

Article

A Biosorption-Pyrolysis Process for Removal of Pb from Aqueous Solution and Subsequent Immobilization of Pb in the Char

Yue Wang, Jinhong Lü *, Dongqing Feng, Sen Guo and Jianfa Li 

College of Chemistry and Chemical Engineering, Shaoxing University, Zhejiang 312000, China; wangyue835@163.com (Y.W.); fengdongqing@yeah.net (D.F.); gsen1041@gmail.com (S.G.); ljf@usx.edu.cn (J.L.)

* Correspondence: lvjinhong@usx.edu.cn; Tel.: +86-575-8834-1524

Received: 19 July 2020; Accepted: 18 August 2020; Published: 25 August 2020



Abstract: The application of biosorption in the removal of heavy metals from water faces a challenge of safe disposal of contaminated biomass. In this study, a potential solution for this problem was proposed by using a biosorption-pyrolysis process featured by pretreatment of biomass with phosphoric acid (PA). The PA pretreatment of biomass increased the removal efficiency of heavy metal Pb from water by sorption, and subsequent pyrolysis helped immobilize Pb in the residual char. The results indicate that most (>95%) of the Pb adsorbed by the PA-pretreated biomass was retained in the char, and that the lower pyrolysis temperature (350 °C) is more favorable for Pb immobilization. In this way, the bioavailable Pb in the char was hardly detected, while the Pb leachable in acidic solution decreased to <3% of total Pb in the char. However, higher pyrolysis temperature (450 °C) is unfavorable for Pb immobilization, as both the leachable and bioavailable Pb increased to >28%. The reason should be related to the formation of elemental Pb and unstable Pb compounds during pyrolysis at 450 °C, according to the X-ray diffraction study.

Keywords: heavy metal; biosorption; biochar; immobilization; phosphoric acid

1. Introduction

Water pollution by heavy metals, such as Pb, is one of the most serious environmental issues in the world. In comparison with other technologies for removing heavy metals from water, biosorption has the advantages of low operation cost, abundant biomass availability, and easy acceptance by the public [1–5]. Many kinds of plant-derived biomass wastes have been used for sorption of heavy metals, such as Pb, Cd, and Cu [6–8]. However, the practical applications of biosorption in the removal of heavy metals face two challenges. The first is that the sorption capacity of many indigenous biosorbents needs to be enhanced. Except for some biosorbents derived from algae and wheat bran, the maximum sorption of Pb by many lignocellulosic materials (seed husks, hulls and leaves, etc.) has shown to be <50 mg/g [6,9]. For seeking the solution of this problem, chemical modifications of biomass have been used for enhancing the sorption capacity [10–12]. The chemical modifying agents, including inorganic bases (e.g., NaOH), mineral acids (e.g., HNO₃), and organic compounds (e.g., urea) can enhance the ion exchange, and increase the functional groups and metal holding capacity of biosorbents. Among these modifying agents, phosphoric acid (PA) has shown to be a good candidate. PA has been used to modify olive pomace [13], corncob [14], rice husk [15], bagasse [16], wheat straw biochar [17] and so forth, so that their sorption to heavy metals was greatly enhanced. The second and more significant challenge is related to the safe disposal of the contaminated biomass after sorption of heavy metals. As the biomass is readily decomposed, the adsorbed heavy metals would be released or leached from the contaminated biomass if it was not properly disposed.

The proposed methods for disposal of heavy metal-contaminated biomass include incineration [18], composting [19], and pyrolysis [20], among others. Both incineration and composting have the problem of secondary pollution because the heavy metals will be dispersed into surroundings. In comparison, pyrolysis is operated in a closed system, and dispersion of heavy metals is controllable. Thus, pyrolysis has been used more frequently for post-treatment of heavy metal-contaminated biomass [21–26]. Pyrolysis is useful for valorization of contaminated biomass by transforming it into bio-fuel [27,28], and has also been used for preparing biochars that are good adsorbents to many pollutants [29–31]. The distribution of heavy metals in various fractions of pyrolysis product (e.g., oil or char) depends on the specific pyrolysis technique and heavy metal species [32–34]. For example, higher pyrolysis temperatures resulted in more emission of heavy metals into volatile fractions (e.g., oil) [27,35]. In contrast, slow pyrolysis at relatively low temperatures is more efficient for retention of heavy metals in the char [36,37]. Furthermore, at the same pyrolysis conditions, the heavy metals Cu, Zn, and Pb are more readily retained in the char than Cd [38]. As the char is more resistant to degradation than the biomass, pyrolysis is a feasible solution for disposal of heavy metal-contaminated biomass if most of the heavy metals are retained in the char and their stability in the char is guaranteed. In our previous studies, we investigated the stability of Pb and Cd in the char, and found that addition of phosphates in the contaminated biomass before pyrolysis enhanced the retention and stability of heavy metals [39–41].

In this work, a novel biosorption-pyrolysis process using PA-pretreated biomass was used to attempt to remove Pb from aqueous solution and subsequently immobilize Pb in the char. The specific objectives were to test two hypotheses: the first is that the PA pretreatment of biomass will enhance its sorption to Pb, and the second and more significant is that the subsequent pyrolysis of the contaminated biomass will increase the stability of Pb in the char. Different from our previous studies using phosphates as the additive for pyrolysis of the contaminated biomass [39], the biomass derived from an aquatic plant was firstly treated with PA, and then used for sorption of Pb in aqueous solution. The Pb-contaminated biomass was pyrolyzed, and the retention and stability of Pb in the char was evaluated. The comparison with the biosorption-pyrolysis process using un-pretreated biomass was also performed, and the immobilization mechanism of Pb in the char was investigated by using X-ray diffraction (XRD) and infrared spectra (IR).

2. Materials and Methods

2.1. Biomass and PA Pretreatment

The plant biomass was derived from the *Hydrocotyle verticillata* species, an aquatic plant that is widely distributed in tropical and subtropical zones. Its great adaptability and vitality makes it a good choice for phytoremediation of polluted or eutrophic water. The floating part (leaves and stems) of the *Hydrocotyle* plant was collected from a local river at Shaoxing, Zhejiang Province of China. The biomass was dried in an oven at 100 °C to a constant weight, and pulverized to a size of <0.15 mm. Elemental analysis using the EA3000 elemental analyser (Euro Vector, Italy) indicates that the pristine biomass (Mass) is composed of C 40.7%, O 29.7%, H 5.9%, N 1.5%, and S 0.6% by weight. The ash content of the biomass measured at 750 °C is 15.7% by weight. Phosphoric acid (H₃PO₄, PA) of analytical grade (Sinopharm Chemical Reagent Co. Ltd., China) was used for pre-treating the biomass. The biomass powder was soaked in 30 wt% PA solution for 24 h, then washed by water until the pH of the effluent reached 6.0. Two PA dosages with the mass ratio of PA/biomass = 0.5 or 1.0 were chosen according to the preliminary experiments. The dry solid residue obtained by PA pretreatment is labeled hereafter as PA_{0.5}Mass or PA_{1.0}Mass, respectively, according to the PA dosage (0.5 or 1.0) used for pretreatment.

2.2. Pb Removal and Sorption Experiments

Pb(NO₃)₂ of analytical grade (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was used to prepare Pb solutions for removal and sorption experiments. Of the biosorbent (un-pretreated biomass (Mass) or PA-pretreated biomass (PA_{0.5}Mass or PA_{1.0}Mass)), 50 mg was added to 20 mL of

aqueous Pb solution with initial concentrations (C_0 , mg/L) ranging from 5 to 50 mg/L. The slurry was adjusted to an initial pH of 5.0 with diluted HNO_3 solution, and placed in a thermostatic shaker bath at 25.0 ± 0.2 °C and shaken for 6 h when the sorption reached equilibrium according to our preliminary experiments. The supernatant solution was sampled and the Pb concentration (C_e) in solution was analyzed by the flame atomic absorption spectrometry (AAS) (AA-7000, Shimadzu, Japan). The removal efficiency (%) was calculated by Equation (1).

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

The isothermal sorption experiments were conducted in a way similar to the removal experiments, except that a higher C_0 range (50–300 mg/L) was used, so as to leave a certain equilibrium Pb concentration (C_e) in the solution. The quantity adsorbed (Q_e , mg/g) was calculated by Equation (2):

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where V is the volume of aqueous Pb solution (0.02 L) and m is the mass of biomass used for sorption experiments (0.05 g). The isothermal sorption data were further analyzed with the Langmuir and Freundlich sorption isotherm models. The Langmuir model has been expressed in Equation (3):

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (3)$$

where Q_m gives the maximum sorption capacity (mg/g) based on the monolayer adsorption model, and b (L/mg) is the Langmuir constant. The empirical Freundlich model has been expressed in Equation (4):

$$Q_e = k_F C_e^{1/n} \quad (4)$$

where k_F is the Freundlich sorption constant, and n gives the sorption intensity of biosorbents.

2.3. Pyrolysis of Pb-Contaminated Biomass

To obtain an adequate amount of contaminated biomass for subsequent pyrolysis, the biomass sample (1.5 g) was mixed with 500 mL of Pb solution with $C_0 = 100$ mg/L at initial pH = 5.0, and the mixture was stirred magnetically at room temperature for 6 h. Then the solid residue was filtered out and dried at 100 °C. The Pb-contaminated biomass powder was marked as Pb@Mass, Pb@PA_{0.5}Mass, or Pb@PA_{1.0}Mass according to the biomass sample used for biosorption. Pyrolysis of the Pb-contaminated biomass was carried out at 350 or 450 °C in a quartz tube furnace filled with N_2 gas. The relatively lower pyrolysis temperature was used because a higher temperature will lead to less retention of Pb in the char, according to a previous report [39]. The resulting Pb-concentrated chars are referred to hereafter as Pb@Char350, Pb@PA_{0.5}Char350, Pb@PA_{1.0}Char350, Pb@Char450, Pb@PA_{0.5}Char450, and Pb@PA_{1.0}Char450, respectively, depending on the temperature and feedstock biomass used for pyrolysis. The amount of Pb loaded in the biomass (Q_{mass} , mg/g) and then concentrated in the chars (Q_{char} , mg/g) was determined using a microwave digestion method [40], and the Pb concentration in the dilute digestion solution was determined using AAS. Retention efficiency of Pb (%) in the char after pyrolysis was calculated by Equation (5).

$$\text{Retention efficiency in the char(\%)} = \frac{Q_{\text{char}}}{Q_{\text{mass}}} \times \text{Yield of char(\%)} \quad (5)$$

2.4. Evaluation of the Stability of Pb in the Solid Samples

The bioavailable Pb, namely that available for utilization by living organisms, was evaluated with the DTPA extraction method using a buffer DTPA (diethylene triamine pentacetate acid) solution

according to the ISO standard (ISO 14870-2001). The leachable Pb in the samples was evaluated based on the amount of extractable Pb with the acid solution used in the Toxicity Characteristic Leaching Procedure (TCLP, EPA Test Method 1311). The details for the DTPA extraction and the TCLP test follow the procedures reported previously [40,42].

2.5. Sample Analysis

Surface composition of the biomass samples was determined with a JSM-6360LV scanning electron microscope (SEM) (JEOL, Tokyo, Japan) equipped with an X-act energy dispersive X-ray spectrometer (EDS) (Oxford, UK). Infrared spectra (IR) were recorded in the 4000–400 cm^{-1} region on a Nexus FT-IR spectrophotometer (Nicolet, Glendale, WI, USA) using a KBr pellet. The crystalline species in the biomass and chars were identified by X-ray diffraction (XRD) using D/MAX3A (Rigaku, Tokyo, Japan) equipment with $\text{CuK}\alpha$ radiation and a goniometer rate of $4^\circ/\text{min}$.

3. Results and Discussion

3.1. Influence of PA Pretreatment on the Removal of Pb by Biomass

The results in Figure 1a indicate that the removal efficiency of Pb by the *Hydrocotyle* biomass (Mass) is enhanced after PA treatment, despite that the sample ($\text{PA}_{1.0}\text{Mass}$) pretreated with more PA performed worse than the counterpart using less PA ($\text{PA}_{0.5}\text{Mass}$). At the dosage of biomass used in this study (2.5 g/L), Pb is almost completely removed by $\text{PA}_{0.5}\text{Mass}$ when the initial concentration (C_0) of Pb (II) ranged from 5–50 mg/L. In contrast, the removal efficiency of Pb by the un-pretreated biomass dropped to <85% with the C_0 increase to 50 mg/L. The enhanced removal efficiency corresponds well to the improved sorption of Pb by biomass after PA pretreatment (Figure 1b). The maximum sorption (Q_m) calculated with the Langmuir model (Equation (3)) increased to 78.7 mg/g for $\text{PA}_{0.5}\text{Mass}$ from 69.6 mg/g for the indigenous biomass (Mass) (Table 1). The Q_m values of the biosorbents in this study are close to those lignocellulosic materials with high sorption capacity to Pb reported in literature [6,7]. In addition, the n values calculated with the Freundlich model are much larger than 1 (Table 1), indicating that all the biosorbents favored the sorption of Pb [17]. The kinetic analysis indicates that the sorption of Pb by all three biosorbents (Mass, $\text{PA}_{0.5}\text{Mass}$, and $\text{PA}_{1.0}\text{Mass}$) fitted well to the pseudo-second-order model ($R^2 > 0.99$), and the sorption rate by the biomass was increased by PA-pretreatment according to the calculated rate constants (Table S1 in the Supplementary Materials). The quantity of Pb adsorbed by all three biosorbents (Mass, $\text{PA}_{0.5}\text{Mass}$ and $\text{PA}_{1.0}\text{Mass}$) increased with the initial pH and the initial Pb concentrations in solution (Figures S2 and S3 in the Supplementary Materials). Therefore, the *Hydrocotyle* biomass and its PA-pretreated derivatives are potential sorbents for removal of heavy metals from water.

The relatively high sorption of Pb by the *Hydrocotyle* biomass and its PA-pretreated derivatives is related to their surface properties. Figure 2 shows the SEM images of the un-pretreated biomass (Figure 2a) and the PA-pretreated biomass (Figure 2b). The rough surface of $\text{PA}_{0.5}\text{Mass}$ favors the sorption by providing more reactive sites. The specific surface area measured by the BET method is $7.24 \text{ m}^2/\text{g}$ for $\text{PA}_{0.5}\text{Mass}$, which is higher than that of the un-pretreated biomass ($1.42 \text{ m}^2/\text{g}$). Thus, PA-pretreatment increases the surface area of biomass and makes more reactive sites available for the sorption of Pb. The EDS analysis indicates that there are some inorganic minerals composed of Ca and K on the biomass surface, which are useful for sorption of Pb through cation exchange. For example, Pb can replace K in carbonate and sulfate to form precipitates, and this is a major pathway for sorption of Pb by those biomasses and biochars rich in inorganic minerals [43–45]. The sorption of Pb by biomass is also related to the surface functional groups. As can be seen in Figure 3, the bands at 1735, 1440, 1160–1060 cm^{-1} indicate oxygen-containing functional groups (C=O, C–OH, and C–O) on the biomass surface, which facilitate the sorption of Pb through surface complexation that has also been reported to contribute much to biosorption of heavy metals [46,47]. Some previous studies have shown that PA treatment can strengthen the acid functional groups of biomass [13,16,48], due to the

dissociation of these groups. In addition, PA pretreatment of the biomass introduces a new PO_4^{3-} group (at 1023 cm^{-1}) that can bind Pb through formation of phosphates, according to the IR spectra (Figure 3). However, pretreatment with a higher dosage of PA (1.0 g/g dry biomass) may result in over-acidification of biomass, which may inhibit the precipitation of Pb, so that the decreased removal efficiency and sorption capacity was observed on $\text{PA}_{1.0}\text{Mass}$ in comparison with $\text{PA}_{0.5}\text{Mass}$ (Figure 1). The over-acidification of biomass is confirmed by the change of pH before and after sorption of Pb. For example, at the same initial Pb concentration (e.g., $C_0 = 250\text{ mg/L}$) and same initial pH = 5.0, pH in the solution after sorption of Pb dropped to 4.8, 4.7, and 4.4, respectively for the sorption systems using Mass, $\text{PA}_{0.5}\text{Mass}$, and $\text{PA}_{1.0}\text{Mass}$. Namely, the pH in the $\text{PA}_{1.0}\text{Mass}$ system is much lower than the other two systems, and lower pH favors dissolution of Pb and impacts its removal by biomass.

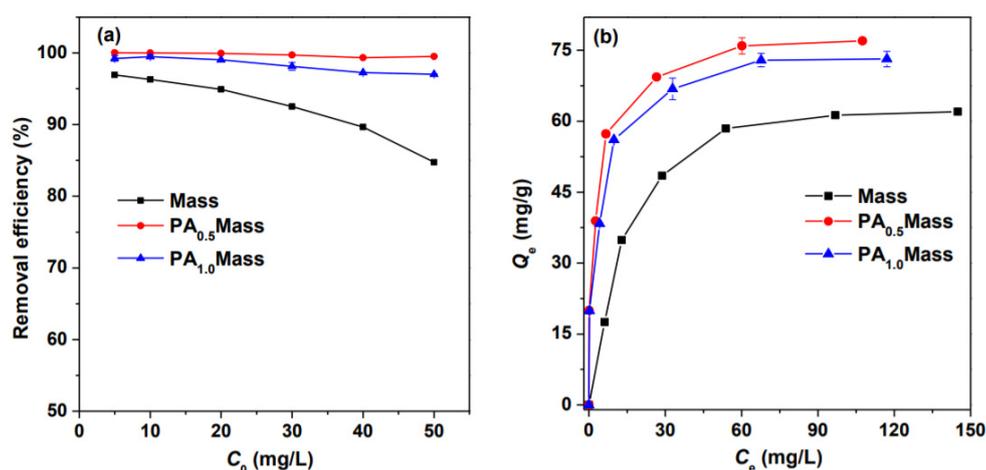


Figure 1. (a) Removal of Pb and (b) sorption isotherms (at $25\text{ }^\circ\text{C}$) of Pb by the *Hydrocotyle* biomass (Mass) and the biomass samples after PA pretreatment ($\text{PA}_{0.5}\text{Mass}$ and $\text{PA}_{1.0}\text{Mass}$).

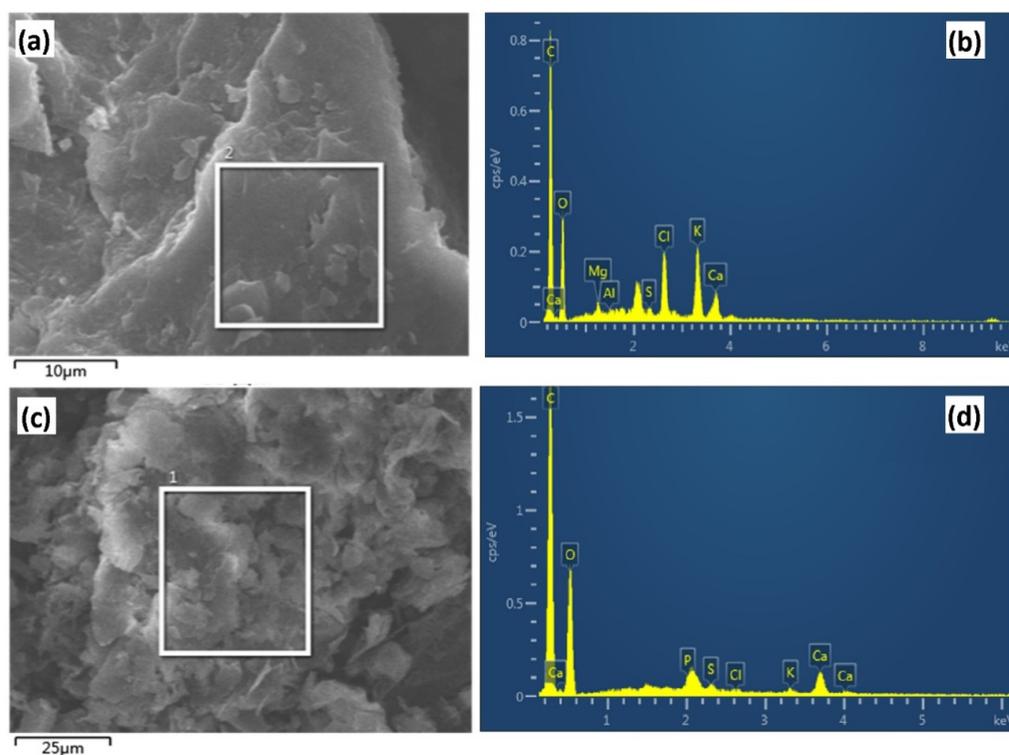
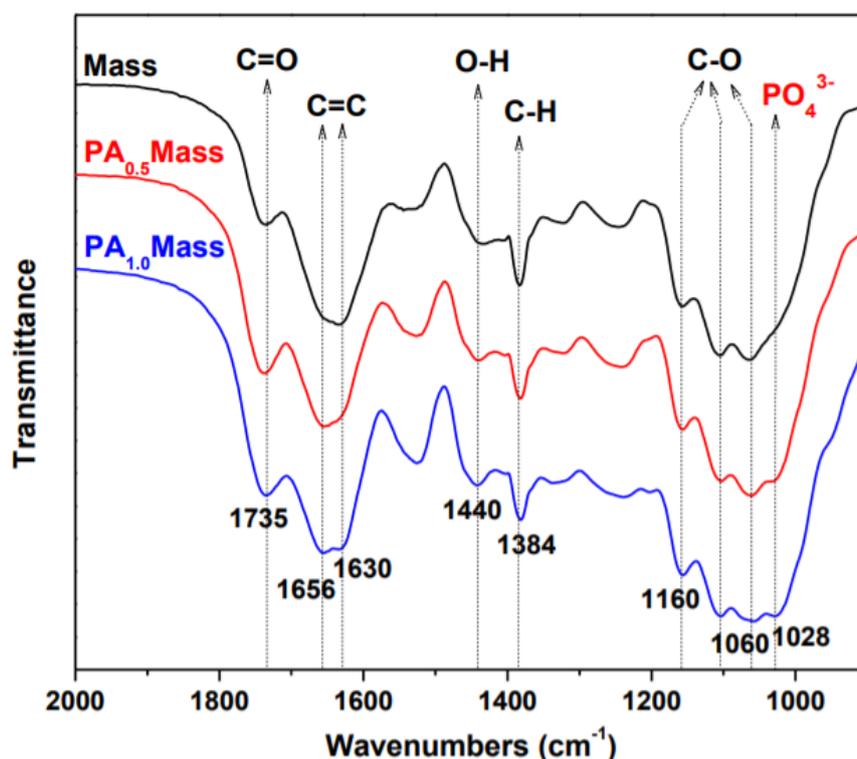


Figure 2. SEM image and EDS mapping results of (a,b) the *Hydrocotyle* biomass, and (c,d) PA-pretreated biomass ($\text{PA}_{0.5}\text{Mass}$).

Table 1. Fitting results of the sorption data with the Langmuir and the Freundlich models.

Models	Langmuir			Freundlich		
	Q_m (mg/g)	b (L/mg)	R^2	k_F	n	R^2
Mass	69.6	0.0788	0.992	20.6	4.21	0.855
PA _{0.5} Mass	78.7	0.373	0.996	36.7	5.72	0.853
PA _{1.0} Mass	76.9	0.242	0.993	32.8	5.39	0.839

**Figure 3.** IR spectra of the *Hydrocotyle* biomass and its PA-pretreated derivatives.

3.2. Influence of Pyrolysis on Pb Retention in the Char

Pyrolysis of the contaminated biomass at high temperatures will increase the risk of emission of Pb with volatile matters, and decrease the retention of Pb in the char, according to the previous studies [40–42]. Thus, two relatively low temperatures (350 and 450 °C) were used for pyrolysis of the Pb-contaminated biomass in this work, and the retention efficiency of Pb in various chars is shown in Figure 4. As can be seen, the Pb retentions in the two chars derived from the un-pretreated biomass were both less than 85%, and higher pyrolysis temperature (450 °C) led to lower retention efficiency due to the emission of Pb with volatile matters [27,35]. In comparison, the Pb retentions in the four chars (PA_{0.5}char350, PA_{1.0}char350, PA_{0.5}char450, and PA_{1.0}char450) derived from the PA-pretreated biomass were all >95%, and a higher dosage of PA used for pretreatment favors retention of more Pb in the char, indicating that PA pretreatment helped inhibit the emission of Pb during pyrolysis. PA is often used for activation of carbonization of biomass [49,50], and has shown to be effective for increasing the yield of char according to the previous reports [51,52], which is in consistency with that observed in this study (Figure 4a). The higher yield of char means less production of volatile matters, and introduction of PO₄³⁻ may also strengthen the binding of Pb to the solid char, which will be investigated in-depth in the following Section 3.4. Therefore, PA pretreatment of the biomass and subsequent pyrolysis enhanced the retention of Pb in the char, which is beneficial for reducing the hazard of secondary pollution due to pyrolysis of heavy metal-contaminated biomass.

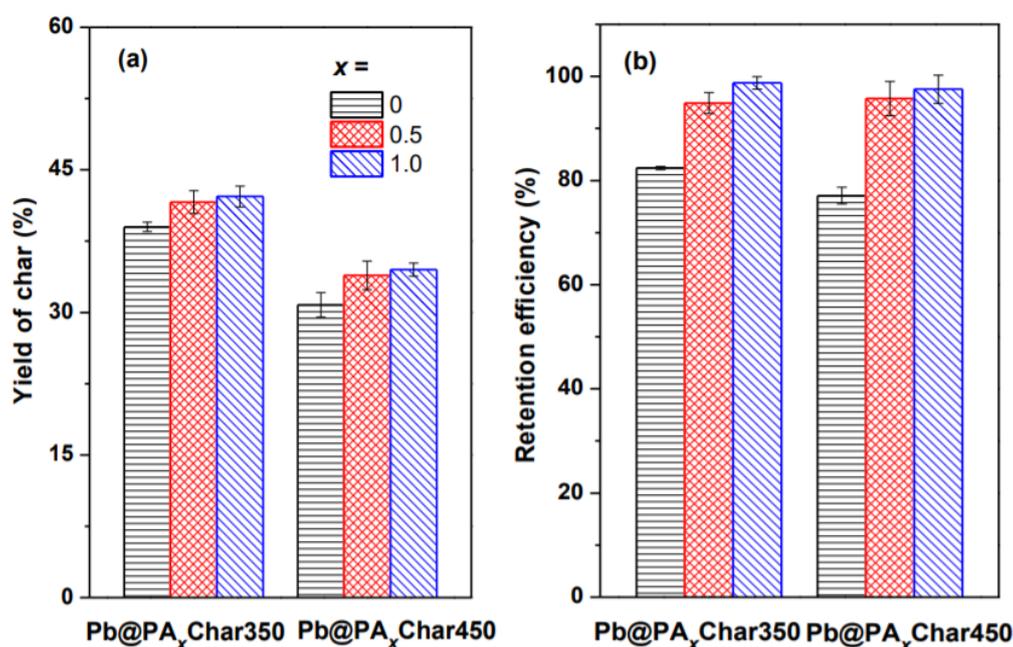


Figure 4. (a) Yield of chars, and (b) retention efficiency of Pb in the chars obtained by pyrolysis of Pb-contaminated biomass pretreated with various dosages of PA (0, 0.5 and 1.0 g/g mass).

3.3. Influence of Pyrolysis on Stability of Pb in the Char

The stability of Pb retained in the chars was first evaluated with the DTPA extraction method. Figure 5a shows the bioavailability of Pb in six chars, and the three Pb-contaminated biomass samples were also included for comparison. As can be seen, Pb adsorbed by biomass is readily bioavailable, whether the un-pretreated biomass or the PA-pretreated biomass was used as the sorbent. The DTPA-extractable Pb from the three biomass are all over 85%, so the sole PA pretreatment could not ensure the stability of Pb, although its sorption was enhanced as that shown in Figure 1b. Pyrolysis of the contaminated biomass sharply reduced the bioavailability of Pb in the char; in particular, the DTPA-extractable Pb is lower than 5% for the three chars obtained by pyrolysis at a lower temperature (Pb@Char350, Pb@PA_{0.5}Char350, and Pb@PA_{1.0}Char350). The DTPA-extractable Pb in the last two chars derived from the PA-pretreated biomass is close to zero. The results show that pyrolysis significantly enhanced the stability of Pb, and PA pretreatment can further reduce the bioavailability of Pb in the char. However, the DTPA-extractable Pb from the chars was lifted to >28% as the pyrolysis temperature increased to 450 °C, indicating that a higher pyrolysis temperature is unfavorable for immobilization of Pb. The similar results about the influence of pyrolysis temperature on stability of heavy metals in the char have been reported by Shi et al. [40]. The reason may be related to the different binding states between Pb and the chars obtained at different pyrolysis temperatures, which will be further discussed in the following Section 3.4.

The Pb immobilization by pyrolysis was further assessed with the TCLP test, and the results of leachable Pb in the biomass and chars are shown in Figure 5b. Interestingly, Pb adsorbed in the biomass was not readily leachable, with the highest leachable ratio of 5.34% observed on the biomass without PA pretreatment, although most of the Pb adsorbed in the biomass was bioavailable (Figure 5a). Such a difference should be related to the interactions between Pb and biomass, which are dominated by surface complexation and cation exchange, because there are plentiful oxygen-containing functional groups and exchangeable cations (e.g., K⁺) on the biomass surface according to the IR and EDS analysis (Figures 2 and 3). These interactions are readily broken down by a chelating agent, such as DTPA, but insensitive to acetic acid used in the TCLP test. Furthermore, pyrolysis increased the amount of leachable Pb in the Pb@Char350 and Pb@Char450 chars, and higher pyrolysis temperatures resulted in more leachable Pb (Figure 5b). The reasons should be mainly related to the change of solid's properties

during the pyrolysis. Pyrolysis makes biomass lose functional groups such as $-OH$ and $C-O$ that are essential for sorption of Pb through surface complexation. At the meantime, inorganic minerals in biomass will be transformed into alkaline matter, such as carbonates or (hydr)oxides [53]. Thus, the interactions between Pb and solid will be changed by formation of Pb oxide or carbonates that are readily dissolved in acid. Therefore, direct pyrolysis, especially at higher temperatures ($450\text{ }^{\circ}\text{C}$), is not favorable for immobilization of Pb in an acidic environment, because nearly half of Pb in the Pb@Char450 sample is leachable (Figure 5b). Despite this result, the encouraging fact is that the two chars (Pb@PA_{0.5}Char350 and Pb@PA_{1.0}Char350) obtained at $350\text{ }^{\circ}\text{C}$ and derived from the PA-pretreated biomass show good immobilization of Pb, with the ratio of leachable Pb accounting for less than 3%. In combination with the results shown in Figure 5a, we conclude that pyrolysis at $350\text{ }^{\circ}\text{C}$ can immobilize Pb adsorbed by the PA-pretreated biomass. The similar immobilization of heavy metals in the char using phosphates as the additive for pyrolysis has been observed in our previous studies [39–41]. What makes this work differently is that the biomass was firstly pretreated with PA, which enhanced its efficiency for removal of Pb before it was immobilized by pyrolysis. In general, such a combined biosorption-pyrolysis will be a promising strategy for removal of heavy metals from aqueous solution and subsequent safe disposal of the contaminated biosorbents.

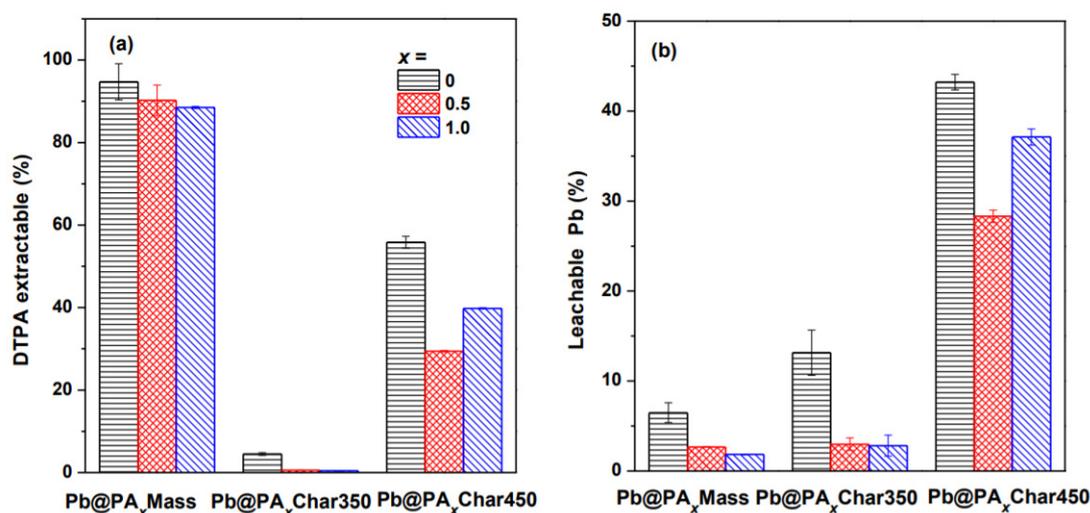


Figure 5. (a) DTPA-extractable Pb from, and (b) TCLP-leachable Pb from the biomass samples pretreated with various dosages of PA (0, 0.5, and 1.0 g/g mass) and the corresponding chars obtained at different pyrolysis temperatures (350 or $450\text{ }^{\circ}\text{C}$).

3.4. Investigations about the Immobilization Mechanisms

The X-ray diffraction (XRD) technique and IR spectra were used to examine the biomass and chars obtained by different treatments, so as to understand the mechanisms of Pb immobilization. The XRD patterns (Figure 6) indicate that there is no crystalline constituent other than cellulose in the Pb-contaminated biomass. However, the stable PbS crystal was found in all the chars, which should be one reason for immobilization of Pb. Furthermore, several strong peaks attributed to the lead phosphates (e.g., $\text{Ca}_8\text{Pb}_2(\text{PO}_4)_6(\text{OH})_2$ at $2\theta = 51.6^{\circ}$, and $\text{Pb}_9(\text{PO}_4)_6$ at $2\theta = 26.8^{\circ}$ and 33.2°) were observed in the Pb@PA_{1.0}Char350 sample. These lead phosphates contribute to the enhanced stability of Pb in this char, so the bioavailability and leachability of Pb were suppressed. However, as the pyrolysis temperature increased to $450\text{ }^{\circ}\text{C}$, the elemental Pb and unstable Pb compounds (PbO and $\text{Pb}_3(\text{CO}_3)(\text{OH})_2$) were formed according to the XRD patterns (Figure 6), which can explain the results obtained in the TCLP test, in which more leachable Pb was observed in the chars obtained at a high pyrolysis temperature ($450\text{ }^{\circ}\text{C}$) (Figure 5). Further, a new peak at 1156 cm^{-1} was found in the IR spectra (Figure 7) of two chars derived from the PA-pretreated biomass (Pb@PA_{1.0}Char350 and Pb@PA_{1.0}Char450), which could be assigned to $C-O$ stretching vibrations in $P-O-C$ (aromatic)

linkage [49]. Thus, Pb phosphates would be bound to the carbon matrix through this linkage, which made Pb be stably anchored on the char [52].

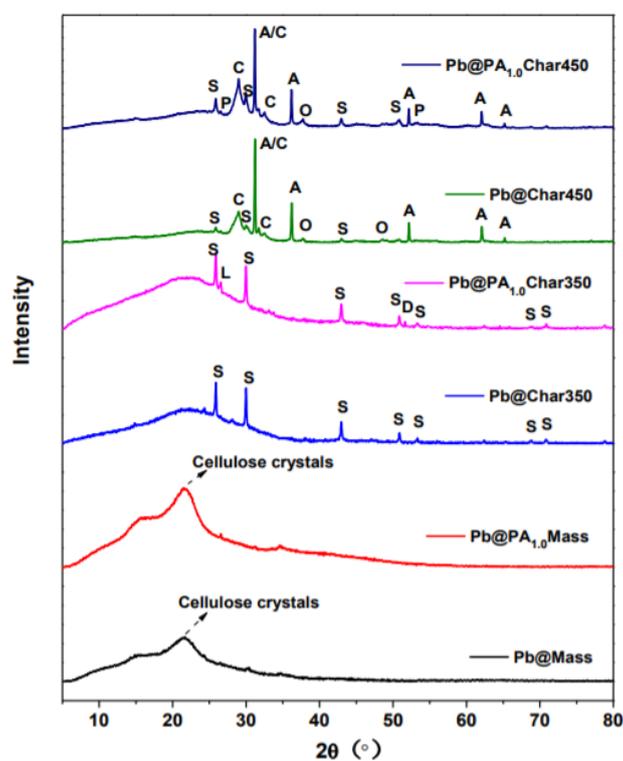


Figure 6. XRD patterns of two biomass and four char samples (A: Pb, C: $\text{Pb}_3(\text{CO}_3)(\text{OH})_2$, D: $\text{Ca}_8\text{Pb}_2(\text{PO}_4)_6(\text{OH})_2$, L: $\text{Pb}_9(\text{PO}_4)_6$, O: PbO, P: $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$, and S: PbS).

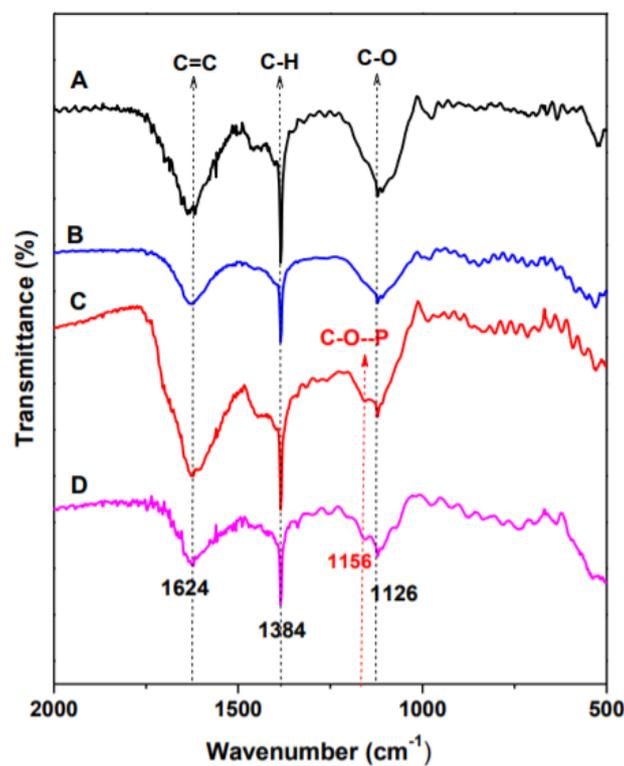


Figure 7. IR spectra of four char samples (A: Pb@Char350, B: Pb@Char450, C: Pb@PA_{1.0}Char350, and D: Pb@PA_{1.0}Char450).

4. Conclusions

The combined biosorption-pyrolysis process can be used for efficient removal of Pb from aqueous solution and then immobilization of Pb in the char, when the *Hydrocotyle* biomass is pretreated with PA. The PA-pretreatment increased the surface area and introduced more functional groups in the biomass, and enhanced the removal efficiency of Pb by biosorption. The subsequent pyrolysis of the Pb-contaminated biomass at relatively low temperatures (350 and 450 °C) retained most of the Pb in the char, and use of the PA-pretreatment further increased the retention efficiency to >95%. Furthermore, both the bioavailability and leaching potential of Pb in the char were significantly reduced by pyrolysis with the aid of PA-pretreatment, and pyrolysis at 350 °C is more favorable for the immobilization of Pb than that at 450 °C. The immobilization mechanisms are related to the formation of Pb phosphates and their linkage to the carbon matrix, according to the investigations with XRD and IR spectra. Despite the promising results obtained in this study, the long-time stability of Pb in the char deserves further investigation by considering more environmental factors, such as pH, temperature, humidity, and microbial effect, before the safe disposal of the char.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/12/9/2381/s1>, Figure S1: Change of the quantity of Pb adsorbed (Q_t) by the biosorbents with the contact time (t), Figure S2: Change of the quantity of Pb adsorbed after equilibrium (Q_e) with the initial pH, Figure S3: Change of the quantity of Pb adsorbed after equilibrium (Q_e) with the initial concentration (C_0), and Table S1: Parameters obtained by fitting the kinetic data (in Figure S1) with the pseudo-second order model.

Author Contributions: Conceptualization, J.L. (Jianfa Li); methodology, Y.W. and J.L. (Jinhong Lü); investigation, Y.W., D.F., S.G. and J.L. (Jinhong Lü); data curation, J.L. (Jinhong Lü); writing—original draft preparation, Y.W.; writing—review and editing, J.L. (Jinhong Lü); funding acquisition, J.L. (Jianfa Li); All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Zhejiang Province, China, grant number LY16B070003, and by the National Natural Science Foundation of China, grant number 41271475.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ungureanu, G.; Santos, S.; Boaventura, R.; Botelho, C. Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption. *J. Environ. Manag.* **2015**, *151*, 326–342. [[CrossRef](#)] [[PubMed](#)]
2. Ayangbenro, A.S.; Babalola, O.O. A new strategy for heavy metal polluted environments: A review of microbial biosorbents. *Int. J. Environ. Res. Public Health* **2017**, *14*, 94. [[CrossRef](#)] [[PubMed](#)]
3. Czikkely, M.; Neubauer, E.; Fekete, I.; Ymeri, P.; Fogarassy, C. Review of heavy metal adsorption processes by several organic matters from wastewaters. *Water* **2018**, *10*, 1377. [[CrossRef](#)]
4. Fernández-González, R.; Martín-Lara, M.Á.; Blázquez, G.; Pérez, A.; Calero, M. Recovering metals from aqueous solutions by biosorption onto hydrolyzed olive cake. *Water* **2019**, *11*, 2519. [[CrossRef](#)]
5. Filote, C.; Volf, I.; Santos, S.C.; Botelho, C.M. Bioadsorptive removal of Pb(II) from aqueous solution by the biorefinery waste of *Fucus spiralis*. *Sci. Total Environ.* **2019**, *648*, 1201–1209. [[CrossRef](#)]
6. Farooq, U.; Kozinski, J.A.; Khan, M.A.; Athar, M. Biosorption of heavy metal ions using wheat based biosorbents—A review of the recent literature. *Bioresour. Technol.* **2010**, *101*, 5043–5053. [[CrossRef](#)]
7. Abdolali, A.; Guo, W.S.; Ngo, H.H.; Chen, S.S.; Nguyen, N.C.; Tung, K.L. Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. *Bioresour. Technol.* **2014**, *160*, 57–66. [[CrossRef](#)]
8. Shaikh, R.B.; Saifullah, B.; Rehman, F.U. Greener method for the removal of toxic metal ions from the wastewater by application of agricultural waste as an adsorbent. *Water* **2018**, *10*, 1316. [[CrossRef](#)]
9. Salman, M.; Athar, M.; Farooq, U. Biosorption of heavy metals from aqueous solutions using indigenous and modified lignocellulosic materials. *Rev. Environ. Sci. BioTechnol.* **2015**, *14*, 211–228. [[CrossRef](#)]
10. Feng, N.; Guo, X.; Liang, S.; Zhu, Y.; Liu, J. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *J. Hazard. Mater.* **2011**, *185*, 49–54. [[CrossRef](#)]

11. Abdolali, A.; Ngo, H.H.; Guo, W.; Zhou, J.L.; Du, B.; Wei, Q.; Wang, X.C.; Nguyen, P.D. Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies. *Bioresour. Technol.* **2015**, *193*, 477–487. [[CrossRef](#)]
12. Pintor, A.M.; Vieira, B.R.; Boaventura, R.A.; Botelho, C.M. Removal of antimony from water by iron-coated cork granulates. *Sep. Purif. Technol.* **2020**, *233*, 116020. [[CrossRef](#)]
13. Martín-Lara, M.A.; Pagnanelli, F.; Mainelli, S.; Calero, M.; Toro, L. Chemical treatment of olive pomace: Effect on acid-basic properties and metal biosorption capacity. *J. Hazard. Mater.* **2008**, *156*, 448–457. [[CrossRef](#)] [[PubMed](#)]
14. Buasri, A.; Chaikut, N.; Tapang, K.; Jaroensin, S.; Panphrom, S. Equilibrium and kinetic studies of biosorption of Zn(II) ions from wastewater using modified corn cob. *APCBEE Procedia* **2012**, *3*, 60–64. [[CrossRef](#)]
15. Dada, A.O.; Olalekan, A.P.; Olatunya, A.M.; Dada, O.J.I.J.C. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk. *IOSR J. Appl. Chem.* **2012**, *3*, 38–45.
16. Xu, Y.L.; Song, S.Y.; Chen, J.D.; Chi, R.A.; Yu, J.X. Simultaneous recovery of Cu²⁺ and Pb²⁺ from metallurgical wastewater by two tandem columns fixed respectively with tetraethylenepentamine and phosphoric acid modified bagasse. *J. Taiwan Inst. Chem. Eng.* **2019**, *99*, 132–141. [[CrossRef](#)]
17. Naem, M.A.; Imran, M.; Amjad, M.; Abbas, G.; Tahir, M.; Murtaza, B.; Zakir, A.; Shahid, M.; Bulgariu, L.; Ahmad, I. Batch and column scale removal of cadmium from water using raw and acid activated wheat straw biochar. *Water* **2019**, *11*, 1438. [[CrossRef](#)]
18. Nzihou, A.; Stanmore, B. The fate of heavy metals during combustion and gasification of contaminated biomass—A brief review. *J. Hazard. Mater.* **2013**, *256*, 56–66. [[CrossRef](#)]
19. Cao, X.; Ma, L.; Shiralipour, A.; Harris, W. Biomass reduction and arsenic transformation during composting of arsenic-rich hyperaccumulator *Pteris vittata* L. *Environ. Sci. Pollut. Res.* **2010**, *17*, 586–594. [[CrossRef](#)]
20. Bădescu, I.S.; Bulgariu, D.; Ahmad, I.; Bulgariu, L. Valorisation possibilities of exhausted biosorbents loaded with metal ions—A review. *J. Environ. Manag.* **2018**, *224*, 288–297. [[CrossRef](#)]
21. Liu, W.J.; Zeng, F.X.; Jiang, H.; Zhang, X.S.; Yu, H.Q. Techno-economic evaluation of the integrated biosorption–pyrolysis technology for lead (Pb) recovery from aqueous solution. *Bioresour. Technol.* **2011**, *102*, 6260–6265. [[CrossRef](#)] [[PubMed](#)]
22. Gonsalvesh, L.; Yperman, J.; Carleer, R.; Mench, M.; Herzig, R.; Vangronsveld, J. Valorisation of heavy metals enriched tobacco biomass through slow pyrolysis and steam activation. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 1585–1595. [[CrossRef](#)]
23. Martín-Lara, M.Á.; Iáñez-Rodríguez, I.; Blázquez, G.; Quesada, L.; Pérez, A.; Calero, M. Kinetics of thermal decomposition of some biomasses in an inert environment: An investigation of the effect of lead loaded by biosorption. *Waste Manag.* **2017**, *70*, 101–113. [[CrossRef](#)]
24. Han, Z.; Guo, Z.; Zhang, Y.; Xiao, X.; Peng, C. Potential of pyrolysis for the recovery of heavy metals and bioenergy from contaminated *Broussonetia papyrifera* biomass. *BioResources* **2018**, *13*, 2932–2944. [[CrossRef](#)]
25. Gong, X.; Huang, D.; Liu, Y.; Zeng, G.; Wang, R.; Wei, J.; Huang, C.; Xu, P.; Wan, J.; Zhang, C. Pyrolysis and reutilization of plant residues after phytoremediation of heavy metals contaminated sediments: For heavy metals stabilization and dye adsorption. *Bioresour. Technol.* **2018**, *253*, 64–71. [[CrossRef](#)] [[PubMed](#)]
26. He, J.; Strezov, V.; Zhou, X.; Kumar, R.; Kan, T. Pyrolysis of heavy metal contaminated biomass pre-treated with ferric salts: Product characterisation and heavy metal department. *Bioresour. Technol.* **2020**, *313*, 123641. [[CrossRef](#)] [[PubMed](#)]
27. Stals, M.; Thijssen, E.; Vangronsveld, J.; Carleer, R.; Schreurs, S.; Yperman, J. Flash pyrolysis of heavy metal contaminated biomass from phytoremediation: Influence of temperature, entrained flow and wood/leaves blended pyrolysis on the behaviour of heavy metals. *J. Anal. Appl. Pyrol.* **2010**, *87*, 1–7. [[CrossRef](#)]
28. Dastyar, W.; Raheem, A.; He, J.; Zhao, M. Biofuel production using thermochemical conversion of heavy metal-contaminated biomass (HMCB) harvested from phytoextraction process. *Chem. Eng. J.* **2018**, *358*, 759–785. [[CrossRef](#)]
29. Chen, B.; Chen, Z.; Lv, S. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour. Technol.* **2011**, *102*, 716–723. [[CrossRef](#)]
30. Li, L.; Zou, D.; Xiao, Z.; Zeng, X.; Zhang, L.; Jiang, L.; Wang, A.; Ge, D.; Zhang, G.; Liu, F. Biochar as a sorbent for emerging contaminants enables improvements in waste management and sustainable resource use. *J. Clean. Prod.* **2019**, *210*, 1324–1342. [[CrossRef](#)]

31. Kim, H.; Ko, R.-A.; Lee, S.; Chon, K. Removal efficiencies of manganese and iron using pristine and phosphoric acid pre-treated biochars made from banana peels. *Water* **2020**, *12*, 1173. [[CrossRef](#)]
32. Stals, M.; Carleer, R.; Reggers, G.; Schreurs, S.; Yperman, J. Flash pyrolysis of heavy metal contaminated hardwoods from phytoremediation: Characterisation of biomass, pyrolysis oil and char/ash fraction. *J. Anal. Appl. Pyrol.* **2010**, *89*, 22–29. [[CrossRef](#)]
33. He, J.; Strezov, V.; Kan, T.; Weldekidan, H.; Asumadu-Sarkodie, S.; Kumar, R. Effect of temperature on heavy metal (loid) deportment during pyrolysis of *Avicennia marina* biomass obtained from phytoremediation. *Bioresour. Technol.* **2019**, *278*, 214–222. [[CrossRef](#)]
34. Li, S.; Zou, D.; Li, L.; Wu, L.; Liu, F.; Zeng, X.; Wang, H.; Zhu, Y.; Xiao, Z. Evolution of heavy metals during thermal treatment of manure: A critical review and outlooks. *Chemosphere* **2020**, *247*, 125962. [[CrossRef](#)] [[PubMed](#)]
35. Han, H.; Hu, S.; Syed-Hassan, S.S.A.; Xiao, Y.; Wang, Y.; Xu, J.; Xiang, J. Effects of reaction conditions on the emission behaviors of arsenic, cadmium and lead during sewage sludge pyrolysis. *Bioresour. Technol.* **2017**, *236*, 138–145. [[CrossRef](#)] [[PubMed](#)]
36. Al Chami, Z.; Amer, N.; Smets, K.; Yperman, J.; Carleer, R.; Dumontet, S.; Vangronsveld, J. Evaluation of flash and slow pyrolysis applied on heavy metal contaminated Sorghum bicolor shoots resulting from phytoremediation. *Biomass Bioenergy* **2014**, *63*, 268–279. [[CrossRef](#)]
37. He, J.; Strezov, V.; Kumar, R.; Weldekidan, H.; Jahan, S.; Dastjerdi, B.H.; Zhou, X.; Kan, T. Pyrolysis of heavy metal contaminated *Avicennia marina* biomass from phytoremediation: Characterisation of biomass and pyrolysis products. *J. Clean. Prod.* **2019**, *234*, 1235–1245. [[CrossRef](#)]
38. Lievens, C.; Yperman, J.; Vangronsveld, J.; Carleer, R. Study of the potential valorization of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part I. Influence of temperature, biomass species and solid heat carrier on the behaviour of heavy metals. *Fuel* **2008**, *87*, 1894–1905. [[CrossRef](#)]
39. Li, S.; Zhang, T.; Li, J.; Shi, L.; Zhu, X.; Lü, J.; Li, Y. Stabilization of Pb(II) accumulated in biomass through phosphate-pretreated pyrolysis at low temperatures. *J. Hazard. Mater.* **2017**, *324*, 464–471. [[CrossRef](#)]
40. Shi, L.; Wang, L.; Zhang, T.; Li, J.; Huang, X.; Cai, J.; Wang, Y. Reducing the bioavailability and leaching potential of lead in contaminated water hyacinth biomass by phosphate-assisted pyrolysis. *Bioresour. Technol.* **2017**, *241*, 908–914. [[CrossRef](#)]
41. Zhang, T.; Wang, Y.; Liu, X.; Lü, J.; Li, J. Functions of phosphorus additives on immobilizing heavy metal cadmium in the char through pyrolysis of contaminated biomass. *J. Anal. Appl. Pyrol.* **2019**, *144*, 104721. [[CrossRef](#)]
42. Zeng, X.; Xiao, Z.; Zhang, G.; Wang, A.; Li, Z.; Liu, Y.; Wang, H.; Zeng, Q.; Liang, Y.; Zou, D. Speciation and bioavailability of heavy metals in pyrolytic biochar of swine and goat manures. *J. Anal. Appl. Pyrol.* **2018**, *132*, 82–93. [[CrossRef](#)]
43. Lu, H.; Zhang, W.; Yang, Y.; Huang, X.; Wang, S.; Qiu, R. Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar. *Water Res.* **2012**, *46*, 854–862. [[CrossRef](#)] [[PubMed](#)]
44. Xu, X.; Cao, X.; Zhao, L. Comparison of rice husk-and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars. *Chemosphere* **2013**, *92*, 955–961. [[CrossRef](#)]
45. Zhang, T.; Zhu, X.; Shi, L.; Li, J.; Li, S.; Lü, J.; Li, Y. Efficient removal of lead from solution by celery-derived biochars rich in alkaline minerals. *Bioresour. Technol.* **2017**, *235*, 185–192. [[CrossRef](#)]
46. Cantrell, K.B.; Hunt, P.G.; Uchimiya, M.; Novak, J.M.; Ro, K.S. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* **2012**, *107*, 419–428. [[CrossRef](#)]
47. Blázquez, G.; Ronda, A.; Martín-Lara, M.A.; Pérez, A.; Calero, M. Comparative study of isotherm parameters of lead biosorption by two wastes of olive-oil production. *Water Sci. Technol.* **2015**, *72*, 711–720. [[CrossRef](#)]
48. Patra, C.; Shahnaz, T.; Subbiah, S.; Narayanasamy, S. Comparative assessment of raw and acid-activated preparations of novel Pongamiapinnata shells for adsorption of hexavalent chromium from simulated wastewater. *Environ. Sci. Pollut. R.* **2020**, *27*, 14836–14851. [[CrossRef](#)]
49. Puziy, A.M.; Poddubnaya, O.I.; Martinez-Alonso, A.; Suárez-García, F.; Tascón, J.M.D. Synthetic carbons activated with phosphoric acid: I. Surface chemistry and ion binding properties. *Carbon* **2002**, *40*, 1493–1505. [[CrossRef](#)]

50. Shu, Y.; Tang, C.; Hu, X.; Jiang, L.; Hu, X.; Zhao, Y. H₃PO₄-activated cattail carbon production and application in chromium removal from aqueous solution: Process optimization and removal mechanism. *Water* **2018**, *10*, 754. [[CrossRef](#)]
51. Zhao, L.; Cao, X.; Zheng, W.; Kan, Y. Phosphorus-assisted biomass thermal conversion: Reducing carbon loss and improving biochar stability. *PLoS ONE* **2014**, *9*, e115373. [[CrossRef](#)] [[PubMed](#)]
52. Zhao, L.; Cao, X.; Zheng, W.; Scott, J.W.; Sharma, B.K.; Chen, X. Copyrolysis of biomass with phosphate fertilizers to improve biochar carbon retention, slow nutrient release, and stabilize heavy metals in soil. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1630–1636. [[CrossRef](#)]
53. Yuan, J.H.; Xu, R.K.; Zhang, H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol.* **2011**, *102*, 3488–3497. [[CrossRef](#)] [[PubMed](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).