

SAND AND PUMICE FILTER AMENDED WITH ACTIVATED CARBON AND BIOCHAR FOR PHOSPHORUS RETENTION

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ABSTRACT

Phosphorus (P) loss via stormwater runoff is a water quality concern. The objective of this study was to investigate two commercial biochars relative to an activated carbon as an additive to geomedia (sand and pumice) for P removal. The batch adsorption experiment was conducted to assess P sorption of the geomedia and carbon materials while the leaching experiment was conducted in sand and pumice columns amended with carbon materials (5 % by weight). The batch adsorption test revealed that only activated carbon showed an appreciable P adsorption up to 19 %. Tested biochar materials showed no adsorption capacity for P and rather released P. The leaching experiment with the P solution (16.3 mg L⁻¹) confirmed that AC-amended sand or pumice columns were more effective in P retention than those amended with biochars. Our results indicated that pristine biomass-based biochars have a limited adsorption for anionic pollutants such as P probably due to limited metal-containing functional groups while activated carbon has reactive functional groups. Future studies for aqueous P removal using biochar should consider surface modification of biochars using metal salts and/or metal-containing feedstock such as biosolids to improve their performance on aqueous P removal.

Keywords: activated carbon; adsorption; biochar; leaching; phosphorus; pumice

1. INTRODUCTION

Eutrophication remains as a major water quality challenge in many countries. Land use change such as the conversion of forest to agricultural and urban land, can contribute to increased inputs

of nutrients such as nitrogen (N) and phosphorus (P) to waterbodies. This, in turn, stimulates the growth of algae and other water plants, thereby initiating the eutrophication process (Correll, 1999). In most freshwater systems, P is the primary limiting nutrient that accelerates eutrophication processes and off-site movement of P to aquatic systems has been a particular concern for water quality management (Sharpley, 2016). Uncontrollable algae growth could be avoided by maintaining P concentration as low as 0.02 mg L⁻¹ (Pei et al., 2015).

The loss of P has been reported from stormwater monitoring projects across the nation in USA (Ma et al., 2009; Hobbie et al., 2017). Excessive P can enter surface water from various sources including atmospheric deposition, malfunctioning septic system, over-fertilization, decaying plant debris, and animal wastes (Bigelow et al., 2019). While conventional stormwater treatment processes such as sedimentation can remove a coarse fraction of particulate matter and particulate-bound P effectively, they are limited in removing dissolved P, allowing P movement to receiving water body (Ma et al., 2019).

Conventionally, aqueous P can be removed via anion exchange membranes, chemical precipitation using coagulants, and adsorption (Sibrell et al., 2009; Chen et al., 2014; Huang et al., 2017). A viable P removal method for stormwater application is to incorporate adsorptive materials into existing and new porous media (Ahmad et al., 2013). Activated carbon (AC) has been the most common adsorptive material in water treatment, but it remains expensive (Vikrant et al., 2018). During the past decade, biochar has been viewed as a low-cost sorbent for organic and inorganic contaminants in soil and water (Mohan et al., 2014; Tan et al., 2015; Mireles et al., 2016). Biochar is a charcoal material produced by the combustion of biomass such as wood or crop residue in an oxygen-limited environment (pyrolysis). The biochar as a soil amendment is known to improve soil structure and fertility while effectively sequestering carbon into the soil (Liang et al., 2008; Lehmann et al., 2011). In addition, favorable physicochemical properties of biochar such as high surface area, porous structure, and active functional groups on its surface, have attracted its use for water treatment and its application to aqueous P removal was critically reviewed in Vikrant et al. (2018).

Green infrastructures such as raingarden, bioswale, and infiltration basin are designed to mimic the natural water cycle to prevent stormwater runoff contaminant with low cost maintenance (Ahiablame et al., 2012; Ho and Kang, 2017). Our previous study evaluated nitrate leaching in sand and pumice media amended with AC and biochars (Kang et al., 2017). Current study presents aqueous P removal with the same materials, mimicking bioswale porous media. The study objectives were to 1) determine P adsorption of the carbon materials (AC and two commercial biochars) and geomedia (sand and pumice), and 2) evaluate P leaching in sand or pumice columns amended with the carbon materials (5% by weight).

2. MATERIALS AND METHODS

2.1. Filter media and pyrogenic carbon materials

The main porous media (Fig. 1) were commercially available play sand (Quikrete International Inc., Atlanta, GA, USA) and pumice (Nature's Footprint, Inc., Bellingham, WA, USA), which were identical materials with Kang et al. (2017). The play sand was in fine sand texture (97.5 % sand, 1.8 % silt, and 0.7 % clay according to hydrometer method), while the pumice was mostly coarser than 2-mm in diameter (Gee and Bauder, 1986; Kang et al., 2017).

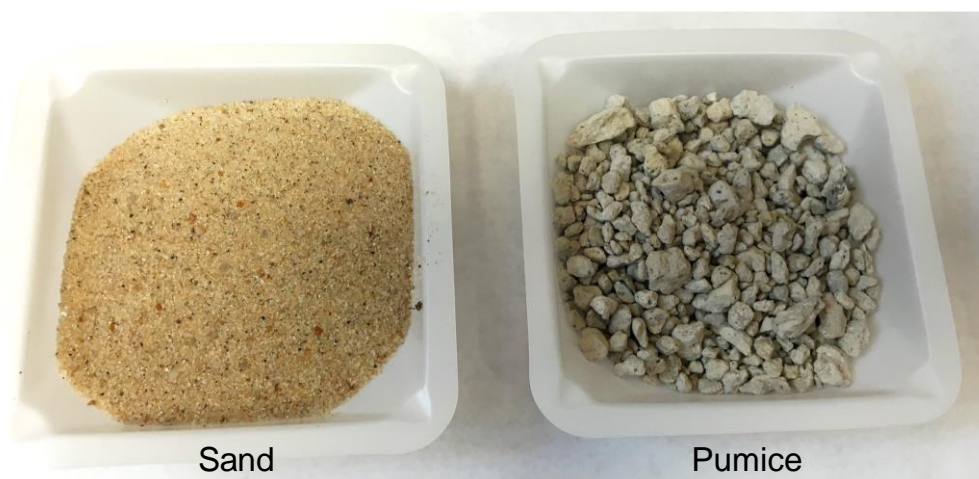


Figure 1: Sand and pumice materials used as main filter media.

A commercial AC and two biochar products, Hoffman biochar (HB) and Wakefield biochar (WB), were the adsorptive carbon materials incorporated into sand or pumice columns in this study. Detailed information on the carbon materials are found in Kang et al. (2017). Briefly, the AC (CR610A, Carbon Resources LLC, Oceanside, CA, USA) was a granular product for aquaculture use. The HB (A.H. Hoffman Inc., Lancaster, NY, USA) was a pelletized biochar product for soil conditioning while the WB (Wakefield Agricultural Carbon LLC, Columbia, MO, USA) was fine grained biochar as a soil amendment. Table 1 shows basic chemical properties of the carbon materials. Biochar pH (1:80 solid-to-solution ratio) was measured using a pH meter (ExTech Instruments, Waltham, MA, USA) and elemental composition (C, O, Fe, and Al in weight %) was measured through Energy-dispersive X-ray spectroscopy in ZEISS EVO LS10 Scanning Electron Microscope (Hitachi, Japan).

Table 1: Basic chemical properties of the carbon materials

Carbon material	pH	C (%)	O (%)	Fe (%)	Al (%)
Activated Carbon	8.03	73.1	11.6	13.7	1.6
Hoffman Biochar	7.88	86.7	13.3	0	0
Wakefield Biochar	10.23	89.8	10.2	0	0

2.2. Batch adsorption experiment

Phosphorus solution was prepared with monopotassium phosphate (KH_2PO_4) in deionized (DI) water at $50 \text{ mg PO}_4 \text{ L}^{-1}$ ($16.3 \text{ mg PO}_4\text{-P L}^{-1}$). AC and biochar samples (0.45 g) were weighted to the 50-mL tubes and equilibrated with 36 mL of $16.3 \text{ mg PO}_4\text{-P L}^{-1}$. Sand or pumice only samples were included. The tubes were equilibrated for 24 h on an end-to-end shaker at 90 oscillations min^{-1} , and supernatants were filtered through 0.2- μm membrane filters. The filtrates were analyzed for $\text{PO}_4\text{-P}$ using a HACH UV-VIS spectrophotometer (DR3900, Loveland, CO, USA) according to the molybdovanadate method (HACH method 10206). The amount of P adsorbed by the tested materials (q) was calculated by (Mireles et al., 2019):

$$q = (C_0V - CV)/M \quad [1]$$

where C_0 is the concentration of P in the initial solution (mg L^{-1}), V is the volume of liquid (L), C is the concentration of P in solution after equilibration, and M is dry weight of tested material (kg). The P adsorption capacity was calculated in percent (%) relative to the initial amount of aqueous $\text{PO}_4\text{-P}$ added (0.59 mg). Blank samples containing individual materials in DI water (1:40 solid-solution ratio) were included to represent water-extractable P (pre-existing P) from the filter media and carbon materials themselves.

2.3. Batch adsorption experiment

A total of 16 columns (7.62-cm diameter by 7.62-cm height) were packed to a depth of 4.56 cm with either sand or pumice (Fig. 2). The sixteen columns corresponded to experimental treatments consisting of two geomedia (sand or pumice) and four carbon amendments including control (no carbon amendment) in duplicates. Sand or pumice with and without carbon amendment (5% by weight) was mixed with the geomedia, which were then dry-packed into the columns to have a bulk density of 1.67 g cm^{-3} for the sand columns and 0.86 g cm^{-3} for pumice columns in a given volume of 191 cm^3 (Table 2). The bottom of each columns was protected with cheese cloth, which minimized the loss of filter materials.



Figure 2: Column experiment setup.

Table 2: The amount of sand or pumice (95 % by weight) and carbon amendment (5 % by weight) for column packing.

Column	Sand or pumice (g)	Amendment (g)	Bulk density (g cm^{-3})
Sand only	318	0	1.67
Sand + amendment	302	16	1.67
Pumice only	165	0	0.86
Pumice + amendment	157	8	0.86

All columns were flushed with 500 mL of DI water on the first day (day 1) according to the procedures employed in Kang et al. (2017). Briefly, the 500 mL of water was irrigated by 100 mL increments through a circular plastic pan placed on the top of column. The pan contained small holes to allow uniform dripping of the water. On the second day (day 2), columns were leached with 500 mL of P solution ($16.3 \text{ mg PO}_4\text{-P L}^{-1}$) by 100 mL increments (leaching event 1-5). The amount of $\text{PO}_4\text{-P}$ applied was 8.2 mg on day 2. On the third day (day 3), columns were leached again with 500 mL of DI water only by 100 mL increments (leaching event 6-10) to assess desorption of the adsorbed P from day 2. Collected column effluents were analyzed for $\text{PO}_4\text{-P}$ according to the molybdo vanadate method (HACH method 10206).

3. RESULTS AND DISCUSSION

3.1. Batch adsorption of phosphorus

AC removed aqueous P up to 19%, while geomeedia only (pumice and sand) showed much lower P removal (1.7 to 2.3 %) (Fig. 3) under batch adsorption condition. It was notable that two biochar materials (HB and WB) released P without adsorption, indicating the dissolution of P from the biochars themselves. DI water extract from geomeedia and carbon materials confirmed that appreciable P concentration was dissolved out from the carbon materials themselves (0.23-0.41 mg L⁻¹) (Table 3).

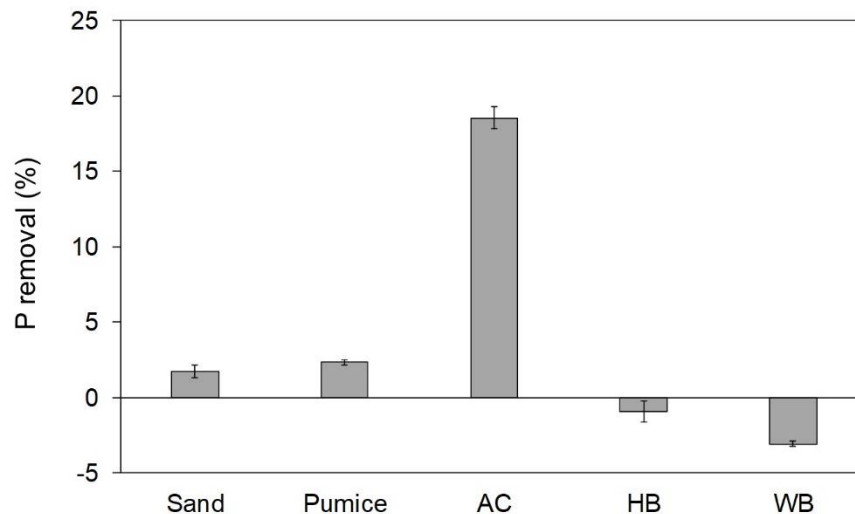


Figure 3: Phosphorus (PO₄-P) removal (%) in batch adsorption experiment.

Table 3: Properties of geomeedia and carbon materials in deionized water extract.

Geomeedia or carbon material	Water-extractable P (mg L ⁻¹)	pH
Sand	0	8.22
Pumice	0	7.67
Activated carbon	0.23	9.04
Hoffman biochar	0.12	7.84
Wakefield biochar	0.41	9.36

Biochar as a soil amendment is known to improve nutrient holding capacity in soils (Beesley et al., 2011; Lehmann et al., 2011). The biochar materials tested in this study (HB and WB), however, showed no adsorption and even release of P under laboratory condition. Similar results were found in Yao et al. (2012) highlighting P release from various biomass-based biochars. They noted that biochars, in general, are effective in removing cationic pollutants from solution due to a net negative surface charge on the surface. In our study, it was notable that AC removed 19 % of aqueous P. The P removal by AC could be explained by additional oxidation step during

activation process, which improves overall adsorptive capacities (Azargohar et al., 2006). Pumice that is often claimed to hold nutrients in gardening was not effective in aqueous P removal (2.3 %). Sand also showed limited aqueous P removal (1.7 %).

3.2. Phosphorus leaching in column experiment

Concentrations of P in column effluents increased with P solution throughout (leaching event 1-5 in Fig. 5) up to 14.4 mg L⁻¹. Sand columns amended with AC (11.6 mg L⁻¹) and pumice columns amended with AC (12.3 mg L⁻¹) showed the lowest P concentration, which suggests that AC-amended columns were effective in P retention in some extent during the adsorption stage (leaching event 1-5), matching the results from batch adsorption experiment. Under desorption stage (leaching event 6-10 by DI water only), overall P concentrations decreased in all columns and reached to their lowest P concentration (1.2-1.3 mg L⁻¹) at the end of leaching event.

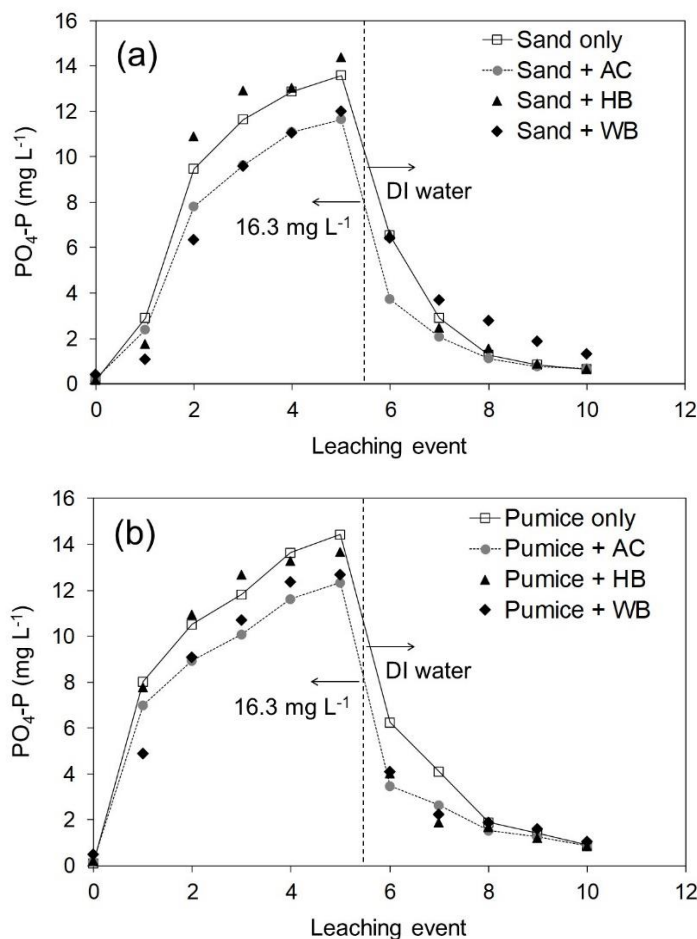


Figure 4: Concentrations of phosphorus ($\text{PO}_4\text{-P}$) in column effluents: (a) Sand and (b) Pumice. Note that leaching event 1 through 5 (adsorption stage) was irrigated with P solution and then only DI water was irrigated afterward (desorption stage).

Phosphorus retention (%) estimated by cumulative amount of P leached (during leaching event 1 through 10) over the amount of P applied (8.15 mg) showed a distinction of AC-amended sand and pumice columns (Fig. 6). AC-amended sand columns yielded the highest P retention (37 %) followed by WB-amended sand columns (30 %). Pumice only columns were the least effective in P retention (13 %). Overall, sand columns produced greater P retention than pumice columns in any carbon amendment by 4-10 %. This difference may be attributed to the greater bulk density and finer particle size in sand columns than those in pumice columns, thus allowing greater retention time of P in sand columns.

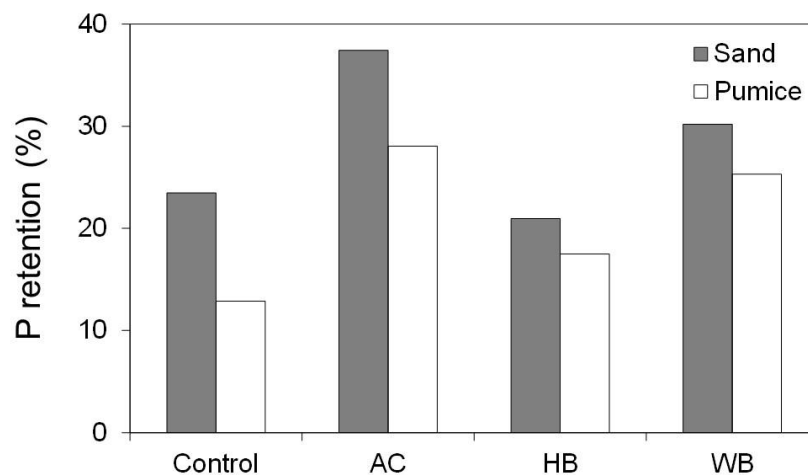


Figure 5: Phosphorus ($\text{PO}_4\text{-P}$) retention (%) in column experiment.

4. CONCLUSIONS

This study presented the performance of sand and pumice filter amended with AC and biochars for aqueous P adsorption. There were limited P adsorption capacities from sand and pumice media themselves (1.7 to 2.3 %) under the batch adsorption experiment. Among the carbon materials, AC exhibited the highest P adsorption (19 %) while biochars even released P from them. The biochar materials tested in this study were pristine biomass-based biochars and their adsorption performance relative to AC was poor. Column experiments confirmed that AC-amended sand columns yielded the lowest P loss by leaching followed by AC-amended pumice column. While the exact feedstock types and manufacturing processes of AC and biochar materials in this study are unknown, the AC contained Fe and Al (Table 1), contributing to the greater P adsorption relative to biochars. While biochar demonstrated strong adsorption capacity

for organic chemicals and cationic pollutants, it has been found to have limited adsorption capacity for oxyanions such as PO₄-P, arsenite, and arsenate (Hu et al., 2015; Cantu et al., 2016; Vikrant et al., 2018). To overcome this weakness, there have been research efforts in producing engineered biochars such as impregnating or loading biochars with metal salts (e.g., AlCl₃, MgCl₂, or FeCl₃) to increase their adsorptive capability on oxyanion pollutants (Yao et al., 2013; Zhang et al., 2013; Wang et al., 2013). In addition, biosolids may serve as an alternative feedstock to conventional biomass in biochar production for the oxyanion removal in water. Biosolids in municipal wastewater treatment plants typically contain metal oxide functional groups on the surface inherited from Al or Fe salt addition during coagulation, which can increase the anion exchange capacity of the mineral surface (Elliot et al., 2013; Deleon et al., 2014; Callegari et al., 2018). The P adsorption by biosolids-derived biochar warrants further investigation particularly with pre-existing P from biosolids themselves.

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