MODIFICATION OF PEANUT SHELL BIOCHAR WITH DIFFERENT METAL OXY-HYDROXIDES FOR IMPROVED REMOVAL OF AMMONIUM AND PHOSPHATE FROM WASTEWATER

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Abstract. The pollution of freshwater by agricultural wastewater is a global threat to ecosystem and human health. The wastewater is mainly disposed of via land application and is a significant source of nutrients such as nitrate (NO_3^-), ammonium (NH_4^+) and phosphate (PO_4^{3-}) in surface and groundwater. We have demonstrated here the sorption of NH_4^+ and PO_4^{3-} onto biochar (black carbon) as a promising mitigation method. Biochar is a low-cost, charcoal-like material made from pyrolysis of waste biomass. It can remove nutrients from wastewater and retain nutrients in soils. However, most biochars are poor at PO_4^{3-} removal. Recently, biochars modified with metals have been shown to be effective for removing PO_4^{3-} from wastewater. Little is known about the relative effectiveness of metal modified biochars for both NH_4^+ and PO_4^{3-} removal from wastewater. The goal of this study was to evaluate the relative effectiveness of metal modified biochars for removing NH_4^+ and PO_4^{3-} from swine wastewater. Solutions of Aluminum (Al), Calcium (Ca), Iron (Fe), and Magnesium (Mg) salts were used to modify peanut shell biochar (PSB). Batch sorption tests were used to compare the effectiveness of the modified PSB for removal of NH_4^+ and PO_4^{3-} from wastewater and PO_4^{3-} from the prepared solutions. All of the modified PSB's except the Ca-PSB showed high PO_4^{3-} removal. The Al-PSB showed the highest PO_4^{3-} removal efficiency from aqueous solutions of PO_4^{3-}, while the Mg-PSB was the best sorbent produced; showing not only high removal of PO_4^{3-} from wastewater, but also enhanced removal of NH_4^+ compared to the unmodified PSB. Fe-PSB showed decreased adsorption of NH_4^+, suggesting iron modification can decrease a biochar's NH_4^+ removal ability. After wastewater treatment, the spent biochar could be applied to soils to increase nutrient holding capacity and soil fertility.

INTRODUCTION

In recent years, as Concentrated Animal Feeding Operations (CAFO's) have become the dominant method of meat production in the developed world, the amount of nutrients from agricultural wastewater (WW) entering waterways has steadily increased (Walker et al., 2005). Nutrients in CAFO WW include nitrogen and phosphorus in the forms of nitrate, ammonium and phosphate. CAFO WW is commonly disposed of via land application on agricultural fields (Burkholder et al., 2007). Nutrient ions that supply bioavailable forms of Nitrogen (N) and Phosphorus (P) easily leach into runoff and groundwater from fields during rain events (Walker et al., 2005) (Carpenter et al., 1998) (Burkholder et al., 2007). Once these nutrients reach waterways, problems such as algae blooms, eutrophication, and dead zones occur. These result in massive fish kills, aquatic ecosystem collapses, and losses in biodiversity (Carpenter et al., 1998). At the same time, contamination of freshwater resources with these nutrients degrades drinking water sources for humans and makes purifying water for drinking more expensive and difficult (Goodrich et al., 1991).

Because this pollution is non-point source, it is difficult and expensive to treat or clean up (Carpenter et al., 1998). However, CAFO WW can be treated before land application, thereby preventing the creation of non-point source pollution. A variety of physical, chemical, and biological treatment methods have been devised for removing these nutrients from CAFO WW, but these are often expensive and unavailable to some farmers (Szögi et al., 2003). Biochar has been shown to effectively remove some of these contaminants from CAFO WW via adsorption (Ahmed et al., 2016).

Biochar is a cheap and renewable charcoal-like adsorbent (black carbon) generated via pyrolysis of biomass. It can easily be made *in situ* from agricultural residue or any source of waste biomass (Ahmad et al., 2013). Biochar has been shown to efficiently remove cations from water, such as ammonium or certain metal ions, but has demonstrated little to no anion sorption capabilities (Hale et al., 2013). This is due to the prevalence of negatively charged functional groups on the surface of the biochar, which preferentially attract and complex with cations (Ding et al., 2014).

Biochar can be modified to manipulate the speciation and abundance of the functional groups that control adsorption using chemical activation or modification treatments. Recent advances in modification of biochar have produced biochars with enhanced abilities to remove ammonium, phosphate, and nitrate (Rajapaksha et al., 2016). In general, oxidation of biochar surfaces increases adsorption of cations such as ammonium, while metal modification increases adsorption of anions (Rajapaksha et al., 2016)

(Wang et al., 2016) (Hestrin et al., 2019). Metal modification attaches metal oxy-hydroxide functional groups to the surfaces of the biochar. This metal impregnation of biochar effectively increases the phosphate sorption capacity of the biochar (Rajapaksha et al., 2016).

Metal modification of biochars has some limitations; the impregnation procedure is costly and requires special chemicals (Ahmed et al., 2016) (Sizmur et al., 2017). There is a need for further research on developing metal impregnated biochars for cost-effective removal of N and P from CAFO and other nutrient rich wastewaters. Also, more work must be done to understand the impact of metal modification on removal of cations in the wastewater. The purpose of this work was to compare the NH_4^+ and PO_4^{3-} removal capacities of Aluminum, Calcium, Magnesium, and Iron modified peanut shell biochar, and identify the most effective of the metal-modified biochars for simultaneous removal of both contaminants in a realistic wastewater treatment scenario.

MATERIALS AND METHODS

Peanut Shell Pellet Biochar (PSB) was obtained via pyrolysis of the pellets at 500°C for 1 hr in a muffle furnace under N_2 atmosphere. Anaerobically digested swine wastewater (CAFO WW) was obtained at the UGA Swine farm in Winterville, GA. The CAFO WW was filtered through coffee filters and stored at 4°C until use. All reagent solutions in this work were prepared using distilled water, except for aqueous solutions of disodium phosphate that were prepared using DI water.

The metal-modified biochars used in the CAFO WW sorption experiments were subjected to ~ 40°C higher oven drying temperatures than the modified biochars used in the prepared aqueous solution PO_4^{3-} experiments due to a malfunctioning dial setting on the lab oven. A sample of Fe-PSB made at the correct drying temperature of 105°C (105°C-Fe-PSB) was included for reference in the array of modified biochars used in the CAFO WW sorption testing. Further work will use biochars dried at the temperatures used in the procedures below.

Biochar Modification

All PSB samples were initially air dried for 24 hours and then crushed and sieved to 106 μm < x < 1.19 mm. To produce Unmodified PSB (UM-PSB), PSB was rinsed 10 times with distilled water, wet sieved to 38 μm < x < 1.19 mm, and then oven dried at 105°C for 24 hrs. Mg-PSB and Ca-PSB were prepared using a modified version of the procedures used in Xia et al., 2016, and Zhang et al., 2013. Al-PSB was prepared using a modified version of the procedure used in Ganvir et al., 2011, and Chen et al., 2016.

To produce Mg-PSB, Ca-PSB and Al-PSB, the PSB rinsed with hot water and dried was mixed with 0.5 M of the corresponding metal chloride solution in a beaker for 12 hrs. The solution pH was adjusted to 10 (pH 7 for AL-PSB) with 1.0 M NaOH (or 1.5 M NaOH for the Al-modification). The pH adjustment also precipitated the metal oxy-hydroxides on the PSB surface. The concentration of PSB in each preparation was 10 mg/L. The mixture was stirred continuously for 12 more hrs, allowed to equilibrate for 24 hrs and then oven dried at 110°C for 24 hrs. After drying, the modified PSBs were rinsed 10 times with distilled water, wet-sieved to 38 μm < x < 1.19 and oven dried at 105°C for 24 hrs.

Fe-PSB was produced using a modified version of the procedure used in Hu et al., 2015. The PSB rinsed with hot water and dried was mixed with 0.5 M Ferric Chloride solution in a beaker for 12 hrs. The mixture was oven dried at 110°C for 24 hrs to precipitate Fe-oxy-hydroxide on the biochar surface. The dried Fe-PSB was rinsed ten times with distilled water, wet-sieved to 38 μm < x < 1.19 before oven dried at 105°C for 24 hrs. Each dried metal-PSB was stored in a sealed glass jar until ready for use in the batch sorption experiments.

Batch Sorption Procedure

Batch sorption of NH_4^+ and PO_4^{3-} by un-modified and the metal modified biochars was measured in CAFO WW. The removal of PO_4^{3-} only was also measured in aqueous solutions of disodium phosphate. The different batch sorption tests performed, the mass of solids, and the initial concentration of each nutrient (NH_4^+ and PO_4^{3-}) in solution are shown in Table 1. Plastic centrifuge tubes with a nominal volume of 50 mL were used in all tests. All tests used 40 mL of the nutrient rich wastewater. The CAFO WW batch sorption tests were performed in triplicates. Batch sorption measurements of PO_4^{3-} in disodium phosphate solutions of 0, 26, and 68 mg/L Total P (initial concentrations) were conducted in replicates with a solid mass (unmodified or metal modified PSB) of 0.5 g.

The prepared samples and their corresponding controls were placed on a rotating mixer (3.3 rpm) and incubated for 24 hours at room temperature (23°C). At the end of the incubation period, the samples were centrifuged at 2000 rpm for 20 min. The supernatant was then decanted off, filtered through 0.45 μm filters to remove any colloids. The solutions were immediately delivered to the UGA Agricultural and Environmental Services Lab to be analyzed for total Phosphorus and NH_4^+ using UV-Vis Spectroscopy.

Data Analysis

The amount of NH_4^+ or PO_4^{3-} (as Total P) adsorbed onto the biochar at equilibrium was calculated using

$$q_e = \frac{(C_o - C_e)V}{M}$$

where q_e is the amount adsorbed after 24 hrs equilibration (mg nutrient/kg biochar), C_o is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of solution (L), and M is the biochar mass (kg).

Each value for q_e shown in the below figures is calculated from the averaged values of the initial and equilibrium concentrations of the triplicate or replicates. Error bars show a 95% Confidence Interval. If error bars between two modified biochars do not overlap for the Figures shown below, then a statistically significant difference exists between their values for adsorption, q_e, of a contaminant.

Table 1 shows the initial concentrations (C_o) of NH_4-N and Total P in the CAFO WW and Pure phosphate solutions, as well as the masses of biochar used in each test, sample sizes (n), and confidence intervals (CI) of each batch sorption experiments.

Table 1. Parameters of batch sorption tests

Round	**NH_4-N (mg/L)**	**Total P (mg/L)**	**Biochar mass (g)**	**Stats**
CAFO R_1 (UM, Fe 105°C)	1378.70	19.19	2.00	n=3, 95% CI
CAFO R_2 (Al, Ca)	1391.09	23.90	2.00	n=3, 95% CI
CAFO R_3 (Fe, Mg)	1111.67	27.69	2.00	n=3, 95% CI
Na2HPO4 R_1	n/a	26.28	0.500	n=2, 95% CI
Na2HPO4 R_2	n/a	68.45	0.500	n=2, 95% CI

RESULTS AND DISCUSSION

The removal of NH_4^+ and PO_4^{3-} from CAFO WW by different metal modified peanut shell biochars are shown in Figure 1 and Figure 2, respectively. The effects of metal modification of biochar on removal of PO_4^{3-} from prepared aqueous solutions are shown below in Figure 3.

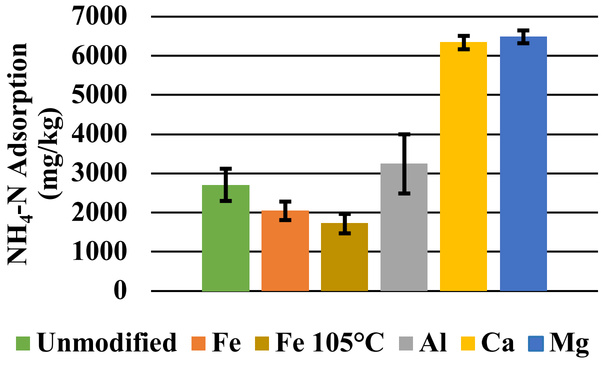

Figure 1. Adsorption of ammonium (NH_4-N) in CAFO WW by unmodified and metal modified biochars dried at 145°C.

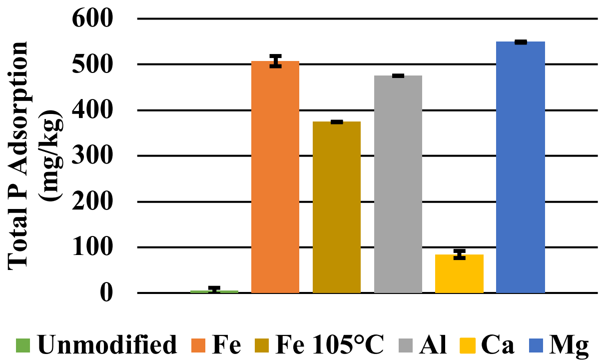

Figure 2. Adsorption of PO_4^{3-} (Total P) in CAFO WW by metal modified biochars dried at 145°C.

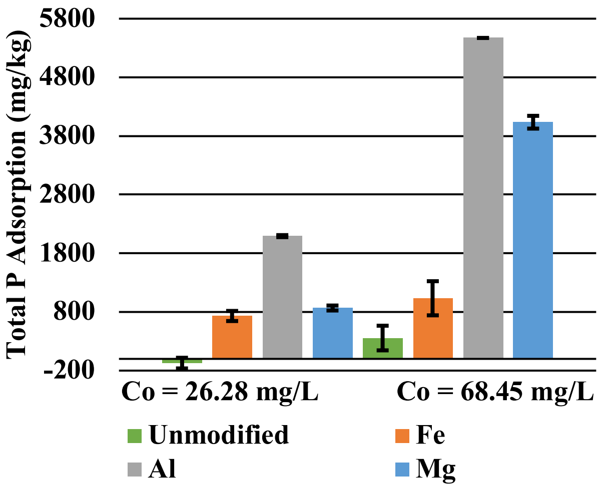

Figure 3. Adsorption of PO_4^{3-} (Total P) in prepared aqueous solutions by unmodified and metal modified biochars dried at 105°C. Results for tests conducted at two different concentrations of PO_4^{3-} (26.28 and 68.45 ppm) are shown.

Batch sorption of NH_4^+ and PO_4^{3-} in CAFO wastewater

Figure 1 shows no enhanced adsorption of NH_4^+ Al-PSB and Fe-PSB over UM-PSB. The adsorption of NH_4^+ by Fe-PSB dried at 105°C and 145°C, respectively was similar and lower than for UM-PSB, indicating that Fe modification may instead inhibit the adsorption of NH_4^+ by some metal impregnated PSB. The latter decrease in adsorption we observed could be attributed to changes in the composition of functional groups and/or hinderance of some sorption sites by the precipitated iron oxy-hydroxides on the Fe-PSB surface and pores. Further research is needed to confirm and better understand this finding. A decrease in adsorption of phosphate by H_2O_2-oxidized biochars was reported by Mia et al., 2017.

The adsorption of NH_4^+ by Ca-PSB and Mg-PSB increased significantly (Figure 1). Specifically, Mg-PSB removed about 29% of the NH_4^+ in the CAFO WW compared to 10% removal by UM-PSB. This finding agrees with the results of Li et al., 2017, who observed that Mg-biochar was most effective for removing NH_4^+ from swine wastewater. The increased removal of NH_4^+ by Ca-PSB is a potentially new finding that may open future directions of research into cheap calcium-modified biochars for removal of NH_4^+ and other cations from wastewater. The precipitation of struvite or related compounds that contain ammonium, phosphate, and divalent base cations is the most likely explanation for the increased NH_4^+ removal. Future work will focus on better understanding the adsorption mechanisms of NH_4^+ by Mg-PSB and Ca-PSB.

Figure 2 shows the relative adsorption of $PO_4^{3-}$from CAFO WW by the unmodified and the different metal modified biochars. All of the modified biochars exhibited significantly higher PO_4^{3-} removal than the unmodified biochar. Of the metal modified biochars, Ca-PSB exhibited the lowest PO_4^{3-}removal from solution, while Mg-PSB, Fe-PSB and Al-PSB showed the highest sorption capacities. It should be noted that the Mg-PSB and Al-PSB treatments removed close to 100% of the Total P from the CAFO WW, indicating that they were the best sorbents for P removal, and could possibly exhibit much higher sorption, if the PO_4^{3-} concentration in solution was higher. Future tests will focus on measuring the maximum loading capacity of PO_4^{3-} in CAFO WW for Mg-PSB and Al-PSB.

The adsorption of PO_4^{3-} by the Fe-PSB dried at 105°C was significantly less than for the Fe-PSB dried at 145°C. This suggests that the drying temperatures for Fe-PSB preparation may determine the effectiveness of Fe-PSB as a filtration media for PO_4^{3-}. It is highly likely that the concentration of colloids in CAFO WW will adversely affect sorption of the nutrients. Thus, we performed addition sorption tests in relatively pure aqueous solutions of PO_4^{3-} described below.

Batch sorption of PO_4^{3-} in prepared aqueous solution

Figure 3 shows the equilibrium PO_4^{3-} adsorption values of the highest performing modified biochars (dried at 105°C) compared to the UM-PSB control in pure solutions of Na_2HPO_4 at about the same concentration of Total P as the CAFO WW (26.28 mg/L) and at a significantly higher PO_4^{3-} concentration of 68.45 mg/L.

The UM-PSB control showed very little or no sorption of PO_4^{3-} from the solution. At the low and high initial PO_4^{3-} concentration in solution, a significant difference in sorption effectiveness was observed among the different biochars. The relative sorption effectiveness of the different biochar was Al-PSB > Mg-PSB > Fe-PSB > UM PSB. It should be noted that the Al-PSB treatment removed close to 100% of Total P at both concentrations. The latter results agree with the results of the CAFO WW experiments and reinforce the finding that the aluminum and magnesium modified biochars produced the most effective metal modified biochars for P removal. Al-PSB shows the highest removal of PO_4^{3-} and indicate that aluminum modification is the best treatment for increasing the PO_4^{3-} removal of biochar for water treatment applications. More batch sorption experiments using higher initial P concentrations and lower masses of biochar are needed to confirm these results and determine the maximum loading of P onto Al-PSB.

For the same range of initial PO_4^{3-} concentration in solution, the q_e values for PO_4^{3-} adsorption onto Al-PSB, Mg-PSB, and Fe-PSB are significantly lower for CAFO WW tests than for phosphate solutions prepared in pure water. This further suggests the inhibition of adsorption or competition for similar adsorption sites for PO_4^{3-} by other anions in the CAFO WW.

CONCLUSION

This work provides compelling preliminary findings on the relative effectiveness of different metal-oxyhydroxide modified biochars for removal of NH_4^+ and PO_4^{3-} from agricultural wastewater and prepared aqueous solutions of phosphate. The results of the batch sorption experiments indicate that Aluminum modification likely results in the largest increases in PO_4^{3-} adsorption capacity for the metal modified peanut shell biochars used in this study. The NH_4^+ adsorption of the PSB unexpectedly increased with Magnesium and Calcium modification, decreased with Iron modification, and did not significantly change with Aluminum modification of the biochar. Mg-PSB was the best modified biochar produced in this work, due to its large increases of both NH_4^+ and PO_4^{3-} removal compared to the unmodified biochar. More work is needed to further confirm these findings and more accurately quantify the adsorption capacities of the metal modified biochars for NH_4^+ and PO_4^{3-} as well as other cations and anions. Metal-modified biochars could be used in bioreactors and manure lagoons to immobilize and recover multiple nutrient ions simultaneously, and the spent biochar could be applied as a nutrient-rich soil amendment.

REFERENCES

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere 99, 19–33. doi:10.1016/j.chemosphere.2013.10.071

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Chen, M., 2016. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresource Technology 214, 836–851. doi:10.1016/j.biortech.2016.05.057

Burkholder, J., Libra, B., Weyer, P., Heathcote, S., Kolpin, D., Thorne, P.S., Wichman, M., 2007. Impacts of Waste from Concentrated Animal Feeding Operations on Water Quality. Environmental Health Perspectives 115, 308–312. doi:10.1289/ehp.8839

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint Pollution Of Surface Waters With Phosphorus And Nitrogen. Ecological Applications 8, 559–568. doi:10.1890/1051-0761(1998)008[0559:nposww]2.0.co;2

Ding, W., Dong, X., Ime, I.M., Gao, B., Ma, L.Q., 2014. Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. Chemosphere 105, 68–74. doi:10.1016/j.chemosphere.2013.12.042

Ganvir, V., Das, K., 2011. Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash. Journal of Hazardous Materials 185, 1287–1294. doi:10.1016/j.jhazmat.2010.10.044

Goodrich, J.A., Lykins, B.W., Clark, R.M., 1991. Drinking Water from Agriculturally Contaminated Groundwater. Journal of Environment Quality 20, 707. doi:10.2134/jeq1991.00472425002000040001x

Hestrin, R., Torres-Rojas, D., Dynes, J.J., Hook, J.M., Regier, T.Z., Gillespie, A.W., Smernik, R.J., Lehmann, J., 2019. Fire-derived organic matter retains ammonia through covalent bond formation. Nature Communications 10. doi:10.1038/s41467-019-08401-z

Li, R., Wang, J.J., Zhou, B., Zhang, Z., Liu, S., Lei, S., Xiao, R., 2017. Simultaneous capture removal of phosphate, ammonium and organic substances by MgO impregnated biochar and its potential use in swine wastewater treatment. Journal of Cleaner Production 147, 96–107. doi:10.1016/j.jclepro.2017.01.069

Mia, S., Dijkstra, F.A., Singh, B., 2017. Aging Induced Changes in Biochar's Functionality and Adsorption Behavior for Phosphate and Ammonium. Environmental Science & Technology 51, 8359–8367. doi:10.1021/acs.est.7b00647

Sizmur, T., Fresno, T., Akgül, G., Frost, H., Moreno-Jiménez, E., 2017. Biochar modification to enhance sorption of inorganics from water. Bioresource Technology 246, 34–47. doi:10.1016/j.biortech.2017.07.082

Szögi, A.A., Vanotti, M.B., 2003. Utilization of nutrients from animal manure: legislation and technology solutions. Journal of Soils and Sediments 3, 260–262. doi:10.1007/bf02988684

Walker, P., Rhubart-Berg, P., Mckenzie, S., Kelling, K., Lawrence, R.S., 2005. Public health implications of meat production and consumption. Public Health Nutrition 8. doi:10.1079/phn2005727

Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2016. Ammonium retention by oxidized biochars produced at different pyrolysis temperatures and residence times. RSC Advances 6, 41907–41913. doi:10.1039/c6ra06419a

Xia, P., Wang, X., Wang, X., Song, J., Wang, H., Zhang, J., Zhao, J., 2016. Struvite crystallization combined adsorption of phosphate and ammonium from aqueous solutions by mesoporous MgO-loaded diatomite. Colloids and Surfaces A: Physicochemical and Engineering Aspects 506, 220–227. doi:10.1016/j.colsurfa.2016.05.101

Zhang, M., Gao, B., Yao, Y., Inyang, M., 2013. Phosphate removal ability of biochar/MgAl-LDH ultra-fine composites prepared by liquid-phase deposition. Chemosphere 92, 1042–1047. doi:10.1016/j.chemosphere.2013.02.050