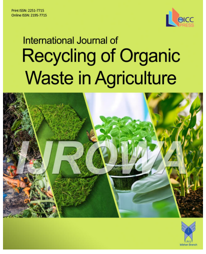

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Cocoa pod husk wastes derived biochar for overcoming potassium deficiency in organic agriculture

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Original Research

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Abstract:

Purpose: Potassium (K) deficiency is emerging as a significant global agricultural challenge impacting 20% of farming areas and posing a threat to food security. In India, the potassium deficit has aggravated due to a focus on nitrogen and phosphorus application, with the net potassium balance declining from −3.29 million tonnes in 2000-01 to −7.2 million tonnes in 2015-16. Cocoa cultivation in Southern states of India like Kerala, Karnataka, Andhra Pradesh, and Tamil Nadu, produce substantial biomass waste, including cocoa pod husks, which are rich in potassium.
Method: This study explores the conversion of cocoa pod husks into biochar as a sustainable potassium source. Cocoa residues, including leaves, pod husks, and bean shells, were sun- and polyhouse-dried before being pyrolyzed in a single-drum charring kiln. The biochar produced from cocoa pod husks was selected for further analysis due to its superior quality, with a conversion efficiency of approximately 40%.
Results: The resulting biochar had a potassium content of 10.9%, with 60% of it being water-soluble, and also contained 13% organic carbon along with nitrogen, phosphorus, and micronutrients. Physico-chemical and microbiological analyses revealed the biochar's alkaline pH (10.7) property, low bulk density (0.41 g/cc), and low native microbial activity, with *Bacillus* spp. being the dominant microbe. An ecotoxicity assay using earthworms indicated no acute toxicity, although earthworms took longer to acclimatize to the cocoa pod husk biochar compared to coconut residue biochar.
Conclusion: Thus, cocoa pod husk biochar, with its high potassium content, organic carbon, and non-toxicity to earthworms, offers a sustainable solution for potassium deficiency in soils, particularly in organic agriculture.

Keywords: Cocoa pod husk biochar; Organic wastes; Potassium nutrition; Organic farming

1. Introduction

Potassium (K) is one of the three essential nutrients required for healthy plant growth and productivity. However, 20% of global agricultural areas face severe potassium deficiency, threatening food security (Brownlie et al., 2024). In India too, the net potassium balance is negative, depleting from −3.29 million tonnes in 2000-01 to −7.2 million tonnes in 2015-16, as farmers focus primarily on nitrogen and phosphorus application (Das et al., 2022). With the rise of organic farming, which promotes soil and environmental health, potassium deficiency remains a critical challenge (Askegaard and Eriksen, 2002; Mikkelson, 2007). Neglecting K management in agriculture is jeopardizing global food security and requires urgent attention (Brownlie et al., 2024). Recycling potassium-rich plant wastes into biochar is emerging as a promising solution. An example is the production of potassium-enriched biochar from *Canna indica* with bentonite to enhance K transformation (Chen et al., 2023). Similarly, cocoa trees could be a sustainable source of organic potassium.
Cocoa (*Theobroma cacao* L.) is the third most important beverage crop globally, after tea and coffee, supporting a $100 billion chocolate industry worldwide from a production of 4.9 million tonnes. Major producers include

Ivory Coast, Ghana, Indonesia, Nigeria, Cameroon, and Brazil. In India, cocoa is primarily grown in Kerala, Karnataka, Andhra Pradesh, and Tamil Nadu, covering 105,975 hectares with a production of 28,426 MT and a productivity of 669 kg/ha (Directorate of Cashew Nut and Cocoa Development, 2021-22). Andhra Pradesh leads with 41,874 hectares and 11,448 MT in production. Traditionally grown in agroforestry systems with permanent shade trees, cocoa later expanded as an intercrop with palms, fruit trees, and other shade trees. This cultivation method conserves natural resources, occupies no extra land, and protects the environment with its dense canopy and substantial litter fall. In the Indian scenario, cocoa has proven to be a profitable and compatible mixed crop, especially in palm-based systems like arecanut, coconut, and oil palm (Elain Apshara, 2019).
Cocoa cultivation generates substantial above-ground biomass, with leaves necessitating annual pruning. These pruned materials, when added to the tree basin, act as mulch, aiding in soil and water conservation during the post-monsoon and summer months. However, addition of excessive pruned residues to the three basins can lead to stem canker, borer infestations, and attract poisonous snakes. In addition, after harvesting cocoa beans, large volumes of pod husks are also discarded on farms. The thickness of these husks varies between 0.6 to 1.58 cm (Elain Apshara and Krithika, 2018), with over 1 cm considered desirable for variety release (Elain Apshara, 2015). Different cocoa varieties can thus produce substantial biomass waste, with only about 5% of fresh pod husks used as cattle feed, leaving 95% as farm waste. In India, cocoa harvesting coincides with the monsoon season, from June to October, when heavy rainfall and high humidity (over 90%) promote black pod rot caused by *Phytophthora* spp (*P. megakarya*, *P. capsici*, *P. palmivora* and *P. citrophthora*). This can result in 20 – 30% pod loss and 10% tree mortality (Chandra Mohanan, 1994; Guest, 2007; Peter and Chandra Mohanan, 2011; Chowdappa et al., 2016). If not promptly removed, pod husks can become active sources of *Phytophthora* infection for the next crop season. The accumulation of leaves and pod husks also creates a microenvironment that fosters the growth of other fungal pathogens like *Colletotrichum* and *Fusarium* species, in addition to the *Phytophthora* spp. (Peter and Chandra Mohanan, 2011).
A one-hectare cocoa garden typically generates around 2 tonnes of leaves, 15 – 17 tonnes of cocoa pod husks, and 500 kg of bean shell residues annually. These residues resist quick decomposition due to their complex phenolic content, causing accumulation if not removed. However, cocoa pod husks contain over 3% potassium (Ankrah, 1974; Lu et al., 2018), making them a valuable natural source of this essential nutrient making them one of the highest natural resources of this major nutrient for crops (Andrews et al., 2021). Effective recycling of these residues (Sujatha et al., 2015), could provide a potassium-rich organic input while also reducing the presence of pathogenic fungi in cocoa fields.
Thus, cocoa pod husks, rich in potassium, present an option as a sustainable potassium source (Yeboah et al., 2016; Rozita et al., 2022). However, raw cocoa pod husks have drawbacks, necessitating post-harvest modification. Composting is a simple option (Fidelis and Rajashekhar Rao, 2017; Vitinaqailevu and Rajashekhar Rao, 2019), but it has been associated with cadmium toxicity (Pinzon-Nunez et al., 2022). We hypothesized that pyrolyzing cocoa pod husks into biochar would be a superior alternative to composting, as this process recycles the waste into a potassium-rich product with high organic carbon too. Previous studies have shown that low-temperature pyrolysis can yield biochar with about 4.03% potassium content (Tsai et al., 2018). In this context, we have standardized the conversion of cocoa residues into biochar through pyrolysis in India for the first time to the best of our knowledge, with the results presented in this paper.

2. Materials and method

Conversion of cocoa pod husk to biochar

Bulked, sun- and polyhouse-dried cocoa residues (leaves, pod husks and bean shells) were used as feedstocks for the biochar production. The process was conducted using a simple, single-drum charring kiln from ICAR-Central Institute of Agricultural Engineering, Bhopal, India, previously utilized for coconut residue biochar (Gopal et al., 2020). The feedstocks were loaded into the kiln and fired, following the same procedure as coconut biochar production. During pyrolysis, temperatures fluctuated between 350 °C and 450 °C with varying residence times. After cooling, the biochar was harvested, and the output from each residue type was measured. Based on these results, only cocoa pod husks were selected for further conversion, with four batches processed using different substrate loading rates and residence times (Table 1).

Physico-chemical analysis

The physico-chemical, microbiological properties, and ecotoxicological assay of the cocoa pod husk (CPH) biochar

Table 1. Details of feedstock inputs and of Cocoa Pod Husk Biochar (CPHB) production in single drum charring kiln.

Batch of CPHB production	Moisture (%) in Cocoa Pod Husk (CPH)	Quantity of CPH substrate (kg)	Residence time (hr)	CPH Biochar output (kg)	Conversion (%)	Moisture (%) in CPHB
1	26	61	3	15	25	14
2	25	53	3	18	34	12
3	18	51	2	20	39	8.5
4	18	53	2	22	42	9

were conducted using the batch with the highest yield. The pH and electrical conductivity (EC) were determined by shaking a 1:10 solid-to-water solution for an hour, allowing it to stand for 30 minutes, and then measuring with a pH/EC meter (Eutech Instruments, Singapore; Lee et al. (2013)). Ash content was estimated by heating the biochar samples in a muffle furnace (SIMECO, India; Slattery et al. (1991)), while organic carbon content was measured using the Walkley and Black (1934). The cation exchange capacity (CEC) of the biochar was assessed through a modified ammonium acetate compulsory displacement method (Gaskin et al., 2008), and bulk density was determined following the procedure outlined by Ahmedna et al. (1997). Total nitrogen content was analyzed by wet digestion with concentrated sulfuric acid (Jackson, 1973). The total phosphorus, potassium, sodium, calcium, magnesium, and micronutrient content in the biochar were determined after acid digestion. Phosphorus concentration was measured using a UV-Visible spectrophotometer (Shimadzu, Japan) through the vanadate-molybdate method (Chapman and Pratt, 1961), while potassium and sodium levels were assessed using a flame photometer (Elico Ltd., India). Calcium and magnesium were estimated by Versenate titration (Cheng and Bray, 1951), and micronutrients were measured using an atomic absorption spectrophotometer (Thermo Scientific iCE 3000 series). Additionally, water-extractable and ammonium acetate-extractable potassium, calcium, and magnesium content were determined by flame photometry and the Versenate method, respectively.

Microbiological analysis

The microbiological characterization of CPH biochar was carried out by serial dilution and spread plate method on general and selective media for general and function-specific microbial communities. Ten-gram powdered biochar, fresh and stored (for 6 months), were added to 90 mL sterile distilled water blanks making it 10^{-1} dilution, vortexed for 5 min with intermittent breaks, serially diluted in sterile water blanks up to million times by transferring 10 mL from previously diluted blank to 90 mL water blank. From different dilutions, an aliquot of 0.1- and 1.0- mL suspension was spread and pour plated, respectively, on selected medium for enumerating bacteria, fungi, actinomycetes and other function-specific microbial groups. The plates were then kept in an incubator at 28 ± 2 °C for 24 to 96 hours and the colonies growing were scored. The results were presented as colony forming units/g of biochar.

Ecotoxicity assay on earthworms

Ecotoxicity assay was performed by introducing the earthworms in circular plastic basins containing one half portion filled with plain soil and another half with soil mixed with different doses of the CPH biochar, with minimum three replications for each dose. The earthworms used in this experiment were the coconut leaf vermicomposting worms, *Eudrilus* sp. (Gopal et al., 2017). In each replication, ten fully grown adult earthworms were added in the Centre of the basin with one half having plain soil and the other half soil mixed with biochar. Sufficient moisture was added to the contents of the basins to allow the earthworms to settle. The movement of earthworms and vermicast output were recorded periodically to ascertain the safety of the biochar towards the worms.

3. Results and discussions

Conversion of cocoa pod husk to biochar

The dried cocoa residues had moisture contents ranging between 12 – 26% as per different batches obtained after their sun and polyhouse drying. Biochar produced from cocoa leaves and bean shells was unsatisfactory, with leaves becoming overly charred and shells either over-charred or under processed, leading to inconsistent biochar quality. In contrast, cocoa pod husk yielded better biochar. Four batches of cocoa pod husk were tried and a variable biochar output was obtained depending upon the input quantities, moisture content and residence time. The highest biochar output (38 – 42%) from husks with the lowest moisture content (18%). The biochar yield from a simple, single-drum charring kiln was 50% lower than that from a specialized charcoal-fired reactor reported in Nigeria (Odesola and Owoseni, 2010), suggesting that there is potential to improve yield by developing a portable double drum charring kiln with agro-waste firing (Pandiselvam et al., 2023).

Physico-chemical and microbiological analysis

The physico-chemical properties of the cocoa pod husk (CPH) biochar were analyzed, revealing a low bulk density of 0.41 g/cc, an alkaline pH of 10.7, and a potassium content of approximately 10.9%, with 60% of it being water-soluble (Fig. 1). The data on physical and major nutrients is furnished in Table 2. The data on secondary and micronutrients is furnished in Table 3 and it showed that calcium and magnesium were also found in significant concentrations. Despite its high potassium content, the CPH biochar exhibited a low organic carbon (OC) content of 13.5%, classifying it as a Class III biochar in terms of OC content. Elemental analysis has shown that raw cocoa pod husks contain about 42.78% carbon (Mansur et al., 2014). However, during pyrolysis in simple singular drum charring kilns, which have unregulated oxygen and burning conditions, the carbon in the husks becomes partially oxidized, leading to lower OC content in the resulting biochar. Unlike sophisticated charring kilns that follow the three stages of i) pre-pyrolysis, ii) main pyrolysis, and iii) biochar formation, simple singular

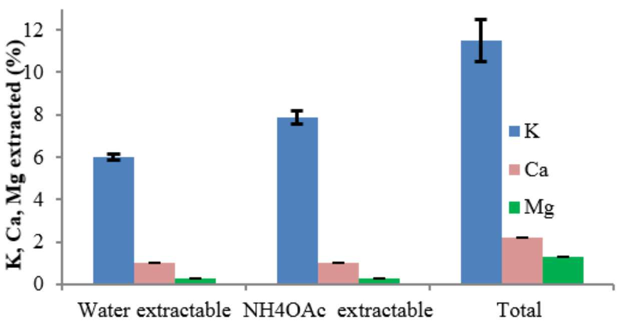

Figure 1. Water and ammonium acetate extractable and total K, Ca and Mg concentrations in cocoa pod husk biochar.

Table 2. Physical properties and major nutrient contents in cocoa pod husk biochar.

Physico-chemical properties	Replications			Mean	Standard deviation
	R1	R2	R3		
Moisture content (%)	6.6	6.2	6.7	6.5	0.26
Bulk Density (g/cc)	0.39	0.41	0.42	0.41	0.015
Ash content (%)	36.03	38.74	40.70	38.49	2.345
CEC (meq/100g)	165.94	177.54	185.14	176.2	9.669
pH	10.72	10.73	10.73	10.7	0.0058
EC (mS/cm)	25.85	26.07	27.77	26.6	1.050
OC (%)	13.5	13.35	13.5	13.45	0.086
Total N (%)	1.09	1.05	1.06	1.07	0.0208
Total P (%)	0.71	0.68	0.75	0.71	0.0351
Total K (%)	11.00	10.15	11.42	10.86	0.0058

drum charring kilns do not regulate these stages effectively, resulting in biochars with lower carbon content (Tomczyk et al., 2020).

The physico-chemical properties of biochar are mainly influenced by the feedstock type. Kiln properties such as temperature and oxygen regulation as well as the residence time, too, have an important role in determining the properties of the biochar. The pH of biochars depends upon the woody or non-woody nature of the feedstock used (Tag et al., 2016). Moreover, pH value is also positively related to ash content. Thus, being a non-wood feedstock, cocoa pod husk biochar had a 36% ash content which must have been the main reason for its high basicity (pH of 10.9). This was quite high compared to pH of biochars from coconut biomass residues, ranging between $7.9-9.3$, and accompanied with lower ash contents (Gopal et al., 2020) than cocoa pod husk biochar produced in this study.

One of the significant properties of cocoa pod husk (CPH) biochar is its high potassium content, approximately 10.9%. This potassium level is at least three times higher than that found in CPH biochar produced under low pyrolysis temperatures (Tsai et al., 2018) and is nearly similar to the 9.8% potassium concentration reported by Rozita et al. (2022), who used a simple clay brick and tank method for biochar production. In our study, this translated to about 10 kg of potassium produced from one tonne of CPH biochar, which is $20-25\%$ more than the potassium extracted from ash when cocoa pod husks are burned or fully oxidized in open air conditions (Gyedu-Akoto et al., 2015). Moreover, the potassium in CPH biochar is not only abundant but also highly available, with up to 60% present in water-extractable form. This makes it an excellent source of readily available potassium for plants. In other studies, to enhance the availability of potassium from biochar, bentonite was added to the substrate during biochar production, as seen in the case of aquatic *Canna indica* plants (Chen et al., 2023).

Further, CPH biochar, with its high pH, could be useful for acid soils, particularly in improving phosphorus nutrition availability as it has been reported that addition of it could reduce P fixation and improve P desorption from acidic soil (Pouangam Ngalani et al., 2023). Beyond its use in

Table 3. The secondary and micronutrient contents in cocoa pod husk biochar.

Secondary & micronutrients	Replications			Mean	Standard deviation
	R1	R2	R3		
Total Na (%)	4.72	4.25	4.95	4.64	0.357
Total Ca (%)	2.2	2.2	2.2	2.20	0
Total Mg (%)	1.3	1.32	1.32	1.32	0.0115
Total Fe (ppm)	6223.2	6238.6	6206.9	6222.9	15.837
Total Mn (ppm)	954.03	944	995.4	964.48	27.245
Total Zn (ppm)	173.20	176.80	204.57	184.86	17.167
Total Cu (ppm)	62.53	64.87	64.60	64.00	1.280
Total B (ppm)	37.50	29.33	34.33	33.72	4.1190

Table 4. Microbial analysis of cocoa pod husk biochar for general and function-specific microflora.

Material analysed	Bacteria		Spore-forming Bacteria		Fungi	Actino mycetes	Free-living Nitrogen-fixers	Phosphate solubilizers	Fluorescent pseudomonads
	CFU g^{-1} dry wt.	log CFU g^{-1} dry wt.*	CFU g^{-1} dry wt.	log CFU g^{-1} dry wt.*					
Cocoa Pod Husk Biochar (CPBH)	20	1.3	14	1.1	ND	ND	ND	ND	ND

CFU: Colony Forming Units
* $\log_{10}$ transformed
ND - Not Detected; it means no bacterial colonies were observed and is to be read as fewer than one CFU g^{-1} CPHB.

farming, CPH biochar has shown potential in environmental applications, particularly for the removal of toxic metals from aqueous solutions (Abbey et al., 2023). Additionally, recycling CPH into biochar has been identified as a more effective method for managing heavy metal contamination compared to composting (Pinzon-Nunez et al., 2022).
Microbiological analysis of the CPH biochar indicated sparse presence of microbiota in the freshly prepared sample (Table 4). Of all the microbial groups studied, only bacteria and spore-forming bacteria were found to be present in the enumeration studies conducted with CPH biochar (Fig. 2). *Bacillus* spp. are the common spore forming bacteria present in several matrices including soil and air. It is possible that while handling the CPH biochar from production stage to powdering stage, some of these bacteria would have found residence in it. Owing to their spore forming capability, *Bacillus* spp. was able to survive in the difficult microenvironments. Similar to CPH biochar, *Bacillus* spp. was observed in coconut palm residue biochars too (Gopal et al., 2020). Other general microbial communities such as fungi and actinomycetes, and the function-specific ones *viz. free*-living nitrogen fixers, phosphate solubilizers and fluorescent pseudomonads were not detected in the CPH biochar. Presence of *Bacillus* spp. and absence of any fungal propagules indicates a good possibility of antagonism property of CPH biochar towards pathogenic fungi such as *Phytophthora*, *Fusarium* and *Colletotrichum*. Biochar addition to soils has been reported to show suppressive action against several soil pathogens including bacteria, fungi and nematodes (Poveda et al., 2021).

Ecotoxicity assay on earthworms

The safety of cocoa pod husk biochar to soil organisms such as earthworms was assayed by earthworm avoidance test. It was observed that when a lower dose of biochar was added to soil, the earthworms did not show avoidance and had easily migrated to the biochar mixed soil portion immediately. Seven out of ten earthworms were observed in the soil + CPH biochar portion in the basins. However, at higher biochar doses, it was observed that the earthworms did not immediately migrate to biochar mixed soil and it took 2 to 3 days for them to get accustomed to the cocoa pod husk biochar. Vermicasts were seen in the biochar + soil portion after two days of introduction of the earthworms indicating their foraging into the biochar mixed soil portion. However, while checking for their presence, it was found that the earthworms had moved back to the only soil portion of the assay container indicating their slow acclimatization to cocoa pod husk biochar. After 3 to 4 days, 6 to 7 earthworms were recorded to remain in the soil + CPH biochar portion in the basins. The results indicated that there was no acute toxicity of the biochar on the earthworms; however, it took them more time to adjust to CPH biochar compared to coconut residue biochar mixed soil (Gopal et al., 2020).

4. Conclusion

With a conversion efficiency of approximately 40%, it is possible to produce about 1.5 tonnes of biochar from 15 tonnes of fresh cocoa pod husks generated from one hectare of a cocoa garden. This 1.5 tonnes of biochar could supply 140 – 150 kg of potassium to the soil, given

Figure 2. Spore forming bacterial colonies from cocoa pod husk biochar.

its 10.9% potassium content. In addition to potassium, the biochar contributes 13% recalcitrant organic carbon, along with nitrogen, phosphorus, and micronutrients. It also exhibits low native microbial activity and is non-toxic to earthworms. With these favorable physico-chemical, microbiological, and earthworm-friendly properties, cocoa pod husk biochar could serve as a sustainable source of potassium, helping to address potassium deficiencies in depleting arable soils and in organic agriculture.

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Authors contributions
The authors confirm the study conception and design: Murali Gopal, Alka Gupta, Elain Apshara, Data generation, collection, analysis and interpretation: Murali Gopal, Alka Gupta, Neenu, S , Manuscript preparation: Murali Gopal, Alka Gupta, Neenu S and Elain Apshara. The results were evaluated by all authors, and the final version of the manuscript was approved.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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