



Low-Cost Biochar Derived from Bamboo Waste for Removal of Heavy Metal in Aqueous Solution

Dusit Angthararuk^{a,b*} Sasamol Phasuk^a & Pannraphat Takolpuckdee^a

^a Faculty of Science and Technology, Valaya Alongkorn Rajabhat University under the Royal Patronage, Pathum Thani, 13180 Thailand

^b Faculty of Science and Technology, Suan Dusit University, Bangkok, 10300 Thailand

Article info

Article history:

Received : 30 January 2022

Revised : 3 August 2022

Accepted : 16 August 2022

Keywords:

Bamboo biochar, Heavy metal, Removal, Groundwater

Abstract

This study assessed the adsorption capacity of heavy metals such as lead (Pb), copper (Cu) and zinc (Zn) in the aqueous solution of biochar. Biochar was obtained from bamboo handicraft scraps by a pyrolysis method and was used as an economical absorbent. The bamboo biochar was characterized by scanning electron microscopy coupled with energy-dispersive x-ray spectroscopy (SEM-EDS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The parameters such as contact time, biochar dosage, pH of the initial solution, and initial concentration of metal ions affected sorption capacity were investigated. Experiment results showed that the bamboo biochar mainly contained carbon and oxygen elements and a high number of C=O, C-O and O-H functional groups. The maximum adsorption uptake on biochar was Pb(II)>Zn(II)>Cu(II) under 1.0 g adsorbent L⁻¹, 20 mg L⁻¹ initial concentration of all metal ions, pH 4, contact time 120 min and at ambient temperature. From Langmuir isotherm fitting showed the maximum adsorption capacity was 41.15, 30.21 and 34.48 mg g⁻¹ for Pb(II), Cu(II), and Zn(II), respectively. Pseudo-second order kinetic model can best describe the adsorption process of all ions in solution mainly via monolayer adsorption onto a homogeneous adsorbent surface and chemisorption as ion exchange, complexation, and surface mineral precipitation of metal ions. Applying the bamboo biochar for the removal of metal ions in groundwater found it was able to eliminate manganese at more than 95% within an hour of contact time. All research findings suggest that bamboo biochar has broad potential for water purification applications.

Introduction

Heavy metals include biologically essential elements such as zinc (Zn), copper (Cu), nickel (Ni), iron

(Fe), chromium (Cr), boron (B) and molybdenum (Mo), and elements that are not essential such as mercury (Hg), cadmium (Cd), lead (Pb), arsenic (As) and silver (Ag). It is high water solubility and due to its low biodegradability

therefore it can accumulate in the microorganisms and environment and then be further transported to the human body (Iqbal et al., 2021; Sherlala et al. 2018). They can be toxic or carcinogenic, which induced disease in the gastrointestinal, renal, and cardiovascular systems and can cause severe problems for humans and aquatic ecosystems (Balali-Mood et al., 2021; Xu et al. 2018). Surface water is threatened by humans, principally heavy metal contamination mainly from the accumulation of chemical fertilizers, pesticides and farm manure used in farming. In addition, surface water can penetrate into shallow groundwater causing heavy metals to spread throughout. They can also affect plant metabolism and growth (Ahmed et al. 2019; Sarker et al., 2022). Kheangkhum, et al., (2020) reported that heavy metals have also been recently detected in major food items, such as rice, vegetables, and meat available in large markets of Thailand. With the continuous evolution of human society and economy, human activities have caused serious pollution to water bodies (Chunhabundit, 2016). The sustainable development of a country depends on the covenant of secure, safe and renewable drinking water. Thai farmers and poor households in some parts of the country rely on groundwater as a significant source of drinking and irrigation.

Various technologies, filtration, precipitation, redox reactions, or ion exchange have been used for the elimination of heavy metals in groundwater. However, these technologies are costly to maintenance, produce harmful by-products, or energy-intensive (Jovarauskaitė & Balund, 2021). The adsorption process is an interesting technique for removing heavy metals. The conventional adsorbent material as the solid material used for the adsorption consists of a porous with a high internal surface area (Da'ana et al., 2021). Activated carbon is an adsorbent derived from carbonaceous raw material. Due to their high surface area, complex pore structure (micro, meso and macro), and a high degree of surface reactivity have been used to adsorb a wide variety of substances. However, traditional activated carbon has some drawbacks, namely high production costs (Siipola et al., 2020). Consequently, research into carbon-based adsorbents with high adsorption efficiency and low expense is limited and is worthwhile in practical applications. An improved low-cost adsorbent can be an appropriate alternative to expensive activated carbon for removing organic pollutants and heavy metal ions contaminating water (Nguyen et al., 2021). Biochar is

an interesting option that is high porous furthermore on the surface has carboxyl ($-COOH$) and hydroxyl ($-OH$) functional groups as sorption sites for the metal ions (Murtaza et al., 2021). However, the chemical and physical properties of biochar are affected by the type of feedstock and pyrolysis technology. Biochar is a carbon material derived from biomass via a pyrolysis process in limited air. Many studies have used biochar to remove contaminants in water. For example, Iamsaard et al., (2022) reported using pineapple leaf biochar that had high efficiency for removing Ni(II), Zn(II), and Cu(II), Deng et al., (2020) used biochar derived from banana stalk to adsorb Zn(II), Mn(II) and Cu(II) from aqueous solution, Chen et al., (2019) studied the kinetics and adsorption mechanisms for adsorption of lead (Pb^{2+}) and cadmium (Cd^{2+}) with dairy manure biochar, however, the biochar were produced by muffle furnace oven. It can be easily controlled during production. Therefore, high-quality biochar production in the field is challenging. Our previous work developed a biochar from bamboo waste by a Top-Lid Updraft Drum (TLUD) equipment for the removal of dissolved organic matter in water (Angthararuk et al., 2022). The Thai Wiang Community, Hin Tung, Mueang Nakhon Nayok District, Nakhon Nayok Province ($14^{\circ}15'03''N$ $101^{\circ}18'18''E$) contains many bamboo plantings and bamboo is used in varies occupations. Some of them are used to produce charcoal for energy by earth kiln, pit kiln and brick kiln. The weakness of conventional charcoal production is its low quality which is not suitable for use as a water contaminant adsorbent. The Thai Wiang Community depends on groundwater for consumption and high-cost anthracite is used for treatment. Therefore, biochar derived from bamboo waste is an affordable adsorbent material that can be a viable alternative to absorbing heavy metals in an aqueous solution.

In this study, biochar was produced from bamboo waste via pyrolysis process by a community low-cost portable biochar kiln to remove heavy metal ions such as Pb(II), Cu(II) and Zn(II) in an aqueous solution. The effects of variables on the initial concentration of metal ion, pH of the solution, contact time, and adsorbent dosage on the adsorption efficiencies were investigated. The kinetics and isotherms of the adsorption process were studied to elucidate this mechanism. Furthermore, the adsorbent was applied to remove the heavy metals in the groundwater.

Materials and methods

1. Reagents and chemicals

All reagents and chemicals utilized in the study were analytical grades. A stock solution of Pb(II), Cu(II), and Zn(II) was prepared from Pb(NO₃)₂, Cu(NO₃)₂.3H₂O, and Zn(NO₃)₂.6H₂O, Sigma-Aldrich, USA. A standard solution 1.0 g L⁻¹ of Pb, Cu and Zn (Merck) was used for the preparation of all standard calibration curves. Double distillation water was used to prepare all the solutions for the experiments.

2. Bamboo biochar

Biochar was converted from bamboo handicraft waste through a slow pyrolysis process under air-limiting conditions. The production used low-cost two-containers as Top-Lid Updraft Drum (TLUD) equipment with available local resources from Hin Tung, Mueang Nakhon Nayok District, Nakhon Nayok Province, Thailand (14°15'03"N 101°18'18"E). The reactive groups on surface bamboo biochar were analyzed by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (IR Tracer-100 FTIR spectrophotometer, Shimadzu, Japan), recording between wavenumber of 4000 and 400 cm⁻¹ with 4 cm⁻¹ resolution and a cumulative number of scans was 40. The background was collected before each measurement. The peak and band positions were obtained using the IR Tracer Software. Morphological characteristics were obtained by scanning electron microscopy (SEM analyzer JSM-6610 LV, JEOL Ltd., Tokyo, Japan) with an accelerating voltage of 20 kV and elemental composition by energy-dispersive x-ray spectroscopy (EDS, Oxford instrument X-Max 50 mm², England).

3. Adsorption experiments

Batch adsorption experiments were carried out with 100 mL of 20 mg L⁻¹ metal ion (Pb²⁺, Cu²⁺ and Zn²⁺) solution mixing 0.1 g (1 g L⁻¹) bamboo biochar placed in a 250-mL Erlenmeyer flask and the mixture was shaken at 150 rpm. Adjustments to the initial pH of the metal ion solution were made using 0.1 mol L⁻¹ HNO₃ or NaOH (Starter 3100 bench, Ohaus pH meter). All experiments were conducted in triplicates at room temperature. After equilibrium, the collected liquid sample was centrifuged at 3,000 rpm for 5 min before being filtered through a 0.45 µm nylon syringe filter. The filtrate was immediately acidified by 0.2% (v/v) HNO₃ for the determination of metal ions by Atomic Absorption Spectroscopy (AAS, GBC3000, Australia).

The adsorption efficiency (Q_e) of metal ions on

biochar was determined by the metal ion concentration adsorbed per unit of adsorbent. The Q_e and adsorption percentage was determined by the following equations:

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\% \text{ Adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e are the concentrations (mg L⁻¹) at initial and equilibrium, respectively. M is the adsorbent amount (g) and V is the volume of solution (L).

4. Factors affecting metal ions adsorption

To investigate the effect of process parameters on adsorption efficiency of metal ions, biochar content (0.1, 0.5, 1.0, 2.0, 5.0 and 10 mg L⁻¹), contact times (15-1140 min), pH (2, 3, 4, 5, 6 and 7) and initial concentration (5, 10, 20, 30, 50, 70 and 100 mg L⁻¹) operates in parallel with the control. The experimental conditions were similar to those previously set in Section 3.

5. Removal of heavy metals in groundwater

The groundwater samples were collected from Hin Tung, Mueang Nakhon Nayok District, Nakhon Nayok Province, Thailand (14°15'03"N 101°18'18"E) during the month of September 2021 by following standard sample collection protocol. Special precautions were conducted during the collection of samples. In the initial step, metal-free sample containers were soaked overnight in 2% nitric acid and then washed with double distilled water and dried. The containers were then rinsed three times with the groundwater sample of the particular location to avoid contamination and then collection of the samples occurred. To prevent the loss of metal ions it was necessary to add 0.5 mL of 1.0 mol L⁻¹ HNO₃ to the sample that was acidified solution. Batch removal of heavy metal ions in groundwater was followed by a 100 mL water sample mixing 0.1 g bamboo biochar (1.0 g L⁻¹) in 250-mL Erlenmeyer flasks with the mixture shaken at 150 rpm for 60 minutes contact time at ambient temperature. At the time, the liquid sample was centrifuged, filtered and determination of metal ions by Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES, Avio 200, Perkin Elmer, USA) was conducted.

Results and discussion

1. Characterization of bamboo biochar

The morphological characteristics of bamboo biochar obtained by scanning electron microscope (SEM) are shown in Fig.1. It is seen as obvious morphological

biochar with a large surface area, tubular shapes, rough surface structures, sharp edges and surface pore morphology as a honeycomb-like structure. An elemental analysis was carried out by energy dispersive spectroscopy (EDS). The results of EDS showed that carbon (C 77.30 %) and oxygen (O 11.93 %) were the major elements of the biochar and the mineral fractions consisted of Si (0.75 %), P (0.33 %), K (1.29 %) and Fe (8.40 %). These results demonstrated that high content C was the main skeleton with O which may come from oxygen-containing functional groups such as carboxylic acid (-COOH), hydroxyl (-OH) or metal minerals such as carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) (Hernández-Mena et al., 2014).

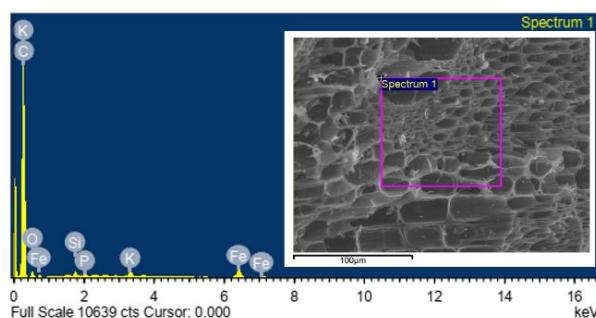


Fig. 1 SEM and EDS for morphological and elemental of bamboo biochar

The FTIR spectrum of bamboo biochar is shown in Fig. 2. It can be seen that the spectrum of adsorbents was characterized. The highest band intensities for the organic functional groups were a band of -OH stretching (3329 cm^{-1}), aliphatic CH_2 ($2914, 2848 \text{ cm}^{-1}$), $\text{C}=\text{O}$ stretching of carboxyl (1700 cm^{-1}), aromatic $\text{C}=\text{O}$ or $\text{C}=\text{C}$ ring stretching (1601 cm^{-1}) (Liu et al., 2021), $\text{C}-\text{O}-\text{C}$ or PO_2^- asymmetric stretching (1236 cm^{-1}) (Bangaoil et al., 2020), $\text{C}-\text{O}$ stretching (1031 and 1098 cm^{-1}) and $\text{Si}-\text{O}-\text{Si}$ stretching ($1154-1031, 798$, and 471 cm^{-1}) (Cui et al., 2019).

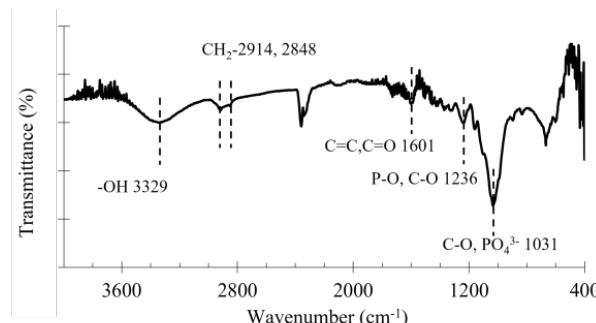


Fig. 2 FTIR spectrum of bamboo biochar

2. Effect of contact time

The contact time of metal ions on absorbent is an important factor, which greatly affects the adsorption process on the surface of biochar. The adsorption effects of Pb(II), Cu(II) and Zn(II) on biochar were determined at different time intervals as shown in Fig. 3. It was observed that the rate of Pb(II) adsorption was rapid with 83% of the ultimate adsorption occurring in the first period of 120 min, while Cu(II) and Zn(II) sorption were 60 and 70%, respectively, followed by a very slow approach to equilibrium. The result showed that after 240 min of contact time the adsorption indicated nearly achieved to the equilibrium phase which was probably the utmost adsorption capacity of the entire samples. The adsorption uptake at the equilibrium state of Pb(II), Cu(II) and Zn(II) on bamboo biochar were $18.82, 15.67$ and 16.25 mg g^{-1} , respectively. Therefore, 6 hours of contact time for the rest of the sorption experiments were chosen.

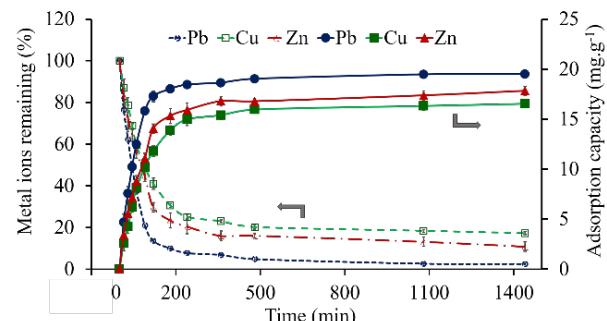


Fig. 3 Adsorption efficiencies and % remaining of metal ions in solution (20 mg L^{-1} initial concentration) on biochar (1.0 g L^{-1}) with function time

3. Effect of biochar dosage

The amount of absorbent directly affects the adsorption efficiency of metal ions, since it determines the capacity of bamboo biochar at a given initial concentration. The results of the batch experiments with various bamboo biochar dosages are presented in Fig. 4. The highest observed metal ions at 0.1 g L^{-1} biochar for Pb(II), Cu(II) and Zn(II) retention capacities were $56.35, 38.30$ and 29.92 mg g^{-1} , respectively. Increasing the absorbent dosage, however, actually decreased the adsorption yield of all metal ions (Fig. 4a). For example, the adsorption efficiency of Pb(II) decreased from 43.2 mg g^{-1} with 0.1 mg L^{-1} absorbent to 1.9 mg g^{-1} at 50 mg L^{-1} which was likely due to aggregation which was clearly visible at higher biochar concentrations. Nevertheless, this reduction in adsorption efficiency,

incremental the adsorbent concentration which did result in increased percentage removal of all metal ions (Fig. 4b). It was likely due to a function of the increased active sites, the data suggested that not all of the added sites were available for binding which is consistent with the observed aggregation (Chen et al., 2011). Whereas, it should be noted that the differences in all metal ions removal were not significantly different at 2 and 10 g biochar L⁻¹. While at 10 g absorbent L⁻¹, the efficient removal of Pb(II), Cu(II) and Zn(II) were 99.60, 98.51 and 94.61 %, respectively.

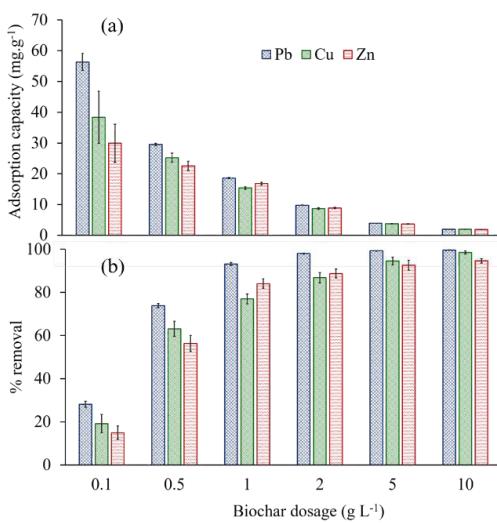


Fig. 4 Effect of biochar dosage on metal ions (a) adsorption efficiencies (b) percentages of heavy metal removal, 20 mg L⁻¹ initial concentration and 6 hours contact time

4. Effect of initial pH

The pH of a solution plays a significant role in the adsorption process affecting the adsorption efficiency due to the effect of the adsorbent surface binding sites with metal ions and the metal ionization process (Qian & Chen, 2014). In this study, the pH between 2 and 7 of the initial solution was investigated and the results are presented in Fig. 5. The adsorption capacity increased with increasing pH value. The best pH of solution for the maximum adsorption capacity was pH 4 for Pb(II) (18.67 \pm 0.13 mg g⁻¹) and pH 5 for Cu(II) (16.08 \pm 0.16 mg g⁻¹) and Zn(II) (17.87 \pm 0.39 mg g⁻¹). At the lower pH of the initial solution, the competition between protons and metal ions, and a lot of hydrogen and hydronium ions in the solution obstructed the cation sorption sites on biochar (Deng et al., 2020). In addition, the surface of the biochar became positively charged and electrostatic repulsion of

cations occurred resulting in low adsorption (Sakhiya et al., 2022). When the pH of the initial solution was increased, the deprotonation of functional groups (through phenolic OH dissociation) on the adsorbent surface can potentially provide more active sites for metal ions, resulting in an enhancement of adsorption effectiveness (Ding et al., 2014). At a pH above 5, the adsorption of heavy metal ions tend to decrease and was likely caused by the hydroxide complexes formation which hydroxido M(OH)⁺ formed that could hinder the interaction between M²⁺ and biochar (Li et al., 2017; Oliveira et al., 2017).

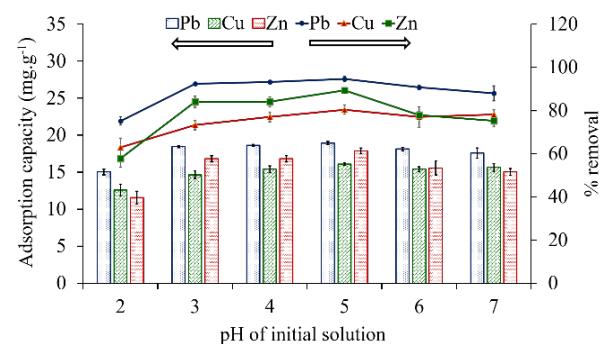


Fig. 5 Effect of initial solution pH on metal ions adsorption capacity

5. Adsorption Kinetics

Heavy metal on biochar sorption rate behaviors were evaluated using the pseudo-first-order (3) and pseudo-second-order (4) model equations as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

Where Q_t (mg g⁻¹) and Q_e (mg g⁻¹) are the biochar adsorption capacity at any time t (min) and equilibrium time, respectively, the adsorption rate constants K_1 (min⁻¹) and K_2 (g mg⁻¹ min⁻¹) are primary and secondary constants, respectively.

The linear relationship of the kinetic model and implicated parameters of the kinetic equations were exhibited in Fig. 6 and Table 1, respectively. The adsorption capacity, Q_e of all metal ions was predicted by the pseudo-second-order kinetic model due to a correlation coefficient ($R^2 > 0.99$) approaching 1 was proved to be more appropriate to fit the kinetics model compared with the pseudo-first-order kinetic model ($R^2 0.75-0.92$). The Q_e calculated value of Pb(II), Cu(II)

and Zn(II) as 20.04, 17.42 and 18.51 mg g⁻¹, which was closer to the actual adsorption capacity, 18.45, 14.97 and 15.92 mg g⁻¹, respectively, obtained from the experiment. Therefore, the adsorption process of all metal ions on bamboo biochar suggested two reactions occur; the first stage is rapid and achieves equilibrium quickly and the second is slow that can continue for a long time. It indicates that the chemisorption of metal ions was the rate-limiting mechanism and adsorbed onto the biochar surface by chemical interaction, such as ion exchange and complexation.

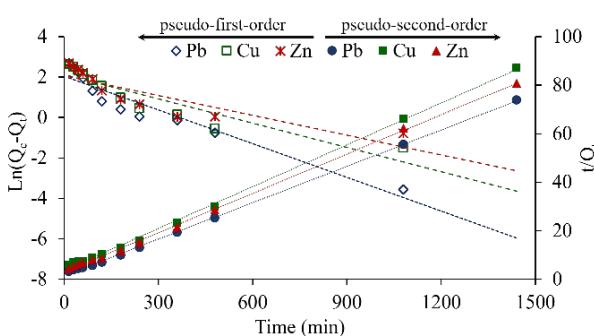


Fig. 6 Adsorption kinetic model of metal ions onto bamboo biochar (a) Pb(II) (b) Cu(II) and (c) Zn(II)

Table 1 Kinetic parameters of Pb(II), Cu(II) and Zn(II) on biochar

Metal ion	Pseudo-first-order model		Pseudo-second-order-model			
	Q_e (mg g ⁻¹)	K_1 (min ⁻¹) $\times 10^{-3}$	R^2	Q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ min ⁻¹) $\times 10^{-3}$	R^2
Pb (II)	7.68	5.6	0.9209	20.24	1.382	0.9994
Cu (II)	8.33	4.0	0.8478	17.42	0.553	0.9985
Zn(II)	7.83	3.3	0.7599	18.51	0.514	0.9990

6. Adsorption Isotherm

Adsorption isotherms are important for describing the relation between the amounts of the adsorbate onto the adsorbent surface and the adsorbate remaining in the solution. It is a mathematical model that plots the solute concentration in the aqueous solution (x-axis) and quantity adsorbed on the adsorbent surface (y-axis) at a constant temperature. It can explain the distribution of the adsorbate molecules or ions on the surface of a material that is related to adsorbate interacting with adsorbents. (Katiyar et al., 2021). Two common models, Langmuir and Freundlich isotherms, were used to study the adsorption behavior. Langmuir's adsorption isotherm model is based on monolayer adsorption onto a homogeneous adsorbent surface and finite adsorption site assumptions without any interactions between adsorbed molecules on neighboring sites. The Freundlich isotherm

model is based on multilayer adsorption that takes into account the adsorbent surface heterogeneity and an exponential distribution of the active sites. The concentrations of metal ions ranged from 5 to 100 mg L⁻¹, pH 4, 1.0 g L⁻¹ adsorbent and 6 hours contact time at constant room temperature were investigated for the adsorption model. The adsorption capacity and behavior of heavy metals onto biochar were evaluated by using the experimental data fitted with linearized form Langmuir (5) and Freundlich (6) equations. The formulas of the two models are shown below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (5)$$

Where C_e (mg L⁻¹) is the metal ion concentration in solution at equilibrium, Q_e (mg g⁻¹) is the quantity of metal ion adsorbed on adsorbent at equilibrium, Q_m (mg g⁻¹) is maximum adsorption capacity, K_L (L mg⁻¹) denotes the Empirical Langmuir constant. Plotting C_e/Q_e versus C_e (5) results in a straight line that Q_m and K_L are calculated from the slope ($1/Q_m$) and intercept ($1/Q_m K_L$), respectively.

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

In which, K_F (L g⁻¹) denotes the Empirical Freundlich constant relating to adsorption capacity, n is Freundlich constant as the heterogeneity related to adsorption intensity. The linear plot of $\log Q_e$ versus $\log C_e$ is evaluated for Freundlich adsorption model that K_F and n are computed from intercept and slope, respectively.

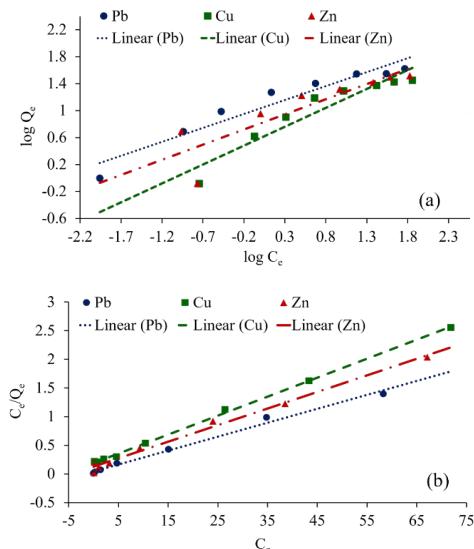


Fig. 7 Adsorption isotherm (a) Freundlich isotherm model (b) Langmuir isotherm model

The curve fitting of two isotherm models acquired in this work are presented in Fig. 7 while the isotherm data obtained are shown in Table 2. The sorption isotherms of Pb(II), Cu(II) and Zn(II) by bamboo biochar recommend, were better fitted to the Langmuir model than the Freundlich model, which can be explained by the correlation coefficients (R^2) 0.990-0.998 for Langmuir model and 0.929-0.772 for Freundlich model. According to the Langmuir model, the maximum adsorption capacities (Q_m) values of Pb(II), Cu(II) and Zn(II) were 41.15, 30.21, and 34.48 mg g⁻¹, respectively.

Table 2 Langmuir and Freundlich isotherm parameters for adsorption of Pb(II), Cu(II) and Zn(II) on biochar

Metal ion	Freundlich model			Langmuir model		
	K_F (g mg ⁻¹ min ⁻¹)	n	R^2	K_L (L g ⁻¹)	Q_m (mg g ⁻¹)	R^2
Pb (II)	10.76	2.415	0.929	1.835	41.15	0.991
Cu (II)	3.91	1.782	0.900	0.173	30.21	0.998
Zn(II)	2.82	2.222	0.772	0.228	34.48	0.990

A comparison of the adsorption capacity of biochar developed in this study with some other adsorbents reported in the literature is presented in Table 3. It was found that the low-cost bamboo biochar produced by the community kiln performed well in comparison with other adsorbents. As a result of the production process at a high temperature of about 600°C,

Table 3 Metal ions adsorption results from this study compared to Metal ions adsorption results in similar studies

Metal	Precursor material	Adsorption capacity (mg g ⁻¹)	References
Pb (II)	Bamboo waste	41.25	This study
	Bamboo*	52.12	commercial
	Corn straw modified with MgCl ₂	5.15	Huang et al. (2020)
	Pomelo peel	21.09	Wu et al. (2021)
	Clostridium powder	9.11	Liu et al. (2021)
	Rice straw	31.15	Sakhya et al. (2022)
Cu (II)	Bamboo waste	30.21	This study
	Bamboo*	43.29	commercial
	Bamboo modified by FeCl ₃	27.5	Zhang et al. (2021)
	Rice husk	21.00	Zhang et al. (2011)
	Apple tree branches	11.41	Zhao et al. (2020)
	Pomelo peel	8.17	Wu et al. (2021)
Zn (II)	Bamboo waste	34.48	This study
	Bamboo*	41.65	commercial
	Bamboo	7.62	Van Hien et al. (2020)
	Rice husk	3.82	Van Hien et al. (2020)
	Wood	4.02	Van Hien et al. (2020)
	Apple tree branches	10.22	Zhao et al. (2020)
	Pomelo peel	4.41	Wu et al. (2021)
	Rice straw	32.81	Sakhya et al. (2022)

* Bamboo biochar purchased from bambooreform, Thailand.

Source: <http://www.bambooreform.com>

that had an effect on biochar porous structure, more micropores and mesopores corresponded to a larger surface area (Angthararuk et al., 2022). However, our biochar's heavy metal adsorption efficiency was inferior compared to the commercial biochar which claims higher temperature production, meanwhile it has a high cost. The low-cost biochar derived from bamboo waste is suitable as an alternative adsorbent for heavy metals removal in water. In order to show the applicability of low-cost biochar, the investigation of adsorbents to remove metal and organic contaminants from wastewater by continuous flow experiments will be conducted in future work.

7. Applied bamboo biochar for heavy metal removal in groundwater

Batch experiment for removal of heavy metals in groundwater with samples being collected from Hin Tung, Mueang Nakhon Nayok District, Nakhon Nayok Province, Thailand (14°15'03"N 101°18'18"E) during September 2021. In this work, the heavy metals such as arsenic (As), cadmium (Cd), copper (Cu), manganese (Mn), lead (Pb), and zinc (Zn) in the groundwater were determined by using an ICP-OES instrument. A four-point calibration curve for each element was created with correlation coefficients of more than 0.999 for quantification. The results found that a concentration of Mn and Cu were 6.74 and 0.068 mg L⁻¹, respectively. While Pb and Zn were less than 0.01 mg L⁻¹ moreover As and Cd were not detected. The results revealed that Mn levels in the water exceeded Thailand's groundwater quality standards. Manganese is not hazardous to health but manganese can cause water to have an unpleasant taste, odor, color, and brownish-black stains (Krishnakumari et al., 2018). The batch test for heavy metal removal in groundwater found that bamboo biochar was able to eliminate Mn more than 95% with an hour contact time while other heavy metals were completely eliminated. The breakthrough data obtained from this study can be utilized to design a point of using low-cost biochar as a filter that would be able to effectively remove heavy metals from groundwater.

Conclusion

Accordingly, this study demonstrates once more that the biochar derived from bamboo handicraft waste by using a simple and low-cost method can be an excellent adsorbent for removing heavy metals from aqueous solutions. The Pb(II), Cu(II) and Zn(II) were

used as representative metals in this experiment and the results showed that biochar had a greater adsorption capacity. The removal efficiency of Pb(II), Cu(II) and Zn(II) were more than 80, 60 and 70 %, respectively, at 20 mg L⁻¹ initial concentration, pH 4, 120 min contact time and 1.0 g absorbent L⁻¹. The adsorption kinetics and behavior were suitably described following the pseudo-second-order kinetic and Langmuir models, respectively, indicating two reactions appear; adsorption rate was rapid in the first stage and then slow to equilibrium adsorbing via monolayer chemical adsorption. Moreover, the function group as C=O, C-O and O-H in the biochar may be essential to metal adsorption, mainly cations can form O-M (M=Pb, Cu and Zn) complexes. Applying the bamboo biochar in the removal of heavy metals in groundwater was successful. Therefore, more research is needed for the application of biochar usage in full-scale systems.

Acknowledgment

This research was supported by Suan Dusit University, Thailand

References

Ahmed, A.S., Sultana, S., Habib, A., Ullah, H., Musa, N., Hossain, M.B., ... Sarker, M.S.I. (2019). Bioaccumulation of heavy metals in some commercially important fishes from a tropical river estuary suggests higher potential health risk in children than adults. *PLoS One*, 14(10), e0219336.

Angthararuk, D., Phasuk, S., & Takolpuckdee, P. (2022). Local production and characterization of biochar from bamboo waste and the removal of natural organic matter from Nakhon-nayok river, Thailand. *Journal of Food Health and Bioenvironmental Science*, 15(1), 18-29.

Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M.R., & Sadeghi, M. (2021). Toxic mechanisms of five heavy metals: mercury, lead, chromium, cadmium, and arsenic. *Frontiers in pharmacology*, 12, 643972.

Bangaoil, R., Santillan, A., Angeles, L.M., Abanilla, L., Lim Jr, A., Ramos, M.C., ... Albano, P.M. (2020). ATR-FTIR spectroscopy as adjunct method to the microscopic examination of hematoxylin and eosin-stained tissues in diagnosing lung cancer. *PLoS One*, 15(5), e0233626.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., & Hay, A.G. (2011). Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*, 102(19), 8877-8884.

Chen, Z.L., Zhang, J.Q., Huang, L., Yuan, Z.H., Li, Z.J., & Liu, M.C. (2019). Removal of Cd and Pb with biochar made from dairy manure at low temperature. *Journal of integrative agriculture*, 18(1), 201-210.

Chunhabundit, R. (2016). Cadmium exposure and potential health risk from foods in contaminated area, Thailand. *Toxicological research*, 32(1), 65-72.

Cui, L., Chen, T., Yin, C., Yan, J., Ippolito, J. A., & Hussain, Q. (2019). Mechanism of adsorption of cadmium and lead ions by iron-activated biochar. *BioResources*, 14(1), 842-857.

Da'ana, D. A., Zouari, N., Ashfaq, M. Y., Abu-Dieyeh, M., Khraisheh, M., Hijji, Y. M., & Al-Ghouti, M. A. (2021). Removal of toxic elements and microbial contaminants from groundwater using low-cost treatment options. *Current Pollution Reports*, 7(3), 300-324.

Deng, H., Li, Q., Huang, M., Li, A., Zhang, J., Li, Y., ... Mo, W. (2020). Removal of Zn (II), Mn (II) and Cu (II) by adsorption onto banana stalk biochar: Adsorption process and mechanisms. *Water Science and Technology*, 82(12), 2962-2974.

Ding, W., Dong, X., Ime, I.M., Gao, B., & Ma, L. Q. (2014). Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere*, 105, 68-74.

Huang, K., Cai, Y., Du, Y., Song, J., Mao, H., Xiao, Y., ... Han, L. (2020). Adsorption of Pb (II) in aqueous solution by the modified biochar derived from corn straw with magnesium chloride. *Nature Environment and Pollution Technology*, 19(3), 1273-1278.

Hernández-Mena, L.E., Pécoraa, A.A., & Beraldob, A.L. (2014). Slow pyrolysis of bamboo biomass: Analysis of biochar properties. *Chem Eng*, 37, 115-120.

Iamsaard, K., Weng, C.H., Yen, L.T., Tzeng, J.H., Poonpakdee, C., & Lin, Y.T. (2022). Adsorption of metal on pineapple leaf biochar: Key affecting factors, mechanism identification, and regeneration evaluation. *Bioresource Technology*, 344, 126131.

Iqbal, Z., Abbas, F., Mahmood, A., Ibrahim, M., Gul, M., Yamin, M., ... Sial, G.Z.H. (2022). Human health risk of heavy metal contamination in groundwater and source apportionment. *International Journal of Environmental Science and Technology*, 19(8), 7251-7260.

Jovarauskaitė, L., & Balundė, A. (2021). A systematic review of drivers of sustainable wastewater treatment technology adoption. *Sustainability*, 13(15), 8584.

Katiyar, R., Patel, A.K., Nguyen, T.B., Singhania, R.R., Chen, C.W., & Dong, C.D. (2021). Adsorption of copper (II) in aqueous solution using biochars derived from *Ascophyllum nodosum* seaweed. *Bioresource Technology*, 328, 124829.

Krishnakumari, B., Abhishek, V.M., Puneeth, T.E., Vignesh, S., & Irfan, M.K.M. (2018). Removal of iron and manganese from ground water. *International Journal of Engineering Research & Technology*, 6(2), 1-4.

Kheangkhun, N., Sringsam, J., Kumpinit, W., Wattanakornnir, A., & Phuengphai, P. (2020). Contaminated heavy metals in rice of Surin province, Thailand. *Naresuan University Journal: Science and Technology (NUJST)*, 28(1), 55-64.

Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., & Ma, L. Q. (2017). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere*, 178, 466-478.

Liu, W., Li, K., Hu, X., Hu, X., Zhang, R., & Li, Q. (2021). Characteristics and mechanism of Pb²⁺ adsorption from aqueous solution onto biochar derived from microalgae and chitosan-modified microalgae. *Front. Environ. Chem*, 2, 693509.

Murtaza, G., Usman, M., Ahmed, Z., Shabbir, R. N., & Ullah, Z. (2021). Molecular understanding of biochar aging on their properties and environmental significances. *EQIA-International Journal of Environmental Quality*, 43, 30-46.

Nguyen, T.T., Chen, H.H., To, T.H., Chang, Y.C., Tsai, C. K., Chen, K.F., & Tsai, Y.P. (2021). Development of biochars derived from water bamboo (*Zizania latifolia*) shoot husks using pyrolysis and ultrasound-assisted pyrolysis for the treatment of Reactive Black 5 (RB5) in wastewater. *Water*, 13(12), 1615.

Oliveira, F.R., Patel, A.K., Jaisi, D.P., Adhikari, S., Lu, H., & Khanal, S.K. (2017). Environmental application of biochar: Current status and perspectives. *Bioresource technology*, 246, 110-122.

Qian, L., & Chen, B. (2014). Interactions of aluminum with biochars and oxidized biochars: Implications for the biochar aging process. *Journal of agricultural and food chemistry*, 62(2), 373-380.

Sakhiya, A.K., Vijay, V.K., & Kaushal, P. (2022). Efficacy of rice straw derived biochar for removal of Pb²⁺ and Zn²⁺ from aqueous: Adsorption, thermodynamic and cost analysis. *Bioresource Technology Reports*, 17, 100920.

Sarker, A., Kim, J.E., Islam, A.R.M., Bilal, M., Rakib, M., Jahan, R., ... Islam, T. (2022). Heavy metals contamination and associated health risks in food webs-a review focuses on food safety and environmental sustainability in Bangladesh. *Environmental Science and Pollution Research*, 29, 3230-3245.

Sherlala, A.I.A., Raman, A.A.A., Bello, M.M., & Asghar, A. (2018). A review of the applications of organo-functionalized magnetic graphene oxide nanocomposites for heavy metal adsorption. *Chemosphere*, 193, 1004-1017.

Siipola, V., Pflugmacher, S., Romar, H., Wendling, L., & Koukkari, P. (2020). Low-cost biochar adsorbents for water purification including microplastics removal. *Applied Sciences*, 10(3), 788.

Van Hien, N., Valsami-Jones, E., Vinh, N.C., Phu, T.T., Tam, N.T.T., & Lynch, I. (2020). Effectiveness of different biochar in aqueous zinc removal: Correlation with physicochemical characteristics. *Bioresource Technology Reports*, 11, 100466.

Wu, Q., Dong, S., Wang, L., & Li, X. (2021). Single and competitive adsorption behaviors of Cu²⁺, Pb²⁺ and Zn²⁺ on the biochar and magnetic biochar of pomelo peel in aqueous solution. *Water*, 13(6), 868.

Xu, J., Cao, Z., Zhang, Y., Yuan, Z., Lou, Z., Xu, X., & Wang, X. (2018). A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism. *Chemosphere*, 195, 351-364.

Zhang, J., Fu, H., Lv, X., Tang, J., & Xu, X. (2011). Removal of Cu (II) from aqueous solution using the rice husk carbons prepared by the physical activation process. *Biomass and Bioenergy*, 35(1), 464-472.

Zhang, Y., Qiu, G., Wang, R., Guo, Y., Guo, F., & Wu, J. (2021). Preparation of bamboo-based hierarchical porous carbon modulated by FeCl₃ towards efficient copper adsorption. *Molecules*, 26(19), 6014.

Zhao, S., Ta, N., & Wang, X. (2020). Absorption of Cu (II) and Zn (II) from aqueous solutions onto biochars derived from apple tree branches. *Energies*, 13(13), 3498.