Assessment of Biochar Adsorption Capacity for Ammonium and Nitrate and Implications on Soil Nitrogen Management

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Abstract—**Biochar has the potential to retain soil nitrogen (N), but inconclusive results are reported. This study aimed to examine the adsorption behavior of ammonium (NH_4^+) and nitrate (NO_3^-) onto biochar and the pH effects to assess retention capability and elucidate the impact on N management. Laboratory experiments were conducted to determine adsorption capacity of NH_4^+ and NO_3^- onto seven biochar products from different feedstocks and Pyrolysis Temperature (PT). All products exhibited adsorption capacity for NH_4^+ with most isotherms fit well by Langmuir and/or Freundlich equations except one by linear equation. Almond shell biochar from 550 °C PT showed the highest adsorption for NH_4^+ in the solution concentration range of 1–200 N mg L^{-1}. Almond shell biochar from 900 °C PT had the lowest adsorption capacity at low solution concentration, but adsorption increased linearly and surpassed all other products as concentration increased. Two softwood biochar products (500 and 540 °C PT) showed a similar trend. Further, NH_4^+ adsorption was highly pH dependent (peaked around pH 9 for all products but reduced by more than half at neutral pH). Except for the almond char at 900 °C PT, no adsorption of NO_3^- was observed for other products at 5 or 50 mg N L^{-1} initial solution concentration. The results concluded that the ability to retain N retention by biochar without modification is limited and varied among feedstocks and pH. The role of biochar to improve N availability or use efficiency should not be overstated to avoid mismanagement decision making.**

Keywords—**ammonium, nitrate, adsorption isotherm, adsorption envelope**

I. INTRODUCTION

The world use of synthetic inorganic nitrogen (N) fertilizers increased from 10 to 110 million tonnes from 1961–2019 [1], but N Use Efficiency (NUE) has declined and is accompanied by detrimental environmental impact [2]. Agricultural fields have been identified as the major source for groundwater pollution with nitrate (NO_3^-) in California [3]. Other major mass loss of N includes ammonia (NH_3) volatilization that has detrimental effects

on air quality and human health. Agricultural production is also the largest source of nitrous oxide (N_2O), a potent greenhouse gas [4]. Thus, effective N management continues to target improving N retention in soil, increasing use efficiency, and minimizing environmental loses.

Biochar, a carbon rich material produced by heating organic materials at high temperature under no or limited oxygen, has been shown to improve soil physical, chemical, and biological properties, and mitigate some environmental contamination problems [5–7]. Studies have indicated that biochar increased N retention, reduced N leaching, and decreased gas emissions [8–10]. There is clear evidence in laboratory determinations that biochar removed N as ammonium (NH_4^+), NO_3^-, or organic N from liquid suggesting that biochar can be used as a decontamination tool [11, 12]. However, variabilities in observed biochar effects are large among studies with many showing no benefits for reducing or even increasing N loss to the environment [13, 14] that could be dependent on conditions [15]. Studies have shown that biochar benefits for N efficiency could be derived from its indirect role in promoting enzyme activities [16–18]. In any case, there is no clear consensus on the direct interaction between biochar and N species that could impact N retention to influence N management decisions at least quantitatively. Field measurements showed that biochar amendment in soil did not reduce N losses including leaching and N_2O emissions [19] or increase plant N uptake [20, 21]. We hypothesize that adsorption by biochar is one of the most important mechanisms to increase N retention and affect the amount of available N in soil for plant uptake. There are significant gaps in understanding how the adsorption characteristics affect the use of N fertilizers, especially by unmodified biochar products to avoid high costs.

Numerous studies investigated how biochar feedstocks and production conditions, such as Pyrolysis Temperature (PT), affect N adsorption. The literature suggests that biochar from low PT favors NH_4^+ adsorption and that from high PT exhibits noticeable NO_3^- adsorption. Fidel *et al.* [22] demonstrated the importance of ion-exchange

mechanisms, sorption of NH_4^+ and NO_3^- to biochar is electrostatic and pH-dependent, whereas NH_4^+ adsorption increased linearly as pH increased while adsorption of NO_3^- peaked at lower pH (3.5–7.5) and decreased as pH increased. Biochar produced at low PT (200–600 °C) showed higher sorption of NH_4^+ and relatively fast sorption kinetics by reaching equilibrium around 10 h [23, 24]. Biochar produced at low PT had more surface functional groups [25]. At 550 °C PT, rice husk biochar showed that the O-H group, −CH₃ and either −C=O or C=C group as well as -COOH group presence enhanced N adsorption [26]. Many studies have attempted to use chemical activation process to promote functional groups on biochar that may lead to high adsorption. For NO_3^-, however, biochar from plant wastes at PT below 700 °C showed limited adsorption or even released NO_3^- [27, 28]. Biochar products showed generally lower sorption to NO_3^- than soil particles [29]. Further, Lv *et al.* [30] showed that although biochar demonstrated certain capacity to adsorb NO_3^- in lab tests, little impact on N leaching in soil columns was observed attributing to weak adsorption. Similarly, although NH_4^+ adsorption by biochar is confirmed in most studies, little impact was observed on soil concentration increase that was attributed to the liberation of ammonia (NH_3) [31].

Many studies characterized the adsorption behavior of mineral N species and many tested modified biochar materials with the attempt to increase N retention for environmental benefits [32–34]. However, these treatments increase production costs. Biochar at commercial scale is currently out of reach as an agronomic practice due to the high costs. Surprisingly few studies have addressed this challenge to focus on biochar materials with low costs that are more feasible for adoption. In this study, we attempted to characterize the adsorption of N by a variety of biochar products including those made from local orchard wastes or materials more widely accessible without post-production treatments. The specific objective was to examine the adsorption behavior of NH_4^+ and NO_3^- onto biochar from the different feedstocks and the pH effects to elucidate the potential impact of biochar on N management. We also attempted to use the information to discuss efforts needed on future work and outlook on biochar adoption.

II. MATERIALS AND METHODS

Laboratory experiments were carried out to characterize biochar products made from seven different feed stocks or PT, determined adsorption capacity of NH_4^+ and NO_3^-, and determined the pH effects. All seven products were used in each determination for comparing differences and summarizing findings.

A. Selection and Characterization of Biochar Products

Seven biochar products were collected and characterized (Table I). The selection was based on potential future availability, diversity in feedstocks, and PT. The biochar products include two from almond shells at two PTs (550 °C and 900 °C), two from softwood (500 °C and 540 °C pyrolysis temperature), and one each

from yard wood/tree trimming (green waste, 900 °C), bamboo or coconut shells (550 °C). The almond shell biochar products were made for testing with the support of Almond Board of California to explore the potential use of orchard waste materials. The two softwood biochar products were commercially available from different companies. The coconut shell biochar has been commercially available and is a relatively more expensive product because of post-treatments to neutralize pH or increased efficiency in retaining chemicals of interest. More research has been done on this product, so it was used as a reference material in our testing of other biochar materials. Other two biochar products were from high PT of green waste (city wood/tree trimming materials) as a byproduct of gasification to produce bioenergy and bamboo, which is known for its good potential due to large quantity of biomass production. Biochar produced from almond shells (orchard harvest by product) and softwood (from dead trees due to drought or fire in the forest) at ~500 °C PT (mostly used for biochar production) are considered with high potential in adoption in terms of costs and local availability in California.

All biochar materials were characterized for basic physiochemical properties and nutrients (NPK, total and available using established extraction methods). Most analyses were done by Control Laboratories (Watsonville, CA, USA) and the method for each determination are provided in Table I. Available N mineral species as NH_4^+ and NO_3^- were analyzed in our lab for the batch of materials used for laboratory studies right before use to ensure accurate values being used.

B. Adsorption of Ammonium on Biochar

All seven biochar products were determined for adsorption capacity of NH_4^+ and NO_3^-. Prior to the experiment, all biochar materials were dried at 105 °C to eliminate adsorbed water and ground to pass through 2 mm sieve. The amount of 0.200 g material was weighed in 15-mL glass screw top vials. Ten mL of 0, 25, 50, 75, 100, 150, and 200 mg L^{-1} NH_4^+-N solution was added to the vial. The different concentration solutions were prepared from the dilution of 1000 mg NH_4^+-N L^{-1} stock solution. The stock solution was made by dissolving 1.9091 g NH_4Cl into 500 mL deionized water in a volumetric flask. Duplicate samples were used for each solution concentration level. The biochar suspension was shaken on a gyratory shaker at 135 rpm for 24 hours (time determined previously to reach equilibrium). The suspension was centrifuged immediately at 1000 g RCF (relative centrifugal force) and then filtered through MF-Millipore™ Membrane Filter (Millipore Sigma-Aldrich, Inc., St. Louis, MO), 0.45 µm pore size of filter using vacuum. The filtration process took less than 10 seconds to complete, thus NH_3 loss from the filtrate was believed minimal. Potential NH_3 loss during shaking was minimal because the vials were closed. The filtrate was immediately transferred to a 10-mL vial, capped, and refrigerated before analyzed for NH_4^+. If the analysis could not be done immediately, the solution was acidified by adding 5 drops (~0.25 mL) of 6M HCl to 5 mL solution. The concentration in the solution represents the

concentration in the liquid phase at equilibrium. The adsorbed NH_4^+ was obtained by the differences between total amount initially in the solution (total added plus the concentration in the control) and the amount in the solution phase at equilibrium. For the control sample when no NH_4^+ was added, the adsorbed NH_4^+ was determined by extraction with 2M KCl for 1 h after the supernatant was decanted by assuming that a major portion of the adsorbed NH_4^+ could be replaced (desorption) by the high concentration of K^+. This method likely underestimates the actual amount of adsorbed because some strongly adsorbed NH_4^+ via surface precipitation may not be exchanged by K^+. Adsorption isotherms were plotted (adsorbed vs concentration in solution at equilibrium) and analyzed with several models (e.g., linear, Langmuir, and Freundlich equations). The linear adsorption isotherm suggests that the distribution or partition of NH_4^+ between solid and liquid phase is consistent as concentration changes:

$$q_e = K_d C_e \qquad (1)$$

where K_d refers to the partition or distribution coefficient, C_e is the equilibrium concentration of NH_4^+ in solution (mg L^{-1}), and q_e is the mass of adsorbed (mg kg^{-1}). Since only one biochar's data fit the linear equation, Langmuir and Freundlich equations were used to fit the adsorption data. The equations and data fitting were based on those described in [35]. The Langmuir equation to calculate NH_4^+ adsorption is:

$$q_e = \frac{q_{max} K_l C_e}{1 + K_l C_e} \qquad (2)$$

where K_l is the Langmuir isotherm constant (L mg^{-1}) related to the binding strength and q_{max} is the maximum amount of ammonium that can be adsorbed based on monolayer coverage. The parameters q_{max} and K_l were obtained by fitting data to the linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{C_e}{q_{max}} \qquad (3)$$

Freundlich adsorption equation is expressed as:

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where k_F is the Freundlich isotherm constant (mg kg^{-1}) (L mg^{-1})$^{1/n}$, and $1/n$ is a constant (dimensionless). The linear form of Eq. (4) is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (5)$$

Eq. (5) is used to obtain parameters K_f and $1/n$ by plotting Log C_e vs Log (q_e). The Freundlich equation is an empirical adsorption model and cannot predict an adsorption maximum. The K_f constant is considered related to adsorption capacity as it has the physical meaning of the amount of adsorbed at unit solution concentration. However, its implication depends on study interests and conditions. As solution concentration increased, the amount of adsorbed varies depending on both K_f and the constant $1/n$. The constant $1/n$ is considered a correction factor, which is always ≤1. When $n = 1$, K_f equals K_d, distribution coefficient in the linear adsorption isotherm. Due to the limitation of Freundlich equation, i.e., no maxima can be predicted and the q_e changes nonlinearly with C_e, to compare the differences in NH_4^+ adsorption between biochar products, we used arbitrary (low or high) solution concentrations in the study range for discussion.

Nitrate adsorption on the seven biochar products were determined following similar procedures as for the NH_4^+, but at only two levels: low (5 mg N L^{-1}) and high (50 mg N L^{-1}) initial solution concentrations because preliminary tests showed no adsorption on biochar at the higher level. These concentrations represent the lower ends of concentration range often found in the field. According to Kabala *et al.* [36], N concentration varied significantly across the season from annual application of 90–180 kg ha^{-1} for sorghum production. Nitrate concentration could go up to 100 mg dm^{-3} at 50 cm depth and 880 at 25 cm depth during a peak month (July) but most other times below 50 mg dm^{-3} during sorghum growing season while NH_4^+-N concentrations remained below 2 mg dm^{-3} in both surface and subsurface soil layer. The concentrations we selected in the test for NH_4^+-N was up to 200 mg L^{-1}.

C. Adsorption Envelopes (pH Effects) of NH_4^+ on Biochar

The pH effects on NH_4^+ adsorption was conducted on all biochar products using similar approach as the isotherm experiment but at one concentration level (100 mg L^{-1} NH_4^+-N). An amount of 0.500 g material (dried at 105 °C and ground to pass through 2 mm sieve) was weighed in 45-mL plastic centrifuge vials. Varying volumes of either 6 M HCl (4–1000 μL) or 5M NaOH (5–400 μL) plus sufficient deionized water were added to the vial to make total liquid volume of 22.5 mL. The different combinations were trying to achieve a pH range of 2–11. The suspension was equilibrated at controlled room temperature for at least 24 hours. Then 2.5 mL of 1000 mg L^{-1} NH_4^+-N solution (prepared from NH_4Cl in deionized water) was added to the vials for an initial solution concentration of 100 mg L^{-1} NH_4^+-N. Another set of vials for each biochar product without adding NH_4^+ solution was prepared and served as blanks. The biochar suspension was shaken on a gyratory shaker for 24 hours, measured for final pH, filtered, and analyzed following the same protocols as for the adsorption isotherm experiment.

D. Chemical Analysis

Chemical analyses for the adsorption experiments were done in our lab including mineral N species [NO_3^-, nitrite (NO_2^-), and NH_4^+] and biochar suspension pH. The pH measurement was accomplished using a digital 420A pH meter with a combined glass electrode (Orion Research Inc., Boston, MA, USA). For mineral N species, the analysis was done using a colorimetric method [37] on a Lachat QuikChem Flow Injection Analysis System

(Lachat Instrument, Loveland, CO, USA). Due to the difference in pH and other factors among biochar products, duplicate runs, reference materials, and spiked samples were all included in each batch analysis for each biochar product to ensure reliable analytical results. Filtrates were diluted 1+4 with deionized water except the almond shell char 550 that were diluted 1+9 with deionized water to minimize color interference for analysis in the analytical standard range of 0.5–20 mg L^{-1} for the pH effect experiment or 1–40 times for the isotherm experiment using a standard range of 1–50 mg L^{-1} for the adsorption isotherm experiment. Duplicate samples showed variation within <5%. Reference material and spiked samples gave a recovery of 95–110% for all runs.

E. Data Analysis

Statistical and regression analyses were performed for all isotherms by the linear or the linear form of Langmuir or Freundlich equations. To correlate the adsorption capacity for NH$_4^+$-N with biochar properties, stepwise regression was performed between q_{max} or K_f and biochar variables using SAS software (version 9.4, SAS Institute, 2013, Cary, NC). The q_{max} or K_f were selected to investigate possible mechanisms for adsorption at high or low concentration ranges, respectively.

TABLE I. SELECTED PROPERTIES OF BIOCHAR PRODUCED FROM VARIOUS FEEDSTOCKS AND PYROLYSIS TEMPERATURE

Biochar feedstock (pyrolysis T °C)[1]	Org-C	Total Ash	Total N	pH	EC$_{20}$	Carbonates	Surface Area	Total K	Total P	Ammonia (NH$_4$-N)	Nitrate (NO$_3$-N)	Organic (Org-N)
	(% dry mass)	(% dry mass)	(% dry mass)		(mS cm^{-1})	(% CaCO$_3$)	(m^2 g^{-1})	(g kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
Almond shell (550)	56.6	19.5	0.96	9.8	5.32	1.5	150	24.3	1,146	23.9	12.9	9,526
Almond shell (900)	23.4	65.2	0.54	12.0	30.7	33.9	262	280.6	12,491	57.8	7.3	5,363
AG Softwood (540)	62	20.2	0.64	10.3	2.31	13.3	317	27.7	4,208	16.6	25.7	6,362
Bamboo[2] (Blue Sky)	75.9	19.8	0.99	9.2	0.351	0.6	153	12.5	767	21.7	1	9,852
CB Softwood (500)	56	43.6	0.5	9.5	2.96	16.6	229	31.1	7,965	25.9	24.5	4,780
Coconut shell (<550)	74.1	5.1	0.7	6.5	0.197	0.4	149	7.9	731	18.7	0.5	6,975
Green waste (>900)	56.8	11.5	2.19	7.3	0.223	2.6	149	5.8	576	23.5	0.5	21,914
Method:	Dry Combust-ASTM D 4373	ASTM D1762-84	Dry Combustion	4.11USCC: dil. Rajkovich	4.11USCC: dil. Rajkovich	ASTM D 4373	Butane activity surf area correl [56]	EPA3050B/EPA 6010	EPA3050B/EPA 6011	Rayment & Higginson [57]	Rayment & Higginson [57]	Calculated

[1] Both almond shell chars and coconut shell char were prepared by Cool Terra (Camarillo, CA). The AG softwood (coniferous tree biomass from forests) char (540 °C) was from AG Biochar, LLC (Modesto, CA). The CB softwood char was obtained from Charborn, LLC (Salinas, CA). The Green waste (wood/tree trimming) char was from CA Greenest (San Jose, CA) and the bamboo char was provided by Blue Sky (Thousand Oaks, CA).
[2] Pyrolysis temperature for the bamboo could not be confirmed but assumed to be <550 °C based on its high org-C content or low ash content and other parameters. All biochar materials were dried before use.

III. RESULTS

A. Biochar Properties

The seven biochar products used in this study varied in physical and chemical properties (Table I) as well as particle size distribution (Fig. 1). These variations were due to the different feedstocks and PTs as well as post-pyrolysis treatment in the coconut shell char, which was the only product with a pH below 7. All other products without modification had a pH above 7 or up to 12. The green waste char had a neutral pH or much lower than the almond shells at similar high pyrolysis temperature (900 °C), likely influenced by bioenergy production process. The almond shell char had a pH 12 as result of much higher ash or mineral as well as nutrient contents as agricultural biomass. The higher PT (900 °C) for the

almond shells resulted in lower C content than that from 550 °C and contained the highest nutrients especially K and P or about ten times of that from the almond shells from 550 °C PT. We do not have information about biochar production efficiency, but it is expected that higher PT produced more nutrient dense materials than C-rich biochar. Particle size distribution is largely dependent on not only on the stock material and PT, but also how the feed stock materials were prepared. The almond shell char from 900 °C PT had higher proportion of finer materials than that from 550°C. The green waste char had ~90% particles larger than 2 mm and >1 mm for bamboo and coconut shell chars. The two softwood biochar products from different companies (AG biochar and CB biochar) from similar PT (500–540 °C) showed similar particle size distributions and similar properties such as pH, EC, nutrient levels (total N, P, and K), and others.
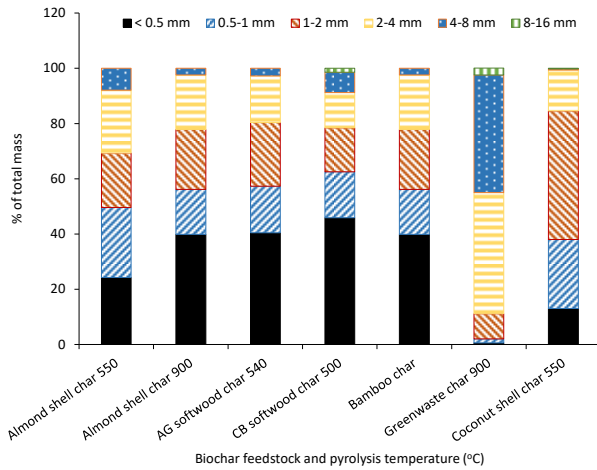
Fig. 1. Particle size distribution in biochar products from different feedstocks.

B. Adsorption of Ammonium on Biochar

Data for NH_4^+ adsorption isotherms and fitting by all three isotherm equations are shown in Fig. 2. The fitting parameters for Langmuir and Freundlich equations are provided in Table II. Not all isotherms fit to one adsorption model (Table III). Among all biochar products, only the almond shell char 900 fit the best to the linear equation ($R^2 = 0.943***$), which suggests different mechanisms dominating the adsorption (most likely surface or co-precipitation in this case). Langmuir equation fit well to all isotherms except almond shell char 900 ($R^2 = 0.50***$) compared to others ($R^2 = 0.94–0.99***$) although several isotherms (AG-softwood char, CB-softwood, bamboo char, and the green waste char) fit better than others (almond shell char 550 and coconut shell char 550) that showed some deviations at higher concentrations. Freundlich model fit all the adsorption isotherms well ($R^2 = 0.88–0.99$). The K_f is related to adsorption capacity at unit concentration of 1 mg kg^{-1}, thus has limited meaning because it was at the lower end of concentration range. We selected the high solution concentration of 200 mg L^{-1} (the higher end of concentration range that was likely to occur in soil following fertilizer application) to project the adsorption capacity in comparison with the maximum adsorption capacity (q_{max}) predicted by Langmuir model. Note the predicted adsorption amount at solution concentration 200

mg NH_4^+-N L^{-1} followed an order that deviated significantly from the order of the K_f as the solution concentration changed, but it followed a similar order of q_{max} except for the almond shell char 900. The difference was caused by its adsorption isotherm that fit better to the linear equation (Fig. 2 and Table II).

Stepwise regression results showed that organic-C content, pH, EC, and surface area of biochar ($p = 0.04$, 0.01, <0.001, and 0.05 respectively) can explain almost all the variation ($R^2 = 0.999$) in adsorption capacity (q_{max}). However, only carbonate in biochar ($p = 0.01$) was significantly contributing ($R^2 = 0.757$) to K_f (adsorption in low concentration range). Although the analyses might be limited by the total number of samples, the results may reflect different sorption mechanisms involved. The high correlation of adsorbed NH_4^+ with EC (indicator for dissolved mineral content) may suggest precipitation or co-precipitation occurred in addition to adsorption affected by surface area and functional groups.

TABLE II. LANGMUIR AND FREUNDLICH ADSORPTION CONSTANTS FOR AMMONIUM ADSORPTION ON BIOCHAR

Biochar Type	Langmuir[†]		Freundlich[‡]		
	K_l	q_{max}	K_f	$1/n$	Estimated q_e C_e = 200 mg NH_4^+-N L^{-1}[§]
Almond shell, 550 °C	0.078	3100	565	0.36	3890
Almond shell, 900 °C	0.000	11,800	23	0.88	2530
AG softwood, 540 °C	0.017	2260	113	0.55	2040
Bamboo, <550 °C	0.120	1110	558	0.14	1160
CB softwood, 500 °C	0.019	2650	160	0.51	2450
Coconut shell, <550°C	0.087	2070	476	0.31	2400
Greenwaste, >900 °C	0.042	2090	301	0.37	2180

[†] K_l is the Langmuir isotherm constant (L mg^{-1}) related to the binding strength and q_{max} (mg kg^{-1}) is the maximum amount of ammonium that can be adsorbed based on a monolayer coverage.
[‡] K_f is the Freundlich isotherm constant and can be considered as the adsorption capacity at unit concentration (mg kg^{-1}) (L mg^{-1})$^{1/n}$, and $1/n$ is a constant (dimensionless). C_e is the equilibrium concentration of NH_4^+ in solution (mg L^{-1}), and q_e is the mass of adsorbed (mg kg^{-1}).
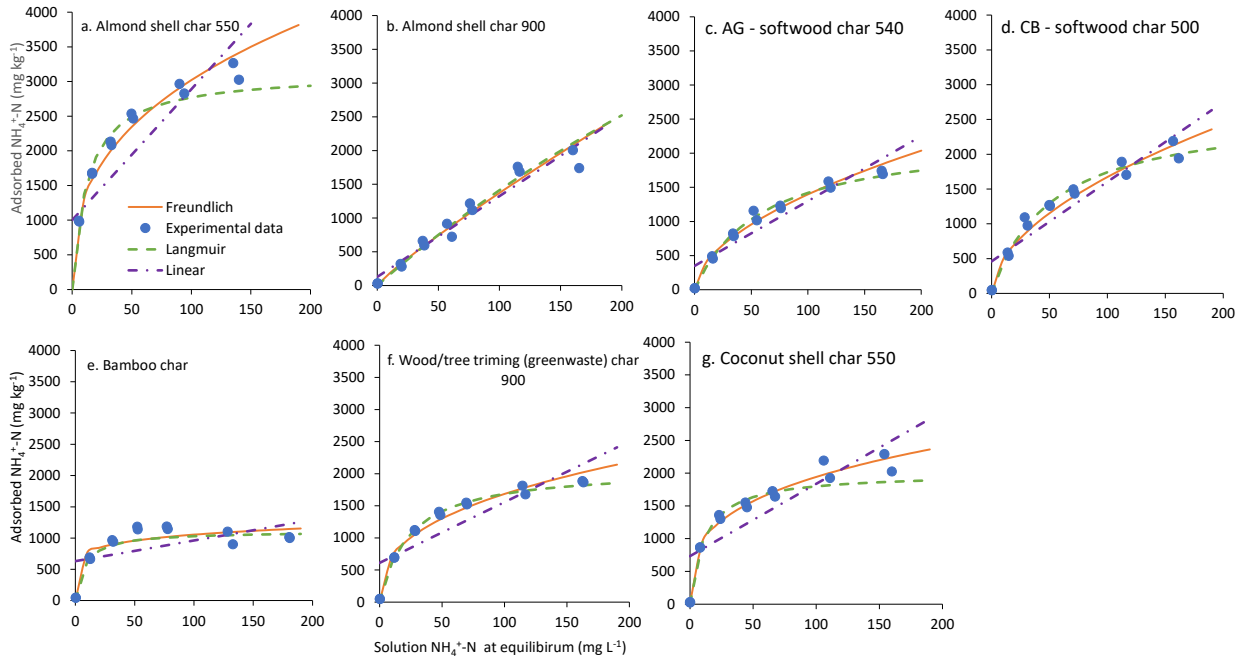[§] The estimation was made for the upper concentration limit tested in this study.

Fig. 2. Adsorption isotherm of ammonium on biochar. The lines are fitted based on linear, Langmuir, or Freundlich equations.
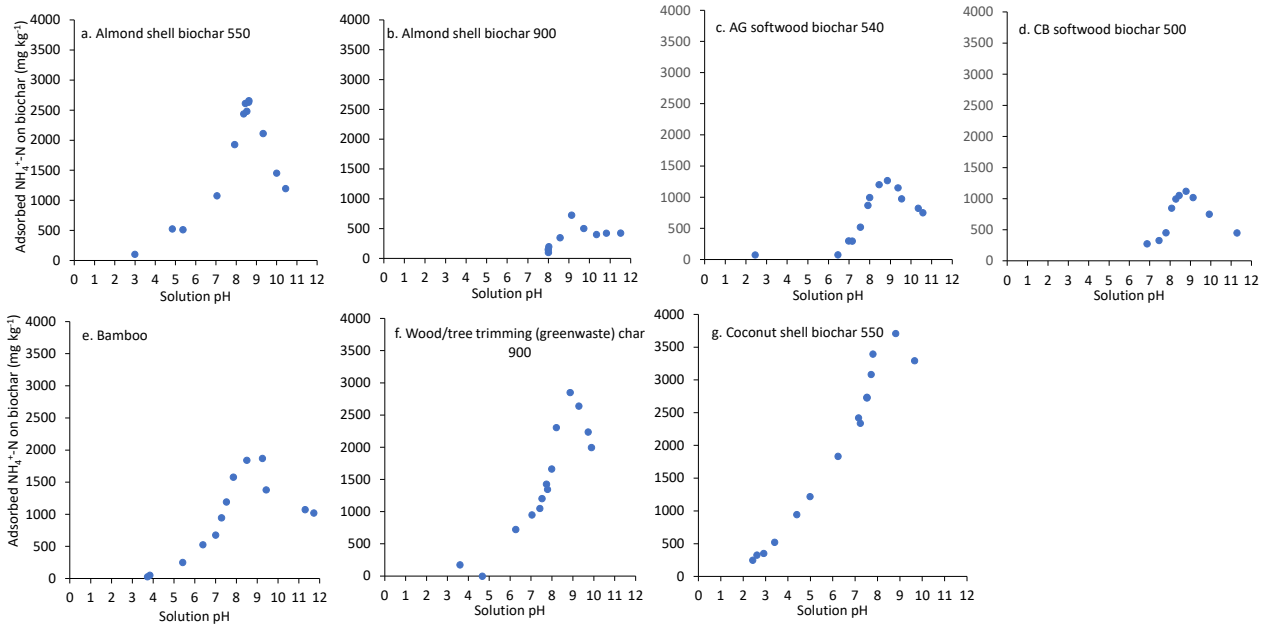

Fig. 3. Adsorption envelopes of NH_4^+ on biochar products from an initial solution concentration of 100 mg NH_4^+-N L^{-1} at a 50:1 (v/w) solution to biochar ratio.

TABLE III. LINEAR REGRESSION ANALYSIS FOR AMMONIUM ISOTHERM FITTING WITH THE LINEAR, LANGMUIR, AND FREUNDLICH EQUATIONS

Biochar	Linear			Langmuir			Freundlich		
	R^2	*p*-values		R^2	*p*-values		R^2	*p*-values	
		Intercept	Slope		Intercept	Slope		Intercept	Slope
Almond shell, 550 °C	0.741	5.63E-04	7.64E-05	0.981	5.72E-04	1.01E-11	0.990	4.75E-21	2.90E-13
Almond shell, 900 °C	0.943	1.01E-01	8.02E-09	0.500	2.48E-04	4.67E-03	0.979	7.29E-14	1.79E-11
AG softwood, 540 °C	0.880	1.71E-03	7.21E-07	0.935	3.63E-05	1.81E-08	0.994	9.40E-18	8.91E-15
Bamboo, <550 °C	0.299	5.14E-04	4.31E-02	0.982	5.37E-01	6.67E-12	0.876	4.88E-11	8.65E-07
CB softwood, 500 °C	0.861	1.19E-03	1.73E-06	0.940	6.48E-05	1.05E-08	0.991	1.26E-17	1.02E-13
Coconut, <550 °C	0.723	5.04E-04	1.17E-04	0.982	3.17E-05	6.66E-12	0.933	1.06E-11	2.03E-08
Greenwaste, >900 °C	0.747	5.77E-04	6.62E-05	0.989	3.21E-06	3.31E-13	0.975	2.63E-15	4.97E-11

C. Adsorption Envelope of Ammonium on Biochar

The pH effect on NH_4^+ adsorption onto biochar is shown in Fig. 3. All graphs show the same pattern. The adsorption of NH_4^+ by all biochar products was very low at low pH, increased as pH increased, and peaked around pH 8.5–9 or near the pKa (9.3), dissociation constant for NH_3(aq) or NH_4OH, and then decreased as pH raised further except the coconut shell char that showed no decline in the study range. The data indicate that the ability of biochar to retain NH_4^+ is highly influenced by the type of biochar and pH is one of the most important factors influencing the adsorption. Notice the two softwood biochar materials with PT of 500–540 °C without post-production treatment had similar peaks ranging around 1500 mg N kg^{-1} adsorption maximum at an initial solution concentration of 100 NH_4^+-N. From similar PT, the almond shell char exhibited the highest peak followed by the bamboo char. The coconut shell and green waste biochar showed highest adsorption (3000–3700 mg NH_4^+-N kg^{-1}) under the study conditions. All the adsorptions, however, were reduced by more than 50% at pH 7.

D. Adsorption of NO_3^- on Biochar

Nitrate adsorption on most biochar products regardless of feedstock or PT were very low (Fig. 4) compared to that for NH_4^+ (Fig. 2). Only the almond shell char from PT 900 °C showed 30% adsorption at low concentration (5 mg L^{-1} initial NO_3^--N concentration). For most biochar products, the ability to retain NO_3^- is very limited with <5% adsorbed at low concentration or nil at the high concentration (50 mg L^{-1} initial NO_3^--N concentration).
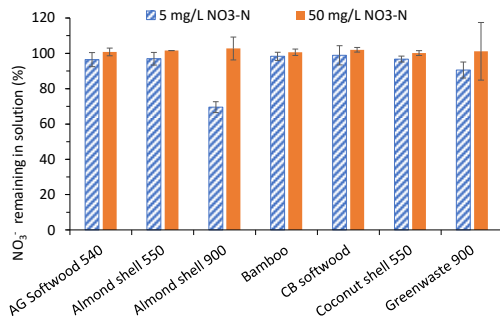

Fig. 4. Solution NO_3^--N concentration at equilibrium after 5 or 50 mg L^{-1} were added to biochar suspension. Error bars are standard deviation of duplicates.

IV. DISCUSSION

A. Adsorption Characteristics of NH_4^+ by Different Biochar Products

Except the almond shell char 900 that had adsorption isotherms for NH_4^+ fit well to the linear equation, all others fit well to either Langmuir and/or the Freundlich equations (Fig. 2). These values imply that different adsorption mechanisms were involved. The estimated q_{max} (Table II) suggested that almond shell char 900 had the highest adsorption capacity followed by the almond shell char 550, then softwood or wood material biochar, and the lowest

from the bamboo char. This prediction may underestimate q_{max} for the almond shell char 550 and coconut shell char 550 because the prediction began to deviate more from experimental data as solution concentration increased (Fig. 2). The deviation does not change the conclusion that almond shell char 550 showed the highest capacity to adsorb NH_4^+ among all the products. Freundlich model predicted adsorption amount by the biochar products at high solution concentration (e.g., 200 NH_4^+) also the highest from almond shell biochar (either PT 550 or 900), suggesting a great potential of this feedstock biochar to retain N.

The higher NH_4^+ adsorption by the almond shell chars than the coconut shell char seems to contradict to what is observed in the pH envelope, but it can be explained due to the difference in product pH, i.e., the higher pH in almond shell char resulted in higher adsorption while the lower adsorption by the coconut biochar was due to its lower pH (Fig. 2). As the pH increased from the coconut shell char, the adsorption increased to a maximum that appeared higher than the almond shell char (Fig. 3). In other words, post biochar treatment by reducing pH in coconut biochar did not increase NH_4^+ adsorption although it provides other benefits and minimize NH_3 loss. The data validate findings by others that pH is one of the most important factors in influencing adsorption [22, 38]. Fidel *et al.* [22] illustrated the same trend that at solution concentration of 10 mg NH_4^+-N L^{-1} its adsorption increased linearly as pH increased from 3.5–9. Our data suggest that NH_4^+ adsorption around pH 9 for all the biochar products regardless PT or feedstock. In most neutral pH, adsorption can be reduced to 50% or lower. The highest adsorption was close to the pKa (9.3) of NH_4^+ that suggest the strong influence of variable charges from functional groups on biochar. However, this high pH favors significant loss of NH_3. Wang *et al.* [39] determined that biochar, which had been acid-aged, did not significantly change chemical properties, functional groups, or chemical bonds on the biochar surface, and their observed NH_4^+-N sorption increase was attributed to physical property changes, such as increasing surface area and porosity.

The relative difference in adsorption capacity changes as a function of solution concentration can be examined further by the Freundlich model to reveal some sorption mechanisms. Foo and Hammed [35] stated that Freundlich model can be applied to multilayer adsorption sites over the heterogeneous surface, demonstrating that the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations. The amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process. The model explains well the adsorption of NH_4^+ on all biochar products in our study as the organic rich materials would involve multiple functional groups or sites [26]. Fig. 5 shows the unaccounted NH_4^+ from the adsorption isotherm experiment. The higher percentage of accounted NH_4^+ at lower concentration is most likely due to stronger

adsorption or co-precipitation that cannot be exchanged by K^+. This fraction was likely getting smaller as the strong adsorption sites or function groups were occupied as concentration increased. Fidel *et al.* [22] clearly demonstrated the importance of ion-exchange mechanisms that the sorption of NH_4^+ to biochar is electrostatic. Adsorption mechanisms include cation exchange, outer-sphere adsorption, inner-sphere adsorption, surface precipitation, and ternary adsorption complexes [40] that were all likely involved in adsorption of NH_4^+ by biochar in our case because of the wide range of solution concentration studied. Fan *et al.* [38] demonstrated that surface complex formation and surface precipitation are responsible for the removal of NH_4^+ from dilute aqueous solution in the presence of bamboo biochar where Fourier Transform Infrared Spectroscopy (FTIR) results showed shift, disappearance, or appearance of specific functional groups on the biochar surface. Surface precipitation or coprecipitation such as $Mg(NH_4)PO_4(s)$ likely occurred especially at high pH and high ash content such as the almond shell char 900 because of the high minerals and P concentrations detected in this product (Table I). The linear adsorption isotherm and high correlation between biochar EC and q_{max} for this product support this assumption.
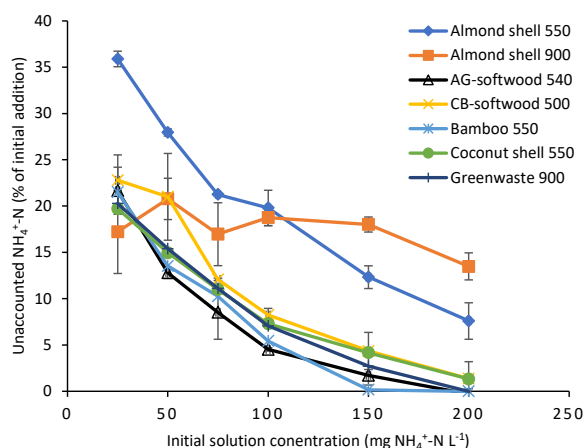

Fig. 5. Unrecovered NH_4^+-N by 2M KCl extraction from isotherm experiment. The higher percentage loss at lower concentration than those from higher concentrations may suggest either stronger adsorption that cannot be exchanged or NH_3 loss. The higher % of the unrecovered from the almond shell char at PT 900 °C may suggest precipitation or coprecipitation of NH_4^+ with other minerals across concentration range.

The data fitting by Freundlich equation also illustrates the differences in NH_4^+ adsorption capacity as solution concentration changed because the adsorbed NH_4^+-N (q_e) at a fixed solution concentration (C_e) depends on both K_f and $1/n$ (Fig. 6 and Table II). The K_f represents the q_e when $C_e = 1$, which represents a very low concentration in soil solution. The order of the adsorption capacity among the biochar products shifted as the C_e increased. The almond shell char (500) showed the highest adsorption across the studied range (1–200 mg N L^{-1}). The bamboo product showed high adsorption at very low concentration (<2 mg N L^{-1} but became the lowest once C_e reached 70 mg L^{-1} in solution. All other products fell into a cluster except the almond shell 900 that showed the lowest adsorption at C_e

<70 mg NH_4^+-N L^{-1} but increased almost linearly and eventually exceeded other products except the almond char 550. The results imply that the same biochar product would have different N retaining efficiency in comparing with other products depending on solution concentrations. For example, the bamboo biochar may adsorb NH_4^+ as effectively as other biochar products at low solution concentrations as in most agricultural fields, but the efficiency would become very low in the removal of NH_4^+ from contaminated water at high concentrations. On the other hand, the almond char at 900 PT could become more efficient in retaining NH_4^+ from contaminated water compared to most other products although the lowest adsorption was measured at low solution concentrations. The PT for biochar production has significant effects on NH_4^+ adsorption. For the same almond shell feedstock, the low PT at 550 °C showed much higher adsorption capacity than that from PT 900 in this study. The results agree with other findings that low PT favors NH_4^+ adsorption when more functional groups are present compared to those from high PT [23–25]. For the feedstock of softwood, the slightly different PT (500–540 °C) from two sources also indicated the same trend as PT changed (Table II and Fig. 6). Almond shells are harvest byproducts that are often considered orchard wastes. Our data showed that converting the material into biochar without further treatment can retain NH_4^+- the highest among the tested products including the coconut shell biochar that was treated to reduce pH. Softwood is considered a large valuable feedstock due to unexpected fire incidents and dead trees from drought. The data suggest that removing these materials from forest to produce biochar can benefit agricultural soils while serving as a strategy for environmental management.
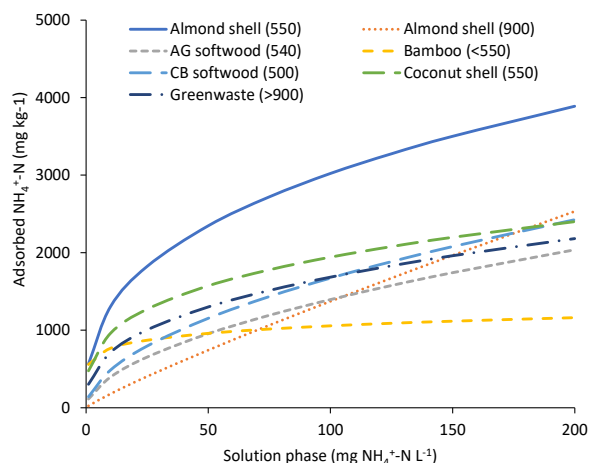

Fig. 6. Prediction of NH_4^+-N adsorption onto biochar products as solution concentrations change based on Freundlich fitted parameters.

B. The Role of Biochar to Retain N in Soil Likely Limited

The biochar products without post-production treatments all showed some capacity to adsorb NH_4^+, but up to a maximum 1500 mg N kg^{-1} around pH 9 (from a 100 mg NH_4^+-N solution, Fig. 3). At neutral pH the adsorption was reduced by about half or more. Assuming a rate at 20 t ha^{-1} biochar is feasible in practice, it can

translate to about 15 kg N ha^{-1} (15% or less of N applied at or above 200 kg N ha^{-1} annual fertilization rate) may be adsorbed. After incorporation to soil, the pH will change and eventually equilibrate with soil pH. An attempt was made to determine NH_4^+ adsorption by acidifying the almond shell char 500 to neutral pH, which resulted in much lower adsorption than without acidifying (data not shown). Considering NO_3^- adsorption is insignificant by biochar, management would mainly depend on the interaction between biochar and NH_4^+. In a more comprehensive study including 10 soils and 4 rates of wood-based biochar, Hailegnaw *et al.* [31] showed that biochar's effect on soil NH_4^+ was inconsistent and insignificant in most of the incubated soils at all biochar rates (0.5–8%) that contradicted to Langmuir model estimated adsorption capacity. They attributed the discrepancies to the potential liberation of NH_3 loss. Biochar without modification tends to have high pH favoring NH_3 volatilization, which presents a challenge for adoption of biochar as a practice in most neutral or alkaline soils but can be highly beneficial in acidic soils. Furthermore, NH_4^+ is not stable in most oxygenated environment and tends to be oxidized to the more stable NO_3^-. Based on the lab experimental data it was not surprising that biochar (up to 58 t ha^{-1}) did not improve crop yield or biomass production, reduce gaseous loss as NH_3 and N_2O, and increase soil N or N uptake for vegetable crops [19–21]. These examinations suggest that biochar can retain N, but the role in significantly improving N availability and reducing loss to the environment is likely limited. However, the results do not deny the positive effects of biochar amendment to significantly improve some of the soil limiting factors such as soil physical and chemical properties or increased water retention in coarse textured soil [41, 42] or neutralized pH in acidic soils [43–45]. Nkoh *et al.* [46] conducted systematic review and revealed that the surface properties of biochar and its associated nutrient content determine its role in the soil while the extent of changes depends on soil properties. Our study did not show correlation between N adsorption and biochar surface area, but by ash or mineral contents and solution concentration level that all subject to change in soil. Thus, both biochar and soil properties determine the outcome of biochar amendment in soil.

To significantly increase N adsorption of biochar materials, many studies explored modifying biochar materials by various treatments. For example, oxidizing biochar by exposure to hydrogen peroxide (H_2O_2) for different periods of time reduced pH and the lowest pH products that were then neutralized to pH 7 increased NH_4^+ adsorption by several fold (from ≤1 mg NH_4^+-N g^{-1} to >41 mg NH_4^+-N g^{-1} [32]. Base (NaOH or KOH)-activated biochar enhanced biochar adsorption for NH_4^+ by 2.9–4.7 times with the maximum adsorption capacity of 14.34 NH_4^+-N [33] (Hsu *et al.* 2019). Magnesium-loaded biochar from production exhibited potential maximum adsorption capacity that could go up to 31.15 mg g^{-1} for NH_4^+-N [47]. While studying NH_4^+ adsorption from biochar at three PTs, three activation

conditions (no oxidation, partial oxidation at 250 °C, and chemical activation), and using three washing methods (no washing, acid washing, and hot water), the highest NH_4^+-N adsorption capacity (1.49 mg/g) was observed from the chemically activated biochar (with potassium carbonate) pyrolyzed at 650 °C without washing with acid or hot water [25]. Oxidized biochar by sodium hypochlorite (NaClO) or H_2O_2 produced at relatively high temperature (500–700 °C) or in combination with acid wash increased NO_3^- adsorption [34]. Although these findings can be valuable for N retention, products with feasible costs are still the key to successful adoption of biochar as an agronomic practice.

C. Biochar Amendment as an Effective Strategy to Sequester C and Improve Overall Soil Productivity

Although biochar may not have a significantly direct impact on N retention via adsorption especially in soils with neutral pH based on the analysis above, the undeniable benefits to sequestrate C and improve soil property make it a good agronomic practice. Field experiments with the same soil showed that the softwood biochar increased Soil Organic C (SOC), increased water retention, and improved soil health [19, 48]. Many studies also reported these benefits [49–51]. Further detailed studies demonstrated the benefits of biochar to improve N use efficiency by promoting enzyme or microbial activities [16–18]. Sequestrating C in soil is a climate smart strategy that also improves soil productivity. Agricultural land uses have resulted in the loss of 133×10^{12} Kg C from the soil and the hotspots are often associated with major cropping regions and degraded grazing lands [52]. Evidence has demonstrated that prehistorically modified soils rich in C are the basis for sustainable agriculture [5]. Depletion of SOC leads to many detrimental effects and threatens sustainability of cropping systems. Biochar can persist in soils on a centennial scale [53]. Thus, biochar can play an important role in sustainable crop production and such practices can and should be exercised whenever feasible. However, the ability of biochar to retain N should not be overstated because inaccurate conclusion can lead to confusions on soil N management for crop production. There are many opportunities or conditions where biochar can be used such as replacing agricultural burning when diseases are concerns or other biomass waste that can be put into good use [54]. Biochar from agricultural biomass can be a significant source of P or K as shown in Table I. Depending on the feedstock, biochar at 20 t ha^{-1} can provide 340 kg K ha^{-1} and then inorganic fertilizer input may be replaced or substantially reduced. Commercial biochar products by far are still too expensive as a feasible practice. At a cost of $350 per ton (for wood biochar), plus application expenses, a rate of 10 ton ha^{-1} would result in $3500+ per ha costs [55], which is substantial for many growers. Without being able to see the benefits in crop yield or other benefits, it is difficult to convince growers to adopt such a practice. A more economical way to produce biochar in situ should be sought to significantly reduce the production and operation costs. There are various low costs methods to produce biochar

(https://biochar-us.org/biochar-production). Modification technology needs to target low costs to make this practice sustainable and environmentally beneficial.

V. CONCLUSION

Based on the determinations of N adsorption, biochar products showed a variable capacity for NH_4^+ retention, which is also highly dependent on pH. The maximum adsorption occurred around pH 9 and the adsorption can be reduced by half at neutral pH. Furthermore, NH_4^+ is unstable in most agricultural soils and the dominant NO_3^- is not adsorbed onto biochar products without modification. Thus, biochar amendment in soil may not result in significant reduction in fertilizer application. Biochar does provide holistic benefits to the soil production system by increasing SOC and improving other properties such as increased water retention and supplying nutrients especially K, thus should continuously be promoted as a conservation practice to improve/sustain the overall soil productivity. Current commercial products are too expensive for growers, and research efforts should be more given to producing low-cost products to promote adoption.

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