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Biochar Types from Latrine Waste and Sewage Sludge Differ in Physico-Chemical Properties and Cadmium Adsorption

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Abstract: Pyrolysis of latrine fecal waste could produce valuable products for minimizing environmental contamination with heavy metals. The objective of this study was to determine yields, characteristics and cadmium (Cd) sorption of biochar from latrine fecal waste and sewage sludge, as affected by pyrolysis temperature. Slow pyrolysis at 350, 550 and 650°C, was used to produce the biochar. In addition to proximate and ultimate analysis, surface area, porosity and functional groups were analyzed. A batch sorption study was conducted to determine the cadmium sorption capacity of the biochar. Biochar from latrine waste had higher yield, ash content, surface area and pore volume and lower total and fixed carbon (C) and volatile matter than from sewage sludge. Yield, volatile matter, total C, nitrogen (N) and hydrogen (H) decreased with pyrolysis temperature, while ash content, surface area and porosity increased. Surface functional groups of the biochar also varied with feedstock and pyrolysis temperature. The Cd sorption capacities were higher for biochar from latrine waste than from sewage sludge. The findings indicated that characteristics of biochar from latrine waste differ from that of sewage sludge origin and has greater potential as an adsorbent for removal of Cd from wastewater.

Keywords: Biochar, Cadmium, Latrine Fecal Waste, Sewage Sludge, Sorption

Introduction

The global generation of human fecal waste has increased over the past decades exacerbating the challenges of waste disposal (Seo *et al*., 2004; Al-Khatib *et al*., 2010). Cities in Southern Africa produce large quantities of human fecal wastes from wastewater treatment plants (sewage sludge) and pit latrines. Zuma *et al*. (2015) reported that 31.3% of households in South Africa depend on pit latrines and 12.5% use the Ventilated Improved Pit latrines (VIP), for their sanitation needs. The processes of filling of the pit with fecal matter (and other wastes), water transfer and biological transformations, over a 5-year cycle (before empting) (Zuma *et al*., 2015) influence the chemical composition of the latrine waste. Communities in the cities largely depend on the sewer systems, which treat wastewater and produce sewage sludge, through the anaerobic digestion and separation of the solid from the liquid (Snyman and Herselman, 2009). Exploitation of these organic wastes, particularly for production of resources like biochar, is essential for minimizing environmental pollution with heavy metals and other benefits (Gerente *et al*., 2007).

Differences in handling of latrine wastes and sewage sludge could result in variation in their characteristics (Tesfamariam, 2009) and those of the resultant biochar. Biochar from organic wastes has shown potential for removal of heavy metals from wastewater (Namgay *et al*., 2010; Major, 2011; Kim *et al*., 2013; Mohan *et al*., 2014; Coumar *et al*., 2016). Heavy metals, a group of elements with at least five times the density of water, are challenging environmental pollutants in places with elevated anthropogenic pressure (di Toppi and Gabbrielli, 1999). The metals enter the soil through pathways including agricultural, mining and other industrial activities (Coumar *et al*., 2016; Kabata-Pendias, 2000; Prasad, 1995). Production of biochar from latrine waste and sewage sludge could have potential uses in heavy metal removal from wastewater. Pyrolysis of these fecal wastes to biochar could recover carbon and nutrients (Hossain *et al*., 2011; Paz-Ferreiro *et al*., 2012; Mendez *et al*., 2012).

The effectiveness of biochar as a sorbent depends on its characteristics owing to the properties of the feedstock (Maraseni, 2010; Mitchell *et al*., 2013) and pyrolysis conditions (Trakal *et al*., 2014; Wan *et al*.,

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2014; Kuppusamy *et al*., 2016; Bogusz *et al*., 2015). Analysis of the literature shows that lignified materials like wheat straw and water hyacinth produce biochar that has lower ash content and higher surface area than from sewage sludge (Xu *et al*., 2014; Tan *et al*., 2015). Differences in chemical composition of fecal wastes, as affected by diets (Mihelcic *et al*., 2011) and management, could influence characteristics of biochar produced from sewage sludge and latrine fecal wastes. Pyrolysis of these marginal organic materials to biochar could maximize their benefits (van Zwieten *et al*., 2010; Buss *et al*., 2016). The objective of this study was to determine effects of pyrolysis temperature on yield, characteristics and cadmium sorption capacities of biochar from latrine wastes relative to sewage sludge.

Materials and Methods

Biochar Feedstock

Latrine fecal wastes and domestic sewage sludge were used for production biocharin this study. The latrine waste was obtained by manually emptying of Ventilated and Improved Pit latrine (VIP) toilets in the eThekwini Municipality, South Africa. Due to non-separation of urine from feces, the waste appeared like pseudo-plastic fluid. The fecal wastes were pelletized by the latrine dehydration and pasteurization process at 200°C for eight minutes. The sewage sludge was collected from drying beds at Howick Wastewater Treatment Plant, 15 km north-west of Pietermaritzburg. The plant produces domestic sewage sludge with minimal industrial contamination. The latrine waste had lower C, N, Na and higher Ca, K, C:N and CEC than sewage sludge (Table 1).

Biochar Production

The feed stocks were dried at 70°C for 24 h and milled to <5mm and slowly pyrolysed in 500 mL crucibles in a muffle furnace, equipped to reduce rapid oxidation and auto-ignition (Yuan *et al*., 2011; Enders *et al*., 2012). The furnace temperature was raised to set levels of 350, 550 or 650°C at a rate of 10°C min^{-1} and pyrolysed for 2 h (Bamminger *et al*., 2014), in triplicate. The biochar was weighed to determine yield before characterization (Herath *et al*., 2013).

Volatile Matter, Ash Content and Fixed C

Volatile matter and ash content were determined using the proximate analyses following the reapproved American Society for Testing and Materials (ASTM) D1762 – 84 protocol (Wu *et al*., 2012). The pulverized samples were oven dried at 105°C for 2 h to determine moisture content. The biochar was subjected to 950°C furnace condition for six min and weight loss was taken as volatile matter, expressed as a percentage on a dry weight basis. Ash was determined after combustion at 750°C for six h. Fixed C was calculated by subtraction of volatile matter (%) and ash (%) from 100% (Liu *et al*., 2014).

Table 1: Chemical properties (means ± standard error) of sewage sludge and latrine waste pellets used for pyrolysis

Property	Latrine waste	Sewage sludge
Total carbon (%)	9.29±0.17	28.6±0.45
Total nitrogen (%)	0.86±0.01	4.97±0.87
C:N	10.8	5.8
Ca (cmol+kg^{-1})	32.2±0.93	20.8±0.74
Mg (cmol+kg^{-1})	24.2±0.54	25.1±1.11
K (cmol+kg^{-1})	4.12±0.02	2.68±0.08
Na (cmol+kg^{-1})	0.69±0.02	14.7±0.59
CEC (cmol+kg^{-1})	17.8±0.37	11.7±0.52

Elemental Composition and Physico-Chemical Properties

Total *C* and *N* were analyzed by dry combustion using LECO Trumac CNS analyzer (LECO Corporation, 2012). Furthermore, CHNS elemental analyzer was used to determine total H.

The pH of biochar was determined in H_2O and KCl at a solid: Solution ratio of 1:20 w/v ratio because of low bulk density of biochar (Cheng and Lehmann, 2009). The concentrations of exchangeable basic cations were extracted with 1M NH_4OAc at pH 7. The air-dried biochar (5.0 g) were suspended in 100 mL^{-1} of 1M ammonium acetate (NH_4OAc) and the mixtures were mechanically shaken at 180 rpm for an hour and then filtered. The filtrate was analyzed for basic cations, using flame photometry (K^+ and Na^+) and atomic absorption spectrometry ($Ca^{2+}$and Mg^{2+}). Cation Exchange Capacity (CEC) was determined as the concentration of NH_4^+ retained after leaching with several portions of ethanol (Ross and Ketterings, 2011).

Functional Groups, Surface Area and Porosity

Chemical functional groups of the biochar were determined using the Fourier Transform Infrared (FTIR) spectroscopy (Coates, 2000). The FTIR transmission spectra were recorded on a PerkinElmer FT-IR at the wave numbers ranging from 550 to 4000 cm^{-1} (Wu *et al*., 2012). Chemical functional groups were then assigned to the wave numbers from the FTIR spectra. Brunauer–Emmett–Teller (BET) surface area and pore volume and size were measured by nitrogen gas sorption analysis at 77K bath temperature using Micromeritics Gemini BET Surface Area Analyser, Poretech, following the method used by Brewer *et al*. (2011).

Batch Cd Sorption Studies

The capacity of the biochar to sorb cadmium (Cd) was evaluated using a batch sorption study. The batch tests were replicated three times and blanks were run concurrently (Mohan *et al*., 2007). A stock solution containing 1000 mg Cd $L^{-1}$was prepared by dissolution of analytical grade of the metal in a 0.01 M $CaCl_2$ as a background electrolyte. The solution was diluted to 5, 10, 15, 20 and 25mg Cd L^{-1} solutions with 0.01 M $CaCl_2$. The 0.01 M $CaCl_2$ solution was used as the 0 mg Cd L^{-1} concentration. The Cd solutions (25 mL^{-1}) were added to centrifuge tubes containing 2.5 g biochar samples. The suspensions were shaken at 180 rpm at constant temperature (25°C) for 24 h (Khodaverdiloo and Samadi, 2011) on a reciprocating shaker. The suspensions were centrifuged at 9440*g for 10 min and the supernatants filtered through Whatman no. 42 filter paper (Khodaverdiloo and Samadi, 2011). A Fast Sequential Atomic Absorption Spectrometer (Model AA280FS) was used to measure metal (Cd) concentration in the supernatant. The pH of the supernatant was also measured. The amount of metal sorbed (S) was calculated as the difference between the amount added and the amount in the equilibrium solution, using Equation 1 (Desta, 2013):

$$S = \frac{(Co - Ce) * V}{W} \qquad (1)$$

where, S is the amount of Cd sorbed (mg kg^{-1}), C_0 and C_e are the initial and equilibrium solution Cd concentrations (mg L^{-1}), V is the solution volume (L) and W is the adsorbent weight (kg).

Data Analysis

All characteristics of biochar were subjected to a two-way analysis of variance (ANOVA) to show effects of pyrolysis temperature and feedstock type using Stata/IC 13.1 for Windows (1985-2013). Adsorption data were fitted using a Langmuir isotherm model and sorption capacities were estimated (Kumar *et al.*, 2011). Step-wise regression analysis was used to identify the best fit model to explain Cd sorption data by removing certain variables based on the t-statistics for estimated coefficients (Gray *et al.*, 1999).

Results and Discussion

Yield, Volatile Matter, Fixed Carbon and Ash Content of Fecal Biochar

Biochar from latrine waste had higher yield than from sewage sludge and the yield decreased with increase in pyrolysis temperature (Table 2). Increasing pyrolysis temperature from 350 to 550°C decreased biochar yield by 6.7% (83.4% to 76.7%) for latrine waste and by 32.9% (74.3 to 41.4%) for sewage sludge. The least latrine waste biochar yield (650°C) was similar to the highest for sewage sludge (350°C). The loss of organic C associated with thermal degradation of ligno-cellulosic biomass and dehydration of organic compounds could explain the decrease in biochar yield with pyrolysis temperature (Liu *et al.*, 2014). Thermal degradation of sewage sludge (higher total C) explains greater decline in yield and increase in total elemental composition than those from latrine waste with increasing pyrolysis temperatures. Sewage sludge biochar yield was lower than reported by Yuan *et al.* (2015), in the similar range as reported by Hossain *et al.* (2011) and higher than reported by Agrafioti *et al.* (2013). The composition of the sludges could explain the differences.

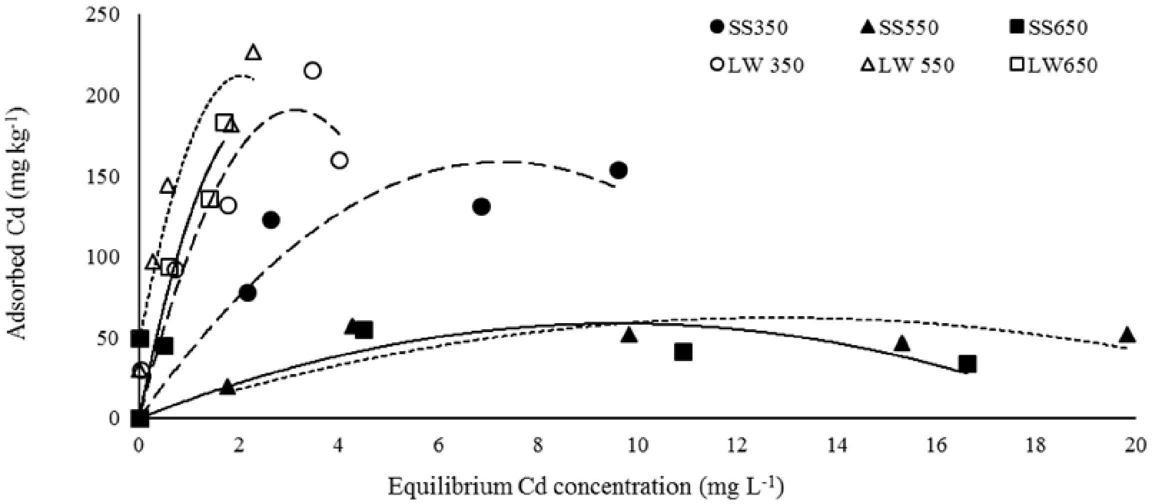

Fig. 1: Adsorption isotherms for six biochars; SS = Sewage Sludge and LW = latrine waste

Volatile matter was higher in biochar from sewage sludge than latrine waste and the composition decreased with increase in pyrolysis temperature (Table 2). There was no significant difference in volatile matter on sewage sludge biochar at 550°C and latrine waste biochar at 350°C. Higher volatiles are indicators of rich organic matter (Liu *et al*., 2014). The decrease in yield and volatile matter with increase in pyrolysis temperature was in agreement with Yuan *et al*., 2011; Enders *et al*., 2012; Wu *et al*., 2012; Mitchell *et al*., 2013; Hmid *et al*., 2014; Liu *et al*., 2014), for a variety of feed stocks. Trends of ash content were the exact opposite of those of volatile matter, with higher levels in biochar from latrine waste than from sewage sludge and the composition increased with increase in pyrolysis temperature (Table 2). Degradation of organic material (loss of volatile solids) during long storage times in the latrine (Zuma *et al*., 2015) could explain the higher ash content in latrine waste(85-93%) than sewage sludge (50-70%) biochar. The higher ash content in the two fecal wastes indicated lower organic C content, when compared with other feed stocks in the literature (Liu *et al*., 2014). Sewage sludge biochar had higher fixed C than from latrine waste (Table 2). Increasing pyrolysis temperature from 350 and 550°C increased fixed C in sewage sludge biochar, while the fixed C decreased for latrine waste biochar. There were no differences in fixed C between 550 and 650°C for both feedstocks. The increase in fixed C with pyrolysis temperature was in agreement with Yuan *et al*., (2011; Enders *et al*., 2012; Wu *et al*., 2012; Mitchell *et al*., 2013; Hmid *et al*., 2014; Liu *et al*., 2014).

Total Carbon, Nitrogen and Hydrogen Composition of Biochar

Biochar from latrine waste had lower total C and N than sewage sludge biochar and the composition decreased with increase in pyrolysis temperature (Table 3). The trends were the opposite of that of ash, indicating that more ash relatively accumulated, as C and N are lost. The C:N ratios were higher for latrine waste biochar than sewage sludge and generally increased with increase in pyrolysis temperature. The increase in pyrolysis temperature from 350 to 550°C resulted in decrease in H content in biochar from both feed stocks (Table 3). The H:C ratios followed the same trend as that of H composition of the biochar. The decrease in H led to a decrease in H:C molar ratio, an index of biochar aromaticity. Generally, the H:C of the biochar ranging 0.02 - 0.1 suggest condensed structure and more recalcitrant constituents (Kloss *et al*., 2012). Hmid *et al*. (2014) and van Zwieten *et al*. (2010) reported that biochar become more aromatic and carbonatious at high temperature due to a decline in H/C. However, the H:C ratios in our study suggest that the biochar did not have significant aromaticity.

pH, Electrical Conductivity, Exchangeable Bases and Cation Exchange Capacity

Biochar pH increased with increase in pyrolysis temperature (Table 4). At 350°C latrine waste biochar had higher pH than sewage sludge, while at 550 and 650°C sewage sludge biochar had higher pH . Generally, biochar pH (Table 4) increased with increase in pyrolysis temperature resulting in alkaline biochar (Wan *et al*., 2014). Electrical conductivity (EC) values of the biochar were low with no significant effects of pyrolysis temperature for latrine waste, while increasing temperature increased EC in sewage sludge biochar. Exchangeable Ca was higher in latrine waste biochar than from sewage sludge, with no effects of pyrolysis temperature. Exchangeable *K* was lower in latrine waste than sewage sludge biochar. The composition decreased in sewage sludge biochar by raising pyrolysis temperature from 350 to 550°C and increased in latrine waste biochar from 550 to 650°C. Exchangeable Mg was lower in latrine waste biochar than sewage sludge at 350°C. Results of Na had no clear trend. Sewage sludge biochar at 550 and 650°C had lower CEC than the others. This was contrary to Mukherjee and Lal (2014), who reported that formation of phenolic functional groups might increase biochar CEC. The functional groups were only present at 650°C for latrine waste and at 350°C for sewage sludge (Table 5). The high ash content and low *C* in fecal waste biochar could explain the difference. The higher CEC in latrine waste biochar could result in higher sorption of metals due to cation exchange (Inyang *et al*., 2016).

Table 2: Yield and proximate analyses results of biochars from human wastes

Feedstock	Temperature (°C)	Yield (%)	Volatiles (%)	Ash (%)	Fixed C (%)
Latrine waste	350	83.55a	10.27b	84.60c	5.10c
	550	76.71b	5.70d	90.23b	4.07d
	650	75.00c	3.10e	92.97a	3.97d
Sewage sludge	350	74.31c	36.13a	49.57f	14.33b
	550	41.42d	9.80b	66.77e	23.37a
	650	37.60e	7.23c	69.77d	22.97a

Means followed by the same letter in each column are not significantly different at $p<0.05$

Table 3: Carbon, nitrogen and hydrogen composition of fecal biochars

Feedstock	Temperature (°C)	C (%)	N (%)	H (%)	C/N	H/C
Latrine waste	350	11.14d	1.04c	1.01b	11:01	1.1
	550	8.73ed	0.71dc	0.36c	12:01	0.3
	650	6.45e	0.44d	0.35c	15:01	0.4
Sewage sludge	350	31.19a	5.45a	2.64a	6:01	1.0
	550	17.27c	2.64b	1.02b	7:01	0.7
	650	20.85b	2.77b	0.71cb	8:01	0.3

Means followed by the same letter in each column are not significantly different at $p<0.05$

Table 4: pH, electrical conductivity, exchangeable bases and cation exchange capacity of the biochars

	Latrine waste			Sewage sludge		
Elements	350°C	550°C	650°C	350°C	550°C	650°C
pH (H_2O)	6.94b	7.02bc	7.14cd	5.89e	7.27d	7.56a
pH (KCl)	6.93d	7.03d	7.17c	6.0 5e	7.47b	7.86a
EC (µS cm^{-1})	36.86b	38.1b	41.6ab	45.30a	9.46c	13.51c
Exchangeable Ca (cmol+kg^{-1})	9.74b	17.3a	18.8a	5.47c	2.78c	3.19c
Exchangeable Mg (cmol+kg^{-1})	3.08b	4.06ab	4.32ab	4.88a	3.44ab	4.65a
Exchangeable K (cmol+kg^{-1})	0.94d	1.04cd	0.58e	3.30a	1.25cb	1.45b
Exchaangeable Na (cmol+kg^{-1})	0.90c	1.40b	0.98c	2.01a	0.44d	1.02c
Cation exchange capacity (cmol+kg^{-1})	5.09a	4.91a	5.65a	4.17ab	2.31c	2.40bc

Means followed by the same letter in each row are not significantly different at $p<0.05$

Table 5: FTIR spectra of fecal biochars produced at different pyrolysis temperatures

		Biochars					
		Latrine waste			Sewage sludge		
Actual group frequency, wave number cm^{-1}	Functional group	350°C	550°C	650°C	350°C	550°C	650°C
*3700-3500	N-H stretching of amide	3694.07	3691.69				
3570-3200	O-H stretching of phenol				3338.16		
*3000-2500	O-H stretching of carboxylic acid	2642.94	2645.18	2646.13	2924.7	2644.1	2795.73
*1740-1690	C=O stretching of aldehyde	1714.77			1706.19		
*1700-1500	C=C bending of aromatic carbon				1559.47	1559.89	1560.98
1650-1550	N-H secondary amine	1559.16	1561.18	1561.22			
1510-1450	C=C-C ring stretching of aromatic C	1497.09	1497.09	1497.04		1497.14	1496.98
1490-1410	Carbonate ions				1446.79		
1410-1310	O-H bending of phenol (tertiary alcohol)			1356.09			
1240-1190	P-O-C stretching of aromatic phosphates	1219.9	1219.86	1219.87	1219.85	1220	1220.03
1100-1000	Phosphate ions						1068.05
1050-990	Aliphatic phosphate	1007.95	1009.67	1046.97	1047.04	1048.24	
995-850	Aromatic phosphates	913.16	914.83				
860-680	C-H bending of aromatic C	772.61	773.06	772.94	772.94	772.52	772.85

Encyclopaedia of Analytical Chemistry (Coates, 2000) *Web Spectra (Merlic, 1997)

Chemical Functional Groups of Fecal Biochar

The chemical functional groups of the biochar are shown in Table 5. The C-H bending of aromatic C, aromatic P-O-C (1240-1190 cm^{-1}) and carboxylic acid O-H functional groups were present in all biochar irrespective of feedstock and pyrolysis temperature. The aldehyde *C* = *O* functional group occurred only in biochar pyrolysed at 350°C irrespective of feedstock. All latrine waste biochar lacked the *C* = *C* bending of aromatic *C* and the aromatic carbon *C* = *O* functional groups, which were present in sewage sludge biochar. All latrine waste biochar had amide N-H (except 650°C) and secondary amine N-H functional groups, which were absent in sewage sludge biochar. All biochar had the ring stretching of aromatic C (C = C-C) except the sewage sludge biochar pyrolysed at 350°C. The phenol O-H functional group (3570-3200 cm^{-1}) and carbonate ion (1490-1410 cm^{-1}) existed only on sewage sludge biochar pyrolysed at 350°C. Increasing pyrolysis temperature could have resulted in formation of C = C-C groups from the phenol O-H and carbonate ion, in sewage sludge biochar. Reduction in biochar yield with increase in pyrolysis temperature is associated with dehydration of organic compounds such as those with hydroxyl, phenolic and carboxylic acid groups (Liu *et al*., 2014; Novak *et al*., 2009). Aromatic phosphate functional group (995-850 cm^{-1}) was only present in latrine waste biochar pyrolysed at 350 and 550°C. On the other hand, the latrine waste biochar produced at 650°C was the only one with the phenol O-H tertiary alcohol functional group (1410-1310 cm^{-1}). The aliphatic phosphate functional group was present in all biochar except sewage sludge biochar pyrolysed at 650°C; the only one with phosphate ions, suggesting that the functional group mineralized at high temperature. On the other hand, C = O stretching of aldehyde on latrine waste biochar diminished with increase in pyrolysis temperature.

Surface Area, Pore Volume and Pore Size

Latrine waste biochar had higher surface area and pore volume than those from sewage sludge (Table 6) The higher surface area and pore volume of latrine waste biochar suggested that these biochar could encourage more physical metal sorption than those from sewage sludge (Inyang *et al*., 2016). Surface area and pore volume increased, whereas pore size decreased, with increase in pyrolysis temperature. There was greater change in surface area, pore volume and pore size as a result of increasing pyrolysis temperature from 350 to 550°C than from 550 to 650°C. As volatile components escape they leave voids, which leads to improvement in the porosity and exposing greater surface area of the carbonized biomass (Ahmad *et al*., 2012; Downie *et al*., 2011). The rapid decline in volatile compounds and associated increase in specific surface area, in our study, supports this view. Lower volatile compounds and high ash content in latrine waste biochar, because of C losses during storage, explains the higher porosity and surface area even at 350°C.

Latrine waste biochar had higher surface area than reported by Agrafioti *et al*. (2013) for sewage sludge. While latrine waste biochar had similar surface area than those reported by Yuan *et al*. (2015), sewage sludge biochar were lower. However, the pore volume in our study was lower, indicating that our biochar were less porous. The increase in surface area and micro-porosity due to pyrolysis could enhance metal retention when used as adsorbents (Masto *et al*., 2013). The higher sorption capacity of latrine waste biochar than sewage sludge appeared related to the surface area. However, the increase in surface area in latrine waste biochar was not correlated with Cd sorption, in agreement with Trakal *et al*. (2014), who reported that removal of Cd was least influenced by biochar morphology and specific surface area.

Cadmium Sorption on Fecal Biochar

The Cd sorption data fitted he Langmuir isotherms (Fig. 1). The different Cd sorption capacities and the constants relating to bonding energy (b) of different biochar are in Table 7. The fit of Langmuir model suggests that Cd sorption on the biochar is a monolayer process (Bogusz *et al*., 2015; Trakal *et al*., 2014). Greater sorption occurred on latrine waste biochar than on sewage sludge biochar, which could be explained by the higher ash, CEC and surface area. Cadmium sorption on both latrine waste and sewage sludge decreased with increase in pyrolysis temperature, except that sorption on latrine waste biochar at 550°C was higher than that on 350°C. The R^2 were > 0.900. The constants relating to bonding energy were higher on latrine waste (≥ 40 L kg^{-1}) than sewage sludge (< 1.2L kg^{-1}).

Relationships of Biochar Characteristics and Cadmium Sorption

Step-wise regression (Table 8) analysis showed that equation Cd sorption capacity could be explained ($p<0.05$) by a combination of ash and total P (**Smax = 1.960 ash -9.028 total P + 255.696**) and of ash and pH (**Smax = 4.177 Ash - 97.429 pH + 525.562**). Although there appears to be relationships between Cd sorption capacity and ash, surface area and CEC, only ash, total P and pH had significant effects. The CEC and surface areas could have been too low and could have been masked by effects of ash and total P and pH. Omission of ash led to insignificant effect with low correlation coefficient and $p>0.05$, which indicated that ash is the most important component in the sorption of Cd on these fecal biochar. The positive correlation of Cd sorption with ash content was in agreement with Xu *et al*. (2014) and suggested that minerals in the ash dominated the sorption process. Calcium hydroxyapatite and calcium carbonates in bone biochar have been shown to promote ion exchange reactions of heavy metals (Inyang *et al*., 2016). The higher Ca than total P in latrine waste biochar indicate that Ca in the ash occurred mainly as carbonates, providing sorption sites for Cd (Xu *et al*., 2014). Phosphorus could have precipitated with Cd at pH 6.0-7.0, resulting in higher sorption than at higher pH. At higher pH, precipitates with Ca and Mg are formed and P becomes less available to precipitate with Cd, lowering sorption. This effect would have been more important for sewage sludge, which had higher P and lower Cd sorption at higher pH (7.5-7.9). The decline in exchangeable Ca with pyrolysis temperature for sewage sludge supported this view. However, this effect could have been lower for latrine waste biochar, which had lower P. In these biochar types, P content and pH did not change because the material was low in volatile solids.

Table 6: Surface area, pore volume and size of the resultant biochars

Feedstock	Pyrolysis temperature (°C)	Surface Area ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)	Pore Size (Å)
Latrine waste	350	7.5	0.0350	183.1
	550	23.7	0.0530	91.0
	650	25.7	0.0520	81.2
Sewage sludge	350	0.3*	0.0008	112.9
	550	1.6	0.0051	129.8
	650	4.2	0.0073	50.6

*Volatiles came off the sample during analysis resulting in negative gas adsorption values (not suitable for BET analysis)

Table 7: Effect of pyrolysis temperature on Cd sorption maximum

Feedstock	Pyrolysis temperature (°C)	Smax (mg kg^{-1} Cd)	b (L kg^{-1} Cd)	R^2
Latrine waste	350	200.0	50.00	0.98
	550	250.0	40.00	0.96
	650	167.0	60.00	0.90
Sewage sludge	350	143.0	0.78	0.98
	550	55.6	1.13	0.97
	650	35.7	-1.56	0.98

Table 8: Multiple and step-wise regression analysis to identify the most influential parameter(s) on Cd Smax; Cd as a model element

Step-wise regression Smax (mg kg^{-1})	Cd regression output coefficients	Standard error	P > |t|	P as a whole
Ash %	2.416	1.509	0.251	0.161
Total P (g kg^{-1})	-7.607	4.042	0.201	
Total Al (g kg^{-1})	-1.591	3.207	0.669	
Constant (*a*)	211.184	163.183	0.325	
Smax (mg kg^{-1})				
Ash %	1.96	1.037	0.155	**0.044**
Total P (g kg^{-1})	-9.028	2.464	**0.035**	
Constant (*a*)	255.696	117.931	0.119	
Smax (mg kg^{-1})				
Ash %	3.995	1.705	0.101	0.169
Total Al (g kg^{-1})	-5.872	3.071	0.152	
Constant (*a*)	-44.703	122.612	0.740	
Smax (mg kg^{-1})				
Total P (g kg^{-1})	-11.204	4.142	0.073	0.127
Total Al (g kg^{-1})	1.531	3.139	0.659	
Constant (*a*)	436.51	101.765	0.023	
Smax (mg kg^{-1})				
Ash %	4.177	0.888	**0.018**	**0.025**
pH_{KCl}	-97.429	21.256	**0.019**	
Constant (*a*)	525.562	144.834	0.036	

Conclusion

Biochar from latrine fecal waste have higher yields, ash, Ca, Fe, surface area, porosity and cadmium sorption capacity and lower fixed C, than those from sewage sludge. Increasing pyrolysis temperature increases surface area and porosity and decreases biochar yield, volatile matter and Cd sorption capacity. Surface functional groups on biochar differ between the fecal wastes and among pyrolysis temperatures. Ash, pH and P content are the most important parameters governing Cd sorption on fecal biochar. Further research is required on sorption of other heavy metals on these fecal biochar when compared with wood derived biochar.

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Author's Contributions

Koetlisi Andreas Koetlisi: Designed all experiments, did data-collection and analysis and wrote the first draft of the manuscript.

Pardon Muchaonyerwa: was the supervisor of the lead author's PhD for which this paper is a part. He participated in the designs and carrying out of all experiments, data-collection and analysis, and writing of the manuscript.

Ethics

This research article is original and has not been published elsewhere and or/does not contain any published material in its content. The authors have read and approved the manuscript and no ethical issues involved.

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