Pyrolysis temperature and steam activation effects on sorption of phosphate on pine sawdust biochars in aqueous solutions

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ABSTRACT
Biochar can be used as an adsorbent for phosphate removal in aquatic environments to treat eutrophication problems. Designing biochars that have large phosphate adsorption capacity through altering pyrolysis conditions and applying activation techniques will improve phosphate removal efficiency. In this study, four pine sawdust biochars were produced at 300 and 550 °C with and without steam activation. Batch sorption experiments including isotherm and kinetic studies were conducted to understand how phosphate removal capabilities and adsorption mechanisms of biochars were affected by pyrolysis temperature and steam activation. Our results showed that the steam activation and pyrolysis temperature did not affect phosphate adsorption by the biochars. The four biochars removed <4% of phosphate from the aqueous solution, which were not affected by the pH of the solution and biochar application rate. The repulsion forces between biochar surfaces and phosphate ions were likely the cause of the low adsorption.

1. Introduction
Phosphorus (P) is a limiting nutrient for the growth of algae in many aquatic environments and increased P concentrations in water bodies such as lakes, ponds and rivers cause eutrophication.[1,2] Human activities such as changing forest land to agricultural or urban use, P fertilisation on agricultural land, and livestock production have greatly increased P abundance in the environment in recent years.[3,4] In a recent study of Lake Winnipeg,[2] the severe eutrophication problem was also related to the increased intensity and frequency of spring floods, which had enhanced the flow of nutrients from the landscape to the lake, as well as draining of wetlands that otherwise could function as buffer zones for runoffs.[2]

The need to reduce P input and remove P from water bodies to minimise eutrophication problems has been widely recognised.[2,5] There are numerous technologies to remove P from water bodies to mitigate eutrophication. Conventional technologies to remove P include electro-dialysis, reverse osmosis, and ion exchange.[6,7] However, these technologies are usually applied on a small scale or require sophisticated equipment. Chemical treatments would require the addition of divalent or trivalent metal salts to precipitate P, and settle the insoluble metal phosphate down in the polluted water. One of the disadvantages of such chemical treatments is that the effective removal of P relies on the application rate, solution pH, reaction temperature, and other co-existing chemicals in the environment. In addition, the creation and handling of a large amount of sludge that result from such treatments can be a problem.[6,8] Biological P removal using activated sludge to uptake P can avoid the use of chemicals, however, more complex operations and hardware configurations with high capital cost are required.[6] Other techniques such as crystallisation and magnetic attraction are either energy intensive or require specialised equipment.[6] Materials that are easy to use and cost effective should be explored to deal with phosphate contamination problems.

Adsorption using waste materials containing lime, alum, and iron salts [6] has been demonstrated to be cost-effective for removing P from aqueous solutions while not generating extra sludge. For instance, iron oxide tailings [9] and red mud [10] were used for P removal in aquatic environments. Karageorgiou et al. [11] reported the effective removal of P by calcite under basic pH and high Ca to P ratios, and the removal effectiveness was time dependent. Ugurlu and Salman [12] used fly ash that contains calcite to adsorb P, which was most effective at 40 °C.

Biochar, as a recalcitrant carbon material, has been widely studied in terms of its role in carbon sequestration
and as a soil amendment. Biochar is usually produced from carbon-rich biomass through thermal decomposition in oxygen-limited environments.[13–15] Biochar can act as an effective adsorbent for both organic and inorganic matters in the soil and water.[16,17] Biochar’s capacity in removing P spans a wide range. For instance, Chen et al. [18] found that biochar made from iron treated orange peel powders had a removal capacity of 1.2 mg P g\(^{-1}\). Yao et al. [19] reported that biochar derived from anaerobically digested sugar beet tailings had a superior P adsorption capacity (133.1 mg P g\(^{-1}\)) under a range of pH and competing ion conditions. In another study, Yao et al. [20] used magnesium-modified biochar with an adsorption capacity over 100 mg P g\(^{-1}\) to recover phosphate from aqueous solutions. The adsorption capacity of biochar is largely dependent on its surface characteristics (e.g. surface area, the type and density of surface charge, elemental composition, and functional groups on the surface) shaped by feedstock type and production condition.[16,21] However, there are few studies conducted to understand the effects of pyrolysis condition on biochar’s removal capability for P in aqueous solutions.

During pyrolysis of biomass, thermal degradation and carbonisation of hemicellulose, cellulose and lignin with subsequent structural transformations are involved.[22] High temperature leads to high degrees of carbonisation, resulting in the formation of aromatic and graphitic structure,[23] and reduction of amorphous content.[24] In order to achieve better adsorption, enlarging surface area by steam activation is a common practice applied during biochar production.[25] In addition, steam activation can improve access to functional groups by releasing volatile matters that block biochar’s pores, and as well as potentially modify surface functional groups.[16,25,26]

Sawdust is a byproduct from timber sawing in sawmills and is often disposed as waste materials or simply burnt for bioenergy production. Making biochar out of sawdust and using the biochar as an adsorbent for removing P from polluted water has the dual function of waste utilisation and pollution reduction. Currently, no study has been conducted to understand the effect of pyrolysis temperature and steam activation on sawdust biochar’s removal capability for P. The objective of this study was to evaluate the effect of pyrolysis temperature and steam activation on the effectiveness of biochars for P adsorption. We hypothesised that pine sawdust biochars produced at a higher temperature with steam activation would have better adsorption capacity for phosphate because of the greater surface area and more functional groups created under those conditions. Batch sorption experiments including isotherm and kinetic studies were conducted to evaluate the adsorption effectiveness and the mechanisms for P sorption. During sorption, effects of biochar application rates and solution pH on the adsorption were also studied.

2. Materials and methods

2.1. Biochar production

Sawdust from Korean pine (Pinus koraiensis) trees was obtained from a sawmill company in Seoul, South Korea. The sawdust was washed with deionised water, air dried, and grounded to less than 1.0 mm in size for biochar production. Based on the Thermal Gravimetric Analysis (data not shown), a drastic weight loss of the pine sawdust biochar occurred at pyrolysis temperature around 350 °C, which indicating a shift of compositional change of biochar, and after 500–550 °C, biochar’s weight remained relatively stable. Thus, we predict that biochars produced at 300 and 550 °C will possess distinct properties from each other. A heating rate of 7 °C min\(^{-1}\) was applied for 2 h with limited oxygen. Steam activation was applied to half of the samples produced at each temperature in a modified N11/H Nabertherm (Germany) furnace.[25] For steam activation, samples were treated with 5 mL min\(^{-1}\) of steam for an additional 45 min at the peak temperature after pyrolysis. Four biochars (BC300, BC300-S, BC550 and BC550-S) were produced. The letters BC and S represent biochar and steam activation, respectively. Values 300 and 550 represent the peak temperatures used in pyrolysis.

2.2. Biochar characterisation

The pH of biochar was determined in 1% (w/v) biochar/deionised water suspension using a pH metre (Thermo Orion, 710A, Beverly, MA, USA). Elemental composition (C, H, O and N) of each biochar was determined through a dry combustion method using an elemental analyser (Carlo Erba, EA1108, Milan, Italy). Moisture, mobile matter, ash, and residence matter contents were determined following Ahmad et al. [27] and Rajapaksha et al. [25]. Surface functional groups of biochars were characterised by Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet, 8700, Madison, WI, USA). All peak assignments in the FTIR spectra were based on previous studies.[21,25] Surface morphologies were examined using a scanning electron microscopy (SEM, Zeiss EVO MA 15, Jena, Germany).

The pH at the point of zero charge (pH\(_{\text{pzc}}\)) was determined by the pH drift method originally developed for activated carbon.[28] This method has been widely used to determine pH\(_{\text{pzc}}\) for biochars.[23,28,29] Briefly, all biochars were washed with 0.1 M HCl (27 g biochar L\(^{-1}\)) by constant stirring for 1 h to remove soluble salts, rinsed with deionised water, and dried overnight at 80 °C. A CaCl\(_2\) solution (5 mM) was then boiled to remove CO\(_2\), and cooled to room temperature. A biochar sample (0.06 g) was added to 20 mL of CaCl\(_2\) solution pre-adjusted to pH 3, 4, 6, 8, 10 using 0.5 M HCl or NaOH followed by equilibration for 24 h in a shaker prior to pH\(_{\text{pzc}}\) measurement. The pH\(_{\text{pzc}}\) was determined after the final pH was
measured and plotted against the initial pH. The pH_{pzc} is the point where the curve pH_{final} vs. pH_{initial} crosses the line where pH_{initial} = pH_{final}. The Brunauer–Emmett–Teller (BET) specific areas of the four biochars were determined in duplicates by nitrogen isotherms at 77 K using a gas adsorption analyser (Quantachrome Autosorb 1 MP, Quantachrome, Boynton Beach, FL, USA).

### 2.3. Sorption experiment

Biochars were washed by deionised water and oven-dried at 80 °C before the sorption experiment. The washing operation removed soluble salts on the biochar surface. Phosphorus solutions with a range of concentrations were prepared by dissolving KH₂PO₄ (certified A.C.S., Fisher Scientific) in deionised water. The isotherm experiment was conducted with a concentration range from 0 to 40 mg P L⁻¹ solution and biochar application rate was 2 g L⁻¹ (0.05 mg biochar applied into 25 mL solution). Since chemical forms of phosphate is pH sensitive, we conducted the sorption without controlling pH or at pH 7.0 ± 0.1 adjusted using 0.1 M of HCl or NaOH. Under uncontrolled pH conditions, the biochar’s solution pH was not adjusted and kept unchanged. Biochar application rates of 2, 4, 12, 20 g L⁻¹ were used to study the effect of solid/solution ratio on phosphate adsorption. Centrifuge tubes (corning) were used for the sorption experiment, and samples were shaken for 48 h to achieve equilibrium. After equilibrium, suspended mixtures were filtered through 0.45 μm nylon membrane filters. The phosphate concentrations in the extracts were determined by the ascorbic acid method.[30] All treatments were replicated three times. The kinetic study was conducted at an initial concentration of 20 mg P L⁻¹ with a biochar application rate of 2 g L⁻¹ at pH 7.0 ± 0.1. The total time used for the kinetic study was 50 h. Samples were collected on the first hour and then every 10 h to determine the phosphate concentrations. All experiments were conducted at room temperature (295 K), and the average values are reported.

### 3. Results and discussion

#### 3.1. Effects of pyrolysis temperature and steam activation on biochar properties

Pyrolysis temperature affected the properties of pine sawdust biochars. Biochars produced at the lower temperature (BC300 and BC300-S) had pH values around 5 while those produced at the higher temperature (BC550 and BC550-S) had basic pH (Table 1). The pH_{pzc} of each biochar was around 4; therefore, the four biochars had negatively charged surfaces under the pH conditions in the study solutions. Increasing the pyrolysis temperature increased the porosity of biochar as more mobile matter was removed, resulting in higher surface areas in BC550 and BC550-S (Table 1). Further, the surface area

![Table](image_url)
that biochars made at 550 °C were more aromatic and less polar, and steam activation did not cause much change in composition or aromaticity, according to the elemental analysis (Table 1).

The O–H stretching from 3200 to 3500 cm$^{-1}$ and the aliphatic C–H stretching from 2820 to 2980 cm$^{-1}$ in BC300 and BC300-S were higher than that in BC550 and BC550-S, indicating that the abundance of hydrogen-bonded hydroxyl groups and aliphatic compounds in BC300 and BC300-S were higher than that in BC500 and BC500-S (Figure 2). The peaks of carboxyl C=O stretching (1700–1740 cm$^{-1}$), aromatic C=C stretching as well as C=O (1600 cm$^{-1}$), aromatic C–H, and symmetric of BC550-S was substantially increased by the steam activation. Steam activation liberates syngas, enables coalescence of small pores and enlarges internal cavities, resulting in increased microporosity.[16,25,31] The SEM images showed that BC550 and BC550-S were more porous than BC300 and BC300-S, and BC500-S with wider edges has the most porous structure (Figure 1). The molar H/C, O/C, and (O + N)/C ratios are indicators of surface aromaticity, polarity and oxygen functionality, respectively.[25] The reduction of these values with increasing temperature indicates carbonisation and development of aromatic and graphitic structures.[23] The lower ratio of O/C and higher fixed carbon concentrations showed that biochars made at 550 °C were more aromatic and less polar, and steam activation did not cause much change in composition or aromaticity, according to the elemental analysis (Table 1).

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Figure 1. SEM images of the four biochars (BC300, BC300-S, BC550, and BC550-S) studied.

Figure 2. FTIR spectra of the four biochars (BC300, BC300-S, BC550, and BC550-S) studied.
C–O stretching (1030–1110 cm$^{-1}$) decreased in BC550 and BC550-S as compared with BC300 and BC300-S, indicating a decrease in polar functional groups with increasing pyrolysis temperature. This is consistent with the elemental analysis where BC500 and BC550-S were more aromatic. The reduction of these polar functional groups resulted from dehydration and depolymerisation reactions, which also led to the growth of aromatic and graphitic structures.[23,32]

### 3.2. Effects of pyrolysis temperature and steam activation on phosphate adsorption

For the four biochars, phosphate was being released at about 0.4 mg P g$^{-1}$ in deionised water (without P addition) in the isotherm study (Figure 3). The four biochars incurred little adsorption when the equilibrium concentrations were below 20 mg P L$^{-1}$. Except for BC550-S, slowly increasing trends were observed when the equilibrium concentrations increased above 20 mg P L$^{-1}$. Maximum adsorbed amounts of phosphate for four biochars were between 1.0 and 1.4 mg P g$^{-1}$ at pH 7 (Figure 3). However, the adsorption patterns of four biochars were not suitable for Langmuir, Freundlich or any other isotherm modelling. At initial concentration of 20 mg P L$^{-1}$ and application rate of 2 g L$^{-1}$, about 2–4% of P was removed by the biochars (Figure 4). Each biochar’s adsorption capacity did not change when the pH was uncontrolled (Figure 4).

Since the biochars have negatively charged surfaces, it is not surprising that the four biochars had little capacity to adsorb P from the solution. The net charge on biochar’s surface was negative because the amount of positive charges was much smaller than the amount of negative charges.[33,34] Mukherjee et al. [35] reported that biochars always have negatively charged surface unless under low pH conditions. The pH affects biochar’s surface charge and further influences biochar’s adsorption capacity.[36] Under ambient conditions, biochars produced at 300 °C were acidic, but the pH was

![Figure 3. Relationships between equilibrium phosphate concentrations and adsorbed amounts of phosphate in isotherm studies for the four biochars (BC300, BC300-S, BC550 and BC550-S). Biochar application rate = 2 g L$^{-1}$, pH 7, T = 295 K, total equilibration time = 48 h.](image)
plateaued out and then remained constant afterwards. The application rate to achieve the highest removal was found to be 4 g L$^{-1}$. The adsorption amount is expected to have a linear relationship with solid/solution ratio or the adsorbent application rate.\[40\] In this study, the lack of relationship between biochar application rate and the amount of P adsorbed further confirms that there was little adsorption of P by the four biochars we studied.

### 3.3. Possible mechanisms for biochar adsorption of P

Physical and chemical interactions including dispersive forces, electrostatic interaction, complexation, and precipitation are possible mechanisms \[16\] that govern the interplay between biochar surface and phosphate ions in the solution. These factors are controlled by the characteristics of biochar surface and solution chemistry. High surface area is usually favourable for adsorption, especially for organic matter.\[13\] In this study, higher surface area or higher oxygen functionality did not improve adsorption. The amount above the pH$_{pzc}$, and as a result little P was adsorbed in BC300 and BC300-S. In the kinetic study with an initial concentration of 20 mg L$^{-1}$, the adsorption pattern was irregular and was difficult to be modelled (Figure 5), and the amount of adsorption was close to zero after 40 h. The initial concentration therefore affected P adsorption.

In Yao et al. \[19\], the greatest sorption capacity for phosphate was observed when pH was around four in biochars made from anaerobically digested sugar beet. But they did not explore details on electrostatic interaction between adsorbent and adsorbate under different pH. Kuma et al. \[36\] observed that the greatest sorption capacity for phosphate was below pH$_{pzc}$ and the sorption capacity decreased sharply when pH was greater than pH$_{pzc}$ because adsorption of anions was mostly favoured when solution pH was lower than pH$_{pzc}$ of the adsorbent. Similar to biochar, the adsorption capacity of activated carbon is also affected by solution pH. Jayson et al. \[37\] used activated carbon to adsorb orthophosphate, and observed a sharp drop of adsorption when solution pH was greater than pH$_{pzc}$ of the activated carbon. For adsorption of negatively charged dyes, the adsorption capacity of activated carbon also decreased when negative charges developed with increasing solution pH.\[38\] In contrast, when pH > pH$_{pzc}$, the uptake of cationic dyes was greatly improved due to increased electrostatic force of attraction.\[39\] In future studies, the most favourable pH condition for adsorption and the surface charge potential of biochar should be determined to assess the potential of the biochars for phosphate removal and for better designing sorption experiments with biochar.

For each biochar, increasing the application rate from 2 to 4, 12, 20 g L$^{-1}$ did not increase adsorption (Figure 6). Determining optimum adsorbent addition rate is critical when considering the cost of application and operation. Kuma et al. \[36\] demonstrated that P removal increased with the increasing adsorbent application rate until it plateaued out and then remained constant afterwards. The application rate to achieve the highest removal was found to be 4 g L$^{-1}$. The adsorption amount is expected to have a linear relationship with solid/solution ratio or the adsorbent application rate.\[40\] In this study, the lack of relationship between biochar application rate and the amount of P adsorbed further confirms that there was little adsorption of P by the four biochars we studied.

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and type of functional groups on biochar surface are important properties that are better preserved at low pyrolysis temperatures and encourage the development of biochar surface amphoteric features and surface charge.[13] For the four biochars used in this study, the surface charges originated from functional groups are mostly from oxygen-related functional groups. Solution chemistry plays an important role in changing surface charges through altering functional groups. When solution pH is greater than the pH_{pzc} of biochars, functional groups act as a Lewis base and display negative charges.

Another possible factor contributing to surface charge is the graphitic structure of the carbon material. [41] For activated carbon, graphene layers where most surface area resides account for most of the surface charges, and when pH > pH_{pzc}, the negative charges are believed to be detrimental to adsorption of the same charged ions.[41] Pyrolysed biochars are, though, not as graphitic as activated carbon, they could likely gain some initial graphitic structure. The developed aromatic structures in BC550 and BC550-S also tend to be π electron donors.[23] On the other hand, phosphate is also known to be able to form inner-sphere complexes with functional groups despite the negative charges.[42] But this likely did not occur on the pine sawdust biochars since the functional groups did not affect the adsorption. The adsorption might be limited to outer-sphere complexation. More research is needed to confirm that the adsorption of phosphate on biochar surfaces did not involve inner-sphere adsorption.

Most adsorption materials used for P removal contain divalent and trivalent metal ions such as magnesium, calcium, aluminium and iron that can precipitate and complex with P, thereby removing P from aqueous solutions.[43] The release of P may also occur due to low Ca content in biochar.[44,45] For biochars that do not contain abundant metal ions, it will be difficult for adsorption to occur when repulsive electrostatic forces exist. For example, Yao et al. [44] tested thirteen biochars for P adsorption and found that most of them had little or no ability to adsorb P in a sandy soil. Recently, Jung et al. [45] found that among the five different biochars they tested only the biochar derived from peanut shell had good adsorptive capacity because of a proper Ca/P ratio. Apparently, biochar’s adsorption capacity largely depends on feedstocks with different mineral compositions.

4. Conclusions

The four pine sawdust biochars produced at two different temperatures with or without steam activation had little affinity for adsorption of phosphate from an aqueous solution, in agreement with many other previous studies. Neither pyrolysis temperature nor the application of steam activation increased phosphate adsorption. For this specific feedstock, the tested temperatures and the steam activation technique were therefore ineffective in changing biochar’s adsorption capacity for phosphate. The adsorption of P by biochars in this study does not support the common belief that a high surface area and oxygen functionality could enhance the adsorption capacity. Our data suggest that the electrostatic repulsion between biochar surfaces and phosphate in the solution was the reason for the disagreement between surface area and oxygen functionality and the adsorption of phosphate by biochar. Our study suggests that even though biochar is an effective adsorbent for cationic elements, one should remain selective and critical when attempting to use biochar to adsorb phosphate from aqueous solutions. In order to produce biochar with better adsorption capacities for P, future research test different feedstocks, particularly those have rich mineral contents and cationic metals, different production conditions and other activation techniques.

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