ARTICLE IN PRESS

Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Characterization of engineered corn cob biochar produced in allothermal pyrolysis reactor

Mari Selvam S [a], Thiagarajan Janakiraman [b], Balasubramanian Paramasivan [a,*]

[a] Department of Biotechnology and Medical Enginnering, National Institute of Technology, Rourkela 769008, India
[b] Department of Mechanical Engineering, Periyar Maniammai Institute of Science and Technology, Thanjavur 613404, India

ARTICLE INFO

Article history:
Received 23 April 2021
Accepted 28 April 2021
Available online xxxx

Keywords:
Allothermal reactor
Biochar
Characteristics
Metal complexation
Soil amendment

ABSTRACT

Biochar production has been explored wisely through different reactors and resulted in higher biochar yield with better quality. Besides the comprehension of production parameters, allothermal reactors has been less explored in terms of biochar production and its potential characteristics after activation. The current study presents the production of corn cob biochar in self-fabricated allothermal reactor and understanding its characteristic features. Corn cob biochar yield of 46.8% with fixed carbon content of 83.9% has been obtained. The produced biochar was modified using magnesium chloride and ferric chloride to produce the engineered biochar. The modified biochar possess numerous pores along with metal complexed and positive functional groups that could adsorb negative charged contaminants and serve as a better soil amendment.

Selection and peer-review under responsibility of the scientific committee of the 12th National Conference on Recent Advancements in Biomedical Engineering.

1. Introduction

Biomass is one of the abundant renewable energy source that shows promising benefits for energy demands in a sustainable manner. Many studies have proved that it could yield different bioproducts like biochar, bio-oil through thermochemical conversion such as pyrolysis which involve heating of the biomass under limited oxygen atmosphere inside a closed container. After complete thermochemical conversion, the produced biochar can be utilized for fuel source and are being explored for various environmental and agricultural applications [1,2]. The product composition of the bioproducts mainly depends on the mode of pyrolysis and the selection of process parameters. Different modes such as slow or fast pyrolysis shall be preferred based on desired properties of final product [3,4]. The exploration of significance and advantages of biochar utilization for different technologies urges the understanding of biomass-to-biochar conversion process. Parameters such as pyrolysis temperature, time, moisture content, feedstock type, biochemical composition, reactor design and type plays vital role in determining the yield of biochar [5,6].

For many centuries, biochar has been produced through earth kilns and used in cooking, heating applications whereas results in higher gaseous emissions. Modern biochar retorts limit the gaseous emissions and produces stable biochar with better physiochemical properties. The reactor designs are typically categorized into either allothermal or autothermal reactors based on the scale of application [7,8]. Autothermal reactors use heat energy to proceed the pyrolysis reaction by biomass oxidation partially within the reactor. Autothermal reactors are commonly being used in small scale applications. On the other hand, allothermal reactors use energy from an external source for heating the biomass to carry out the endothermic pyrolytic reactions where heat is conducted through either surface or transport bed material [9]. The gas product produced in allothermal reactor consists of higher heating values in comparison with autothermal reactor [10]. Haryati *et al.* [11] produced palm kernel shell biochar through fixed bed allothermal reactor with 33–52 percent of yield and found its suitability for soil amendment and sequestration of carbon in degraded soil. However, large investment is required for technology implementation, since the reactor operation is difficult and complicated for small scale production. Proper study of the parameters in allothermal reactor is essential to determine the perfect combination of parameters to make the better quality biochar.

* Corresponding author.
E-mail address: biobala@nitrkl.ac.in (B. Paramasivan).

https://doi.org/10.1016/j.matpr.2021.04.469
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the 12th National Conference on Recent Advancements in Biomedical Engineering.

Please cite this article as: S Mari Selvam, T. Janakiraman and B. Paramasivan, Characterization of engineered corn cob biochar produced in allothermal pyrolysis reactor, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2021.04.469

This study investigates the production of biochar in a self-fabricated allothermal biochar reactor and explore its properties for its applications. The produced biochar has been modified with magnesium and ferric chloride and characterized for analyzing the surface functional groups, morphology and charge to analyze its recovering potential of specific nutrients in soil. These studies will help to understand the biochar production in allothermal reactor and the properties after modification with metal aqueous solutions.

2. Materials and methods

2.1. Fabrication of biochar reactor

The biochar reactor of volume 10 kg was fabricated using mild steel with thickness of 0.006 m since it serves the purpose in cost effective manner and better with its lighter characteristics. The height of the reactor was kept at 0. 580 m and the diameter as 0. 440 m which is far enough to satisfy minimum reactor volume (332.43×10^{-3} m^3) criteria for analyzing corn cob biochar properties. The prototype was designed to be taller in order to load more biomass that would increase the yield of biochar. A chimney was attached with a height of 0. 200 m and diameter of 0.050 m to release the exhaust gas out of the reactor. The reactor was fabricated and tested for different biomass however the production of corn cob biochar has been discussed here along with the modification and characterization for its use in sustainable agriculture.

2.2. Production of biochar

The locally collected corn cobs sticks were allowed to dry in sunlight for 3 days. The dried biomass of 8 kg was loaded into the pyrolysis reactor from the top as shown in Fig. 1. After loading the biomass, the reactor was closed by top lid with the chimney. The excess corn cob was used as fuel and ignited from the bottom to provide sufficient heat for the pyrolysis. The temperature of the process had been monitored with K- type thermocouple connected with data logger. Pyrolytic gas was allowed to release through chimney and it could be observed by naked flame torch. When the pyrolytic gas continues burning with flame, top lid was removed after 20 min and the burning feed was extinguished by tube flow of water. After extinguishing, the converted biochar material was collected, dried and stored. The produced biochar was modified using 1 M $MgCl_2$ and 1 M $FeCl_3$ to produce engineered biochar. 2 g of biochar was added to 10 ml of metal aqueous solutions and kept for overnight at 50 °C. Then the solutions were subjected to centrifugation and filtered. The biochar obtained was dried and stored in desiccator till further use.

2.3. Physiochemical characterization of the prepared biochar

Standard protocols of American Society for Testing and Material (ASTM) D1762-84 was utilized to analyze the proximate composition of the biochar [12]. The Hydrogen to Carbon (H/C) and Oxygen to Carbon (O/C) ratios were estimated according to Klasson *et al.* [13].

2.4. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was done to observe the surface functional groups in the pristine samples and after its modification. Infrared spectrum of biochar and modified biochar was recorded under ambient conditions using Perkin-Elmer spectrophotometer with 4.0 cm^{-1} resolution. Each sample was prepared by mixing the biochar with infrared (IR) spectroscopy grade potassium bromide (KBr) in the mass ratio of 1:100, which was then pressed in a hydraulic press to form pellets. The FTIR spectrum for each of the pellets were analyzed under attenuated reflectance mode with the wavenumber scan done between 400 cm^{-1} to 4000 cm^{-1} by taking an average of 8 scans per sample

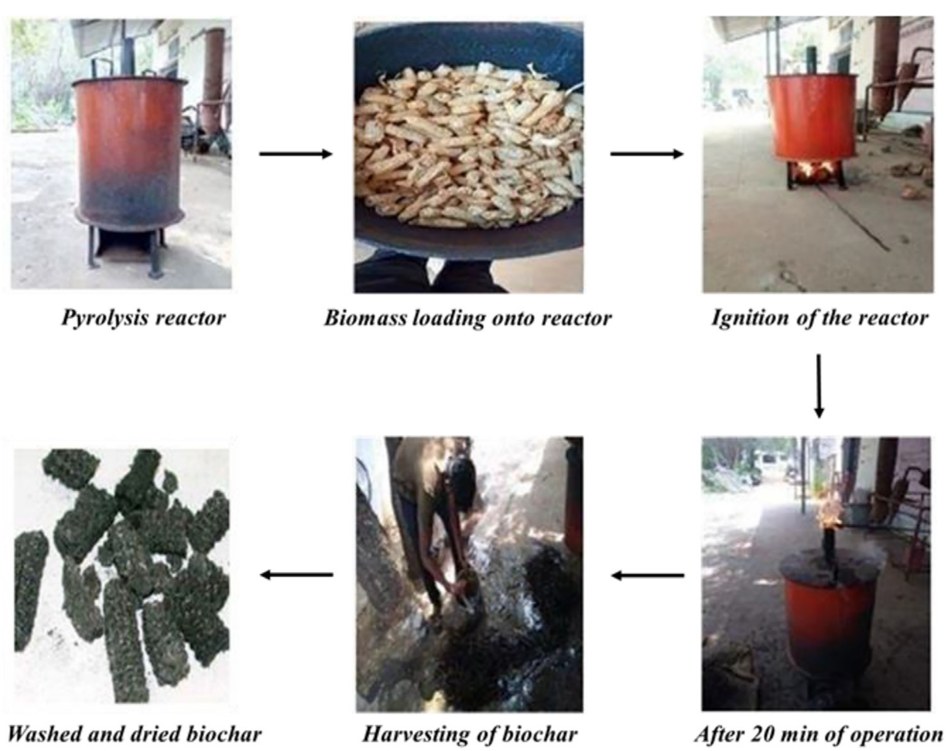

Fig. 1. Process description of production of corn cob biochar in self-fabricated allothermal reactor.

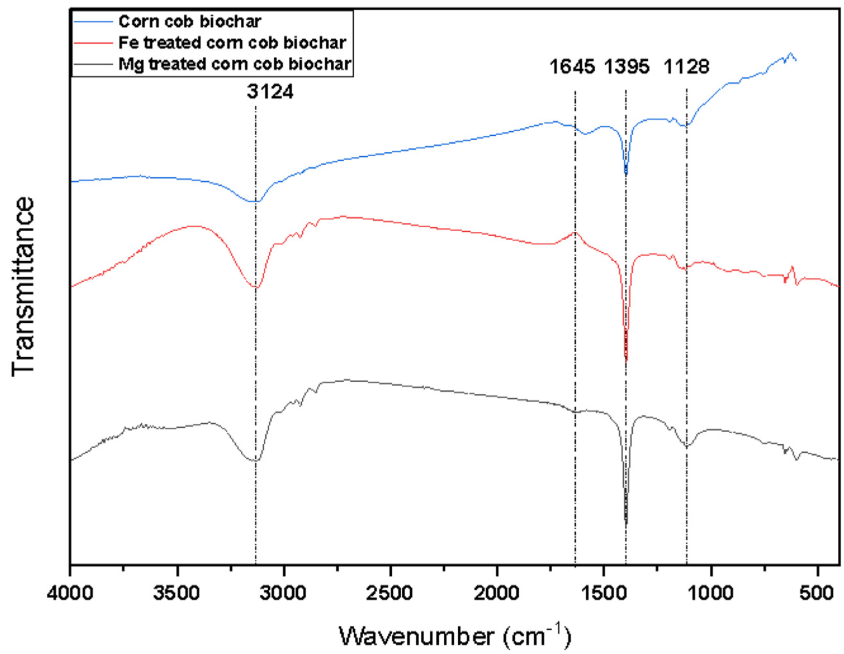

Fig. 2. FTIR spectrum of corn cob biochar and Fe, Mg treated corn cob biochar.

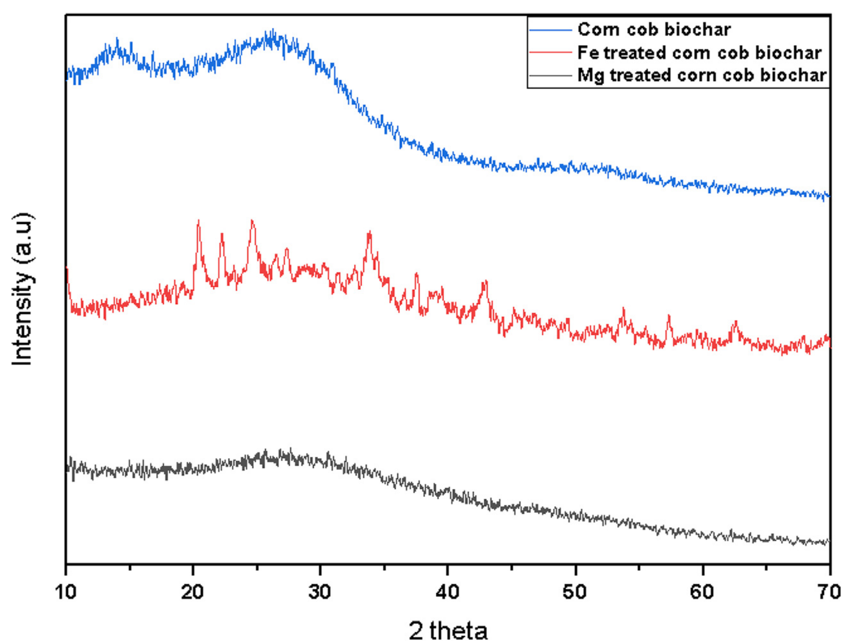

Fig. 3. XRD spectrum of corn cob biochar and Fe, Mg, treated corn cob biochar.

2.5. X-ray diffraction (XRD) spectroscopy

XRD patterns for powdered samples of biochar and modified biochar was done through Philips Pan analytical X'Pert. X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm) to analyze the changes in carbon sheet structure following modification. Diffractogram were obtained with 2 theta ranging from 10° to 70° having scan rate of 10° per min at a step size of 0.01.

2.6. Scanning electron microscope (SEM) & energy dispersive X-ray (EDX) analysis

The morphological porous structure was observed through the scanning electron microscope (SEM) [JSM-6480 LV, JEOL] with theoretical resolution of 1 nm and acceleration of 15 kV. The cross sections of samples were analyzed in longitudinal and transverse directions. The JEOL JSM-6480LV scanning electron microscope was equipped with an INCAPentaFET-x3 X-ray microanalysis system with high-angle ultra-thin window detector and a 30 mm^2 Si(Li) crystal to analyse the surface elemental content. An accelerating voltage of 25 kV was used with a 1 nm probe with ~ 1nA of current on the sample

3. Results and discussion

3.1. Yield and properties of biochar

After the initial ignition, the burning of the biomass was slowly propagated with increase of temperature. The release of enormous

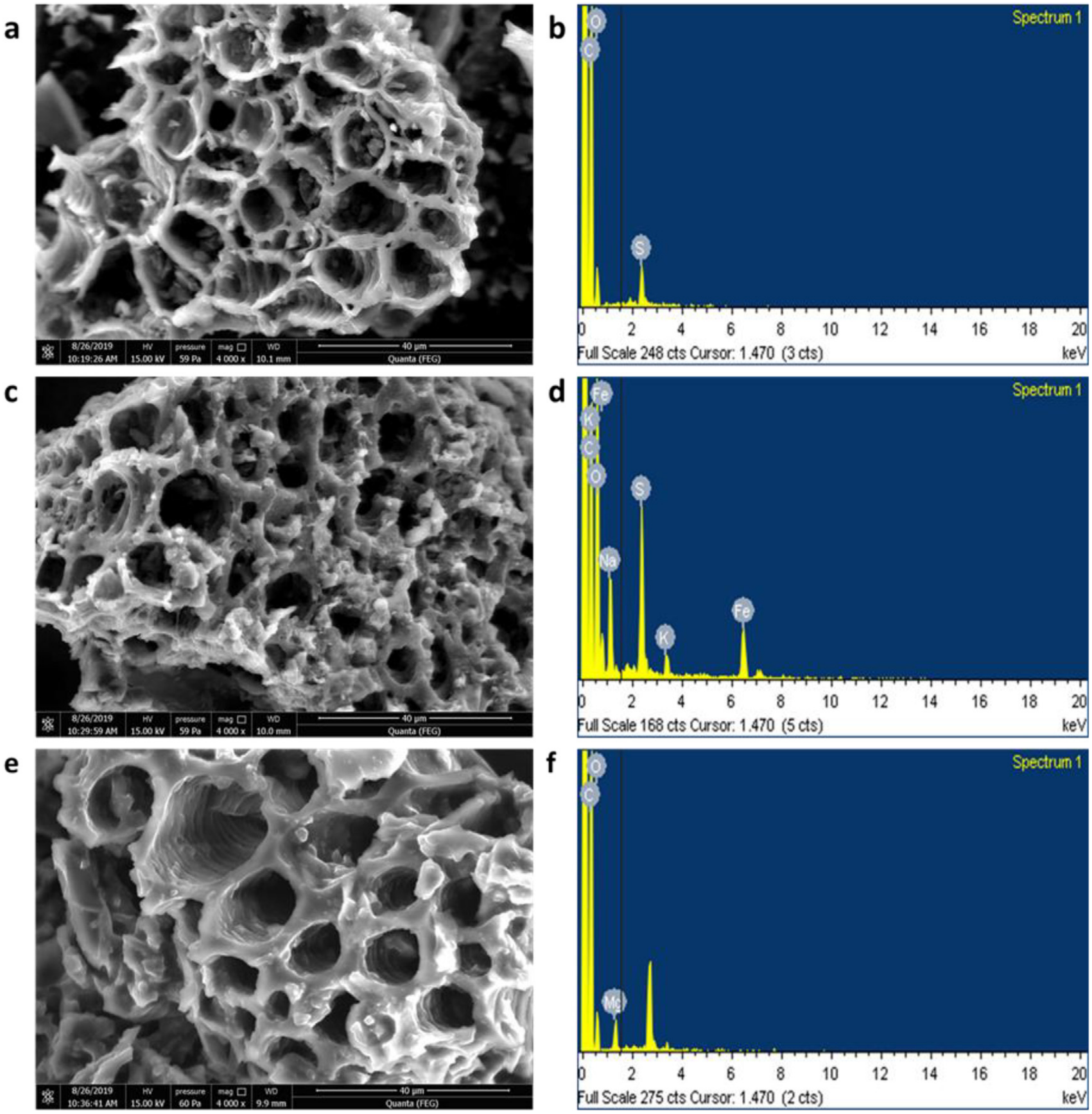

Fig. 4. Scanning Electron Microscopic (SEM-EDX) images of (a, b). corn cob biochar; (c, d). Fe treated corn cob; biochar (e, f). Mg treated corn cob biochar.

Table 1
Elemental composition of corn cob biochar and modified biochar.

Elemental Composition (%)	Corn cob biochar	Fe treated corn cob biochar	Mg treated corn cob biochar
Carbon (C)	76.18	43.76	72.68
Oxygen (O)	19.16	34.25	24.55
Sulphur (S)	4.65	6.00	ND
Iron (Fe)	ND	11.05	ND
Magnesium (Mg)	ND	ND	2.76

*ND – Not detected.

smoke was observed after 5 min of ignition. It took 35 min to reach the temperature of 550 °C. Around 20 min of operation at this temperature, a continuous flame of pyrolysis gas burning was observed. The system was extinguished and biochar was washed with water to remove the ash. Corn cob biochar of yield 46.8% has been obtained from the self-fabricated allothermal biochar reactor whereas Haryati *et al.* [11] reported the yield of 33.4% at 600 °C for 60 min. The ash free biochar of 3.75 kg was obtained and stored. The pH of biochar is found to be 9.1 which is alkaline and electrical conductivity of 404 μS cm^{-1}. The volatile matter (VM) content of 11.42% and fixed carbon (FC) content of 83.9% was observed. VM/FC ratio of biochar is found to be 0.136 which is similar to that anthracite coal reported by Yan *et al.* [14]. H/C and O/C ratio is found to be 0.305 and 0.0606 respectively which confirms the produced biochar is stable and is highly resistant to biological and thermal decomposition [15]. Thus, the produced alkaline biochar could be applied for improving the fertility of acidic soil and will be stable in soil for longer years.

3.2. Functional group analysis of produced biochar

The FTIR spectrum of pristine and modified biochar has been given in Fig. 2. The intensity of peak 1395 cm^{-1} was enhanced after modification with 1 M $MgCl_2$ and 1 M $FeCl_3$ aqueous solutions that have been reported as the characteristic peak of metal cation's complexation with carboxyl groups [16]. The shifting of band at 1645 cm^{-1} is due to binding to the carbonyl group from the aldehyde/ester [17]. The band at 1128 cm^{-1} is owing to the oxygen complexation from C=O=C functional group with metal atom and leads to change in peak intensity [18]. The peak at 3128 cm^{-1} indicates the presence of dissociative hydroxyl group whereas the peak shifts from 3128 cm^{-1} to 3134 cm^{-1} represents

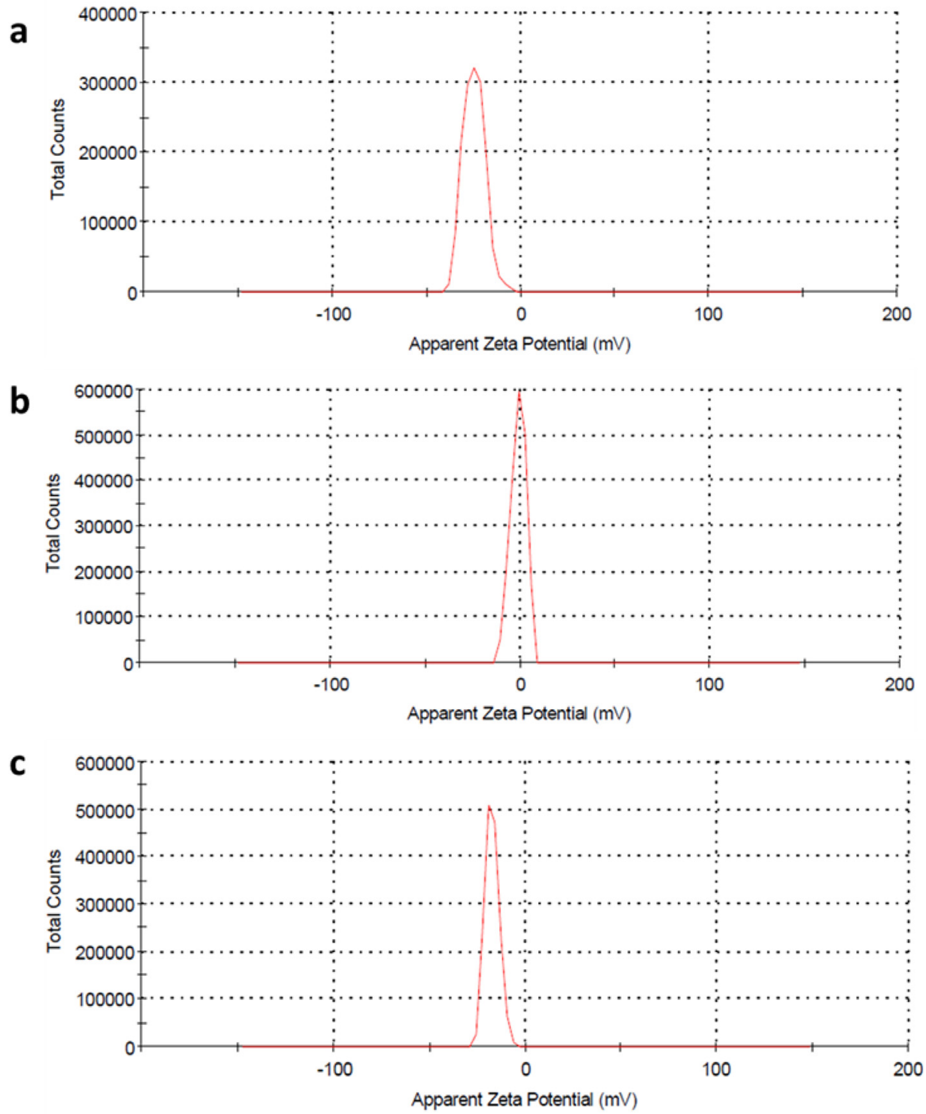

Fig. 5. Zeta potential of a). corn cob biochar; b). Fe treated corn cob biochar; c). Mg treated corn cob biochar.

the bonding of metal cations [19]. The infrared spectrum of biochar treated with metal aqueous solution shows significant changes of metal complexation with respect to that of pristine biochar.

3.3. X-ray diffraction spectrum of pristine and modified biochar

The XRD patterns of the raw, Mg and Fe corncob biochar were illustrated in Fig. 3. Two broad peaks that appeared at 15° and 21° in the crystalline pattern of the raw corncob are typical of the XRD pattern of alpha cellulose as reported by Nwadiogbu *et al.* [20], and pristine structure of carbonaceous materials [21]. The sharp peaks at 23°, 25°, and 26° in the Fe treated corncobs were explained by the presence of Fe ions [22]. The intensity of cellulose peak is declined in Mg treated corn cob which indicate that $MgCl_2$ treatment modifies the cellulose present in the corn cob.

3.4. Surface morphology and elemental composition of pristine and modified biochar

The SEM images of corn cob biochar and Mg, Fe treated biochar has been given in Fig. 4. As shown in the figure, the surface texture morphology has been significantly improved by metal complexation. The Mg treated biochar shows more porous structure compared to Fe treated biochar. These biochar has pores of different size and the metal particle could get easy access to complex with the surface owing to larger pore. The carbon and oxygen content has been changed after metal complexation as shown in Table 1. This is due to catalytic effect of Mg and Fe species in the form of C—O—Mg, C—O—Fe bond on the surface of carbon [17], and get precipitated as metal oxides. The presence of 2.06% Mg and 11.03% Fe has been detected in Mg and Fe modified biochar respectively confirms the metal complexation.

3.5. Zeta potential of corn cob biochar and modified biochar

The adsorption properties of biochar could be reflected by zeta potential and it is measurement of Van der waals and electrostatic repulsive forces [23]. The zeta potential of pristine and modified biochar were given in Fig. 5. The corn cob biochar shows zeta potential of −24.7 mV which is potentially stable and does not agglomerate. The Fe and Mg treated corn cob biochar showed zeta potential of −0.909 mV and −17.3 mV respectively. The electronegativity of pristine biochar is higher and could able to adsorb positive charged metal cations which act as contaminants in soil.

The oxygen containing functional groups (OCFG) has been decreased in treated biochar which indicates that the electrostatic repulsion between OCFGs and negative charged adsorbates could be minimized and the adsorption efficiency can be enhanced after optimization [24,25].

4. Conclusion

Corn cob biochar of 46.8% has been obtained through self-fabricated allothermal biochar reactor. The produced alkaline biochar has higher fixed carbon content of 83.9% and H/C ratio of 0.305 which is expected to be potentially stable and helps in carbon sequestration. The metal complexed biochar could adsorb negative charged contaminants and aids in remediating the soil. The surface porosity has been enhanced after treating with metal aqueous solutions.

The electronegativity of pristine corn cob biochar could assist in adsorbing positive charged contaminants and the treated biochar could be used for immobilizing the negative charged contaminants. In a nutshell, the corn cob biochar produced from the allothermal biochar reactor has good physiochemical properties with higher yield and is suited for amendment in acidic soil and carbon sequestration.

Declaration of Competing Interest

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.

Acknowledgements

The authors thank the Department of Biotechnology and Medical Engineering of National Institute of Technology Rourkela for providing the research facility. The authors thank the Science and Engineering Research Board (SERB), Department of Science and Technology (DST) of Government of India for the research grant [File No: ECR/ES/2017/003397] and for sponsoring the PhD programme of the first author.

References

[1] J. Wang, S. Wang, J. Clean. Prod. 227 (2019) 1002–1022.
[2] S.K. Bhatia, S.S. Jagtap, A.A. Bedekar, R.K. Bhatia, A.K. Patel, D. Pant, Y.H. Yang, Bioresour. Technol. (2020) 122724.
[3] L. Wang, Y.S. Ok, D.C. Tsang, D.S. Alessi, J. Rinklebe, H. Wang, D. Hou, Soil Use Manag. 36 (3) (2020) 358–386.
[4] A. Tomczyk, Z. Sokolowska, P. Boguta, Rev. Environ. Sci. Bio/Technol. 19 (1) (2020) 191–215.
[5] M. Tripathi, J.N. Sahu, P. Ganesan, Renew. Sustain. Energy Rev. 55 (2016) 467–481.
[6] I. Cabeza, T. Waterhouse, S. Sohi, J.A. Rooke, Anim. Feed Sci. Technol. 237 (2018) 1–7.
[7] M. Milhe, L. Van De Steene, M. Haube, J.M. Commandre, W.F. Fassinou, G.J. Flamant, Anal. Appl. Pyrolysis 103 (2013) 102–111.
[8] H.K. Nsamba, S.E. Hale, G. Cornelissen, R.T. Bachmann, J. Sustain. Bioenerg. Sys. 5 (01) (2015) 10.
[9] S.H. Kong, S.K. Loh, R.T. Bachmann, H. Zainal, K.Y.J. Cheong, Oil Palm Res. 31 (3) (2019) 508–520.
[10] N.B. Rasmussen, N. Aryal, Fuel 263 (2020) 116706.
[11] Z. Haryati, S.K. Loh, S.H. Kong, R.T.J. Bachmann, Oil Palm Res. 30 (3) (2018) 485–494.
[12] A.S.T.M. Standard, ASTM, Conshohocken, PA. (2009)
[13] K.T. Klasson, Biomass Bioenerg. 96 (2017) 50–58.
[14] M. Yan, S. Zhang, H. Wibowo, N. Grisdanurak, Y. Cai, X. Zhou, X.E. Kanchanatip, Waste. Dis. Sustain. Energy. 1-10 (2020).
[15] S. Ghysels, F. Ronsse, D. Dickinson, W. Prins, Biomass Bioenerg. 122 (2019) 349–360.
[16] P. Khare, U. Dilshad, P.K. Rout, V. Yadav, S. Jain, Arab. J Chem. 10 (2017) S3054–S3063.
[17] D. Feng, Y. Zhao, Y. Zhang, H. Xu, L. Zhang, S. Sun, Fuel 212 (2018) 523–532.
[18] Q. Zhou, X. Jiang, X. Li, C.Q. Jia, W. Jiang, RSC Adv. 8 (53) (2018) 30171–30179.
[19] J. Bai, Y. Chao, Y. Chen, S. Wang, R. Qiu, J. Environ. Sci. 78 (2019) 328–337.
[20] J. Nwadiogbu, V. Ajiwe, P. Okoye, J. Taibah Univ. Sci. 10 (1) (2016) 56–63.
[21] E.A. Assirey, L.R. Altamimi, J. Taibah Univ. Sci. 15 (1) (2021) 111–121.
[22] X.Q. Wang, P. Wang, P. Ning, Y.X. Ma, F. Wang, X.L. Guo, Y. Lan, RSC Adv. 5 (32) (2015) 24899–24907.
[23] D.J. Wang, W. Zhang, X.Z. Hao, D.M. Zhou, Environ. Sci. Technol. 47 (2013) 821–828.
[24] L. Zhao, X. Cao, W. Zheng, Q. Wang, F. Yang, Chemosphere 136 (2015) 133–139.
[25] L. Zhou, D. Xu, Y. Li, Q. Pan, J. Wang, L. Xue, A. Howard, Water 11 (8) (2019) 1559.