

Evaluating the Potential of Pineapple Peel Biochar and Lateritic Soil in the Adsorption of Phosphorous from Human Urine

Austine O. Otieno, Patrick G. Home, James M. Raude, Sylvia N. Murunga, Gerryshom Munala and Tuula Tuhkanen

Abstract—the diminishing phosphate rock reserves and the increasing cost of fertilizer production is a major driver for seeking alternative sustainable sources of phosphate fertilizers to meet the growing food demand. Extracting nutrients from human urine to obtain fertilizers for crop production can contribute in achieving phosphorous fertilizer demand in addition to protection of fresh water bodies from pollution. This study aimed at evaluating the potential of pineapple peel derived biochar (PPB) and lateritic soil (LS) in adsorbing phosphorous (P) from human urine. The effect of contact time and initial concentration of P on adsorption was evaluated. Langmuir and Freundlich isotherm models were employed to correlate the experimental equilibrium adsorption data. The results indicate that PPB adsorbs P from human urine but releases into the solution thus not attaining equilibrium. There was an increase in the amount of adsorbed P on LS upto equilibrium. Langmuir model ($R^2=0.984$) best described P adsorption on LS with a maximum monolayer adsorption capacity of 45.25 mg/g calculated from the model. These results indicate that LS can hold P for crop use if enriched with human urine whereas the adsorbed P by PPB can be easily leached.

Keywords—Equilibrium, Freundlich, Isotherms, Langmuir, Phosphorous

I. INTRODUCTION

Phosphorous (P) is an essential macronutrient required for healthy crop growth [1]. Seeking alternative P sources to augment the already declining the non-renewable phosphate rock reserves [2] is therefore necessary. Human urine has a potential of meeting global P demand by approximately 22% [3]. According to Randall et al. [4], the P concentration in undiluted human urine ranges from 260 to 740 mg/L. Already

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field scale application of fresh urine for crop fertilization has demonstrated that it produces higher yields than chemical fertilizers with no potential threat to humans [5], [6]. Although WHO recommends storage of urine for duration of 6 months at 20 °C to achieve complete elimination of pathogenic micro-organisms [7], the prolonged storage of human urine may not be convenient in urban and peri-urban areas due to huge space requirements for storage and odour problems.

Nutrient extraction or capture from urine could therefore enable ease of application and handling. Various approaches have been explored in phosphorous extraction and capture from urine such as forward osmosis [8], anion exchange [9], struvite precipitation [3] and adsorption [10]. Adsorption process is considered an efficient, simple and low-cost method for phosphates removal even at low P concentrations [11]. Biochar has recently attracted attention of researcher for adsorption of nutrients from aqueous solutions [12]. Biochar is a carbon material formed by pyrolysis of biomass under no or minimal oxygen conditions. Although biochars are effective in adsorption of cationic species, they are not efficient in removal of anionic species from aqueous solutions since their surfaces are commonly negatively charged [13], [14]. Modification of biochar surfaces using metal oxides preferably magnesium oxides has been demonstrated to recover significant amount of P from aqueous solutions [15]. Adsorption of phosphate ions to the MgO sites could therefore be considered to be the main reason for phosphate removal from aqueous solutions. Although many studies have reported on the inability of non-modified biochars to attract phosphates, investigations on effect of initial P concentrations in urine and contact time on their adsorption characteristics has not been widely reported. This is important because the positively charged surface of modified biochar using metal oxides might inhibit simultaneous adsorption of cations such as ammonium from urine.

The use of geological materials such as zeolite [16] and natural loess [17] has been reported to be effective in phosphates recovery from urine. Lateritic soil is a widely abundant geological material within the tropical climates. However, it is normally nutrient deficient since it is formed under rapid weathering and high rates of leaching and thus majorly used for construction purposes [18]. Although its use

for adsorption has majorly focused on fluorides and heavy metal removal, its application for nutrients recovery is minimal.

Herein, we have investigated the use of non-modified biochar derived from pineapple peels (PPB), and lateritic soil (LS) in adsorption of P from source separated human urine. The effect of initial P concentration in urine and contact time on the adsorption behaviour of PPB, and LS were determined. We further investigated the adsorption capacity of P on LS using the Langmuir, and Freundlich isotherm models.

II. MATERIALS AND METHODS

A. Materials

Fresh undiluted urine was collected from volunteers. Fresh pineapple peels were collected from vendors, dried in a greenhouse to constant moisture content and then carbonized at 400 °C for 4 hours. The resulting char was then crushed and particles < 300µm sieved. The powders were then kept in air tight plastic containers for use in the experiment. Lateritic soil was excavated at 20 cm from the ground surface and impurities removed. It was then dried in an oven at 104±1°C for 24 hours, crushed, sieved to < 300µm and kept in air tight plastic containers for use in the experiment.

B. Materials Characterization

Human urine was characterized for pH and temperature using a Mettler Toledo SevenEasy S20 pH meter. Procedures for P determination in the human urine samples was carried out according to Finnish standard (SFS, 3026) for determination of total phosphorous in water [19] with UV-Spectrophotometer (880 nm wavelength) used to obtain the readings. The elemental composition of lateritic soil was determined using a Bruker S1 Titan 500 X-ray fluorescence (XRF) spectrometer.

C. Batch adsorption experiments

D. Effect of initial concentration of P in urine and contact time on the adsorption behaviour of PPB and LS

Six different concentrations of P in urine (164.12, 283.55, 309.82, 439.95, 555.04, and 680.21 mg/L) were obtained by diluting the original urine sample with deionized water. 25 mL of urine was placed in each 250 mL conical flask and dosed with 0.2g of adsorbent with each dosing having three replicates. The samples were agitated continuously at 100 revolutions per minute (rpm) for 30, 60, 90 and 120 minutes with a laboratory shaker and then filtered using whatman filter paper no. 42 to separate the adsorbent from the filtrate. The batch experiment was conducted at a room temperature of 21 °C and urine pH = ~7.50 ± 0.30. The amount of P adsorbed was calculated using Eq.1

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

where, Co and Ct are the concentrations of P in the urine at the initial time and at certain time t (mgL-1), respectively, V is

the volume of urine (mL), W is the mass of adsorbent (g) and qt is the amount of P (mg) adsorbed per unit mass (g) of the adsorbent (mg/g).

E. Langmuir and Freundlich modelling of adsorption of P on LS

Langmuir model assumes a monolayer adsorption occurring on a homogenous surface, while Freundlich model assumes a multi molecular layer adsorption on a heterogeneous surface. The linearized form of Langmuir [20] and Freundlich [21] adsorption isotherms models shown in Eq. 2 and 4, respectively, were used to evaluate the adsorption;

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (2)$$

where qe (mg/g) is the amount of P adsorbed per unit mass of adsorbent (mg/g), Ce (mg/L) is the equilibrium concentration of P, qm (mg/g) is a constant representing maximum monolayer saturation capacity, KL (L/mg) is the constant representing affinity between molecules in the adsorbate and the adsorbent. The plot of 1/qe against 1/Ce gives a linear plot from which the Langmuir constants qm(mg/g) and KL(L/mg) are obtained.

The Langmuir model constant (KL) which represents the affinity between molecules in the adsorbate and the adsorbent can further be used to compute the dimensionless separation factor (RL) as shown in Eq.3

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

where, Co (mg/L) is the initial concentration of P, KL (L/mg) is the Langmuir constant, RL is dimensionless separation factor. If RL is found to be in the range (0 < RL < 1), then sorption of molecules onto the adsorbent is considered favourable [22].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where, qe (mg/g) is the amount of P adsorbed per unit mass of adsorbent, Ce (mg/L) is the equilibrium concentration. The plot of log qe versus log Ce gives a linear plot, from which the Freundlich constants Kf and n are determined.

III. RESULTS AND DISCUSSION

A. Chemical Composition of Lateritic Soil (LS) and Pineapple Peel Biochar (PPB)

The main components of lateritic soil as revealed by XRF data are SiO2 = 55.83 wt.%, Al2O3 = 20.02 wt.%, and Fe2O3 = 9.50 wt.% while pineapple peel biochar was dominated by CaO = 36.27 wt.%, K2O = 7.12 wt.%, Fe2O3 = 6.88 wt.% (Table 1).

TABLE 1
 CHEMICAL COMPOSITION OF LS AND PPB
 (wt.%)

Element	Lateritic Soil (wt.%)	Pineapple Peel Biochar (wt.%)
SiO ₂	55.83	ND
Al ₂ O ₃	20.02	1.18
CaO	1.01	36.27
MgO	ND	ND
Na ₂ O	1.00	5.20
K ₂ O	1.80	7.12
TiO ₂	1.20	2.54
MnO	0.14	1.86
Fe ₂ O ₃	9.50	6.88
P ₂ O ₅	0.79	2.80
S	0.18	2.00
LOI	7.69	33.32

ND: Not detected; LOI: weight loss on ignition

It can be deduced from the results of elemental analysis that LS was infertile medium for crop growth compared to PPB based on its lower amount of soluble alkaline oxides (CaO, K₂O, and P₂O₅) and organic matter as depicted by lower weight loss on ignition (LOI) of 7.69 wt.%. However, LS is a potential adsorbent for removal of anionic phosphates from human urine since it has significant amount of Al and Fe which have been widely reported to form complexes with phosphate molecules thereby removing P from aqueous phases [19]–[21]. On the other hand, magnesium oxides (MgO) is considered to be the major compound in biochars responsible for removal of P from human urine through electrostatic attraction to form magnesium ammonium phosphates on biochar surfaces [15]. MgO was however not detected in the PPB. Although calcium oxides can remove the phosphate species from human urine through formation of amorphous calcium phosphates, CaO are highly soluble in urine resulting to the dissolution of the complexes [4]. Hence the PPB could potentially adsorb P from human urine but release it back into the solution through dissolution of the complexes formed by CaO.

B. Phosphorous (P) adsorption behaviours and capacities of PPB and LS in human urine

C. Effect of contact time and the initial concentration of P in urine on the amount of P adsorbed on LS and PPB

The effect of contact time and the initial concentration of P in urine on the amount of P adsorbed on LS and PPB are presented in Fig.1.

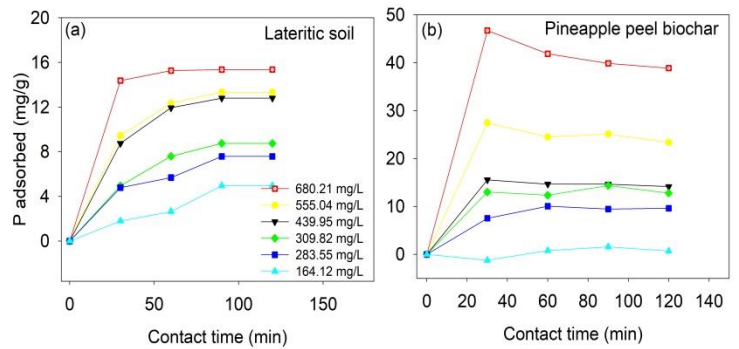


Fig.1 Effect of contact time and the initial concentration of P in urine on the amount of P adsorbed on (a) lateritic soil and (b) pineapple peel biochar

As illustrated in Fig.1a, it is evident that an increase in initial P concentration in urine resulted to an increase in the amount of P adsorbed on LS at equilibrium. At higher initial P concentrations, the ionic gradient between the adsorption surface and the solutes was higher resulting to higher mass transfer of phosphate ions to the adsorption sites. With regards to effect of contact time on P adsorption, there was rapid adsorption between 0-30 min, followed by a gradual decline in sorption rate between 30-90 min, beyond which negligible amount of P was adsorbed. The initial rapid uptake was due to availability of more unoccupied sorption sites. However, these sites gradually got occupied towards equilibrium thereby reducing the sorption rate. At equilibrium, all the active sorption sites were occupied hence negligible uptake could occur. Similar findings have been reported by previous studies [22], [23].

D. Adsorption isotherms for the adsorption of P from human urine on the LS

The adsorption isotherms of the Langmuir and Freundlich models describing the behaviour of P adsorption on LS are presented in Fig. 2, while the isotherm parameters are summarized in Table 2. Lateritic soil was chosen for equilibrium studies due to its potential to hold phosphorous unlike PPB that shows a tendency to release P in urine solution.

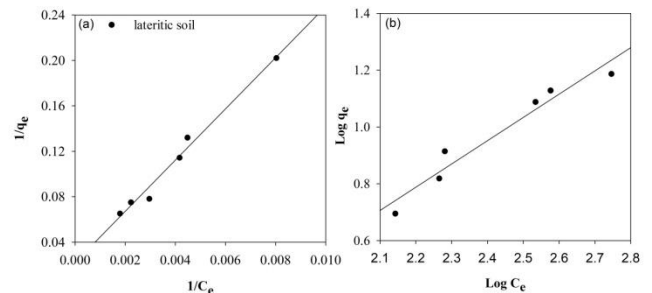


Fig. 2 (a) Langmuir, and (b) Freundlich isotherm model fits of lateritic soil

On the basis of the R² values presented in Table 2, both

Langmuir and Freundlich isotherm models yielded satisfactory fit to the experimental data but Langmuir model gave the best fit. Therefore, it can be interpreted that the available adsorption sites for P on LS have the same adsorption energy and that the process is reversible. Studies by Bhattacharjee et al. [23], and Fulazzaky et al. [24] have also reported the Langmuir model to best describe P adsorption on LS with Al and Fe cations considered to be responsible for the removal of P from aqueous phase through electrostatic attraction to form complexes. The R_L value of 0.6 indicates favourable conditions for adsorption of P on LS.

TABLE 2
LANGMUIR, AND FREUNDLICH ISOTHERM
PARAMETERS FOR THE ADSORPTION OF P ON LS

Isotherm parameters	
Langmuir	
q_{max} (mg/g)	45.25
K_L	0.001
R_L	0.6
R^2	0.984
Freundlich	
K_f	0.119
$1/n$	0.778
R^2	0.966

IV. CONCLUSION

The maximum adsorption capacity of 45.25 mg/g exhibited by LS indicates that it can be used to effectively recovery P from human urine. Langmuir model best described P adsorption on LS, an indication that monolayer adsorption on homogenous active sites was the dominant mechanism of adsorption. PPB exhibited a tendency to adsorb and release P in human urine simultaneously thereby not attaining equilibrium, an indication of dissolution of amorphous calcium phosphates formed on the PPB surface in human urine solution.

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REFERENCES

- [1] B. Mndzebele *et al.*, "Effects of cowpea-amaranth intercropping and fertiliser application on soil phosphatase activities, available soil phosphorus, and crop growth response," *Agronomy*, vol. 10, no. 1, 2020, doi: 10.3390/agronomy10010079.
- [2] D. P. Van Vuuren, A. F. Bouwman, and A. H. W. Beusen, "Phosphorus demand for the 1970-2100 period: A scenario analysis of resource depletion," *Glob. Environ. Chang.*, vol. 20, no. 3, pp. 428-439, 2010, doi: 10.1016/j.gloenvcha.2010.04.004.
- [3] S. G. Barbosa, L. Peixoto, B. Meulman, M. M. Alves, and M. A. Pereira, "A design of experiments to assess phosphorous removal and crystal properties in struvite precipitation of source separated urine using different Mg sources," *Chem. Eng. J.*, vol. 298, pp. 146-153, 2016, doi: 10.1016/j.cej.2016.03.148.
- [4] D. G. Randall, M. Krähenbühl, I. Köpping, T. A. Larsen, and K. M. Udert, "A novel approach for stabilizing fresh urine by calcium hydroxide addition," *Water Res.*, vol. 95, pp. 361-369, May 2016, doi: 10.1016/j.watres.2016.03.007.
- [5] E.-L. Viskari, G. Grobler, K. Karimäki, A. Gorbatova, R. Vilpas, and S. Lehtoranta, "Nitrogen Recovery With Source Separation of Human Urine—Preliminary Results of Its Fertiliser Potential and Use in Agriculture," *Front. Sustain. Food Syst.*, vol. 2, Jun. 2018, doi: 10.3389/fsufs.2018.00032.
- [6] S. K. Pradhan, A.-M. Nerg, A. Sjöblom, J. K. Holopainen, and H. Heinonen-Tanski, "Use of Human Urine Fertilizer in Cultivation of Cabbage (*Brassica oleracea*)—Impacts on Chemical, Microbial, and Flavor Quality," *J. Agric. Food Chem.*, vol. 55, no. 21, pp. 8657-8663, Oct. 2007, doi: 10.1021/jf0717891.
- [7] WHO, "WHO Guidelines for the Safe Use of Wasterwater Excreta and Greywater - World Health Organization - Google Books," 2006. [Online]. Available:
- [8] F. Volpin, H. Heo, M. A. Hasan Johir, J. Cho, S. Phuntsho, and H. K. Shon, "Techno-economic feasibility of recovering phosphorus, nitrogen and water from dilute human urine via forward osmosis," *Water Res.*, vol. 150, pp. 47-55, 2019, doi: 10.1016/j.watres.2018.11.056.
- [9] A. Sendrowski and T. H. Boyer, "Phosphate removal from urine using hybrid anion exchange resin," *Desalination*, vol. 322, pp. 104-112, 2013, doi: 10.1016/j.desal.2013.05.014.
- [10] P. Kini and H. Sridevi, "Removal of phosphorus from human urine by adsorption method using GGBS," *Int. J. Civ. Eng. Technol.*, vol. 8, no. 3, pp. 1061-1069, 2017.
- [11] N. Y. Acelas, B. D. Martin, D. López, and B. Jefferson, "Selective removal of phosphate from wastewater using hydrated metal oxides dispersed within anionic exchange media," *Chemosphere*, vol. 119, pp. 1353-1360, 2015, doi: 10.1016/j.chemosphere.2014.02.024.
- [12] Y. Qin *et al.*, "Enhanced removal of ammonium from water by ball-milled biochar," *Environ. Geochem. Health*, vol. 5, 2019, doi: 10.1007/s10653-019-00474-5.
- [13] S. E. Hale, V. Alling, V. Martinsen, J. Mulder, G. D. Breedveld, and G. Cornelissen, "The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars," *Chemosphere*, vol. 91, no. 11, pp. 1612-1619, 2013, doi: 10.1016/j.chemosphere.2012.12.057.
- [14] P. Vassileva, P. Tzvetkova, and R. Nickolov, "Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation," *Fuel*, vol. 88, no. 2, pp. 387-390, Feb. 2009, doi: 10.1016/j.fuel.2008.08.016.
- [15] O. Oginni *et al.*, "Phosphorus adsorption behaviors of MgO modified biochars derived from waste woody biomass resources," *J. Environ. Chem. Eng.*, vol. 8, no. 2, p. 103723, 2020, doi: 10.1016/j.jece.2020.103723.
- [16] S. Caspersen and Z. Ganrot, "Closing the loop on human urine: Plant availability of zeolite-recovered nutrients in a peat-based substrate," *J. Environ. Manage.*, vol. 211, pp. 177-190, Apr. 2018, doi: 10.1016/j.jenvman.2018.01.053.
- [17] S. Jiang, X. Wang, S. Yang, and H. Shi, "Characteristics of simultaneous ammonium and phosphate adsorption from hydrolysis urine onto natural loess," *Environ. Sci. Pollut. Res.*, vol. 23, no. 3, pp. 2628-2639, 2016, doi: 10.1007/s11356-015-5443-1.
- [18] N. Ehujuo, * Ehujuo, N. N. Okeke, and O. C. Akaolisa, "Geotechnical Properties of Lateritic Soils Derived from Various Geologic Formations in Okigwe Area, Southeastern Nigeria," *Geotech. Prop. of... Futo J. Ser.*, vol. 3, no. 2, pp. 178-189, 2017.
- [19] Y. Yang, D. Tomlinson, S. Kennedy, and Y. Q. Zhao, "Dewatered alum sludge: A potential adsorbent for phosphorus removal," *Water Sci. Technol.*, vol. 54, no. 5, pp. 207-213, 2006, doi: 10.2166/wst.2006.564.
- [20] B. S. Chittoo and C. Sutherland, "Adsorption of Phosphorus Using Water Treatment Sludge," *J. Appl. Sci.*, vol. 14, no. 24, pp. 3455-3463, 2014, doi: 10.3923/jas.2014.3455.3463.
- [21] M. Razali, Y. Q. Zhao, and M. Bruen, "Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution," *Sep. Purif. Technol.*, vol. 55, no. 3, pp. 300-306,

- 2007, doi: 10.1016/j.seppur.2006.12.004.
- [22] S. M. Ragheb, "Phosphate removal from aqueous solution using slag and fly ash," *HBRC J.*, vol. 9, no. 3, pp. 270–275, 2013, doi: 10.1016/j.hbrcej.2013.08.005.
- [23] A. Bhattacharjee, B. B. Jana, S. K. Mandal, S. Lahiri, and J. N. Bhakta, "Assessing phosphorus removal potential of laterite soil for water treatment and eco-technological application," *Ecol. Eng.*, vol. 166, no. April, p. 106245, 2021, doi: 10.1016/j.ecoleng.2021.106245.
- [24] M. A. Fulazzaky, M. H. Khamidun, M. F. M. Din, and A. R. M. Yusoff, "Adsorption of phosphate from domestic wastewater treatment plant effluent onto the laterites in a hydrodynamic column," *Chem. Eng. J.*, vol. 258, pp. 10–17, 2014, doi: 10.1016/j.cej.2014.07.092.