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Incorporation of biochar and semiinterpenetrating biopolymer to synthesize new slow release fertilizers and their impact on soil moisture and nutrients availability

Muhammad Imran Rafique^{1 \boxtimes}, Mohammad I. Al-Wabel¹, Abdullah S. F. Al-Farraj¹, Munir Ahmad¹, Taieb Aouak², Hamed Ahmed Al-Swadi¹ & Mohammed Awad Mousa¹

Chemical fertilizers (CFs) are indispensable nutrients source for plants replenishing them with essential nutrients. However, their over-utilization imposed destructive consequences of excessive loss of major nutrients resulting in low nutrient use efficiency and further environmental concerns. Therefore, to counter excessive application of CFs and to regulate sustainable agriculture, a novel biochar (BC)-based slow-release fertilizer (SRF) was developed by incorporating mica (MI) and semi-interpenetrating chitosan polymer (Semi-IPN) via graft co-polymerization. Fabricated SRFs were characterized and their nutrient release dynamics as well as soil water holding (WH) and water retention (WR) capacity were investigated. The results revealed that BC-based SRFs, particularly BC-SRF and BCMI-SRF, enhanced soil WH capacity by 40.61% and 47.80%, respectively, whereas the highest soil WR capacity was recorded as 32.55% and 35.52% respectively, after 30 days. The nutrients (NH⁺-N, P, K) release ratio of CF and MI was recorded in the range of 85–100%, however BC and MI incorporated SRFs showed splendid slow release nutrients dynamics and release 75.53% of NH, +-N, 65.66% of P and 71.83% of K in a 30 days incubation experiment. Nutrient release kinetics exhibited diffusion and mass transport as the major nutrient release mechanisms, which was confirmed by the best fitted parabolic diffusion and first order kinetics models. Hence, current study inclusively demonstrated new routes for synthesis of innovative and eco-friendly SRFs with substantial slow-release performance to overcome excessive nutrient loss by application of CF.

Keywords Slow-release fertilizer, Water retention, Polymer, Nutrient release kinetics, Mica

During last few decades conspicuous increase in application of chemical fertilizers (CFs) was recorded, which was quite anticipated to increase crop production to fulfil increasing food demand globally. An estimated global demand of CFs (N, P, and K) reached 185.1 million tons in 2022¹. Farmers reaped sufficient fortune in securing higher food production by employing conventional CFs; however, it resulted in some calamity such as secondary pollution caused by excessive nutrient release from CF, lower fertilizer use efficiency (FUE), higher production cost, and poor soil health due to degraded soil structure, nutrient imbalance, and accumulation of pollutants². Liu et al.³ and Jain et al.⁴ reported that only 30–60% of N, 10–20% of P and 30–50% of K is absorbed and utilized by plants and crops, while rest is either fixed or precipitated in soil, which ultimately restrained in soil matrix unavailable for plant uptake, while, ground water leaching, surface runoff, and volatilization also result in major loss of nutrients. To ensure incessant, copious, and sustainable production of food, it is very important to maintain better soil quality and improved soil health of arable lands. Healthy soil with profuse moisture contents, plenteous organic compounds, and essential nutrients supports better plant growth and enhances crop yield which consequently fortify sustainable and enormous food production⁵.

Recently, evolution of slow release fertilizers (SRFs) has emerged as one of the key strategies to subside nutrient loss and ultimate enhancement in plant production and crop yield. Generally, SRFs release nutrients at

¹Soil Sciences Department, College of Food & Agricultural Sciences, King Saud University, P.O. Box 2460, 11451 Riyadh, Kingdom of Saudi Arabia. ²Department of Chemistry, College of Science, King Saud University, 11451 Riyadh, Saudi Arabia. ^{Semenail}: mrafique@ksu.edu.sa controlled and slow rate than traditional fertilizers for prolonged period which is conducive for plants to ensure better nutrient uptake. Additionally, SRFs are regarded as an effective way to recover aquatic and terrestrial environment by mitigating negative impacts of CFs pollution such as eutrophication, ground water leaching of nutrients, phosphorus fixation with soil particles and greenhouse gasses emission⁶. In recent years ample work is being done on formulation and development of SRFs and different types of SRFs has been formulated such as urea based SRFs, (formaldehyde, isobutylidene diurea, and triazone), magnesium ammonium phosphates, and nutrient enriched compost with persistent nutrient supply and slow release mechanism⁷.

In addition to precision fertilization, irrigation and optimum soil moisture are the key factor for promoting plant growth and enhancing agriculture production, especially in arid and semi-arid environments. Soils in arid and semi-arid regions are denoted with infrequent rains, hot climate and insufficient water resources and farmlands in these areas suffer water shortage which compels wise and effective utilization of limited water resources. Intensive water shortage in such regions threatens to food shortage, potential health issues, disturbance in ecosystem and lower crop production⁸. In addition to this, contamination of groundwater resources by agricultural load, excessive implication of CFs, and salinization has been reported by earlier studies^{9–11}. Thus, understanding of such water shortage problems urges to search efficient solution to conserve quality and quantity of water resources in these regions.

In recent times, synthesis and application of super adsorbent polymers (SAPs) has emerged as an efficient strategy to conserve water resources. Owing to their excellent water absorption and water retaining capacities, application of such SAPs encouraged agricultural activities in arid and semi-arid soils with improved water holding (WH) and water retention (WR) capacity of soil, reduced irrigation frequency and better crop growth¹². Besides all of their beneficial and lucrative characteristics, SAPs exhibits weak mechanical strength, and poor resistance to external force which ultimately effects their performance in conserving water resources and improving soil moisture¹³. Recently development of semi-interpenetrating (Semi-IPN) polymer network showed superior performance in retaining soil moisture over single polymer substrate. Semi-IPN polymer network is blend of couple of polymers which hold linear and elastic polymer chains diffused into monomer and polymer network with non-covalent interaction¹⁴. The product developed by Semi-IPN polymer network technology could be helpful in improving soil WR capacity and provide plant with moisture for prolonged period.

Researchers have developed various technologies to formulate and synthesize different kinds of SRFs such as polymer coated SRFs, hydrogel based SRFs, brown coal based SRFs, clay and biochar (BC) based SRFs, carbon based SRFs and nano structured SRFs^{15,16}. Engaging BC in designing and synthesizing SRFs could improve its nutrient release performance and improve overall soil health. The carbon enriched solid material BC, which is generated by thermal degradation of organic waste in an oxygen limited environment, is a low cost, permeable, and greener material¹⁷. Synthesis of BC provides a suitable pathway for better recycling of organic waste and transforming it into some useful material which could ultimately mitigate soil nutrient loss, greenhouse gases emission effect, and land air pollution caused by open burning of organic waste¹⁸. Likewise, BC is known for having ample surface area, porous structure, plenty of surface functional groups, high cation exchange capacity (CEC), sufficient sorption potential, and nutrient retention capacity^{19,20}. Moreover, BC has enough nutrient holding and retention ability, which could be further refined by engaging it to generate BC based SRFs (BC-SRFs)²¹. Application of BC-SRFs in soil aided higher nutrient uptake by plants through slow release pathway with ultimately reduced nutrient loss from soil⁶. However, BC-SRFs showed inconsistent performance specially in arid and semi-arid soil with zero to marginal increase in soil moisture¹⁶. Therefore, developing SRFs based on BC and Semi-IPN polymer network could be an anticipative strategy to ensure consistent nutrient supply and maintain optimum soil moisture specially in water strained environment.

Among several natural polymers, chitosan has emerged as biodegradable, non-hazardous, and linear copolymer with numerous useful agricultural and biomedical applications²². Chitosan is also recognized for its excellent binding ability, chelating properties, bundle of diverse surface functional groups and biocompatibility, which make it a suitable surface coating and carrier material in SRFs production²³. Mica (MI), a silicate clay mineral, has been extensively used as reinforcing filler for polymer and provide polymer with resistance against chemical abrasion, mechanical and dimensional stability and refined particle-matrix interaction^{24,25}. Additionally, it is also pronounced as a good soil available K supplement²⁶. To best of our knowledge, very little research work is reported regarding employing chitosan in Semi-IPN polymer along with BC to develop SRF. Therefore, utilization of chitosan in producing MI filled Semi-IPN polymers and its combination with nutrient enriched BC could be very useful technique to produce new SRFs with excellent WH and WR ability. Insight to this context, new kind of SRFs based on BC with MI filled Semi-IPN polymer were synthesized. Freshly synthesized SRFs were tested for their performance in improving soil WH and WR capacity in research experiment. Additionally, an incubation study was conducted to explore nutrient release performance of synthesized SRFs.

Materials and methods

Production and nutrient enrichment of biochar

Conocarpus (*Conocarpus erectus* L.) waste was used as a feedstock (biomass) to produce BC. Biomass (BM) was collected from King Saud University campus, Riyadh, Saudi Arabia. Prior to slow pyrolysis in the Digital Muffle furnace (Wisetherm FH14, Germany), the collected BM was washed with deionized water, air dried, cut into small pieces. Pyrolysis temperature was set at 400 °C with a residence time of 3 h and 5 °C per minute temperature rise. Later on, the produced BC was collected, cooled at room temperature, crushed, grinded to small particle and sieved through 1 mm mesh aperture, stored in an airtight acrylic container and tagged as BC. To generate nutrient loaded BC (BC-NPK), nutrient solutions of N, P, and K containing 0.25 M concentration of each element was prepared in deionized water by using CH_4N_2O (Urea) and KH_2PO_4 (Potassium dihydrogen phosphate) as source compounds. Subsequently, in a glass beaker, filled with 100 mL of NPK solution, 20 g of BC was added. The beaker was placed at hot plate and stirred at 40 °C and 700 rpm until homogeneous mixture.

After acquiring a homogeneous mixture, the solution was removed from hot plate, cooled, filtered through a Whatmann filter paper and solid material from the filter paper was collected and oven dried at 50 °C. The resultant solid material was crushed, grounded and sieved by 0.5 mm size mesh, stored in air tight container and tagged as BC-NPK.

Synthesis of SRFs

To generate SRFs, the BC-NPK was initially mixed with finely grounded MI powder in an aqueous solution, which was latterly grafted with chitosan particles by following solution polymerization procedure (high density pure Chitosan powder was purchased from Chemsavers chemicals). Briefly, 20 g BC-NPK and 5 g MI powder were added in 500 mL glass beaker having 250 mL deionized water and stirred vigorously. After a homogeneous mixture, 2 g chitosan powder was added in solution and mixed thoroughly . To generate Semi-IPN polymer network, 5 g acrylamide monomer and 0.2 g N, N', methylenebisacrylamide (N, N-MBA) cross linker were added to above solution and to initiate polymerization process 5 g ammonium persulfate (initiator) was added. The beaker with solution was placed on a hot plate at 70 °C and stirred vigorously at 700 rpm for 5 h. Later on, solution was removed from hot plate and after cooling at room temperature it was filtered by Whatman filter papers. The solid material on filter paper surface was further washed with deionized water to remove possible impurities. After washing, solid material was cooled at room temperature, grinded and sieved to a fine powder and stored in acrylic container. Similar procedure was repeated by using either BC-NPK or MI alone. In this way, different types of SRFs were produced including BC-based SRFs without MI (BC-SRF), MI-based SRFs without addition of BC (MI-SRF), BC and MI-based composite SRFs (BCMI-SRF).

Characterization of BCs and SRFs

Synthesized BCs (BC and BC-NPK) and SRFs (BC-SRF, MI-SRF, and BCMI-SRF) along with BM were analyzed for their physio-chemical characteristics by following standard procedures. Firstly, the yield of produced BC was calculated using Eq. (1). The ASTM D1762-84²⁷ method was used to measure moisture contents, volatiles, ash, and fixed carbon fraction of BCs and BM.

$$Yield \ (\%) = \frac{Weight of \ biomass - Weight of \ biochar}{Weight of \ biomass} \times 100$$
(1)

In this context, Energy-dispersive X-ray spectroscopy (EDS, JSM-6380 LA, JEOL, Japan) was used to observe elemental analysis of produced BCs and SRFs. The BM and its derived BCs and SRFs samples were analyzed by Scanning Electron Microscopy (SEM, EFI S50 Inspect, Netherlands) for their surface morphology, while crystallinity in synthesized materials was determined by X-ray diffractometer (MAXima_X XRD-7000, Shimadzu, Japan). Surface area, total pore volume, and pore diameter were analyzed following the Brunauer–Emmett–Teller (BET) method using surface area and porosity analyzer (TriStar II 3020, Micromeritics, USA). Fourier transform infrared spectroscopy (FTIR) was used to identify abundance of surface functional groups in synthesized materials. Synthesized materials were analyzed for pH and electrical conductivity (EC) by making suspension in deionized water at 1:10 w/v ratio. The suspension was latterly analyzed by using pH meter (WTW-pH 523), EC meter (YSI Model 35) to determine pH and EC value of synthesized materials. Likewise, CEC of synthesized materials was measured by following Sparks method²⁸.

Soil samples: collection, preparation, and characterization

Soil samples (agricultural soil) were collected from Derab Agriculture Research Center, King Saud University, Riyadh, Saudi Arabia. Collected soil samples were stored in air tight plastic bags and moved to Soil Chemistry Laboratory, Soil Science Department, King Saud University Riyadh, Saudi Arabia. Soil samples were air-dried and sieved through a 2 mm sieve and a composite sample was prepared. Soil samples were analyzed chemically (pH, EC, and CEC) following standard procedures²⁸. A soil suspension was prepared at 1:2.5 ratio (w/v) and analyzed for pH and EC. Soil texture was determined by following Bouyoucos method²⁹, while Walkley and Black method³⁰ was followed to determine soil organic matter (OM) content. A soil sample was digested by Hossner method³¹ and the digestate was analyzed by Inductively coupled plasma-optical emission spectrometry (Perkin Elmer Optima 4300 DV ICP-OES) to investigate total trace elements.

Evaluation of water-holding and water retention performance of synthesized materials

The WH and WR performance of the produced materials was determined by adding materials in acrylic container containing soil. Acrylic containers with porous bottom were selected and each container was filled with 200 g soil (W_s) amended with synthesized materials at the rate of 1% (w/w) ratio. Prior to addition of soil and materials, the bottom of containers was covered with a layer of filter paper and after adding soil each container was weighed (W_o). Each container was drained with deionized water at steady and consistent flow rate. After a complete halt of gravitational flow of water from container weight of the container was recorded (W1). The samples were placed at room temperature for a period of 30 days and weighed at regular intervals (Wi) (1, 3, 7, 10, 14, 21, 30 days). The WH and WR performance of materials was assessed by using following equations (Eqs. 2–3).

$$WH \% = \frac{W1 - W0}{W_S} \times 100 \%$$
 (2)

$$WR\% = \frac{Wi - W0}{W1 - Wo} \times 100\%$$
(3)

Nutrients release behavior of synthesized materials

The synthesized charred materials and SRFs were employed in incubation experiments to investigate their nutrient release behavior in soil. Acrylic containers were filled with 500 g soil and materials were added at 2% (*w/w*) ratio. Moreover, in separate containers, CFs (CFs) including urea, triple super phosphate (TSP) and potassium chloride (KCl) were also added with soil to observe the release of N, P, and K in comparison to synthesized SRFs. A control treatment was also added with soil only and no addition of chemical and synthesized SRFs. The soil was kept at field capacity throughout the experiment by regular weighing and adding deionized water when needed. After a set of time intervals of 1, 3, 7, 10,14, 21, and 30 days of incubation, the soil samples were taken from each container and extracted with ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) and potassium KCl^{32,33}. Each sample was examined in triplicate including a control treatment. In addition, to observe nutrient release from prepared materials, experimental data was also interpreted by applying some kinetic models to observe kinetics release of nutrient³⁴.

First order :
$$Inq_t = Inq_o - k_1 t$$
 (4)

Pseudo-second order :
$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q} t$$
 (5)

Power function :
$$Inq_t = Inb + k_f (Int)$$
 (6)

Parabolic diffusion :
$$q_t = a + k_p t^{0.5}$$
 (7)

where q_t and q_o are the mass percentage of nutrient release in different time interval, the rate constant of first-order and second-order are described by k_1 and k_2 respectively, k_p is parabolic diffusion constant, k_f is rate coefficient value, and a is a constant.

Statistical analysis

The data were analyzed statistically using analysis of variance (ANOVA) and a Tukey's honest significant difference (HSD) test was conducted to inspect the significant variations and comparisons among the data of the pairwise treatments at $P = 0.05^{35}$. All the treatments were performed in triplicate for each sample.

Results and discussion Characterization of BCs and SRFs

Chemical and proximate analyses showed distinctive variations among surface and chemical properties of raw BM and its derived BCs and SRFs. Pyrolysis of conocarpus BM at 400 °C produced BC with 34.7% yield, which indicated thermal degradation of raw BM and loss of various volatiles, decomposition of organic compounds and release of moisture from BM¹⁹ (Table 1). Lower moisture contents (2.80%) were anticipated in pristine BC, while the highest moisture contents (9.96%) were found in raw BM. The decrease in moisture contents could be due to dehydration and removal of water molecules and surface functional groups, which were also responsible for decrease in yield of BC. Comparatively higher moisture contents were recorded in BC-NPK (4.85%) and BCbased SRFs (3.03-5.00%), and that could be due to washing and pretreatment of these materials³⁶. Additionally, BC-based SRFs have broad channeled and cross-linked network of Semi-IPN polymers pronounced with diffused layers of polymers and deeply entrapped water molecules suggesting comparatively higher moistures contents in synthesized BC-based SRFs¹⁴. Similar to moisture contents, mobile matter was found higher in BM (43.20%), which was subsequently decreased in BCs (20.58-23.91%) and synthesized SRFs (16.96-25.07%). Contrarily to moisture and mobile matter, an increment in ash% and fixed carbon fraction was found after converting raw BM in to BCs. Ash contents were increased from 8.85% in BM to 11.42-22.85% in BCs and SRFs while fixed carbon contents were found as high as 57.16-65.20% in produced BCs and SRFs, which were 37.98% in raw BM. The increase in ash contents could be due to interaction between organic and inorganic constituents, and concerted mineral contents subsequent to thermal treatment of raw BM³⁷. The enhanced carbon fraction in BCs and SRFs against BM is the reflection of formulation and accumulation of condensed, aromatic and more stable

| Material | BM | BC | BC-NPK | BC-SRF | MI | MI-SRF | BCMI-SRF |
|---|-------|-------|--------|--------|-------|--------|----------|
| Yield % | - | 34.7 | - | - | - | - | - |
| Moisture % | 09.96 | 2.80 | 04.85 | 05.00 | - | - | 3.03 |
| Mobile matter % | 43.20 | 20.58 | 23.91 | 25.07 | - | - | 16.96 |
| Resident matter % | 37.98 | 65.20 | 61.67 | 59.00 | - | - | 57.16 |
| Ash % | 08.85 | 11.42 | 09.56 | 10.92 | - | - | 22.85 |
| pH (1:25) | 05.53 | 09.14 | 07.60 | 06.27 | 06.51 | 06.90 | 07.48 |
| $EC^{\dagger} (dSm^{-1})$ | 01.62 | 01.00 | 0.66 | 03.95 | 00.21 | 00.81 | 00.94 |
| $\text{CEC}^{\dagger\dagger} \text{ (cmol kg}^{-1}\text{)}$ | 52.25 | 40.72 | 46.16 | 55.54 | 16.44 | 17.18 | 43.03 |

Table 1. Yield, Proximate, and chemical analysis of Conocarpus BM and its derived BCs and SRFs. [†]Electrical conductivity, ^{††}Cation exchange capacity, *BM* Biomass, *BC* Biochar, *BC-NPK* Nutrient enriched biochar, *BC-SRF* Biochar slow release fertilizer, *MI* Mica, *MI-SRF* Mica slow release fertilizer, *BCMI-SRF* Biochar and mica based slow release fertilizer.

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components of carbon, describing excellent recalcitrant potential and soil stability especially in pristine BC, that exhibited the highest carbon fraction (65.20%). Due to respective condensation and dehydration of basic and acidic functional groups by heating BM the pH of BC increased by 3.61 units against BM (5.53). Pretreating and loading BC with nutrients (N, P, and K) resulted in lower pH value of BC-NPK (7.60), BC-SRF (6.27) and BCMI-SRF (7.48), that adorned its potential application in alkaline soil for improved nutrient availability³⁸. Additionally, washing of BCs during solution polymerization hydrolyzed organic constituents and generated organic acids resulting in relative decline in BCs pH and EC value with exception of BC-SRF (3.95 dSm⁻¹)¹⁹. The increase in EC value of BC-SRF could be due to loosely bounded nutrients and soluble salts, while abundance of K elements in BC-SRF could also contribute to raise its EC value³⁹. Higher CEC value of BC-SRF (55.54 cmol kg⁻¹) indicated presence of oxygenated surface functional groups and ample nutrient holding capacity of BC-SRF. The CEC value was decreased in BC (40.72 cmol kg⁻¹) against BM (55.25 cmol kg⁻¹), signifying the potential impact of thermal degradation of organic compounds (cellulose, hemicellulos and lignin) and attached functional groups in BM⁴⁰.

SEM visualization indicated structural and morphological assessment of raw BM and showed that BM has rough and amorphous surface with irregular microspheres, suggesting abundance of cellulose, hemicellulose and lignin compounds (Fig. 1). Tubular channels and regular surface porosity were noted in pristine BC indicating effective degradation of organic substances in BM and release of clogged impurities and volatile compounds¹⁹ Fairly smooth surface and flakes were found in of MI and MI-SRF. In synthesized SRFs, microspheres and tubular channels were found covered and locked by several crystals indicating triumphant impregnation of nutrients (N, P, and K) on BC surface to produce SRFs. Additionally, hollow broad channels with smooth and homogeneous surface were found in BC-SRF and few wrinkles with porous surface were found in BCMI-SRF. Likewise, during polymerization reaction between BC and polymers resulted in irregular and amorphous aggregates on surface of BC-SRF, and some pores with open channels were also observed⁴¹. Additionally, white particles on smooth surface of BC-NPK and SRFs (MI-SRF and BCMI-SRF) endorsed sturdy joined nutrients and polymers constituents on BC surface, along with well dispersed mica particles, that also enhanced surface pore configuration and generated broad channels²⁶. Surface area detection analysis (BET) showed that owing to amorphous surface structure BM predicted lowest surface area (2.182 m² g⁻¹), pore volume (0.000668 cm² g^{-1}) and pore size (12.252 Å), while pristine BC possessed highest surface area (296.762 m² g⁻¹), highest pore volume (0.125575 cm² g⁻¹) and pore size (16.926 Å) (Table 2). Similar to pristine BC, BC-NPK also showed significantly higher surface area (209.987 m² g⁻¹) and pore characteristics (0.089227 cm² g⁻¹, 16.996 Å) against synthesized SRFs. In comparison to BM, slightly higher surface area (3.657 m² g⁻¹) and pores characteristics $(0.001261 \text{ cm}^2 \text{ g}^{-1}, 13.796 \text{ Å})$ were found in MI, which was decreased slightly in MI-SRF $(3.179 \text{ m}^2 \text{ g}^{-1})$, with smaller pore volume (0.000988 cm² g⁻¹) and pore size (12.427 Å), while BCMI-SRF indicated a slight increase in surface characteristics (4.154 m²g⁻¹, 0.001876 cm² g⁻¹, 12.190 Å). Higher surface area in BC and BC-NPK was quite anticipated indicating its porous surface and it could be due to pyrolysis of BM that led the release of volatiles and clogged impurities resulting in tubular, broad channeled and porous surface^{42,43}. Furthermore, higher surface in woody BC could be attributed to composition of organic compounds (lignin, cellulose, and hemicellulose) in BM⁴³. In comparison to pristine BC a slight decrease in BC-NPK surface area could be due to clogging of pores by nutrient particles after enrichment with nutrients⁴⁴. Sharp decrease in surface area of BC-SRF indicated presence of Semi-IPN network of infused layer of acrylamide and chitosan polymers, and it also showed adsorption of NPK particles which was also confirmed by decline in average pore size of BC-SRF^{42,44}. Likewise, SEM analysis suggested flaky surface of MI and MI-SRF that could be possible reason behind lower surface area and smaller pore size along with nutrients impregnation³⁶.

The XRD analysis of conocarpus BM and its derived BCs and synthesized SRFs indicated characteristic variations in crystallinity and mineralogical composition (Fig. 2). An anticipated sharp and elevated peak of muscovite was observed at 7.58 Å in crystallinity of MI^{45} . While broad peaks of whewellite ($CaC_2O_4H_2O$) and cellulose lattice were found at 3.15–4.06 Å in raw BM and MI. These peaks were thinned and disappeared latterly in synthesized BCs and shifted to the left in BC-SRF indicating thermal degradation of organic framework of cellulose and destruction of ordered structures in BM by polymerization⁴⁶. The distinctive reflections at 7.64 Å were disappeared lately in BC-based SRFs suggesting uniform dispersion and integration of polymer matrix and formation of Semi-IPN polymer structure, and that facilitated excellent water holding capacity of synthesized SRFs⁴⁷. Similarly, the presence of calcite compounds was confirmed by appearance of small peaks in BCs at 2.22 Å. Similar mineral composition and crystallinity was found in conocarpus derived BC⁴⁸ and jujube wood waste derived BC¹⁹.

The FTIR analysis results showed low intensity bands of O-H and Al-OH group at 3326.91 cm⁻¹, 3615.01 cm⁻¹ and 3675.01 cm⁻¹ wavenumber in BM, MI and MI-SRF, respectively, that belongs to water molecules and found absent in BCs (Fig. 3). The absence of -OH groups could be due to release of volatiles and water molecules by heat treatment of BM. Also, the absence of -OH stretching in BC-based SRFs could be due to participation of -OH group in polymerization reaction⁴⁹. Furthermore, Si-O bending and Si-O-Si stretching were observed at 1023.09 cm⁻¹ in BM, MI, MI-SRF, these were thinned in BCMI-SRF and disappeared in BC, BC-NPK and BC-SRF¹³. Additionally, band of C-H group was found in BM indicating the presence of cellulose and hemicellulose compounds⁵⁰. The broad band at wavenumber 1700–1300 cm⁻¹ was due to the presence of -COOH functional groups, which were appeared in BM and latterly weakened in BCs and SRFs. Likewise, shifting of -COOH peaks from 1710.23 cm⁻¹ in BC and 1731.15 cm⁻¹ in BC-NPK to 1631.15 cm⁻¹ in BC-SRF and 1641.23 cm⁻¹ in MI-SRF could be due to intermolecular hydrogen bonding interaction during polymerization and it affirmed successful integration of Semi-IPN polymer network in SRFs³⁸. Broad peaks and vibrations of C-N (amine) groups at 1008.27 cm⁻¹, 1051.10 cm⁻¹, 1131.10 cm⁻¹, and 1641.13 cm⁻¹ wavenumber in BC-SRF, MI-SRF and BCMI-SRF suggested polymerization reaction and involvement of urea by nutrient enrichment of BCs and MI⁵¹.



Fig. 1. Structural assessment (SEM-analysis) of BM and synthesized BCs and SRFs.BM (biomass), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer).

The elemental analysis of all the synthesized materials indicating relative weight percentages of selected elements by using EDS is shown in Table 3. The analysis endorsed porous nature of BC, that was also supported by SEM analysis and it helped to accommodate nutrient ions by BC to generate SRF. Furthermore, owing to its porous structure, BC showed higher affinity and enrichment for added nutrients against MI and almost two folds higher concentration of N (3.94%) and P (3.21%) were found in BC-SRF which was 1.55% and 1.79%, respectively in MI-SRF. While K concentration was found consistently higher in MI (11.96%) and MI-SRF (12.66%) against BC-NPK (4.47%) and BC-SRF (4.26%). Additionally, successful loading and dispersion of nutrients on BC and MI surface was also confirmed by higher concentration of N, P and K in BC-NPK, BC-SRF, MI-SRF and BCMI-SRF against pristine BC and MI. All produced BCs showed significantly higher fraction of carbon (C) (70.09-73.53%), followed by oxygen (O) (18.16-20.07%), while silica (Si) magnesium (Mg) and calcium (Ca) were found as dominant minerals. Similar trend was observed in BC-based SRFs with higher C (64.12-67.88%) and O contents (11.21-19.51%). The C contents were slightly higher in BCs than SRFs which could be due to washing and polymerization process of synthesized SRFs³⁸. Overall O was second dominant element with some minor elements (Na, Mg, Al, Si, S, Cl, K, Ca, and Mn) in BM and all synthesized BCs and SRFs. The higher contents of C and O in skeletal composition of synthesized materials enlightened ample abundance of O-containing surface functional groups (-COOH, OH)⁵². In addition to higher abundance C and O, MI was found with higher mineral contents in its composition including 33.20% Si and 32.26% Al in MI and 29.86% Si and 31.72% Ål in MI-SRF. Higher mineral contents in MI could be due to occurrence of muscovite mineral in its composition and presence of muscovite mineral was also confirmed XRD analysis (Fig. 2).

| | BET surface area | Pore volume | Pore size | | |
|----------|------------------|-----------------|-----------|--|--|
| Sample | $(m^2 g^{-1})$ | $(cm^3 g^{-1})$ | (Å) | | |
| BM | 2.182 | 0.001 | 12.252 | | |
| BC | 296.762 | 0.126 | 16.996 | | |
| BC-NPK | 209.987 | 0.089 | 16.196 | | |
| BC-SRF | 6.409 | 0.001 | 14.889 | | |
| MI | 3.657 | 0.001 | 13.796 | | |
| MI-SRF | 3.179 | 0.001 | 12.427 | | |
| BCMI-SRF | 4.154 | 0.001 | 12.190 | | |





Fig. 2. The X-ray diffraction analyses of BM, synthesized BCs and SRFs. BM (biomass), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer).

Characterization of soil samples

Collected soil samples were analyzed for their physio-chemical characteristics. Table S1 (supplementary data) indicates that soil was found slightly alkaline (pH = 7.66) with low EC (0.38 dSm⁻¹) and OM contents (1.31%). The CEC was found as 9.82 cmol kg⁻¹ and soil texture was pronounced as sandy loam. Total contents of heavy metals were found below permissible limits except for Fe, while average available contents of N (NH₄⁺-N) (194.04 mg kg⁻¹), P (55.04 mg kg⁻¹) and K (388.45 mg kg⁻¹) ascribed that soil was low in fertility⁵³. Experimental study of soil samples also showed that soil has low WH and WR capacity (Fig. 4).

Water holding and water retention performance of synthesized materials

The prepared BCs and synthesized SRFs were examined for their potential impacts on soil WH and WR capacity. Addition of BC and BC-NPK enhanced soil WH capacity by 23.59-23.77% against un-amended (CK) soil (Fig. 4a). While 40.61–47.80% higher WH capacity if soil was recorded after application of BC-SRF and BCMI-SRF, respectively, suggesting almost two folds increase in WH capacity of soil over BCs. A moderate increase in soil WH capacity was noted by addition of MI and its derived SRF (MI-SRF), which was quite less than BCs and BC-based SRFs. Furthermore, the impacts of synthesized materials on WR capacity of soil were also observed at regular time interval up to 30 days (Fig. 4b). In a period of 21 days and 30 days, water was lost completely in



Fig. 3. The FTIR analysis of BM, synthesized BCs and SRFs. BM (biomass), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer).

| | С | 0 | N | Р | Na | Mg | Al | Si | Cl | K | Ca | Mn |
|-----------|--------|-------|------|------|------|-------|-------|-------|------|-------|------|------|
| Materials | Wt (%) | | | | | | | | | | | |
| BM | 56.96 | 37.62 | | | - | 0.34 | 0.24 | 0.90 | - | 0.95 | 3.00 | - |
| BC | 73.53 | 20.07 | 1.98 | 1.23 | - | 0.86 | - | 0.58 | - | 0.91 | 0.79 | - |
| BC-NPK | 70.09 | 18.16 | 3.55 | 2.68 | - | 0.31 | - | 0.21 | - | 4.47 | 0.53 | - |
| BC-SRF | 67.88 | 19.51 | 3.94 | 3.21 | 0.21 | 0.37 | - | 0.33 | | 4.26 | 0.29 | - |
| MI | - | 16.53 | | | 0.51 | 03.65 | 32.26 | 33.20 | 0.06 | 11.96 | 1.61 | 0.22 |
| MI-SRF | 1.15 | 16.44 | 1.55 | 1.79 | 0.70 | 02.18 | 31.72 | 29.86 | 0.14 | 12.66 | 1.02 | 0.79 |
| BCMI-SRF | 64.12 | 11.21 | 3.44 | 3.14 | 1.25 | 2.19 | 0.41 | 1.96 | 0.28 | 11.09 | 0.53 | 0.38 |

Table 3. Relative weight percentages of selected elements in BM and its derived BCs and SRFs as obtained by multi-point analyses using energy dispersive X-ray spectroscopy. *Wt* weight, *BM* Biomass, *BC* Biochar, *BC-NPK* Nutrient enriched biochar, *BC-SRF* Biochar slow release fertilizer, *MI* Mica, *MI-SRF* Mica slow release fertilizer, *BCMI-SRF* Biochar and mica based slow release fertilizer.

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un-amended soil and in soil receiving MI at 1% *w/w*. A gradual decrease in soil water contents was found in soil treated with BCs (BC and BC-NPK) and at the end of 30 days period BC treated soil held 19.37% of added water, 16.35% of water was recorded in soil treated by BC-NPK. As mentioned earlier addition of MI did not impact soil WR capacity and lost 96.27% of added water after a period of 21 days, subsequent to complete water loss after 30 days incubation period. MI based SRFs showed some resistance towards water release from soil and MI-SRF treated soil held 11.23% water after 30 days. On the other hand, BC-SRF and BCMI-SRF illustrated excellent potential in improving soil WR capacity by demonstrating minimum water loss and held 32.55% and 35.52% of added water, respectively.

Increasing soil moisture and its WH capacity indicated plausible ability of BC to hold water, while further increment in soil WH capacity narrated positive impact of accompanying Semi-IPN in synthesis of SRF. Enhanced soil moisture could be attributed to improved soil porosity and hydraulic properties subsequent to addition of BCs which enable soil to hold more water for longer period⁵⁴. In a research study on potential impacts of BC on soil porosity and WH capacity, Liu et al.⁵⁵ reported an increment in plant available water with effective crop uptake by treating agricultural soil with fine BC particles. Moreover, such promising impacts on boosted soil moisture and better WH capacity is largely believed due to surface characteristics and physiochemical properties of BC such as high surface area and porous structure which hold water by capillarity^{56,57}. Some indirect effects of BC addition in soil which increase soil water contents include soil aggregation, better soil structure and bulk density. Combination of carbonaceous material such as BC with polymer network to produce SRFs entrapped more water molecules in elastic and cross-linked network of polymer chains and porous channels on BC surface by capillary action⁵⁸. Additionally, in Semi-IPN polymer network the N,



Fig. 4. Water holding (WH %) (**a**), and water retention (WR %) (**b**) performance of synthesized materials. CK (control), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer).

N-MBA crosslinker induced hydrophilic surface functional group on BC surface such as –OH, and –COOH which reinforced SRFs efficiency in absorbing and holding more volume of water⁵⁹. Coexistence of BC with MI particles and chitosan-based polymer network provide SRF with better mechanical strength and higher water adsorption capacity which ultimately increased WH capacity of soil and improve soil water content for shorter and longer period. Likewise, combination of MI with chitosan polymer network provides unique advantage of moisture absorption adsorption, water molecules adhesion, swelling and stability to SRF which induces positive impact on soil moisture^{16,24}.

Capturing water molecules in hydrophilic surface functional groups, broad tubular and porous channels of SRFs could be possible mechanism for retaining higher soil water contents in SRFs treated soil, subsequent to minimum water loss by percolation as well^{60,61}. Hollow channels and tubular surface of SRFs was also confirmed by SEM analysis of SRFs (Fig. 1). Also, homogeneous mixing of soil with BCs and SRFs underwent aggregation which might have improved soil physical structure, induced interparticle and intraparticle porosity and enhanced its ability to hold larger volume of water. The addition of BC in soil regulate inter particle pores largely depending on its own surface area and particle size which optimize soil moisture and WR capacity of soil⁶². In a previous research work on synthesis and application of BC based polymer coated SRFs, An et al.⁶³ reported that incorporation of nutrients with SAP and BC enhanced nutrient and water retaining capacity especially in sandy soils. Moreover, the electrostatic interaction and hydrogen bonding between surface functional groups and SRFs particles could be responsible for higher water retention and sustained soil moisture in soil treated with BC based SRFs. The three dimensional and elastic cross-linked structure of Semi-IPN embedded SRFs encouraged retention of soil moisture and held higher content of water in its cross-linking structure, which also inhibited water loss from soil⁶⁴. Furthermore, a water blocking layer developed between soil particles after incorporation of Semi-IPN polymer ingrained SRFs in soil which inhibited water loss from soil to atmosphere⁶⁵. In addition to enhanced WH and WR capacity, decrement in soil water loss by soil evaporation in corn cob based Semi-IPN embedded SRF treated soil was observed by Lu et al.⁶⁶ and Wen et al.⁶⁷, suggesting excellent water absorbency and gradual release of absorbed water by Semi-IPN polymer network. The existence of chitosan based Semi-IPN polymer network played key role in retaining higher volume of water in soil due to its crosslinking polymer chains, higher water absorption and retaining capacity, swelling behavior and elastic nature⁶⁸. Furthermore, solution polymerization treatment of BCs to produce SRFs induced additional hydrophilic amine groups on its surface, which enhanced WH and WR capacity of soil mixed with SRFs. Thus, synthesizing and soil application of BC based Semi-IPN polymer embedded SRFs simultaneously provide soil with water and water-soluble nutrient which release drought stress in plants and improve their overall growth.

Nutrients release behavior of synthesized materials

An incubation experiment was conducted to examine the nutrient release behavior of newly synthesized SRFs (Fig. 5). The AB-DTPA and KCl extracts of soil collected at regular time intervals (1, 3, 7, 14, 21 and 30 days) declared quick supply of nutrient initially, which latterly moved towards gradual equilibrium and was further interpreted by kinetics models to validate nutrient release behavior and possible mechanism. It was found that among synthesized SRFs, BC-SRF and BCMI-SRF showed better performance in controlling the release of nutrients against commercial fertilizer. After 30 days incubation period CK and CF treated soil released 100% of NH_4^+ -N contents, while lowest release was found in BC-SRF treated soil (69.76%) followed by BCMI-SRF (73.53%) and MI-SRF (77.35%). Similar trend was observed for P release, with better nutrient release performance by BCMI-SRF (65.66%), followed by BC-SRF (70.36%) and MI-SRF (75.08%). Comparatively higher contents



Fig. 5. The performance of synthesized BCs and SRFs for kinetics release of nutrient (%) in soil [(**a**) N, (**b**) P, (**c**) K]. CK (control), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer), CF (chemical fertilizer).

of extractable K were found in MI (90.78%) treated soil which is a silicate clay mineral and rich in K contents⁶⁹. Among examined nutrients like NH_4^+ -N release CK and CF released 100% of K and P contents in incubation period while distinctive treatment effect was observed on release of these nutrients during soil incubation period. Overall K and P release was quick as compared to NH_4^+ -N release which also increased gradually with increasing time period. Initially rapid release of K and P was found which could be due to dissolution of loosely attached and mass flow of nutrients, while on the other hand NH_4^+ -N ion showed better sorption on BCs and SRFs surface initially. However, a gradual increase in nutrients release dynamics was observed in tested SRFs which was comparatively swift in CK and CF treated soils.

The potential of BC-based synthesized SRFs to control nutrients release could be due to porous surface of BC, which generated loose porous network and cross-linking sites to attach and hold nutrients. Moreover, it aided Semi-IPN polymer network in SRFs and acted as a nutrient carrier. The SEM images showed infused and surface deposited nutrient particles in BC porous surface and cavities, which further support slow release behavior of synthesized SRFs. The prolonged release of N by BC-SRF and BCMI-SRF could be due to Semi-IPN polymer network structure and graft polymerization of chitosan with BC and MI³. In different studies, Wen et al.¹³ and Wen et al.⁶⁷ reported 61.3% and 56.1% release of N from BC-based slow release nitrogen fertilizer embedded with acrylic acid and acrylamide polymer network and bentonite. Surface fixation of P on BC via electrostatic interaction and chemical complexation with functional groups and surface deposition could be responsible for slow release of P in soil^{70,71}. Additionally, surface characteristics such as specific surface area and porous structure mainly attributed to resisting chemical corrosion and leaching of P in soil⁶². Co-polymerization of BC and MI with chitosan-based polymer was mainly attributed to well fixation of K contents in branched and chained network of Semi-IPN in as-prepared SRFs which resulted in slow and consistent supply of K contents in soil for prolonged period⁷². Among synthesized SRFs BC-SRF showed excellent performance in slow release of NH4+-N suggesting plausible ability of BC for adsorption of NH4+-N on its charged surface while surface porosity aided its slow release. On the other hand, BCMI-SRF performed better for P and K release indicating incorporation of cross-linking network of Semi-IPN helped P sorption on porous surface of SRFs and controlled mass flow of K by diffusion from SRFs to soil solution. MI illustrated quick and higher K release in soil while Semi-IPN polymer network aided MI-SRF showed its potential in regulating slow release of K in soil.

Kinetics study of nutrient release

To further illuminate slow release of nutrient and possible mechanism, experimental data was examined by several mathematical kinetics models including First-order, Pseudo second-order, Power function and Parabolic diffusion (Table 4). The results revealed that parabolic diffusion and first order described nutrients release better than pseudo second order and power function. Regression correlation value (R²) which helps to find out better fitness and aptness of mathematical model to interpret experimental data and explain kinetics release process, was found highest for parabolic diffusion ($R^2 = 0.94 - 0.99$) and first order (0.90-0.99) indicating that nutrient release followed constant mass transport and Fickian diffusion through polymer matrix of SRFs⁷³. Parabolic diffusion described mass transfer of nutrients by diffusion through porous surface of SRFs. Specifically, for N and P release is more suitably pronounced by dissolving through porous matrix of SRFs when it come in contact with water. Also, owing to its porous structure, BC could hold NPK particles for longer period and delayed nutrient release process in BC based SRFs⁷⁴. Lower values of diffusion constant (k_{id}) of SRFs (BC-SRF, MI-SRF, and BCMI-SRF) endorsed their slower diffusion from polymer matrix of SRFs against CF, which has highest diffusion constant value for NH_4^+ -N (606.42 mg g⁻¹), P (155.16 mg g⁻¹) and K (57.37 mg g⁻¹). It also confirmed that induced Semi-IPN network of chitosan-based polymers by co-polymerization of BC and MI stalled NPK diffusion process and regulated slow release of NPK from porous matrix of SRFs. Moreover, SEM analysis showed white amorphous layer of polymers matrix and nutrients diffused in broad channels and pores on BC surface which regulated slow release mechanism of nutrients when SRFs encountered with soil/water medium. Furthermore, the aiding BC with phyllosilicate MI mineral along with branched polymer network generated more complex path for nutrient diffusion through SRFs and ensured slow release of nutrient. The release of K was more suitably explained by first order kinetics which could be controlled by both desorption and diffusion of K from synthesized materials¹⁶ While spongy network of SRFs could hinder K release and K diffusion process, which could be rate limiting for K release. Power function kinetics depicted lowest R² value and was found unfit to describe nutrient release process

| NH ₄ ⁺ -N | | | | | | | | | | |
|---------------------------------|-----------------------|----------------|-----------------------|---------------------|------------------------|-----------------------|-------------------|-----------------------|----------------|--|
| | First | order | Pseud order | lo-second | Parabolic diffusion | | Power function | | | |
| Treatments | R ² | k ₁ | R ² | k ₂ 'h | | R ² | k _{id} | R ² | k _f | |
| Ck | 0.91 | 0.13 | 0.84 | 63×10 ⁻³ | 31.36 | 0.97 | 38.68 | 0.72 | 1.27 | |
| BC | 0.94 | 0.13 | 0.82 | 23×10^{-3} | 86.23 | 0.97 | 101.56 | 0.68 | 1.29 | |
| BC-NPK | 0.93 | 0.13 | 0.74 | 71×10^{-3} | 125.67 | 0.99 | 142.76 | 0.60 | 1.28 | |
| BC-SRF | 0.95 | 0.14 | 0.78 | 26×10^{-3} | 83.10 | 0.97 | 96.67 | 0.71 | 1.31 | |
| MI | 0.91 | 0.12 | 0.79 | 62×10^{-3} | 40.38 | 0.98 | 44.08 | 0.70 | 1.15 | |
| MI-SRF | 0.96 | 0.13 | 0.74 | 44×10^{-3} | 45.60 | 0.97 | 54.34 | 0.73 | 1.20 | |
| BCMI-SRF | 0.93 | 0.02 | 0.76 | 27×10^{-3} | 75.05 | 0.98 | 87.68 | 0.67 | 0.99 | |
| CF | 0.90 | 0.02 | 0.81 | 05×10^{-4} | 587.77 | 0.98 | 606.42 | 0.54 | 1.16 | |
| Phosphorus | | | | | | | | | | |
| | R ² | k ₁ | R ² | k2' | h | R ² | k _{id} | R ² | kf | |
| Ck | 0.94 | 0.126 | 0.87 | 60×10^{-3} | 29.02 | 0.96 | 51.45 | 0.72 | 1.19 | |
| BC | 0.92 | 0.128 | 0.74 | 41×10^{-3} | 73.85 | 0.95 | 91.08 | 0.62 | 1.21 | |
| BC-NPK | 0.92 | 0.115 | 0.79 | 40×10^{-3} | 128.62 | 0.99 | 96.43 | 0.52 | 1.14 | |
| BC-SRF | 0.92 | 0.116 | 0.75 | 33×10^{-3} | 134.08 | 0.98 | 106.71 | 0.52 | 1.14 | |
| MI | 0.95 | 0.121 | 0.79 | 78×10^{-3} | 46.21 | 0.97 | 62.32 | 0.51 | 1.14 | |
| MI-SRF | 0.92 | 0.114 | 0.81 | 66×10^{-3} | 89.31 | 0.98 | 73.36 | 0.64 | 1.09 | |
| BCMI-SRF | 0.92 | 0.015 | 0.81 | 29×10^{-3} | 132.02 | 0.98 | 112.41 | 0.54 | 0.97 | |
| CF | 0.90 | 0.014 | 0.85 | 24×10^{-3} | 203.72 | 0.98 | 155.16 | 0.51 | 0.99 | |
| Potassium | | | | | | | | | | |
| | R ² | k ₁ | R ² | k2' | h | R ² | k _{id} | R ² | k_{f} | |
| Ck | 0.95 | 0.08 | 0.84 | 97×10^{-2} | 26.40 | 0.92 | 8.74 | 0.54 | 0.73 | |
| BC | 0.96 | 0.10 | 0.82 | 40×10^{-2} | 65.12 | 0.91 | 21.63 | 0.50 | 0.87 | |
| BC-NPK | 0.98 | 0.11 | 0.81 | 29×10^{-2} | 95.20 | 0.92 | 30.09 | 0.47 | 0.90 | |
| BC-SRF | 0.96 | 0.12 | 0.77 | 17×10^{-2} | 50.37 | 0.90 | 30.99 | 0.60 | 1.01 | |
| MI | 0.98 | 0.10 | 0.74 | 33×10^{-2} | 73.76 | 0.92 | 25.57 | 0.51 | 0.91 | |
| MI-SRF | 0.97 | 0.10 | 0.74 | 35×10^{-2} | 67.95 | 0.90 | 24.11 | 0.53 | 0.92 | |
| BCMI-SRF | 0.97 | 0.12 | 0.85 | 40×10^{-2} | 70.87 | 0.91 | 22.08 | 0.48 | 1.18 | |
| CF | 0.99 | 0.09 | 0.18 | 19×10^{-2} | 250.55 | 0.92 | 57.37 | 0.41 | 1.12 | |

Table 4. Derived parameters of the kinetics models for nutrient release from synthesized BCs and SRFs. CK (control), BC (biochar), BC-NPK (nutrient enriched biochar), MI (mica), BC-SRF (biochar based slow release fertilizer), MI-SRF (mica based slow release fertilizer), BCMI-SRF (biochar and mica based slow release fertilizer), CF (chemical fertilizer).



Fig. 6. Schematic mechanism of nutrient release from biochar based Semi-IPN polymer network embedded slow release fertilizer.

while pseudo-second order narrated chemical interaction between BC and nutrient particles was also found unsuitable to explain nutrient release process due to lower coefficient correlation value for SRFs.

Slow release mechanism of SRFs

The slow release mechanism of nutrients by SRFs is illustrated in Fig. 6. A multi staged diffusion process could better explain nutrient release from SRFs⁷⁵. It began with enrichment and fixation of nutrients on porous surface of BC by electrostatic interaction and interlayer diffusion, which was latterly described by entrapment in cross-linked chained network of Semi-IPN polymers. After soil application and interaction with soil moisture, hydrophilic MI and polymer matrix of SRFs absorbed moisture which resulted in swelling of SRFs, closed permeability of porous surface of BC and partially prevent nutrients dissolution. Subsequently, osmotic pressure built up which allowed water to penetrate in channeled and spongy shell of BC to condense on the solid fertilizer, followed by partial nutrient dissolution. Water molecules were adsorbed by polymer network and BC which latterly stored as nutrient solution in BC pores and tubular channels. Then, the dissolved nutrients were released slowly via diffusion, under concentration or pressure gradient, or a combination of these as the driving force, thereof referred as the "diffusion mechanism"⁶⁸. In the beginning, large nutritional gradient occurred which regulated quick and higher mass transport and which gradually slow down to equilibrium release with time. Diffusion of nutrients through porous surface of SRFs was also confirmed by kinetics study of nutrient release and explained well by mathematical equation of parabolic diffusion model.

Conclusion

The current research work was led to examine to potential of synthesized BCs and SRFs in improving overall soil moisture and nutrient availability. Conocarpus BM derived BC was synthesized at 400 °C pyrolysis temperature which was subsequently enriched with NPK. Nutrients enriched BC was further modified with polymer by solution polymerization to generate BC based SRFs. Additionally, MI and MI based SRF were also synthesized following similar method without addition of BC. Synthesized BCs and SRFs illustrated distinctive characteristics variations, and BC-SRF recorded highest CEC value (55.54 cmol kg⁻¹), BC recorded highest specific surface area (296.762 m² g⁻¹), residual C contents (65.21%) and broad channeled porous structure. Among synthesized materials BCMI-SRF recorded highest increase in soil WH capacity (91.58%) followed by BC-SRF (68.37%) while addition of BC and BC-NPK slightly increased soil WH capacity by 30.89% and 31.19%, respectively. BC-SRF and BCMI-SRF recorded 28.63% and 46.35% higher increase in soil WH capacity over pristine BC. Similarly, soil with BCMI-SRF showed highest WR capacity with retaining 35.52% of added water after 30 days period, while BC-SRF treated soil held 32.55% water, which was significantly higher than WR capacity of BC (19.37%) and MI (11.23%) treated soil. BC-SRF performed best among synthesized SRFs for NH₄⁺-N release indicating 69.76% release of total NH₄⁺-N, which was 73.53% in BCMI-SRF treated soil, 77.35% in MI-SRF treated soil and 83.56% in soil with BC. BCMI-SRF exhibited excellent performance for slow release of P (65.66%) and K (71.83%), that was 70.36% for P and 75.47% for K release in BC-SRF treated soil. In comparison to synthesized SRFs higher nutrients release was recorded in pristine BC (85.71% and 86.57% for P and K, respectively) and MI (80.68% and 90.78% for P and K, respectively) added soil. Application of mathematical kinetics model to experimental data showed that nutrient release followed first order and parabolic diffusion kinetics model. Additionally, along with bulk mass transport parabolic diffusion was found as dominant mechanism of nutrient release in soil. Over all the produced SRFs were based on combined characteristics of organic polymer (chitosan) and organic adsorbent (biochar) and have ample efficiency of releasing nutrients at controlled and slow rate to ensure enough availability of nutrients in soil for plants. The slow release mechanism of SRFs counter the effect of excessive nutrients loss from CFs such as urea and other P and K fertilizers which cause environmental pollution and enhances production cost. Especially the leaching of nutrients which are excessively released from CF caused ground water pollution such as eutrophication and surface soil fixation of nutrients making them unavailable for plants and resulting in low nutrients use efficiency. On the other hand, slow release of nutrients by SRFs not only enhances nutrients use efficiency and also promote plant growth for prolonged availability of nutrients in soil. Conclusively, our findings manifested that application of BC based Semi-IPN embedded SRFs could be a suitable and feasible technique to counter excessive nutrient loss by CFs application, improves nutrient availability in soil and also it improves overall soil moisture by holding and retaining larger volume of water in soil. Since this is preliminary research, future research work should focus to improve quality and optimize production costs of the synthesized SRFs and to assess the potential impacts of polymer residues on soil health.

Data availability

The data analyzed during the current study is available from the corresponding author on reasonable request.

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References

- 1. World Fertilizer Trends. And Outlook to 2022: Summary Report (FAO, 2019).
- Banik, C., Bakshi, S., Laird, D. A., Smith, R. G. & Brown, R. C. Impact of biochar-based slow-release N-fertilizers on maize growth and nitrogen recovery efficiency. 52(3), 630–640 (2023).
- 3. Liu, X. et al. A biochar-based route for environmentally friendly controlled release of nitrogen: urea-loaded biochar and bentonite composite. *Sci Rep.* **9**(1), 9548 (2019).
- Jain, A., Balasubramanian, R. & Srinivasan, M. P. Hydrothermal conversion of biomass waste to activated carbon with high porosity: a review. Chem. Eng. J. 283, 789–805 (2016).
- 5. Islam, M. M. Synthesis of biochar-based slow-release fertilizer from nutrient-rich organic waste an abstract of entire text (Doctoral dissertation) (2022).
- Chen, Z. S. et al. Sustainable application for agriculture using biochar-based slow-release fertilizers: a review. ACS Sustain. Chem. Eng. 11 (1), 1–12 (2022).
- Al-Rawajfeh, A. E., Alrbaihat, M. R. & AlShamaileh, E. M. Characteristics and types of slow-and controlled-release fertilizers. In Controlled Release Fertilizers for Sustainable Agriculture 57–78. (Academic, 2021).
- Morante-Carballo, F., Montalván-Burbano, N., Quiñonez-Barzola, X., Jaya-Montalvo, M. & Carrión-Mero, P. What do we know about water scarcity in semi-arid zones? A global analysis and research trends. *Water* 14 (17), 2685 (2022).
- 9. Paul, M., Negahban-Azar, M., Shirmohammadi, A. & Montas, H. Developing a multicriteria decision analysis framework to evaluate reclaimed wastewater use for agricultural irrigation: the case study of Maryland. *Hydrology* **8** (1), 4 (2021).
- Ricart, S. & Rico-Amorós, A. M. Constructed wetlands to face water scarcity and water pollution risks: learning from farmers' perception in Alicante, Spain. Water 13 (17), 2431 (2021).
- 11. Minhas, P. S., Saha, J. K., Dotaniya, M. L., Sarkar, A. & Saha, M. Wastewater irrigation in India: current status, impacts and response options. *Sci. Total Environ.* 808, 152001 (2022).
- Rashidzadeh, A. & Olad, A. Slow-released NPK fertilizer encapsulated by NaAlg-g-poly (AA-co-AAm)/MMT superabsorbent nanocomposite. *Carbohydr. Polym.* 114, 269–278 (2014).
- 13. Wen, P. et al. Microwave-assisted one-step synthesis and characterization of a slow release nitrogen fertilizer with inorganic and organic composites. RSC Adv. 6 (44), 37337–37346 (2016).
- 14. Tally, M. & Atassi, Y. Optimized synthesis and swelling properties of a pH-sensitive semi-IPN superabsorbent polymer based on sodium alginate-g-poly (acrylic acid-co-acrylamide) and polyvinylpyrrolidone and obtained via microwave irradiation. *J. Polym. Res.* 22, 1–13 (2015).
- 15. Fu, J., Wang, C., Chen, X., Huang, Z. & Chen, D. Classification research and types of slow controlled release fertilizers (SRFs) used-a review. *Commun. Soil. Sci. Plant. Anal.* 2219–2230 (2018).
- 16. An, X. et al. Incorporation of biochar into semi-interpenetrating polymer networks through graft co-polymerization for the synthesis of new slow-release fertilizers. J. Clean. Prod. 272, 122731 (2020).
- 17. Lehmann, J. Bio-energy in the black. Front. Ecol. Environ. 381-387 (2007).
- Abiola, W. A., Diogo, R. V. C., Tovihoudji, P. G., Mien, A. K. & Schalla, A. Research trends on biochar-based smart fertilizers as an option for the sustainable agricultural land management: bibliometric analysis and review. *Front. Soil. Sci.* 1136327 (2023).
- Rafique, M. I., Usman, A. R., Ahmad, M. & Al-Wabel, M. I. Immobilization and mitigation of chromium toxicity in aqueous solutions and tannery waste-contaminated soil using biochar and polymer-modified biochar. *Chemosphere* 266, 129198 (2021).
- 20. Rafique, M. I. et al. Clay-biochar composites: emerging applications in soil. *Clay Compos. Environ. Appl.* 143–159 (2023).
- 21. Liu, T. et al. Preparation of magnetic hydrochar derived from iron-rich *Phytolacca acinosa* Roxb. For cd removal. *Sci. Total Environ.* 145159 (2021).
- 22. Das, L., Das, P., Bhowal, A. & Bhattachariee, C. Synthesis of hybrid hydrogel nano-polymer composite using graphene oxide, Chitosan and PVA and its application in waste water treatment. *Environ. Technol. Innov.* **18**, 100664 (2020).
- Das, L. et al. Calcium alginate-bentonite/activated biochar composite beads for removal of dye and biodegradation of dye-loaded composite after use: synthesis, removal, mathematical modeling and biodegradation kinetics. *Environ. Technol. Innov.* 24, 101955 (2021).
- 24. Pan, X. F. et al. Transforming ground mica into high-performance biomimetic polymeric mica film. *Nat. Commun.* **9** (1), 2974 (2018).
- Deshmukh, S. P., Rao, A. C., Gaval, V. R. & Mahanwar, P. A. Mica-filled PVC composites: effect of particle size, filler concentration, and surface treatment of the filler, on mechanical and electrical properties of the composites. *J. Thermoplast. Compos. Mater.* 24 (5), 583–599 (2011).
- 26. Das, S. K. Qualitative evaluation of fodder trees and grasses in hill region. J. Krishi Vigyan. 7 (2), 276-279 (2019).
- 27. ASTM, D. Standard Method for Chemical Analysis of Wood Charcoal 1762-1784 (USA, 1989).
- 28. Sparks, D. L. Methods of Soil Analysis (Soil Society of American, 1996).
- 29. Bouyoucos, G. J. Hydrometer method improved for making particle size analysis of soils. Agron. J. 54, 464–465 (1962).
- 30. Walkley, A. & Black, I. A. An examination of the Degtjareff method for determining soil organic matter, and a proposed
- modification of the chromic acid titration method. Soil Sci. 29–38 (1934).
 31. Hossner, L. R. Dissolution for total elemental analysis. In Methods of Soil Analysis: Part 3e Chemical Methods (eds. Sparks, Bigham, J. M.) 49–64 (SSSA and ASA, 1996).
- Soltanpour, P. N. & Workman, S. Modification of the NH4- HCO3-DTPA soil test to omit carbon black. Commun. Soil. Sci. Plant. Anal. 10, 411–1420 (1979). (1979).

- 33. SEPA (State Environmental Protection Agency). Water and Waste Water Monitoring Analysis Method (China Environmental Science, 2002).
- 34. Sparks, D. L. Kinetics of soil chemical phenomena: future directions. Future Prospects Soil. Chem. 55, 81-101 (1998).
- 35. StatSoft Inc. Statistica for Windows (Computer Program Manual) (StatSoft, Inc., 1995).
- Zhang, S. et al. Bio-based interpenetrating network polymer composites from Locust Sawdust as coating material for environmentally friendly controlled-release urea fertilizers. J. Agric. Food Chem. 64 (28), 5692–5700 (2016).
- Hu, Z. & Wei, L. Review on characterization of biochar derived from biomass pyrolysis via reactive molecular dynamics simulations. J. Compos. Sci. 7 (9), 354 (2023).
- Wang, C. et al. Biochar-based slow-release of fertilizers for sustainable agriculture: a mini review. *Environ. Sci. Ecotechnol.* 10, 100167 (2022).
- 39. Wali, F. et al. Formulation of biochar-based phosphorus fertilizer and its impact on both soil properties and chickpea growth performance. *Sustainability* **12** (22), 9528 (2020).
- Lee, J. W. et al. Characterization of biochars produced from cornstovers for soil amendment. *Environ. Sci. Technol.* 44 (20), 7970– 7974 (2010).
- Li, X. et al. A novel wheat straw cellulose-based semi-IPNs superabsorbent with integration of water-retaining and controlledrelease fertilizers. J. Taiwan. Inst. Chem. Eng. 55, 170–179 (2015).
- 42. Kizito, S. et al. Role of nutrient-enriched biochar as a soil amendment during maize growth: exploring practical alternatives to recycle agricultural residuals and to reduce chemical fertilizer demand. *Sustainability* **11** (11), 3211 (2019).
- Rehrah, D. et al. Production and characterization of biochars from agricultural by-products for use in soil quality enhancement. J. Anal. Appl. Pyrol. 108, 301–309 (2014).
- 44. Zhang, H. W. et al. Preparation and characterization of biochar-based slow-release nitrogen fertilizer and its effect on maize growth. Ind. Crops Prod. 203, 117227 (2023).
- Kumar, A., Tanvar, H. & Dhawan, N. Processing of mica for extraction of alumina and potash values. *Trans. Indian Inst. Met.* 73, 23–33 (2020).
- 46. Xie, L., Liu, M., Ni, B. & Wang, Y. Utilization of wheat straw for the preparation of coated controlled-release fertilizer with the function of water retention. J. Agric. Food Chem. 6921–6928 (2012).
- 47. Wen, P. et al. Microwave-assisted synthesis of a semi-interpenetrating polymer network slow-release nitrogen fertilizer with water absorbency from cotton stalks. ACS Sustain. Chem. Eng. 4 (12), 6572–6579 (2016).
- Al-Wabel, M. I., Al-Omran, A., El-Naggar, A. H., Nadeem, M. & Usman, A. R. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresour. Technol.* 131, 374–379 (2013).
- 49. Ma, Z. et al. Synthesis and characterization of a novel super-absorbent based on wheat straw. *Bioresour. Technol.* **102** (3), 2853-2858 (2011).
- Ahmed, M. B. et al. Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment. *Bioresour. Technol.* 238, 306–312 (2017).
- Meri, N. H. et al. Effect of chemical washing pre-treatment of empty fruit bunch (EFB) biochar on characterization of hydrogel biochar composite as bioadsorbent. In *IOP Conference Series. Mater Sci Eng*, vol. 358, No. 1, 12018. (IOP Publishing, 2018).
- Liang, H., Chen, L., Liu, G. & Zheng, H. Surface morphology properties of biochars produced from different feedstocks. In 2016 International Conference on Civil, Transportation and Environment 1205–1208 (Atlantis Press, 2016).
- Aggag, A. M. & Alharbi, A. Spatial analysis of soil properties and site-specific management zone delineation for the South Hail Region, Saudi Arabia. Sustainability 14 (23), 16209 (2022).
- 54. Liu, Z. et al. Impacts of biochar concentration and particle size on hydraulic conductivity and DOC leaching of biochar-sand mixtures. J. Hydrol. 533, 461-472 (2016).
- Liu, Z., Dugan, B., Masiello, C. A. & Gonnermann, H. M. Biochar particle size, shape, and porosity act together to influence soil water properties. *PLoS One.* 12 (6), e0179079 (2017).
- 56. Batista, E. M. et al. Effect of surface and porosity of biochar on water holding capacity aiming indirectly at preservation of the Amazon biome. *Sci. Rep.* **8** (1), 10677 (2018).
- 57. Ndede, E. O., Kurebito, S., Idowu, O., Tokunari, T. & Jindo, K. The potential of biochar to enhance the water retention properties of sandy agricultural soils. *Agronomy* **12** (2), 311 (2022).
- Wang, W., Yang, Z., Zhang, A. & Yang, S. Water retention and fertilizer slow release integrated superabsorbent synthesized from millet straw and applied in agriculture. *Ind. Crops Prod.* 160, 113126 (2021).
- 59. Baki, M. & Abedi-Koupai, J. Preparation and characterization of a superabsorbent slow-release fertilizer with sodium alginate and biochar. J. Appl. Polym. Sci. 135 (2018).
- Głąb, T., Pałmowska, J., Zaleski, T. & Gondek, K. Effect of biochar application on soil hydrological properties and physical quality of sandy soil. *Geoderma* 281, 11–20 (2016).
- Khajavi-Shojaei, S., Moezzi, A., Norouzi, Masir, M. & Taghavi, M. Synthesis modified biochar-based slow-release nitrogen fertilizer increases nitrogen use efficiency and corn (*Zea mays* L.) growth. *Biomass Convers. Biorefin.* 13 (2), 593–601 (2023).
- 62. Ibrahim, A. et al. Effects of conocarpus biochar on hydraulic properties of calcareous sandy soil: influence of particle size and application depth. Arch. Agron. Soil Sci. 63(2), 185–197 (2017).
- 63. An, X. et al. A new class of biochar-based slow-release phosphorus fertilizers with high water retention based on integrated copyrolysis and co-polymerization. *Chemosphere* **285**, 131481 (2021).
- Hu, X. et al. Synthesis and characterization of a novel semi-IPN hydrogel based on Salecan and poly (N, N-dimethylacrylamideco-2-hydroxyethyl methacrylate). Carbohydr. Polym. 105, 135–144 (2014).
- 65. Yang, L., Yang, Y., Chen, Z., Guo, C. & Li, S. Influence of super absorbent polymer on soil water retention, seed germination and plant survivals for rocky slopes eco-engineering. *Ecol. Eng.* **62**, 27–32 (2014).
- Lu, S. et al. Multifunctional environmental smart fertilizer based on L-aspartic acid for sustained nutrient release. J. Agric. Food Chem. 64 (24), 4965–4974 (2016).
- 67. Wen, P. et al. Microwave-assisted synthesis of a novel biochar-based slow-release nitrogen fertilizer with enhanced water-retention capacity. ACS Sustain. Chem. Eng. 5 (8), 7374–7382 (2017).
- Cheng, D., Liu, Y., Yang, G. & Zhang, A. Water-and fertilizer-integrated hydrogel derived from the polymerization of acrylic acid and urea as a slow-release N fertilizer and water retention in agriculture. J. Agric. Food Chem. 66, 5762–5769 (2018).
- 69. Basak, B. B. Waste mica as alternative source of plant-available potassium: evaluation of agronomic potential through chemical and biological methods. *Nat. Resour. Res.* 28 (3), 953–965 (2019).
- Xia, Y., Tang, Y., Shih, K. & Li, B. Enhanced phosphorus availability and heavy metal removal by chlorination during sewage sludge pyrolysis. J. Hazard. Mater. 382, 121110 (2020).
- Andelkovic, I. B. et al. Graphene oxide-Fe (III) composite containing phosphate–A novel slow release fertilizer for improved agriculture management. J. Clean. Prod. 185, 97–104 (2018).
- Said, A. et al. Mechanochemical activation of phlogopite to directly produce slow-release potassium fertilizer. *Appl. Clay Sci.* 165, 77–81 (2018).
- Rizwan, M., Gilani, S. R., Durrani, A. I. & Naseem, S. Kinetic model studies of controlled nutrient release and swelling behavior of combo hydrogel using Acer platanoides cellulose. J. Taiwan. Inst. Chem. Eng. 131, 104137 (2022).
- 74. Tang, X. et al. The response of arsenic bioavailability and microbial community in paddy soil with the application of sulfur fertilizers. *Environ. Pollut.* 264, 114679 (2020).

75. Azeem, B., KuShaari, K., Man, Z. B., Basit, A. & Thanh, T. H. Review on materials & methods to produce controlled release coated urea fertilizer. *J Control. Release.* 181, 11–21 (2014).

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Author contributions

M.I.R.: Investigation, conceptualization, methodology, writing original draft, editing, data interpretation. M.I.A.-W.: Project administration, funding acquisition, resources, review and editing, supervision. A.S.A.-F.: Conceptualization, methodology, re-sources, supervision. M.A.: Statistical analyses, review and editing. methodology, data interpretation. T.A: Supervision, methodology, resources. H.A.A.-S: Formal analysis, data interpretation. M.M.A.; Formal analysis. All authors have read and agreed to the published version of the manuscript.

Declarations

Competing interests

The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to M.I.R.

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