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ORIGINAL RESEARCH

Biochar as a waste management strategy for cadmium contaminated cocoa pod husk residues

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Abstract

Purpose The role of cocoa pod husk waste in soil cadmium contamination has been largely overlooked. Hence, this study aims to provide a strategy for the management of cocoa pod husk waste when representing a pollution menace for cocoa plantations.

Method Cocoa pod husks waste was subjected to composting and pyrolysis for decreasing the heavy metal content. Biochar and compost were characterized using SEM-EDS, and FTIR-ATR. Macro and micronutrients (Mg, K, Zn, Fe, Cu, Zn, Mn, and Na), and Cd were measured by atomic absorption spectroscopy (AAS). Sorption experiments and soil incubation experiments for two months were also carried out looking for an application of CPH materials in Cd sorption and remediation.

Results Pyrolysis showed more effectiveness for Cd reduction in cocoa pod husk waste (90%) than composting (66%), 700 °C was the optimal temperature. Equilibrium isotherm experiments showed maximum Cd adsorption of 21.58 mg g^{-1} for Bc700 in solution. Biochar showed a small reduction of available Cd in naturally contaminated soil. Both materials have the potential to be used as organic fertilizer because of their high nutrient contents.

Conclusion Biochar is an alternative to compost for the management of post-harvest cocoa wastes contaminated with Cd.

Keywords Biomass valorization, Pyrolysis, Composting, Soil pollution, Sustainable agriculture

Introduction

Cocoa is a valuable crop that has played an important role since ancient times. Native from the Amazon, cocoa trees were domesticated around 8000 years ago on the foothills of the Andes and around the banks of the largest tributaries of the Amazon River covering the present Colombia, Peru, Ecuador, and Bolivia (Miller and Nair 2006). Cocoa was grown in small areas often associated with other fruit crops of large plantations where indigenous authorities and later colonizers controlled the harvest (Thomas et al. 2012). Currently, the harvesting practices have not changed much. Cocoa is primarily produced by smallholder farmers with little capital and hence, there is less scope for the development of technical innovations. The yield rates are low due to poor quality planting material associated with low fertilization (Vaast and Somarriba 2014). However, in Latin American countries, cocoa trees are grown as intercrop in agroforestry systems, and thus, it has helped in sustainable land use, biodiversity conservation, and mitigation of climate change. It has also served as socio-economic alternatives for replacing illegal coca crops (Abbott et al. 2018).

The cocoa bean production in Latin America is around 875 thousand tonnes in 2020, as estimated by the International Cocoa Organization (ICCO 2021). In Colombia, its production has increased from 37.202 tons in 2011 to 63.416 tons by 2020 (FEDECACAO 2020). Each ton of cocoa dry beans generates about 10

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tons of cocoa pod husks (CPH) (Figueroa et al. 2020) and thus generates a considerable amount of CPH wastes. In the last year, there were about 8 million tons of CPH wastes in Latin America. In Colombia, the average cocoa beans productivity is 446 kg per hectare and generates about 4 tons of CPH waste per hectare (Ortiz-Rodríguez et al. 2014).

The residual biomass of CPH is usually abandoned on the plantations at the place of cocoa stripping itself, thus, it becomes a significant source of inoculation of diseases and pests for healthy plants (Vriesmann et al. 2012) that limits and disrupts the expansion of cocoa production and reduces the cocoa bean yield. Some of the CPH wastes from plantations with high cadmium (Cd) contents are a serious risk. The Cd(II), a heavy metal, is one of the most toxic and dangerous environmental pollutants (Han et al. 2009). It poses a major problem for cocoa production in Colombia and restricts its exportation potential (Casteblanco 2018), thereby limiting economic development and expansion (Cely-Torres 2017). Furthermore, high mobility and extreme toxicity of Cd (Prokop et al. 2003) present in the accumulated CPH will pose a major problem as it is taken up by cocoa trees and it can also diffuse deeper and contaminate groundwater supplies (Mirsal 2008).

Maintenance of soil in cocoa tree plantations with Cd-free environment has been a major problem faced by cocoa producers (Cilas and Bastide 2020). With Cd as a growing concern, the need to transform these biomass wastes into materials that can return to the soil becomes evident, and the production of CPH by-products could accomplish this goal. Cocoa producers in Latin America either drop out the CPH in stripping sites after harvest or are composted in designed places as a strategy to fertilize the soils (Salazar et al. 2018). The use of tons of CPH produced in the form of compost through the decomposition of harvested residues provides nutrient supply opportunities on cacao ecosystems (Hartemink 2005). However, any treatment without reduction of Cd, can increase its content in soils, as noted by Ramtahal et al. (2018). In their experiments, lime treatment to soil in cocoa trees recorded a slow accumulation of Cd from cocoa litter.

An alternative to compost for the CPH waste contaminated with Cd is the production of biochar. Biochar is the product of thermal decomposition of biomass in a reducing atmosphere that can be used to reduce and recycle large amounts of waste from agriculture, with other added benefits as greater efficiency in fertilizer uses, pathogen pest elimination, soil deacidification (Nguyen and Nguyen 2017), and remediation of heavy metals from agricultural soils, along with a positive effect in the biological properties of the soil (Lu et al. 2018) thus contributing to soil resilience. Although biochar has been used since ancient times in agriculture (Ahmad et al. 2014), it is currently unknown to Latin American cocoa producers and can be cheap and easily produced by smallholder cocoa producers (Odesola and Owosen 2010).

In this study, preparation and characterization of cocoa pod husk-based biochar and compost was carried out to assess the nutritive qualities and the reduction of Cd contents in CPH biomass. Furthermore, as we hypothesized that biochar or compost might have a beneficial influence on reducing Cd contents in cocoa plantations, the Cd adsorption capacities of those materials were investigated in adsorption and incubation studies with biochar and compost mixtures and compared with natural zeolite, inorganic material that despite are not part of organic agriculture, it has been extensively studied for Cd remediation (Shi et al. 2009) and is used by many Latin American cocoa producers to improve the production efficiency.

Materials and methods

Characteristics of CPH used for composting and biochar making

Cocoa fruit samples were randomly collected from northern Colombia, in the municipalities of San Vicente del Chucurí (SVC) and Rionegro (RN) from plantations with previously determined high and low Cd contents, respectively. From each area, three of the most commonly grown cocoa varieties namely, Criollo, Calabazon, and Caucasia from SVC; and Criollo, CCN-5,1 and ICS-39 from RN were used. Cocoa pod husks (about 77% of the total cocoa fruit) were first washed with deionized water and chopped to sizes about 5 cm for composting and to sizes about 10 mm, and oven-dried for 24 h at 60 °C for biochar preparation according to Kiggundu and Sittamukyoto (2019).

Preparation and characterization of compost

Composting was carried out in the facilities of a nursery of seedlings and cocoa beans and was protected from direct sunlight. The chopped CPH were stacked and arranged in 100 L plastic tanks, and the heap was covered with black polyethylene plastic for maintaining humidity. For aeration, small holes were made at equal distance on the sides and at the base of each tank. Periodically, molasse was added to adjust the moisture content of the composting materials between 60 and 65% by weight, its excess was regulated by completely turning the heap every two weeks or as required (Munongo et al. 2017). The monitored temperature of the heap ranged from 20-27 ℃. After 18 weeks (Echeverria 2018), compost was ready, sun-dried, and macerated. Macro and micronutrients in compost and biochar were measured following the Colombia technical standard NTC5167 (2011) for determination of Ca, Mg, K, Zn, Fe, Cu, Zn, Mn, and Na, by atomic absorption spectroscopy (AAS) with acid digestion (HCl: HNO_3) (3:1).

Preparation and characterization of biochar

Biochar was produced under limited oxygen and slow pyrolysis heating program in crucibles covered in a muffle furnace (Igalavithana et al. 2019). Pyrolysis temperature was reached at a heating rate of 10 °C min^{-1} (Tsai et al. 2018) and maintained for 2 h (Kim et al. 2017). Pyrolysis temperatures were 400 °C, 600 °C, 700 °C and 800 °C.

Moisture, ash content, pH, water holding capacity, and Electrical Conductivity (EC) with a ratio of 1:5 were determined as explained in Song and Guo (2011), and a ratio of 1:2 was used in compost and zeolite for pH and EC analysis. Secondary electron (SE) imaging of the morphology of biochar and energy dispersive X-ray spectroscopy (EDS) analysis were carried out, along with structural characterization of functional groups to determine changes in functional groups regarding temperature and composting using FTIR-ATR. Surface morphological comparison and porous structures were analyzed according to Tan and Yuan (2017). After characterization of porous structure, biochar produced at 600 °C and 700 °C were chosen for batch adsorption experiments. Posteriorly, based on batch experiments, the maximum sorption capacity was obtained with the biochar produced at 700 °C (Bc700), which also showed the highest decrease of Cd contents without a collapse of the porous structure. Therefore, Bc700 was selected for the soil incubation experiment.

Determination of total Cd contents

The determination of ‘total Cd in CPH was carried out in 5 samples of each cocoa variety used for composting and biochar making. Posteriorly, It was analyzed is there was any reduction in the Cd content by conversion of CPH to other material. Approximately 10 g of CPH was heated at a rate of 50 °C h^{-1} until it reached 450 °C for 2 h. After letting samples overnight, 1-3 mL of water was added, and each crucible was placed on a heating plate to allow evaporation. Then, the samples were placed back in a muffle furnace and heated. The samples were treated with 5 mL of 6 M HCl and 10-30 mL of 0.1M HNO_3, and evaporated until reached a volume of 5 mL and diluted to volume with deionized water. Biochar samples only required acid digestion.

Determination of 0.05M DTPA-extractable Cd contents

Cd availability analysis, using 0.05 M DTPA extraction solution (Ramtahal et al. 2015), was carried out to determine if either biochar or compost can influence the available Cd content in soils. The solution was prepared using 1.96 g of DTPA, 1.028 g of $CaCl_2$, and 14.92 g of TEA which were dissolved separately in deionized water and then combined according to Lindsay and Norvel (1978). The pH was adjusted to 7.3 using concentrated HCl and the volume was made up to 1 L with deionized water. Cd contents were quantified by atomic absorption spectroscopy with a graphite furnace (AAS-HG) in an Agilent FS240 equipment.

Quality control

To monitor and control the determination of Cd, the INM-061 and SPE001 ‘total’ Cd in soil and internal reference materials were used, with recovery rates ranging between 94% - 103% to CPH and soils from incubation experiment, respectively. Controls were analyzed with each batch of samples. Additional controls as internal samples were carried out. It was used replicated of the samples, method blanks, and spiked samples. All controls full fill Quality Criteria: Replicated samples with RPD < 10% and spiked samples with recovery percentage between 85-115%. To ensure that macro and micronutrients (Ca, Mg, K, Zn, Fe, Cu, Zn, Mn, and Na) in biochar were not a result of the difference in ash fractions, biochar was rinsed with deionized water, filtered, and dried for 24 h at 60 °C prior to nutrient analysis.

Determination of the maximum Cd adsorption capacities of biochar and compost

In order to investigate the possible applications of these materials for Cd remediation of water systems, the maximum Cd adsorption capacities and behavior of the material were analyzed at natural pH (Jordão et al. 2011), through batch experiments carried out by adding 5 mL of Cd solution to a 50 mL of electrolyte 0.01M $CaCl_2$ solution previously equilibrated at room temperature (23 °C) for 24 h. After applying 100 mg L^{-1} Cd, the solution was stirred for 4, 8, 24, and 48 h at variable weights of 2.5, 1.25, 0.5, and 0.25 g, until identifying the equilibrium time that was 4 h. Following OECD (2000) methodology, samples were subjected to mechanical agitation at 29 oscillations per min. The Cd solution was prepared from $Cd(NO_3)_25H_2O$ and added at contents of 0, 50, 100, 150, 200, 250, 300 mg L^{-1}. The Cd contents of 120 and 275 mg L^{-1} were used to strengthen the data. The different capacities of Cd sorption in equilibrium (q_m) expressed in mg/g and efficiencies in the removal of Cd in solution were determined following the methodology in Roy et al. (2002).

The maximum Cd adsorption capacity and affinity of the material for Cd adsorption were evaluated and mathematically modeled using ISOFIT (Matott and Rabideau 2008) for Langmuir (Langmuir 1918) Freundlich (Freundlich 1907) isotherms. The curve fitting was assessed using the Standard Error of the regression (SE) instead of the coefficient of determination R^2, more suitable to nonlinear methods (Yaneva et al. 2013) and ranked through the Corrected Akaike Information Criterion (AICc), (Davila-Jiménez et al. 2014). All experiments were conducted in triplicate.

Soil incubation experiment

A separate incubation experiment was carried out to determine the efficacy of biochar and compost in reducing the 0.05M DTPA-extractable Cd content in soils and when used along with zeolite. Thus, three materials used in the incubation experiment were biochar (Bc700), compost, and natural zeolite (type clinoptilolite and supplied as powder by ZEOCOL S.A.S was screened in grain sizes °C 0.145 mm before use). They were mixed at the rate of 0 to 6 % by weight, with a sandy clay loam soil created to get graded levels of Cd in soils as found in different cocoa plantations.

The properties of this soil were characterized according to Amacher (1996) and are listed in Table 1. Cd analysis was performed every week to monitor the Cd concentration of the soil compound sample of 2.07 ± 0.14 mg kg^{-1} 0.05M DTPA-extractable Cd. Water holding capacity was up to 60% (Park et al. 2011). The experiment was carried through a factorial arrangement: Bc700 (6%), Cp (6%), Z (6%), Bc700 (3%) + Cp (3%), Bc700 (3%) + Z (3%), Cp (3%) + Z (3%), Bc700 (2%) + Cp (2%) + Z (2%), Control. The experiment was carried out with 50 g of soil (Illera et al. 2004). To simulate real field application conditions intermittent periods of moisture and soil drying were maintained. Mixtures were placed in 50 mL plastic containers to avoid Cd adsorption on glass walls (King et al. 1974). During the incubation time of 2 months (Rajaie et al. 2006), samples were weighed periodically, adding deionized water after each drying. Plastic containers were covered with parafilm with a small perforation to maintain aeration (Brewer et al. 2011). As 0.05M DTPA-extractable Cd represents an available fraction of Cd to the plant and can be used to interpret the extent of remediation, the influence of the materials was determined by the decreasing 0.05 M DTPA-extractable Cd when compared to control samples. Total organic carbon (TOC) was measured according to Walkley and Black (1934).

Table 1 Physicochemical properties of soil

Compound soil	Sand %	Silt %	Clay %	OC^a %	pH^b	Exchangeable Cations (cmol $^{(+)}$ kg^{-1})				Available
						Ca	K	Mg	Na	Cd mg kg^{-1}
Sandy clay loam	58	22	20	2.48	6.57	14	0.3	0.8	0.2	2.07

Soil contamination Cd warning limit is higher than 1 mg kg^{-1} (Salmanzadeh 2017)

a Organic carbon

b 1:2 soil to deionized water ratio

Data analysis

Data were statistically analyzed using SPSS 23.0 software package (SPSS Inc.). Treatments and pyrolization effects were studied by t-test and one-way analysis of variance ANOVA with Tukey HSD test at probability (p) level of < 0.05 at 95% interval confidence. Pearson correlation analysis (r) was conducted among all data.

Results and discussion

Nutritive value and characteristics of compost

Cocoa pod compost has already shown high NPK (nitrogen, phosphorus, and potassium) contents with better outputs for fertilization than the usual NPK fertilizers (Adegunyole and Olotu 2018). The macronutrients and micronutrients contents analyzed confirm CPH–based compost capacities for organic fertilization (Table 2). As the composting conditions were similar, differences in nutrient values can be explained by differences in the cocoa varieties used. Compost from CPH has fertilization characteristics that make it suitable for application in tropical acidic soils (Campos et al. 2017), high nutrients content in CPH has been suggested as an alternative for the partial substitution of conventional fertilizers, especially K, Ca, and P, which CPH have important quantities (Gyedu-Akoto et al. 2015), that also contribute as an input of organic matter when returned to the soil. This study only described the macro and micronutrients found in the prepared CPH based compost and biochar, the effects of compost on the change of soil nutrients and assessments in a real field application, along with other characteristics that have been studied by Doungous et al. (2018) and Lu et al. (2018).

Table 2 Nutritive value (macro and micronutrient contents) of CPH based composts and biochars, Cd concentrations, the yield efficiency, and ash contents product of the pyrolysis process

Analysis / Variety	Bc600 (RN) (ICS-39)	Bc700 (SVC) (Caucacia)	Cp (RN) (Mix)	Cp (SVC) (Mix)
pH	11.16	10.21	9.13	9.76
EC (us/cm)	45200	58700	10110	13720
Cd (mg Kg^{-1})	0.36	0.56	0.98	7.86
CaO (%)	2.15	0.95	0.92	1.60
MgO (%)	0.60	0.99	0.59	0.83
K_2O (%)	18.17	14.13	6.03	7.87
Na (%)	0.04	0.03	0.02	0.02
Zn (mg Kg^{-1})	281.25	198.53	120.95	100.48
Fe (mg Kg^{-1})	100.19	0.00	379.17	530.03
Cu (mg Kg^{-1})	32.92	9.24	8.57	7.57
Yield efficency (%)	27.09	26.31	-	-
Biochar Ash (%)	24.9	35.71	-	-

Nutritive value and characteristics of biochar

Biochar did not show significant variations in the contents of metal ions (Ca, Zn, Cu, Na Fe, Mg, and Cu) when compared to these in compost, which can be an effect of removing the ash fraction before the macro and micronutrient analysis (Hale et al. 2020). Except for K, mainly because residualization and mineralization (Karim et al. 2017), this macronutrient showed an important increment in the char fraction of biochar-based CPH. Hence, biochar based CPH shows also a potential in returning nutrients to soil, which have been uptaken by the crop in significant quantities (Aikpokpodion 2010), particularly the K, which is mainly removed from the soil by the cocoa plant and accumulated in CPH (Fidelis and Rajashekhar 2017) and can be returned to the soil through the pyrolization process of CPH.

Regarding pyrolysis temperatures, changes in the morphology of structural pores arrangement but not in pore sizes were seen. Pore sizes ranged between 5 and 40 µm, which are capable of keeping water readily available to plants and improving nutrient retention in soil (Batista et al. 2018). Porous carbon-like structural arrangement (Fig. 1) is shown in few areas at 400 °C with relicts of the CPH primary structure, at 600 and 700 °C there are indications of the beginning of rupture in porous structures that reach their peak of structural collapse at 800 °C.

Assignment of spectral peaks obtained using ATR-FTIR (Fig. 2) was interpreted based on biochar charac-

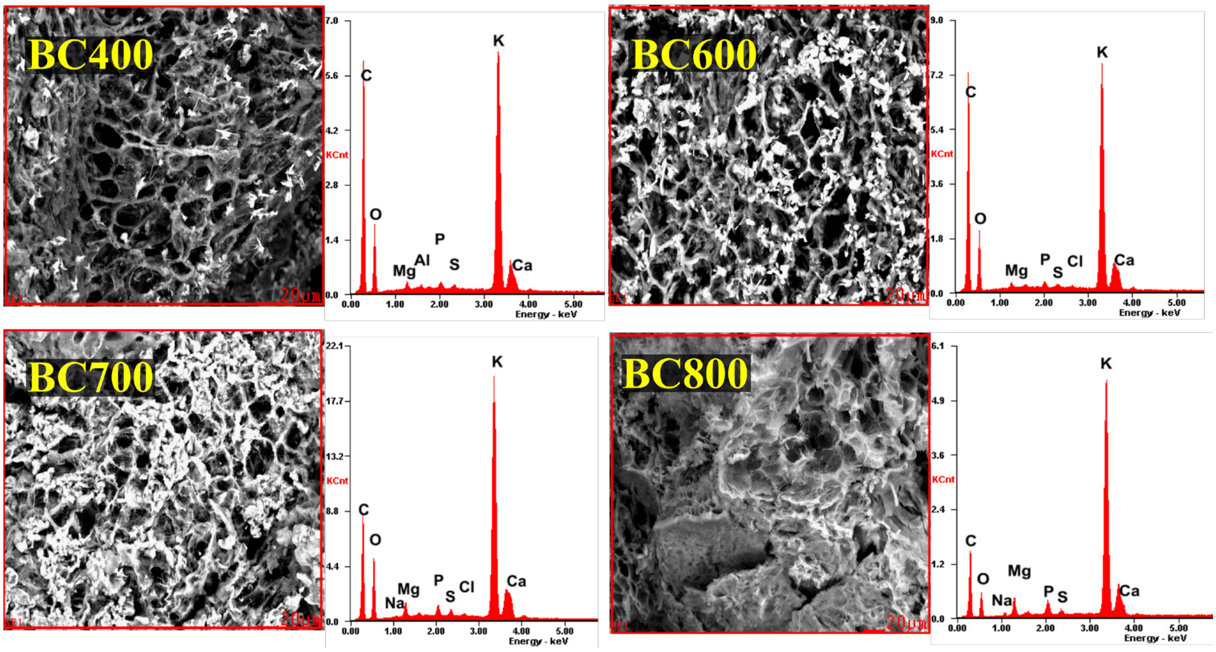

Fig. 1 Representative SEM photomicrographs with EDS analysis showing the morphology of biochar obtained at several temperatures of pyrolysis

Note: The slight differences in C contents are due to surface ash fractions.

teristic vibrations (Cantrell et al. 2012) detailed changes regarding temperature (Keiluweit et al. 2010), organic matter (Wen et al. 2007), and composting (Spaccini and Piccolo 2007). Changes in functional groups were evidenced by temperature variation. Hence, there were no significant changes in functional groups concerning CPH composting. As pyrolysis temperature increased, many functional groups disappeared to give formation to inorganic salts. Which may be explained by dehydration of cellulosic and lignose components that showed the most noticeable change in spectral area 4000 to 3000 cm^{-1} and 2000 to 100 cm^{-1}. Beginning of decomposition occurs at temperatures below 400 °C for cellulose and from 160 °C to lignin (Li et al. 2014), evidenced from 400 °C, temperature at which intensity decreasing has started and reaches a maximum at 800 °C, in which only peaks of low intensity attributed to some aromatic components and functional groups are observed.

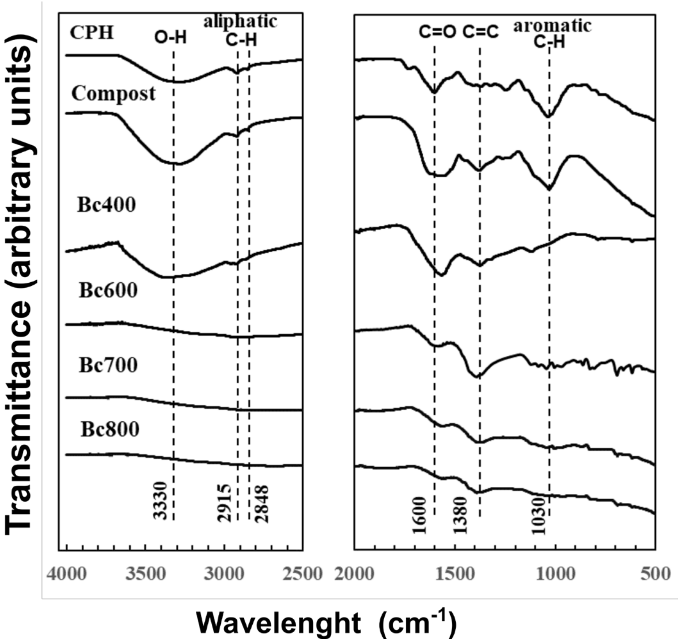

Fig. 2 Characterization of functional groups

Reducing of Cd contents in CPH through composting

The cocoa varities analysed are shown in Table 3. It can be inferred from the Table 2 and 3 that cocoa pod husks from SV with a starting Cd content mean of 23.48 (mg kg^{-1}) after composting ended in a compost material with Cd contents of 7.86 ± 0.15 (mg kg^{-1}), which despite was a sharp decrease in Cd contents, continued to be high for application back to the soil. Composting as predicted by Godlewska et al. (2017) and Wu et al. (2017), did not reduce to a safe level high total heavy metal contents in organic agricultural residues. It is suggested to explore other composting methods, such as the use of earthworms in composting process (Usmani et al. 2017).

Table 3 Cadmium contents in the cocoa varieties used for composting and biochar (n=5)

Cocoa variety	Cd (mg Kg^{-1})	SD
Criollo (SV)	31.99	6.71
Calabazon (SV)	18.78	4.13
Caucasia (SV)	19.67	3.77
Criollo (RN)	0.95	0.50
CCN-51 (RN)	0.34	0.10
ICS-39 (RN)	0.42	0.08

Reducing of Cd contents in CPH through pyrolisis

The conversion of CPH to biochar by pyrolisis significantly affected the Cd contents by volatilization as the main mechanism in reducing Cd contents in CPH biomass. The three CPH varieties from SV examined (Criollo, Calabazon, Caucasia) subjected to temperatures of 600 °C, 700 °C, and 800 °C showed significant Cd reduction contents ($p < 0.05$ Tukey's HSD test). As noted in (Fig. 3), this reduction was over 70% at 600 °C and over 90% at 700 and 800 °C. As Cd contents might be reduced in safe levels starting from 700 °C is suggested the choice temperature starts from 700 °C to preparation of biochar from CPH biomass contaminated with Cd or applied to other agricultural residues contaminated with Cd. Biochar produced at 700 °C prepared from SV of Caucasia variety and biochar at 600 °C from RN of ICS-39 variety were used to analyze the biochar remediation capabilities.

Application of CPH-based biochar and compost for the sorption of Cd °C

Effect of dose and removal time

Biochar and compost showed high adsorption no matter the dose added (Fig. 4a). Pearson correlation analysis

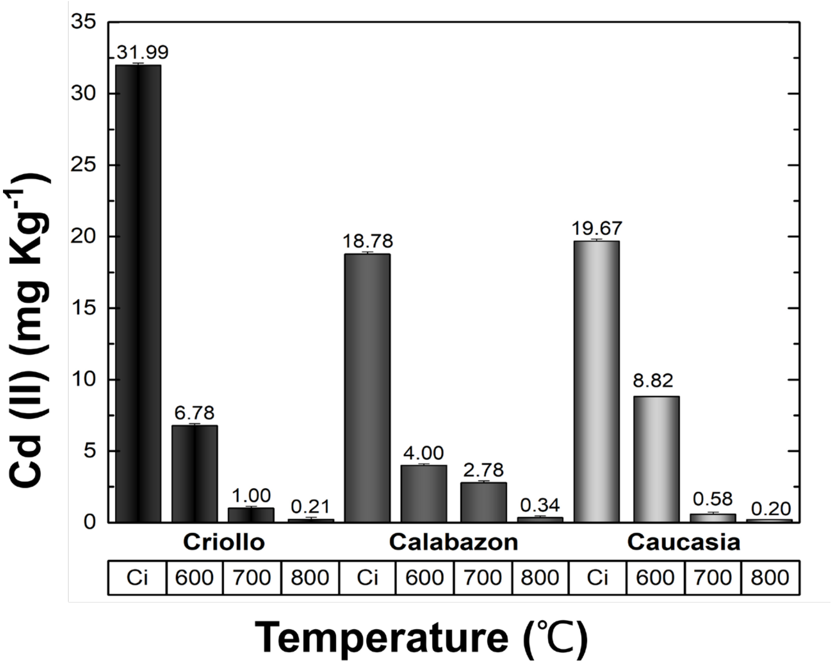

Fig. 3 Total Cd (II) decreases with increasing of pyrolysis temperature

Note: Cadmium contents in the three CPH varieties from (SV) subjected to increasing pyrolysis temperatures, starting from the initial concentration (Ci). Cd decreases are higher than 90% from 700 °C.

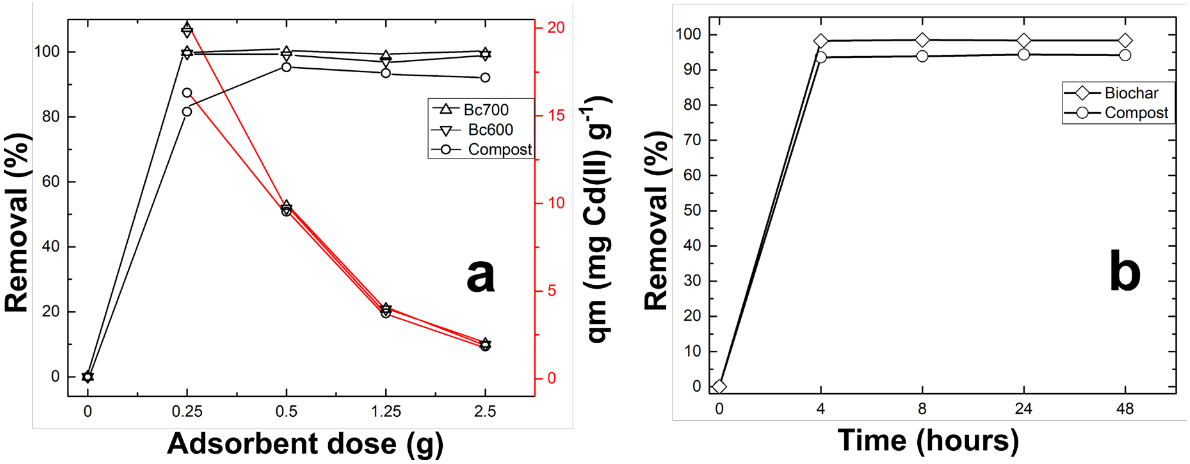

Fig. 4 **a)** Effect of adsorbent doses on Cd removal, red lines represent the amount of Cd adsorbed qm, **b)** Effect of time on Cd removal

revealed a significant negative linear trend correlation between the amount of Cd adsorbed (qe) and the adsorbent dose ($r = -0.584$, $p < 0.05$). Therefore, it might be concluded that increases of total surface area and sorption sites in those materials did not play an important role in their sorption capabilities, which were poorly affected even at a low adsorbent amount. The equilibrium time was less than 4 hours, during which biochar and compost reach removal yields above 90% with variations less than 5% (Fig. 4b).

Influence of the pH on Cd sorption

Statistical analysis showed that pH in adsorbents had a significant positive linear trend correlation ($r = 0.777$, $p < 0.01$) with the adsorption capacity, which is in inverse relation with the EC ($r = -0.693$, $p < 0.01$). Because Cd adsorbed on the surface of biochar and compost depended on their initial pH, which decreased as regards the concentration of the initial Cd (Fig. 5a), the pH was perhaps the most important parameter in the adsorption process of Cd. Thus, its influence on the adsorption of Cd on those materials was investigated. In this manner, pH solution was varied at 4, 7, and 9 using 0.1M HCl or 0.1M NaOH. Cd concentration was kept in 100 mg L^{-1} and doses of adsorbent were 0.25 g. The results confirm the influence of pH on adsorption process (Fig. 5b), where adsorption was ineffective at pH 4 because this acidic pH favored the liberation of cations adsorbed onto the surface of the adsorbent. The adsorption capacity was maximum at pH 9.

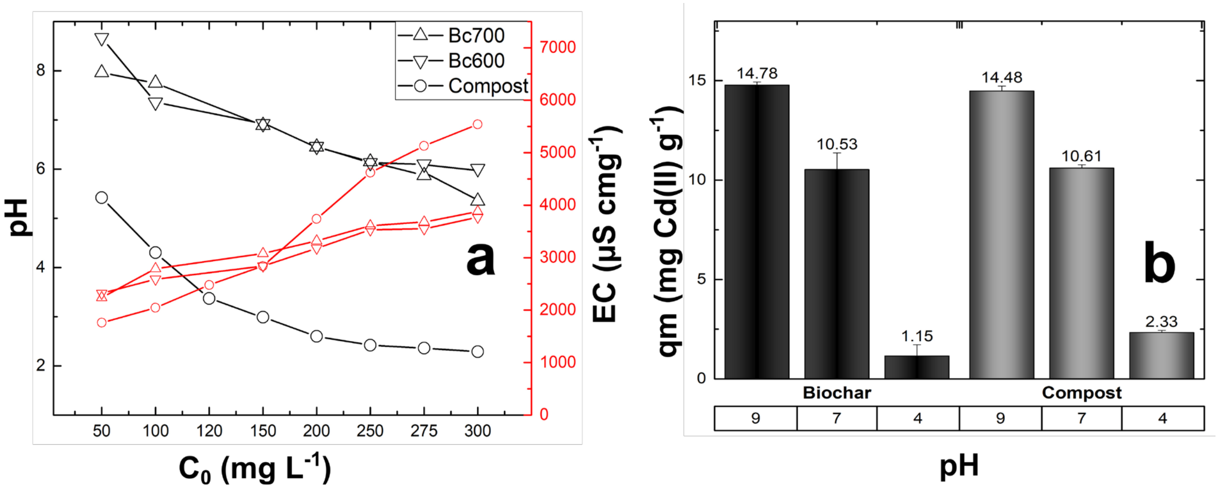

Fig. 5 **a)** Relation of pH and EC (red lines) with ^{o}C (initial concentration), **b)** Cd adsorption under pH variation

Sorption Isotherms and maximum capacities of adsorption

The AICc values show that Langmuir model fitted the equilibrium data only for biochar (Table 4). The parameter K_f related to sorption relative capacity was a sign of a higher affinity of Cd in the adsorbents. At pH < 6, the sorption process showed a break in which the initial pH of the material could not dampen the high amounts of Cd added, declining the adsorbed amount (q_m).

Table 4 Parameters of the Freundlich and Langmuir models in the sorption of Cd (II) at 23 °C

	Freundlich $q_e = K_f C^{1/n}$				Langmuir $q_e = q_m bc_e/1+bc_e$			
Material	**K_f ($mg^{1-1/n} g^{-1} L^{1/n}$)**	**n/1**	**SE**	**AICc**	**b ($L\ mg^{-1}$)**	**q_m ($mg\ g^{-1}$)**	**SE**	**AICc**
BC700	13.68	0.09	3.60	20.2	1.00	21.58	1.95	14.1
BC600	10.16	0.12	2.56	17.8	0.23	19.21	1.73	12.3
Compost	9.37	0.00	2.95	12.1	1.00	9.47	3.22	19.3

The results of the sorption isotherms on the adsorption of Cd on biochar and compost are shown in (Fig. 6a). The effect of pH was stronger in compost, with an initial pH of 7.5 could not efficiently dampen the increasing acidity of the solution. Although AICc ranking indicates that compost sorption process is better described by Freundlich model, which has been suggested by Chavez et al. (2016) and Pinto et al. (2016), the sorption isotherm diverges from the model (SE = 2.95) which is due to the influence of its comparatively lower initial pH that does not promote the binding of Cd ions onto the active surface of the heterogeneous groups in compost. Those ions are strongly dependent on the particle surface charge. Therefore, a pH above six has to be kept to enhance its capacities in the remediation of water highly contaminated with Cd.

Maximum sorption capacity values according to q_m parameter were 21.58 mg g^{-1} and 19.21 mg g^{-1} for Bc700 and Bc600, respectively. Hence, higher temperature pyrolysis improves the adsorption of Cd by biochar, as noted in Chen et al. (2018). These results are in accordance with those reported in the literature for other similar adsorbents such as 25.8 mg g^{-1} for biochars at 700 °C derived from water hyacinth invasive plant (Li et al. 2016), 18 mg g^{-1} for biochar derived from rice bran (Xu and Chen 2015), 40.8 mg g^{-1} for biochar at 600 °C derived from pine tree residues (Park et al. 2019), and 13.36 mg g^{-1} derived from buffalo weed (Roh et al. 2015). Thus, cocoa pod husk-based biochar is a promising alternative for Cd removal. Further studies might determine whether desorption could occur to avoid the risk for soil and further for the plant.

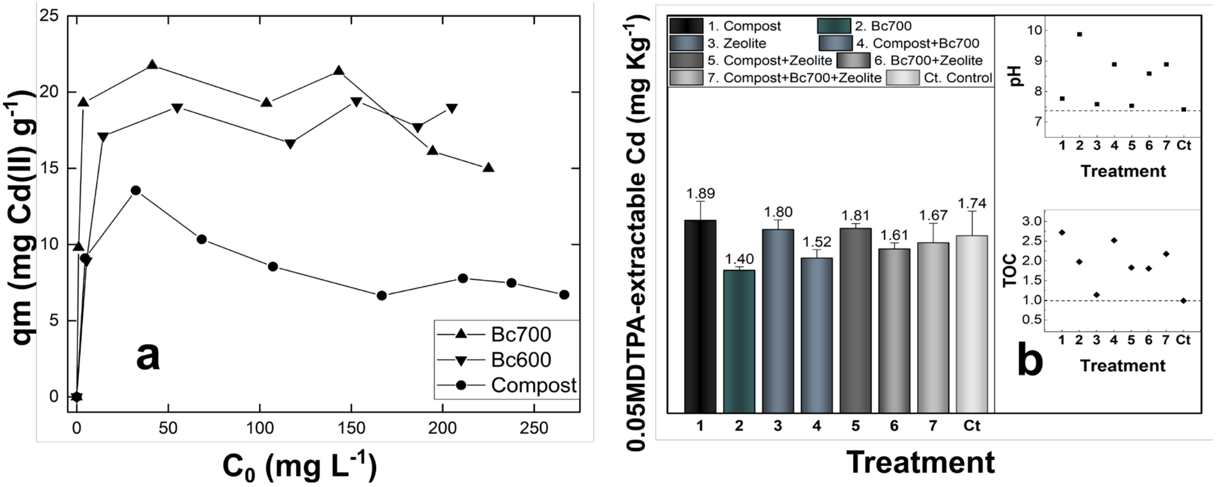

Fig. 6 a) Sorption isotherms on the adsorption of Cd in biochar and compost, **b)** Effect of the treatment in the Cd (II) 0.05 DTPA-extractable in soil, pH variations, and TOC percentage

Application of CPH-based biochar and compost for remediation of Cd contaminated soils

The 0.05 M DTPA-extractable Cd was used to interpret the extent of remediation. Concentrations of 0.05 M DTPA-extractable Cd from control soil during the incubation period of 2 months (Fig. 6b) were close to treatments values. Therefore no significant statistical difference was found. T-test values indicated that biochar and its mixtures had an effect on decreasing the 0.05M DTPA-extractable Cd. On the contrary, compost, zeolite, and their mixture were slightly higher than those in control soils. The ANOVA statistical analysis indicated that pH changed significantly ($p < 0.05$). Based on the Tukey HSD test, those changes are seen for biochar, biochar + zeolite, and biochar + compost + zeolite. Pearson correlation analysis supported those results; 0.05M DTPA-extractable Cd and pH showed a negative correlation ($r = -0.724$ $p < 0.001$). Hence, it is concluded that increases of pH in soil might be the main factor affecting the reduction of the 0.05M DTPA-extractable Cd. And even though the absorption capabilities were not affected by very low pH variable as noted in the aforementioned Cd sorption experiment in solution, the fact that neither compost nor zeolite had any sorptive effect on Cd present in the soil as far as the 0.05M DTPA-extractable Cd concerns, is due to compost and zeolite could not significantly increase the pH of soil. An alkaline pH promotes the reduction of leachable and interchangeable Cd fractions in contaminated soils (Li and Gao 2019) and the precipitation and complexation reactions (Van Poucke et al. 2018).

The long duration of the experiment may have also caused that Cd concentration changed to less mobile forms over time as shown by Mann and Ritchie (1994) and even more so the design of the experiment with periods of humidity and drying could have affected the concentration of the labile form of Cd and having decreased it as shown in Stafford et al. (2018) with a possibility that Cd availability could have also been influenced by short-term periods of soil saturation and subsequent drying. For future research strategies, it is advisable to use not only a single extraction but also multiple extractions to analyze the Cd behavior of each fraction in the soil after amendmentapplication and also to take into account the periods of moisture-drying as a variable. This might help to explain the variation in soil extractable Cd concentrations as observed in this study.

The amount of organic carbon and the pH have been pointed out as the main variables that regulate Cd immobilization with an inverse relationship between these variables and the content of bioavailable Cd (Muehe et al. 2013). Filipović et al. (2018) suggested that a high amount of organic matter contained in compost usually reduces the mobility of Cd by redistributing it to a fraction less available to the plant through the formation of stable complexes with humic substances present in it. However, the present study did not find any relationship since it was the pH that mainly regulated the Cd sorption process in the compost.

Lime has been proven effective in reducing bioavailable Cd (Yan-bing et al. 2017). To which a synergism between lime and compost and or biochar is suggested, since lime can help to regulate the pH, especially for compost, while both compost and biochar can provide essential nutrients and compensate for the deficit of such nutrients in the top layers of the soil. This can prevent cacao plant increases the activity of deep roots in deeper layers by searching for nutrients that are already available in the top layers. Indeed, Arguello et al. (2020) have pointed out that the aforementioned reason, together with a limited alkalinity penetration after surface application, makes the application of lime ineffective when subsurface soils are also a substantial source of Cd. A limitation that have most surface applications of amendments. Nevertheless, biochar with a high content of nutrients can help. Particularly, the effectiveness of the application of biochar in field experiments has already been verified by Ramtahal et al. (2019) with plantations of old cocoa trees, where the root system is quite developed and extended.

Biochar has a complex porous structure that can sequester Cd ions inside and improve crop nutrition in contaminated soils (Tandy et al. 2009). The high EC in biochar that increased with temperature indicates the enrichment of biochar in inorganic salts that can be combined with Cd and stabilize when ashes have not been removed (Stella Mary et al. 2016). According to Tan et al. (2017), biochar can fuse strongly with soil, which is promoted due to water action by moisture added to the soil. Cd is subjected to a series of physical and chemical adsorption in the soil, being fixed to biochar, blocking its mobility and achieving soil remediation. Furthermore, high contents of TOC in soil amendments with biochar or compost produced from CPH increase soil resilience. In turn, it can help reduce the carbon footprint of cocoa production in Colombia (Ortiz- Rodríguez et al. 2016).

Environmental implications

The Cd contamination found in cocoa cultivation systems is a reality that compromises the socio-economic development of more than 65.341 Colombia rural families (Colombian Ministry of Agriculture 2020) who mainly develop their activity with old plantations, traditionally exploited with low technology (Franzen and Borgerhoff-Mulder 2007). On the first of January 2019, a European regulation came into force that establishes new maximum permissible limits of cadmium (Cd) in cocoa beans and products derivates (European Commission 2014). Which represents a socio-economic problem for these families whose Cd pollution problem might worsen over time due to mishandling of the high amount of CPH residues dropped out on the crop after harvesting.

Therefore, the needed solution to change this pollution scenario must involve a range of economic, environmental, and social considerations, pillars for sustainable agriculture (Ramírez-Sulvarán et al. 2014). The solution presented in this study is using the CPH mishandled residue to produce biochar. It is effective in removing Cd in solution and can help to reduce Cd availability in soil. These, in turn, help manage organic crop residue preventing infection focus and insect proliferation, and it can be a source of organic fertilizer. In addition, the contribution of this work is to provide cocoa farmers an improvement in the management of the crop through its understanding, opening possibilities for commercialization of their products in international markets, as well as national markets, also decreasing the use and expenditure on chemical fertilizers and promoting the sustainability of cocoa plantations.

Conclusion

Biochar produced under optimal pyrolysis temperature of 700 °C was able to decrease total Cd contents in CPH residues to safe levels. Also, biochar influenced the reduction of 0.05M DTPA-extractable Cd in soils. Composting on the other hand could not significantly reduce the Cd content for agricultural applications, and compost Cd adsorption capacity was highly influenced by the pH, to which it is suggested to explore other composting options and increases of pH in the case of high Cd contents in CPH waste.

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Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

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