Synthesis and Characterization of rice husk nanobiochar-based N and K Fertilizers: Promoting Environmental Sustainability in Agriculture

Abstract

This study focuses on the synthesis and characterization of nanobiochar-based nitrogen (N) and potassium (K) fertilizers derived from rice husk. The aim is to address the agricultural by-products generated during the rice milling process and convert them into valuable products. The nanobiochar particles, with dimensions in the nanoscale range, exhibit enhanced physical, chemical, and surface characteristics compared to macrobiochar counterparts. The particle size analysis revealed hydrodynamic diameters of 42.5 nm for RHNB N and 10.9 nm for RHNB K, while the zeta potentials were found to be -32.4 mV and -31.8 mV, respectively. Fourier transform infrared spectroscopy (FT-IR) confirmed the presence of functional groups and nutrient incorporation in the fertilizers. X-ray diffraction (XRD) analysis indicated the crystalline structure of the samples, attributed to the presence of SiO2. Scanning electron microscopy (SEM) provided insights into the porous structure and surface morphology of the nanobiochar fertilizers. The elemental analysis using energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of various elements. The developed rice husk nanobiochar-based N and K fertilizers offer promising properties for sustainable agriculture, including slow-release nutrient delivery and mitigation of environmental issues associated with conventional fertilizers. These fertilizers have the potential to enhance soil fertility and contribute to environmental sustainability in agricultural systems. Further research and field trials are necessary to evaluate their efficacy in agricultural practices.

Key word: Nanobiochar, magnetic stirring, soil fertility, waste management, slow release, sustainable agriculture

Introduction

Rice, being a primary food source for over half of the global population, generates agricultural by-products such as rice straw and rice husk during the milling process [1]. The husk, which constitutes the outermost layer of the rice grain, is often considered waste and disposed of. According to reports, the combustion of 1 ton of rice husk in the field results in approximately 0.15 kg of CO_2 being released into the atmosphere. Conversely, when rice hulls are left on the ground and undergo natural decomposition, around 0.09 kg of methane gas is generated [2]. Reducing the particle size to the micro range (10-600 µm) enhances the availability of adsorption sites, thereby leading to improved adsorption capacity (Lonappan et al. [3], Naghdi et al. [4]. By further reducing the size of biochar particles to the nanoscale, reaching dimensions of 100 nm or below, its properties are significantly enhanced. This reduction in size results in a higher surface-to-volume ratio, thereby increasing surface energy, adsorption potential and ultimately improving its biological effectiveness (Naghdi et al. [4], Sulaiman et al. [5]. These unique attributes of nanobiochar have been recently highlighted [6]. Furthermore, nanobiochar exhibits more negative zeta potentials, smaller hydrodynamic radius and a higher concentration of functional groups containing oxygen and carbon defects. These characteristics contribute to the generation of reactive organic species (ROS), ultimately enhancing its adsorption capability beyond that of macrobiochar counterparts (Ramanayaka et al. [7]. The utilization of physical modification methods like ball milling has not yet gained widespread popularity. However, the limited research conducted in this area has shown promising results, indicating the need for further investigation and exploration (Lyu et al. [8], Ramanayaka et al. [9]. In a recent study, a novel investigation introduced a polymer matrix comprising of cotton stalks (CSs), acrylic acid (AA), 2-acrylamide-2 methylpropane sulfonic acid (AMPS), and bentonite. This matrix was combined with $NH4^{+}$-loaded biochar (N-BC) to develop slow-release nitrogen fertilizers known as biochar-based slow-release nitrogen fertilizers (BSRFs) (Wen et al. [10]. Additionally, this experimental study aims to address waste agricultural residue by either dealing with it or converting it into a more valuable product. The environmentally friendly rice husk nanobiochar-based fertilizers developed in this study helps resolve leaching issues commonly associated with conventional fertilizers, thus mitigating environmental problems and reducing nutrient loss.

Material and Methods

Development of rice husk biochar based N and K fertilizers

To develop the rice husk nanobiochar-based nitrogen (N) fertilizer, the method described by Yiman et al. [11] and Gong et al. [12] was followed. The process involved the following steps: Solution A preparation: In a 250 mL beaker, 1 mL of glycerol and 5 mL of ethanol were mixed and stirred on a magnetic stirrer at a speed of 60 revolutions per minute for 1 hour. Subsequently, 5 g of CTAB was added to the stirring mixture and stirred for an additional 20 minutes. Solution B preparation: In a 2 L beaker, 100 g of dried rice husk nanobiochar was weighed, and 217.08 g of ammonium sulphate was added. The mixture was stirred for 20 minutes at a speed of 60 revolutions per minute. Solution A was slowly added to Solution B, and the combined mixture was stirred at room temperature with a speed of 400 revolutions per minute for 60-90 minutes. The resulting mixture was collected and dried for 24-32 hours at 60 °C in an oven. After drying, it was ground into a fine powder using a pestle and mortar. The final product obtained was rice husk nanobiochar-based N fertilizer weighing between 305-315.98 g, which was then packaged in a polythene bag. The developed rice husk nanobiochar-based N fertilizer contained 20.98% nitrogen after the process of magnetic stirring and drying, starting from an initial ammonium sulphate content of 46%. Same procedure followed for rice husk nanobiochar-based K fertilizer. To create the rice husk nanobiochar-based K fertilizer, 133.66 g of potassium sulphate with an initial potassium content of 60% was added to 100 g of rice husk biochar. Following electric stirring and drying, the rice husk nanobiochar-based K fertilizer exhibited a potassium content of 41.65%. The resulting product was a rice husk nanobiochar-based potassium (K) fertilizer weighing between 203-210.41 g, which was carefully stored in a polythene bag.

Characterization of rice husk nanobiochar-based N and K fertilizers

Spectral analysis

DLS (Dynamic Light Scattering) analysis

The size and zeta potential of dispersed particles were assessed using DLS with a Nanopartica (HORIBA, SZ-100) compact scattering spectrometer. Prior to analysis, the synthesized particles were filtered through a 0.22 µm syringe-driven filter unit, and DLS provided valuable information on particle size, dispersion properties and stability, particularly at low negative zeta potentials.

Fourier transform infrared spectroscopic analysis (FT-IR)

FTIR spectroscopy analyzes infrared radiation absorption and transmission to study a sample's wavelength-dependent absorption. It is valuable for identifying organic molecular groups based on their distinct vibration frequencies. Samples were scanned in transmittance mode from 400 to 4000 cm^{-1} using a finely ground sample mixed with KBr (1:200) to create a transparent film, which was pressed with a Tensor 27, BRUKER instrument.

XRD (X-Ray Diffraction analysis)

XRD analysis was performed at Yogi Vemana University (YVU), Kadapa, using a Rigaku Ultima IV X-ray diffractometer. The purpose was to assess sample crystallinity, identify phases in nanoscale particles, and locate Bragg's reflection peaks. The measurements were conducted at 40 kV and 20 mA, utilizing CuK radiation, with scans acquired at a rate of 10° per minute. Comparison with relevant literature helped determine the phases corresponding to the observed peaks.

Scanning electron microscopy (SEM)

Biochar samples were analyzed for morphology, physical properties, spectral composition, and chemical composition using scanning electron microscopy (SEM) (Chia et al. [13] and energy-dispersive X-ray spectroscopy (EDX) (Purakayastha et al. [14]. Prior to analysis, a 1-2 mm layer of palladium and gold alloy was coated on the samples using a 20 kV beam energy (Downie et al. [15]. The Hitachi S4800 SEM instrument was utilized to provide a detailed description of the surface morphology of the biochar fertilizers.

Results and Discussion

Particle Size and Zeta-Potential Analysis

The hydrodynamic diameter of RHNB N was 42.5 nm Fig. 1(a**)**, whereas RHNB K had a hydrodynamic diameter of 10.9 nm Fig. 1(c)**.** Additionally, RHNB N exhibited a negative zeta potential of 32.4 mV Fig 1(b), while RHNB K displayed a negative zeta potential of 31.8 mV Fig 1(d).

Fourier transform - infrared spectroscopy (FT-IR)

By comparing the FT-IR spectra of RHNB N and RHNB K (as depicted in the Fig. 2(a, b), it was observed that all samples exhibited peaks in the range of 3900-3600 cm^{-1}. These peaks were attributed to the stretching of hydroxyl bonds (-OH). The presence of these peaks suggests the possible presence of moisture content in the samples, a finding that was further supported by the physical parameters examined. The observed peaks at 2979-2983 cm^{-1} in the FT-IR spectra were attributed to the stretching of -COOH and C-H bonds. Additionally, peaks at 1392, 1131, and 1073 cm^{-1} indicated vibrations and stretching of the C-O bond, as previously reported in studies by Mukome et al. [16], Zhang et al. [17] and Zornoza et al. [18]. Furthermore, there was a noticeable peak shifting in the case of RHNB N and RHNB K, which occurred at positions of 2983, 1073, and 613 cm^{-1}. This shift in peaks confirmed the incorporation of nutrients in both rice husk nanobiochar-based fertilizers, as supported by the work of Nurhidayati and Mariati [19].

Powder X-ray diffraction (XRD)

The examination of various biochar samples involved the utilization of X-ray diffraction (XRD) analysis to investigate the presence of crystalline or amorphous silica formation. The powder XRD diffractograms of RHNB N and RHNB K were obtained by scanning the range of 2θ = 5-80° and are depicted in Fig. 2(c, d). The peaks observed at 2θ values of 17.15°, 21.63°, 26.53° and 35.02° in the diffractograms correspond to the intensity values reported in the literature (Yu et al. [20]; Zornoza et al. [18]. The XRD data revealed an enhanced crystalline structure in both samples, which was attributed to the existence of SiO_2 in the rice husk biochar. The presence of SiO_2 creates high-energy sites that promote favorable adsorption, as corroborated by the findings of Strnad et al. [21].

Scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDX)

To achieve successful visual and morphological characterization of RHNB N and RHNB K, as well as to analyze their pore properties, scanning electron microscopy (SEM) was employed. These investigations were documented by Saeed et al. [22] and Chia et al. [23].

SEM images taken at different resolutions (500 µm, 100 µm, 20 µm and 10 µm) provide valuable information about the porous structure of and RHNB N and K samples, enhancing their surface area and adsorption capacity [24]; Yu et al. [20]. The white coating observed on the samples' surfaces indicates the presence of doped salts (Fig. 3(a-h).

The elemental analysis of the surface using energy-dispersive X-ray spectroscopy (EDS) was performed to investigate the presence of carbon (C), oxygen (O), nitrogen (N), iron (Fe), sodium (Na), silicon (Si), phosphorus (P), chlorine (Cl), potassium (K) and fluorine (F) in various regions of interest. The obtained EDS measurements, depicted in **Fig. 4(a-d)** along with a corresponding, showcase the respective peaks and values related to the elements on weight percentage.

Conclusion

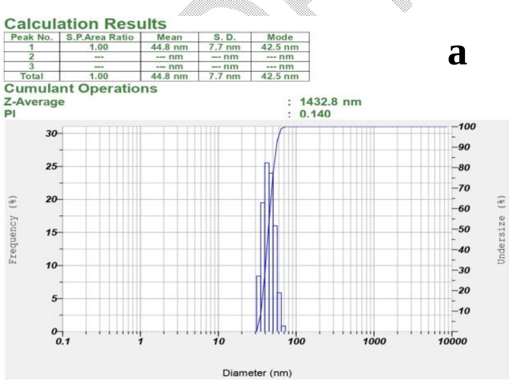
In conclusion, this study focused on the synthesis and characterization of nanobiochar-based nitrogen (N) and potassium (K) fertilizers derived from rice husk. The developed fertilizers exhibited enhanced physical, chemical and surface characteristics due to the nanoscale dimensions of the biochar particles. Based on the characterization results, it can be concluded that nanobiochar-based N and K fertilizers derived from rice husk exhibit promising properties for sustainable agriculture. These fertilizers have the potential to enhance soil fertility, promote slow-release nutrient delivery and mitigate environmental issues associated with conventional fertilizers. Overall, the synthesis and characterization of nanobiochar-based N and K fertilizers offer a sustainable approach for eco-friendly agriculture and contribute to environmental sustainability. Further research and field trials are warranted to assess their efficacy in promoting sustainable crop production and soil health in real-world agricultural systems.

References

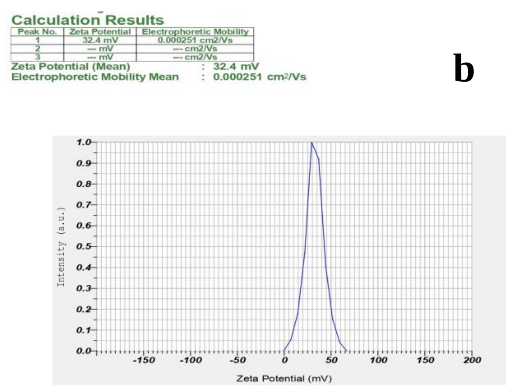
1. Tateda M. Production and effectiveness of amorphous silica fertilizer from rice husks using a sustainable local energy system, Journal of Scientific Research & Reports, 2016;9(3): 1-12.
2. Umeda J, Kondoh, K. High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic impurities removal, Industrial Crops and Products, 2010;32(3): 539-544.
3. Lonappan L, Rouissi T, Das RK. Adsorption of methylene blue on biochar microparticles derived from different waste materials, Waste Management. 2016;49:537–544.
4. Naghdi M, M. Taheran M,. Pulicharla R. Pine-wood derived nanobiochar for removal of carbamazepine from aqueous media: adsorption behavior and influential parameters, Arabian Journal of Chemistry. 2019;12:5292–5301.
5. Sulaiman GM, Mohammed WH, Marzoog TR, Al-Amiery A, Kadhum AH. Greensynthesis, antimicrobial and cytotoxic effects of silver nanoparticles using Eucalyptus chapmaniana leaves extract, Asian Pacific Journal of Tropical Biomedicine. 2013;3:58–63.
6. Noreen S, Abd-Elsalam KA. Biochar-based nanocomposites: a sustainable tool in wastewater bioremediation, in: K.A. Abd-Elsalam, M. Zahid (Eds.), Applications of Nanomaterials for Water Purification, Micro and Nano Technologies, Aquananotechnology. 2021;185–200.
7. Ramanayaka S, Vithanage M, Alessi D,. Liu WJ, Jayasundera ACA, Ok YS. Nanobiochar: production, properties and multifunctional applications, Environmental Science:Nano. 2020;7:3279–3302.

8. Lyu H, Gao B, He F, Zimmerman AR, Ding C, Huang H, Tang J. Effects of ball milling on the physicochemical and sorptive properties of biochar: experimental observations and governing mechanisms, Environmental Pollution. 2018;233:54–63.
9. Ramanayaka S, Tsang DCW, Hou D. Green synthesis of graphitic nanobiochar for the removal of emerging contaminants in aqueous media, Science of the total environment. 2019;310:107306.
10. Wen P, Wu, Z, He Y, Ye BC, Han Y, Wang J, Guan X. Microwave–assisted synthesis of a semi–interpenetrating polymer network slow–release nitrogen fertilizer with water absorbency from cotton stalks, ACS Sustainable chemistry & Engineering. 2016;4(12): 6572–6579.
11. Yiman Jia, Zhengyi Hu, Jing Mu, Wantong Zhang, Zijian Xie and Guoxi Wang. Preparation of biochar as a coating material for biochar-coated urea. Science of the Total Environment. 2020;731:139063.
12. Gong, Shang Li, Xiaolong Song, Fangxiang Lu, Dinghui Chen, Qianlin. Preparation and application in HDPE of Nano-$CaSO_4$ from phosphogypsum, ACS Sustainable Chemistry & Engineering. 2020;8(11): 4511-4520.
13. Chia CH, Gong B, Joseph SD, Marjo CE, Munroe P Rich AM. Imaging of mineral−enriched biochar by FTIR, Raman and SEM–EDX, Vibrational Spectroscopy, 2012;62:248−257.
14. Purakayastha TJ, Kumari S and Pathak H. Characterisation, stability, and microbial effects of four biochars produced from crop residues, Geoderma. 2015;239:293−303.
15. Downie AE, Van Zwieten L, Smernik RJ, Morris S, Munroe PR. Terra Preta Australis: Reassessing the carbon storage capacity of temperate soils. Agriculture, Ecosystems and Environment, 2011;140(1−2):137−147.
16. Mukome FN, Zhang X, Silva LC, Six, J, Parikh, SJ. Use of chemical and physical characteristics to investigate trends in biochar feedstocks, Journal of Agricultural and Food Chemistry. 2013;61:2196–2204.
17. Zhang Y, Li Z, Mahmood I. Recovery of NH_4^+ by corn cob produced biochars and its potential application as soil conditioner, Frontiers of Environmental Science & Engineering. 2014;8:825–834.
18. Zornoza R, Moreno-Barriga F. Acosta J, Munoz M, Faz A. Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments, Chemosphere. 2016;144:122–130.
19. Nurhidayati N, Mariati M. Utilization of maize cob biochar and rice husk charcoal as soil amendment for improving acid soil fertility and productivity, Degraded and Mining Lands Management. 2014;2:223–230.
20. Yu J, Zhao Y, Li Y. 2014. Utilization of corn cob biochar in a direct carbon fuel cell, Power Sources. 2014;270:312–317.
21. Strnad S, Kreze T, Stana KK, Ribitsch V. Correlation between structure and adsorption characteristics of oriented polymers, Material Research Innovations 2001;4(2-3):197-203.
22. Saeed, A H, Harun N Y, Sufian S, Afolabi H K , Al Qadami E H H, Roslan F A S., Rahim SA, Ghaleb AS. Production and characterization of rice husk biochar and Kenaf biochar for value-added biochar replacement for potential materials adsorption, Ecological Engineering & Environmental Technology. 2021;22:1-8.
23. Chia C H, Gong B, Joseph S D, Marjo C E, Munroe P Rich AM. Imaging of mineral−enriched biochar by FTIR, Raman and SEM–EDX, Vibrational Spectroscopy 2012;62:248-257.

24. Lehmann J. A handful of carbon. Nature. 2007;447:143–144.



a



b

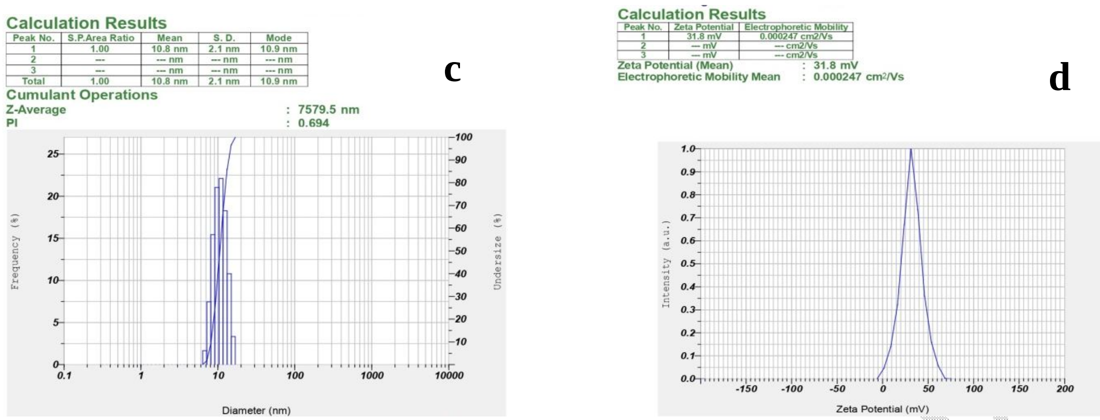
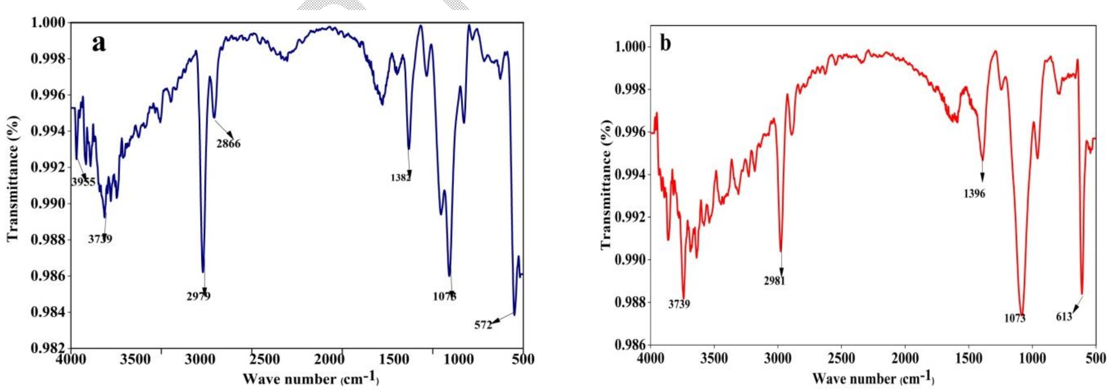


Fig.1. (a-d) Size and zeta potential of synthesized of (a) RHBB N - (size: 2085.7 nm), (b) RHBB N – (zeta potential: -37.1 mV) and (c) RHBB K (size: 1644.1 nm), (d) RHBB K (zeta potential: 33.2 mV).



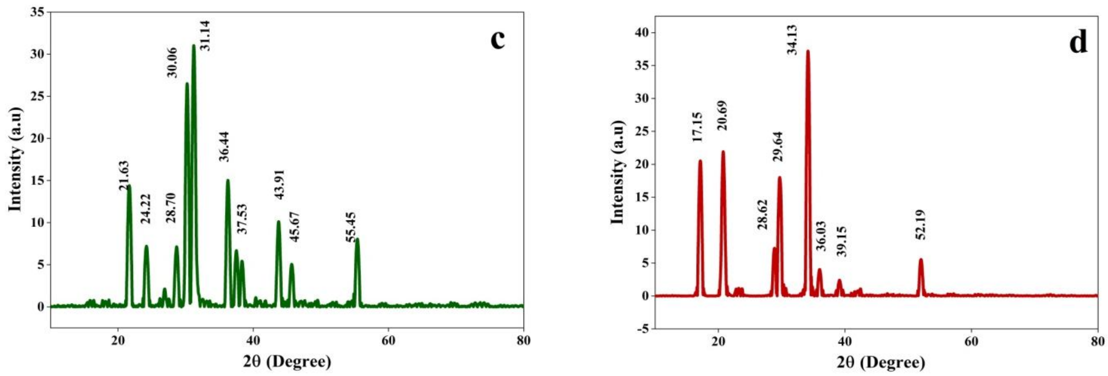
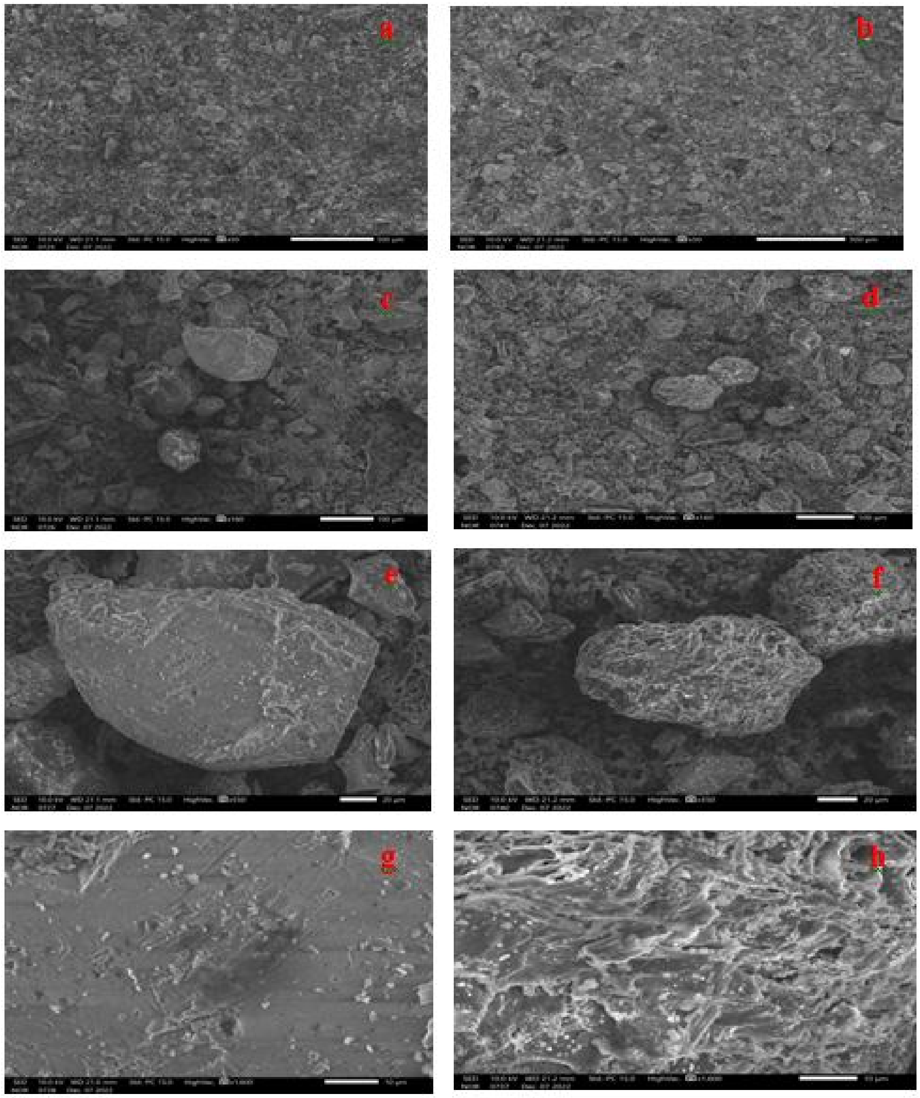
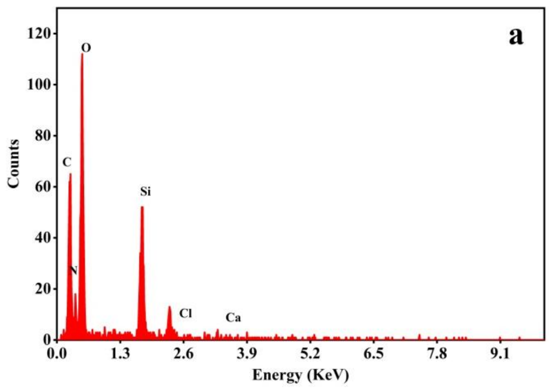


Fig. 2. (a-d) FT-IR micrograph provides evidence of distinct functional groups present on the surfaces of RHNB N and RHNB K and more noticeable peak size is observed in case of RHNB K (b) compare to RHNB N (a). If peak size is more, more react with the materials. Crystal structure of the synthesized RHNB N (c), RHNB K (d) were analyzed using XRD (X-ray diffraction). Distinctive diffraction peaks were observed in the crystal structure analysis of RHNB N, specifically at 21.63, 30.06 and 31.14 and 36.44, while RHBB K exhibited notable peaks at 17.15, 20.69, 29.64 and 34.13.



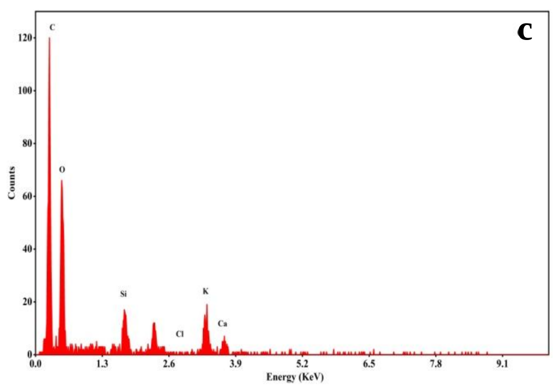
h

Fig. 3. SEM images of RHNBB N and RHNBB K at resolutions of 500 µm (a & b), 100 µm (c & d), 20 µm (e & f) and 10 µm (g & h), respectively, showing more porous structure of rice husk nanobiochar-based N and K fertilizers while white colour represents the impregnation of nutrients.



b

Element	Weight %	Atomic %	Error %
C K	18.95	27.53	20.17
N K	6.02	7.5	35.96
O K	41.68	45.47	11.32
FeL	0.9	0.28	81.27
NaK	2.13	1.61	30.27
SiK	21.82	13.56	8.53
P K	1.42	0.8	23.62
ClK	2.19	1.08	31.68
K K	3.2	1.43	23.44
CaK	1.69	0.74	23.75



d

Element	Weight %	Atomic %	Error %
C K	24.29	37.68	13.39
N K	2	2.66	88.92
O K	32.76	38.15	13.59
FeL	1.27	0.42	77.52
NaK	2.06	1.67	29.62
SiK	7.24	4.8	13.16
P K	1.06	0.64	22.92
ClK	2.22	1.16	30.56
K K	19.38	9.23	11.52
CaK	7.71	3.59	17.65

Fig. 4. Elemental analysis (EDX) of RHNB N (a, b), RHNB K (c, d) represents the detailed composition of macro, secondary and micro nutrients.