Biosolid-derived Biochar for Phosphate (P) Remediation

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Introduction

❑ Introduction

According to a 2004 E.P.A. report, approximately 7.1 million tons of biosolids are produced in the US each year. Biosolids are a nutrient-rich organic materials resulting from the treatment of sewage sludge. Up until now, these byproducts of waste treatment have been incinerated, buried in a landfill, or field-applied as fertilizers. Land applied biosolids receive additional treatment to remove pathogens and trace metals. In this study, the biosolid was characterized as a possible precursor for biochar as a remediation source for excess phosphates (P) in the environment through adsorption processes. Biochar is the carbonaceous product of pyrolysis, which is a thermochemical process in the absence of oxygen at elevated temperature. Due to the high ash content of sewage sludge, it was hypothesized that biosolid-derived biochar would contain more metal oxide functional groups on its surface when compared to biomass-derived biochars. These groups increase the anion exchange capacity (AEC) of the mineral surface. In addition, higher pyrolysis temperatures were used to increase the concentration of metal oxides on the biochar surface to provide maximum bonding sites for anion adsorption. The pyrolytic conversion of biosoilds to biochar can be a promising method for improving the management of sewage sludge and increasing the value-added products from this byproduct of waste treatment.

❑ Objective

The objective of this study was to investigate the P adsorptive characteristics of the biosolid-derived biochars that were produced at different temperatures through slow pyrolysis. Evidence of changing surface functionality with varying temperatures was investigated, with the intent to define what temperature produced the best biochar to remediate excess P concentration in effluent.

Experimental set-up

Materials and Methods

❑ Characterization

➢ Biochar ash and yields were gravimetrically determined. Biochar pH was determined using the international Biochar Initiative Protocols. Inorganic elements were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) after microwave digestion.

❑ FTIR and PCA

➢ The surface functionality of the biochar was analyzed by Fourier transform infrared spectroscopy with an attenuated total reflectance attachment (FTIR-ATR, Perkin Elmer). Spectra were recorded in the range of 4000 – 600 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were analyzed using principal component analysis (PCA) to identify major and minor differences between the samples.

❑ Adsorption Kinetics

➢ A batch mixture of 0.2 grams of biochar per 50mL of 60 mg/L phosphate solution was made and shaken at 140 rpm. 10mL samples were extracted at the appropriate times (for 96 hours) and then filtered and prepared for ICP analysis for P concentration. Solution pH 7 was maintained throughout the experiment.

❑ Adsorption Isotherms

➢ Mixtures of 0.2 grams of biochar per 50 mL of phosphate solution at different concentrations ranging from 4 to 60 mg/L were prepared. The mixed solutions were shaken at 140 rpm for 96 hours, enough time to reach equilibrium. Inorganics were determined by ICP-OES.

Biosolid-derived Biochar Characterization

Table 1. Properties and inorganic analysis of bio-solid and the resulting biochars produced at pyrolysis temperatures 400°C, 600°C, and 750°C

					Inorganic elements (mg/g)		
	Pyrolysis Temp.(°C)	Yield (wt %)	pH	Ash %	Ca	Cu	Fe
Biosolid	N.A.	N.A.	7.0	33	18.5 ± 1.3	0.2 ± 0.0	20.3 ± 0.1
Biochar	400	35	7.0	60	54.7 ± 5.8	0.6 ± 0.0	36.0 ± 2.6
	600	42	8.1	72	53.4 ± 4.0	0.6 ± 0.1	31.4 ± 5.8
	750	39	10.7	79	33.6 ± 3.0	0.6 ± 0.0	35.5 ± 2.0

		Inorganic elements (mg/g)							
		K	Mg	Mn	Na	P	S	Zn	Si
Biosolid	N.A.	2.3 ± 0.1	1.6 ± 0.2	0.7 ±0.0	0.7 ± 0.0	14.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.00	43.9 ± 1.7
Biochar	400	5.2 ± 0.2	8.0 ± 1.0	1.4 ± 0.0	1.6 ± 0.1	29.5 ± 1.7	9.1 ± 0.0	1.4 ±0.02	49.3 ± 6.7
	600	6.0 ± 0.6	5.9 ± 1.0	1.7 ± 0.0	1.9 ± 0.1	30.0 ± 1.8	10.5 ± 0.6	1.6 ± 0.1	22.2 ± 0.5
	750	4.4 ± 0.6	2.5 ± 0.3	1.6 ± 0.1	1.7 ± 0.1	36.9 ± 1.3	10.3 ± 0.3	1.5 ± 0.06	93.7 ± 7.4

*All samples were average values calculated from N = 3 replicate measurements and concentrations were calculated on the basis of the dry weight of the biochar (mg/g).

➢ Ash content increased from 33 to 79 wt% with increasing pyrolysis temperatures to 750°C.
➢ The pH of biosolid and its biochars produced at 400-600°C ranged from 7.0-8.1 whereas the pH of biochar at 750°C was 10.7.
➢ Alkali and Alkali earth metals such as Ca, K, Mg, Na and other inorganic compounds including Fe, P and Si were found at high concentrations in all the biochars.

FTIR and Principal Component Analysis (PCA)

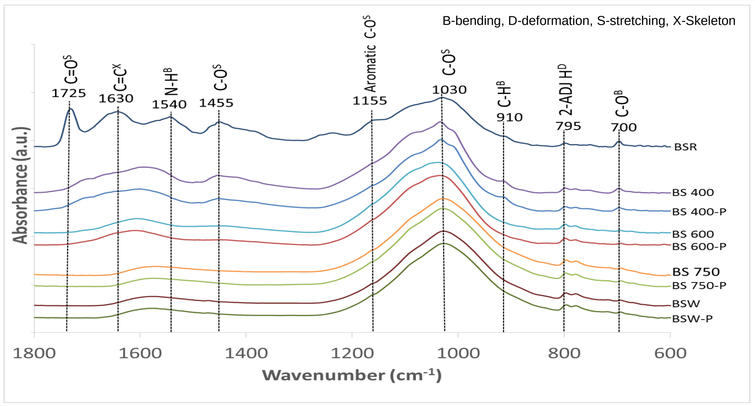


Fig. 1. FTIR spectra of the feedstock

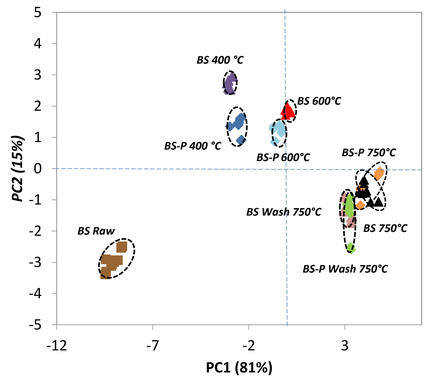


Fig. 2. PCA of FTIR spectra data

➢ As pyrolysis temperature increased, surface functionality of the biochars was significantly decreased [Fig. 1].

➢ Biosolid and its biochars produced at different pyrolysis temperatures were separated by PC1 with 81% of the total variance [Fig 2].

➢ The results indicate that increasing pyrolysis temperature removes surface oxygenated functionality present in the biochars.

Adsorption Kinetics

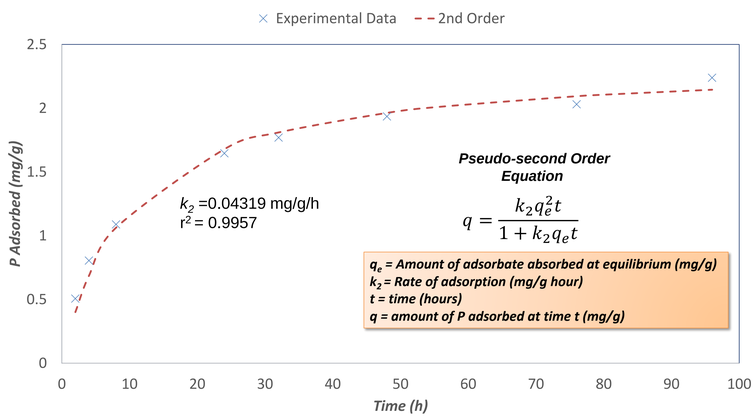


Fig. 3. Adsorption kinetics of P on BS750 and the fitted model using the pseudo-second order model

➢ The data set was well fit to the pseudo-second order rate law. As the concentration of the adsorbate (P) was doubled, the reaction speed increased by the square of the rate.
➢ The rate constant (k) was found to be 0.04319 (mg/g hour).
➢ The best fit to the pseudo-second order kinetics model implies that the rate limiting factor is due to chemical adsorption (chemisorption).

(P) Adsorption Isotherms and Models

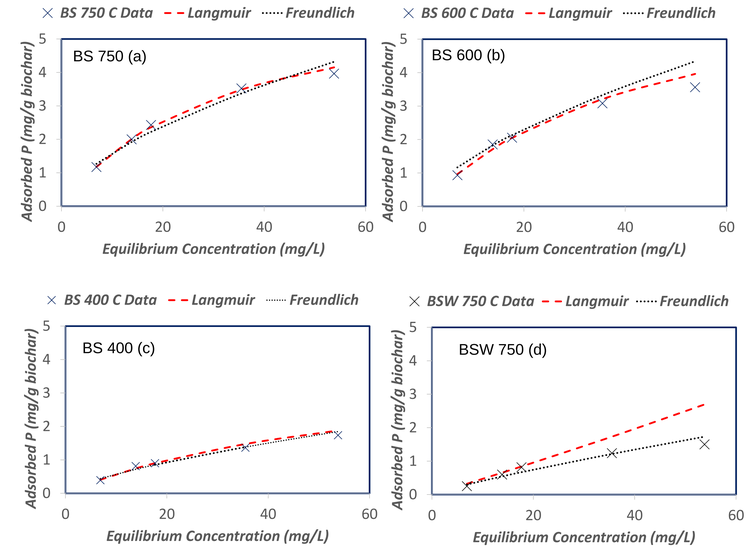


Fig 4. P adsorption isotherms and models by biosolid-derived biochars produced at 400, 600 and 750ºC. (a) BS750, (b) BS600 (c) BS400, and (d) BSW750 (Washed). The red dash line represents the Langmuir isotherm model and the black dotted line represents the Freundlich isotherm model

Table 2. Best-fit parameter values for isotherm model data

	Langmuir			Freundlich		
	Q^0 (mg/g)	K (L/mg)	r^2	K_f (mg/L)	1/n	r^2
BS 750 C	6.603	0.031	0.996	0.401	0.596	0.971
BS 600 C	7.293	0.022	0.988	0.340	0.639	0.966
BS 400 C	4.014	0.016	0.987	0.115	0.696	0.965
BSW 750 C	-33.417	-0.001	0.974	0.058	0.853	0.947

❑ The Langmuir model was found to fit well with the adsorption isotherm data of biosolid-derived biochars.
- The Langmuir model assumes monolayer adsorption on a homogeneous surface with no interaction between the adsorbed ions.
- The experimental data from biosolid-derived biochar made at 750˚C fit the Langmuir model best with an r^2 of 0.996.

❑ The Freundlich model better fit the adsorption isotherm of the washed biochar implying the removal of metal oxides from the biochar and the production of porosity for P adsorption.

Langmuir Isotherm

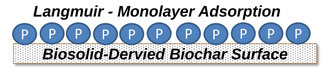
$$q_e = \frac{Q^0.K.C_e}{1+K.C_e}$$

Freundlich Isotherm

$$q_e = K_F C_e^{1/n}$$

q_e = Amount of adsorbate absorbed at equilibrium (mg/g).
C_e = Equilibrium Concentration (mg/L)
K = affinity coefficient
Q^0 = monolayer maximum adsorption capacity (mg/g)
K_F = relative adsorption capacity constant of the adsorbent (mg/g)
n = intensity of the adsorption constant

Langmuir - Monolayer Adsorption



i.e. mononuclear: $S_{MgO}\text{-}OH_2^+ + H_2PO_4^- \leftrightarrow S_{MgO}H_2PO_4 + H_2O$

Conclusion

➢ As pyrolysis temperature increased, the ash content increased and the surface functionality decreased.
➢ Biosolid-derived biochar produced at 750°C by slow pyrolysis fit well the pseudo-second order kinetics model for P adsorption.
➢ The P adsorption isotherm data of biosolid-derived biochars was better fit into the Langmuir isotherm model than the Freundlich isotherm model.
➢ We concluded that 600°C can be the optimum temperature if cost was an issue.
➢ Biosolids-derived biochars can be an environment-friendly and cost-effective adsorbent for phosphate adsorption in the environment.
➢ **Future studies:**
- Repurposing of P-laden biochar for soil amendment on field application.
  - Adsorption with controlled ionic strength at different pH.
  - Identify the ions that leach out of biosolid biochar into solution.
- Field application of the bio-solid biochar in various systems and soil types.

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