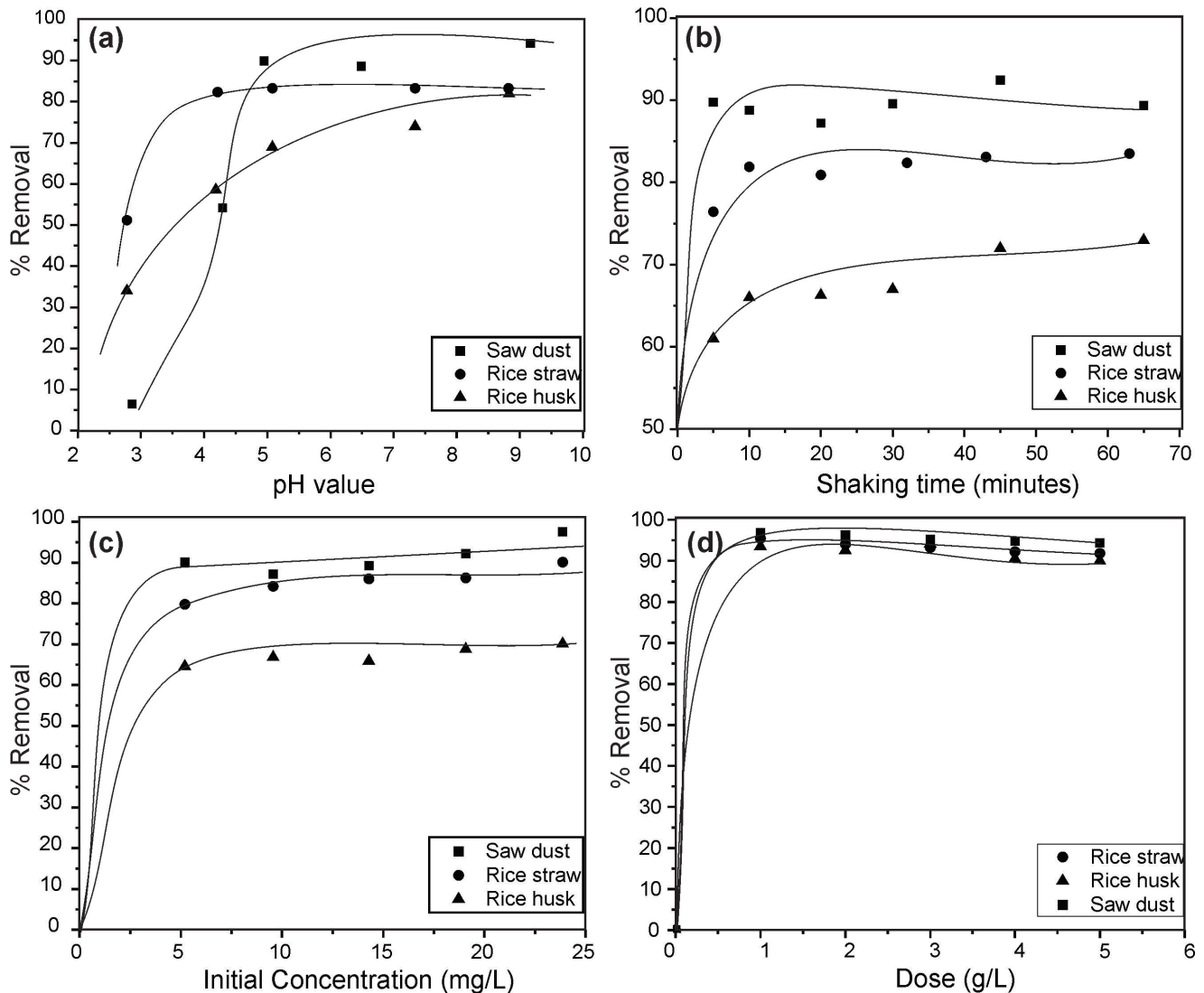


Fig. 2. Adsorption of Pb(II) on to studied biochars as a function of (a) pH, (b) shaking time, (c) initial Pb(II) concentration and (d) biochar dosage (for <math><0.125\text{ mm}</math> fraction).

the contact time from 1 to 9 h using different size fractions. It was found that most of the Pb(II) adsorption occurs within the first hour and then reached equilibrium. Therefore, further investigations were carried out for the first 70 min and measurements were taken at different time intervals (Fig. 2b). It was found that Pb(II) adsorbed readily in the first few minutes onto biochar and attained equilibrium. Among the three studied biochars, saw dust shows over 90% of adsorption within the first 10 min followed by rice straw and risk husks. The higher rate of adsorption in the first 10 min could be attributed to the availability of a higher concentration of adsorption sites in the saw dust biochar surface. With longer time intervals, the adsorption sites become saturated and the uptake rate will be controlled by the rate at which the adsorbate Pb(II) is transported from the solution to the interior sites of the biochar particles, so the adsorption become much slower [46].

Adsorption experiments were carried out using different initial Pb(II) concentrations. This showed that higher initial concentrations tends to be adsorbed more onto biochar

(Fig. 2c). This indicates that the over 90% of Pb(II) ions readily adsorbed onto the biochar surface; however, saw dust biochar shows slightly higher adsorption of Pb(II) from the aqueous solution. This may be due to the high probability of collision between metal ions with the biochar surface and high rate of metal ions diffusion onto biosorbent surface. The ratio of metal ions to active sites is low at low initial metal concentrations and relatively high at higher initial metal concentrations. Therefore, the adsorption efficiency was rather low at lower initial metal concentrations. Near similar observations were made in the study conducted by Rafatullah et al. [47] using saw dust. They have achieved the maximum adsorption of Pb(II) (34.2%) with increasing in concentration and dosage of adsorbent.

The result of varying adsorbent dose was shown in Fig. 2d in which adsorbent dosages varied from 1.0 to 5.0 mg/L. As shown in Fig. 2d, the adsorbent dose of 1.0 mg/L is sufficient for the optimal removal of metal ions. Approximately 85% rapid adsorption in the initial stage was attributed to

the availability of active sites. Thus, the progressive change of adsorption sites resulted in a decreased adsorption process. Increasing the dose further decreased the percentage removal. The removal percentage was rapidly increased up to 95% at 1.0 g/L dosage and it became nearly constant at a higher dose rate due to metal concentration shortage in the solution at high dose rates.

3.2. The adsorption isotherms of Pb(II)

Adsorption equilibrium measurements are used to determine the maximum adsorption capacity. There are six models of adsorption isotherms that are used to describe the metal adsorption on to solid surfaces [19,48]. From these, Langmuir, Freundlich and Temkin isotherms were considered in this study as they have been widely used to describe the interaction between metal ions in solution and adsorbents.

Langmuir isotherm (linear form) is expressed as follows [49]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

Essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant separation factor R_L (equilibrium parameters) that is given by

$$R_L = \frac{1}{1 + bC_i} \quad (4)$$

in which q_e is the amount mg/g of Pb(II) adsorbed at equilibrium state, Q_0 is the maximum adsorption capacity, C_e and C_i are the equilibrium and initial concentrations of Pb(II) (mg/L) and b is the Langmuir constant. As shown in Fig. 3a, saw dust and rice straw biochars fitted the Langmuir model while rice husk biochar only obeys the model at low concentrations. Equilibrium concentration (C_e) and equilibrium adsorption capacity (q_e) were calculated for each initial metal concentration. The correlation coefficients for Pb(II) were respectively

0.97, 0.95 and 0.95 for saw dust, rice straw and rice husk. The q_0 (monolayer adsorption capacity) and Langmuir constants (b) were calculated from the slope and intercept and is given in Table 1.

The maximum adsorption capacities (Q_0) estimated from the Langmuir isotherm model for Pb(II) was observed for saw dust biochar. The separation factor (R_L) for saw dust and rice straw biochars were 0.234 and 0.128 that indicates a favourable sorption isotherm for Pb(II). Therefore, the results show that saw dust and rice straw biochars have the potential as good sorbents for Pb(II) ions that follow monolayer adsorption isotherms. Table 2 compares the maximum adsorption capacity of Pb(II) ions by various biochar adsorbents.

The Freundlich isotherm model is widely used to describe adsorption characteristics for the heterogeneous surfaces [50] and assumes a monolayer capacity, but is accompanied by interaction between the adsorbed molecules. The Freundlich equation (linear form) is given as follows:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (5)$$

where K_F is a constant related to the adsorption capacity of the adsorbent and the constant $1/n$ indicates the intensity of the adsorption. The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the sorbate. The obtained values of $1/n$ and K_F are calculated from the plot of $\log q_e$ vs. $\log C_e$ (Fig. 3b). The $1/n$ obtain for saw dust, rice straw and rice husk biochar were 1.27, 1.65 and 1.26, respectively, and indicates the cooperative sorption of Pb(II). The values indicated the affinity of the sorbent towards the uptake of Pb(II) ions and the adsorption of metal ions was favourable.

The Temkin isotherm model assumes the effect of some indirect interactions among adsorbate particles and suggests a linear decrease in the heat of adsorption of all the molecules in the layer. The Temkin linear isotherm form is expressed as follows [51]:

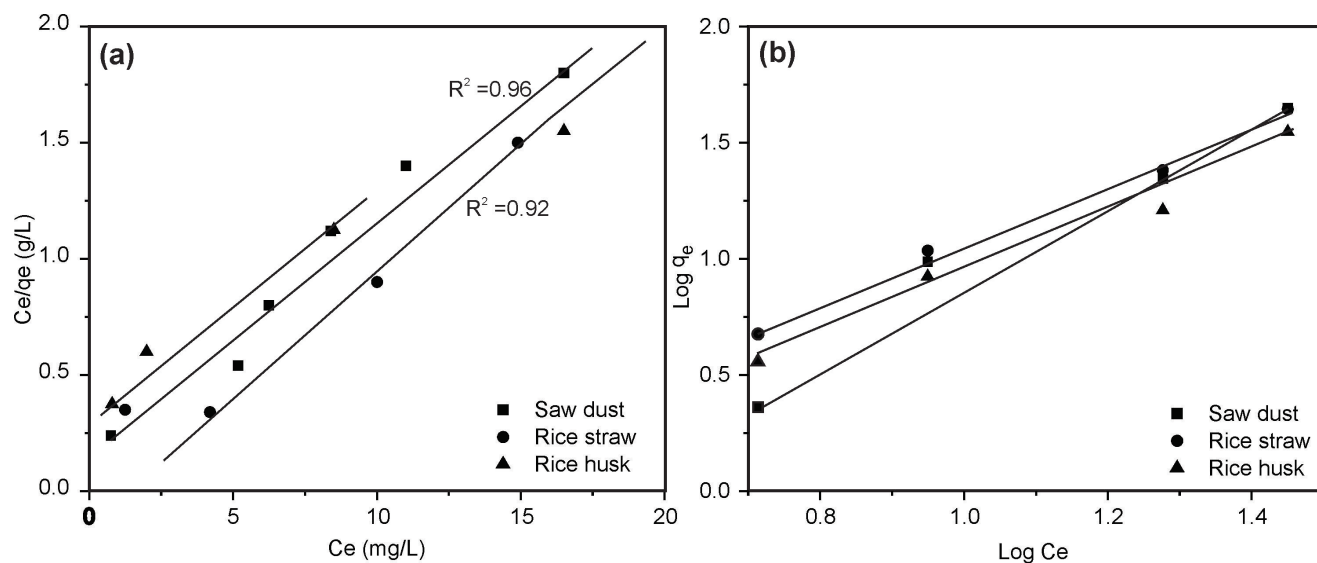


Fig. 3. Pb(II) sorption in batch experiment (a) Langmuir and (b) Freundlich isotherm models.

Table 1
Parameters obtained from Langmuir, Freundlich and Temkin isotherm models

Isotherm models	Adsorption parameters	Types of biochar		
		Saw dust	Rice straw	Rice husk
Surface area (m^2/g^{-1})		1,091.5	46.6	193.7
Langmuir	q_0	9.621	10.947	6.66
	b	0.6325	1.313	0.588
	R_L	0.234	0.128	0.63
	R^2	0.971	0.955	0.956
Freundlich	K_F	0.60	0.18	0.46
	$1/n$	1.27	1.65	1.26
	R^2	0.99	0.95	0.97
Temkin	B	Not obey the model		110.26
	R^2			0.9962

Table 2
Comparison of the maximum adsorption capacity of Pb(II) ions by various adsorbents

Absorbent	Maximum Pb(II) adsorption capacity ($mg\ g^{-1}$)	Reference
Rice rusks	2.4	[18]
Pine wood char	4.13	[63]
Pine bar char	3.00	[63]
Oak bar char	13.10	[63]
Dairy manure biochar	109.40	[13]
Pig manure biochar	230.7	[60]
Coe manure biochar	212.77	[60]
Rice husk	6.66	This study
Rice straw	9.621	This study
Saw dust	10.947	This study

$$q_e = B \log A + B \log C_e \quad (6)$$

where A and B are the Temkin isotherm constant (L/g) and heat of sorption (J/mol), respectively. R is the gas constant ($J/mol/k$), b is the Temkin isotherm constant linked to the energy parameter, B , as shown in the following equation:

$$b = \frac{RT}{B} \quad (7)$$

The Temkin isotherm model was also used in this study in which the quantity adsorbed q_e against, $\log C_e$ were plotted (Fig. 4) and the constants A and B were determined and listed (Table 1). Considering the values for Langmuir, Freundlich and Temkin adsorption isotherms, it can be suggested that the Freundlich isotherms fitted well with all biochar materials. However, rice straw and saw dust biochars perform better for the sorption of Pb(II) and the data fitted well into the Langmuir adsorption isotherms. Temkin isotherm fits only with rice husk biochar. Therefore, it can be suggested that the

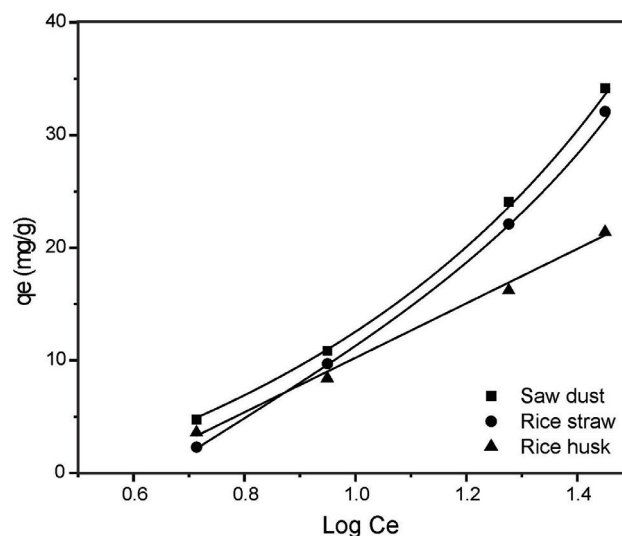


Fig. 4. Temkin isotherm for Pb(II) adsorption for studied biochar.

suitable biomass should be identified before applying them to remove specific metal ions from wastewater.

3.3. Effect of Pb(II) adsorption on biochar surfaces

The FTIR spectra obtained for biochar from byproducts of biomass that were pyrolyzed in moderate temperature of $400^\circ C$, are characteristics of different oxygen containing surface groups of C–O; C=O and C–OH and other lingo cellulose materials since the materials were pyrolyzed at a lower temperature. Absorption bands observed at $1,581$ and $1,408\ cm^{-1}$ are typical for C–C bonds, $1,054\ cm^{-1}$ for CO–C stretching, $3,360\ cm^{-1}$ for hydroxyl (–OH) stretching and $575\ cm^{-1}$ for alkyl halide groups. The spectrum of rice straw biochar was characterized by four bands (Fig. 5) at $3,374$; $1,090$; 791 and $1,587\ cm^{-1}$ that are attributed to, CO–C stretching of secondary hydroxyl, aliphatic CH_2 deformation, and aromatic C=C ring or COO– group stretching, respectively [52]. Adsorption bands for several functional groups in rice husk biochar revealed that –NH amine groups at $1,589\ cm^{-1}$, aliphatic amine peak at $1,054\ cm^{-1}$, CH aromatic groups at $787\ cm^{-1}$ and alkyl halide peaks at $599\ cm^{-1}$, $554\ cm^{-1}$ and $586\ cm^{-1}$. The FTIR spectrum of the saw dust biochar identified functional groups at $1,579\ cm^{-1}$ for NH amine, $1,031\ cm^{-1}$ for aliphatic amine, and 628 , 602 , 597 , 584 , 572 and $562\ cm^{-1}$ for the alkyl halide groups. A peak at $586\ cm^{-1}$ has been formed for the alkyl halide group, two peaks at $872\ cm^{-1}$ and $757\ cm^{-1}$ for CH aromatic active sites and the other two peaks appeared at $3,202\ cm^{-1}$ and $2,833\ cm^{-1}$ corresponds to the stretching vibration of –OH and the extension vibration of –NH [52]. The band at $2833\ cm^{-1}$ can be assigned to CH stretching.

The FTIR analysis also elucidates the possible mechanism(s) involved in metal ion adsorption on to biochar surfaces. The spectrum of rice straw biochar after Pb(II) adsorption clearly shows that the hydroxyl band ($3,360\ cm^{-1}$) had to $3,332\ cm^{-1}$ due to the formation of a complex between the Pb(II) and hydroxyl function groups [53]. Moreover, the band at $1,054\ cm^{-1}$ was shifted to $1,073\ cm^{-1}$ indicating coordination of Pb(II) with carboxylate groups. Bands

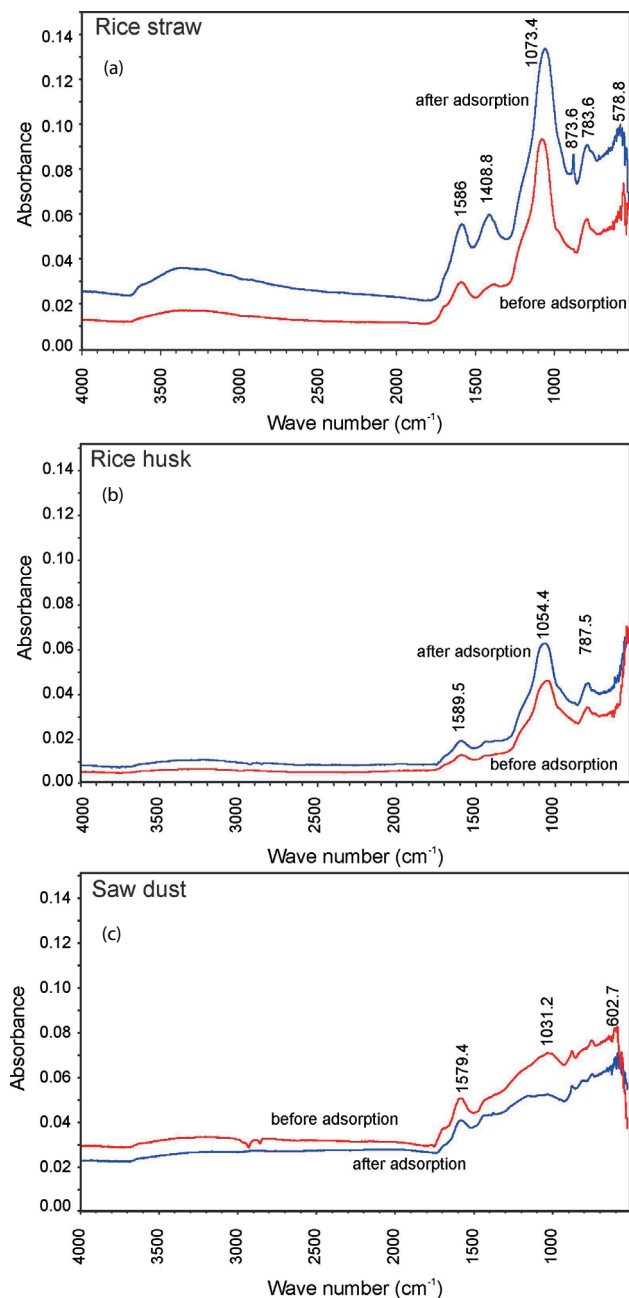


Fig. 5. FTIR spectra for (a) rice straw, (b) rice husk and (c) sawdust biochar before and after Pb (II) adsorption.

appeared at 1,408 and 1,581 cm^{-1} were shifted and merged together at 1,586 cm^{-1} . The peak appeared at 575 cm^{-1} split into two peaks at 575 cm^{-1} and 555 cm^{-1} after the uptake of Pb(II) onto rice straw biochar. The C-H stretching peak at 873 cm^{-1} had been shifted to 784 cm^{-1} due to Pb adsorption. After interaction with Pb(II) with rice husk biochar (Fig. 5), the absorption band of -NH amine and aliphatic amine groups were shifted to 1,585 cm^{-1} and 1,046 cm^{-1} , respectively. The CH aromatic peak which was at 787 cm^{-1} moved to 784 cm^{-1} , alkyl halide peaks at 599 cm^{-1} , 554 cm^{-1} and 586 cm^{-1} have been shifted to 594 cm^{-1} and 568 cm^{-1} . Two other peaks at 629 cm^{-1} and 618 cm^{-1} have been identified

due to the change in absorption intensity, and interaction of metal ions with active sites of rice husk biochar. With the interaction of Pb(II) onto sawdust biochar, a wide band was appeared in the FTIR spectrum between the wavelengths of 1,570 to 3,200 cm^{-1} . This may be due to metal ions bound to active sites of the biosorbents through either electrostatic attraction or complex formation mechanisms. The electrostatic attraction is between the metal ion and carbonate group. Meanwhile, the complex formation involves an electron pair sharing between electron donor atoms (O and N) [52]. The FTIR results from this study suggest that carbonyl, hydroxyl and amine are the main adsorption sites in sawdust, rice straw and rice husk biochar. The Pb(II) ions can be adsorbed by biochars specifically through the formation of surface complexes between Pb(II) and the functional groups on the adsorbate.

4. Conclusions

This study reveals that the percentage removal of Pb(II) is dependent on the dose of the adsorbent, pH of the solution and the initial metal concentration. The contact time necessary for maximum adsorption was found to be less than an hour. The Pb(II) adsorption increased with the increase of pH in the solution. The optimum pH range for Pb adsorption was 5.0–7.0. Based on the experimental conditions, it was found that the removal of Pb(II) ions from their aqueous solution could reach between 90% and 94% by sawdust biochar. Rice husk and rice straw biochars were also good adsorbents at higher pH for the removal of Pb(II) from an aqueous phase. The sorption capacity is dependent on the type of the adsorbent and the nature of the wastewater treated. The FTIR spectra of three biomass indicated that Pb(II) metal can be adsorbed by the biochars specifically through the formation of surface complexes between Pb(II) and the functional groups on the biochars surface. Adsorbent materials derived from low-cost agricultural wastes can therefore be used as an effective removal and recovery of lead ions from wastewater. The cost of individual sorbents varies depending on the degree of processing and availability of materials locally. This study proved that biochar produced from agricultural and forest wastes can be used as an alternative sorbent to activated carbon or other water purifiers to treat heavy metals in wastewater.

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