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Synthesis and Chemical Modification of Walnut Shell Biochar for Enhancing Water Retention Capacity of Sandy Soil

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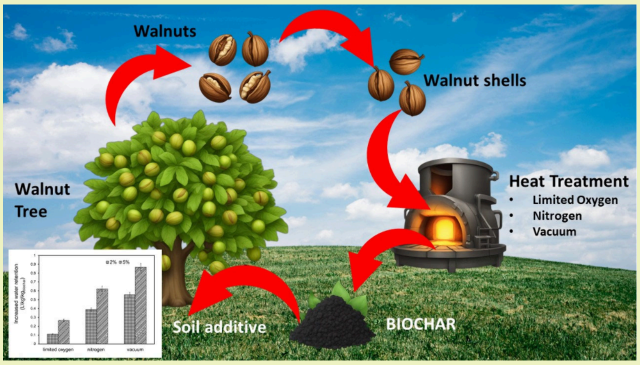

ABSTRACT: The Jammu district of the Indian subcontinent has sandy soil that has low water retention, leading to low agricultural produce. This region is also the largest producer and supplier of walnuts, where walnut shells tend to become local agro-industrial waste. The current study deals with the thermochemical treatment of walnut shells using three different atmospheres, i.e., limited oxygen, nitrogen, and vacuum. The walnut shell biochars were tested for water retention capacity and hydraulic conductivity. All the synthesized biochars were then chemically treated with acid or base to increase their water retention capacity. Surface analysis was done using SEM and FTIR and suggested surface modification and hydrophilic functionalization. The highest water retention capacity was observed in untreated biochar synthesized under limited oxygen atmosphere and sodium carbonate treated biochar synthesized under nitrogen and vacuum environments. The increase in water retention can be associated with hydrophilic functionalization and microstructure of the biochar surface, modified by chemical treatment, supported by contact angle measurements. Incorporation of biochar with soil (locally sourced) shows an enhancement in water retention capacity and lowering of hydraulic conductivity. The highest enhancement for water retention was observed to be 11% for the biochar−soil mixture (5%) using sodium carbonate treated vacuum biochar as compared to the control.

KEYWORDS: *Thermochemical treatment, Shell; Biochar, Sandy Soil, Water retention, Solid waste management*

1. INTRODUCTION

The global climate change has led to a high variation in the rate of precipitation. The occurrences of flash floods and droughts have increased over the years. This has led to a huge uncertainty in agricultural produce. Thus, it is important that the water availability of soil for plants to grow and its retention in soil be enhanced. This will not only benefit the agro ecosystem but also improve the microbial communities in soil leading to better health of the soil.[1]

In order to improve the soil health by increasing both water content and microbial growth, biochar is being considered as one of the leading contenders for this abatement.[2−4] Biochar can be produced using various thermochemical alterations of biomass. It is considered "*to sustainably sequester carbon and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health*".[5] This has provided an impetus for the use of biochar for soil health abetment for the last few decades.[6,7] Biochar has shown a considerable increase in water retention capacity itself, owing to the internal porosity and surface functionalization.[8,9] Thus, the addition of biochar to different kinds of soil has led to an enhancement in its water retention capacity.[10,11]

The Jammu district is in the northern part of the Indian subcontinent and has sandy soil due to the geographical location.[12] The soil that has at least 85% of sand, less than 15% silt and less than 10% clay is classified as sandy soil which has very low water-holding capacity,[10] this affects the vegetation growth in sandy soil.[13] Thus, there have been reports on the use of different biochars that have been tried for abatement of sandy soils.[10,14−17] Additionally, the addition of biochar also improves carbon sequestration (i.e., greenhouse gas mitigation), removes harmful contaminants from the soil, improves crop production by boosting soil fertility, and increases microbial activity and drought mitigation.[13,18] It has been observed that the use of biochar with high hydrophilicity tends to increase the water-holding capacity of sandy soil.[13,19−21] Contradictorily, Jeffery et al.[22] reported that they did not observe any enhancement in the water retention capacity of

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sandy soil by adding Maize biochar. This was attributed to the hydrophobicity of the biochar particles. Wiersma et al.[23] also reported no observable change in the water retention capacity of sandy soil with the addition of Miscanthus straw biochar. Alternatively, Zhang et al.[21] in another study reported that water retention in sandy soil-pine biochar mixture depends on the mixing method. When they arranged the biochar in a layered format, they found no enhancement in water retention capacity; however, when it was uniformly mixed, the water retention capacity decreased. Additionally, they found that larger biochar particles improved the hydraulic properties of sandy soil compared to finer particles. This was due to the destruction of the pore structure of biochar during grinding.[21]

In the current study, the aim was to try and test the effect of walnut shell biochar on the water retention capacity of sandy soil available locally. India is the seventh largest producer of walnuts in the world,[24] and Jammu and Kashmir regions are the largest producers of walnuts in the country.[25] The total production of walnuts in Jammu and Kashmir was 290,000 metric tonne in 2022.[26] The shells of the walnuts form a waste of the agro industry.[24] As the majority of the walnuts produced (~80%) are distributed deshelled,[27] the total shell waste can be estimated to be about 92,800 metric tonne.[28] The walnut shell has found various applications like thermochemical conversion to biofuels[24,29,30] and char, which has been used for various applications, for example, electrode synthesis for batteries,[31] quantum dots,[32] water retention in soil,[16] carbon capture,[33] wastewater treatment,[28] etc. A local survey suggests that the walnut shells are generally collected and disposed of by the municipal corporation in the city of Jammu.

The current study aims to utilize the walnut shell waste for agricultural reuse. The idea is to convert the walnut shell biomass to biochar and study its effect on the water retention capacity and hydraulic conductivity of soil obtained from nearby fields in Jammu. In the case of water retention in soil, it is known that the thermochemical treatment temperature has an effect on the hydrophobicity and hydrophilicity of the biochar.[9] Three different thermochemical environments have been used for the synthesis of walnut shell biochar, and their water retention capacity was tested. Later, chemical treatment of the low water-holding capacity biochar was done in order to enhance the water-holding capacity of the biochar. The three highest water retaining biochars were mixed with soil, and their water retention capacity and hydraulic conductivity were evaluated and compared with literature.

2. METHODOLOGY

2.1. Feedstock. The walnut shells (WS) utilized in this study were obtained from a Dialgam village, India [33.6805° N, 75.1649° E]. In the laboratory, hard walnuts were cracked with a stone. The shells were separated from the kernel. The shells were washed with DI water to remove dirt and other impurities and dried for 24 h at 100 °C (7051-091, Equitron India). The dried shells were ground with a domestic grinder and stored in an air tight container until further use.

2.2. Chemicals. Sodium hydroxide, sodium carbonate anhydrous, hydrochloric acid, and glacial acetic acid were obtained from SD Fine-chemicals limited. Sodium bicarbonate was purchased from Sigma-Aldrich (India). All chemicals were analytical reagent grade and used without further purification. A N_2 cylinder was bought from Sigma Gases, India (99.99% pure). Deionized (DI) water in this study was generated from a double distillation unit (GLDD50AQ, Glassco, India).

2.3. Char Synthesis. The cleaned walnut shells were dried in an oven (7051-091, Equitron India) at 100 °C for 24 h. The dried walnut shells were crushed to form finer particles using a mortar and pestle. The ground shells were kept in closed ceramic crucibles and then placed in a vacuum muffle furnace (Stericox India) for 3 h at 500 °C with initial heating rate of 5 °C/min. The char thus obtained was stored in air tight containers.[9]

The muffle furnace was operated under three different conditions. During the first condition, the inlet and outlet valves of the furnace were kept open to the atmosphere and air was allowed to pass under natural convection. In the second case, N_2 gas was passed through the furnace at a flow rate of 2 L/min. In the third case, the inlet valve was closed, and a vacuum pump was connected to the outlet and was used for the entire process. For 60 g of walnut shell sample, 18 g of biochar was obtained in all three conditions. The ultimate analysis of three different biochar samples was determined using an elemental analyzer (Elementar UNICUBE, Germany). The ultimate analysis was done in duplicates. Proximate analysis was carried out in accordance with standard methods ASTM D1037 (1991), ASTM D2017 (1998) and ISO 562 (1974) to determine moisture content, ash content, and volatile matter, respectively. The fixed carbon was calculated by subtracting the sum of ash, moisture, and volatile percentage from 100. All the proximate analysis was done in triplicates.

2.4. Chemical Treatment. All the three biochars thus synthesized were treated chemically using 1 M solutions of either hydrochloric acid (HCl), acetic acid (CH_3COOH), sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), or sodium carbonate (Na_2CO_3). The process followed for chemical treatment involved adding 10 g of biochar to 100 mL of solution (e.g., 1 M hydrochloric acid) and kept in an incubator shaker (C24 Plus, Remi, India) for 24 h at 180 rpm at 27 °C. The chemically treated biochar was separated by vacuum filter. The sample was dried in an oven for 48 h at 100 °C. The dried biochar was kept in air tight container until further use. This was repeated for all the three biochars in triplicate.

2.5. Characterization. Fourier transform infrared spectroscopy (FTIR) (Spectrum Two N, PerkinElmer, USA) was used to identify and analyze different functional groups on the surface of the chemically treated and untreated biochar samples. The system has a KBr window for attenuated total reflectance mode (ATR) system with $LiTO_3$ detector with SNR of 9300:1. Scanning Electron Microscopy (SEM, JSM-7900F, JEOL, JAPAN) was used for morphological analysis of chemically treated and untreated biochar samples.

2.6. Water Retention in Biochar. A percolation based water retention test was carried out for the chemically treated and untreated biochar as reported previously[9,14,21,34] with a few modifications. A packed bed was created using 15 mL of a graduated centrifuge tube with a cap. The bottom tip of the centrifuge tubes was cut, and five holes of 2 mm diameter were drilled on its lid. A Whatman class-1 (Sigma Adrich) cellulose filter paper was used at the bottom to stop the flow of solid from flowing away with the water. 3 g of chemically treated and untreated biochar samples was loaded to a centrifuge tube to form the biochar bed, and the sample was gently tapped until the bed settled completely. A known amount of double distilled water was passed through the bed, and the water that percolated through the bed was collected at the bottom and measured. All percolation experiments for water retention were carried out in triplicate, and the standard deviation has been presented in the data.

2.7. Contact Angle Measurements. The contact angle was measured using optical tensiometer (Theta Flex, Biolin Scientific, Germany). The biochar samples were kept on the sample holder of an instrument, and 0.6 μL of deionized water (>18 MΩ resistivity) was placed on a sample surface. The image was analyzed by software using the sessile drop method to determine the contact angle. The process was repeated five times for each sample.

2.8. Water Retention in Soil with and without Biochar. The soil sample was collected from the local field of village Jagti, India [32.8206° N, 74.9063° E], using a cylindrical core-cutter having an internal diameter of 10 cm, height 13 cm, and wall thickness 3 mm, which was placed on the ground with a steel dolly having 2.5 mm height and 10 cm internal diameter to be fitted on the top of core cutter. The steel rammer having a weight of 9 kg was blown on the dolly to insert the core cutter into the soil. The soil samples were collected for nearby fields (multiple fields) and were mixed well before use; this is representative of the nearby fields of the nearby region of Jammu (Tawi valley). The soil type evaluated is concurrent with the literature.[12] The motivation was to develop a local technology that would benefit people in the surrounding region for both waste management and livelihood development. The undisturbed soil core sample was taken to the laboratory, and the field density, dry density, and water content test of soil was determined as per Indian Standards IS 2720 (part XXIX)-1975. The pH of soil sample was determined as per Indian Standards IS 2720 (part 26), 1983, using a pH meter (HI2550, Hanna Instruments). A 30 g portion of soil was mixed with 75 mL of water as per the standard for pH measurements. Bulk density was determined as per Indian Standards IS 2720-1980 (Part III/section 1). Particle size analysis of the soil was done by using a standard sieve set (Indian Standards IS 460-1, 1985).

The field soil was kept in an oven for 24 h at a temperature of 110 °C. The obtained soil sample was crushed and then sieved through a 2 mm sieve. The soil sample which was passed through 2 mm sieve was packed in an air tight polythene bag, and the sample bags were kept in a vacuum desiccator. Biochar sample was also ground using mortar and pestle and was passed through a 2 mm sieve. The obtained biochar sample was kept in an airtight container and kept in a vacuum desiccator. 30 g of soil was taken as constant, and 2% and 5% (wt) biochar were mixed uniformly with the soil, and all these samples were used for percolation water retention test.[9,15,35]

The percolation experiments for water retention in soil were done in a similar manner, as stated in the previous section.[9,15,21,34] The packed bed was created using a 50 mL graduated centrifuge tube, the conical end was cut, and five holes of 2 mm diameter were drilled on the cap. Whatman 1 cellulose filter paper was used to retain all the solid within the cap. 30 g of soil or biochar–soil mix was added to the centrifuge tube to form a bed, and the tube was tapped gently until the packing height became constant. 30 mL of double distilled water was added to the packed bed, soaked for 30 min, and allowed to freely drain for 20 min for all excess water to drain. The percolate was collected at the bottom, measured, and corrected for the water retention of the filter paper. The same was repeated for the biochar–soil mix. All experiments were repeated in triplicates.

2.9. Hydraulic Conductivity of Soil with and without Biochar. The hydraulic conductivity was determined per IS:272O (Part 17)-1986. The sample of soil (or soil–biochar mix) that has been compacted and soaked is placed inside of a permeameter mold having 100 mm diameter and 127 mm height. A constant head reservoir is attached to ensure that the water level above the sample remains constant. As soon as a steady flow has been established, water runs continuously through the soil, while being subjected to a constant hydraulic head. The water that is collected in a measuring cylinder over a certain amount of time is the water that is collected from the sample, and both the amount of water and the amount of time are recorded. After that, the hydraulic conductivity (K) is determined by using Darcy's law,[36] taking into account the flow rate, cross-sectional area, length of the soil sample, and head difference. The hydraulic conductivity was repeated thrice.

3. RESULT AND DISCUSSION

3.1. Ultimate Analysis of the Three Different Biochars. The ultimate analysis was done in order to characterize the chemical composition of the biochar obtained. The results of the ultimate analysis of the biochar synthesized using three different thermochemical treatment processes is listed in Table 1. It can be observed that the biochar obtained with limited oxygen atmosphere has the highest carbon content, whereas the biochar obtained from vacuum treatment has the lowest carbon content. Additionally, it can be observed that there is negligible difference in both hydrogen and nitrogen content in all the char samples. The biochar obtained using a vacuum environment retained high oxygen content followed by biochar prepared under nitrogen environment, and the limited oxygen environment synthesized biochar sample has the minimum oxygen content. The carbon to hydrogen ratio for all biochar samples shows negligible change; however, the carbon to nitrogen ratio follows similar trend as the carbon content. Proximate analysis data of the char samples in Table 1 show that all samples have a high amount of volatile matter and fixed carbon. The moisture content in all the different types of char is near to 10% with low ash content. The results are similar to previous study for walnut biochar analysis of Indian walnuts.[29]

Table 1. Ultimate and Proximate Analysis of the Synthesized Biochar Samples

	Proximate Analysis			
Treatment	Moisture	Fixed Carbon	Volatiles	Ash
Limited oxygen	5.61 ± 0.5	24.55 ± 1.5	70.14 ± 2.5	1.25 ± 0.3
Nitrogen	11.17 ± 1.5	15.19 ± 0.5	68.59 ± 3.6	3.5 ± 0.8
Vacuum	10.86 ± 1.0	17.64 ± 1.2	70.46 ± 5.1	1.04 ± 0.2

	Ultimate Analysis					
	N (%)	C (%)	H (%)	O (%)	C/N	C/H
Limited oxygen	0.43	86.35	2.87	10.34	199	30.01
Nitrogen	0.43	83.90	2.75	12.92	195	30.48
Vacuum	0.43	78.99	2.59	17.99	182	30.46

3..2. Water Retention Tests of Three Different Biochars. Figure 1 shows the water retention in a packed bed of the biochar synthesized using three different

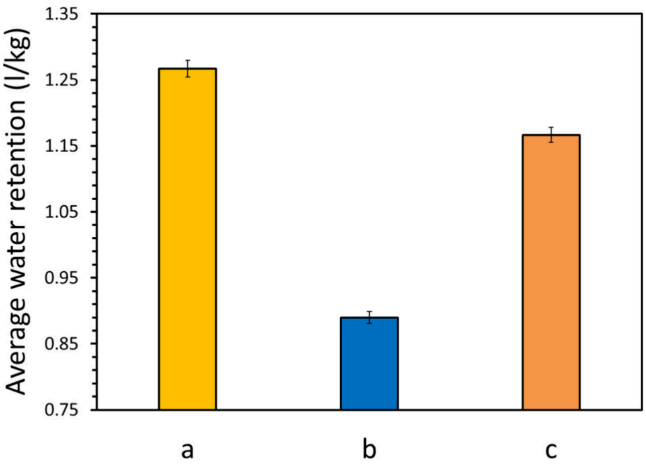

Figure 1. Water retention with standard deviation of three replicates in packed bed of biochar synthesized using three different methods: (a) limited oxygen, (b) nitrogen, and (c) vacuum.

thermochemical treatments. It can be observed that the biochar synthesized using limited oxygen atmosphere shows the highest water retention as compared to the other treatments. Alternatively, the biochar that was synthesized using nitrogen treatment shows the minimum water retention capacity. In order to understand the reason for the variation in water retention capacity, the surface chemistry and morphology of the char samples were studied.

3.3. Surface Chemistry and Morphology of Three Different Biochars. In order to understand the surface chemistry of the biochar, FTIR analysis of the three biochar samples was performed (Figure 2). It can be observed from Figure 2 that the gas space atmosphere of the muffle furnace has an effect on the chemical composition of the biochar formation. The FTIR spectrum of all the char samples can be divided into three regions, 700−900, 900−1500 and 1500−1700 cm^{-1}. All of the assignments can be seen in Table 2. The peaks at 1418 ± 4 cm^{-1} can be assigned to the O−H bending vibration of carboxylates and carbonic acids,[37,38] which is evident in the biochar synthesized under nitrogen and vacuum conditions and absent in the limited oxygen sample. Carboxylic and amine/amino groups tend to be polar in nature, thus showing hydrophilic characteristics.[9,15] It can be observed from Figure 2 that, for limited oxygen synthesized biochar, the amine group peak resonance seems to be stronger as compared to the other two biochar. Thus, all the biochar have hydrophilic surface groups.

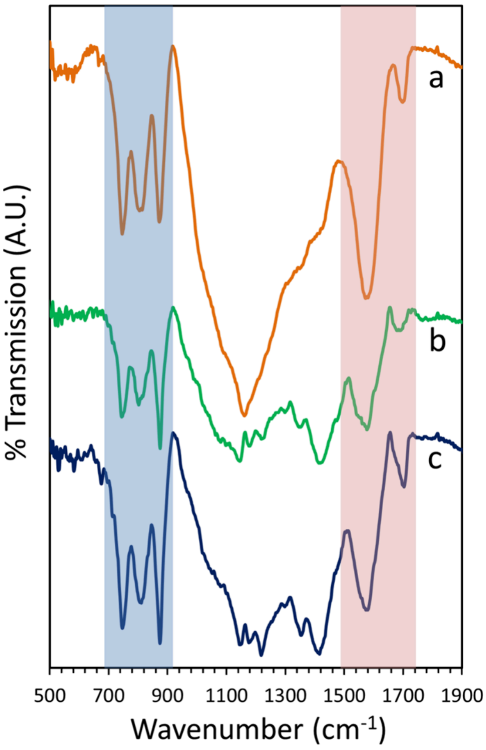

Figure 2. FTIR of the biochar samples synthesized using three different methods: (a) limited oxygen, (b) nitrogen, and (c) vacuum.

Table 2. Assignment of FTIR Peaks of Walnut Shell Biochar

Peak positions (cm^{-1})	Assignment	Reference
700−900	substituted aromatics	39
1180−1220	C−N stretching of amine/amino groups	40
1418 ± 4	carboxylates and carbonic acids	37, 38
1580 ± 5	stretching vibration of lignin	41
1695 ± 10	carboxylic acids/conjugated acid	39

Figure 3 shows the surface morphology of the biochar samples synthesized using three thermochemical treatment methods. It can be observed from Figure 3 that all three samples have a sponge-like structure, which is characteristic of walnut shells and biochar.[41−43] Comparing Figure 3a with Figure 3b,c, one can observe that there are small microcraters within the macropores of the biochar. This suggests that the surface of the biochar may be rougher in the case of nitrogen and vacuum synthesized biochar as compared to biochar synthesized under limited oxygen. The microporous nature and surface roughness of the biochar would lead to low wettability of water (discussed later, Figure 9), thus enhancing easy runoff from the macrocraters (lotus leaf effect).[44] Therefore, from the SEM and FTIR results, it can be suggested that water retention in the packed bed of the three biochars (Figure 2) can be associated with surface morphology as compared to surface functionalization.

3.4. Water Retention after Chemical Treatment of Three Different Biochars. It was observed that the change in hydrophobicity increases the water-holding capacity of biochar.[8] In order to further enhance the water retention, the three different biochar chemical treatments (acidic and basic) were performed. Figure 4 shows that the chemical treatment of the three biochars had an effect on its water retention capacity. It can be observed from the figure that the water retention capacity of all the samples decreased under acidic treatment. However, it was observed that basic treatment had a varying effect on the water retention capacity of the biochar. Biochar obtained from nitrogen treatment shows an enhancement in water retention when chemically treated with sodium bicarbonate and sodium carbonate. It shows reduction in water retention when chemically treated with sodium hydroxide compared to untreated biochar. Alternatively, biochar synthesized using vacuum treatment shows enhancement in water retention when treated with sodium carbonate as compared to sodium bicarbonate or sodium hydroxide, which shows a reduction in the water retention capacity. For the biochar synthesized using limited

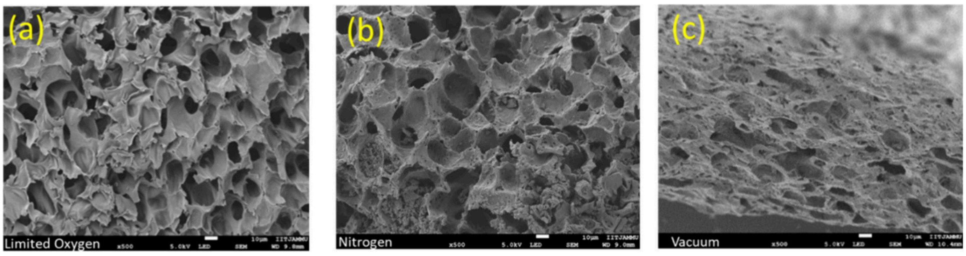

Figure 3. SEM images of biochar synthesized using three different methods: (a) limited oxygen, (b) nitrogen, and (c) vacuum.

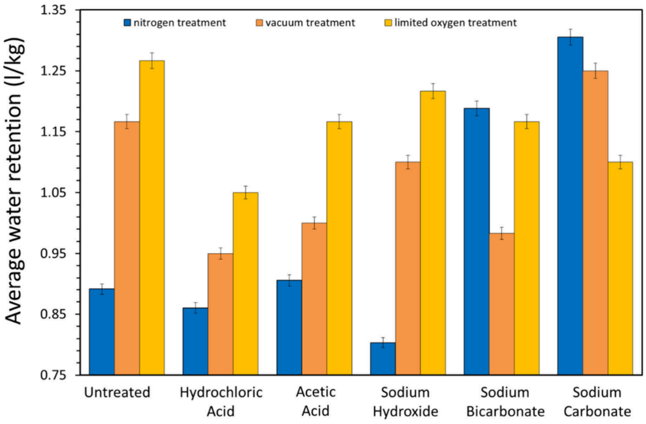

Figure 4. Water retention with standard deviation of three replicates in chemically treated and untreated biochar synthesized using three different thermochemical treatments (i.e., limited oxygen, nitrogen, and vacuum).

oxygen, basic treatment shows reduction in the water retention capacity as compared to untreated sample. Therefore, in order to understand the cause for the variation in water retention capacity of the chemically treated biochar, the surface chemistry and morphology were studied.

3.5. Surface Chemistry and Morphology of Chemically Treated Biochar. The FTIR analysis of the chemically treated biochar samples is presented in Figure 5. It can be seen from Figure 5A that significant changes are observed in the IR spectral peaks due to the chemical treatment. There are additional peaks observed at 1418 ± 4 cm^{-1} when chemically treated, which can be assigned to −OH stretching vibration of carboxylic acid.[41] However, on analysis of Figure 5B,C, it can be observed that there are no significant changes in the spectra, as there are no new peaks formed, but the relative intensities of the peaks have changed.

Figure 6, 7, and 8 show SEM images of chemically treated and untreated biochar samples. It can be observed from Figure 6 that, in most of the samples except Figure 6a, the pores are filled with small particles. This can be one of the major reasons for the reduction in the water retention capacity for the biochar sample after chemical treatment and of the biochar synthesized under limited oxygen atmosphere. In Figure 7 and Figure 8, similar phenomena of pore blocking due to smaller particles can be observed, except for Figure 7f and Figure 8f, respectively. Thus, the enhancement in water retention in the biochar samples can be attributed to the clear macroporous structure of the walnut shell.

3.6. Hydrophobicity of the Chemically Treated and Untreated Biochar. There exists a strong correlation between hydrophilicity and water retention capacity of the

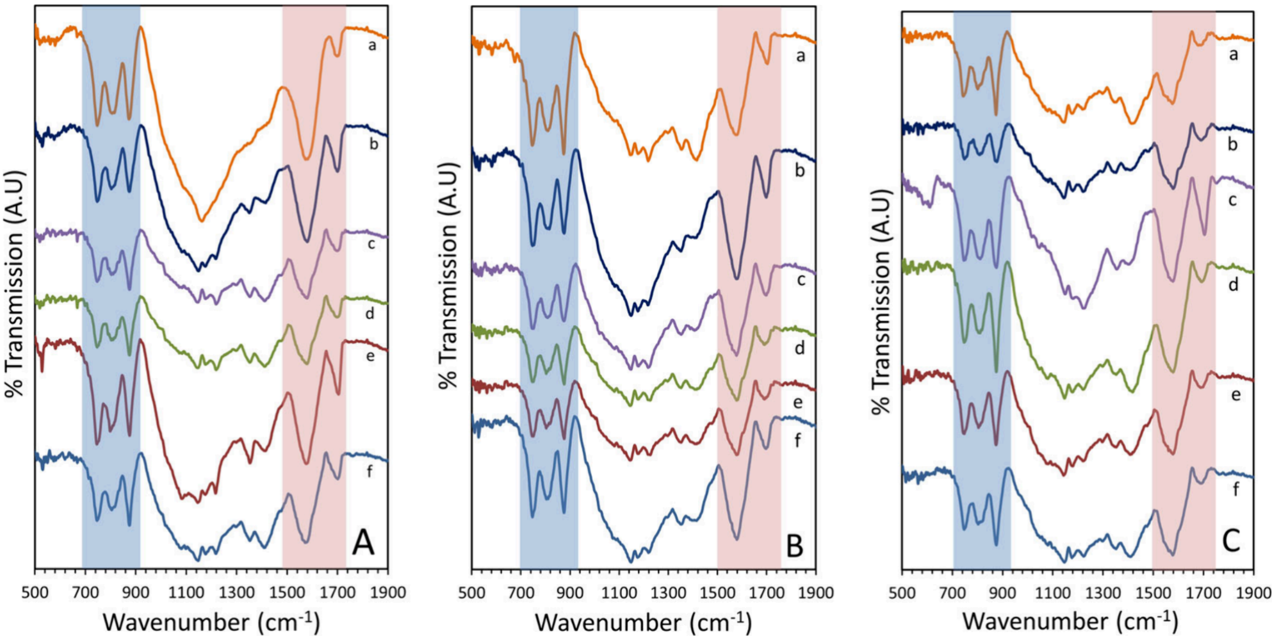

Figure 5. FTIR spectra of chemically treated biochar [(A) limited oxygen, (B) vacuum] and (C) nitrogen (a) untreated and treated with (b) hydrochloric acid, (c) acetic acid, (d) sodium bicarbonate, (e) sodium carbonate, and (f) sodium hydroxide.

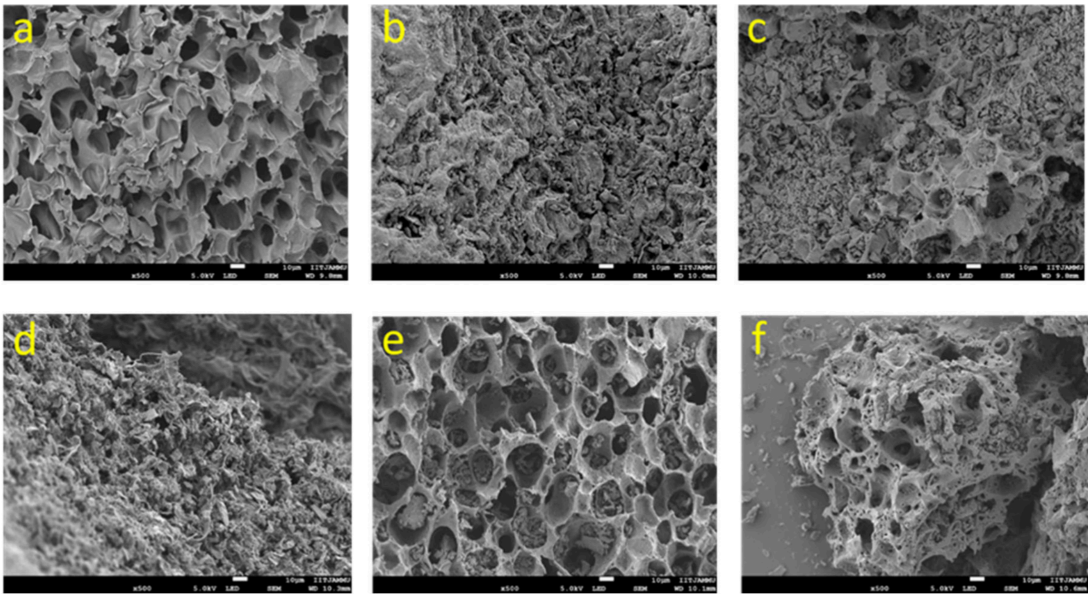

Figure 6. SEM images of the biochar synthesized under limited oxygen atmosphere: (a) untreated and with chemical treatment using (b) hydrochloric acid, (c) acetic acid, (d) sodium hydroxide, (e) sodium carbonate and (f) sodium bicarbonate.

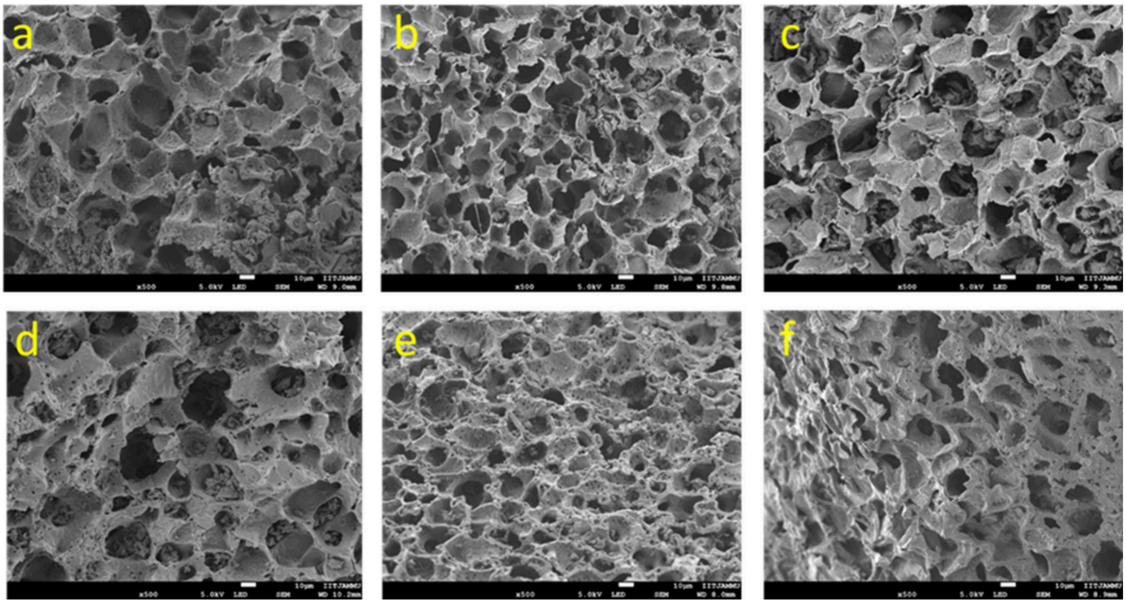

Figure 7. SEM images of the biochar synthesized under nitrogen atmosphere: (a) untreated and with chemical treatment using (b) hydrochloric acid, (c) acetic acid, (d) sodium hydroxide, (e) sodium carbonate, and (f) sodium bicarbonate.

biochar.[8] The hydrophilicity of the biochar was identified using contact angle measurements,[38,45] which determines the adhesive properties of liquids and solid surfaces. The numerical value of the angle allows one to predict the nature of the liquid−surface interaction and the ability of the material to absorb and retain moisture. It is considered that, if the value of the contact angle is less than 90°, then there is high affinity of the liquid to the solid, suggesting high wettability. If the angle value is more than 90°, it suggest that repulsive force is higher between the solid and liquid, suggesting low wettability.[45,46] It can be seen from Figure 9 that there is a considerable change in the hydrophobicity of the biochar with and without chemical treatment. All the biochar samples that show high water retention capacity in Figure 4 show low contact angles in Figure 9, confirming the effect of chemical treatment on the water retention capacity biochar. Thus, surface features and functionalization both are collectively responsible for the surface wettability of water and the processed biochar, leading to high water retention.[46]

3.7. Influence of Biochar in Soil Water Retention. The properties of the soil obtained from the field in Jammu are listed in Table 3. Sieve analysis of the soil was done as per IS 460-1 to determine the particle size distribution of the soil. It can be seen in Table 3 that the soil contains more than 91% sand and 0% of gravel. It also contains a lower percentage of clay and silt, classifying the soil as sandy. The results are similar to reported literature.[12]

Sandy soils have been observed to have low water-holding capacity, as they drain water easily.[10] To increase the water-holding capacity of the soil, 2% and 5% of the biochar were

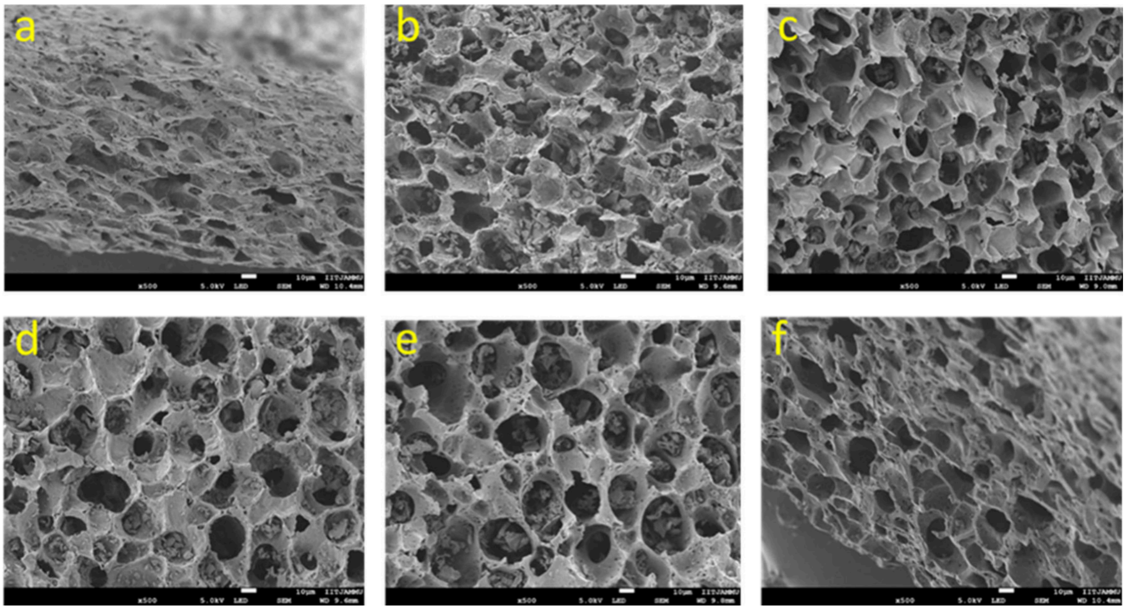

Figure 8. SEM images of the biochar synthesized under vacuum atmosphere: (a) untreated and with chemical treatment using (b) hydrochloric acid, (c) acetic acid, (d) sodium hydroxide, (e) sodium carbonate, and (f) sodium bicarbonate.

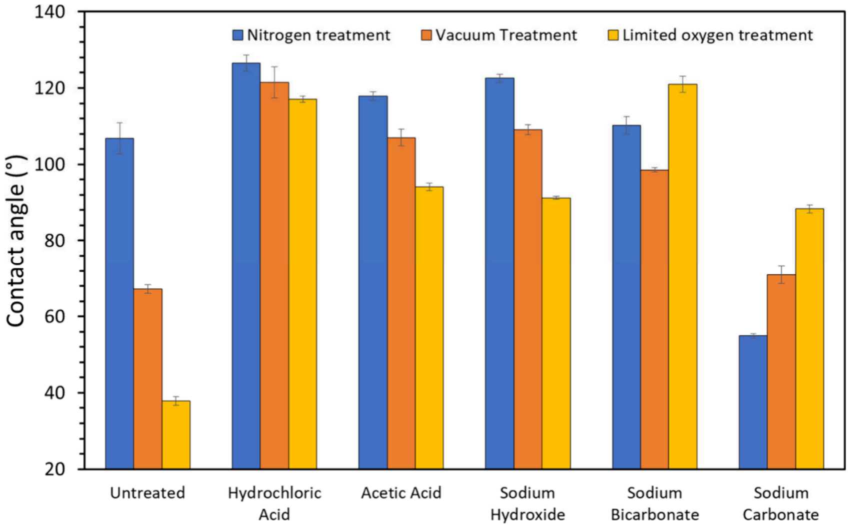

Figure 9. Contact angle with standard deviation of five replicates in chemically treated and untreated biochar synthesized using three different thermochemical treatments (i.e., limited oxygen, nitrogen, and vacuum).

Table 3. Properties of Soil Obtained from Field near IIT Jammu, India

Field Density	1940 ± 20 kg/m^3
Dry density	1720 ± 28 kg/m^3
Water Content	13.10 ± 3.5%
Specific gravity	2.77 ± 0.15
pH	7.25 ± 0.3
Clay%	1.82 ± 0.3
Silt%	6.53 ± 1.1
Sand%	91.65 ± 4.1

mixed with the soil,[9,15,21] and the water retention capacity was evaluated using the percolation technique. Figure 10 shows the increased water retention capacity and percentage water retention enhancement of the soil−biochar mix. It can be observed from Figure 10a that there is an increase in the water retention capacity of soil when the three previously identified biomasses were mixed with the soil. The water retention capacity of bare soil was 0.4 L/kg. When 2% biochar was mixed with soil, an increase in water retention capacity was observed between 0.1 ± 0.004 and 0.55 ± 0.033 L/kg/kg biochar, i.e., about 1 ± 0.04% to 3 ± 0.05%, with a maximum of 0.55 ± 0.033 L/kg/kg biochar for chemically treated vacuum char in addition to that of the bare soil. When 5% biochar is mixed with soil, it increases the water-holding capacity between 0.27 ± 0.0135 L/kg and 0.8 ± 0.072 L/kg/kg biochar, i.e., 3 ± 0.05% to 11 ± 0.09%. Similarly, in this case also chemically treated biochar synthesized under vacuum conditions shows an enhancement in water retention of 0.8 ± 0.072 L/kg/kg biochar (i.e., 11 ± 0.09%) as compared to bare soil. The biochars synthesized using wood chips tend to show a lower water retention at 5% biochar loading in sandy soil.[16] However, it was reported that maze and pine biochar did not show any enhancement in water retention in sandy

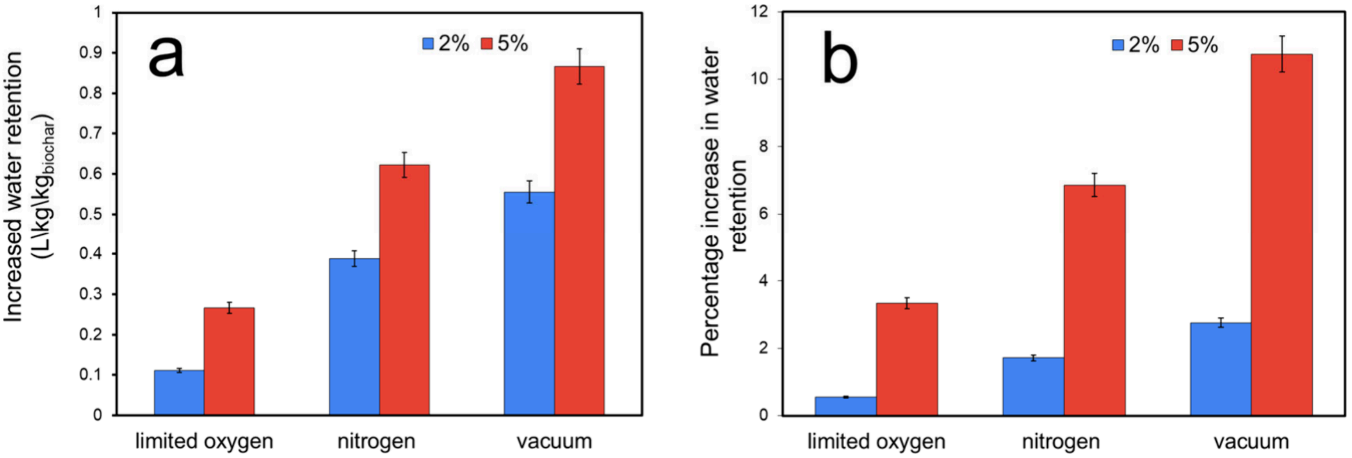

Figure 10. Increase in water retention with standard deviation of three replicates of biochar−soil mix at different char loadings of 2% and 5% (wt %), respectively.

Table 4. Comparison of Water Retention Enhancement in Different Types of Sandy Soil Using Biochar

	Soil type	Biomass	Biochar (%)	Pyrolysis temperature (°C)	Water retention (%)	Reference
1	Sandy	Wood chips	5	450−500	10	48
2	Sandy	Poultry litter hydrochar	0.5	220	2	35
		1	5			
		2	5			
3	Sandy	Mesquite	2	400	14	10, 47
4	Sandy	Walnut shell	2	500 (Vacuum)	3 ± 0.05	This Study
			5	500 (Vacuum)	11 ± 0.09	

soils.[15,21] Contradictory to the report by Zhang et al.[21] in the current study, it has been observed that uniformly mixed biochar−sandy soil mixture has enhanced water retention. Table 4 shows the comparison of the use of different biochars synthesized using different thermochemical temperatures (mostly pyrolysis) for enhancement of water retention in sandy types of soil. From Table 4, it can be observed that the results obtained in this study compared with the results reported in the literature for soil types were similar to the ones used for this study.

Both interparticle and intraparticle pore structure of the soil can be altered by biochar amendment. It has been observed that the soil particles can readily fill in the interparticle pore structure generated by irregular-shaped biochar particles.[16,47] In this study it can be observed from the SEM images that the walnut shell biochar tends to have many macropores that can be filled in by fine soil particles, suggesting a reason for the variation in water retention in soil. In contrast, it was previously reported[15] that, for sandy soil, biochar had no effect on the water retention capacity, though the pore diameter of the biochar used there was smaller than the one observed in this study. It is thus reasonable to deduce that the ratio of biochar porosity to that of the soil layers has a close relationship with the water content ratios in soil layers.[21] This provides a new impetus toward more research toward incorporation of biochar with sandy soils to increase the usability of more land for agricultural purpose.

3.8. Hydraulic Conductivity of Biochar Mediated Soil.

The saturated hydraulic conductivity, K_s, describes the measure of effortless movement of water through saturated porous media, i.e., soil. The hydraulic conductivity of the soil and soil biochar mix was evaluated. The change in hydraulic conductivity of the soil with and without different biochar abatements can be observed from Figure 11. The hydraulic conductivity of the bare soil was 0.8013 ± 0.012 cm/min. This is consistent with some previously reported literature on soil hydraulic conductivity.[21] It can be observed from Figure 11 that there is a decrease in the hydraulic conductivity of the soil with addition of the biochar. The results tend to follow a trend similar to that for the moisture retention capacity in Figure 10a. Ajayi et al.,[20] Barnes et al.,[34] Zhang et al.[21] and Šurda et al.[13] also found a strong correlation between hydraulic conductivity and biochar composition for sandy soil. They found that the K_s of sandy soil decreased with increasing ratios of added biochar. They attributed this to either to the water-repellent nature of biochar or the infilling of large water-conducting pores with biochar. The same may be attributed in

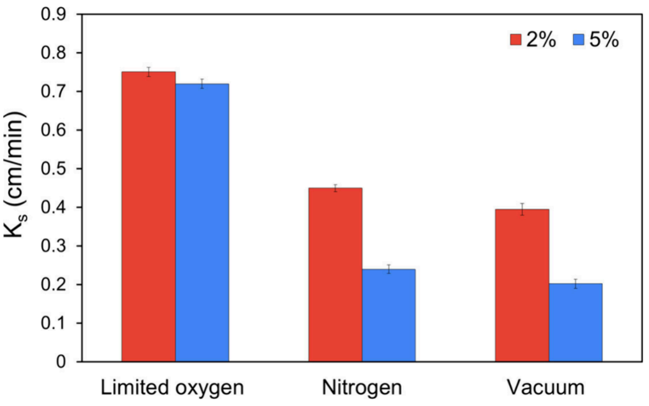

Figure 11. Increase in hydraulic conductivity with standard deviation of three replicates of biochar−soil mix at different char loadings of 2% and 5% (wt %), respectively.

this study as per the FTIR and contact angle measurements. However, Jeffery et al.[22] and Wiersma et al.[23] reported no significant enhancements of the hydraulic conductivity with biochar addition to sandy soil.

4. CONCLUSION

In this study, walnut shells were thermochemically treated under three different atmospheric conditions to synthesize biochar. It was observed that the biochar synthesized under limited oxygen condition showed the best results for water retention as compared to the biochar synthesized using nitrogen and vacuum environments. However, in order to enhance the water retention capacity of the biochar, chemical treatment was done for all the biochar. Following this, an enhanced water retention in nitrogen and vacuum environment synthesized biochar was observed after sodium carbonate treatment. The biochar having the highest water retention was then mixed with soil in a ratio of 2% and 5% and water retention was studied. The best water retention was observed for a sodium carbonate treated vacuum environment synthesized biochar when mixed with soil, giving an enhancement of 11% compared to bare soil. The use of vacuum and post treatment provides an economic limitation for wide scale application. However, for field application, the untreated biochar synthesized with limited oxygen seems to be a plausible contender that can be easily implemented for rural field applications. The technology for synthesis of this biochar is simple and easy to implement with low economic investment, as most households in the Jammu and Kashmir region char the walnut shell to use as heating fuel in the winter. Lifecycle analysis and economic evaluation of the implementation of this technology can be further studied.

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Notes

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