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A New Direction in Wheat Cultivation by Preparation of Biochar and Rice Straw NPK Slow-Release Fertilizers to Improve Nutrient Release Performance

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Abstract

It is documented that biochar has a well-established solute adsorption capability and a few studies on the subject have been published, our goal in using slow-release fertilizers is to reduce the amount of vital nutrients that are lost during the agricultural process. In this study, commercial fertilizer was enhanced with biochar and rice straw, and the patterns of nutrient release were compared to those of conventional fertilizer. The production of Blank slow-release fertilizer (BL),Rice straw slow-release fertilizers (RSSRF) and Biochar slow-release fertilizers (BSRF) was revealed by X-ray powder diffraction (XRD), Infrared (IR) measurements, Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX). Fertilizer release is conducted using a column technique which verified that BSRF exhibits lower release behavior of NO_3^-, PO_4^{3-}, and K^+ than both commercial fertilizers and RSSRF. BSRF might be able to lower nutrient leaching and hence raise crop nutrient efficiency. This outcome inspires us to Subsequent investigations ought to concentrate on comprehending the processes involved in nutrient release, aligning nutrient release with plant uptake, and utilizing the BSRF in environmental remediation.

Keywords: Biochar, Slow-release fertilizers, Rice straw and commercial fertilizers.

1. Introduction

The growing world population raises the need for food. This necessitates intensifying and raising the caliber of the harvested crops in addition to the restricted quantity of arable land. Fertilizers, both natural and synthetic, are utilized to address this issue [1]. The process of fertilizing soil involves adding the right amount of mineral materials to it to enrich it with nutrients for plants [2]. Since the qualities of these elements govern the soil's fertility, fertilizers' purpose is to supply nutrients (primarily nitrogen (N), potassium (K), and phosphorus (P) [3]. Due to quick losses to the environment, only 40%–70% of the nitrogen and 80%–90% of the phosphorus included in conventional fertilizers are not absorbed by crops [4]. Potassium fertilizer is lost by leaching and surface runoff; phosphate fertilizer is lost through ineffective transformation and surface runoff; and nitrogen fertilizer is lost through denitrification, volatilization, and leaching [5]. Slow-release fertilizers decrease environmental contamination and increase nutrient utilization as compared to regular fertilizers. As contrast to other straw types including wheat straw (5.0–8.5%), barley straw (7.4%), corn straw (5.1–7.9%), and sugarcane straw (4.1%), pristine rice straws often have a higher ash concentration (8.5–20.4%) [6]. According to [7], rice straw also contains approximately 40% carbon, 30% oxygen, 5%–6% hydrogen, 1% nitrogen, and less than 2% sulfur. These straw-type biomasses typically have a low moisture content of less than 10% and a comparable elemental makeup (C, H, N, S, and O), making them an excellent feedstock for pyrolysis to produce biochar [8]. Furthermore, rice straw's moderate fixed carbon content makes it a better option for carbon-based adsorbent synthesis than other straw-type biomass like sugarcane and wheat straw [9]. Direct mixing, encapsulating, and pelletizing are the methods used to produce biochar-based fertilizer [10]. In order to create nitrogen-enriched organic matter that has been enhanced with high-quality fertilizer, biochar is thought to be an excellent carrier material [11]. Biochar is a carbon-rich substance obtained from the pyrolysis of biomass in the absence of oxygen, and it is one of the agricultural products [12], [13]. The application of biochar to a soil can also improve plant

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productivity and soil fertility [14]. However, a number of studies indicate that this material should be modified before being added to the soil [15], [16]. Furthermore, biochar has the ability to enhance a number of soil properties, including soil organic carbon content and cation exchange capacity (CEC) [17], [18]. The majority of research studies have focused on using biochar as a supporting material for the impregnation process, which involves soaking the powdered biochar in a commercial fertilizer solution to create a controlled-release fertilizer[19]. This study was to produce biochar and rice straw with N, P and K commercial fertilizers, which are uncoated slow-release fertilizers, and to examine the wheat planted in soil. Biochar is thought to be an excellent carrier material to create nitrogen-enriched organic matter that has been enhanced with high-quality fertilizer.

2. Experimental

2.1. Raw materials and chemicals

Raw material; Ricehusk (Sakha 101 c. v, Oryza sativa L.) was collected in summer season,2021 from the farm of Rice Research and Training Center, Sakha, Kafr El-Sheikh, Egypt. The dried straw was washed by distilled water to remove dust, oven-dried at 70 °C for 10 h, and ground. Biochar was prepared by using rice husk as a raw material. Rice husk (Sakha 101 c. v, Oryza sativa L.) was collected in summer season, 2021 from rice hulling machine near to Kafr El sheikh city at the north part of Egypt. Chemicals including Urea (46% N) was bought from Alexandria Fertilizers Company (Egypt),commercial fertilizers, single super phosphate (12% P_2O_5)Egyptian Financial and Industrial Company (Egypt)and Potassium sulfate (50% K)from Sesoda corporation company (Taiwan).Sulfuric acid from Merck (USA),Sodium hydroxide El-Nasr Pharmaceutical Chemicals Company (Egypt) and boric acid ADWIC (Egypt).

2.2. Biochar production

The rice husk was heated at 420 °C in oxygen-limited conditions and was held for1 h. Biochar was then cooled to room temperature in stainless steel sealed container to prevent the biochar from exposure to oxygen. Prior to being used at the field site or used to make fertilizers based on biochar, the biochar was powdered, put through a 0.25 mm sieve.

2.3. Synthesis of BL, RSSRF and BSRF

12.6 g of Urea (NH_2CONH_2), 7.2 g of Single Super Phosphate (SSP), and 3.6 g of Potassium Sulfate (K_2SO_4) were dissolved in distilled water to prepare an N-P-K nutrient solution. The rice straw for RSSRF, rice husk biochar for BSRF, and nothing for BL were combined with the N-P-K nutrient solution in a beaker and left to stand for three days at room temperature. The three mixtures were passed through a bean mincer fitted with a 10-mm die extruder. The slow release fertilizers (SRFs) were thus produced as around 10-mm cubic strands, which were subsequently hand-cut into smaller bits measuring roughly 10 mm in length. After being air-dried at room temperature, the SRF cubes were kept in tightly sealed glass bottles until they were subjected to nutrient analysis.

2.4. Determination of nutrient release patterns

The purpose of these investigations was to confirm that nutrients were released from the BSRF. Every experiment was run in a glass column for 21 days. The glass column contains 5 gm of sand soil then 1 gm of BSRF was added. After 3, 7, 14, and 21 days, 30 milliliters of distilled water were taken out of the glass column. To track the nutrient leakage, it was labeled and described, respectively. A U-V visible spectrophotometer was utilized to calculate the concentrations of phosphate, while a flame photometer was used to evaluate the water samples for potassium ions.

2.5. Analytical characterization techniques

The sample morphology and crystal structure were characterized using X-ray powder diffraction (XRD)(Shimadzu XRD- 6000), Scanning electron microscope (SEM)(JEOL JSM-IT100),(SEM/EDX) and Fourier-Transform Infrared Spectroscopy (FT-IR)(JASCO FT/IR-6800).

2.6. Statistical analysis

Data collection and analysis were computed using Origin software and MS Excel. The experiments conducted for the physical parameters and slow release of nutrients in water were repeated three times, the results generated were taken as average results of all the three experiments for the research.

3. Results

3.1. Fourier transform infrared spectroscopy (FTIR)

Biochar has always been reported as a material of carbon nature along presence of many oxygen groups including carboxylic groups (-COOH) and hydroxylic groups (-OH) on its surface plane with pores throughout its structure [20]. Figure 1a shows the FTIR spectra of biochar prepared, the main bands in the range 1042–1512 cm^{-1}, implying the existence of large numbers of hydroxyl groups (-OH) and carboxylate group (-COOH) on the biochar[21]. Peaks arising at 1622 and1650 $cm^{-1}$are characterized for the ν(C=O) and $\nu(C = C)_{aromatic\ ring}$, certain peaks in the range of 3422–3446 cm^{-1} confirmed the hydroxyl group on the outside surface of the biochar indicating presence of moisture content also confirmed by Proximate analysis, so this spectrum should be assigned to ν (O–H)[22]. Furthermore, the peak at 2923 cm^{-1} were accredited to ν (–CH)[23]. The FTIR spectrum of pure urea (Fig. 1b) shows that ν(C=O)frequency appears at 1685 cm^{-1}.The bands of $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ appear at 3445 and 3345cm^{-1}, respectively while N-H deformation frequency appears at 1609 cm^{-1}. The ν(C–N)frequency band was observed at 1461 cm^{-1} [24]. The spectrum of SSP shows the band at 837 cm^{-1} which corresponds to HPO_4^{2-}[25].The bands observed at 3553 and 3413 $cm^{-1}$are attributed toν (H_2O) frequencies. The δ(H_2O) frequencies appear at 1693 and 1631 cm^{-1}.The ν_{as} (PO_2) and ν_s (PO_2) bands were observed at 1158 $cm^{-1}$and 1110 cm^{-1}, respectively. The band observed at 670 cm^{-1} is assignable to ν_L (H_2O) vibration mode and the $\nu_4(SO_4^{2-})$ frequency appears at 601 cm^{-1}.The band at 509 cm^{-1} is attributed toPO_2in plane symmetric deformation. The ν_2 (SO_4^{2-}) frequency appears at 460 cm^{-1}.The band observed at 424 cm^{-1} is assigned as bending mode of P $(OH)_2$[26].The infrared spectrum of potassium sulfate shows that the peaks observed at 3450 – 3224 cm^{-1} are due to ν (OH) of the HSO_4 groups. The band appeared at 1108 cm^{-1} is attributed to $\nu_{as}(SO_4^{2-})$ and ν_s (SO_4^{2-}) appears at 973cm^{-1} [27]. Hence we have assigned the frequency 496 cm^{-1} to symmetric bending of the SO_4 groups. The band observed at 620 cm^{-1} is assigned as asymmetric bending of the SO_4 groups [28].Figure 1c compares the FTIR spectra of the three samples; BL (Blank slow release fertilizer); RSSRF (RSSRF) and BSRF (biochar slow-release fertilizer), respectively. An insight at the figure indicates that in sample BSRF there is an enhancement in intensity of bands around 1621-1631cm^{-1}attributable to ν(C=O) and ν $(C=C)_{aromatic\ ring}$ and those at 3440 and 3444 cm^{-1}due to ν (OH) on the outside surface of the biochar indicating presence of moisture content so this spectrum should be assigned to O–H stretching. This in turn supports the existence of biochar in slow release fertilizer.

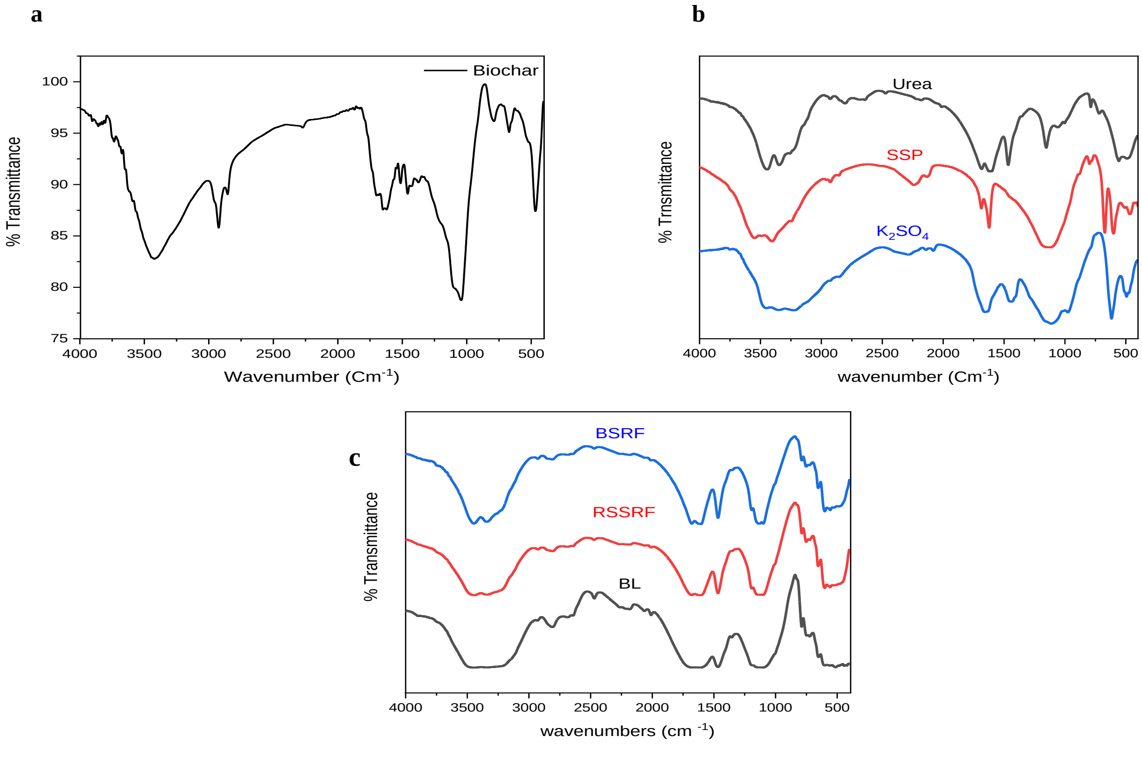

Figure 1: FTIR Spectra of Biochar (a),Urea, SSP (Single super Phosphate) and K_2SO_4(Potassium sulfate) (b) BL (Blank slow release fertilizer), RSSRF(rice straw slow-release fertilizer) and BSRF (biochar slow-release fertilizer) (c).

3.1.2. X-ray diffraction (XRD)

The peaks of urea (fig 2a) were indexed to the face-centered tetragonal structure, which is in good agreement with the JCPDS card no. 01-083-1436. The characteristic diffraction pattern shows sharp intense and narrow peaks at 21.86^o, 28.89^o, 24.19^o, 35.11^o, and 37.72^{o}2θ angles, corresponding to hkl parameters of (110), (111), (101), (210) and (201), respectively[29].The XRD pattern of single super phosphate fertilizer shows peaks at 2θ values of 11.38^o, 20.39^o, 23.06^o, 28.77^o, 30.94^o, 33.06^o, 40.08^o and 43.90^o as the main observed crystalline phases were Gypsum [$Ca(SO_4).xH_2O$] (PDF2 pattern files #01-089-1445 and #00-006-0226), and a phosphate-rich phase corresponding to dihydrogen calcium phosphate [$Ca(H_2PO_4)_2.xH_2O$] (PDF2 pattern file #00-009-0347). This result confirms the stages envisaged in the chemical reaction for the manufacture of P-fertilizer products [26].Figure 2b shows Peaks at 2θ values of 20.86^o, 30.01^o, 30.55^o, 36.45^o, 37.34^o, 39.76^o, 40.49 and 43.87^o corresponding to hkl parameters of (111), (022), (130), (040), (013), (212), (141) and (042), respectively match well with the result of the reported arcanite K_2SO_4 (JCPDS NO. 05-0613) [30], [31]. XRD pattern of the ricehusk biochar (fig 2c) Shows the intense peak at 21.7 ^{o} which represents to presence of SiO_2 into the sample as expected. The rice husk mostly contains silicon [32].The XRD patterns shows characteristic peaks at 2θ values 21.80^o, 24.16^o, 28.88^o,35.11^{o}and 37.80^o due topresence of urea. Peaks at 2θ values 30.88^o and36.69^o appeared dueto presence of K_2SO_4. On the other hand, small intensity peakat 2θ value 11.74^{o}is attributed to presence of single super phosphate fertilizer in spectrum (fig 2d).

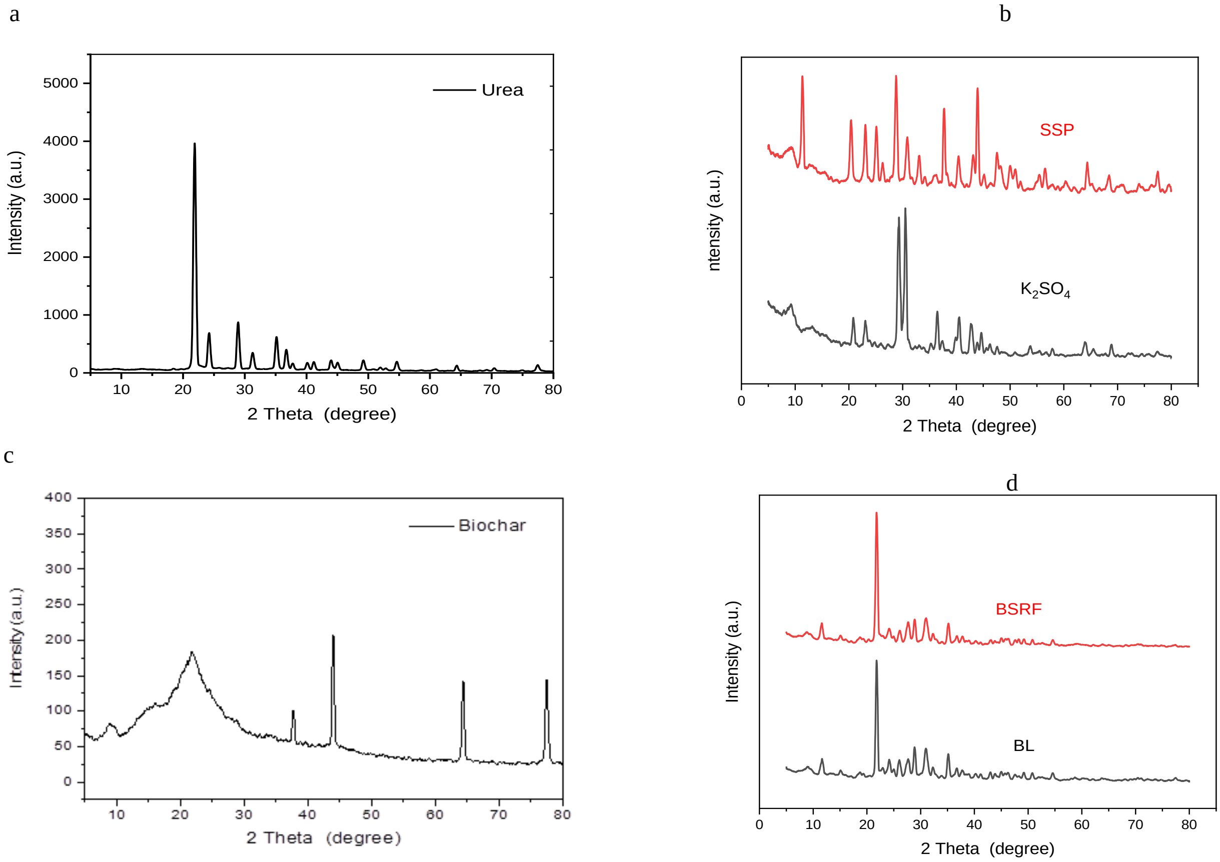

Figure 2: Powdered X.R.D diffraction patterns of urea (a), SSp and K_2SO_4 (b), Biochr (c) and BSRF (biochar slow-release fertilizer) and BL (Blank slow release fertilizer) (d).

3.1.3. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX)

To examine the impacts of rice husk biochar consumption on NPK commercial fertilizers, a surface morphology study was conducted on the biochar slow-release fertilizer. SEM pictures (Fig. 3) show the intricate morphology of the samples that were generated in order to see structural alterations in the NPK fertilizers in the Blank slow-release fertilizer sample. As opposed to figure 3 (C, D), figure 3 (A, B) shows that the morphological structure of commercial NPK fertilizer was moredense. The morphological structure of the slow-release fertilizer made of biochar is more porous because the rice husk biochar has pores that create an elongated structure with a smooth surface [33]. The high temperature pyrolysis process that released the volatile materials from the biomass sample resulted in the formation of the porous and spongy structure of biochar[34]. The attachment of micronutrient components to the biochar causes the surface of the slow-release fertilizer made of biochar to become somewhat rough. This is another phenomena [35]. Using EDX, the various samples' elemental analysis was carried out (Fig. 4 A and B). When the two figures are compared, it is evident and verified that rice husk biochar is impregnated with N, P, and K to create BSRF.

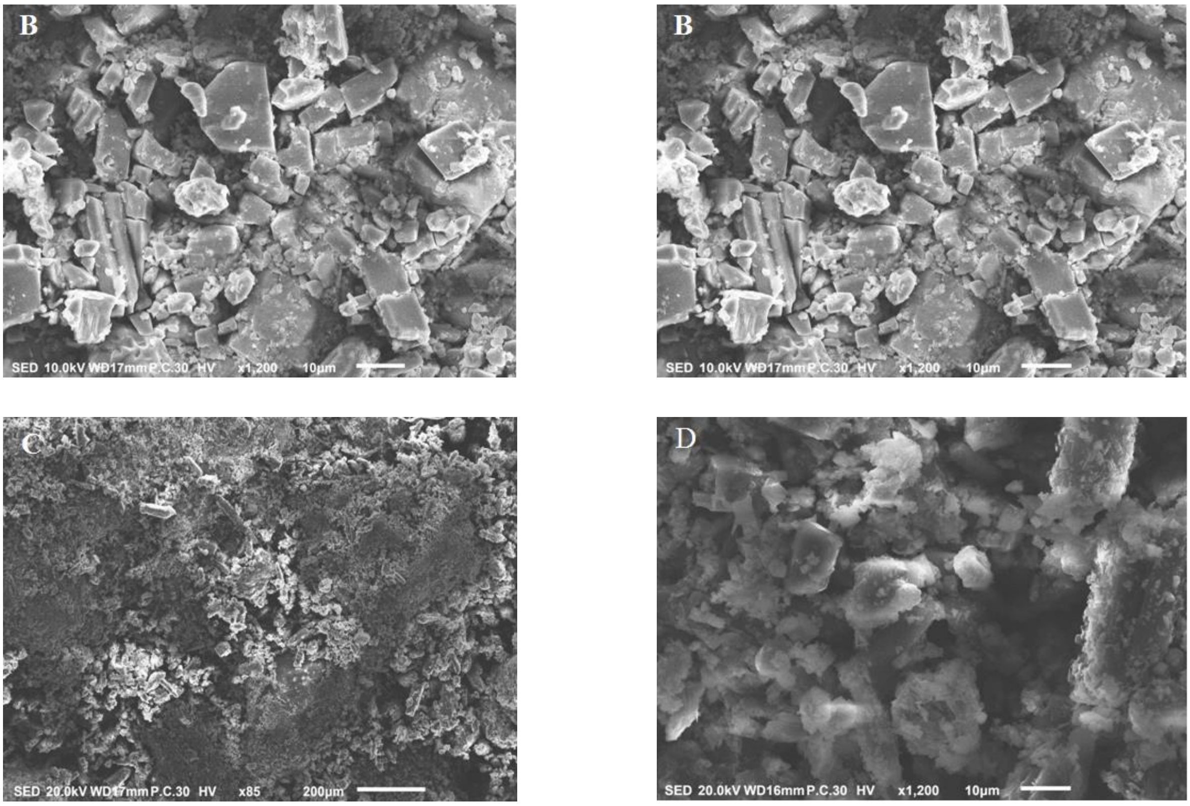

Figure 3: SEM images of BL at (A and B at 200 µm and 10 µm resolution)and BSRF(C and D at 200 µm and 10 µm resolution).

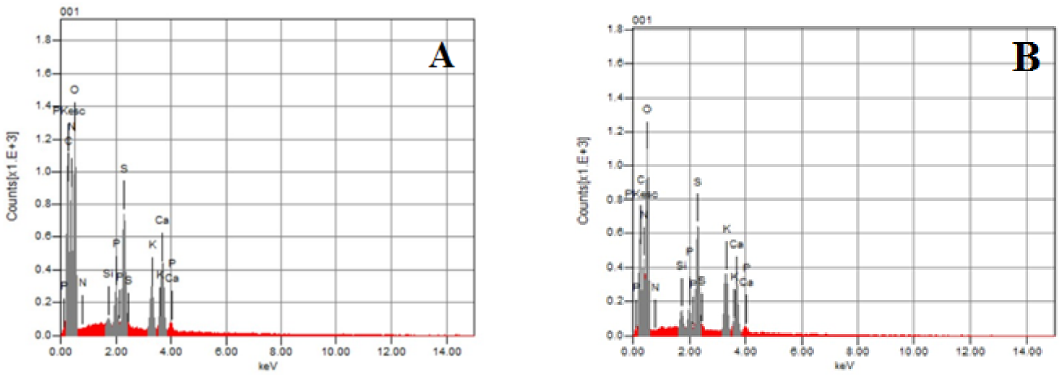

Figure 4: EDX spectra for BL(A) and BSRF(B).

3.2. Evaluation of metal concentrations from commercial and Slow-release fertilizers

Figure 5 shows the values of leached metal ions from commercial fertilizers (C), blank slow release fertilizer (BL), biochar slow-release fertilizer (BSRF) and rice straw slow-release fertilizers (RSSRF) by the applied extracting agents H_2SO_4 and $HClO_4$. The results indicated that the contents of the investigated metals in the commercial fertilizer (C) are greater than that of the slow-release fertilizers (BL, BSRF and RSSRF).

Table 1: Analysis of N, P and K ions in (C, BL, RSSRF and BSRF)

sample	N (mg L^{-1})	P(mg L^{-1})	K(mg L^{-1})
C	230384	14880	67470
BL	224840	9552	64350
RSSRF	218064	10992	65910
BSRF	229768	10272	64350

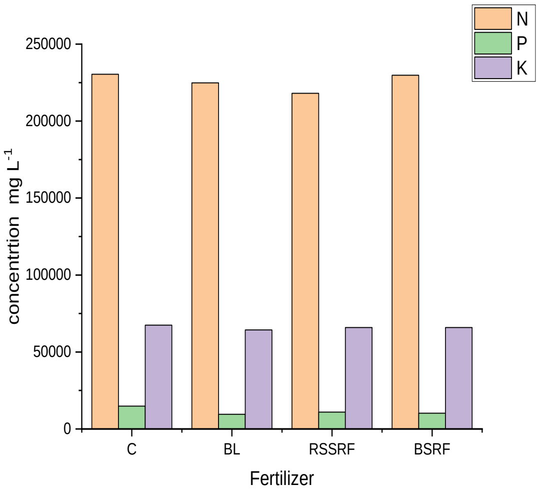

Figure 5: Analysis of N, P and K ions in (C, BL, RSSRF and BSRF).

3.2. Slow-release studies

Fertilizer nutrient release patterns were characterized by an initial high release of phosphorus and nitrogen within the first seven days, and potassium and nitrogen within the first three days (table 2). This discovery was attributed to nutrient washout and quick diffusion. The biochar slow release fertilizer's cumulative nitrogen release rate is displayed in fig. 6b. On the seventh day, the cumulative nitrogen release rate of BSRF was nearly 69.65 %, and on the twenty-first day, it exceeded 88.86 %. On the seventh day, nevertheless, the cumulative nitrogen release rates of B and the rice straw slow release fertilizer RSSRF were 98.24 % and 100.0%, respectively. The slow-release performance of BSRF was good. Hydrophobicity and a porous structure characterize biochar. Initially, just a portion of the pores in biochar may be utilized to transmit nutrients and allow water to pass through [36]. Because water is difficult to enter the pores of biochar, the diffusion of water may be limited, thus limiting nitrogen release [37]. Furthermore, through nitrogen adsorption (NH_4^+-N and NO_3^--N), biochar with a large specific surface area and negative surface functional groups might further limit nitrogen loss [38]. After seven days, the cumulative rate of P releases from BSRF (64%) is substantially lower than that of BL and RSSRF fertilizers (88 and 74%). Fertilizer P release patterns showed an overall downward trend over time (fig. 6c). Since the cumulative rate releases for the BSRF, RSSRF, and B fertilizers were 90%, 96%, and 97% of the monitoring period, respectively, the full release of P was not measurable at the conclusion of the experiment (fig. 6d). Fig. 4e displays the K slow-release performance of several SRFs. For a period of fourteen days, it was found that the cumulative rate of K release from BSRF was substantially lower than that of compounds BL and RSSRF. For BL and RSSRF, complete release of K is attained in 14 days and for Band RSSRF in 21 days, respectively, indicating that BSRFs function better during slow releases. Compound BL released a higher cumulative rate of K than did compound BSRF overall (fig. 6f). In fact, a number of published research have also discovered that the pore structure of biochar, which would slow down fertilizer diffusion, may be responsible for the release of K from biochar-based fertilizers.[19]. For fertilizers (C, BL, RSSRF and BSRF), K release generally decreased over time [39].

Table 2: Instantaneous concentration and cumulative rate of N, P and K released from C (Commercial fertilizers), BL (Blank slow release fertilizer), RSSRF (rice straw slow-release fertilizer) and BSRF (biochar slow-release fertilizer) during a 21-day period of sequential leaching.

sample	Time (day)	Concentration (mgL^{-1})			Cumulative rate (%)		
		N	P	K	N	P	K
C	3	221760	10073.7	66456	96.25	67.61	98.45
	7	9240	4535.7	1064.7	100	98.05	100
	14	0	0	0	100	98.05	100
	21	0	0	0	100	98.05	100
BL	3	160776	5272.8	41652	71.52	54.93	64.68
	7	60060	3209.7	21762	98.24	88.36	98.47
	14	0	592.8	1170	98.24	94.53	100
	21	0	292.5	0	98.24	97.58	100
RSSRF	3	148764	5050.5	41652	68.21	45.91	63.20
	7	71148	3170.7	21294	100	74.74	95.52
	14	0	1283.1	1404	100	86.40	97.65
	21	0	1068.6	0	100	96.12	97.65
BSRF	3	115500	3942.9	36972	50.26	38.28	57.41
	7	44352	2694.9	18954	69.56	64.44	86.84
	14	34188	1641.9	4563	84.44	80.39	93.93
	21	10164	1080.3	3861	88.86	90.87	99.92

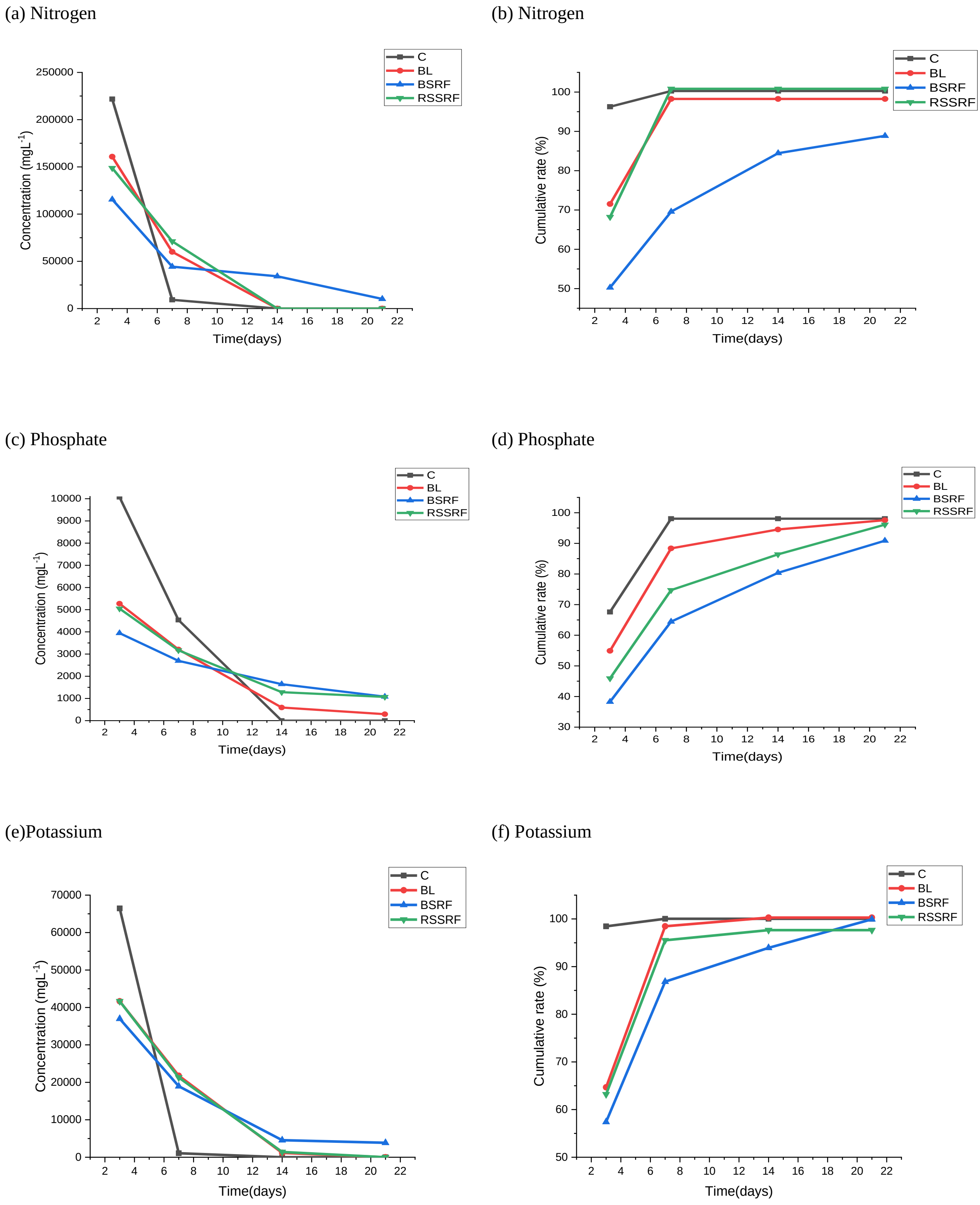

Figure 6: Instantaneous (a, c, e) and cumulative (b, d, f) concentration of Nitrogen, phosphate and potassium released from C (Commercial fertilizers), BL (Blank slow release fertilizer), RSSRF (rice straw slow-release fertilizer) and BSRF (biochar slow-release fertilizer) during a 21-day period of sequential leaching.

3.3. Effect of BSRF on N, P and K in soil and wheat plant

Figures (7& 8) showed that there is no discernible difference between the control and other treatments in terms of soil accessible nitrogen concentrations. The biochar slow-release fertilizer (BSRF) treatment had the lowest accessible potassium and phosphorus levels at 15.34 ppm and 382.20 ppm, respectively (table 3). This is because BSRF can severely limit the release of these nutrients into the soil. Over time, biochar has the ability to bind, adsorb, and retain mineral minerals; the nutrients are only released when required by plant roots [40]. The balance between the concentration of nutrients in the biochar and those in the soil controls this natural process of nutrient release in the soil [41].The release of potassium and phosphorus from biochar slow-release fertilizer (BSRF) increases over time, albeit at a decreasing rate. Figure (9) and table 4 indicated that BSRF has the highest nitrogen and phosphorus uptake of wheat grains 540.40 and 124.60 mg/pot, respectively.

Table 3: Soil chemical prosperities after harvesting wheat plants.

Properities / Sample	EC_e dS/m	pH	available N(ppm)	Available P(ppm)	Available K(ppm)
C	0.31	7.46	30.80	17.68	471.90
BL	0.32	7.55	30.80	19.67	391.30
BSRF	0.33	7.49	30.80	15.34	382.20

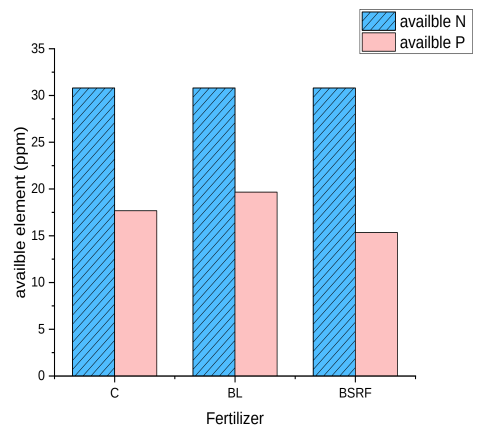

Figure 7: Concentrations of available nitrogen (shadowed) and harvesting wheat plants.

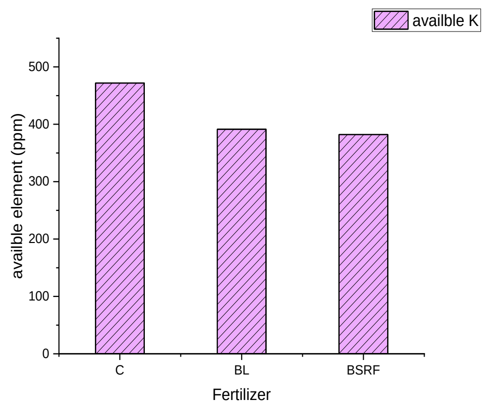

Figure 8: Concentrations of available potassium after available phosphorus (plain) after harvesting wheat plants.

Table 4: Effect of different slow-release fertilizers on N, P and K uptake of Wheat grains**.**

Treatment	N-Uptake (mg/pot)	P-Uptake (mg/pot)	K-Uptake (mg/pot)
C	520.72	91.60	123.5
BL	394.85	83.34	73.19
BSRF	540.40	124.60	90.93

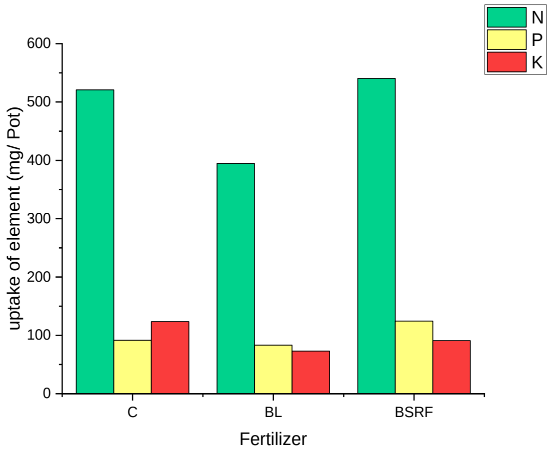

Figure 9: Effect of different slow-release fertilizers on N, P and K uptake of Wheat grains.

4. Conclusion

Biochar was created by pyrolyzing rice husk. SEM scans demonstrate that the generated samples have a superior porous pattern. The nutrient release patterns of a slow-release fertilizer made of biochar were compared to those of standard chemical fertilizers. Biochar proved to be a useful ingredient for the production of an N-P-K fertilizer, as demonstrated by SEM and EDX tests. The slow-release biochar fertilizer released nutrients less than compound C, suggesting that it could be a better option than traditional chemical fertilizers. Increased crop nutrient use efficiency is implied by the gradual release characteristic, which also suggests decreased nutrient leaching.

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