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Article

# Phosphorus and Nitrogen Adsorption Capacities of Biochars Derived from Feedstocks at Different Pyrolysis Temperatures

Lei Zhou <sup>1,2</sup>, Defu Xu <sup>1,2,3,4,\*</sup>, Yingxue Li <sup>4</sup>, Qianchen Pan <sup>2</sup>, Jiajun Wang <sup>1,2</sup>, Lihong Xue <sup>3</sup> and Alan Howard <sup>5,\*</sup>

<sup>1</sup> Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing 210044, China

<sup>2</sup> School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

<sup>3</sup> Key Laboratory of Agro-Environment in downstream of Yangze Plain, Ministry of Agriculture, Nanjing 210014, China

<sup>4</sup> Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Nanjing 210044, China

<sup>5</sup> Department of Geography and Environmental Science, University of Reading, Reading RG6 6AB, UK

\* Correspondence: defuxu1@163.com (D.X.); a.howard@reading.ac.uk (A.H.); Tel.: +86-025-5869-5684 (D.X.); +44-118-378-8763 (A.H.)

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**Abstract:** This study investigates the P and NO<sub>3</sub><sup>-</sup> adsorption capacities of different biochars made from plant waste including rice straw (RSB), *Phragmites communis* (PCB), sawdust (SDB), and egg shell (ESB) exposed to a range of pyrolysis temperatures (300, 500 and 700 °C). Results indicate that the effect of pyrolysis temperature on the physiochemical properties of biochar varied with feedstock material. Biochars derived from plant waste had limited adsorption or even released P and NO<sub>3</sub><sup>-</sup>, but adsorption of P capacity could be improved by adjusting pyrolysis temperature. The maximum adsorption of P on RSB700, PCB300, and SDB300, produced at pyrolysis temperature of 700, 300 and 300 °C, was 5.41, 7.75 and 3.86 mg g<sup>-1</sup>, respectively. ESB can absorb both P and NO<sub>3</sub><sup>-</sup>, and its adsorption capacity increased with an increase in pyrolysis temperature. The maximum NO<sub>3</sub><sup>-</sup> and P adsorption for ESB700 was 1.43 and 6.08 mg g<sup>-1</sup>, respectively. The less negative charge and higher surface area of ESB enabled higher NO<sub>3</sub><sup>-</sup> and P adsorption capacity. The P adsorption process on RSB, PCB, SDB and ESB, and the NO<sub>3</sub><sup>-</sup> adsorption process on ESB were endothermic reactions. However, the NO<sub>3</sub><sup>-</sup> adsorption process on RSB, PCB and SDB was exothermic. The study demonstrates that the use of egg shell biochar may be an effective way to remove, through adsorption, P and NO<sub>3</sub><sup>-</sup> from wastewater.

**Keywords:** biochar; pyrolysis temperature; nitrogen; phosphorus; adsorption capacity

## 1. Introduction

Discharges of phosphorus (P) and nitrate (NO<sub>3</sub><sup>-</sup>) into the natural environment from agricultural, industrial, and domestic wastewater have increased in many countries. The resulting nutrient enrichment and eutrophication of water-bodies has become a serious environmental concern around the world [1,2]. Under eutrophic conditions, rapid growth of organisms, especially algae, may be stimulated resulting in depletion of dissolved oxygen and deterioration of the aquatic environment [3]. In addition, human health could be affected by high levels of NO<sub>3</sub><sup>-</sup> in water. For example, infant methemoglobinemia and several types of cancers could occur due to human uptake of excess

$\text{NO}_3^-$  [4]. Therefore, removing excess P and  $\text{NO}_3^-$  from wastewaters has important ecological and social implications.

Technologies used to remove P and  $\text{NO}_3^-$  from wastewaters are mainly divided into three categories: chemical, biological and physical methods [5]. Chemical treatments may produce additional pollutants, such as sludge, due to the precipitation of P [6]. Biological treatments may increase the cost of wastewater treatment because of the requirement for aeration or other pre-treatments [7]. Physical treatments include many methods, such as electrodialysis, reverse osmosis and adsorption. Compared to electrodialysis and reverse osmosis, adsorption is a widely used and promising method of purifying wastewater in situ because it is relatively low-cost and efficient and is less likely to generate secondary pollution [8,9]. Therefore, investigation of economical and effective adsorbents to remove P and  $\text{NO}_3^-$  from wastewaters has much potential value.

Large amounts of bio-wastes, such as straw and manure, are produced from agriculture and industrial activities [10]. For example, the annual production of agricultural waste is approximately 0.7 billion tonnes in China, of which 70% is rice straw, wheat straw, and corn stalk [11]. Egg shell is a waste from daily life, and its annual production is about 3.7 million tonnes in China [12]. Large quantities of bio-waste have resulted in many environmental problems, such as water pollution due to its leachate, and air pollution due to its burning. Therefore, it is very important to find sustainable solutions to solve bio-waste issues, and biochar production offers a viable approach. As well as possibly aiding the removal of P and  $\text{NO}_3^-$  from wastewaters, biochars may be applied to soil to serve as an amendment to increase plant growth, and reduce bioavailability, phytotoxicity, and uptake of heavy metals in contaminated soil [13]. Biochars that are used as adsorption agents in wastewater, could, therefore, be subsequently re-used as a soil amendment.

There have, however, been inconsistent results on  $\text{NO}_3^-$  and P adsorption by biochars. Yao et al., for example, found that  $\text{NO}_3^-$  leaching was reduced by 14.0–34.0% when a biochar produced from Brazilian pepper wood and peanut hull at 600 °C was added to soil [14]. However, Hale et al. [15] found that cacao shell and corn cob biochar did not adsorb  $\text{NO}_3^-$  and, in fact, sometimes increased the release of  $\text{NO}_3^-$  into the environment. Jung and Hong [16], for example, found an adsorption of 8.3 mg g<sup>-1</sup> of phosphate in a biochar from seaweed pyrolysis at 600 °C. Michalekova-Richveisova et al. [17] demonstrated that the maximum phosphate adsorption capacity was 0.036 mg g<sup>-1</sup>, 0.132 mg g<sup>-1</sup> and 0.296 mg g<sup>-1</sup>, respectively for a corn cobs biochar, garden wood waste biochar and wood chips biochar. However, Novaisa et al. [18] demonstrated that biochars would not be able to adsorb significant amounts of phosphate due to the large amount of phenolic and carboxylic groups and a high proportion of fulvic and humic acids. Similarly, some biochars, such as wild fire biochar, Jarrah biochar, greenwaste biochar, sugarcane bagasse biochar and blady grass biochar, do not have the capacity to adsorb phosphate and can actually release P into solution [19]. Therefore, research to identify the physiochemical properties of biochars most suitable for removal of P and N from wastewater remains very important.

Adsorption of nitrogen (N) and P may be influenced by many factors, including its CEC, acidic functional groups, surface oxygen-containing functional groups [20], surface charges and available anion exchange sites [21]. In addition, Chintala et al. [22] found that P adsorption by biochars was significantly affected by initial P concentration in the solution. Therefore, P and  $\text{NO}_3^-$  adsorption is related to the biochar's physiochemical properties, and the initial P and  $\text{NO}_3^-$  concentration. However, there is little information on how biochars derived from plant waste and egg shell affect P and  $\text{NO}_3^-$  adsorption at varying pyrolysis temperatures. The objectives of this study therefore include: (1) to examine capacity of P and  $\text{NO}_3^-$  adsorption of different biochars produced under different pyrolysis temperatures; (2) to investigate the adsorption process of P and  $\text{NO}_3^-$  by the biochars. The results will offer a theoretical and practical foundation for removal of P and  $\text{NO}_3^-$  from eutrophic or wastewaters using biochars.

## 2. Materials and Methods

### 2.1. Materials

Four types of materials, i.e., rice straw, *Phragmites communis*, sawdust and egg shell were obtained from Nanjing University of Information Science and Technology, Nanjing, China. The materials were rinsed with water and air-dried, then ground and sieved to < 2.0 mm particles using a stainless grinding machine. The powdered biomass was tightly placed in a ceramic pot, and then pyrolyzed in a muffle furnace. The pyrolysis was programmed to drive temperature to 300 °C, 500 °C and 700 °C at a rate of 5 °C min<sup>-1</sup>, respectively, and held at the peak temperature for 2 h before being cooled to room temperature. The biochars produced from rice straw, *Phragmites communis*, sawdust and egg shell under 300 °C, 500 °C and 700 °C were referred to as RSB300, RSB500, RSB700, PCB300, PCB500, PCB700, SDB300, SDB500, SDB700, ESB300, ESB500 and ESB700, respectively. All biochar samples were ground to pass through a 0.5 mm sieve prior to use.

### 2.2. Adsorption Kinetics Experiments

The stock solutions of P and NO<sub>3</sub><sup>-</sup>-N were prepared using KH<sub>2</sub>PO<sub>4</sub> and KNO<sub>3</sub>, respectively. Sorption kinetics were evaluated at room temperature (30 °C) and the initial pH for each sorption solution was adjusted to 7 prior to the experiments. The biochar (0.2 g) was added into 20 mL solutions containing 20 mg P or NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>. Subsamples were taken after 30 min, 60 min, 180 min, 300 min, 420 min, 780 min, 1080 min and 1440 min, and shaken at 180 rpm in a mechanical shaker. The subsamples were then filtered with a syringe filter. The concentrations of NO<sub>3</sub><sup>-</sup>-N and P in the filtrate were determined by ultraviolet spectrophotometry and ammonium molybdate spectrophotometry, respectively.

The amount of P and NO<sub>3</sub><sup>-</sup> adsorbed by the biochars was calculated by the following equation (Equation (1)).

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (1)$$

where  $q_t$  (mg g<sup>-1</sup>) is the amount of P and NO<sub>3</sub><sup>-</sup> adsorbed by the biochars;  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) are the initial and  $t$  time concentrations of the pollutants, respectively;  $V$  (L) is the volume of adsorption solution; and  $W$  (g) is the mass of biochar.

The experimental results were fitted using three typical kinetic models (Pseudo-first-order Equation (2), Pseudo-second-order Equation (3) and Intraparticle diffusion Equation (4)).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} = \frac{1}{h} + \frac{t}{q_e} \quad (3)$$

$$q_t = k_3 t^{0.5} + C \quad (4)$$

where  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the amounts of P and NO<sub>3</sub><sup>-</sup> adsorbed by the biochars at the equilibrium time and at time  $t$ , respectively;  $k_1$  (h<sup>-1</sup>),  $k_2$  (g mg<sup>-1</sup> h<sup>-1</sup>), and  $k_3$  (mg g<sup>-1</sup> h<sup>-0.5</sup>) are the rate constants of the corresponding model; and  $C$  (mg g<sup>-1</sup>) is a constant.

### 2.3. Adsorption Isotherm Experiment

Sorption isotherms of P or NO<sub>3</sub><sup>-</sup>-N were determined using batch experiments in the centrifugal tube under the same conditions as above, and the concentration of P varied from 0 to 320 mg L<sup>-1</sup> (0, 5, 10, 20, 40, 80, 160 and 320 mg L<sup>-1</sup>) or concentration of NO<sub>3</sub><sup>-</sup>-N varied from 0 to 320 mg L<sup>-1</sup> (0, 5, 10, 20, 40, 80, 160 and 320 mg L<sup>-1</sup>). After being shaken for 24 h, the final suspensions were centrifuged,

filtered, and the supernatant solution was separated for analysis of P or  $\text{NO}_3^-$ . The concentration of P or  $\text{NO}_3^-$  was calculated Equation (5).

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (5)$$

where  $q_e$  is the equilibrium P or  $\text{NO}_3^-$  concentration in  $\text{mg g}^{-1}$ ;  $V$  is the volume of P or  $\text{NO}_3^-$  aqueous solution in L;  $W$  is the adsorbent mass in g;  $C_0$  is the initial P or  $\text{NO}_3^-$  concentration in  $\text{mg L}^{-1}$ ; and  $C_e$  is the aqueous P or  $\text{NO}_3^-$  concentration at equilibrium in  $\text{mg L}^{-1}$ .

Sorption isotherms were fitted to the Langmuir (Equation (6) and Freundlich (Equation (7)) equations to quantify the adsorption capacity of different biochars.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the adsorption capacity;  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration after the adsorption or desorption;  $1/n$  is the intensity of adsorption or affinity;  $K_F$  ( $\text{mg g}^{-1}$ ) is the Freundlich adsorption constant;  $q_{\max}$  ( $\text{mg g}^{-1}$ ) is the maximum sorption capacity;  $K_L$  ( $\text{L mg}^{-1}$ ) is a Langmuir constant.

#### 2.4. Adsorption Thermodynamics

Sorption data of RSB700, PCB300, SDB300, and ESB700 using initial P or  $\text{NO}_3^-$  concentration (20, 40, 80, 160 and 320  $\text{mg L}^{-1}$ ) at a temperature range of 20, 30 and 40 °C were collected after 24 h equilibration time. Three parameters (Gibb's free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ )) were calculated using the following equations.

The thermodynamic equilibrium constant  $K_c$  was defined as (Equation (8)):

$$K_c = \frac{C_0 - C_e}{C_e} \quad (8)$$

where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium concentration of P or  $\text{NO}_3^-$  solution.

$\Delta G^0$  was calculated by the following equation (Equation (9)):

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

where,  $T$  is temperature in K,  $R$  the ideal gas constant = 8.314  $\text{J mol}^{-1} \text{K}^{-1}$ .

$\Delta H^0$  and  $\Delta S^0$  was calculated by the following equation (Equation (10)).

$$\ln K_c = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (10)$$

Thus, from the linear plot of  $\ln K_c$  versus  $1/T$ , the enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) values were calculated from the slope ( $\Delta H^0/RT$ ) and intercept ( $\Delta S^0/R$ ), respectively.

#### 2.5. Analysis Method

The pH of biochars was measured by adding the biochars to deionized water at a mass/water ratio of 1:20 (PHS-3C). Each sample was analyzed in duplicate. The specific surface area and porosity properties of the biochars were measured by  $\text{N}_2$  adsorption isotherms at 77 K with the Brunauer–Emmett–Teller (BET) method and by  $\text{CO}_2$  isotherms at 273 K using a Quadrasorb Si-MP surface area analyzer. Zeta-potential measurements were performed at pH 7 with a potential analyzer (Zetasizer Nano ZS90, Malvern, UK).

## 2.6. Statistical Analysis

The average was calculated from three replicates of each experimental treatment using Origin Pro 8.0, and the results were indicated as mean  $\pm$  standard deviation. The kinetics and sorption isotherms were fitted using Origin Pro 8.0, and  $R^2$  values were used to compare the performance of different models. Statistical analysis was performed using SPSS 12.0. A one-way analysis of variance (ANOVA) was conducted for biochar characteristics. The tukey test was performed to detect the statistical significance of differences ( $p < 0.05$ ) among means of treatments.

## 3. Results and Discussion

### 3.1. Characteristics of Biochar

According to Table 1, total volume, specific surface area and pH of RSB, PCB, SDB and ESB increased with pyrolysis temperatures, and the parameters were significantly higher at 700 °C than at 300 °C ( $p < 0.05$ ).

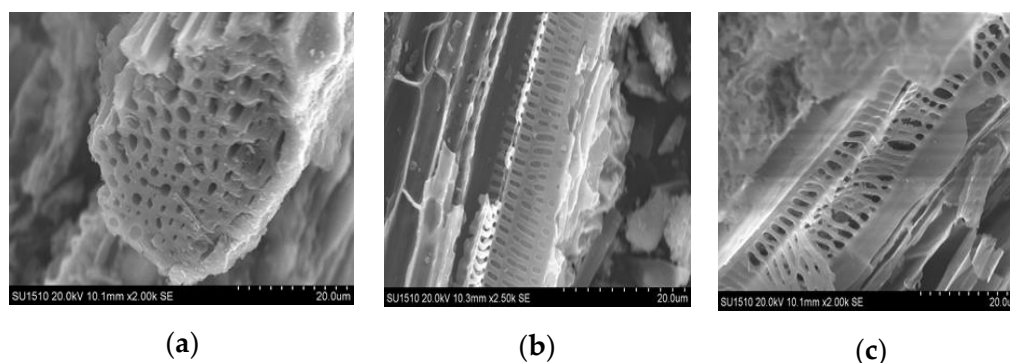
**Table 1.** Textural properties of different biochars.

Sample	Total Volume (cm <sup>3</sup> g <sup>-1</sup> )	Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> )	pH	Zeta Potential (mV)
RSB300	0.022 $\pm$ 0.003 <sup>a</sup>	5.9 $\pm$ 0.6 <sup>a</sup>	6.61 $\pm$ 0.05 <sup>a</sup>	-30.50 $\pm$ 0.70 <sup>a</sup>
RSB500	0.072 $\pm$ 0.008 <sup>b</sup>	34.0 $\pm$ 3.6 <sup>b</sup>	9.28 $\pm$ 0.07 <sup>b</sup>	-41.90 $\pm$ 1.05 <sup>b</sup>
RSB700	0.189 $\pm$ 0.002 <sup>c</sup>	122.6 $\pm$ 14.3 <sup>c</sup>	10.06 $\pm$ 0.1 <sup>c</sup>	-19.35 $\pm$ 1.92 <sup>c</sup>
PCB300	0.008 $\pm$ 0.0009 <sup>a</sup>	3.5 $\pm$ 0.4 <sup>a</sup>	6.43 $\pm$ 0.03 <sup>a</sup>	-39.30 $\pm$ 0.76 <sup>a</sup>
PCB500	0.106 $\pm$ 0.002 <sup>b</sup>	131.5 $\pm$ 14.3 <sup>b</sup>	6.82 $\pm$ 0.02 <sup>b</sup>	-30.33 $\pm$ 2.01 <sup>b</sup>
PCB700	0.415 $\pm$ 0.05 <sup>c</sup>	441.7 $\pm$ 45.6 <sup>c</sup>	9.42 $\pm$ 0.04 <sup>c</sup>	-23.41 $\pm$ 0.70 <sup>c</sup>
SDB300	0.006 $\pm$ 0.0007 <sup>a</sup>	2.9 $\pm$ 0.4 <sup>a</sup>	4.55 $\pm$ 0.14 <sup>a</sup>	-25.63 $\pm$ 0.54 <sup>a</sup>
SDB500	0.233 $\pm$ 0.03 <sup>b</sup>	378.7 $\pm$ 39.6 <sup>b</sup>	6.03 $\pm$ 0.02 <sup>b</sup>	-39.90 $\pm$ 1.20 <sup>b</sup>
SDB700	0.278 $\pm$ 0.04 <sup>b</sup>	594.9 $\pm$ 60.3 <sup>c</sup>	7.88 $\pm$ 0.08 <sup>c</sup>	-16.60 $\pm$ 0.29 <sup>c</sup>
ESB300	0.004 $\pm$ 0.0005 <sup>a</sup>	2.0 $\pm$ 0.2 <sup>a</sup>	7.89 $\pm$ 0.04 <sup>a</sup>	-9.99 $\pm$ 0.92 <sup>a</sup>
ESB500	0.006 $\pm$ 0.0007 <sup>ab</sup>	3.7 $\pm$ 0.4 <sup>ab</sup>	8.02 $\pm$ 0.11 <sup>a</sup>	-4.94 $\pm$ 1.63 <sup>b</sup>
ESB700	0.009 $\pm$ 0.0008 <sup>b</sup>	5.3 $\pm$ 0.5 <sup>b</sup>	9.46 $\pm$ 0.07 <sup>b</sup>	-2.99 $\pm$ 1.37 <sup>b</sup>

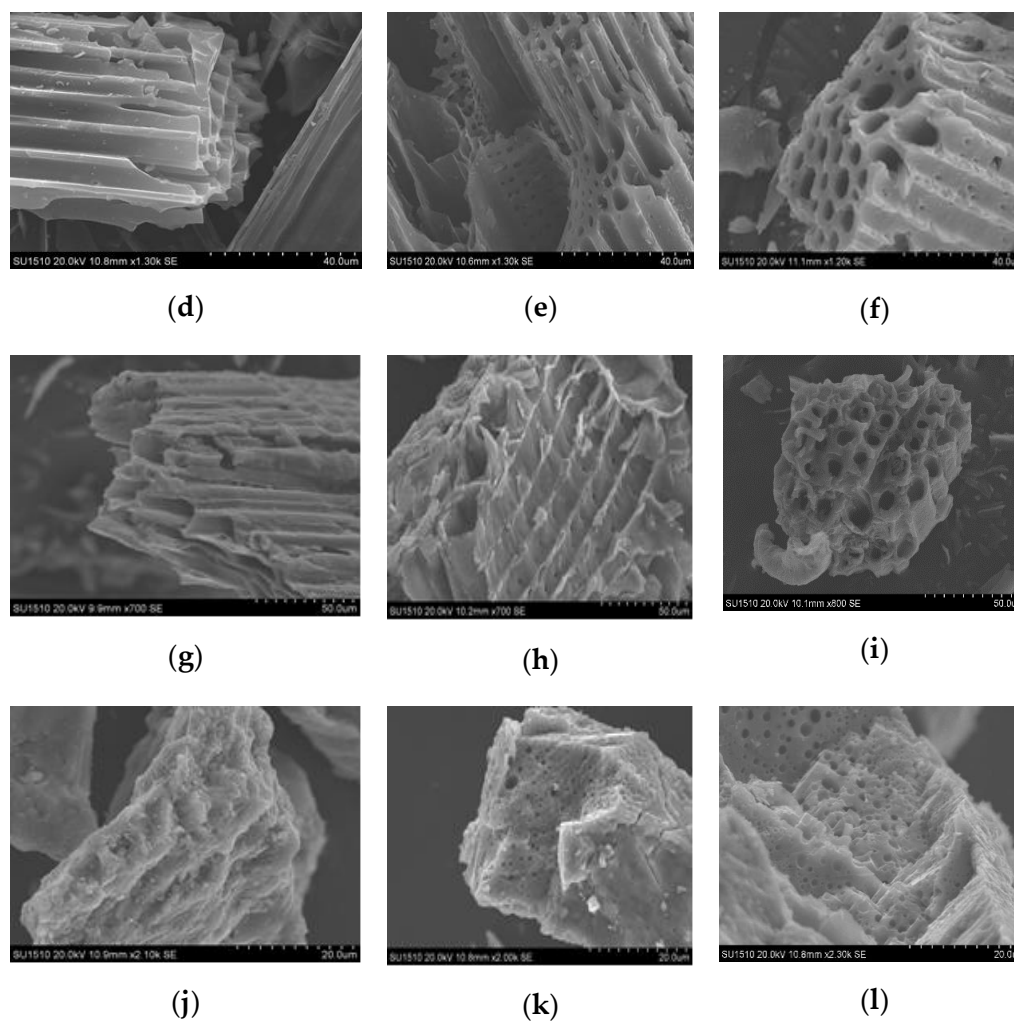
Data are means  $\pm$  SD of  $n = 3$ . Different letters in the same column indicate significant differences in different pyrolysis temperature for each biochar ( $p < 0.05$ ).

Zeta potential of PCB and ESB increased with pyrolysis temperatures (Table 1). The zeta potential significantly decreased for RSB and SDB produced from pyrolysis at 500 °C than at 300 °C ( $p < 0.05$ ). However, zeta potential significantly increased for RSB and SDB produced from pyrolysis at 700 °C than at 300 °C or 500 °C ( $p < 0.05$ ). Results showed that the response of zeta potential of biochars on pyrolysis temperature varied with biochar type.

The SEM images of the studied biochars are shown in Figure 1, the more and uniform hollow channels for each biochar occurred with increasing pyrolysis temperature. Compared to RSB, PCB and SDB biochar, ESB biochar had less small pore size with relatively lower porosity (Figure 1).



**Figure 1.** Cont.

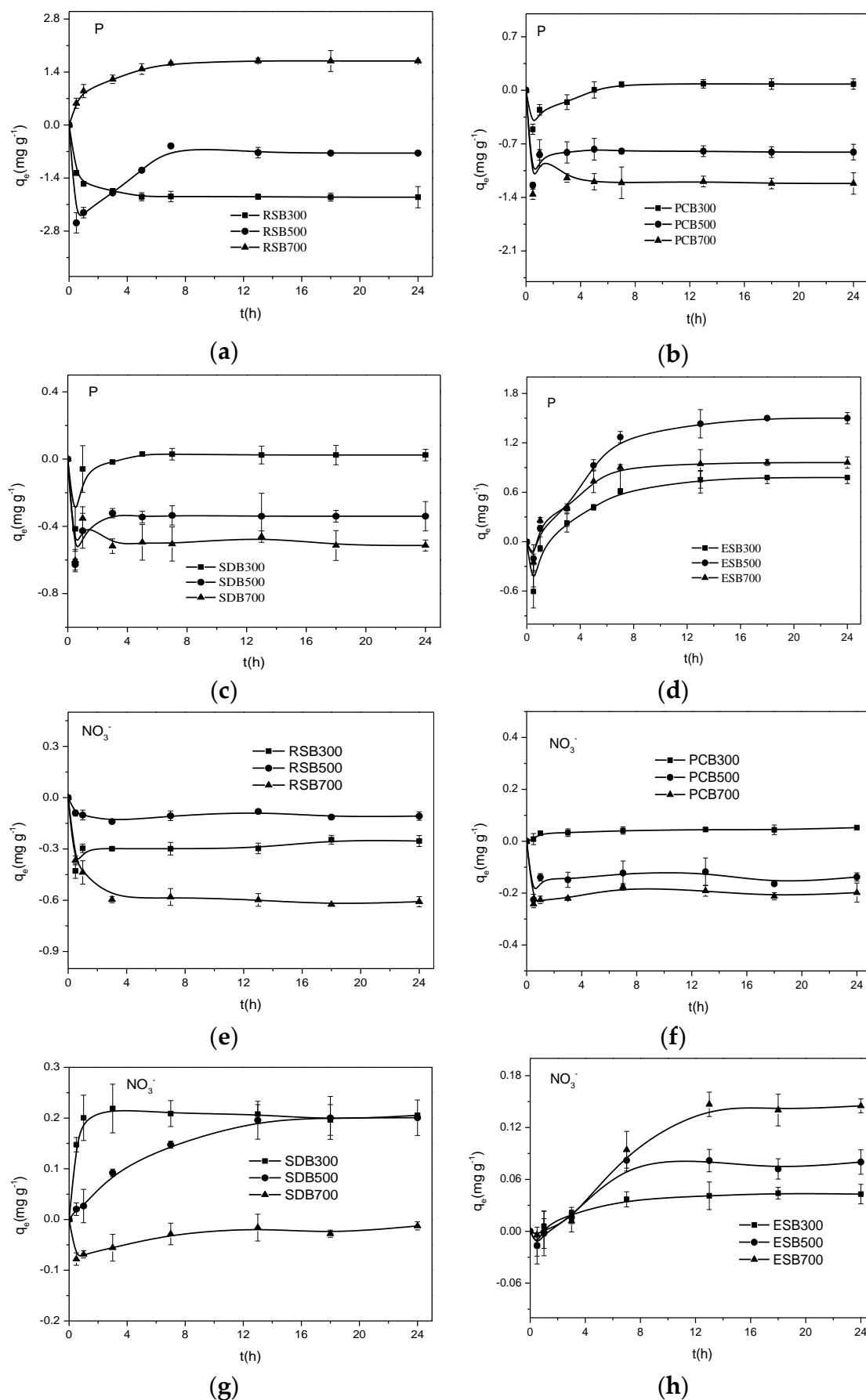


**Figure 1.** Scanning electron microscope (SEM) photos of RSB300 (a), RSB500 (b), RSB700 (c), PCB300 (d), PCB500 (e), PCB700 (f), SDB300 (g), SDB500 (h), SDB700 (i), ESB300 (j), ESB 500 (k) and ESB 700 (l), respectively.

### 3.2. Sorption Kinetics of Biochar

Adsorption or desorption of P on the biochars is shown in Figure 2. Release of P occurred in RSB300 and RSB500, PCB500 and PCB700, and SDB500 and SDB700 (Figure 2a–c), respectively. Similarly, PCB300 and SDB300 presented lower P adsorption capacity (Figure 2b,c): Novais et al. [23] showed that some biochars have very low or zero P adsorption, due to its behavior as “great anion”, which prevents the adsorption of anions such as phosphates. Schneider and Haderlein [24] demonstrated that the dissolved organic matter released from the biochar pyrolysis at 200 °C when placed into the P solution competed for sorption sites and inhibited P sorption. However, our results show that P was adsorbed by ESB300, ESB500 and ESB700 (Figure 2d), P adsorption capacity is therefore dependent on biochar type and the rate of adsorption is affected by pyrolysis temperature.





**Figure 2.** Adsorption kinetics of P and  $\text{NO}_3^-$  on RSB (a), PCB (b), SDB (c), ESB (d), RSB (e), PCB (f), SDB (g), and ESB (h), respectively. Data are means  $\pm$  SD of  $n = 3$ .

Release of  $\text{NO}_3^-$  occurred in RSB, PCB500, PCB700 and SDB700 (Figure 2e–g), respectively. However, adsorption of  $\text{NO}_3^-$  by ESB increased with time, and increased with pyrolysis temperature (Figure 2h). Therefore, ESB could adsorb both P and  $\text{NO}_3^-$ . As shown in Figure 2d,h, when the initial P and  $\text{NO}_3^-$  concentration was 20 mg/L, rapid adsorption on ESB was observed in the first 8h, which suggested that P and  $\text{NO}_3^-$  in solution was impelled to adhere to the surface of biochar.

To investigate adsorption mechanisms of P and  $\text{NO}_3^-$ , the sorption data were fitted with kinetic models, including the pseudo-first-order, pseudo-second-order and intra-particle diffusion model. According to Table 2, the pseudo-second-order kinetic model for adsorption P on RSB700, PCB300 and SDB300 showed the best fit to the experimental data with the highest  $R^2$  in a range of 0.994–0.999. These results are similar to those of Elsa et al. [25], who demonstrated that the pseudo-second-order kinetic model fits the experimental data better than the pseudo-first-order kinetic model for P adsorption. However, the pseudo-first-order kinetic model for ESB showed the best fit to the experimental data with the highest  $R^2$  in a range of 0.984–0.995 (Table 2). In this study, the intra-particle diffusion model didn't fit the data well with low  $R^2$  in a range of 0.601–0.893 (Table 2), indicating that intrapore diffusion does not dominate the adsorption process of P on the biochars.

**Table 2.** Parameters of P adsorption kinetics of different biochars.

Sample	Pseudo-First-Order			Pseudo-Second-Order			Intra-particle Diffusion		
	$K_1$ ( $\text{h}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_2$ ( $\text{g mg}^{-1} \text{h}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_3$ ( $\text{mg g}^{-1} \text{h}^{-0.5}$ )	C ( $\text{mg g}^{-1}$ )	$R^2$
RSB700	0.005	0.998	0.865	0.009	1.790	0.999	0.032	0.703	0.778
PCB300	0.006	0.430	0.868	0.622	0.084	0.998	0.016	−0.392	0.706
SDB300	0.008	0.100	0.800	4.480	0.024	0.994	0.002	−0.046	0.601
ESB300	0.006	1.879	0.966	0.012	0.827	0.951	0.038	−0.411	0.800
ESB500	0.004	2.027	0.995	0.020	1.514	0.919	0.054	−0.231	0.893
ESB700	0.006	1.534	0.984	0.011	1.026	0.947	0.033	−0.053	0.753

According to Table 3, the pseudo-second-order kinetic model for  $\text{NO}_3^-$  adsorption on PCB300, SDB300 and SDB500 showed the best fit to the experimental data with the highest  $R^2$  in a range of 0.974–0.992. This suggests that  $\text{NO}_3^-$  adsorption process is mainly chemical adsorption. However, the pseudo-first-order kinetic model for  $\text{NO}_3^-$  adsorption on ESB showed the best fit to the experimental data with the highest  $R^2$  in a range of 0.906–0.989. The results suggest that the intra-particle diffusion model didn't fit the data well with low  $R^2$  in a range of 0.784–0.914 (Table 3). The pseudo-first-order model is widely used to describe reversible physical adsorption between the adsorbent and the adsorbate [26]. The pseudo-second-order model indicated that the adsorption of P onto calcium-flour biochar was a chemisorptions-dominated process [27]. Therefore, in this study, the pseudo-second-order model could be used to predict the kinetic process for P and  $\text{NO}_3^-$  sorption on PCB and SDB, which was a chemisorptions-dominated process. However, the pseudo-first-order model could be suitable to predict the kinetic process for P and  $\text{NO}_3^-$  sorption on EBS, which is a physisorption-dominated process.

**Table 3.** Parameters of  $\text{NO}_3^-$  adsorption kinetics of different biochars.

Sample	Pseudo-First-Order			Pseudo-Second-Order			Intra-Particle Diffusion		
	$K_1$ ( $\text{h}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_2$ ( $\text{g mg}^{-1} \text{h}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_3$ ( $\text{mg g}^{-1} \text{h}^{-0.5}$ )	C ( $\text{mg g}^{-1}$ )	$R^2$
PCB300	0.001	0.028	0.764	0.153	0.053	0.984	0.001	0.015	0.771
SDB300	0.001	0.023	0.700	0.287	0.216	0.992	0.001	0.177	0.328
SDB500	0.006	0.300	0.968	0.010	0.267	0.974	0.006	−0.002	0.928
ESB300	0.004	0.047	0.970	0.449	0.044	0.966	0.002	−0.009	0.804
ESB500	0.008	0.127	0.906	0.097	0.05	0.878	0.003	−0.021	0.814
ESB700	0.003	0.193	0.989	0.024	0.112	0.935	0.005	−0.036	0.914

### 3.3. Sorption Isotherms of Biochar

The amount of P adsorption by RSB700 increased with P concentration in the initial solution. Release of P from RSB300 and RSB500 occurred when P concentration was  $< 80 \text{ mg L}^{-1}$  in the

initial solution (Figure 3a). The amount of P adsorption by PCB300 and PCB500 increased with P concentration in the initial solution (Figure 3b). However, release of P from PCB700 occurred for different P concentrations in the initial solution (Figure 3b). Zhang et al. [19] showed that timber biochar and peanut shell biochar released P when the P concentration was < 100 mg P L<sup>-1</sup>, but they retained 1–2% P when the P concentration in the solution was 200 mg P L<sup>-1</sup>. It can be seen from Figure 3c that SDB300, SDB500 and SDB700 released P when the P concentration was < 5 mg L<sup>-1</sup>, but they adsorbed P when P concentration was >80 mg L<sup>-1</sup>. Therefore, the P adsorption capacity of the biochars was influenced by the P concentration in the initial solution. These results are similar to those of Chintala et al. [22], who demonstrated that P adsorption on biochars was significantly affected by initial P concentration and biochar types. According to Figure 3d, ESB300, ESB500 and ESB700 had a capacity to adsorb P, and ESB700 exhibited the highest P sorption capacity.

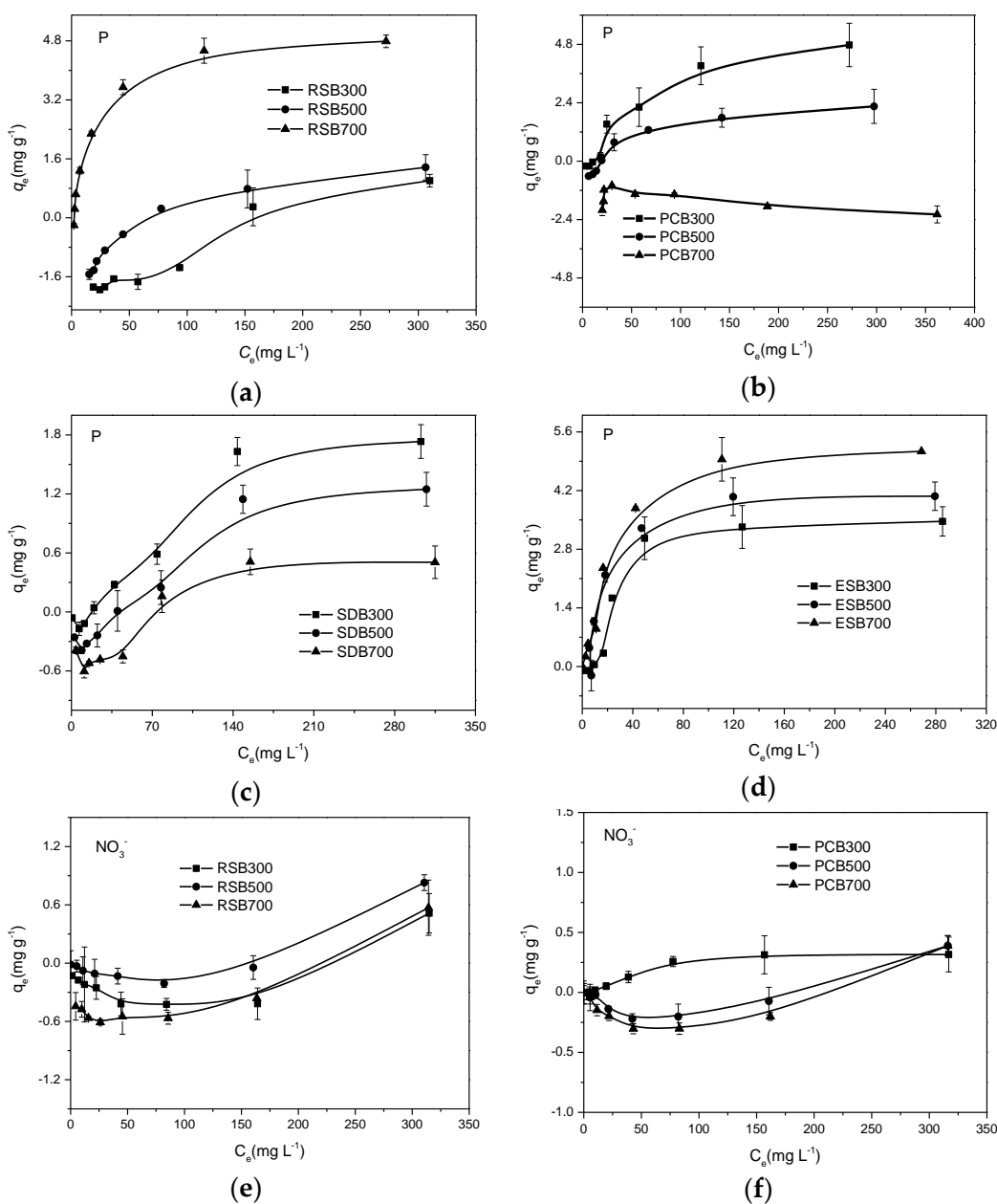
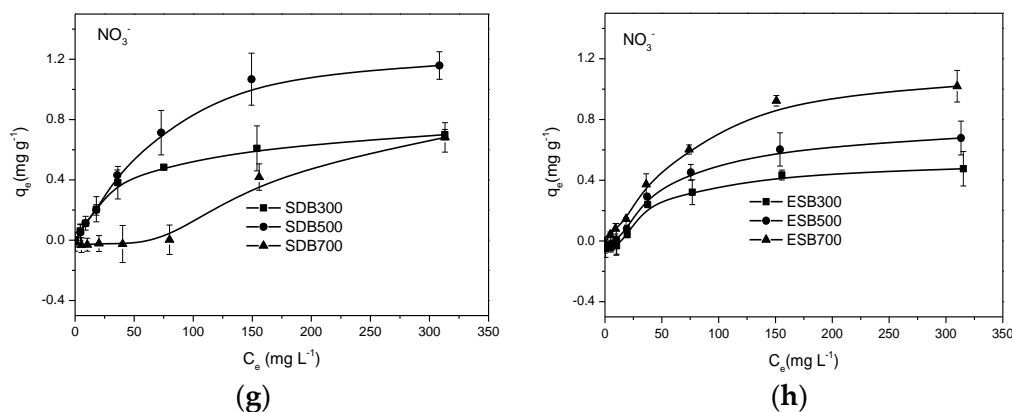


Figure 3. Cont.



**Figure 3.** Adsorption isotherms of P and  $\text{NO}_3^-$  on RSB (a), PCB (b), SDB (c), ESB (d), RSB (e), PCB (f), SDB (g), and ESB (h), respectively. Data are means  $\pm$  SD of  $n = 3$ .

It can be seen from Figure 3e,f, RSB and PCB cannot adsorb  $\text{NO}_3^-$  in the lower initial  $\text{NO}_3^-$  concentration. The results are similar to those of Hale et al. [15], who found that cacao-shell derived biochar could not adsorb  $\text{NO}_3^-$ . The amount of adsorption  $\text{NO}_3^-$  on SDB and ESB increased with initial  $\text{NO}_3^-$  concentration (Figure 3g,h). The order of  $\text{NO}_3^-$  adsorption capacity on ESB was that of  $\text{ESB700} > \text{ESB500} > \text{ESB300}$  (Figure 3h). However, the order of  $\text{NO}_3^-$  adsorption on SDB was shown as following:  $\text{SDB500} > \text{SDB300} > \text{SDB700}$  (Figure 3g). These results showed that the  $\text{NO}_3^-$  adsorption capacity on biochars was also influenced by types of biochar and pyrolysis temperatures.

RSB700, PCB300, PCB500, SDB300, SDB500, and ESB have the ability to adsorb P from P solutions, so their P adsorption isotherms were investigated to elucidate the adsorption mechanisms. The model parameters for P on biochars for both Langmuir and Freundlich models are presented in Table 4, which show that the Langmuir model fits the experimental data better ( $0.981 > R^2 > 0.852$ ) than the Freundlich model ( $0.897 > R^2 > 0.728$ ). Similarly, PCB300, SDB300, SDB500, ESB300, ESB500 and ESB700 have the ability to adsorb  $\text{NO}_3^-$ . Therefore, their model parameters for  $\text{NO}_3^-$  on biochars for both Langmuir and Freundlich models are presented in Table 5, which show that the Langmuir model fits the experimental data better ( $0.996 > R^2 > 0.919$ ) than the Freundlich model ( $0.949 > R^2 > 0.850$ ). Therefore, the Langmuir equation fitted the data better than the Freundlich equation for adsorption P and  $\text{NO}_3^-$  (Tables 4 and 5). This is consistent with Tan et al. [28], who showed that the Langmuir equation had the best fit for the experiment. Elsa et al. [25] demonstrated that the Freundlich constant ( $K_F$ ) increased with the calcium content, which confirms the increase in adsorption intensity of the biochar due to the chemical reaction between phosphate ions and  $\text{Ca}^{2+}$ . In this study,  $K_F$  for P and  $\text{NO}_3^-$  adsorption on ESB increased with pyrolysis temperature.

**Table 4.** Parameters of P adsorption isotherms of different biochars.

Sample	Langmuir			Freundlich		
	$q_{\max}$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg g}^{-1}$ )	n	$R^2$
RSB700	5.407	0.039	0.981	0.611	2.558	0.876
PCB300	7.747	0.007	0.942	0.125	1.501	0.897
PCB500	3.270	0.008	0.933	0.026	1.246	0.760
SDB300	3.859	0.003	0.903	0.019	1.230	0.872
SDB500	3.395	0.002	0.911	0.002	0.871	0.728
ESB300	4.538	0.018	0.852	0.244	2.009	0.760
ESB500	4.922	0.030	0.920	0.482	2.458	0.800
ESB700	6.084	0.031	0.973	0.598	2.542	0.855

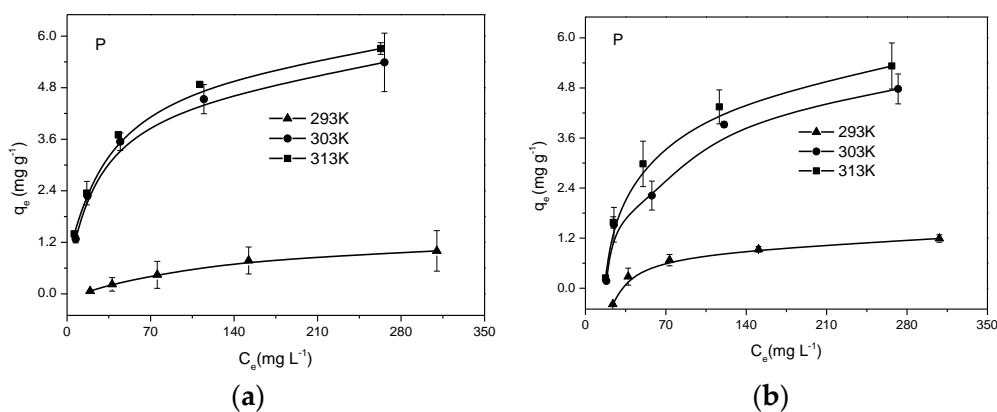
**Table 5.** Parameters of  $\text{NO}_3^-$  adsorption isotherms of different biochar.

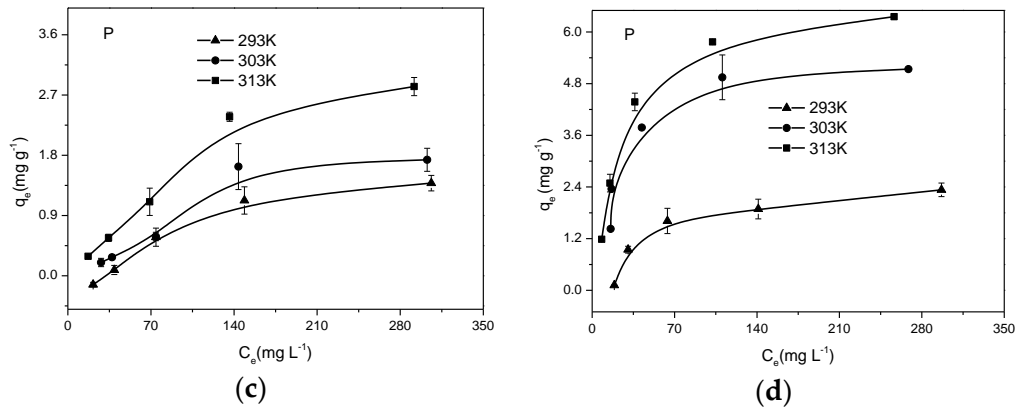
Sample	Langmuir			Freundlich		
	$q_{\max}$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg g}^{-1}$ )	n	$R^2$
PCB300	0.433	0.012	0.955	0.021	2.006	0.876
SDB300	0.804	0.021	0.996	0.070	2.416	0.949
SDB500	1.574	0.011	0.989	0.067	1.941	0.941
ESB300	0.671	0.010	0.919	0.020	1.735	0.850
ESB500	0.937	0.010	0.963	0.032	1.810	0.901
ESB700	1.426	0.010	0.987	0.051	1.855	0.941

The maximum adsorption of P and  $\text{NO}_3^-$  ( $q_{\max}$ ) on ESB was lower in the biochar produced through pyrolysis at 300 °C than at 700 °C (Tables 4 and 5), indicating that the maximum adsorption of P and  $\text{NO}_3^-$  increased with pyrolysis temperature. Our results are similar to those of Zhang et al. [20], who found that biochar, produced from horse manure and bedding compost at pyrolysis of 200 °C, released the P and  $\text{NO}_3^-$ . However, the maximum adsorption of P ( $q_{\max}$ ) on PCB and SDB was lower in the biochar produced at pyrolysis temperature of 500 °C than at 300 °C. Therefore, the maximum adsorption of P on biochar was influenced by pyrolysis temperature. The maximum adsorption of P ( $q_{\max}$ ) on RSB700, PCB300, SDB300 and ESB700 was 5.407, 7.747, 3.859 and 6.084  $\text{mg g}^{-1}$ , respectively. The maximum adsorption of P ( $q_{\max}$ ) on PCB300 was approximately two times that of SDB300. The maximum adsorption of  $\text{NO}_3^-$  ( $q_{\max}$ ) on PCB300, SDB300 and ESB700 was 0.443, 1.574 and 1.426  $\text{mg g}^{-1}$ , respectively. Kameyama et al. [21] found that only 1.2 and 0.7  $\text{mg g}^{-1}$   $\text{NO}_3^-$  could be adsorbed by the bamboo powder charcoal and sugarcane bagasse derived biochar, respectively. In this study, the  $\text{NO}_3^-$  adsorption capacity was between 0.443 to 1.426  $\text{mg g}^{-1}$ . Therefore, the capacity to absorb  $\text{NO}_3^-$  was lower but varied with the biochars from different feedstock materials.

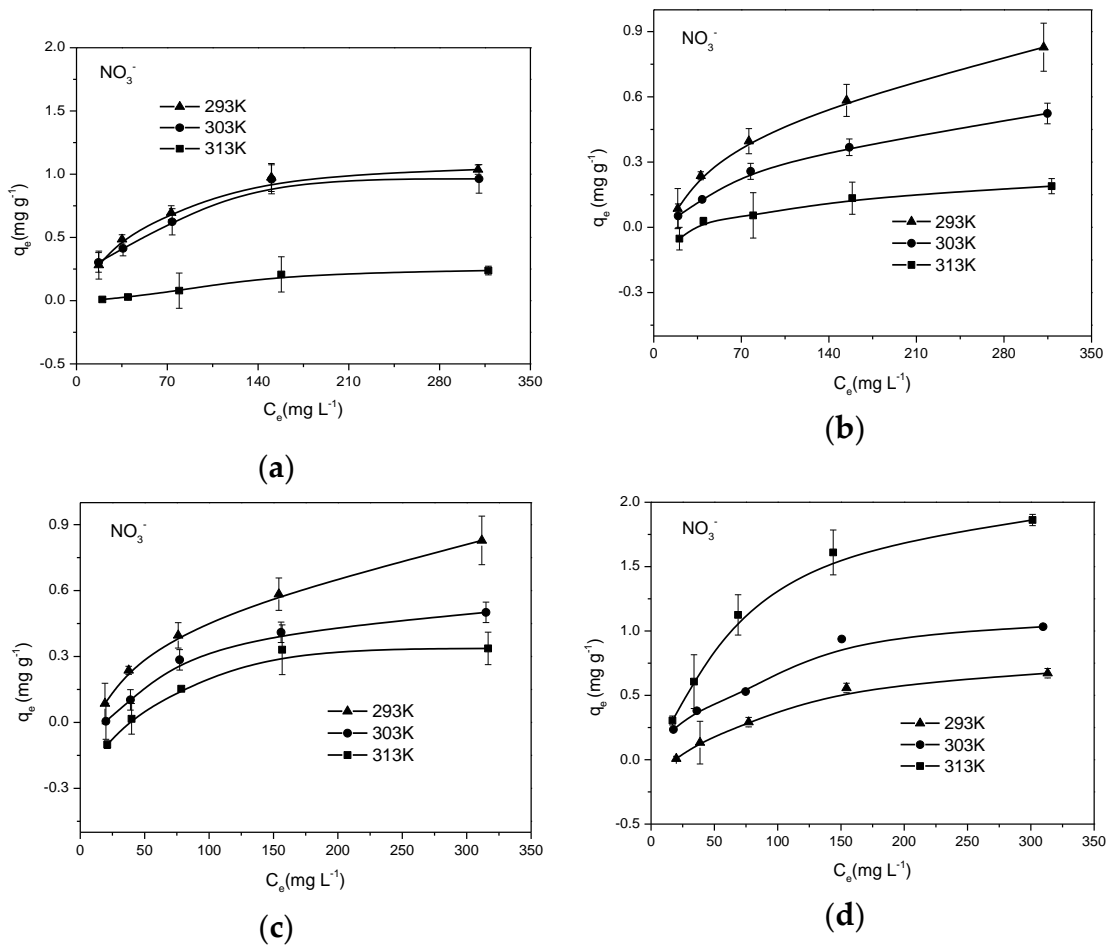
### 3.4. Adsorption Thermodynamics of Biochars

The thermodynamics of P and  $\text{NO}_3^-$  adsorption on the biochars at 293, 303, and 313 K were analyzed (Figures 4 and 5). As shown in Table 6, the  $\Delta H^0$  value for RSB700, PCB300, SDB300 and ESB700 was 83.54, 44.63, 27.53 and 39.68  $\text{kJ mol}^{-1}$ , respectively, indicating that P adsorption process was endothermic. The  $\Delta S^0$  value for RSB700, PCB300, SDB300 and ESB700 was 0.33, 0.19, 0.13 and 0.19  $\text{kJ mol}^{-1} \text{K}^{-1}$ , respectively, indicating increased disorder and randomness of liquid-solid phase interaction at the biochar surface [29]. Zhang et al. [30] demonstrated that P tended to be adsorbed on the surface of biochar when the  $\Delta S^0$  values were positive. The  $\Delta G^0$  values were in a range of  $-10.48$  to  $-18.41$   $\text{kJ mol}^{-1}$  indicating that the process of  $\text{PO}_4^{3-}$  adsorption onto the biochar was mainly spontaneous [31,32]. Furthermore, the  $\Delta G^0$  decreased with increasing adsorption reaction temperature, indicating a better P adsorption efficiency at a higher solution temperature [33].

**Figure 4.** Cont.



**Figure 4.** Amount of P on RSB700 (a), PCB300 (b), SDB300 (c) and ESB700 (d) under different temperature. Data are means  $\pm$  SD of  $n = 3$ .



**Figure 5.** Amount of  $\text{NO}_3^-$  on RSB500 (a), PCB300 (b), SDB500 (c) and ESB300 (d) under different temperature, respectively. Data are means  $\pm$  SD of  $n = 3$ .

**Table 6.** Thermodynamic parameters for P and NO<sub>3</sub><sup>−</sup> adsorption.

T(K)	Sample	P			Sample	NO <sub>3</sub> <sup>−</sup>		
		$\Delta H^0$ (kJ mol <sup>−1</sup> )	$\Delta S^0$ (kJ mol <sup>−1</sup> K <sup>−1</sup> )	$G^0$ (kJ mol <sup>−1</sup> )		$\Delta H^0$ (kJ mol <sup>−1</sup> )	$\Delta S^0$ (kJ mol <sup>−1</sup> K <sup>−1</sup> )	$\Delta G^0$ (kJ mol <sup>−1</sup> )
293	RSB700	83.54	0.33	−11.95	RSB500	−70.80	−0.19	−13.47
303				−17.70				−12.69
313				−18.41				−9.73
293	PCB300	44.63	0.19	−11.27	PCB300	−25.37	−0.05	−10.79
303				−13.92				−10.70
313				−15.07				−9.73
293	SDB300	27.53	0.13	−10.48	SDB500	−27.44	−0.06	−10.79
303				−11.99				−10.70
313				−13.07				−8.67
293	ESB700	39.68	0.19	−14.53	ESB300	39.20	0.17	−9.81
303				−17.47				−12.45
313				−18.20				−13.11

The  $\Delta H^0$  value for RSB500, PCB300 and SDB500 was  $-70.8$ ,  $-25.37$  and  $-27.44$  kJ mol<sup>−1</sup> (Table 6), respectively, indicating that NO<sub>3</sub><sup>−</sup> adsorption process was an exothermic reaction. However, the  $\Delta H^0$  value for ESB was  $39.2$ , indicating this was endothermic. The  $\Delta S^0$  value for RSB, PCB and SDB was  $-0.19$ ,  $-0.05$ , and  $-0.06$  kJ mol<sup>−1</sup> k<sup>−1</sup>, respectively, indicating decreased disorder. However, the  $\Delta S^0$  value for ESB was  $0.17$  kJ mol<sup>−1</sup> k<sup>−1</sup>, suggesting increased disorder. The  $\Delta G^0$  values were in the range of  $-8.67$  to  $-13.47$  kJ mol<sup>−1</sup> indicating that the process of NO<sub>3</sub><sup>−</sup> adsorption onto the biochars was also spontaneous in nature. The  $\Delta G^0$  of RSB, PCB and SDB increased with adsorption reaction temperatures, indicating a better NO<sub>3</sub><sup>−</sup> adsorption efficiency at a lower solution temperature. However, the  $\Delta G^0$  of ESB decreased with increasing adsorption reaction temperature, indicating a better NO<sub>3</sub><sup>−</sup> adsorption efficiency at a higher solution temperature [33]. Results show that NO<sub>3</sub><sup>−</sup> adsorption process on the biochars produced from feedstocks rich in cellulose, hemicellulose and lignin was an exothermic reaction, but an endothermic reaction occurred for the biochar produced from egg shell.

### 3.5. Effect of Characteristic of Biochar on Capacity of Nitrate and Phosphate Adsorption

Cellulose, hemicellulose, and lignin are essential constituents of plant cell walls. In this study, RSB, PCB and SDB derived from the plants waste showed limited adsorption of, or even released, NO<sub>3</sub><sup>−</sup> and P. These findings agree with Zhang et al. [34] who found that the pristine biochar surface is negatively charged, and thus cannot easily adsorb the negatively charged NO<sub>3</sub><sup>−</sup> and P. Plant-derived biochar used in this study had a low zeta potential ( $-16.6$  to  $-41.9$  mV), meaning that electrostatic repulsion between the negatively charged surface sites and electronegative phosphate species resulted in the lower phosphate adsorption [35]. Yang et al. [36] demonstrated that positive zeta potential is desirable to the adsorption of anion by electrostatic attraction and in this study egg shell biochar (ESB) had a positive zeta potential in the range  $-2.9$  to  $-4.9$  mV.

The NO<sub>3</sub><sup>−</sup> and P adsorption capacity of egg shell biochar was influenced by surface area and porosity characteristic. The SEM images of ESB showed that there was more porosity of ESB produced at  $700$  °C than at  $300$  °C (Figure 1). The P and NO<sub>3</sub><sup>−</sup> adsorption capacities were higher in ESB700 than in ESB300, which was related to more porous structure and higher surface area in ESB700 than in ESB300 (Table 1). These findings agreed with those of Yin et al. [37], who demonstrated that the porous structure and higher surface area could contribute to better PO<sub>4</sub><sup>3−</sup> and NO<sub>3</sub><sup>−</sup> adsorption. Therefore, the higher surface area of egg shell biochar seems to improve adsorption of NO<sub>3</sub><sup>−</sup> and P.

The NO<sub>3</sub><sup>−</sup> and P adsorption capacity of biochars could be improved by adjusting pyrolysis temperature. Many methods have been used to improve NO<sub>3</sub><sup>−</sup> and P adsorption capacity. It was reported that the dashed activated carbon could adsorb  $9.84$  mg NO<sub>3</sub><sup>−</sup> g<sup>−1</sup> [38]. The NO<sub>3</sub><sup>−</sup> adsorption on the La-modified biochar was  $8.81$  mg g<sup>−1</sup>, which was considerably higher than that on the pristine biochar ( $2.81$  mg g<sup>−1</sup>) [39]. The Mg-modified sugar beet tailing biochar showed a P adsorption capacity of  $6.67$  mg g<sup>−1</sup> [35]. The sesame straw biochar activated by ZnCl<sub>2</sub> showed the highest phosphorus adsorption capacity of  $9.39$  mg g<sup>−1</sup> [40]. The poplar chips biochar modified by Al showed its high P

adsorption capacity of 43.98 mg g<sup>-1</sup> [37]. Results of this study showed that the NO<sub>3</sub><sup>-</sup> and P adsorption capacity could be enhanced by adjusting pyrolysis temperature. For example, the maximum sorption of P on RSB, produced at pyrolysis temperature of 700 °C, was 5.40 mg g<sup>-1</sup>. Compared with RSB300 and RSB500, RSB700 with higher P adsorption capacity could be attributed to higher surface area and total volume (Table 1). Similarly, the maximum sorption of NO<sub>3</sub><sup>-</sup> on SDB, derived from pyrolysis at 300 °C, was 1.574 mg g<sup>-1</sup>. Iida et al. [38] demonstrated that the NO<sub>3</sub><sup>-</sup> adsorption process would be restricted under basic conditions because the OH<sup>-</sup> competes with NO<sub>3</sub><sup>-</sup> for the adsorption sites on the biochar surface. Ketcha et al. [41] also found that the optimum pH value of NO<sub>3</sub><sup>-</sup> adsorption on activated carbon was in the range of 2.8–6.5. Therefore, the ability of SDB300 to adsorb NO<sub>3</sub><sup>-</sup> could be related to their lower pH derived from pyrolysis at 300 °C (Table 1). Results suggested that the P and NO<sub>3</sub><sup>-</sup> adsorption capacity could be improved through screening biochars derived from different feedstock materials and pyrolysis temperatures.

#### 4. Conclusions

The physicochemical characteristics of biochars were influenced by feedstock type and pyrolysis temperature, which affected the N and P adsorption capacity. Biochars derived from plant wastes, including RSB, PCB and SDB, had limited adsorption or even released NO<sub>3</sub><sup>-</sup> and P. However, their PO<sub>4</sub><sup>3-</sup> adsorption capacity improved by adjusting pyrolysis temperature. Egg shell biochar (ESB) has an ability to adsorption both NO<sub>3</sub><sup>-</sup> and P, which increased with increasing pyrolysis temperatures. The maximum NO<sub>3</sub><sup>-</sup> and P adsorption on ESB700, produced at pyrolysis temperature of 700 °C was 1.426 and 6.084 mg g<sup>-1</sup>, respectively. Surface area and zeta potential of ESB could be the two predominant factors affecting NO<sub>3</sub><sup>-</sup> and P adsorption. The influences of pyrolysis temperature on adsorption of both NO<sub>3</sub><sup>-</sup> and P varied between feedstock materials.

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