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Communication

# Effects of Biochar Production Methods and Biomass Types on Lead Removal from Aqueous Solution

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**Featured Application:** This study produced biochars from a conventional lab tube furnace vs. a Do-It-Yourself (DIY) biochar maker and compared the biochar properties and their efficacy for aqueous lead removal. It tested four different biomasses as feedstock materials. It would be a good reference for those who are considering household-scale biochar production and its application as a sorbent for cationic heavy metal.

**Abstract:** Biochar has proven its potential in removing heavy metal ions from water. The objective of this study was to evaluate locally obtained biomass feedstocks for biochar production and their efficiency as a sorbent for aqueous lead (Pb<sup>2+</sup>) removal. The biomass feedstocks consisted of avocado seed, avocado peel, grapefruit peel, and brown seaweed, which represent agricultural and marine biomasses. The biochar materials were produced in two different methods: (1) a laboratory tube furnace at 300 °C and (2) a Do-It-Yourself (DIY) biochar maker, “BioCharlie Log”. The biochars were characterized for selected physicochemical properties, and batch adsorption tests with 10 mg Pb<sup>2+</sup> L<sup>-1</sup> were conducted. All biochars exhibited >90% Pb<sup>2+</sup> removal with the avocado seed and grapefruit peel biochars being the most effective (99%) from the tube-furnace-produced biochars. BioCharlie-produced-biochars showed similar Pb<sup>2+</sup> removal (90–97%) with brown seaweed and avocado seed biochars being the most effective (97%). Land-based biochars showed a higher carbon content (>53%) than the brown seaweed biochar (28%), which showed the highest ash content (68%). Our results suggested that oxygen-containing surface functional groups in land-based biochar and mineral (ash) fraction in marine-based biochar play a key role in Pb<sup>2+</sup> removal.

**Keywords:** biochar; adsorption; lead; pyrolysis; avocado seed; avocado peel; brown seaweed; grapefruit peel



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## 1. Introduction

Heavy metals are a water pollutant of concern as they are increasingly discharged into the environment [1]. Lead (Pb) is of particular concern due to its toxicity and its potential to enter the public water supply system. High levels of exposure to Pb may cause damage to the kidney, liver, reproductive systems, and brain functions [2]. In children and infants, Pb can cause delays in mental or physical development and deficits in attention span and learning ability [3]. Most Pb contamination in drinking water occurs from corrosion of Pb-containing pipes or brass fixtures in homes, or in water treatment plants when water treatment changes alter water chemistry [4,5]. Under the United States Environmental Protection Agency (USEPA)’s Lead and Copper Rule (1991), the maximum contaminant level goal of Pb in drinking water is zero as any exposure to Pb leads to health risks. The rule sets an action level of 15 ppb (µg L<sup>-1</sup>) for Pb in drinking water [6]. If 10 percent of a

water system's customers (the 90th percentile) sample above this level, then further action is needed to diminish Pb exposure. In the USA from 2001 to 2004, hundreds of homes had Pb concentrations of up to 300 ppb in Washington D.C., while a 2015 citizen science effort testing Pb in home water samples in Flint, Michigan determined a 90th percentile of 27 ppb with samples ranging up to 108 ppb [5,7]. The global average of Pb concentrations in lakes and rivers was reported to be  $116 \pm 29$  ppb (mean  $\pm$  standard error) during 2010–2017 [1].

Biochar is a charcoal-like substance derived from agricultural or forestry waste (biomass) under limited or no oxygen conditions (pyrolysis) and it has been used as a soil amendment. By charring the biomass, carbon dioxide (CO<sub>2</sub>) in the biomass material is “fixed” into a stable, solid form while reducing the potential release of CO<sub>2</sub> into the atmosphere. The use of biochar as a low-cost adsorbent to remove metallic contaminants from aqueous solutions has been an emerging research topic [8–10]. In addition, adsorption is regarded as an efficient method of the contaminant removal due to its low operating cost and simple design [11]. A promising opportunity is the conversion agricultural residues from food production into biochar and its subsequent use for water treatment [12]. A biochar-based water treatment system has the potential to be used when biochar production is feasible (e.g., flame curtain kiln for developing countries or biomass gasifier for developed countries) [13].

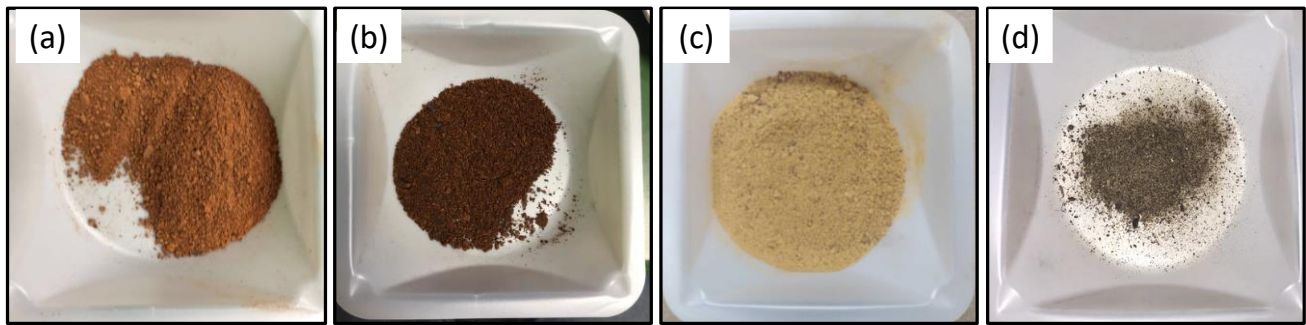
In this study, biochar materials were produced from locally sourced biomasses and tested for their adsorptive properties of aqueous Pb ion (Pb<sup>2+</sup>). The Pb<sup>2+</sup> was chosen as a model divalent heavy metal cation due to its potential to make its way into drinking water systems. Four biomass sources (avocado seed, avocado peel, brown seaweed, and grapefruit Peel) were used as the biochar feedstock due to the abundance of these biomasses. For example, worldwide production of avocado is 6.4 million tons per year with a waste proportion of 24% [14]. Citrus waste represents 50–60% of the 100 million tons of fruits produced per year [15]. Seaweed is also an abundant and seasonal marine waste, which is highly undesired by the coastal tourism industry [16].

Biochars were produced through two different methods in this study: (1) through a laboratory tube furnace in which the temperature was controlled, and (2) through a Do-It-Yourself (DIY) biochar maker, “BioCharlie Log”, in which the pyrolysis temperature is not controlled and represents a household biochar production. To the best of our knowledge, there was no study directly comparing the BioCharlie-produced biochars against laboratory-produced biochars for Pb<sup>2+</sup> removal. The biochar production by BioCharlie is highlighted by the ease of production in an open fire, and it has the potential to be used on a household scale where a temperature-controlled pyrolysis unit is not available. The produced biochars by both methods were characterized for selected physicochemical properties and evaluated for Pb<sup>2+</sup> removal. The specific objectives of this study were to (1) evaluate Pb<sup>2+</sup> removal across four biomass types through a single-point batch adsorption experiment (e.g., screening test), and (2) investigate the effects of production methods on the Pb<sup>2+</sup> removal and selected physicochemical properties of the produced biochars. A commercial activated carbon was included as a reference sorbent for Pb<sup>2+</sup>.

## 2. Materials and Methods

### 2.1. Biochar Production

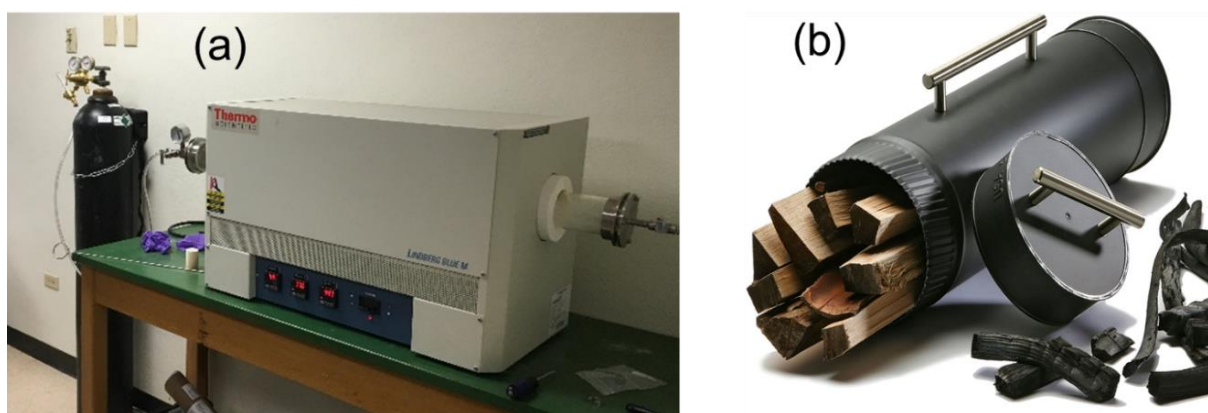
Avocado seed, avocado peel, and grapefruit peel were obtained from local grocery stores and collected after consumption, while brown seaweed (*sargassum*) was collected from the Laguna Madre, a hypersaline lagoon near the shoreline in South Padre Island, Texas, USA. The biomass materials were washed thoroughly with tap water and then oven-dried at 105 °C for 24 h. The oven-dried biomasses were then ground using a coffee grinder (Figure 1).



**Figure 1.** Ground biomass feedstock used for biochar production: (a) avocado seed, (b) avocado peel, (c) grapefruit peel, and (d) brown seaweed.

One group of biochars was produced through a tube furnace (Lindberg/Blue MTM Tube Furnace, ThermoFisher Scientific, Waltham, MA, USA) at 300 °C (Figure 2a). The pyrolysis temperature at 300 °C was chosen because low temperature biochars were found to contain active surface functional groups such as hydroxyl, phenolic, and carboxylic functional groups, and were favorable for removing heavy metals from aqueous solutions in previous studies [17,18]. The individual biomass was weighed and placed in a crucible and then placed inside the tube furnace. The tube furnace was purged with nitrogen (N<sub>2</sub>) gas at a rate of 5 L min<sup>-1</sup> for 1 h to remove oxygen from the system, and then the biomass was pyrolyzed for 1 h at 300 °C. The tube furnace was allowed to cool down to room temperature under a N<sub>2</sub> flowing condition to prevent any oxidation before collecting and weighing the biochar samples. Biochars produced through the tube furnace are henceforth abbreviated AST for avocado seed (the letter T indicating tube furnace), APT for avocado peel, GPT for grapefruit peel, and BST for brown seaweed.

A second group of biochars were produced through BioCharlie Log (BioCharlie, America Sequesters CO<sub>2</sub>, Clarence, NY, USA) (Figure 2b). The BioCharlie pyrolyzed the biomass by minimizing oxygen inflow and has been advertised as a DIY biochar maker. The individual biomass was weighed and placed inside the BioCharlie Log, which was pyrolyzed on a grill over a fire. The BioCharlie Log was removed from the fire and allowed to cool at room temperature before opening it to weigh the produced biochar. Biochars produced through BioCharlie are henceforth abbreviated ASB for avocado seed (the letter B indicating BioCharlie), APB for avocado peel, GPB for grapefruit peel, and BSB for the brown seaweed.



**Figure 2.** Two different biochar production methods employed in this study: (a) tube furnace that is commonly used for material synthesis; (b) BioCharlie Log, a Do-It-Yourself biochar maker (photo adapted from Amazon product page).

For all the produced biochars, the percent yield of the biochars (mass fraction of biochar over dried biomass) was determined by:

$$\text{Yield (\%)} = 100 \times (W_f/W_i) \quad (1)$$

where  $W_f$  represents the weight of the produced biochars and  $W_i$  represents the weight of the dried biomass.

## 2.2. Biochar Characterization

Biochar samples were diluted in a 1:10 solid-to-solution ratio with deionized (DI) water and shaken for 1 h to measure pH and electrical conductivity (EC) using a pH-conductivity multimeter (EC500, Extech Instruments, Waltham, MA, USA). Carbon (C) and nitrogen (N) contents in the biochars were determined using an elemental analyzer (ECS 4010 Nitrogen/Protein Analyzer, Costech Analytical Technologies, Inc., Valencia, CA, USA). Surface functional groups on the surface of the biochars were examined by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) via a Perkin Elmer Spectrum One FTIR (Perkin Elmer, Waltham, MA, USA). The FTIR spectra were collected from a 700–4000  $\text{cm}^{-1}$  range using an average of 20 scans at a resolution of 2  $\text{cm}^{-1}$ . Only tube-furnace-produced biochars were analyzed for the FTIR due to the incidental loss of BioCharlie-produced biochar samples.

Proximate analysis including the percent moisture, volatile matter (mobile matter), fixed matter, and ash content were determined in accordance with the method by Karunanithi et al. (2017) [19]. Note that the BST sample was excluded for proximate analysis due to the lack of sample remaining for this analysis. Briefly, a 1–2 g sample of the biochar in a crucible was heated for 2 h at 105 °C to determine the moisture content. Then, the biochar sample was heated in a top-covered crucible at 450 °C for 0.5 h to determine the volatile matter. Lastly, the remaining sample after the volatile matter was heated in an open-top crucible at 700 °C for 1 h to determine ash content. The mass of the sample before and after each of the heating periods was used to determine moisture content, volatile matter, and ash content. The fixed matter of biochar was calculated by subtracting the sum of moisture, ash, and volatile matter from 100.

$$\text{Fixed matter (\%)} = 100 - [\text{moisture (\%)} + \text{ash (\%)} + \text{volatile matter (\%)}] \quad (2)$$

## 2.3. Lead Adsorption

A single-point batch adsorption experiment was performed in duplicates to evaluate the biochar performance in removing  $\text{Pb}^{2+}$ . An activated carbon for aquaculture use (Aqua-Tech, Spectrum Brands, Inc., Blacksburg, VA, USA) was included to compare biochar performance against the commercial activated carbon product. For the adsorption tests, a 1:40 ratio of biochar mass to  $\text{Pb}^{2+}$  solution was employed based on Mireles et al.'s work (2019) that used the same solid-to-solution ratio [18]. While adsorbent dosage, solid-to-solution ratio, co-existed ions, and equilibration time are important experimental parameters in determining the adsorption efficiency of target contaminant [20], the scope of the current study was to cross-compare  $\text{Pb}^{2+}$  removal across 9 different adsorbents at a fixed, initial  $\text{Pb}^{2+}$  concentration (10  $\text{mg L}^{-1}$ ) during a relatively short equilibration time (1 h). Individual biochar material (0.8 g) was equilibrated with 32 mL of 10  $\text{mg L}^{-1}$   $\text{Pb}^{2+}$  solution in a centrifuge tube and then shaken for 1 h in an end-to-end shaker. After shaking, the biochar suspension was filtered through 0.2  $\mu\text{m}$  membrane filter paper, and the resulting solution was measured for its final  $\text{Pb}^{2+}$  concentration by HACH DR3900 spectrophotometer (HACH, Loveland, CO, USA) via the HACH method 10216 (TNT 850, HACH, Loveland, CO, USA). The  $\text{Pb}^{2+}$  removal by the biochar material (%) was calculated by:

$$\text{Pb}^{2+} \text{ removal (\%)} = 100 \times (1 - C_f/C_i) \quad (3)$$



where  $C_i$  is the initial concentration of  $Pb^{2+}$  in the solution ( $mg L^{-1}$ ) and  $C_f$  is the final concentration of  $Pb^{2+}$  in the solution after equilibration.

### 3. Results and Discussion

#### 3.1. Biochar Yield and Properties

The biochar yield differed by production method and biomass type (Table 1). The yield from the tube furnace was 42–63%, while the yield from the BioCharlie was 36–51%. Previous studies reported that the biochar yield from slow pyrolysis at 300 °C ranged between 42 and 61% [21–23]. Overall, the BioCharlie-produced biochar resulted in lower yields than those from the tube furnace when compared to individual biomass. This difference may be attributed to the BioCharlie Log's uncontrolled temperatures and potential exposure to oxygen. The BioCharlie Log was not completely sealed off from the surrounding environment and thus may have fueled combustion processes (oxidation) or uneven carbonization, allowing for more biomass to be turned into ash or volatile matter components. This is supported by the greater volatile matter content in BioCharlie produced biochars in land-based biomasses (ASB, APB, and GPB). By biomass type, brown seaweed biochars showed the highest yield in both production methods (BST = 63%, BSB = 51%), while avocado seed biochars showed the lowest yield (AST = 42%, ASB = 37%). In general, increasing the pyrolysis temperature tends to decrease biochar yield% [24]. Note that the pyrolysis temperature in the tube furnace was maintained at 300 °C for 1 h, while the pyrolysis temperature in the BioCharlie reached >300 °C within 20 min in a separate trial equipped with a grill thermometer. A previous biochar study using a top-lit updraft (TLUD) stove also found that the temperature reached over 500 °C within 20 min for pinewood and bamboo biochars until the end of the charring period [25].

Table 1. Selected properties of biochar materials.

Properties	Tube Furnace				BioCharlie Log			
	Avocado Seed (AST) <sup>2</sup>	Avocado Peel (APT)	Grapefruit Peel (GPT)	Brown Seaweed (BST)	Avocado Seed (ASB) <sup>2</sup>	Avocado Peel (APB)	Grapefruit Peel (GPB)	Brown Seaweed (BSB)
Yield (%)	42.50	56.18	47.57	63.15	36.65	48.65	41.72	51.12
pH	7.66	9.40	9.04	7.94	8.85	9.65	8.30	6.88
EC ( $\mu s/cm$ ) <sup>1</sup>	125	272	855	1534	4466	3330	2400	2057
Moisture (%)	1.67	3.46	1.02	N/A	3.67	5.45	1.15	0.86
Volatile Matter (%)	28.17	23.85	30.00	N/A	33.87	58.71	35.52	8.27
Ash Content (%)	34.38	28.81	23.10	N/A	17.57	6.25	17.33	68.06
Fixed Matter (%)	35.78	43.88	45.88	N/A	44.89	29.59	46.00	22.81
C (%)	60.33	54.21	53.50	27.87	N/A	N/A	N/A	N/A
N (%)	1.38	1.02	1.59	1.6	N/A	N/A	N/A	N/A

<sup>1</sup> Electrical Conductivity. <sup>2</sup> Letter T indicating tube furnace for avocado seed (AST); B indicating BioCharlie for avocado seed (ASB).

Biochar pH ranged from 6.88 to 9.65 depending on production method and biomass type (Table 1). BioCharlie-produced avocado seed and avocado peel biochars (pH 8.85 for ASB, pH 9.65 for APB) showed higher pH values than their tube-furnace-produced counterparts (pH 7.66 for AST, pH 9.40 for APT). However, a higher pH was observed with tube-furnace-produced grapefruit peel and brown seed biochars (pH 9.04 for GPT, pH 7.94 for BST) compared to those from BioCharlie (pH 8.30 for GPB, pH 6.88 for BSB), indicating an inconsistent effect of production methods on the biochar pH across biomass types. Typically, the pH of the biochars increases slightly with increasing pyrolysis temperature [26]. This general relationship was found for BioCharlie-produced avocado seed and avocado peel biochars (ASB and APB) assuming higher peak temperature in the biochar production by BioCharlie, but it was not the case for GPB and BSB. This discrepancy may be attributed to biomass-specific characteristics (e.g., lower C content and less carbonization in GPB and BSB) but the firm relationship between pH and production method was not clear in the given data. Other studies found that pH values for biochars pyrolyzed at 300 °C ranged

from 6.89–8.29, which were comparable to the AST, BST, BSB, and GPB in the current study [22,27–29].

EC for tube-furnace-produced biochars was 125–1534  $\mu\text{s cm}^{-1}$  and that for BioCharlie-produced biochars was 2057–4466  $\mu\text{s cm}^{-1}$  (Table 1). For the same biomass, BioCharlie-produced biochars showed consistently higher EC than tube-furnace-produced biochars. It was notable that ASB and APB (BioCharlie) showed 12–36 times greater EC than AST and APT (tube furnace), indicating that the pyrolysis temperature condition was likely to affect the difference. Biochars produced under higher pyrolysis temperatures generally have higher EC values, which is often attributed to higher concentrations of residues or ash [26,27]. Brown seaweed biochars showed relatively high EC in both production methods ( $>1500 \mu\text{s cm}^{-1}$ ). EC values in the current study were comparable to those (150–6000  $\mu\text{s cm}^{-1}$ ) from eight different biochars pyrolyzed at 300 °C [22].

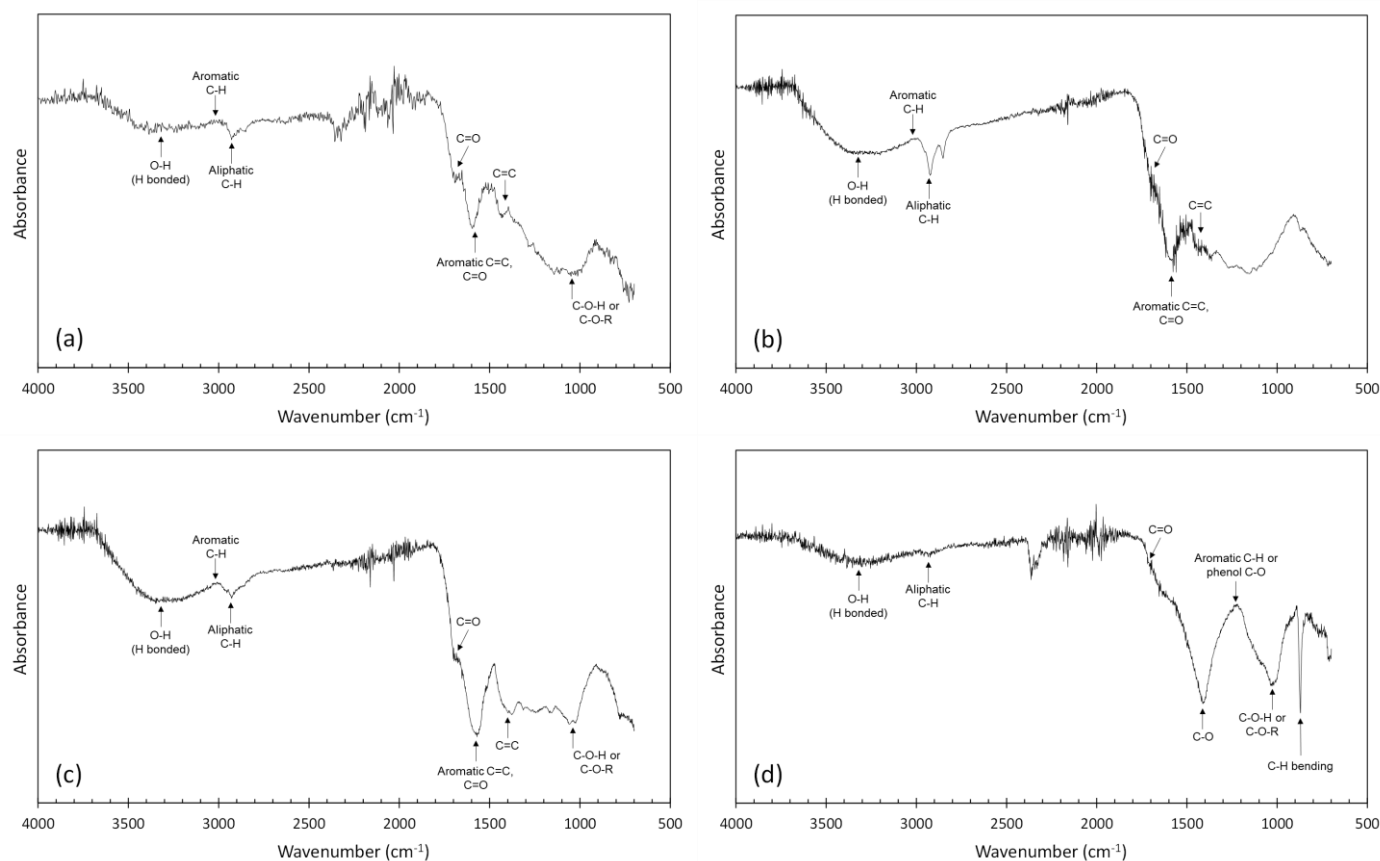
With the exclusion of the BST biochar, BioCharlie-produced biochars showed higher volatile matter but less ash content than tube-furnace-produced biochars (Table 1). It was notable that BST biochar had a 68% ash content, reflecting the nature of marine biomass with the lowest volatile matter (8%). The fixed matter of biochar as a proxy for recalcitrant matter ranged from 23 to 46%. Grapefruit peel biochars showed the highest fixed matter (46%) in both production methods. Previous studies reported that the volatile matter ranged between 37 and 66%, the fixed matter ranged between 20 and 66%, and ash content ranged between 2 and 20% for similar biochars produced at 300 °C [21–23,25,30].

The C and N contents were examined for the tube-furnace-produced biochars only (due to the sample loss for BioCharlie-produced biochar), where the carbon content was 28–60% by weight, with AST being the highest carbon percentage (60%) and BST being the lowest (28%). The higher C content in AST and APT indicates a higher stability of C (i.e., a higher proportion of aromatic C and condensed aromatic structures) [31]. However, the C contents of AST and APT were lower than other land-based biochars (66–69%) from hickory wood, bagasse, and bamboo biochars pyrolyzed at 300 °C [28]. The C content of brown seaweed biochar in this study (28%) was in a similar range to a previous study that used cultivated seaweed as a biochar feedstock material (29%), reflecting its low C content in the original feedstock [32]. The N content was less than 2% by weight, which was a typical range for non-manure-derived biochars [27].

### 3.2. FTIR Analysis

The FTIR results of AST, APT, GPT, and BST biochar samples are shown in Figure 3. Land-based biochars (AST, APT, and GPT) showed a broad peak (3500–3200  $\text{cm}^{-1}$ ) by O-H stretching in varying degree, indicating dehydration of cellulosic and ligneous components [18,33,34]. Marine-based biochar (BST) was relatively flat in that region. The land-based biochars showed absorption of the aromatic component (C-H stretching at 3050  $\text{cm}^{-1}$ ) and aliphatic component (C-H stretching at 2935 and 2885  $\text{cm}^{-1}$ ). The land-based biochars displayed the stretching of carbonyl bonds (C=O) at 1740–1700  $\text{cm}^{-1}$ , indicating the presence of carboxylic groups and possibly traces of aldehydes, ketones, and esters [33]. Aromatic C=C stretching (1600  $\text{cm}^{-1}$ ) was also observed in the land-based biochars. The band at 1030  $\text{cm}^{-1}$  was assigned to C-O-H or C-O-R representing oxygenated functional groups [33], and it was observed in all biochars except APT.

BST biochar showed unique features in the fingerprint region ( $<1400 \text{cm}^{-1}$  in wavelength). The band at 1047  $\text{cm}^{-1}$  was assigned to C-O stretching indicating the presence of carbonate and calcium atoms [35]. The broad peak at around 1210  $\text{cm}^{-1}$  was assigned to C-H bonds of aromatic rings or axial deformation vibrations of C-O bonds in phenols [36]. A sharp bend can be observed at 870  $\text{cm}^{-1}$ , indicating aromatic C-H deformation in the BST [37].



**Figure 3.** Fourier transform infrared (FTIR) spectra of tube-furnace-produced biochars: (a) avocado seed biochar, (b) avocado peel biochar, (c) grapefruit peel biochar, and (d) brown seaweed biochar.

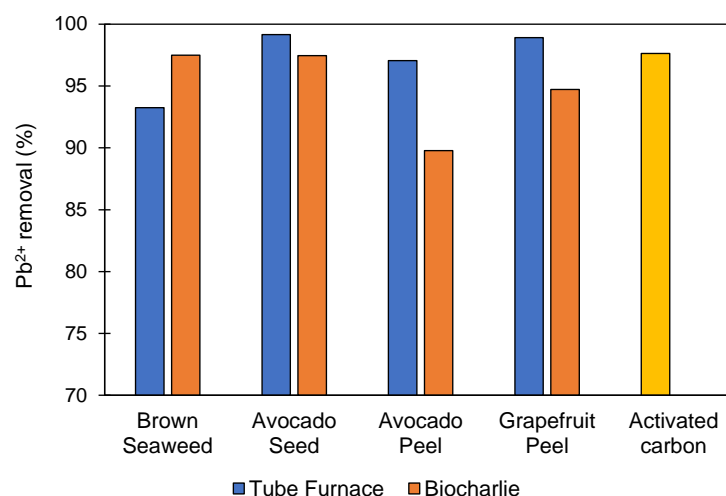
### 3.3. Lead Adsorption

All biochar materials exhibited  $\text{Pb}^{2+}$  removal greater than 90% (Figure 4). Note that %  $\text{Pb}^{2+}$  removal in the current study was used as a relative index in comparing eight different biochars, and it does not indicate the absolute amount of  $\text{Pb}^{2+}$  removal. Of the tube-furnace-produced biochars, avocado seed (AST) and grapefruit peel biochars (GPT) performed the best with 98–99%  $\text{Pb}^{2+}$  removal. The high  $\text{Pb}^{2+}$  removal from GPT agrees with a previous study that found 96%  $\text{Pb}^{2+}$  removal when low temperature (300 °C) organic peel biochar was equilibrated with 10 mg  $\text{Pb}^{2+} \text{L}^{-1}$ . Of the BioCharlie-produced biochars, brown seaweed and avocado seed biochars performed equally well (97%). It is notable that brown seaweed biochar from BioCharlie performed well as it is not a carbon-rich biomass.

The biochars from the tube furnace showed slightly greater  $\text{Pb}^{2+}$  removal than the BioCharlie counterparts except brown seaweed biochars. Avocado seed and grapefruit peel biochars from the tube furnace were particularly effective and their performance was comparable to commercial activated carbon (98%). From the FTIR data (Figure 3), land-based biochars (AST, APT, and GPT) showed oxygen-containing surface functional groups, while BST did not. This absence of oxygen-containing groups can explain the lower  $\text{Pb}^{2+}$  adsorption of BST (tube furnace). The enhanced performance of BSB (BioCharlie) may be attributed to its high ash content (68%, Table 1). The positive role of biochar mineral fraction has been postulated to enhance heavy metal adsorption onto the biochar in a previous study, and both C and mineral (ash) fractions of biochar likely contributed to the effective  $\text{Pb}^{2+}$  removal in the current study [38,39]. It is important to note that the current study does not reveal the adsorption mechanism of  $\text{Pb}^{2+}$  (e.g., physisorption or chemisorption) on the biochar materials. As the current study used relatively low-temperature biochars with no surface activation, chemisorption processes (e.g., precipitation, ion exchange, electrostatic



attraction, and surface complexation) were likely to be dominant for  $Pb^{2+}$  adsorption, but there was no mechanistic information to support this statement in the current study [20,39].



**Figure 4.** Percent removal of aqueous lead ( $Pb^{2+}$ ) affected by biomass types and biochar production methods.

#### 4. Conclusions

This study compared the selected properties of biochars produced under two different methods (lab tube furnace vs. BioCharlie) and evaluated their performance as a sorbent for  $Pb^{2+}$ . BioCharlie-produced biochars exhibited higher EC and volatile matter than tube-furnace-produced biochars. The batch adsorption tests at  $10 \text{ mg } Pb^{2+} \text{ L}^{-1}$  showed that overall tube-furnace-produced biochars performed better at  $Pb^{2+}$  removal than the BioCharlie-produced-biochars, except for the brown seaweed biochar. Four biochars (AST, GPT, ASB, and BSB) were top performers in removing  $Pb^{2+}$  across both production methods. Further investigation determining biochars' adsorption capacity in various ranges of  $Pb^{2+}$  concentrations (adsorption isotherm), pH and biochar dosage effects on  $Pb^{2+}$  adsorption, and their performance under the flowing condition is desired to confirm the biochars as an effective sorbent for  $Pb^{2+}$ .

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