Batch and Fixed Bed Column Studies on Cadmium (II) and Lead (II) Adsorption from Aqueous Solution by Coffee Pulp Biochar

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***Abstract*—**Biochar prepared from pyrolysis of coffee pulp was used as adsorbent for the removal of Cd(II) and Pb(II) from aqueous solution using batch and fixed bed column adsorption methods. The derived biochar from coffee pulp was characterized by ultimate analysis, SEM with EDS and FTIR. The effect of the operating parameters such as pH of the solution, biochar dosage and initial metal ion concentration was studied in batch experiments. Adsorption isotherms results showed that the Langmuir isotherm model (R^2 > 0.99) was better fitted for Cd(II) and Pb(II) adsorption by coffee pulp biochar as compared with Freundlich isotherm model. The predicted maximum adsorption capacities for Cd(II) and Pb(II) adsorption were 46.51 mg/g and 54.05 mg/g, respectively. In fixed bed column experiments, rate of flow of the solution (2 mL/min) and bed height (15 cm) influence the breakthrough time of Cd(II) and Pb(II) adsorption. Biochar derived from coffee pulp could therefore be used as low cost effective adsorbent for the removal of Cd(II) and Pb(II) contaminated industrial wastewater effluent**.**

***Keywords*—**Adsorption, biochar, cadmium, coffee pulp, isotherms, lead.

I. Introduction

Coffee (*Coffea* sp.) is one of the most important agricultural commodities in the world. Industrial processing of coffee cherries is done to isolate coffee powder by removing the shell and the mucilaginous part from the cherries [1]. Coffee pulp is an abundant agricultural by-product of handling and processing coffee for it represents approximately 28 – 43% of the weight of the coffee fruit. Some major problems in the disposal of this type of by-products include agglomeration, fouling and excessive emissions, etc. and there are no profitable uses for this type of residue [2].

Cadmium and lead are considered as some of the most toxic heavy metals [3]. These heavy metals can pose a danger to the human and environmental health due to their hazardous effects, persistency and the accumulation tendency. The exposure to heavy metals can cause damage to many parts of human bodies, even at very low concentrations [4]. Therefore, the removal of heavy metals from aqueous solutions is of extreme importance. Various conventional methods such as chemical precipitation, electro dialysis, coagulation/flocculation, etc. were already recommended for the removal of heavy metals from aqueous solution. However, these methods have their own existing limitations such as high operational cost, sensitive operating conditions, less efficiency and further the disposal is a costly matter [5]. The adsorption using agricultural wastes and by-products (AWBs) is a practical option due to their unique chemical composition, available in abundance, renewable, low cost, and more efficient to remove heavy metals in aqueous solution [6]. AWBs as low-cost adsorbents are used either in natural form or even after some physical or chemical modification. Biochar, usually generated from pyrolysis of agricultural wastes and by-products, exhibits a great potential to remove various heavy metals in the water due to its wide availability of feedstock, low cost and favorable physical/chemical characteristics [7]–[17].

The potential alternative use of coffee pulp as biochar adsorbent for the purpose of removing heavy metals in the environment was believed to reduce wastes in an eco-friendly way. Hence, it agrees well with concepts of innovative, effective and sustainable waste management.

In this study the adsorption capacity of coffee pulp biochar for the removal of Cd(II) and Pb(II) ions from aqueous solution in batch studies was investigated. The effect of the operating parameters such as pH of the solution, biochar dosage and initial metal ion concentration was studied. Furthermore, the influence of flow rate and bed height were also investigated in fixed bed column studies.

II. Materials And Methods

A. Preparation of the Adsorbent

The coffee pulp was obtained from the National Coffee Research, Development and Extension Center (NCRDEC) at the Cavite State University, Cavite, Philippines. It was acquired after the de-pulping of coffee fruit in wet processes. Then, the pulp was sun dried for 3 days.

The production of biochar samples was done in the chemical laboratory at the Mapúa Institute of Technology, Manila, Philippines. The dried coffee pulp was ground to pass through a less than the 0.5 mm sieve. Pyrolysis took place in a temperature-controlled furnace (Vecstar muffle furnace) at 500°C for 10 mins. The obtained samples of coffee pulp biochar were sealed in a container before experimental use. It was used directly without further treatment in subsequent experiments.

B. Characterization of the Biochar Adsorbent

Physical and chemical properties of the coffee pulp biochar samples, including elemental content, biochar morphology and

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spectral properties were characterized. The pH of biochar was measured by adding the biochar to de-ionized water at a 1:5 w/w ratio, then shaking the mixture, allowing it to equilibrate for 5 min, and then measuring the pH of the solution using a pH meter. The presence of carbon, hydrogen, and nitrogen in the coffee pulp biochar was determined by ultimate analysis using a combustion method. The oxygen content of the samples was determined by energy dispersive spectroscopy (EDS) through Dual Beam Helios Nanolab 600i (accelerating voltage: 15 kV). The surface morphology and particle size of the coffee pulp biochar were studied by using a scanning electron microscopy (SEM) through Dual Beam Helios Nanolab 600i (accelerating voltage: 1 kV). Fourier Transform Infrared (FTIR) analysis (Perkin Elmer FT-IR Spectrometer Frontier, range: 4000 – 600 cm^{-1}) was carried out to determine the surface functional group existing in the coffee pulp biochar.

C. Preparation of the Aqueous Solutions

Standard solutions (1,000 mg/L each) of cadmium(II) ion and lead(II) ion were prepared by dissolving appropriate amount of respectively cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$) and anhydrous lead nitrate ($Pb(NO_3)_2$) powders in a beaker with one liter (1 L) of distilled water. The standard solutions were diluted to the designed concentrations to be used in the batch adsorption experiments.

D. Batch Adsorption Experiments

All batch experiments were carried out at room temperature (25 °C). For the effect of initial pH of the solution, each of the experiments was performed in a 250 mL Erlenmeyer flask containing 100 mL of 150 mg/L of each metal ion solution and 0.5 g of the coffee pulp biochar. The initial pH values of each of the mixtures were adjusted by adding 0.1 M NaOH and 0.1 M HCl (pH 3.0, 4.0, 5.0, 6.0, 7.0). The effect of biochar dosage was determined by using 250 mL Erlenmeyer flask containing 150 mg/L of each metal ion solution and different biochar dosages: 0.1, 0.3, 0.5, 0.7, and 1 g. For the initial metal ion concentration, five concentration levels ranging from 50 mg/L to 250 mg/L were individually evaluated. All of these mixtures were shaken by using an automatic shaker for 24 h at 100 rpm, filtered using Whatman filter paper, and washed with 50 mL distilled water. The residual metal ions were determined by atomic absorption spectroscopy (AAS). These residuals were used as the equilibrium heavy metal concentrations for the analysis of adsorption capacities of the coffee pulp biochar.

The adsorption capacity (q_e) of the coffee pulp biochar in the equilibrium state was calculated according to (1).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

Where q_e is the amount of heavy metals adsorbed at equilibrium in mg/g, C_0 and C_e are initial and equilibrium heavy metal concentrations in mg/L, respectively, V is the volume of the solution in L and m is the weight of coffee pulp biochar in g.

E. Fixed Bed Column Experiments

Fig. 1 shows the schematic diagram of the fixed bed column setup in this study. The column is 2 cm in diameter and 40 cm length. The column was partially packed up to the desired bed height of coffee pulp biochar. Using a peristaltic pump, the artificial wastewater was pumped at different flow rates from the container with cadmium(II) and lead(II) contaminated water (separated system). Samples on the outlet were collected at definite time intervals and examined for its heavy metal ion concentration. The metal ion concentration of the samples was determined using AAS. The breakthrough curves for each metal were obtained by concentration-time data (plotting C/Co versus time). The breakthrough time corresponding to 90% removal (or C/Co = 0.1) was chosen as a point for comparison for the removal efficiency of each metal.

III. Results And Discussion

A. Characterization of Coffee Pulp Biochar

The physicochemical properties of the coffee pulp biochar were measured and the results were tabulated in Table 1. It was found that the pH of coffee pulp biochar rose to 8.45. High pH of a biochar suggest that it has potential as an amendment to neutralize soil acidity, which can be an important factor in metal ions mobility. The average particle size of the coffee pulp biochar is 63.24 µm, it is in the same range of a very fine sand (62.5 – 125 µm). Finer particles generally have a greater specific surface area thus providing a number of adsorption sites, thereby increasing adsorption capacity [18]. The molar H/C ratio can be used to describe the degree of carbonization or aromaticity [19]. The observed H/C ratio of 0.55 for the coffee pulp biochar indicate that this biochar is weakly carbonized and are consistent with only moderate amounts of aromatization [20]. This high H/C ratio suggests that the coffee pulp biochar likely still contain a certain amount of original plant organic residues such as cellulose [20]. The O/C ratio (0.22) and (O+N)/C ratio (0.30) of the coffee pulp biochar is likely to present a relatively hydrophilic and polar structure [9]. The SEM image of Fig. 2 reveals the porous structure of the coffee pulp biochar surface. It reveals that the coffee pulp biochar is a macro porous material with a pore size > 50 nm. The summary of the peaks of the FTIR spectra of the coffee pulp biochar and their assignment are in Table 2. As can be inferred from the FTIR analysis, the functional groups present on the coffee pulp biochar surface were hydroxyl, alkyl and ether groups. These surface functional groups had been reported to play an important role in the adsorption capacity and the removal mechanism of the adsorbates [11].

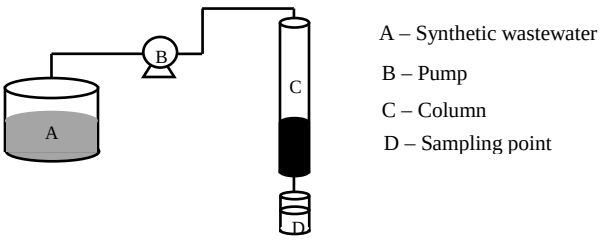


Fig. 1. Fixed bed column set up

TABLE I

PHYSICOCHEMICAL PROPERTIES OF THE COFFEE PULP BIOCHAR

Parameters	Values
pH	8.45
Average particle size (µm)	63.24
C (%)	68.66
H (%)	3.16
N (%)	6.60
O (%)	20.03
H/C	0.55
O/C	0.22
(O+C)/N	0.30

H/C – ratio of hydrogen to carbon, (O + N)/C – polarity index, O/C –ratio of oxygen to carbon

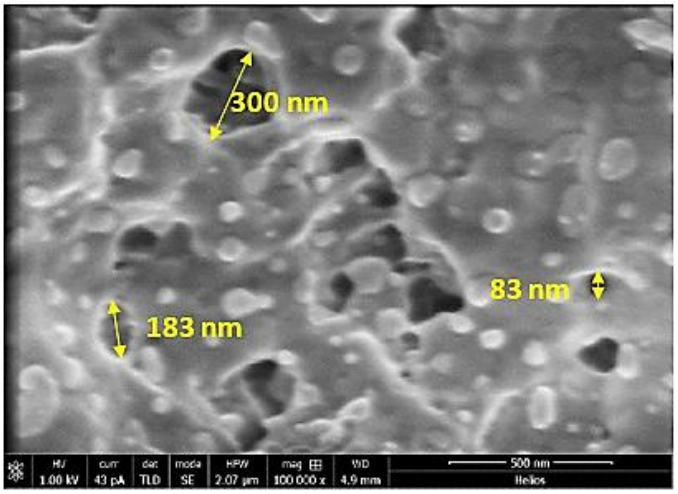


Fig. 2. SEM images of the coffee pulp biochar for surface morphology

TABLE II:
PEAKS FROM COFFEE PULP BIOCHAR SPECTRUM AND THEIR POSSIBLE ASSIGNMENTS

Band position/cm	Possible assignments
3335.71 – 3177.14	O – H stretch (alcohol)
2917.85	C – H stretch (alkane)
1568.91	C = C stretch (aromatic)
1394.00	O – H bend (alcohol)
1381.14	C – H bend (alkane)
1258.08	O – H bend (alcohol)
1234.90 – 1149.29	C – OH stretch (alcohol)
1067.26	C – O – C stretch (ether)
1011.97 – 755.15	C – H bend (alkane)
702.31 – 618.89	O – H bend (alcohol)

B. Effect of Initial pH of the Solution

To study the effect of the initial pH on the Cd(II) and Pb(II) adsorption onto coffee pulp biochar, metal uptake of the solutions with an initial pH ranging from 3.0 to 7.0 was verified. Metal uptake was affected by the initial pH of the solution as shown in Fig. 3. The highest adsorption capacities for Cd(II) (28.30 mg/g) and Pb(II) (28.95 mg/g) were observed at pH values of 6 and 5, respectively. Lower adsorption capacities were also observed at lower pH. This was attributed to the surface charge of the biochar adsorbent, H^+ ions compete with the metal cations for the adsorption sites at a low pH value of the solution causing a low adsorption capacity [13]. As the pH value of the solution increases, the amount of negatively charged surface groups also increases, which favors the metal ion uptake due to electrostatic interaction. However, at very high pH, the adsorption stops and the hydroxide precipitation start [11], [21]

C. Effect of Biochar Dosage

The highest adsorption capacities of coffee pulp biochar for Cd(II) and Pb(II) ions were observed at 0.1 g biochar dosage. These were 104.87 and 128.48 mg/g, respectively. Fig. 4 shows that the adsorption capacities were found to decrease with increasing the dosage of biochar. For Cd(II), the adsorption capacity of the coffee pulp biochar sharply decreased from 104.87 mg/g at 0.1 g of biochar dosage to 14.16 mg/g at 1 g of biochar dosage. This was likely due to overlapping of adsorption sites leading to a decrease in the total surface area [9].

D. Effect of Initial Metal Ion Concentration

As shown in Fig. 5, the amount of metal ions adsorbed per gram of coffee pulp biochar increased with the increase of the initial metal ion concentration. The highest adsorption capacities were observed at the initial concentration of 250 mg/L with 41.13 and 46.74 mg/g for Cd(II) and Pb(II), respectively. This trend was attributed to the rate of transporting metal ions from solution to the adsorbent surface owing to a driving force made by the initial metal ion concentration [22].

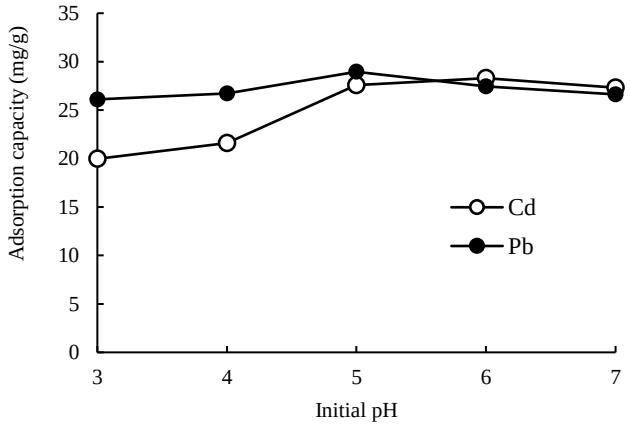


Fig. 3. Effect of the initial pH on adsorption capacities of Cd(II) and Pb(II) ions by coffee pup biochar

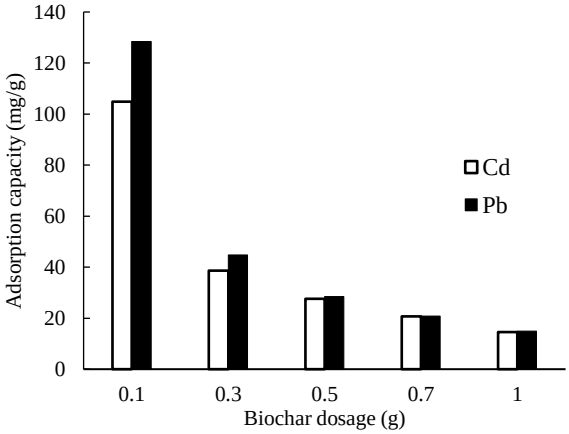


Fig. 4. Effect of biochar dosage on adsorption capacities of Cd(II) and Pb(II) ions by coffee pulp biochar

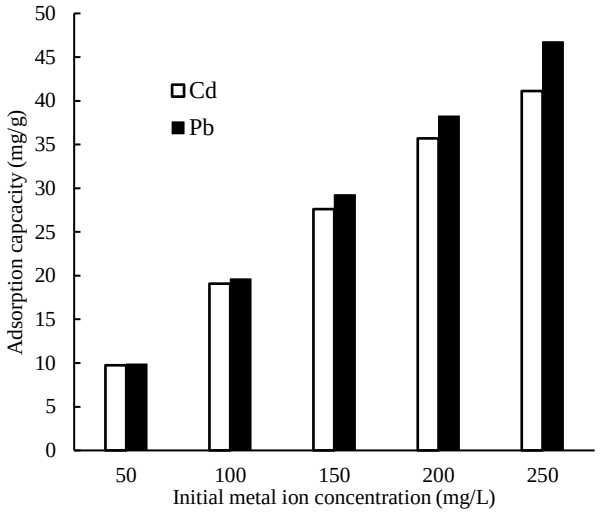


Fig. 5. Effect of initial metal ion concentration on adsorption capacities of Cd(II) and Pb(II) ions by coffee pulp biochar

E. Adsorption Isotherms

The Langmuir and Freundlich isotherm models were used to examine the maximum amount of metal ions that could be adsorbed by the coffee pulp biochar.

Langmuir isotherm in (2) assumes monolayer adsorption over an actively homogeneous adsorbent surface [23].

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

Where q_e is the amount of heavy metals adsorbed at equilibrium in mg/g, q_{max} is the monolayer adsorption capacity in mg/g, b is the Langmuir constant, C_e is the equilibrium heavy metals concentrations in mg/L. Equation (3) shows its linear form.

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

A straight line was formed with a slope of $1/q_{max}$ and an intercept of $1/bq_{max}$ by plotting C_e/q_e versus C_e.

Freundlich isotherm in (4) is an empirical model based on heterogeneous adsorption over independent sites [23].

$$q_e = K_f C_e^{1/n} \quad (4)$$

Where K_f is related to binding energy and adsorption capacity and n is related to the intensity of adsorption. Equation (5) shows its linear form.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

The plot of ln q_e versus ln C_e yield a straight line with $1/n$ as slope and ln K_f as intercept.

The isotherm fitting of the equilibrium data for Cd(II) and Pb(II) adsorption by coffee pulp biochar are shown in Fig. 6. Correlation coefficients suggested that the Langmuir model fits the data better than the Freundlich model (R^2 > 0.99 for Langmuir model vs 0.9819 and 0.9858 for Freudlich model). The maximum predicted adsorption capacities of coffee pulp biochar for Cd(II) and Pb(II) ions were 46.51 and 54.05 mg/g, respectively. The parameter b is related to the affinity of the binding sites, which allows comparisons of the affinity of biochar towards the metal ions [11]. The coffee pulp biochar had a higher affinity for Pb(II) (0.34 L/mg) than Cd(II) (0.16 L/mg).

F. Effect of varying bed heights

The breakpoint time at 90% removal (C/Co = 0.1) for the effect of varying bed height at a constant flow rate (2 mL/min) on Cd(II) and Pb(II) adsorption by coffee pulp biochar are shown in Table 3, while their breakthrough curves are in Fig 7. As the bed height increases from 5 cm to 15 cm, it was observed that the breakpoint time also increases from 21 to 41 min for Cd(II) and 40 to 60 min for Pb(II). The increase of breakthrough time is due to higher amount of adsorbent dose in column with higher bed height, which provide greater functional sites and broadened mass transfer zone for each metal adsorption. The breakthrough time is directly proportional to the amount of adsorbent in the column.

G. Effect of varying flow rates

Table 3 shows also the breakpoint time at 90% removal (C/Co = 0.1) for the effect of varying flow rate at the constant bed height (15 cm) on Cd(II) and Pb(II) adsorption by coffee pulp biochar, while Fig. 8 shows their breakthrough curves. The longest breakpoint time occurred when running at a flow rate of 2 mL/min while the shortest breakpoint time occurred when running at a flow rate of 6 mL/min for all single metal adsorption systems. The breakpoint time decreased with the increase of the of the flow rate. This implies that it would take a longer time for the adsorbent to be completely saturated at slow flow rates since decreasing the movement of the fluid decreases the flow of the ions entering the pores of the adsorbent resulting to a slower clogging of the adsorbent pores.

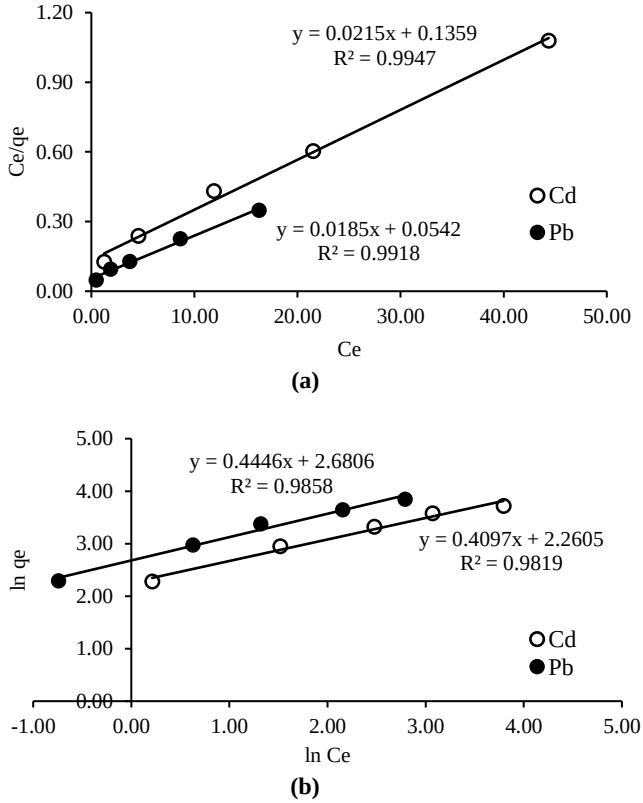
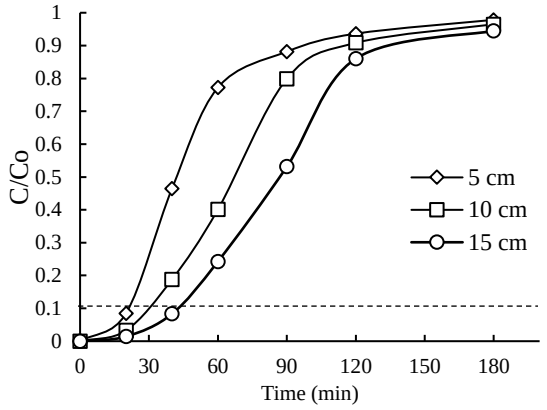


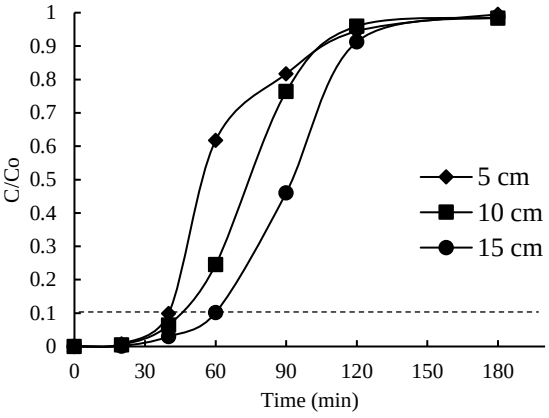
Fig. 6. Fitting the equilibrium data in (a) Langmuir and (b) Freundlich isotherm model

TABLE III
BREAKPOINT TIME FOR EACH METAL AT DIFFERENT OPERATING CONDITION

Parameters	Value	Breakpoint time (min) of 90% removal for each metal	
		Cd	Pb
Bed height	5 cm	21	40
	10 cm	30	45
	15 cm	41	60
Flow rate	2 mL/min	41	60
	4 mL/min	31	46
	6 mL/min	23	41

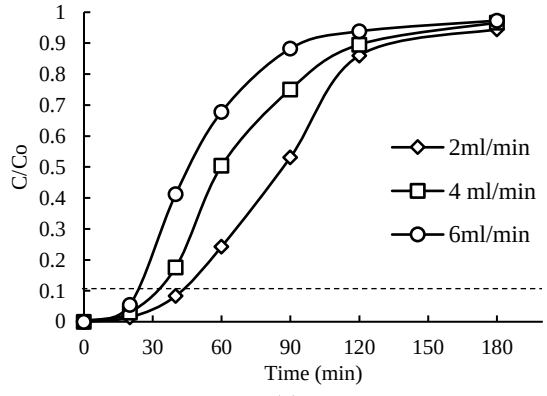


(a)

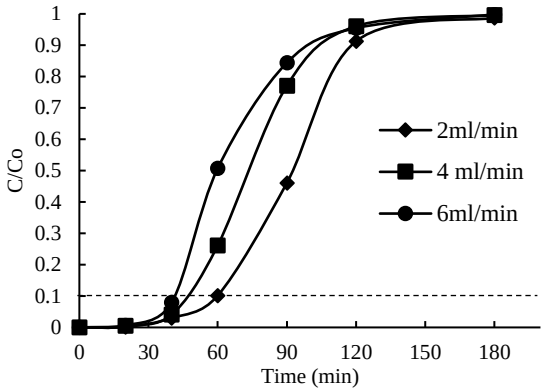


(b)

Fig. 7. Breakthrough curves for the effect of varying bed height on (a) Cd(II) and (b) Pb(II) adsorption by coffee pulp biochar



(a)



(b)

Fig. 8. Breakthrough curves for the effect of varying flow rate on (a) Cd(II) and (b) Pb(II) adsorption by coffee pulp biochar

IV. CONCLUSION

This study revealed that the coffee pulp biochar was an effective adsorbent and can be used for the removal of Cd(II) and Pb(II) ions from aqueous solution through batch and fixed bed column. The physicochemical characteristics of the coffee pulp biochar were found to be favorable for the Cd(II) and Pb(II) ions adsorption. The optimum initial pH was observed at pH value of 6 for Cd(II) adsorption and pH value of 5 for Pb(II) adsorption. The adsorption capacity of coffee pulp biochar decreased with increasing biochar dosage while increasing the metal ion concentration resulted in the increasing adsorption capacity of the coffee pulp biochar. The experimental data fitted well with the Langmuir isotherm model (R^2>0.99) and the predicted maximum adsorption capacity of the coffee pulp biochar was 46.51 mg/g for Cd(II) adsorption and 54.05 mg/g for Pb(II) adsorption. The breakthrough time is directly proportional to the amount of adsorbent, however, inversely proportional to the rate of flow of the solution.

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