

Determination of the phosphate adsorption potential of biochar derived from *Ananas comosus* (pineapple) peels in aqueous solution

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Abstract

The increased demand and use for phosphate around the world have caused the global phosphate level to rise. Adsorbents such as biochar are commonly used to remediate heavy metals, but research has also shown its potential to remediate excess nutrients. Pineapple peels were proven to contain magnesium which can aid phosphate adsorption and can be used as a potential biochar feedstock. The study aimed to determine the potential of pineapple peel derived biochar in adsorbing phosphates. Pineapple peel biochar were produced via pyrolysis at 300 °C, 400 °C, and 500 °C, and then characterized using a Fourier Transform Infrared (FTIR) spectrometer. Biochar analysis showed biochar decomposition as pyrolysis temperature was increased. Phosphate analysis showed positive adsorption rates at 25 ppm concentrations but showed negative adsorption rates at lower concentrations. The results showed a general inverse relationship between the biochar adsorption capacity and pyrolysis temperature which directly contradicts previous research.

Keywords: *pineapple peels, Ananas comosus, phosphate, adsorption, biochar*

Introduction. The increased industrial and agricultural demand and use for phosphate around the world caused the global phosphate levels to exceed the assimilation capacity in river basins which covers a total of 38% of the world's land surface area [1]. Locally, the phosphate levels in the local rivers have been nearing or have reached the 0.5 mg/L limit set by the Environmental Management Bureau [2].

Biochar is a pyrolyzed biomass used for remediation or sequestration purposes [3]. The speed and temperature of the pyrolysis of the biomass can affect the structure and functional groups that comprise the biochar. Biochar pyrolyzed at slower rates and lower temperatures tend to have more diversified organic characters including aliphatic and other types of molecular structures, more functional groups and a higher possible ion exchange capacity [4,5]. On the other hand, biochar pyrolyzed at higher temperatures has more pores. Therefore, it has a greater surface area yet is more carbonized and has less functional groups [5,6].

Biocharcoal have specific ions that can positively affect the biochar adsorption capacity of excess nutrients in the water, for example, correlation between the magnesium ions in the biochar and the phosphorus adsorption capacity of the biochar can be used as a basis for choosing the biomass stock for the production of biochar [5,6].

Pineapple peels have been used for the production of biochar for the remediation of chromium and oxytetracycline [8,9].

Since there are limited studies on the potential use of pineapple peel biochar on the remediation of excess phosphates, this study aimed to determine the potential of biochar derived from the peels of *Ananas comosus* (pineapple) pyrolyzed at different temperatures (300, 400, and 500°C) in adsorbing phosphates.

Studying the adsorption capacity of pineapple peels on phosphate can contribute to the current understanding of the relationship between the biochar adsorption capacity of a specific pollutant, and its structure and composition. The study specifically aimed to:

- (i) characterize biochar pyrolyzed at 300, 400, and 500°C using Fourier Transform Infrared (FTIR) spectroscopy;
- (ii) measure the phosphate concentration of phosphate solution samples before and after treatment with biochar;
- (iii) calculate the adsorption potential of biochar by using the concentration of phosphates removed from the water; and
- (iv) compare the adsorbed amounts of phosphates of the biochars pyrolyzed at 300, 400 and 500°C.

Methods. Pineapples were dried, powdered, and then pyrolyzed at three different temperatures - 300, 400, and 500 °C. The resulting treatments were referred to as PP300, PP400, and PP500. The yield of

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each sample was calculated and the adsorbents were characterized using FTIR analysis. The adsorption potential of the different biochars were determined through conducting five replicates of batch adsorption experiments, and calculating their removal rates and adsorption capacity after measuring the phosphate levels in the treated water using the 18th edition of American Public Health Association (APHA 1992) 4500-P standard methods for phosphate analysis [10]. Lastly, one-way analysis of variance (ANOVA) and paired t-Test were used to determine a significant difference among the means of the phosphate adsorption capacity of each biochar. All analyses unless otherwise stated were performed at the Biology and Chemistry Instrument laboratories at Philippine Science High School – Western Visayas Campus.

Pre-pyrolysis procedures. Pineapples were obtained from Leganes Public Market, Iloilo. The peels were thoroughly separated from the flesh by careful scraping. The peels were air-dried for 24 hours, and then oven-dried at 70°C for 12 hours. The oven-dried peels were ground using a blender and passed through a 1 mm sieve. Five grams of pineapple peels were weighed using an analytical balance, and were placed into ten constant-weighted ceramic crucibles for each pyrolysis temperature.

Pyrolysis. The powdered peels were stored in a plastic container with silica desiccant, and were brought to the Department of Science and Technology - Regional Standards and Testing Laboratory (DOST - RSTL) for slow pyrolysis. The crucibles were covered with lid to ensure oxygen-poor conditions, and charred under three different temperatures- 300, 400, and 500 °C using a muffle furnace, at a ramp rate of 5°C/minute. The crucibles were incubated at the peak temperature for 2 hours before cooling down to room temperature using a desiccator [8].

Ash and Biochar Separation. The resulting products of pyrolysis were immersed in 0.1M of HCl solution overnight. It was then rinsed with distilled water and oven-dried overnight at 60°C. After cooling down to room temperature, the solids were passed through a No. 100 mesh 149-µm sieve to obtain the final biochar samples [8]. The final samples were named PP300, PP400, and PP500, respectively. The biochar was stored in a desiccator until usage.

Biochar characterization. The functional groups present on the surface of the biochar were identified using Fourier Transform Infrared (FTIR) analysis, following the Attenuated Total Reflection (ATR) method for solids.

Sorption Tests. Five phosphate solutions were prepared by dissolving respective amounts (10, 20, 30, 40, 50 mg) of anhydrous monopotassium dihydrogen phosphate (KH_2PO_4) in 1 L distilled water. All glassware used were washed using 1:1 HCl and rinsed with distilled water to prevent contamination of other chemicals [10]. In separate Erlenmeyer flasks, 150 mL of each phosphate solution were treated with 0.3 g of biochar, shaken for 24 hours at 200 rpm using a mechanical shaker [11].

The agitated phosphate solutions were filtered with Grade 1 Whatman 11-µm filter paper, and then with 0.45-µm nylon membrane filters previously soaked in two liters of distilled water for 24 hours. The phosphate content of the treated solutions was determined using the stannous chloride acid method from APHA 1992 [10].

Spectrophotometry Analysis. The phosphate analysis was conducted by batches of five to maximize the capacity of the UV-1800 Shimadzu Ultraviolet-visible (UV-Vis) spectrophotometer. A volume of 25 mL of the phosphate solution samples were placed in 50-mL Erlenmeyer flasks. One (1) mL of the ammonium molybdate solution was added and mixed. Then, two drops of the stannous chloride solution were added and swirled. Samples were transferred to cuvettes within 5 to 15 minutes. Absorbance of samples were measured using a UV-Vis spectrophotometer at a wavelength of 650 nm [10]. The concentration limit of detection of the analysis was determined to be at 9.94 ppm.

Data Analysis. Using Microsoft Excel 2016, paired t-Test was conducted to determine if there is a significant difference between the means of the phosphate content of the solutions pre- and post-treatment of each biochar at each concentration. One-way ANOVA analysis was used to determine if there is a significant difference between the performance of each biochar. All analyses used a significance level (α) of 0.05.

Safety Procedure. Laboratory gowns, gloves and masks were worn every time chemicals were being handled. Excess SnCl_2 solution was turned over to the school's Chemistry Science Research Assistant (SRA). Solutions were disposed of in waste bottles which were labeled "Inorganic Waste", and were turned over to the Chemistry SRA for proper disposal.

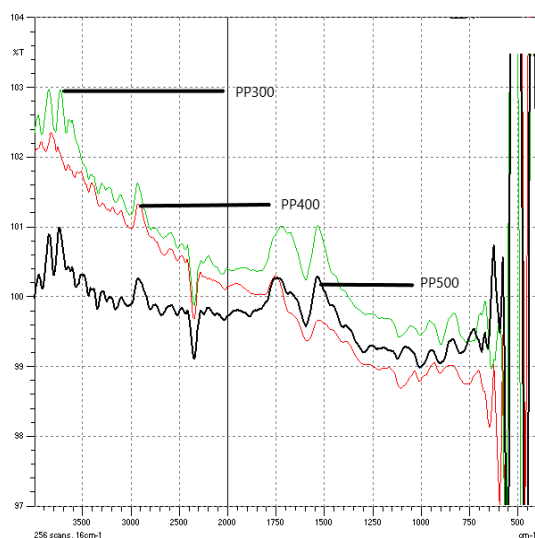
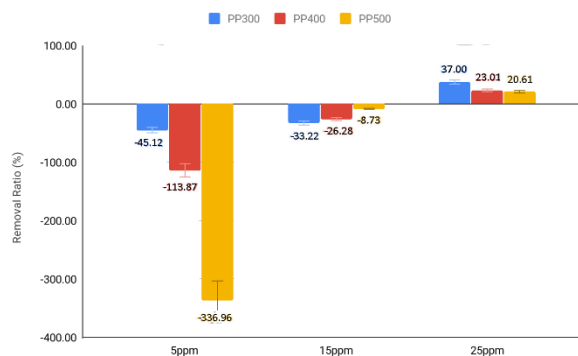
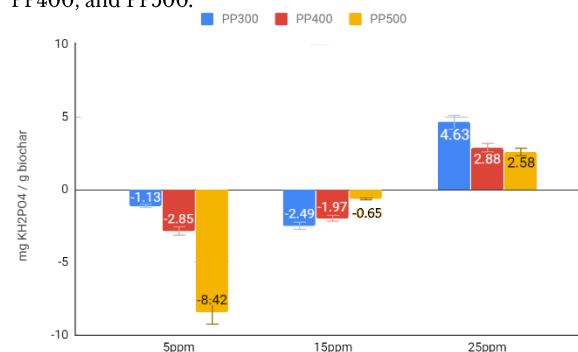
Results and Discussion. In Table 1, it is shown that as the pyrolysis temperature increases, the biochar yield decreases. This is mainly due to the cellulose-hemicellulose degradation and lignin decomposition as the pyrolysis temperature increases [12,14]. The degradation of cellulose is governed by parallel and competing steps that consequently produce products such as charcoal, water, tar and gas [13]. In addition, as the pyrolysis temperature increases, the increased decomposition of the organic matter of the biochar, the progressive concentration of inorganic compounds and the destructive volatilization of ligno-cellulosic matter led to the ashing of inorganic compounds and therefore caused further decrease in biochar yield [9]. This decrease in the biochar yield was also evident in related literature that pertained to the pyrolysis of pineapple peels and other biomass [7,9,12].

Table 1. Biochar yield of pineapple peels pyrolyzed at 300°C, 400°C, and 500°C.

Biochar	Yield (g)	Yield (%)
PP300	~ 14.9197	29.84%
PP400	~9.6137	19.23%
PP500	~8.3028	16.61%

These trends were also substantiated by the FTIR analysis which showed similar peaks and increasing transmittance. As seen in Figure 1, there is a notable decrease in the number of functional groups as temperature increases indicating the increased degradation of the pineapple peel at higher temperature. The results of the FTIR spectroscopy showed distinct peaks at about 3050, 1725, and 1610 cm^{-1} , signifying the presence of aliphatic alkane (C=C) and carbonyl groups (C=O). The individual peaks generated by C=O stretching at 1725 and 1610 cm^{-1} indicate possible formations of aliphatic and conjugated ketones (has C=C unit attached directly to the carbon of the carbonyl group) [14]. In addition, the peaks at 2300 and at 3050 cm^{-1} refer to the stretching of the alkyl functional group, and the molecular bonds of the C=C which denote presence of benzene rings, respectively.

FTIR analysis also showed that the transmittance of the C=C bonds increased slightly at biochar pyrolyzed at 400 °C but decreased at 500°C while there was a general increase of the transmittance of other functional groups as temperature increases. These changes might signify that most of the functional groups decreased in number as there are few bonds to absorb that light in the sample and therefore can transmit higher amounts of light. This decrease indicates the increased thermal degradation of the pineapple peel biochar due to increased energy availability which can destabilize the molecular bonds. Furthermore, previous studies showed that biochar prepared at higher temperatures exhibited lower (O/C) and (H/C) ratios, which corresponded to the loss of functional groups on biochar pyrolyzed at higher temperatures [7,9,11].

**Figure 1.** Zoomed FTIR spectra of PP300, PP400 and PP500.**Figure 2.** KH_2PO_4 removal ratio (%) of biochars PP300, PP400, and PP500.**Figure 3.** Adsorption capacity of PP300, PP400, and PP500 in different concentrations of phosphate solutions.

The predominantly negative results (-0.65 to -8.42 $\text{mg KH}_2\text{PO}_4/\text{g biochar}$) could suggest that using pineapple peel biochar for the overall remediation might be inefficient and cannot adsorb high amounts of pollutants. However, earlier studies using pineapple peel biochar for the adsorption of oxytetracycline and chromium (VI) showed positive potential in treating pollutants [8,9]. Although pineapple peel biochar was used for the remediation of other pollutants, it must be taken into consideration that pineapple peel biochar might not be suited for nutrient pollutant adsorption in general as biochar is often negatively charged, making it repel negatively charged ions such as phosphate [11]. However, previous research established that pineapple peels have 107 ± 5.2 mg of magnesium per 100g of the peel in dried basis [10], and SEM analysis of Wang et al. [8] showed that amounts of magnesium ions were still present which have a positive effect in the adsorption capacity of phosphates [7,11]. Considering the previous literature regarding the use and chemical composition of pineapple peel biochar [8,9], together with the fact that the biochar used for the adsorption of 25 ppm phosphate solutions showed positive adsorption capacity, the inconsistent data cannot be attributed to the inefficiency of the pineapple peel biochar itself.

Furthermore, it should be noted that time during pyrolysis and agitation was standard in other research concerning the remediation of phosphates. According to Trazzi et al. [5], like adsorption, the desorption process of phosphate was influenced by the phosphate concentration in solution, carbonization temperature, and agitation time. This implies that the biochar pyrolyzed at higher temperatures, had longer agitation time in the phosphate solution and had been

utilized for the adsorption of more saturated phosphate solutions is more likely to undergo 50% desorption of phosphate [5], but the desorption of the biochar used does not seem to follow this trend.

Biochar also exhibits variable physicochemical properties that can directly influence adsorption such as pyrolysis temperature and biochar feedstock. The latter directly affects the chemical composition and surface characteristics that can influence phosphate sorption and desorption capacity causing varied and contrasting findings on the effect of biochar on phosphate (PO_4) sorption. For example, magnesium (Mg) enrichment of corn and peanut biochar enhanced the anion exchange capacity of phosphate [6,15].

The phosphate adsorption results showed that the standard deviation of all the replicates of the 5 mg/L concentration ($\sigma = 3.66$), regardless of pyrolysis temperature, was much higher than those of the replicates at 15 mg/L ($\sigma = 0.98$) and 25 mg/L ($\sigma = 1.44$). These results could imply inaccuracies in the concentrations used for the adsorption. This could be due to errors, human or otherwise, during the weighing of the solute, but it should be taken into consideration that the standard deviation generally decreases as the concentration increases which denotes a possible constant error during the weighing.

These erratic results may also be due to the possible desorption of phosphate, normal effects of the pyrolysis temperature, or the possible constant error during the weighing and preparation of the monopotassium phosphate solute. In addition, the long storage of the biochar can be a possible cause of the low phosphate adsorption rates. Research on the effect of biochar ageing on the adsorption of diuron and glyphosate herbicides by Zhelezova et al. [16] showed that the ageing of soil-biochar mixtures decreased the adsorption of both herbicides in comparison with freshly biochar-amended soil. This showed a relationship between the degradation of the biochar with the decrease of its adsorption capacity which might have caused the low adsorption rates of the pineapple peel biochar.

The high standard deviations and the conflicting adsorption results of different pyrolysis temperatures and phosphate concentrations mean results showing no cohesion, from which no conclusion can be made that can neither prove or disprove the hypothesis.

Limitations. The study included no characterization of the specific elemental composition and topography of the biochar using scanning electron microscopy and energy dispersive X-ray spectroscopy. Sorption isotherms used to determine adsorption kinetics were not applied in the study. The study also lacked the use of proper reference materials for blanks and pretrials.

Conclusion. The produced biochar showed decreasing yields and functional groups such as C=C, C-H, and C=O, which implied further biochar degradation, as pyrolysis temperature increased. The adsorption of phosphate increased from negative

values to positive values as concentrations of the phosphate solutions increased. The high standard deviation and the pattern of adsorption values at lower concentrations imply desorption of phosphate, and errors that are more noticeable at lower phosphate concentrations. Based on these findings, there is no evidence to support nor to dismiss the efficiency of biochar as a phosphate adsorbent.

Recommendations. Further analysis is recommended for the determination of sorption kinetics and isotherms that establish the processes that govern the sorption capacity of the pineapple peel biochar. Furthermore, it is recommended that dilution should be used in order to make solutions with low concentrations to reduce the constant error of weighing apparatus. The addition of sorption pretrials and the usage of proper industrial or reference materials for blanks are also recommended.

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