

## Article

# Removal Efficiencies of Manganese and Iron Using Pristine and Phosphoric Acid Pre-Treated Biochars Made from Banana Peels

Hyunjoon Kim <sup>1,†</sup>, Ryun-Ah Ko <sup>1,†</sup>, Sungyun Lee <sup>2,\*</sup> and Kangmin Chon <sup>1,\*</sup> 

<sup>1</sup> Department of Environmental Engineering, College of Engineering, Kangwon National University, Kangwondaehak-gil, 1, Chuncheon-si, Gangwon-do 24341, Korea; guswns863@naver.com (H.K.); rh6468@naver.com (R.-A.K.)

<sup>2</sup> Department of Civil Environmental Engineering, School of Disaster Prevention and Environmental Engineering, Kyungpook National University, 2559, Gyeongsang-daero, Sangju-si, Gyeongsangbuk-do 37224, Korea

\* Correspondence: sungyunlee@knu.ac.kr (S.L.); kmchon@kangwon.ac.kr (K.C.); Tel.: +82-54-530-1446 (S.L.); +82-33-250-6352 (K.C.)

† These authors contributed equally to this work and should be considered as co-first authors.

Received: 2 March 2020; Accepted: 15 April 2020; Published: 20 April 2020



**Abstract:** The purpose of this study was to compare the removal efficiencies of manganese (Mn) and iron (Fe) using pristine banana peel biochar (BPB) and phosphoric acid pre-treated biochars (PBPB) derived from banana peels. The removal efficiencies of Mn and Fe were investigated under different adsorbent dosages (0.4–2 g L<sup>−1</sup>), temperatures (15–45 °C), and ionic strengths (0–0.1 M), and were directly correlated to the differences in physicochemical properties of BPB and PBPB, to identify the removal mechanisms of heavy metals by adsorption processes. The removal of Mn by PBPB obeyed the Freundlich isotherm model while the removal of Mn and Fe by BPB followed the Langmuir isotherm model. However, the removal of Fe by PBPB followed both Freundlich and Langmuir isotherm models. The removal efficiencies of Mn and Fe by BPB and PBPB increased with increasing temperatures and decreased with increasing ionic strengths. PBPB more effectively removed Mn and Fe compared to BPB due to its higher content of oxygen-containing functional groups (O/C ratio of PBPB = 0.45; O/C ratio of BPB = 0.01), higher surface area (PBPB = 27.41 m<sup>2</sup> g<sup>−1</sup>; BPB = 11.32 m<sup>2</sup> g<sup>−1</sup>), and slightly greater pore volume (PBPB = 0.03 cm<sup>3</sup> g<sup>−1</sup>; BPB = 0.027 cm<sup>3</sup> g<sup>−1</sup>). These observations clearly show that phosphoric acid pre-treatment can improve the physicochemical properties of biochar prepared from banana peels, which is closely related to the removal of heavy metals by adsorption processes.

**Keywords:** biochar; manganese; iron; banana peel; adsorption; pre-treatment; phosphoric acid

## 1. Introduction

Water pollution by heavy metals released from various industrial activities such as metal plating and cleaning, mining, refineries, coatings, batteries, and automobile radiators, is an emerging environmental issue in water treatment engineering since heavy metals may pose adverse effects on human health and aquatic ecosystems due to their high toxicity, carcinogenicity, and non-biodegradability [1,2]. Among various heavy metals used in industrial activities, manganese (Mn) and iron (Fe) are known to be major inorganic pollutants affecting water quality [3]. Although Mn is essential to activate enzymes in the human system, high Mn concentrations can generate respiratory diseases, and continuous administration can cause neurotoxicity risk in humans [3,4]. In the case of Fe, it can cause undesirable aesthetic concerns (i.e., metallic tastes) and lead to the growth of ferrobacteria

related to odor problems [3]. The World Health Organization (WHO) have set a safe drinking water concentration of 0.05 and 0.3 mg L<sup>-1</sup> for Mn and Fe, respectively [5]. Based on these reasons, there is great need to develop an economic and efficient method for removing heavy metals from wastewater.

Several treatment techniques, including membrane filtration (e.g., reverse osmosis and nanofiltration), chemical precipitation, and oxidation/reduction, are available for the removal of heavy metals, including Mn and Fe, from industrial wastewater [6–10]. A commonly practiced Mn and Fe treatment approach is to chemically oxidize dissolved Mn(II) to particulate Mn(IV) or dissolved Fe(II) to particulate Fe(III), followed by physical separation of the insoluble precipitates from water using clarification and filtration processes [9,11]. However, most of those are not applicable for wastewater treatment due to their low removal efficiencies when the heavy metal concentrations are lower than 100 mg L<sup>-1</sup> [12]. In contrast, activated carbon may effectively remove heavy metals from wastewater even at low concentrations [13]. Despite this advantage, the use of the activated carbon adsorption process for the removal of heavy metals has been limited as it requires high maintenance and operational costs [14]. In recent years, biochars, which can be produced at low cost, have attracted great attention as an alternative to activated carbon [15–18]. Biochar is an ecofriendly adsorbent produced using by-products of the agricultural industries and wastes from various crops, and is effective for removing heavy metals from wastewater [18–21].

Over the wide range of crops, bananas cultivated in more than 130 countries are regarded to be one of the most widely grown tropical fruits in the world [22]. The world production of bananas was approximately 117.9 million tons in 2015 [23], and about 7 million tons of banana peel wastes are produced annually (the proportion of banana peels in total dry weight = 25–30%) [24]. Currently, most banana peel wastes are used as natural fertilizers on soils in agricultural fields, and some of them are fed to animals [25]. Banana peels contain a large amount of pectins which are complex polysaccharides consisting of galacturonic acids, arabinoses, galactoses, and rhamnoses. Among them, galacturonic acids have a strong binding capacity to the metal cations in the aqueous phases due to the presence of carboxyl groups [22,26]. Therefore, biochar derived from banana peels is considered to be a promising option for removing heavy metals effectively from wastewater.

Raw biochars have showed feasibility for adsorbent material to remove contaminants including heavy metals and organic pollutants [17,18,21,27,28]. However, the sorption capacities can be enhanced by treatment with acids, nanocomposites, and activation agents [17,29,30]. For example, Chu et al. showed that phosphoric acid treatment improved the porosity of biochars from pine sawdust, cellulose, and lignin [31]. The modified biochars provided better sorption of carbamazepine and bisphenol A. The sorption for 15 different pesticides by biochars from rice straw and corn stover was also increased by phosphoric acid treatment due to increased functional groups and aromatization of the biochars [32]. Considering the effects of phosphoric acid treatment on porosity and the modification of functional groups of biochars, the treatment method can be applied to improve removal efficiencies of heavy metals by biochars from other sources. In addition, phosphoric acid has advantages in low pyrolysis temperature, low cost, and low corrosivity to the equipment [31]. Nevertheless, to the best of our knowledge, phosphoric acid pre-treatment has not been used to enhance the physicochemical properties of biochars from banana peels in association with the adsorption of heavy metals.

The main purpose of this study was to evaluate the effects of phosphate pre-treatment on the adsorption of heavy metals (i.e., Mn and Fe) using biochars prepared from banana peels. First, the physicochemical characteristics of pristine and phosphoric acid pre-treated biochars derived from banana peels were rigorously characterized. Then, various adsorption experiments were conducted to investigate optimum adsorbent dosages, adsorption kinetics, adsorption isotherms, and effects of temperature and ionic strengths on adsorption. The improved adsorption efficiencies by phosphoric acid treatment were analyzed based on the physicochemical characteristics of the biochar, and the adsorption mechanisms of Mn and Fe were discussed. This study improves our understanding of the effect of phosphoric acid treatment on modification of the surface structure and functional groups of biochars for heavy metal removal.

## 2. Materials and Methods

### 2.1. Materials

Banana peel wastes were collected in Chuncheon-si (Gangwon-do, Korea). Mn ( $\text{KMnO}_4$ , oxidation state = +7, concentration =  $1000 \text{ mg L}^{-1}$ ) and Fe ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ , oxidation state = +2, concentration =  $1000 \text{ mg L}^{-1}$ ) AA standard solutions and phosphoric acid ( $\text{H}_3\text{PO}_4$ ), were purchased from Daejung Chemicals & Metals (Siheung-Si, Gyeonggi-Do, Korea). Mn(VII) and Fe(II) solutions for adsorption experiments were prepared by diluting the concentrated standard solutions in deionized water.

### 2.2. Production of Biochar

The banana peel wastes were dried in an oven at  $105^\circ\text{C}$  for 24 h, ground using a mortar, washed several times with deionized (DI) water to remove impurities on their surfaces, and then dried in the oven at  $105^\circ\text{C}$  for 12 h. From the resulting banana peel powder, 50 g was immersed in a 500 mL phosphoric acid solution (20 wt. %) for 2 h to activate adsorption sites, and dried at  $105^\circ\text{C}$  for 12 h. Pristine and phosphoric acid pre-treated banana peel wastes (weight of each banana peel waste = 20 g) were pyrolyzed in the tubular furnace (PyroTech, Namyangju, Gyeonggi-do, Korea) at  $600^\circ\text{C}$  (heating rates =  $0.2^\circ\text{C min}^{-1}$ ) under  $\text{N}_2$  conditions ( $\text{N}_2$  flow rate =  $0.25 \text{ L min}^{-1}$ ) for 2 h and then cooled to room temperature. Biochars prepared from banana peel wastes were washed several times with DI water, filtered with a  $0.7 \mu\text{m}$  GF/F filter (Whatman, Maidstone, UK), and then dried in the oven at  $105^\circ\text{C}$  for 12 h. Biochars produced from pristine and phosphoric acid pre-treated banana peel wastes are defined as BPB (banana peel biochar without pre-treatment) and PBPB (pre-treated banana peel biochar), respectively.

### 2.3. Characterization of Biochar

Element composition of BPB and PBPB was analyzed using an elemental analyzer (EuroEA3000 CHNS-O, Euro Vector S.p.A, Via Tortona, Milan, Italy). The ash content was calculated by subtracting the quantities of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) from the total mass fraction of the adsorbents. The specific surface area of biochar was determined with a Bronauer–Emmett–Teller (BET) analyzer (BELSORP-mini II, MicrotracBEL, Japan). The functional group composition of the adsorbents was identified using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (Frontier Optica, Perkin Elmer, Waltham, MA, USA).

### 2.4. Adsorption Experiments

#### 2.4.1. Optimal Adsorbent Dosages

Prior to the adsorption kinetics experiments, the optimum dosage of BPB and PBPB for each heavy metal was determined. The adsorbents (dosage =  $0.02\text{--}4 \text{ g L}^{-1}$ ) were added to 25 mL of heavy metal solution (each metal concentration =  $10 \text{ mg L}^{-1}$ , pH = 7.0) and then mixed at 150 rpm and  $25^\circ\text{C}$  using a shaking incubator (VS-8480, Vision Scientific, Daejeon-Si, Korea) for 3 h. All the adsorption tests were repeated three times to minimize experimental errors.

#### 2.4.2. Adsorption Kinetics Analysis

For adsorption kinetics experiments, the optimum dosage of each adsorbent was added to 25 mL of sample solutions (each heavy metal concentration =  $10 \text{ mg L}^{-1}$ ) and mixed at 150 rpm using the shaking incubator for 0–24 h (temperature =  $25^\circ\text{C}$ , pH = 7.0). The concentrations of Mn and Fe at the initial and equilibrium states were measured using colorimetric methods with a UV-Vis spectrophotometer (UV-1280, Shimadzu, Kyoto, Japan) at UV absorbances of 525 and 510 nm, respectively. All the

adsorption tests were repeated three times to minimize experimental errors. The amount of adsorbed heavy metals at time  $t$  ( $q_t$  (mg g<sup>-1</sup>)) was calculated as follows [14]:

$$q_t = \frac{(C_0 - C)V}{m} \quad (1)$$

where  $C_0$  and  $C$  are the initial and final concentrations (mg L<sup>-1</sup>) of heavy metals in the solutions,  $V$  is the volume (L) of the solution, and  $m$  is the mass (g) of the used adsorbents.

The removal efficiencies of heavy metals were calculated using Equation (2) [14]:

$$\text{Removal efficiency of heavy metal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $C_e$  represents the concentrations of each heavy metal (mg L<sup>-1</sup>) at equilibrium of the solutions.

The adsorption kinetics of Mn and Fe were investigated using Equations (3) and (4):

$$\text{Pseudo-first-order model :} \quad \log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (3)$$

$$\text{Pseudo-second-order model :} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_1$  (min<sup>-1</sup>) is the constant of the pseudo-first-order equation, and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the constant of the pseudo-second-order equation.  $q_e$  (mg g<sup>-1</sup>) is the adsorption capacity at equilibrium.

#### 2.4.3. Adsorption Isotherm Analysis

The adsorption isotherms of Mn and Fe by BPB and PBPB were identified with 6 different initial concentrations (each heavy metal concentration = 1–10 mg L<sup>-1</sup>) under controlled conditions (agitation time = 24 h, mixing speed = 150 rpm, temperature = 25 °C, pH = 7.0). The adsorption results were analyzed using the Langmuir and Freundlich isotherm models.

$$\text{Langmuir isotherm :} \quad q_e = \frac{q_{\max} K_L c_e}{1 + K_L c_e} \quad (5)$$

where  $q_e$  (mg g<sup>-1</sup>) is the maximum monolayer adsorption capacity of heavy metals, and  $K_L$  (L mg<sup>-1</sup>) is the equilibrium constant of the Langmuir equation.

$$\text{Freundlich isotherm :} \quad q_e = K_F c_e^{1/n} \quad (6)$$

where  $K_F$  (mg<sup>1-(1/n)</sup> L<sup>1/n</sup> g<sup>-1</sup>) is the Freundlich adsorption constant, and  $n$  is the dimensionless empirical coefficient related to adsorption strength, which depends on the surface heterogeneity.

#### 2.4.4. Effects of Temperatures and Ionic Strengths

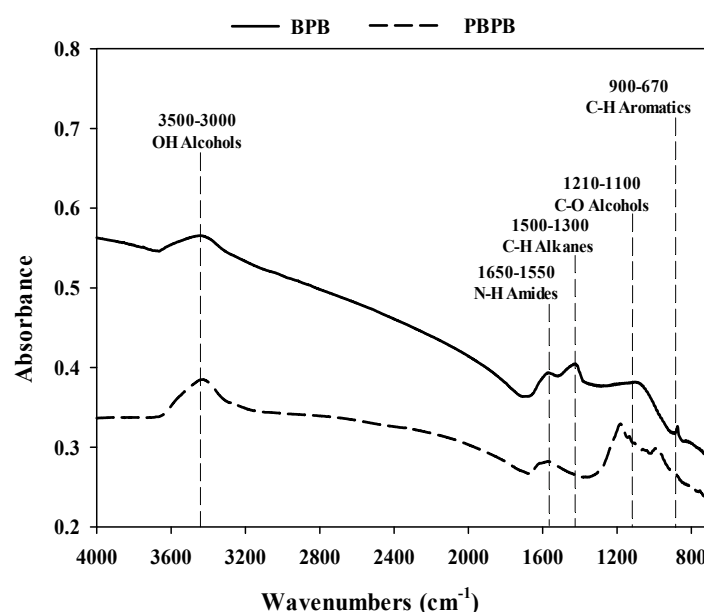
The effects of temperature and ionic strength on the adsorption of heavy metals by BPB and PBPB were investigated at various temperatures (15–45 °C) and ionic strength conditions (0.005–0.1 M) (each heavy metal concentration = 10 mg L<sup>-1</sup>, agitation time = 6 h, mixing speed = 150 rpm, temperature = 25 °C, pH = 7.0). The removal efficiencies of Mn and Fe using BPB and PBPB were calculated using Equations (2) and (3) as described in the previous section.

### 3. Results and Discussion

#### 3.1. Physical Properties of Biochar

Figure 1 illustrates the functional group composition of BPB and PBPB, measured using ATR-FTIR. The functional group composition of BPB and PBPB was similar, but the intensities of the IR peaks of

the functional group composition affecting the adsorption of heavy metals were different. The IR peaks related to O-H stretching and C-O stretching of alcohols appeared at 3500–3000  $\text{cm}^{-1}$  (BPB = 3443  $\text{cm}^{-1}$ , PBPB = 3431  $\text{cm}^{-1}$ ) and 1210–1100  $\text{cm}^{-1}$  (BPB = 1103  $\text{cm}^{-1}$ , PBPB = 1180  $\text{cm}^{-1}$ ) due to the presence of alcohol functional groups ( $-\text{CH}_2\text{OH}-$ ) derived from the cellulose component of the banana peels [33]. The IR peaks related to N-H stretching of amides were found in the range of 1650–1550  $\text{cm}^{-1}$  (BPB = 1565  $\text{cm}^{-1}$ , PBPB = 1575  $\text{cm}^{-1}$ ). Furthermore, C-H stretching of alkanes and C-H stretching of aromatics exhibited relatively strong IR peaks in the range of 1500–1300  $\text{cm}^{-1}$  and 900–670  $\text{cm}^{-1}$ , respectively [34]. The IR peak derived from C-O stretching of alcohols exhibited a relatively high IR intensity in PBPB compared to BPB in the range of 1210–1100  $\text{cm}^{-1}$  because the phosphoric acid pre-treatment promoted the formation of oxygen-containing functional groups closely associated with the adsorption of heavy metals [34,35].



**Figure 1.** Attenuated total reflectance (ATR)-FTIR spectra of banana peel biochar without pre-treatment (BPB) and pre-treated banana peel biochar (PBPB).

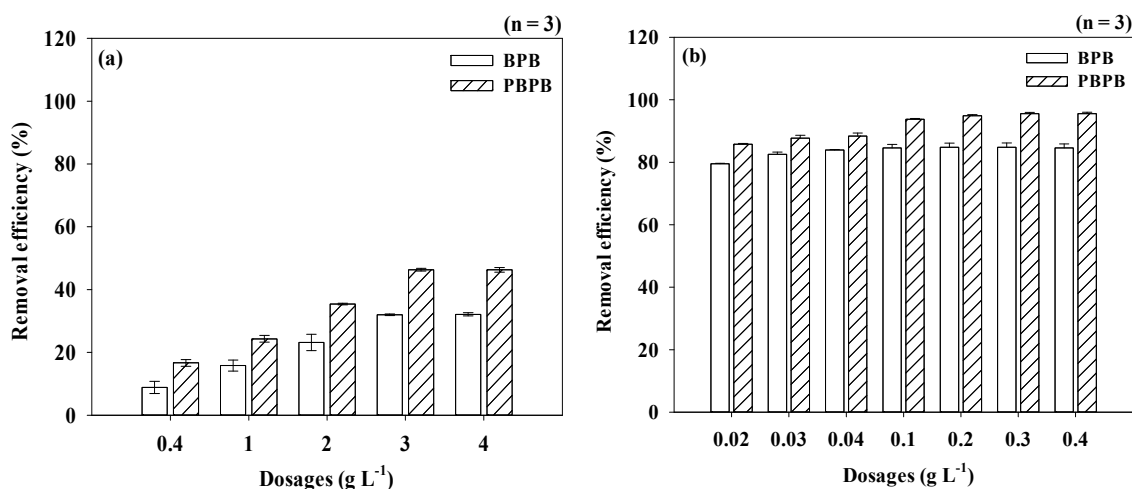
Table 1 shows the elemental composition and surface properties of BPB and PBPB. Although the hydrogen, nitrogen, and ash content of BPB and PBPB were similar (H content of BPB = 1.6%, H content of PBPB = 1.9%; N content of BPB = 2.9%, N content of PBPB = 2.2%; ash content of BPB = 19.0%, ash content of PBPB = 16.4%), PBPB had lower carbon content (54.7%) and higher oxygen content (24.8%) compared to BPB (C content = 75.4%, O content = 1.1%). Therefore, the H/C, O/C, and N/C ratios of PBPB were much higher than those of BPB. These observations indicate that increases in hydroxyl and carboxyl functional groups in PBPB after phosphoric acid pre-treatment may enhance electrostatic attractions between heavy metals and the adsorbent surfaces intimately related to the adsorption of heavy metals [36]. Furthermore, the specific surface area and total pore volume of PBPB (specific surface area = 27.41  $\text{m}^2 \text{g}^{-1}$ ; total pore volume = 0.032  $\text{cm}^3 \text{g}^{-1}$ ) were considerably greater compared to BPB (BPB = 11.32  $\text{m}^2 \text{g}^{-1}$ ; total pore volume = 0.027  $\text{cm}^3 \text{g}^{-1}$ ). These results suggest that heavy metals can be adsorbed more readily by PBPB than BPB due to its abundance of adsorption sites [12].

**Table 1.** Physicochemical properties of BPB and PBPB.

|      | Elements Composition (%) |     |      |     |      | Atomic Ratio |       |       | $S_{\text{BET}}$<br>( $\text{m}^2 \text{g}^{-1}$ ) | Pore Volume<br>( $\text{cm}^3 \text{g}^{-1}$ ) |
|------|--------------------------|-----|------|-----|------|--------------|-------|-------|----------------------------------------------------|------------------------------------------------|
|      | C                        | H   | O    | N   | Ash  | H/C          | O/C   | N/C   |                                                    |                                                |
| BPB  | 75.4                     | 1.6 | 1.1  | 2.9 | 19.0 | 0.022        | 0.014 | 0.038 | 11.32                                              | 0.027                                          |
| PBPB | 54.7                     | 1.9 | 24.8 | 2.2 | 16.4 | 0.035        | 0.453 | 0.039 | 27.41                                              | 0.032                                          |

### 3.2. Effects of Adsorbent Dosages

Figure 2 presents the change in the removal efficiencies of Mn and Fe as a function of adsorbent dosages. The removal efficiencies of Mn and Fe using BPB and PBPB were increased with increasing adsorbent dosages because of the increased availability of adsorption sites on the adsorbent surfaces [14]. The lower removal efficiencies of Mn by BPB and PBPB compared to those of Fe might be attributed to differences in the electronegativity and ion radius of Mn and Fe. Since Fe has a higher electronegativity than Mn (Fe = 1.8, Mn = 1.5) and a small ion radius, it can more easily diffused into the pores of PBPB and BPB [37,38]. In the equilibrium state, PBPB exhibited higher removal efficiencies of Mn and Fe than BPB (removal efficiency of Mn by BPB = 32%, removal efficiency of Mn by PBPB = 46%, removal efficiency of Fe by PBPB = 96%, removal efficiency of Fe by BPB = 85%). These results mean that phosphate pre-treatment promoted the formation of functional groups on the biochar surfaces capable of adsorbing heavy metals [27,39]. The removal efficiencies of Mn by BPB and PBPB reached the steady state at an adsorbent dosage of  $3 \text{ g L}^{-1}$  while the steady states of Fe adsorption occurred at  $0.1 \text{ g L}^{-1}$  for BPB and  $0.3 \text{ g L}^{-1}$  for PBPB, respectively. Hence, the PBPB and BPB dosages obtained at their steady states for Mn and Fe were applied for further adsorption experiments.

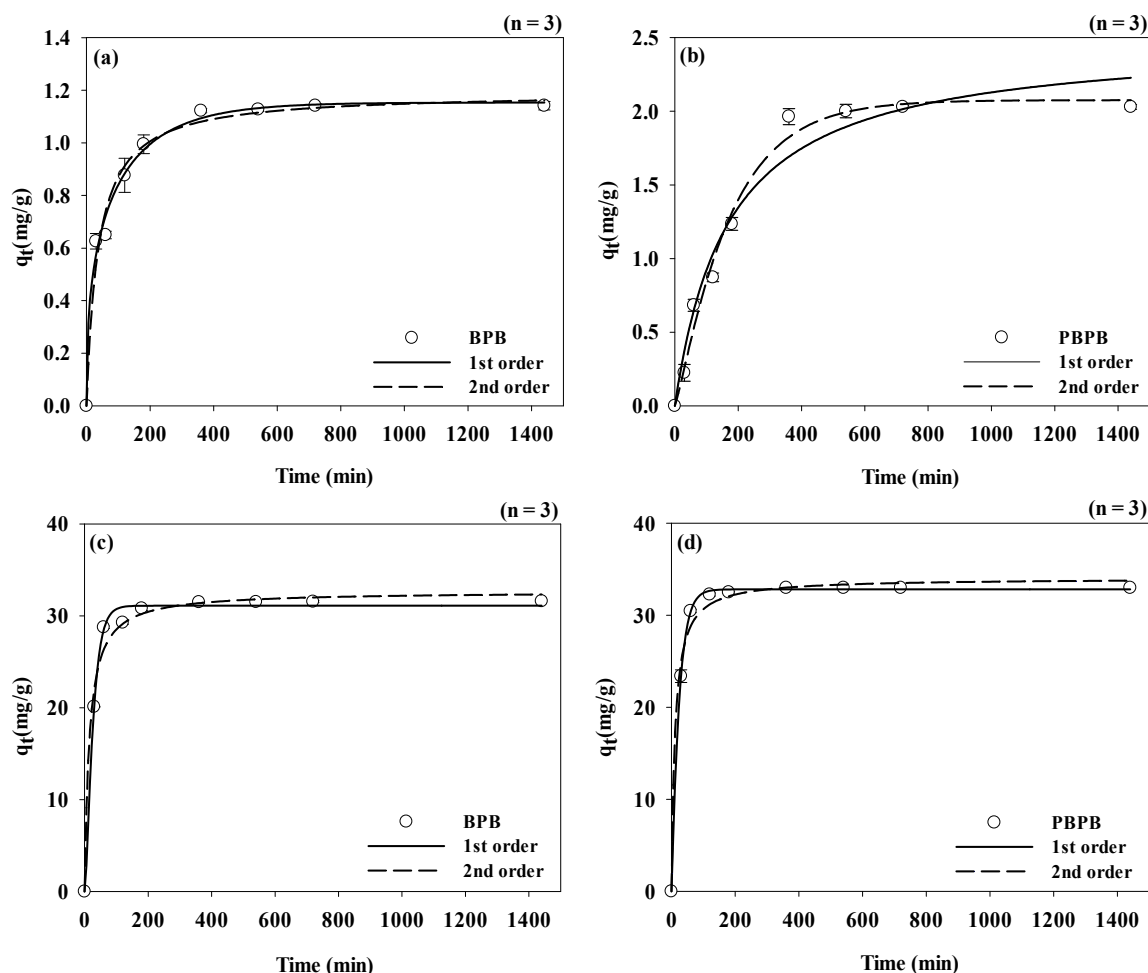


**Figure 2.** Effects of biochar dosages on the adsorption of heavy metals using BPB and PBPB: (a) Mn and (b) Fe (agitation time = 3 h, agitation speed = 150 rpm, initial concentration of Mn and Fe =  $10 \text{ mg L}^{-1}$ , pH = 7, and temperature =  $25^\circ \text{C}$ ).

### 3.3. Adsorption Kinetics of Mn and Fe

Figure 3 depicts the adsorption kinetics of Mn and Fe by BPB and PBPB. The adsorption proceeded rapidly in the beginning for both heavy metals (Mn  $\leq 360 \text{ min}$ ; Fe  $\leq 180 \text{ min}$ ) and almost reached equilibrium at 10 h. A possible explanation for these results is that the availability of adsorption sites plays key roles in the adsorption of Fe and Mn by BPB and PBPB [19]. Table 2 presents the kinetic model parameters for the adsorption of Mn and Fe by BPB and PBPB. Based on the correlation coefficient values ( $R^2$ ), the pseudo-second-order model better described the adsorption of Mn and Fe by BPB and PBPB than the pseudo-first-order model. These observations indicate that the adsorption of Mn and Fe by BPB and PBPB is predominantly governed by chemical adsorption (i.e., covalent

bonding or ion/electron exchange) [27]. As shown in Figure 3, the adsorption capacities at equilibrium ( $q_e$ ) of Mn and Fe by BPB were 1.14 and 31.61 mg g<sup>-1</sup>, respectively. Meanwhile, the  $q_e$  of Mn and Fe by PBPB were 2.03 and 32.99 mg g<sup>-1</sup>, respectively. The higher  $q_e$  values by PBPB support the assumption that PBPB is more effective for the adsorption of heavy metals than BPB due to its higher content of oxygen-containing functional groups [34,35].



**Figure 3.** Adsorption kinetics of heavy metals onto BPB and PBPB: (a,b) Mn and (c,d) Fe (agitation time = 24 h, agitation speed = 150 rpm, adsorbent dosage of BPB and PBPB for Mn = 3 g L<sup>-1</sup>, adsorbent dosage of BPB for Fe = 0.1 g L<sup>-1</sup>, adsorbent dosage of PBPB for Fe = 0.3 g L<sup>-1</sup>, initial concentration of Mn and Fe = 10 mg L<sup>-1</sup>, pH = 7, and temperature = 25 °C).

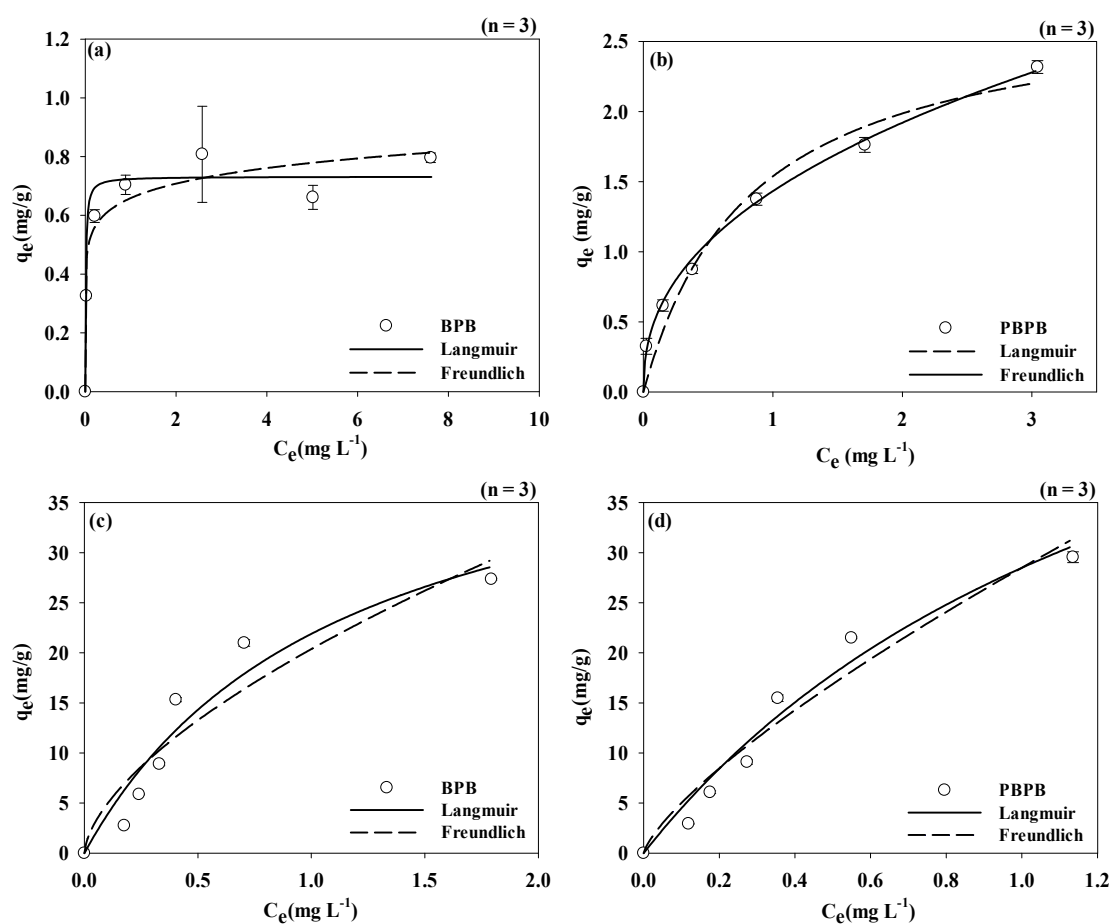
**Table 2.** Kinetic model parameters for the adsorption of Mn and Fe by BPB and PBPB (n = 3).

|      |    |                                                      | k     | R <sup>2</sup> |
|------|----|------------------------------------------------------|-------|----------------|
| BPB  | Mn | First-order (min <sup>-1</sup> )                     | 0.008 | 0.944          |
|      |    | Second-order (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.029 | 0.999          |
|      | Fe | First-order (min <sup>-1</sup> )                     | 0.007 | 0.867          |
|      |    | Second-order (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.004 | 0.999          |
| PBPB | Mn | First-order (min <sup>-1</sup> )                     | 0.009 | 0.965          |
|      |    | Second-order (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.003 | 0.977          |
|      | Fe | First-order (min <sup>-1</sup> )                     | 0.019 | 0.892          |
|      |    | Second-order (g mg <sup>-1</sup> min <sup>-1</sup> ) | 0.006 | 0.999          |



### 3.4. Adsorption Isotherms of Mn and Fe

The adsorption mechanisms of Mn and Fe by BPB and PBPB were analyzed using the Langmuir and Freundlich adsorption isotherm models (Figure 4 and Table 3). The Langmuir isotherm model was well-fitted to the adsorption of Mn and Fe by BPB ( $R^2$  of Mn = 0.972,  $R^2$  of Fe = 0.869). These results imply that monolayer adsorption is responsible for the adsorption of Mn and Fe by BPB [7]. The adsorption of Mn by PBPB followed the Freundlich isotherm model ( $R^2 = 0.993$ ) more closely than the Langmuir isotherm model ( $R^2 = 0.898$ ). It is evident that multilayer adsorption strongly contributes to the adsorption of Mn by PBPB [13]. However, the adsorption of Fe by PBPB followed both Freundlich ( $R^2 = 0.933$ ) and Langmuir isotherms ( $R^2 = 0.949$ ). The  $n$  value of the Freundlich isotherm model was used to examine the adsorption affinity of Mn and Fe onto BPB and PBPB (Table 3): (i)  $n > 1$  (favorable), (ii)  $n = 1$  (linear), and (iii)  $n < 1$  (unfavorable) [30]. The adsorption of Mn and Fe by BPB ( $n$  value of Mn = 7.267,  $n$  value of Fe = 1.069) and the adsorption of Mn by PBPB ( $n$  value = 2.471) were favorable whereas the adsorption of Fe by PBPB ( $n$  value = 0.977) was not favorable. The separation parameter  $R_L$  value, based on  $R_L = 1/(1 + K_L C_0)$  of the Langmuir isotherm model, was also calculated to assess the adsorption preference of Mn and Fe toward BPB and PBPB: (i)  $R_L > 1$  (unfavorable), (ii)  $R_L = 1$  (linear), (iii)  $1 > R_L > 0$  (favorable), and (iv)  $R_L = 0$  (irreversible) [40]. Since the  $R_L$  values of Mn and Fe by BPB and PBPB were in the range of 0–1 ( $R_L$  of Mn by BPB = 0.003;  $R_L$  of Fe by BPB = 0.146;  $R_L$  of Mn by PBPB = 0.012;  $R_L$  of Fe by PBPB = 0.156), the adsorption of Mn and Fe by BPB and PBPB seemed to be favorable.



**Figure 4.** Adsorption isotherms of heavy metals onto BPB and PBPB: (a,b) Mn and (c,d) Fe (agitation time = 24 h, agitation speed = 150 rpm, adsorbent dosage of BPB and PBPB for Mn = 3 g L<sup>−1</sup>, adsorbent dosage of BPB for Fe = 0.1 g L<sup>−1</sup>, adsorbent dosage of PBPB for Fe = 0.3 g L<sup>−1</sup>, initial concentration of Mn and Fe = 10 mg L<sup>−1</sup>, pH = 7, and temperature = 25 °C).

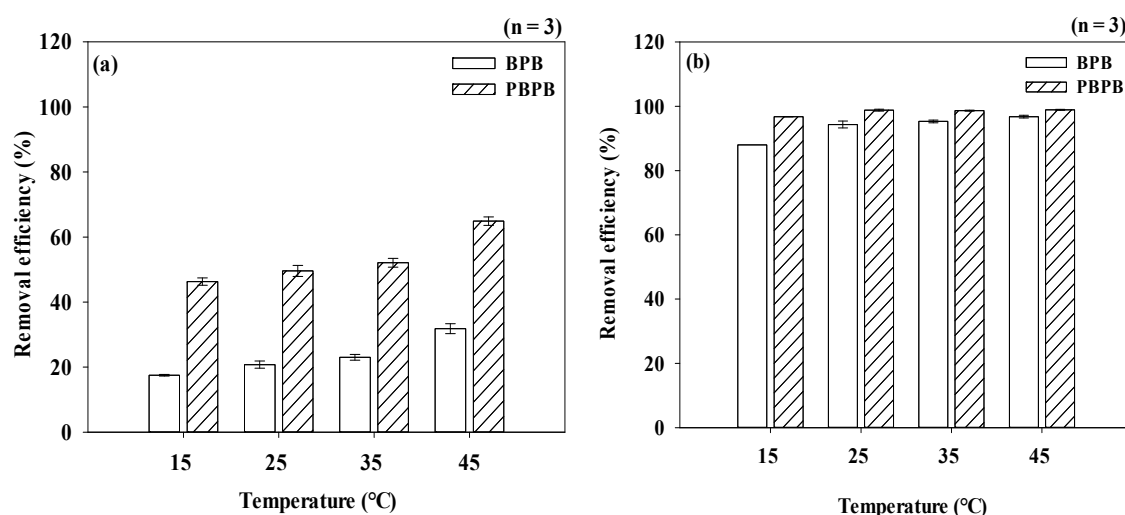


**Table 3.** Isotherm model parameters for adsorption of Mn and Fe by BPB and PBPB (n = 3).

|      |            |                                                                 | Mn     | Fe     |
|------|------------|-----------------------------------------------------------------|--------|--------|
| BPB  | Langmuir   | $K_L$ (L mg <sup>-1</sup> )                                     | 32.204 | 0.583  |
|      |            | $q_e$ (mg g <sup>-1</sup> )                                     | 0.796  | 27.355 |
|      |            | $R_L$                                                           | 0.003  | 0.146  |
|      |            | $R^2$                                                           | 0.972  | 0.869  |
|      | Freundlich | $K_F$ (mg <sup>1-(1/n)</sup> L <sup>1/n</sup> g <sup>-1</sup> ) | 0.821  | 3.864  |
|      |            | n                                                               | 7.267  | 1.069  |
|      |            | $R^2$                                                           | 0.81   | 0.826  |
|      |            |                                                                 |        |        |
| PBPB | Langmuir   | $K_L$ (dm <sup>3</sup> mg <sup>-1</sup> )                       | 7.943  | 0.540  |
|      |            | $q_e$ (mg g <sup>-1</sup> )                                     | 2.319  | 29.55  |
|      |            | $R_L$                                                           | 0.012  | 0.156  |
|      |            | $R^2$                                                           | 0.898  | 0.949  |
|      | Freundlich | $K_F$ (mg <sup>1-(1/n)</sup> L <sup>1/n</sup> g <sup>-1</sup> ) | 1.161  | 4.611  |
|      |            | n                                                               | 2.471  | 0.977  |
|      |            | $R^2$                                                           | 0.993  | 0.933  |
|      |            |                                                                 |        |        |

### 3.5. Effects of Temperature on Adsorption of Mn and Fe

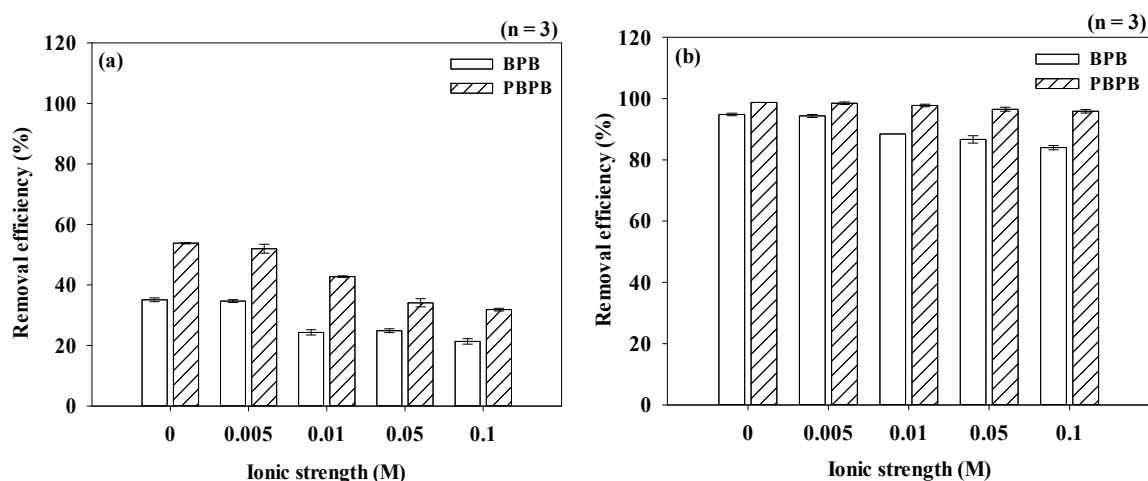
The effects of temperature on the adsorption of Mn and Fe by BPB and PBPB are compared in Figure 5. The removal efficiencies of Mn and Fe by both BPB and PBPB were increased with increasing temperatures from 15 (removal efficiency of Mn by BPB = 17%, removal efficiency of Mn by PBPB = 46%, removal efficiency of Fe by BPB = 88%, removal efficiency of Fe by PBPB = 97%) to 45 °C (removal efficiency of Mn by BPB = 32%, removal efficiency of Mn by PBPB = 65%, removal efficiency of Fe by BPB = 97%, removal efficiency of Fe by PBPB = 99%). These results suggest that high temperatures may provide sufficient energy for the adsorption of heavy metals on the surficial and interior layers of biochars [41]. From the higher removal efficiencies of Mn and Fe by PBPB than BPB, it can be concluded that the abundance of oxygen-containing functional groups facilitates the adsorption of heavy metals by carbonaceous adsorbents [36].



**Figure 5.** Effects of temperature on the adsorption of heavy metals using BPB and PBPB: (a) Mn and (b) Fe (agitation time = 6 h, agitation speed = 150 rpm, adsorbent dosage of BPB and PBPB for Mn = 3 g L<sup>-1</sup>, adsorbent dosage of BPB for Fe = 0.1 g L<sup>-1</sup>, adsorbent dosage of PBPB for Fe = 0.3 g L<sup>-1</sup>, initial concentration of Mn and Fe = 10 mg L<sup>-1</sup>, pH = 7, and temperature = 15–45 °C).

### 3.6. Effects of Ionic Strength on Adsorption of Mn and Fe

Figure 6 illustrates the effects of ionic strength on the removal of heavy metals by BPB and PBPB. The removal efficiencies of Mn and Fe by BPB and PBPB were gradually decreased with increasing ionic strengths. For example, when ionic strength was increased from 0 to 0.1 M, the removal efficiencies of Mn by BPB and PBPB were decreased from 35% and 54% to 21% and 32%, respectively. Meanwhile, the removal efficiencies of Fe by BPB and PBPB were decreased from 95% and 99% to 84% and 96%, respectively. These observations imply that increases of ionic strength may reinforce the electrostatic repulsion between heavy metals and the biochar surfaces and reduce the availability of adsorption sites on the biochar surfaces through the aggregation of biochars [42]. The removal efficiencies of Fe by BPB and PBPB were less affected by the changes in ionic strength compared to the removal efficiencies of Mn by BPB and PBPB because Fe has a smaller ion radius and higher electronegativity than Mn [37,38]. These inherent natures allowed Fe to exhibit higher attractive charges in the nucleus on the electron orbital [37,38]. Therefore, Fe more easily penetrated into the pores of biochars compared to Mn [37,38]. In addition, the higher removal efficiencies of Mn and Fe by PBPB (removal efficiency of Mn = 32–54%; removal efficiency of Fe = 96–99%) than BPB (removal efficiency of Mn = 21–35%; removal efficiency of Fe = 84–95%) at all the tested ionic strengths provide evidence that the surface structural features and oxygen-containing functional group abundance govern the adsorption of heavy metals by carbonaceous adsorbents [12,21,22].



**Figure 6.** Effects of ionic strength on the adsorption of heavy metals using BPB and PBPB: (a) Mn and (b) Fe (agitation time = 6 h, agitation speed = 150 rpm, adsorbent dosage of BPB and PBPB for Mn = 3 g L<sup>-1</sup>, adsorbent dosage of BPB for Fe = 0.1 g L<sup>-1</sup>, adsorbent dosage of PBPB for Fe = 0.3 g L<sup>-1</sup>, initial concentration = 10 mg L<sup>-1</sup>, pH = 7, and temperature = 25 °C).

## 4. Conclusions

In this study, phosphoric acid pre-treatment on banana peel biochar was investigated for enhancement of Mn and Fe removal efficiencies. The physicochemical characteristics of pristine and phosphoric acid pre-treated biochars were characterized using the elemental analyzer, BET, and ATR-FTIR. These characterizations revealed that phosphoric acid pre-treatment facilitated the formation of oxygen-containing functional groups (i.e., hydroxyl and carboxyl functional groups), which could enhance the adsorption of heavy metals on the biochar surfaces. In addition, phosphoric acid pre-treatment improved specific surface area and pore volume for more adsorption sites for heavy metals. The adsorption experiments showed that phosphoric acid pre-treatment can improve the removal of Mn and Fe significantly. The results of the adsorption kinetics of Mn and Fe by BPB and PBPB were well-matched to the pseudo-second-order, indicating that adsorption was predominantly governed by chemical adsorption. The adsorption of Mn and Fe by BPB obeyed the Langmuir

isotherm model, whereas the Freundlich isotherm model described the adsorption of Mn by PBPB well. The adsorption of Fe by PBPB followed both Freundlich and Langmuir isotherm models. Furthermore, the adsorption of Mn and Fe by both BPB and PBPB increased with increasing temperature. However, the removal efficiencies were decreased with increasing ionic strength. From the excellent adsorption performance of Mn and Fe by PBPB compared to BPB, it can be concluded that phosphoric acid pre-treatment is a promising method to enhance Mn and Fe removal by banana peel biochar.

**Author Contributions:** H.K.: methodology and conceptualization, R.-A.K.: formal analysis and data curation, S.L.: writing—original draft preparation, K.C.: writing—review, editing, and funding acquisition. All authors have read and agree to the published version of the manuscript.

**Funding:** This study was supported by the Basic Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2018R1D1A1B07044718) and partially supported by a 2017 Research Grant from Kangwon National University (Republic of Korea).

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

## References

1. Ihsanullah; Abbas, A.; Al-Amer, A.M.; Laoui, T.; Al-Marri, M.J.; Nasser, M.S.; Khraisheh, M.; Atieh, M.A. Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Sep. Purif. Technol.* **2016**, *157*, 141–161. [\[CrossRef\]](#)
2. Wang, F.; Yuanfeng, P.; Cai, P.; Guo, T.; Xiao, H. Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. *Bioresour. Technol.* **2017**, *241*, 482–490. [\[CrossRef\]](#)
3. Elsehly, E.M.; Chechenin, N.G.; Bukunov, K.; Makunin, A.V.; Priselkova, A.B.; Vorobyeva, E.A.; Motaweh, H.A. Removal of iron and manganese from aqueous solutions using carbon nanotube filters. *Water Supply* **2015**, *16*, 347–353. [\[CrossRef\]](#)
4. Idrees, M.; Batool, S.; Ullah, H.; Hussain, Q.; Al-Wabel, M.I.; Ahmad, M.; Hussain, A.; Riaz, M.; Ok, Y.S.; Kong, J. Adsorption and thermodynamic mechanisms of manganese removal from aqueous media by biowaste-derived biochars. *J. Mol. Liq.* **2018**, *266*, 373–380. [\[CrossRef\]](#)
5. Kwakye-Awuah, B.; Sefa-Ntiri, B.; Von-Kiti, E.; Nkrumah, I.; Williams, C. Adsorptive Removal of Iron and Manganese from Groundwater Samples in Ghana by Zeolite Y Synthesized from Bauxite and Kaolin. *Water* **2019**, *11*, 1912. [\[CrossRef\]](#)
6. Al-Rashdi, B.; Johnson, D.; Hilal, N. Removal of heavy metal ions by nanofiltration. *Desalination* **2013**, *315*, 2–17. [\[CrossRef\]](#)
7. Chen, Q.; Yao, Y.; Li, X.; Lu, J.; Zhou, J.; Huang, Z. Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. *J. Water Process. Eng.* **2018**, *26*, 289–300. [\[CrossRef\]](#)
8. Bazrafshan, E.; Mohamadi, L.; Ansari-Moghaddam, A.; Mahvi, A.H. Heavy metals removal from aqueous environments by electrocoagulation process- a systematic review. *J. Environ. Health Sci. Eng.* **2015**, *13*, 74. [\[CrossRef\]](#)
9. Khatri, N.; Tyagi, S.; Rawtani, D. Recent strategies for the removal of iron from water: A review. *J. Water Process. Eng.* **2017**, *19*, 291–304. [\[CrossRef\]](#)
10. Patil, D.S.; Chavan, S.M.; Oubagaranadin, J.U.K. A review of technologies for manganese removal from wastewaters. *J. Environ. Chem. Eng.* **2016**, *4*, 468–487. [\[CrossRef\]](#)
11. Tobiasson, J.E.; Bazilio, A.; Goodwill, J.; Mai, X.; Nguyen, C. Manganese Removal from Drinking Water Sources. *Curr. Pollut. Rep.* **2016**, *2*, 168–177. [\[CrossRef\]](#)
12. Pérez-Marín, A.B.; Zapata, V.M.; Ortuño, J.F.; Aguilar, M.I.; Saez, J.; Lloréns, M. Removal of cadmium from aqueous solutions by adsorption onto orange waste. *J. Hazard. Mater.* **2007**, *139*, 122–131. [\[CrossRef\]](#)
13. Demirbas, A. Heavy metal adsorption onto agro-based waste materials: A review. *J. Hazard. Mater.* **2008**, *157*, 220–229. [\[CrossRef\]](#)
14. Pellerá, F.-M.; Giannis, A.; Kalderis, D.; Anastasiadou, K.; Stegmann, R.; Wang, J.-Y.; Gidarakos, E. Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products. *J. Environ. Manag.* **2012**, *96*, 35–42. [\[CrossRef\]](#)

15. Liu, Z.; Zhang, F.-S. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *J. Hazard. Mater.* **2009**, *167*, 933–939. [\[CrossRef\]](#)
16. Liu, Z.; Zhang, F.-S.; Wu, J. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. *Fuel* **2010**, *89*, 510–514. [\[CrossRef\]](#)
17. Jun, B.-M.; Kim, Y.; Han, J.; Yoona, Y.; Kim, J.; Park, C.M. Preparation of Activated Biochar-Supported Magnetite Composite for Adsorption of Polychlorinated Phenols from Aqueous Solutions. *Water* **2019**, *11*, 1899. [\[CrossRef\]](#)
18. Lucaci, A.R.; Bulgariu, D.; Ahmad, I.; Lisa, G.; Mocanu, A.M.; Bulgariu, L. Potential Use of Biochar from Various Waste Biomass as Biosorbent in Co(II) Removal Processes. *Water* **2019**, *11*, 1565. [\[CrossRef\]](#)
19. Gupta, P.; Ann, T.-W.; Lee, S.-M. Use of biochar to enhance constructed wetland performance in wastewater reclamation. *Environ. Eng. Res.* **2016**, *21*, 36–44. [\[CrossRef\]](#)
20. Zhao, J.; Shen, X.-J.; Domene, X.; Alcañiz, J.-M.; Liao, X.; Palet, C. Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions. *Sci. Rep.* **2019**, *9*, 9869. [\[CrossRef\]](#)
21. Wang, X.; Li, X.; Liu, G.; He, Y.; Chen, C.; Liu, X.; Li, G.; Gu, Y.; Zhao, Y.; He, Y. Mixed heavy metal removal from wastewater by using discarded mushroom-stick biochar: Adsorption properties and mechanisms. *Environ. Sci. Process. Impacts* **2019**, *21*, 584–592. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Vilardi, G.; Di Palma, L.; Ochando-Pulido, J.M. Heavy metals adsorption by banana peels micro-powder: Equilibrium modeling by non-linear models. *Chin. J. Chem. Eng.* **2018**, *26*, 455–464. [\[CrossRef\]](#)
23. Martínez-Ruano, J.A.; Caballero-Galván, A.S.; Restrepo-Serna, D.L.; Alzate, C.A.C. Techno-economic and environmental assessment of biogas production from banana peel (*Musa paradisiaca*) in a biorefinery concept. *Environ. Sci. Pollut. Res.* **2018**, *25*, 35971–35980. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Sagar, N.A.; Pareek, S.; Sharma, S.; Yahia, E.M.; Lobo, M.G. Fruit and Vegetable Waste: Bioactive Compounds, Their Extraction, and Possible Utilization. *Compr. Rev. Food Sci. Food Saf.* **2018**, *17*, 512–531. [\[CrossRef\]](#)
25. Omulo, G.; Banadda, N.; Kabenge, I.; Seay, J.R. Optimizing slow pyrolysis of banana peels wastes using response surface methodology. *Environ. Eng. Res.* **2018**, *24*, 354–361. [\[CrossRef\]](#)
26. Ibarra-Rodríguez, D.; Lizardi-Mendoza, J.; López-Maldonado, E.A.; Oropeza-Guzman, M.T.; Diana, I.-R.; Jaime, L.-M. Capacity of ‘nopal’ pectin as a dual coagulant-flocculant agent for heavy metals removal. *Chem. Eng. J.* **2017**, *323*, 19–28. [\[CrossRef\]](#)
27. Zhou, N.; Chen, H.; Xi, J.; Yao, D.; Zhou, Z.; Tian, Y.; Lu, X. Biochars with excellent Pb(II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization. *Bioresour. Technol.* **2017**, *232*, 204–210. [\[CrossRef\]](#)
28. Amin, M.T.; Alazba, A.A.; Shafiq, M. Removal of Copper and Lead using Banana Biochar in Batch Adsorption Systems: Isotherms and Kinetic Studies. *Arab. J. Sci. Eng.* **2017**, *43*, 5711–5722. [\[CrossRef\]](#)
29. Tan, X.; Liu, S.; Liu, Y.; Gu, Y.-L.; Zeng, G.-M.; Hu, X.; Wang, X.; Liu, S.-H.; Jiang, L. Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage. *Bioresour. Technol.* **2017**, *227*, 359–372. [\[CrossRef\]](#)
30. Wang, Z.; Wu, J.; He, T.; Wu, J. Corn stalks char from fast pyrolysis as precursor material for preparation of activated carbon in fluidized bed reactor. *Bioresour. Technol.* **2014**, *167*, 551–554. [\[CrossRef\]](#)
31. Chu, G.; Zhao, J.; Huang, Y.; Zhou, D.; Liu, Y.; Wu, M.; Peng, H.; Zhao, Q.; Pan, B.; Steinberg, C.E. Phosphoric acid pretreatment enhances the specific surface areas of biochars by generation of micropores. *Environ. Pollut.* **2018**, *240*, 1–9. [\[CrossRef\]](#)
32. Taha, S.M.; Amer, M.E.; Elmarsafy, A.E.; Elkady, M.Y. Adsorption of 15 different pesticides on untreated and phosphoric acid treated biochar and charcoal from water. *J. Environ. Chem. Eng.* **2014**, *2*, 2013–2025. [\[CrossRef\]](#)
33. Wu, C.; Wang, Z.; Huang, J.; Williams, P.T. Pyrolysis/gasification of cellulose, hemicellulose and lignin for hydrogen production in the presence of various nickel-based catalysts. *Fuel* **2013**, *106*, 697–706. [\[CrossRef\]](#)
34. Coates, J. Interpretation of infrared spectra, a practical approach. In *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2006; pp. 10815–10837.
35. O’Connell, D.W.; Birkinshaw, C.; O’Dwyer, T.F. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresour. Technol.* **2008**, *99*, 6709–6724. [\[CrossRef\]](#) [\[PubMed\]](#)

36. Wang, Z.; Liu, G.; Zheng, H.; Li, F.; Ngo, H.-H.; Guo, W.; Liu, C.; Chen, L.; Xing, B. Investigating the mechanisms of biochar's removal of lead from solution. *Bioresour. Technol.* **2015**, *177*, 308–317. [[CrossRef](#)] [[PubMed](#)]
37. Dastgheib, S.A.; Rockstraw, D.A. A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells. *Carbon* **2002**, *40*, 1843–1851. [[CrossRef](#)]
38. Bin Jusoh, A.; Cheng, W.; Low, W.; Nora'Aini, A.; Noor, M.M.M. Study on the removal of iron and manganese in groundwater by granular activated carbon. *Desalination* **2005**, *182*, 347–353. [[CrossRef](#)]
39. Moreno-Castilla, C.; Álvarez-Merino, M.A.; López-Ramón, M.; Rivera-Utrilla, J. Cadmium Ion Adsorption on Different Carbon Adsorbents from Aqueous Solutions. Effect of Surface Chemistry, Pore Texture, Ionic Strength, and Dissolved Natural Organic Matter. *Langmuir* **2004**, *20*, 8142–8148. [[CrossRef](#)]
40. Gorgievski, M.; Božić, D.; Stanković, V.; Strbac, N.; Šerbula, S. Kinetics, equilibrium and mechanism of Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions biosorption using wheat straw. *Ecol. Eng.* **2013**, *58*, 113–122. [[CrossRef](#)]
41. Abdelhafez, A.A.; Li, J. Removal of Pb(II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. *J. Taiwan Inst. Chem. Eng.* **2016**, *61*, 367–375. [[CrossRef](#)]
42. Park, C.M.; Han, J.; Chu, K.H.; Al-Hamadani, Y.; Her, N.; Heo, J.; Yoona, Y. Influence of solution pH, ionic strength, and humic acid on cadmium adsorption onto activated biochar: Experiment and modeling. *J. Ind. Eng. Chem.* **2017**, *48*, 186–193. [[CrossRef](#)]



© 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/>).