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Maximum phosphate adsorption capacity as influenced by some biochar properties

[1]Abdu N., *[2]Solomon, R. I., [1]Yusuf A. A., and [3]Bello M.

1. Ahmadu Bello University Zaria, Faculty of Agriculture, Department of Soil Science
2. Modibbo Adama University of Technology, Yola, School of Agriculture and Agricultural Technology, Department of Soil Science
3. Ahmadu Bello University Zaria, Faculty of Engineering, Department of Chemical Engineering

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Corresponding Author's E-mail Address: **rejoice605@gmail.com**

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ABSTRACT

The use of biochar as a low-cost adsorbent to remove nutrients from aqueous solutions is getting great attention lately due to its many environmental applications and benefits. Although biochar has been widely used to remove phosphate from aqueous solutions, inconsistencies still exist with regards to biochar properties responsible for the adsorption process. This research was therefore, carried out to determine the influence of some biochar properties on the maximum phosphate adsorption capacity of biochar produced from four different feed-stocks. The biochars used for this study were prepared from two plant materials; (Maize cob and rice husk) and two animal wastes (cow dung and poultry litter) at 600 ° C. The different biochars were subjected to a laboratory batch sorption experiment. Data obtained were fitted into the linear forms of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) adsorption isotherms while least square regression analysis was used to test the goodness of fit using the coefficient of determination (R^2)., stepwise regression analysis was carried out to determine the nature and extent of relationships between the biochar properties and maximum phosphate adsorption capacity using statistical analysis software (SAS 9.4). Results revealed higher R^2 values for the D-R adsorption isotherm (> 0.97) across all the treatments suggest a better fit of the D-R adsorption isotherm for phosphate adsorption onto the biochar materials. The maximum phosphate adsorption capacity of the biochar materials is in the order: maize cob biochar > poultry litter biochar > cow dung biochar > rice husk biochar. Stepwise regression analysis revealed that 99 % of the change in maximum phosphate adsorption is influenced by the combined effects of biochar EC, moisture content and specific surface area. Hence, modification of biochar EC, moisture content, and specific surface area is essential for improving phosphate adsorption by biochar.

1.0 Introduction

Incessant fertilizer application to meet the food production demand of the ever-growing human population has been the leading cause of phosphate release from both point and non-point sources into a runoff. This has led to the accumulation of high nutrient concentrations in surface and/or groundwater a condition called eutrophication; excessive production of photosynthetic aquatic microorganisms in freshwater and marine ecosystems (Karaca *et al*., 2004). Jung *et al.* (2015) reported that eutrophication is a serious environmental issue responsible for the degradation of the quality of water ecosystems, global loss of biodiversity with undesirable influence on the economy, and has caused great danger on environmental health (Yao *et al*., 2011).

So many methods have been proposed for phosphate removal from contaminated media, which include; chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and adsorption (Adegoke *et al*., 2013). However, these techniques are not without some setbacks, for instance, reverse osmosis as effective as it maybe is expensive as membranes get easily spoiled and therefore needs frequent replacement while chemical precipitation is not very sensitive especially where the contaminants are in a small amount. Solvent extraction or electrolytic processes can be economical only when working with more concentrated solutions while ion exchange is expensive and requires skilled manpower for its operation. Therefore, adsorption is a more preferred method for the removal of toxic contaminants from wastewater because it is cheap, very effective with any concentration, and simple (Tran *et al*., 1999). Other benefits of adsorption include its effectiveness at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, the possibility of regeneration and re-use (Mohanty *et al*., 2006).

Sparks (2003) defines adsorption as one of the most significant chemical processes that affect the movements of nutrients and contaminants. It is a widely used technique for removing pollutants from contaminated media. Zhou *et al.* (2019); Takaya, *et al*. (2016) reported that phosphate adsorption may be affected by many factors, which include its CEC, acidic functional groups, surface charges, and anion exchange capacity. Biochar symbolizes a developing technology that is progressively being accepted for its potential role in carbon sequestration, waste management, soil improvement, crop productivity enhancement, and environmental remediation (Kuppusamy *et al*., 2016, Takaya, *et al*., 2016). It is a fine-grained, carbon enriched product mainly produced from biomass feedstocks by pyrolysis under no/limited oxygen condition (Lehmann, 2007). The physical properties of biochar which include; low biodegradability, high porosity, and high surface area make biochar an important source of soil amendment which promotes beneficial soil microorganisms, binding of nutrient cations and anions, and may enhance nutrients availability (Karer 2013). However, theseproperties differ widely based on feedstock material and method of pyrolysis thereby shaping their suitability for specific purposes (Ogonek 2016). Although biochars have been generally used to remove phosphate from aqueous solutions, inconsistencies still exist with regards to biochar properties responsible for the adsorption process. Similarly, the phosphate adsorption capacity of biochar is feedstock specific (Trazzi *et al*. 2015) and is greatly influenced by biochar properties. Therefore exploring the relationship between maximum phosphate adsorption capacity and biochar properties to ascertain the physiochemical properties of biochars that affect phosphate removal from contaminants is imperative. This research was therefore, carried out to determine the influence of some biochar properties on the maximum phosphate adsorption capacity of biochar produced from four different feed-stocks.

2.0 Materials and methods

2.1 Biochar Preparation

Biochar was prepared from two plant materials (Maize cob and rice husk) and two animal wastes (cow dung and poultry litter). In each case, 47.6, 37.2, 45.0, and 39.5 kg of Maize cob, rice husk, cow dung, and poultry litter respectively were placed in an airtight stainless steel container separately before putting it into the oven. This process lasted for about two hours. The oven was heated to 600 °C (to obtain high surface area) at a heating rate of 20 °C per minute and kept at that temperature for 45 min. After each run, the oven was turned off and the biochar was left inside to cool. This process was carried out in a 60-litre capacity oven. The pyrolysis resulted in 11.2, 11.2, 15.20, and 12.40 kg of Maize cob biochar (MCB), Rice husk biochar (RHB), Cow dung biochar (CDB), and Poultry litter biochar (PLB) respectively. The biochar mass was then grinded and sieved through a 2 mm mesh sieve to obtain a powder consistency that would mix uniformly with the soils.

The biochar samples were characterized for pH, total ash content, total organic C, phosphates, volatile matter, biochar yield, as described by Jindo *et al*. (2014). The pH was determined using the pH drift method as described by (Cataldo *et al*., 1975) while the specific surface area was determined using the methylene blue method and the Langmuir surface area calculated as described by Itodo *et al*. (2010).

2.2 *Batch Sorption Experiment*

The different biochars were subjected to a laboratory batch sorption experiment to determine their ability for phosphates adsorption. One gram (1g) of biochar samples were equilibrated with three different concentrations; 15, 30, 60 mgL^{-1} phosphate in a 1:50 biochar to solution ratio using potassium di-hydrogen phosphate as the source of phosphate in a 50 ml flask. The flasks were shaken on a mechanical shaker to allow the suspension to equilibrate. Samples were filtered after 60 minutes. Phosphate concentration in the filtrate was measured using the ascorbic acid method in a spectrophotometer. The amount of phosphate adsorbed by biochar was calculated based on the following relationship as proposed by Mulu (2013):

$$Q = \frac{V_i (C_i - C_e)}{M}$$

Q = Quantity of adsorbed phosphate

V_i = Volume of solution

C_i = Initial ion concentration

C_e = Equilibrium ion concentration

M = Mass of adsorbent (Biochar)

Data Analysis

The results obtained from the batch adsorption experiment were fitted into the linear form of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) adsorption isotherms using the least square fit method to determine which isotherm suites the adsorption process as described by Agarwal *et al*. (2014). Coefficient of determination (R^2) was used to test the goodness of fit of the adsorption isotherms as described by Abdu (2006). Similarly, correlation and regression analyses were carried out to determine the nature and extent of relationships between the biochars and phosphate adsorption capacities of the soil using statistical analysis software (SAS 9.4).

3.0 Results and Discussion

Results of some biochar properties are presented in Table 1. Data obtained revealed that all the biochar produced were alkaline. However, Maize cob biochar (MCB) recorded the highest pH value of 10.3 and 9.5 in water and $CaCl_2$ respectively while the lowest pH value of 7.6 and 7.1 in water and $CaCl_2$ respectively were recorded in cow dung biochar. Results also revealed lower pH values across all the biochar materials in calcium chloride solution (Table 1). Similarly, the highest EC value of 3.5 dS m^{-1} was recorded in MCB while the lowest EC of 2.6 dS m^{-1} was recorded in Cow dung biochar (CDB). High pH and EC recorded in MCB may be associated with the high ash contents of the biochar. Yue *et al*. (2017) obtained a similar result and opined that ash content in biochar has a direct effect on its pH and EC values and attributed it to the increased pyrolysis temperature. Similarly, Mukherjee *et al*. (2011) opined that with increasing production temperature, EC and pH increased and linked it to the production of more ash content. Furthermore, they linked the high pH values to a progressive loss of acidic surface functional groups, mainly aliphatic carboxylic acids. Lower pH values observed across all the biochar in calcium chloride solution may not be unconnected to the increased ionic strength of the solution compared to those measured in water. Gavriloaiei (2012) opined that small increases in the electrolyte concentration cause a decrease in pH values. Based on bulk density, Poultry litter biochar (PLB) recorded the highest bulk density value with 0.58 Mg m^{-3} while the lowest bulk density of 0.35 Mg m^{-3} was recorded in CDB (Table 1). This may be due to a few macro and micropores observed in the PLB biochar. This is in agreement with the findings of Mary *et al*. (2016) who recorded different bulk density of biochar for different feedstock and associated it to the intra and inter-particle voids of the biochar.

Maize cob biochar recorded the highest moisture content with 1.9 % while the lowest moisture content of 1.32 % was recorded in Rice husk biochar (RHB) and may be attributed to its high ash content which results in greater moisture absorption. Higher moisture contents were reported by Ronnse *et al*. (2013) for biochar with high ash contents. Highest and lowest biochar yield of 33.8 % and 23.6 % were recorded in CDB and MCB biochar respectively and may not be unconnected to the nature of the feedstocks. Similarly, relatively low biochar yield was recorded across the biochar samples and may be attributed to the high pyrolysis temperature. Similar results were reported by Lawrinenko and Laird (2015); Fang *et al*. (2014)); Jindo *et al*. (2014), they opined that biochar yield tends to decrease with increasing pyrolysis temperature and the type of feedstock and linked it to loss of labile elements from the biochar. Results revealed that all the biochars have their pH_{ZPC} lower than their pH in both water and $CaCl_2$ solution (Table 1). This suggests that the biochars have net negative charges on their surfaces. Fiol and Villaescusa (2009) reported that at solution pH higher than pH_{ZPC}, there is an excess of negatively charged ions while at pH lower than pH_{ZPC}, solid surfaces have net positive charges.

Table 1: Biochar Characterization

Parameters	MCB	RHB	CDB	PLB
pH (1:10 Biochar: H_2O)	10.30	7.90	7.60	7.80
pH(1:10 Biochar:0.01M $CaCl_2$)	9.50	7.20	7.10	7.50
EC (dS m^{-1})	3.50	2.70	2.60	3.10
Bulk density (Mg m^{-3})	0.41	0.41	0.35	0.58
Moisture content (%)	1.90	1.32	1.67	1.66
Biochar yield (%)	23.60	30.10	33.80	31.40
pH_{ZPC} (NaCl)	8.00	6.90	6.70	6.90
Total ash (g kg^{-1})	690.00	490.00	589.00	480.00
Total C (g kg^{-1})	292.00	395.00	300.00	400.00
Volatile matter (%)	0.66	0.65	1.45	1.36
Phosphates (mg kg^{-1})	13.32	6.26	18.83	23.80
specific surface area (cm^2 g^{-1}) (Langmuir)	2.735 x 10^3	3.107 x 10^3	2.955 x 10^3	2.896 x 10^3

MCB= Maize cob Biochar, RHB=Rice husk biochar, CDB= Cow dung biochar, PLB= Poultry litter biochar

The highest total ash content of 690 g kg^{-1} was recorded in MCB followed by CDB with 589 g kg^{-1}. The lowest total ash content of 480 g kg^{-1} was recorded in PLB biochar. This may be associated with the nutrient content in the original feedstock. Crombie and Masek (2014) reported differences in ash content of biochar produced from different feedstock and linked it to the nature of the original feedstock. However, the highest total carbon content of 400 g kg^{-1} was recorded in PLB followed closely by RHB with 395 g kg^{-1}. While the lowest total carbon content of 292 g kg^{-1} was recorded in MCB r and may be due to the low volatile matter observed in the biochar samples. This contradicts the findings of Domingues *et al*. (2017) who reported that biochars produced from plant biomass gave maximum C contents and linked it to greater polymerization, which results in an increased condensation of the carbon structure of the biochar. However, the result of this study may be due to a significant amount of wood shavings in the poultry litter used for this study. Similarly, total carbon content for RHB was reported by Jindo *et al*. (2014). They observed varying carbon content in biochar of different feedstock and linked the wide variations to a composition of the original materials. However, Ma *et al*. (2016) observed a significant negative correlation between the total carbon contents of some biochars with the volatile matter.

Results of the Langmuir surface area revealed that RHB recorded the largest specific surface area with 3.107 x 10^3 cm^2 g^{-1} followed by CDB with 2.955 x 10^3 cm^2 g^{-1} while lowest specific surface area of 2.735 x 10^3 $cm^2 g^{-1}$ was recorded in MCB (Table 1). This may be attributed to the higher ash content recorded in the biochar at such high temperature. This agrees with the findings of Jindo *et al*. (2014) who observed reduced surface area of some biochar with increasing ash content in the biochar and opined that the high ash content occupied and obstructed the access to micropores, causing the surface area to reduce. The high surface area recorded in RHB is in line with the findings of Jindo *et al*. (2014) who reported consistently high surface area in rice husk biochar with increasing pyrolysis temperature of up to 800 °C. Similarly, Lei and Zhang (2013); Liu and Zhang (2007) reported increased porosity and surface area when rice husk biochar was applied to soils and attributed it to the large surface area of the added biochar.

3.1 The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) Isotherm Constants for the Description of Phosphate Adsorption onto RHB, MCB, CDB, and PLB

The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm constants for the description of phosphate adsorption onto RHB, MCB, CDB, and PLB are presented in Table 2. With respect to the Langmuir adsorption isotherm, R^2 values of 0.647 and 0.999 were recorded for MCB and PLB respectively. Lowest q_m of -2.496 mg g^{-1} was recorded in RHB while the highest q_m of 4.87 mg g^{-1} was recorded in MCB with K_L values of 110.99 and -150.15 L mg^{-1} for RHB and MCB respectively. Highest Langmuir R^2 value for PO_4^{3-} was recorded in PLB biochar. However, negative K_L value suggests that despite the high R^2 value PO_4^{3-} adsorption onto PLB biochar could not be described by a monolayer adsorption process. Higher maximum phosphate adsorption capacity recorded by MCB and PLB may be due to the high electrical conductivity of these biochars. It may also be attributed to the high ash content of MCB. This is in line with the findings of Dugdug *et al*. (2018); Bai *et al*. (2017) who observed increased phosphorus adsorption with increasing electrical conductivity and linked it to differences in soluble salts concentrations particularly calcium and sodium. Also, Zhou *et al.* (2019) reported a significant increase in phosphate adsorption with increasing ash contents of biochar. Based on the Freundlich adsorption isotherm, R^2 values of 0.875 to 0.998 were recorded for CDB and PLB respectively. Highest PO_4^{3-} K_f value of 1.06 X 10^6 was recorded in RHB while the lowest K_f value of 36.19 was recorded in MCB. Highest n value of 2.62 was recorded in MCB while the lowest n value of -2.04 was recorded in PLB (Table 2). Highest Freundlich isotherm R^2 value for PO_4^{3-} adsorption recorded in MCB biochar suggests multilayer adsorption onto the heterogeneous surface of the biochar rather than the charge on the surface. However, negative adsorption intensity (n) values recorded by RHB, CDB, and PLB suggest that phosphate adsorption onto these biochar samples could not be described effectively with the Freundlich adsorption isotherm model. Mulu (2013); Kumar *et al.* (2010) reported that the nature of adsorption depends on n value.The Temkin adsorption isotherm constants B_T for phosphate adsorption on the different biochars revealed negative values (Table 2). However, K_T values of 0.62 and 0.72 Lg^{-1} were recorded for

Table 2: The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) Isotherm Constants for Phosphate Adsorption onto RHB, MCB, CDB, and PLB

Langmuir	Constants	RHB	MCB	CDB	PLB
	K_L (L mg^{-1})	110.9878	-150.15	52.51549	-134.048
PO_4^{3-}	q_m (mg g^{-1})	-2.49644	4.871443	-1.14176	3.132086
	R^2	0.9903	0.6469	0.7495	0.9999
Freundlich					
	R^2	0.9736	0.9781	0.8745	0.9981
	K_f (mg g^{-1})	1.06E+6	36.19412	942.0371	903.9804
	1/n	-1.494	0.381	-1.953	-0.49
	n	-0.66934	2.62467	-0.51203	-2.04082
Temkin					
	B_T	-2760.76	-1247.7	-2176.98	-2405.13
	K_T (Lg^{-1})	0.718	0.617	0.699	0.655
	R^2	0.8129	0.8873	0.901	0.9023
Dubinin-Radushkevich					
	Q_{DR} (mg kg^{-1})	5449.615	2671.459	1449.192	5052.234
	B_{DR} (mol^2 J^{-2})	0.050201	0.053319	0.004559	0.009314
	E (J mol^{-1})	3.155956	3.062274	10.47307	7.326646
	R^2	0.9736	0.8745	0.9781	0.9981

RHB=Rice husk biochar, MCB= Maize cob Biochar, CDB= Cow dung biochar, PLB= Poultry litter biochar, qm = maximum quantity adsorbed, R_L= Langmuir Separation factor, K_L= Langmuir adsorption rate, K_f = Freundlich adsorption capacity, n= adsorption intensity, B_T =Temkin constant values relating to the heat of sorption, K_T =Temkin adsorption potential, Q_{DR}=maximum quantity, B_{DR} = D-R isotherm constants, E =free energy of adsorption

MCB and RHB respectively. Highest R^2 value of 0.90 was recorded in both CDB and PLB while lowest R^2 of 0.81 was recorded in RHB (Table 2). High Temkin isotherm R^2 recorded on PO_4^{3-} adsorption onto all biochar samples revealed a decrease in heat of adsorption with increasing surface coverage and that the adsorption energies are uniform. Low negative B_T observed across the samples suggests exothermic physical adsorption of phosphate onto the biochar samples. This is in line with the report of Dada *et al.* (2012) who associated low Temkin adsorption isotherm (B_T) with physical adsorption. Based on the D-R adsorption isotherm, highest Q_{DR} value of 5449.62 mg kg^{-1} was recorded in RHB while the lowest Q_{DR} value of 1449.19 mg kg^{-1} was recorded in CDB. Similar to what was observed on NO_3^- adsorption; low B_{DR} values were observed across all the biochar samples (Table 2). However, relatively low E values were observed and values ranged from as low as 3.06 to 10.47 J mol^{-1} for MCB and CDB respectively. Coefficient of determination (R^2) of 0.87 for MCB and 0.998 recorded in PLB suggesting a good fit of the isotherm for phosphate adsorption onto the biochars. MCB showed the least suitability as evident by its lowest R^2. This may be linked to the net positive charges of MCB at the adsorption pH, hence making phosphate adsorption onto this biochar to be through electrostatic attraction rather than a pore filling process. Adegoke *et al*. (2013) reported that positive or negative surface sites are developed on the surface of solids in aqueous suspensions and ZPC determines the ion adsorption preference onto the adsorbent. Similarly, the low free energy of adsorption (E) recorded in RHB, MCB, and PLB is an indication of physical adsorption. High D-R isotherm R^2 value recorded in RHB, PLB, and CDB samples may not be unconnected to phosphate affinity to the large surface area of the biochar samples. Dada *et al*. (2012); Ayawei *et al*. (2017) stated that The D-R adsorption isotherm effectively explains the adsorption of gases and vapours onto microporous materials.

3.2 *Relationship between Biochar Properties and Phosphate Adsorption*

Result of Pearson's correlation revealed significant (P<0.05) positive relationships between adsorbed phosphate and EC, and sulphate and specific surface area (Table 3). Nevertheless, high negative correlations were observed between adsorbed phosphate and biochar pH, moisture content and pHzpc with R values of -0.77, -0.82, and -0.71 respectively. High significant positive correlation observed on adsorbed phosphate with EC, sulphate, and specific surface area, indicate increasing phosphate adsorption with increasing EC, sulphate, and specific surface area. Dugdug *et al*. (2018); Bai *et al*. (2017); reported increased phosphorus adsorption with increasing electrical conductivity and associated it with differences in soluble salts concentrations particularly calcium and sodium. Similarly, Zhou *et al.* (2019) opined that Ca and Mg have a greater influence on phosphate adsorption compared to the other components of the ash. Negative correlations were observed between adsorbed phosphate and biochar pH, moisture content and ZPC revealed that increasing biochar pH, moisture content, and ZPC will lead to a decrease in phosphate adsorption and vice versa. Results of the stepwise regression analysis retained EC, moisture content, and specific surface in the model with a combined R^2 value of 0.99 (Table 4). The retention EC, moisture content, and specific surface area in stepwise regression analysis model indicate a profound influence of these variables on phosphate adsorption. It also suggests that combined effect of these variables accounted for about 99 % of the change in adsorbed phosphate. Dugdug *et al*. (2018); Bai *et al*. (2017); Abdu (2006); Agbenin (2003) reported a significant effect of pH, clay contents of soil, EC among others on phosphate adsorption

Table 3: Pearson Correlation between Adsorbed Phosphates with some Biochar Properties

pH (1:2.5 soil to 0.01 $CaCl_2$) **Biochar Properties**	**R Values**	**P. Value**
pH (1:2.5 soil to water)	-0.675	0.016
	-0.77	0.003
EC	0.93	<.0001
Moist. content	-0.819	0.001
ZPC Na	-0.707	0.01
ZPC KCl	-0.696	0.012
PO_4^{3-}	-0.467	0.126
SO_4^{2-}	0.944	<.0001
Specific surface area	0.909	<.0001

Table 4: Summary of Stepwise Regression Analysis for Adsorbed Phosphate with some Biochar Properties

Step	**Variable** Entered	**Variable** Removed	**Number** Vars In	**Partial** R-Square	**Model** R-Square	**C(p)**	**F Value**	**Pr > F**
1	EC		1	0.8609	0.8609	2009.39	61.88	<.0001
2	Moist. content		2	0.066	0.9268	1054.72	8.12	0.0191
3	Specific surface area		3	0.0726	0.9944	4	1052.72	<.0001
	Model	Qmax Phosphate= 32.335+19.900 EC - 6 8.844 Moist. content + 0.8998 specific surface area						

Qmax= maximum adsorbed quantity, moist. =moisture

3.0 Conclusion

The findings of this study revealed that only maize cob biochar (MCB) and poultry litter biochar (PLB) can adsorb phosphate under the experimental conditions. Although the Langmuir adsorption isotherm was used to determine the maximum phosphate adsorption capacity of the biochar materials, it was not appropriate for describing PO_4^{3-} adsorption onto any of the biochar. However, phosphate adsorption onto MCB was best described by the Freundlich adsorption isotherm while, the D-R adsorption isotherm was suitable for describing phosphate adsorption onto RHB, CDB, and PLB. Phosphate adsorption was significantly influenced by EC, moisture content, and specific surface. Hence, modification of biochar EC, moisture content, and the specific surface area should be a prerequisite for using biochar to effectively remove phosphate from aqueous solution.

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