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RESEARCH ARTICLE

Ameliorative effects of *Daniellia*- and *Vitellaria*-derived biochars on the chemistry of oil-contaminated soils and germination indices of cowpea

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Abstract: The study assessed the effectiveness of biochars derived from *Daniellia oliveri* and *Vitellaria paradoxa* in ameliorating waste lubricant oil contaminated soils and improving germination of cowpea seeds. *Daniellia oliveri* and *Vitellaria paradoxa* biochars were applied at 0.5 and 1.0 % levels to soils contaminated with 2 % v/w waste lubricant oil (WLO). The unpolluted soil and WLO-contaminated soil without biochar were also used as controls. All treatments in three replicates were arranged in a randomized block design in a screen house. Biochars and soils were analyzed for pH, organic carbon (OC), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) and total petroleum hydrocarbon (TPH exclusively analyzed for soil). Ten cowpea seeds sown in soils were observed for sprouting from 1 to 10 days after sowing (DAS). Germination percentage and indices were determined from the number of sprouted seeds at 10 DAS. *Vitellaria*-derived biochar (BV) had higher N, K and Mg than *Daniellia*-derived biochar (BD). WLO contamination significantly reduced soil P but slightly affected pH, OC and exchangeable cations. Addition of BD and BV reduced TPH and improved soil quality. Oil contamination delayed and reduced cowpea germination by 9.3 % in un-amended WLO-contaminated soil. 1 % BV addition was effective in improving germination velocity and indices of cowpea seeds in oil-contaminated soils.

Keywords: Biochar, cowpea, germination, soil improvement, waste lubricant oil.

INTRODUCTION

Soil pollution from petroleum derivatives, previously considered a problem of petroleum producing or processing countries, is fast becoming a global problem posing a starting challenge to non-petroleum producing countries as well (Odjegba and Sadiq, 2002). The surge in the number of automobiles has consequently increased the demand for automobile repairers (mechanics) who ignorantly dispose waste lubricant oils, after servicing engines, in gutters, water drains, open plots and farms (Lale *et al*., 2014). Oil contamination affects the biological, physical, chemical components of the soil in various ways (Atuanya, 1987; Odjegba and Sadiq, 2002; Agbogidi and Ejemeta, 2005: Agbogidi, 2010), and its effects on the growth, development, productivity and yield of plants cannot be undermined. Apart from the introduction of trace metals such as lead, nickel, zinc and barium, chemical additives such as amines, phenols, sulphur associated with waste lubricant oils (Lale *et al*., 2014) also contribute to impede growth and development of plants. Oil in soil creates anaerobic condition by impeding moisture content (Shukry *et al*., 2013), excluding air and increasing the production of hydrogen sulphide (Udo and Oputa, 1984) which ultimately induces considerable retardation in germination and plant growth (Adam and Duncan, 2002). Several authors have reported a lower rate of germination in soil contaminated by petroleum or its derivatives (Amakiri and Onofeghara, 1984; Adam and Duncan, 1999; Vavrek and Campbell, 2002; Méndez-Natera *et al*., 2004; Achuba, 2006; Smith *et al*., 2006; Sharifi *et al*., 2007; Korade and Fulekar, 2009; Bona *et al*., 2011; Udom *et al*., 2012). Apart from seed germination impairment, reductions in yield and premature death of crops have also been reported in soils contaminated with waste lubricant oil (Udom *et al*., 2012). Since soil health is the foundation of a vigorous and sustainable food system, corrective measures are needed to alleviate the effects of contamination while improving crop production.

Various techniques, including the use of plants and/or associated microorganisms, have been studied to be efficient in ameliorating polluted soils through removal, inhibition or decontamination of harmful materials (Cunningham and Ow, 1996; Schwab and Banks, 1999; Merkl *et al*., 2005). Recent focus on biochar, a stable carbon-rich charred biomass and its utilization as a soil amendment (Qayyum *et al*., 2014) have proved highly effective due to its sorption ability for organic pollutants (Zhang *et al*., 2010) and heavy metals (Beesley *et al*., 2010).

Biochar has been produced from numerous biological residues ranging from wood to manures and feedstocks to plant materials (Beesley *et al*., 2011). Although the use of charcoal (wood biochar) is common, biochar production using organic wastes or feedstocks such as wood waste, crop residues (including straw, nut shells, and rice hulls), switch grass, bagasse from the sugarcane industry, chicken litter, dairy manure, sewage sludge and paper sludge is relatively new. More recently biochar obtained derived

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from wheat residue (Yu *et al*., 2006), eucalyptus (Yu *et al*., 2009), *Gossypium* (Yang *et al*., 2010) and orchard prune residue (Fellet *et al*., 2011) have been tested as amendment on contaminated soils. Typically, biochars have high cation exchange capacity and with potential benefits in increasing soil biological activity (Lehmann *et al*., 2011; Paz-Ferreiro *et al*., 2014), diminishing soil greenhouse gas emissions from agricultural sources and thus enhancing soil carbon sequestration due to its elevated content of recalcitrant forms of carbon (Gascó *et al*., 2012). Biochar production through pyrolysis does not only offer a way of reducing air pollution from open burning of crop biomass, but also a favorable agriculture sustainable model for reutilizing agricultural waste (Wang *et al*., 2013). This residue conversion approach will be particularly useful in vegetation types, such as savannas, where most of the tree species are deciduous.

The present study assessed the effectiveness of biochars derived from *Daniellia oliveri* and *Vitellaria paradoxa* in ameliorating waste lubricant oil contaminated soils and improving germination of cowpea seeds. This is with the aim of sustainably utilizing the huge wastes of litters from these tree species, growing abundantly in savanna-type (Guinea, Sudan and Sahel) vegetation in Nigeria, in crop production, most especially cowpea which account for major protein in the diet of average Nigerians.

MATERIALS AND METHODS

Biochar was produced separately from leaf litters of *Daniellia oliveri* and *Vitellaria paradoxa* using a muffle furnace (Gallenkamp model) maintained at 450 °C. Chemical properties including pH, total organic carbon, total nitrogen, available phosphorus and exchangeable cations (K, Ca and Mg) of the biochars were determined using standard procedures. Biochar pH was determined in 1:2.5 w/v of biochar powder to 0.02M $CaCl_2$ solution. Organic carbon was determined using wet digestion method as outlined by Walkley and Black (1934). Total nitrogen was determined using macro Kjeldahl method of digestion, distillation and back titration (Bremner, 1996). Available P was determined using colorimetric method as outlined by Olsen and Sommers (1982). Potassium, calcium and magnesium concentrations were determined using filtrate of mixed acid ($HClO_4$-HNO_3) (Faridullah *et al*., 2014) digests read at 766.5 nm, 422.7 nm and 285.2 nm with atomic absorption spectrophotometer (Buck Scientific Model - 210VGP).

Soil was collected from 0 to 15 cm soil depth from an un-disturbed area in the Botanical Garden, University of Ilorin, Nigeria. Soils in the area are predominantly lateritic with loamy sand texture classified as Afisols based on USDA Soil Taxonomy (Oyedeji *et al*., 2017). Soil was air dried at room temperature (25 °C) for 2 weeks, sieved through < 2 mm and any debris was removed. Soil was then homogenized and 5 kg weighed separately into 18 polyethylene bags which represented five treatments and the control replicated three times. Waste lubricant oil (WLO) and biochars from *Daniellia oliveria* (BD) or *Vitellaria paradoxa* (BV) were then incorporated into the treatments; Control (T_0): 5 kg soil; T_1: 5 kg soil + 2% v/w WLO contamination; T_2: 5 kg soil + 2% v/w WLO contamination + 0.5% w/w BD; T_3: 5 kg soil + 2% v/w WLO contamination + 1.0% w/w BD; T_4: 5 kg soil + 2% v/w WLO contamination + 0.5% w/w BV and T_5: 5 kg soil + 2% v/w WLO contamination + 1.0% w/w BV.

The experimental set-up in the screen house was set in a randomized complete block design and watered to field capacity for two weeks. Samples of soil were collected from each polyethylene bag, air dried to constant weight and analyzed for pH, total petroleum hydrocarbon, organic carbon, total nitrogen, available phosphorus, and exchangeable K, Ca and Mg. Soil pH, organic carbon, total nitrogen and available phosphorus were determined using the procedure described for biochar. Total petroleum hydrocarbon was determined by gravimetric method as described by Villalobos *et al*. (2008). Exchangeable K, Ca and Mg were extracted using 1M ammonium acetate buffered to pH 7.0. Concentrations of K and Ca were determined using flame photometer (Jenway PFP7 model) while Mg was determined using atomic absorption spectrophotometer (Jenway 6305 model).

Ten cowpea seeds obtained from National Centre for Genetic Resources and Biotechnology (NACGRAB), Ibadan were sown to 2 cm depth into soil treatments in the polyethylene bags. Germination (%) records were taken at commencement of germination for up to 10 days after sowing and seeds which failed to sprout after that time were considered dead. Final germination percentage (FGP), mean germination time (MGT), germination index (GI), coefficient of velocity of germination (CVG), germination rate index (GRI), first day of germination (FDG), last day of germination (LDG) and time spread of germination (TSG) were determined using the formulae outlined by Kader (2005) and mean germination rate (MR) was according to the formula by Ranal *et al*. (2009).

$$FGP\ (\%) = \frac{Total\ of\ seeds\ germinated\ in\ a\ seed\ lot}{Total\ No.of\ seeds\ sown} \times 100 \quad (1)$$

$$MGT\ (day) = \frac{\sum nt}{\sum n} \quad (2)$$

Where n is the number of seed(s) that germinated on day t.

$$MR\ (day^{-1}) = \frac{1}{MGT} \quad (3)$$

$$GI = (10 \times n_1) + (9 \times n_2) + \cdots + (1 \times n_{10}) \quad (4)$$

$$CVG = \frac{100(n_1 + n_2 + \cdots + n_x)}{(n_1 t_1 + n_2 t_2 + \cdots + n_x t_x)} \quad (5)$$

Where n is number of seeds germinated each day, t is number of days from seeding corresponding to n.

$$GRI\ (\%day^{-1}) = \frac{G_1}{1} + \frac{G_2}{2} + \cdots + \frac{G_x}{x} \quad (6)$$

Where G_1, G_2 and G_x are germination percentages at day 1, 2 and x respectively.

$$FDG\ (day) = Day\ on\ which\ the\ first\ germination\ event\ occurred \text{ in a seed lot} \quad (7)$$

$$LDG\ (day) = Day\ on\ which\ the\ last\ germination\ event\ occurred \text{in a seed lot} \quad (8)$$

$$FDG\ (day) = time\ (days)\ between\ the\ first\ and\ last\ germination\ events \quad (9)$$

Data obtained were subjected to one way proc ANOVA in SAS 9.1.3 Software. Significantly different means were separated using Fisher's LSD at 0.05 α level.

Table 1: Chemical properties of biochars from *Daniellia oliveri* and *Vitellaria paradoxa.*

Biochar	pH	OC	TN	P	K	Ca	Mg
		(%)			(mg kg^{-1})		
BD	8.60^{a}	16.91^{a}	0.43^{b}	53.54^{a}	128.45^{b}	14.80^{a}	15.2^{b}
BV	8.49^{a}	16.51^{a}	1.55^{a}	33.01^{a}	283.45^{a}	11.5^{b}	55.0^{a}
$LSD_{0.05}$	0.44	3.91	0.29	23.92	37.18	28.00	13.37

$LSD_{0.05}$ is least significant difference at α=0.05 and means with the same superscripted letter in a column are not significant; BD is *Daniellia oliveri* biochar and BV is *Vitellaria paradoxa* biochar.

Table 2: Chemical properties of control, oil-contaminated and biochar-amended soils.

Treatment	pH	TPH	OC	TN	P	K	Ca	Mg
			(%)				(mg kg^{-1})	
T_0	5.31^{c}	0.00^{e}	15.58^{b}	0.47^{c}	16.57^{a}	0.32^{d}	0.29^{b}	0.18^{d}
T_1	5.30^{c}	0.93^{a}	15.48^{b}	0.73^{b}	12.07^{c}	0.28^{d}	0.25^{b}	0.16^{d}
T_2	5.71^{b}	0.55^{b}	16.41^{a}	0.96^{a}	14.11^{b}	5.15^{c}	0.91^{a}	0.46^{c}
T_3	6.07^{a}	0.26^{d}	16.63^{a}	0.93^{ab}	16.25^{a}	5.64^{c}	1.07^{a}	1.51^{b}
T_4	5.43^{c}	0.40^{c}	16.38^{a}	1.13^{a}	12.17^{c}	6.59^{b}	0.79^{a}	1.48^{b}
T_5	5.84^{ab}	0.10^{e}	16.59^{a}	0.96^{b}	12.89^{bc}	8.36^{a}	1.00^{a}	1.60^{a}
$LSD_{0.05}$	0.25	0.12	0.31	0.20	1.44	0.58	0.32	0.07

$LSD_{0.05}$ is least significant difference at α=0.05 and means with the same superscripted letter in a column are not significant.

Table 3: Germination indices for cowpea sown in uncontaminated and WLO-contaminated soils amended with different biochars.

Treatment	FGP	MGT	MR	GI	CVG	GRI	FDG	LDG	TSG
	(%)	(day)	(day^{-1})			(%day^{-1})	(day)	(day)	(day)
T_0	100.0^{a}	4.07^{d}	0.25^{a}	34.67^{a}	24.60^{a}	24.67^{a}	4.00^{b}	4.33^{b}	1.33^{c}
T_1	90.7^{b}	6.05^{a}	0.17^{d}	24.33^{c}	16.56^{d}	14.71^{d}	5.00^{a}	7.67^{a}	3.67^{ab}
T_2	97.6^{ab}	5.02^{b}	0.20^{c}	28.00^{b}	19.96^{c}	18.99^{c}	4.33^{b}	6.00^{b}	2.67^{ab}
T_3	100.0^{a}	4.67^{bc}	0.22^{bc}	31.67^{ab}	21.49^{bc}	21.78^{abc}	4.00^{b}	5.33^{bc}	2.33^{bc}
T_4	100.0^{a}	4.80^{bc}	0.21^{bc}	31.00^{ab}	20.93^{bc}	21.11^{bc}	4.33^{b}	5.33^{bc}	2.00^{bc}
T_5	100.0^{a}	4.40^{cd}	0.23^{ab}	33.00^{a}	22.76^{ab}	23.11^{ab}	4.00^{b}	5.33^{bc}	2.33^{bc}
$LSD_{0.05}$	7.37	0.50	0.02	3.91	2.07	3.15	0.59	1.19	1.19

$LSD_{0.05}$ is least significant difference at α=0.05 and means with the same superscripted letter in a column are not significant. FGP values were arcsine transformed before statistical analysis and retransformed to percentage.

RESULTS

The chemical properties of biochars from *Daniellia oliveri* (BD) and *Vitellaria paradoxa* (BV) are presented in Table 1. BV had significantly higher ($P < 0.05$) total nitrogen, potassium and magnesium than BD. BD had higher calcium while pH, organic carbon, phosphorus concentrations in the biochars was not significantly different. The chemical properties of the native soil, WLO-contaminated and biochar-amended soils are presented in Table 2. Soil pH was significantly low in T_0 (Control), T_1 and T_4. T_3 had the significantly highest ($P < 0.05$) pH and followed by T_5. Biochar amended soils (T_2 to T_5) had significantly higher OC, TN, K, Ca, Mg but lower TPH compared with T_1. T_1 had the least concentration of P but significantly higher N than T_0. BD significantly improved pH, OC and exchangeable Ca concentrations. BV significantly reduced TPH concentration in the soil but improved exchangeable Ca and Mg.

Germination characteristics of the cowpea seeds in the control, WLO-contaminated and biochar-amended soils are presented in Table 3. Final germination percentage (FGP) significantly varied and reached 100% in the control

and treatments, except T_1 and T_2. Mean germination time (MGT) was significantly highest in T_1 (6.05 days) and least in T_0 (4.07 days). Mean germination rate or germination speed (MT) was fastest in T_0 (0.25 day^{-1}) and slowest in T_1 (0.17 day^{-1}). The germination index (GI) and coefficient of velocity of germination (CVG) were highest in T_0 (34.67 and 24.60) while T_1 had the least GI and CVG (24.33 and 16.56). Germination rate index (GRI) was also highest in T_0 (24.67 % day^{-1}) and lowest in T_1 (14.71 % day^{-1}). The first, last day, and time spread of germination (FDG, LDG and TSG) also varied significantly ($P < 0.05$). Seeds in T_0, T_3 and T_5 started germination earliest (i.e. on the 4th day). Seeds in T_1 had the longest period of germination (7.67 days). TSG was shortest in T_0 (1.33 day) and longest in T_1 (3.67 day).

DISCUSSION

The variation in the chemical properties of *Daniellia*-derived and *Vitellaria*-derived biochars was in line with earlier report by Jindo *et al*. (2014) that the nature or type of feedstock strongly influences the physicochemical properties of biochars. pH of *Daniellia*-derived and *Vitellaria*-derived biochars in this study exceeded the pH (8.32) reported by Gulyas *et al*. (2014) for wood chip (WC) but fall within the range of 7 - 9 reported by Beesley *et al*. (2011). Hunt *et al*. (2010) also asserted that the initially high (alkaline) pH of biochar is desirable when used with acidic, degraded soils. Also, the percentage carbon of biochars from the two species was higher than 9.9 % reported by Gulyas *et al*. (2014) for animal bone biochar (ABC). The result of total nitrogen concentrations in the two biochars were similar to that of wood chip and animal bone biochars reported by Gulyas *et al*. (2014), but phosphate and exchangeable cations concentrations in this study varied considerably.

The higher pH in the biochar-amended soils in this study confirms earlier report by Beesley *et al*. (2011) that addition of biochar, which typically have a pH of 7-9, to acidic soils will result in an increase in the soil pH. The significant reduction in TPH concentration in the biochar-amended soils confirms earlier report by Beesley *et al*. (2010) and Gomez-Eyles *et al*. (2011) that biochar amendment in soil reduces petroleum hydrocarbons contamination. In addition to pH modification, Beesley *et al*. (2011) also affirm the potential of biochar to increase soil OC and exchangeable cations. According to Granatstein *et al*. (2009), biochar represents a stable form of carbon in the soil and thus provides an intriguing potential carbon storage strategy.

The high N content in the waste lubricant oil-contaminated soils in relation to the control could be linked to input from the oil. Posthuma (1970) asserted that petroleum contains nitrogen and oxygen in low concentrations as well as metals such as lead, nickel, sodium, calcium, copper and uranium. Apart from direct nitrogen addition from the biochars, improvement in soil N in the amended soils could be linked to increased activity of beneficial microorganisms due concomitant nutrient and water retention created by the large surface area and porosity of biochars (Hunt *et al*., 2010). Low phosphate in WLO-contaminated soils is due to presence of hydrocarbons as affirmed by Amadi *et al*. (1996). Higher P levels in the soils amended with *Daniellia*-derived biochar is related to P content in the biochar. Cao and Harris (2010) found that biochar is rich in P, and unlike C and N, an increase in the production temperature increase P likewise Mg and Ca. High exchangeable cations in the biochar-amended soils is characteristic of the biochars from the two sources in this study. The result is consistent with Biederman and Harpole (2013) report that biochar addition to soils may increase concentrations of exchangeable cations, depending on the intrinsic properties of the soil and the biochar. Nwite (2013) also reported improvement in K, Ca and cation exchange capacity in oil-contaminated soils amended with charred rice husk. Generally, chemical properties of the biochar-amended soils varied with concentration and source material of the biochar.

The reduction in the final germination percentage (FGP) of cowpea seeds in the unamended WLO-contaminated treatment corroborates the findings of Lale *et al*. (2014), who observed slow and low germinability of cowpea seeds in the soil contaminated with 2% waste engine oil. Udo and Fayemi (1975) concluded oil-pollution affect seed germination as seeds absorb oil in the soil and get destroyed. The high mean germination time (MGT) and low mean germination rate (MT) for seeds in the WLO-contaminated treatment indicate the inhibitory effect of oil on germination. The results of FDG and LDG in the control and the biochar-amended soils fall within the range (4 to 5 days) reported by Akinyosoye (1976) and Gbadebo and Adenuga (2012). The extended germination period of 5 to 7 days observed in the unamended WLO treatment also coincides with 6-8 days interval observed by Gbadebo and Adenuga (2012) for cowpea seedling emergence in the highest oil treatment. According to Adam and Duncan (2002), volatile components of light hydrocarbons in oil capable of penetrating plant cell wall can be phytotoxic thus delaying or decreasing seed germination. These effects of delayed and decreased germination accounted for the variation in germination indices including germination index (GI), germination rate index (GRI) and coefficient of velocity of germination (CVG) in this study. The closeness of seed germination results in the control (T_1) and T_5 (oil contaminated soil amended with 1% *Vitellaria*-derived biochar) showed the biochar application is effective in ameliorating the effects of waste lubricant oil contamination.

CONCLUSION

The present study showed that waste lubricant oil significantly increased soil N but decreased available P. Incorporation of *Daniellia*- and *Vitellaria*-derived biochars to the waste lubricant oil contaminated-soils significantly improved the soil pH, OC and exchangeable cations, which ultimately facilitated the germination of cowpea seeds compared to the un-amended WLO-contaminated soils. *Vitellaria*-derived biochar at (higher concentration) showed greater potential in ameliorating the effects of oil contamination and enhancing germination of cowpea seeds than *Daniellia*-derived biochar.

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