Volume 10, Issue 2, 2020, 5224 - 5228 ISSN 2069-5837
Biointerface Research in Applied Chemistry
www.BiointerfaceResearch.com
https://doi.org/10.33263/BRIAC102.224228
Original Research Article **Open Access Journal**
Received: 26.12.2019 / Revised: 01.02.2020 / Accepted: 02.02.2020 / Published on-line: 04.02.2020

Irreversible sorption of carbofuran by moderately acidic soil amended with biochar

Vijetha Ponnam [1,*], Ramesh Naidu Mandapati [1], Satyavathi Bankupalli [2]
[1]Department of chemical engineering, Vignan's Foundation for Science, Technology and Research, Andhra Pradesh, India
[2]Process Engineering & Technology Transfer Department, CSIR -Indian Institute of Chemical Technology, Hyderabad, Telangana 500 007, India.
*corresponding author e-mail address: ***vijetha.ponnam@gmail.com*** | Scopus ID 37462235200

ABSTRACT
An ecofriendly technique to on farm burning of biomass by making biochar from agricultural waste was provided. Characteristic studies of biomass and biochar such as SEM, Ultimate and proximate analysis, pH, Cation exchange capacity, Water holding capacity, Electrical conductivity, Soil organic matter and Dry matter production were examined. Adsorption and desorption of carbofuran in soil were studied in batch experiment mode. From the experimental studies, it was observed that pH, Cation exchange capacity, Water holding capacity, Electrical Conductivity, Soil organic content and dry matter production increases with biochar addition. Adsorption Studies show that carbofuran adsorbed with control is 0.45 mg/g whereas with 3%BC it was 6.375 mg/g and desorption studies show that with 3% biochar carbofuran desorption is less. Hence Capsicum Annuam Biochar could be one of the promising option for improving the soil health as well as for adsorbing the pesticides.
Keywords: *Carbofuran; Capsicum Annuam; Adsorption; amendment; Cation exchange capacity.*

1. INTRODUCTION

Carbofuran is a broad-spectrum insecticide mostly used in Andhrapradesh for controlling the pests. Carbofuran efficiency depends on its properties and terms and its ability to attain the target in reasonable time. Pesticides because of their toxicity have gained profound importance . Application of carbofuran in the fields results in its surface water runoff whose levels were observed to be 1.9 % of the total application. The maximum carbofuran in drinking water as given by the U.S environmental protection agency was 40mg mL^{-1}. Adsorption is one of the best solution for adsorption of the carbofuran [1,2]. The studies carried over related to this concept was proved by Bailey and White, Cheng and Wauchope et al. [3]. Some experimental studies were carried out to test the adsorption of carbofuran on to soils, clays, flyash and synthetic inorganic ion exchangers [4,5]. Recent studies reported the role of organic co solvents on the adsorption of carbofuran in soils.

Properties of the soil like organic matter content, composition, pH etc., influence the adsorption of pesticides in the soil.[6,7] So both soil conditions and climatic conditions effect the movement of carbofuran in the soil. On-point groundwater pollution is a major concern in many countries[]8,9]. The growth in agricultural productivity over the past decade has been closely linked to the use of agrochemicals such as fertilizers and pesticides. Excessive fertilizer and chemical levels added to plants have often led to soil and surface water pollution [10,11].

Capsicum Annuam (CA) is widely grown in India with an annual production of about 1.2 million tons, contributing to about 27.24 percent of the total spice cultivation area and 25.65 percent of total spice production in India [12]. According to the Ministry of New and Renewable Energy (MNRE), India produces 500 MT of plant debris each year. The peasants are burning the unused on the field. Upon planting, the farmers burn the discarded CA stem on the farm as a low cost disposal method to minimize the turnaround time for the second crop between harvesting and sowing, resulting in pollution caused by the release of greenhouse gasses as reported by the Indian Agricultural Research Institute on crop residue management [13]. The present study therefore explores biochar production from Capsicum Annuam and its applicability as an adsorbent for a sustainable management option. The desirable properties required to be good adsorbent for Capsicum Annuam biochar (CABC) is its high capacity to absorb pollutants. CABC's applicability for carbofuran removal and soil health improvement has been tested in this study.

2. MATERIALS AND METHODS

2.1. Preparation of samples.

The soil sample used in our study was collected from the surface layer of vadlamudi region at VFSTR (deemed to be university) campus. The soil sample was air dried in an oven, crushed and sieved through 2mm sieve and thoroughly mixed. Analytical grade carbofuran, purity of 98%, a white crystalline solid was purchased from Sigma Aldrich, India. All other chemicals for this study were procured from National Scientific Products, Guntur. Double distilled water was used for preparing all the solutions.

2.2. Preparation of Biochar from Capsicum Annuam.

CA was collected from the nearby fields in the Guntur region of Andhra Pradesh. This biomass was sun dried, crushed into small pieces and kept in the oven for removal of residual moisture. The dried biomass was loaded and sealed in an earthen pot to carry out the pyrolysis in muffle furnace under depleted oxygen environment. Pyrolysis was performed at low temperature

(300 $°C$) for 120 min. The pyrolysed biomass i.e., CABC was crushed, grinded and sieved to the desired sizes and packed in airtight covers for soil amendment experiments. Double distilled water was used for preparing all the solutions and all other chemicals used in this study are procured from National scientific products, Guntur.

2.3. Nomenclature:

CEC : Cation exchange capacity
WHC : Water holding capacity
EC : Electrical Conductivity
SOC : Soil Organic matter
DMP : Dry matter Production
CA : Capsicum Annuam
CABC : Capsicum Annuam Biochar

Table 1. Details of soil samples.

S.No	Sample	
1	Control	Pure Soil Sample
2	1%BC	1/100 w/w ratio of biochar to soil
3	3%BC	3/100 w/w ratio of biochar to soil
4	1%BC-NPK	1/100 w/w ratio of biochar to soil+ NPK
5	3%BC-NPK	1/100 w/w ratio of biochar to soil+NPK

2.4. Characterization Of CABC.

CA and CABC were analyzed for its physico-chemical properties such as elemental analysis using Elementar Vario Micro cube–CHNS elemental analyzer; morphology using a scanning electron microscopy (HITACHI S-3000 N made in Germany); specific surface area BET (Brunauer, Emmett and Teller)N2 adsorption method using surface area analyzer (Smart Sorb 92/93).

Figure. 1. Pot trial experiments.

2.5. Pot Trails.

Capsicum Annuam plant was used as the test plant for the present study. Seedlings of 10 cm height of CA plants were collected from the nearby plant nursery of VFSTR campus, Vadlamudi. Plant experiments were conducted in clay pots placed where there is enough sunlight in VFSTR campus, vadlamudi and care is taken that there is no leaching loss of carbofuran or water. Each pot is filled with nearly 3 kg of five (Control, 1%BC, 3%BC, 1%BC NPK, 3%BC NPK) different soil treatments(Fig 1). The five different biochar amendments used in this study are given in table 1 . The combination of five biochar treatments was carried out in 10 replicates. Sample of 3 g was taken from each replicate to make carbofuran concentrations in the range of 2 to 20 mg/L (2,4,6,8,10,12,14,16,18,20 mg/L). All these samples were thoroughly mixed and shaken for 24 hrs in an orbital shaker. The samples were filtered and analysed to determine the carbofuran concentration.

2.6. Biochar amendment on Soil physical and chemical properties.

After harvesting from the pots , soil from each pot was collected, air-dried at 36 °C , mixed and passed through 2mm sieve .These samples were further analyzed to measure pH, Cation exchange capacity, Water holding capacity, Electrical conductivity, Soil organic matter and Dry matter production.

2.7. pH analysis.

The growth of plants strongly depends on pH value of the samples.1N KCl was used to determine pH with soil and solution ratio of 1: 2.5. 10 gm air dried soil samples were mixed with 25 ml of 1 N KCl solution in a beaker and the probe of the pH meter in Deluxe Soil and Water analysis kit – National Instruments Corporation, measures the pH value of the solution.

2.8. Cation Exchange Capacity (CEC).

The Cation Exchange Capacity (CEC) is the capacity of soil to hold an exchangeable cations. The higher the CEC of soil, the more cations it can retain. High clay soil can hold more exchangeable cations than low clay soils. CEC also increases as organic matter increases. Cation exchange capacity was calculated according to ammonium acetate method [14] of which is buffered at pH 7.

2.9. Water holding capacity.

Increasing soil water keeping ability after biochar treatment may be a potential main mechanism for yield increase[15]. Biochar has a high total porosity and can also retain water in tiny pores, thereby increasing water retention potential and allowing water to penetrate through the wider pores from the ground surface to the top soil during heavy rain[16]. All the 10 air-dried soil samples of 2 gm each were collected from the pots and are placed in filter paper which in turn is placed on a separating funnel in a 250 ml conical flask.100 ml of distilled water was poured through these samples until distilled water was completely passed through the filter paper. Water holding capacity of these 10 samples was measured by knowing the amount of distilled water absorbed by the samples which can be known by the increase in the weight of the samples.

$$Water\ holding\ capacity(\%) = \frac{wt\ of\ wet\ soil - wt\ of\ dry\ soil}{wt\ of\ dry\ soil}$$

2.10. Electrical Conductivity.

Electrical conductivity determines the presence of soluble salts in the soil.10 gm of air dried soil samples were mixed with 25 ml of distilled water, stirred for 30 min and was kept overnight so that left over soil settles down and the conductivity probe in the soil and water analysis kit measures the electrical conductivity of the samples.

2.11. Soil organic matter (SOM).

SOM is the organic matter portion of soil, consisting of residues of plants and animals at different stages of decomposition, soil organism cells and tissues, and soil organism synthesized substances.

The organic matter content in the soil is obtained by the relation

Soil organic matter content $=1 - \left[\frac{(W_4-W_1)}{(W_2-W_1)}\right] * 100$

Where,
W_1 is the weight of the container,
W_2 is the weight of container + wet soil,
W_3 is the weight of container + dry soil,
W_4 is the weight of the container+ burnt soil.

2.12. Dry matter Production.

Chilli plants after harvesting for 42 days, the above ground matter of the chilli plant was collected and dried in an oven for 70 °C for 5 hrs. Then the weight of the above ground matter for all the treatments was noted down.

2.13. Batch Sorption process.

The combination of five biochar treatments with carbofuran pesticide together was carried out in 10 replicates. The carbofuran concentrations were made in the range of 1 to 20 mg/L (2,4,6,8,10,12,14,16,18,20 mg/L).All these samples were thoroughly mixed and shaken for 24 hrs in an orbital shaker till the equilibrium was achieved. An aliquot of 5 g of soil from each treatment was taken to determine the carbofuran concentration using UV/VIS spectrophotometer at 273 nm. All the carbofuran sorption experiments were performed in triplicate.

2.14. Desorption Studies.

All the samples loaded with carbofuran were taken for analysis. These samples were shaken in an orbital shaker at 100 rpm and 25 °C for 24 hrs till the equilibrium was achieved. 10 ml of the Supernatant solution obtained was taken for analysis and is replaced by 10 mL of 0.01 M CaCl2 solution and then shaken in an orbital shaker for another 24 hrs. This process was repeated twice and the carbofuran desorbed from the samples were determined by using UV/VIS spectrophotometer at 273nm. All the carbofuran desorption experiments were conducted in triplicate.

3. RESULTS

3.1. Proximate and Ultimate analysis of biochar.

Elemental compositions of Raw Chilli stalk and CABC (300 °C) are reported in Table 2. Proximate analysis for CABC was determined according to ASTM D 1762-84 standard method. The % volatile matter and ash composition steadily declines with a rise in temperature. Ultimate analysis reveals that carbon content in CABC increased from 40.53 to 45.32 %. Highest values for C/N ratio and lowest values for H/C ratio were observed. With an increase in the temperature, the volatile constituents of CABC evaporate gradually, illustrating that the yield of CABC is temperature dependent . The BET surface area and pore volume for the biochar formed at 300 °C was marked to be 32.07 m^2/g and 0.0635 cm^3/g respectively. Calculated H/C and O/C molar ratios are the indicators of CABC aromaticity and polarity, respectively. Scanning microscopic images of biomass and biochar were taken to compare the surface morphology modifications between biomass and biochar(Fig 2).

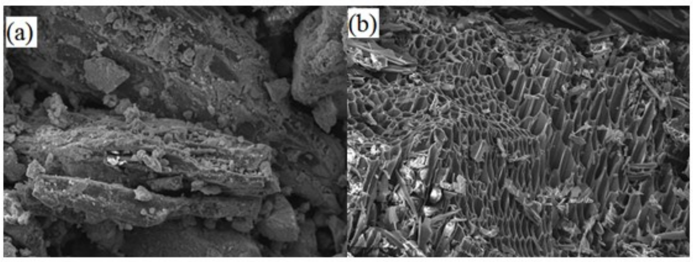

Figure 2. SEM images of (a)Biomass (b)Biochar.

Table 2. Basic property analysis of biomass and biochar.

Characteristics	Biomass	CABC (300 °C)
Ultimate Analysis (wt. %)		
C	40.53	45.32
H	5.02	3.64
N	0.77	1.3
S	0.14	0.20
O	40.23	35.22
Proximate Analysis (wt. %)		
Ash	0.82	15.32
Volatile Matter	80.23	35.62
Fixed carbon	18.95	49.06
Moisture	3	-
Other Properties		
H/C	0.12	0.08
O/C	0.99	0.77
C/N	52.63	34.86
surface area m^2/g		32.07
pore volume cm^3/g		0.0635
Higher heating value, HHV (kJ/g)	15.9	16.5

3.2. Effect of biochar amendment on soil physical and chemical properties.

From the pH studies, it was observed that the soil under the present study is an acidic soil and its PH increased with biochar amendment. Soil PH was more sensitive and its value increased from 5.4 to 7.32 with just an addition of 3 % BC. The high biochar pH values are due to the basic oxides, hydroxides, and carbonates formed during pyrolyses process. Similar trend was observed in the previous studies.

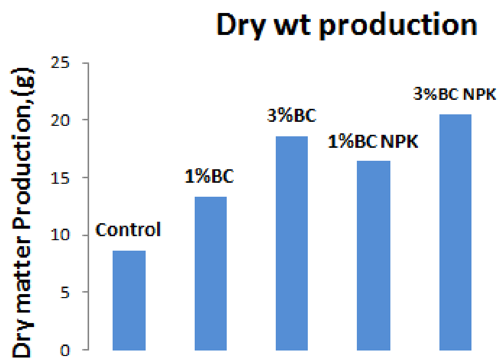

Figure 3. Amount of Dry matter production for different treatments.

From the present study, it was also observed that biochar addition to acidic soils increases Cation exchange capacity as it adds free bases to the soil which was also proved in the previous studies[17]. Water holding capacity of the soil is increased from 140 w/w % to 170 w/w % with an increasing percentage of biochar which shows that the biochar amendment can help farmers not only to improve the soil health but also for water absorption for food security assurance. Since biochar is a carbon rich organic material, soil amended with biochar has high soil organic content In control, SOC was only 0.81 wt % where as in case of 3% BC NPK, it was increased to 7.11 wt%Table 3. Dry Chilli plant weight was calculated after harvesting and it was observed that DMP increases with an increasing rate of biochar. In control , DMP was 8.7 g whereas in 3%BC NPK it was 20.5g (Fig 3).

3.3. Effect on adsorption and desorption studies.

The Concentration of carbofuran present in aliquots of all treatments w.r.t time(up to 6 weeks) was calculated by collecting the supernatant of all the samples and filtered them by using 0.45 µm filter cloth and analyzing by using UV spectrophotometer . The amount of carbofuran adsorbed was shown in the Fig 4. From the figure it was clear that the amount of carbofuran adsorbed increases with an increasing percentage of biochar in soil. During 6th week (42nd day, after harvesting), carbofuran adsorbed with control is 0.45 mg/g whereas with 3%BC it was 6.375 mg/g.

In desorption experiments, the supernatants (with carbofuran)in adsorption studies were replaced with 0.01M $Cacl_2$ (without carbofuran), and the samples were shaken for 24 hrs. After equilibrium has been achieved , the aliquots were again analyzed by sing UV spectrophotometer to find the amount of carbofuran desorbed (Fig 5) . It was observed that carbofuran desorption is less in the case of 3%BC with a value of 0.175 mg/g whereas in control it was 0.375 which is higher than any other treatment involving biochar.

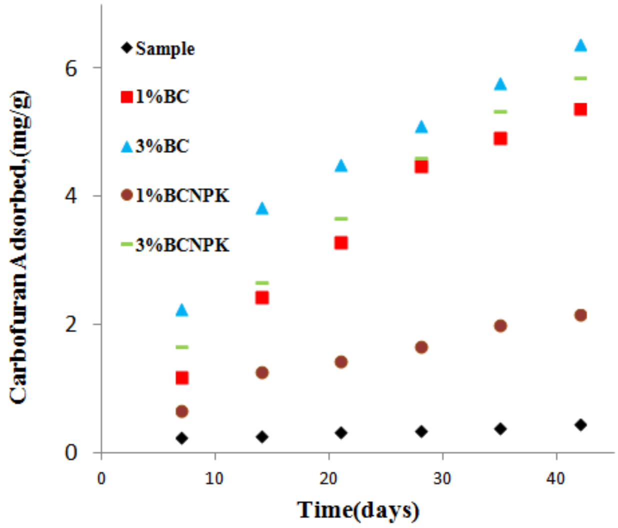

Figure 4. Amount of carbofuran adsorbed vs Time.

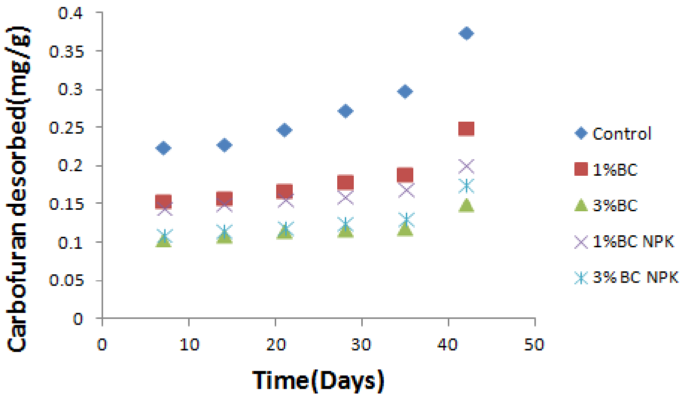

Figure 5. Amount of carbofuran desorbed vs Time.

Table 3. Effect of biochar on soil properties.

Parameter	Control	1%BC	3%BC	1%BC NPK	3%BCNPK
pH	5.4	5.9	6.32	6.36	7.32
CEC($cmolkg^{-1}$)	8.23	9.54	10.66	10.75	11.23
WHC(w/w)%	140	150	170	139	141
EC($\mu s\ cm^{-1}$)	250	320	483	330	495
SOC (wt %)	0.81	1.65	6.23	2.32	7.11
Dry Matter Production (g)	8.7	13.3	18.6	16.4	20.5

4. CONCLUSIONS

Capsicum Annuam Biochar was prepared from Capsicum Annuam and was characterized and successfully used as soil amendment to enhance soil health and to adsorb carbofuran pesticide. Water holding capacity of the soil is increased from 140 w/w % to 170 w/w % with an increasing percentage of biochar. Cation exchange capacity increases with biochar amendment since it adds bases to the soil. From the adsorption studies it was clear that the amount of carbofuran adsorbed increases with an increasing percentage of biochar in soil. From the desorption studies It was observed that carbofuran desorption is less in case of 3%BC with a value of 0.175 mg/g whereas in control it was 0.375. From the above overall observations, instead of burning the biomass in the fields after harvesting, biomass can be converted to biochar through pyrolysis process which in turn will help in soil conditioning by improving its nutritional quality and also for adsorbing the synthetic organic contaminants.

5. REFERENCES

1. Gopinathan, R.; Bhowal, A.; Garlapati, C. Adsorption Studies of Some Anionic Dyes Adsorbed by Chitosan and New Four-Parameter Adsorption Isotherm Model. *Journal of Chemical & Engineering Data* **2019**, *64*, 2320-2328, https://doi.org/10.1021/acs.jced.8b01102.
2. Andelescu, A.; Nistor, M.A.; Muntean, S.G.; Rădulescu-Grad, M.E. Adsorption studies on copper, cadmium, and zinc ion removal from aqueous solution using magnetite/carbon nanocomposites. *Separation Science and Technology* **2018**, *53*, 2352-2364, https://doi.org/10.1080/01496395.2018.1457696.
3. Wauchope, R.D.; Yeh, S.; Linders, J.; Kloskowski, J.R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kordel, W.; Grestl, Z.; Lane, M.; Unsworth, J.B. Pesticide soil sorption parameters:

theory, measurement, uses, limitations and reliability. *Pest Manag. Sci.* **2002**, *58*, 419, https://doi.org/10.1002/ps.489.
4. Neagu, M.; Vijan, L.E.; Giosanu, D. Adsorption Study of Phenolic Compounds Substituted with NO2 and Cl Groups on Activated Carbon. *Journal of Environmental Protection and Ecology* **2013**, *14*, 552–558.
5. Dar, B.A.; Wani, A.; Rather, S.A.; Singh, B. Isothermal Studies of Sorption of Acetic Acid from Wastewater Using Shed Needles of Pine Trees. *Journal of Environmental Protection and Ecology* **2013**, *14,* 559–565, https://doi.org/10.1007/s13369-012-0492-y.
6. Ebrahimi, E.; Asadi, G.; von Fragstein und Niemsdorff, P. A field study on the effect of organic soil conditioners with different placements on dry matter and yield of tomato (*Lycopersicon esculentum* L.). *Int J Recycl Org Waste Agricult* **2019**, *8*, 59, https://doi.org/10.1007/s40093-018-0228-4.
7. Rajput, R.; Panwar, P.; Arunachalam, A. Soil nutrients, microbial biomass, and crop response to organic amendments in rice cropping system in the Shiwaliks of Indian Himalayas. *International Journal of Recycling of Organic Waste in Agriculture* **2018**, *8*, https://doi.org/10.1007/s40093-018-0230-x.
8. Mehdizadeh, M.; Izadi-Darbandi, E.; Yazdi, N.P.; Rastgoo, M.T.; Malaekeh-Nikouei, B.; Nassirli, H. Impacts of different organic amendments on soil degradation and phytotoxicity of metribuzin. *Int J Recycl Org Waste Agricult* **2019**, *8(Suppl 1)*, https://doi.org/10.1007/s40093-019-0280-8.
9. Anwar, Z.An Ping,Bushra Haroon·Muhammad Irshad·Gary Owens**,** Nutrients losses via runoff from soils amended with cow manure composted with leaf litter. *J. Soil Sci. PlantNutr.* **2018**, *18,* http://dx.doi.org/10.4067/S0718-95162018005002501.
10. Deng, S.; Wipf, H.M.; Pierroz, G.; Raab, T.; Khanna, R.; Coleman-Derr, D. A Plant Growth-Promoting Microbial Soil Amendment Dynamically Alters the Strawberry Root Bacterial Microbiome. *Sci Rep* **2019**, *9*, https://doi.org/10.1038/s41598-019-53623-2.
11. Cobb, A.B.; Wilson, G.; Goad, C.L.; Grusak, M.A. Influence of alternative soil amendments on mycorrhizal fungi and cowpea production. Heliyon **2018**, *4,* e00704, https://doi.org/10.1016/j.heliyon.2018.e00704.
12. Velayutham, L.K.; Damodaran, K. Growth Rate of Chilli Production in Guntur District of Andhra Pradesh. *IJRHSS* **2015**, *2,* 1-5.
13. Vijetha, P.; Subbaiah, T.; Vineet, A.; Alka, K.; Satyavathi, B.; Rameshnaidu, M. Torrefied and unmodified capsicum annuam biochar for the removal of synthetic hazardous pesticide (carbofuran) from watershed. *BRIAC* **2019**, *9*, 4384–4393.
14. Ross, D. Recommended soil tests for determining soil cation exchange capacity. In: *Recommended soil testing procedures for the Northeastern United States.* Northeast Regional Bull. Sims, J.T.; Wolf, A. (ed.) Agric. Exp. Stn., Univ. of Delaware, Newark, DE. Volume 493, 1995; pp. 62–69.
15. Jeffery, S.; Verheijen, F.G.A.; Van Der Velde, M.; Bastos, A.C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric Ecosyst Environ* **2011**, *144*, 175–187, https://doi.org/10.1016/j.agee.2011.08.015.
16. Asai, H.; Samson, B.K.; Stephan, H.M.; Songyikhangsuthor, K.; Homma, K.; Kiyono, Y.; Inoue, Y.; Shiraiwa, T.; Horie, T. Biochar amendment techniques for upland rice production in Northern Laos, 1. Soil physical properties, leaf SPAD and grain yield. *Field Crop Res* **2009**, *111,* 81–84, https://doi.org/10.1016/j.fcr.2008.10.008.
17. Yuan, J.H.; Xu, R.K.; Qian, W.; Wang, R.H. Comparison of the ameliorating effects on an acidic ultisol between four crop straws and their biochars. *J. Soils & Sediments* **2011**, *11,* 741–750, https://doi.org/10.1007/s11368-011-0365-0.

6. ACKNOWLEDGEMENTS

The study was supported by Council of Scientific and Industrial research (CSIR), Indian institute of Chemical Tehnology, Hyderabad, Telangana, India.