

# ENGINEERED BIOCHAR DERIVED FROM GRASS JELLY TREE WASTE

Chatlada Chaiwong<sup>1</sup>, Sunan Siphai<sup>2</sup>, Supattra Budsareechai<sup>3</sup>, Jesper Theodorus Nicolaas Knijnenburg<sup>4</sup>, and Yuvarat Ngernyen<sup>1,\*</sup>

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## Abstract

The aim of this study was to prepare biochar from grass jelly tree waste, which is a solid waste of the dessert industry, and investigate the effects of chemical modification with  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$  on the porous properties. The grass jelly tree waste was pyrolyzed at 500, 600 and 700°C for 1 hour to obtain biochar, and subsequently impregnated with 30 wt%  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$  for 24 hours. Porosity measurements showed that the engineered biochar derived from pyrolysis at 700°C and modified with  $\text{H}_3\text{PO}_4$  had the highest surface area of 111  $\text{m}^2/\text{g}$ . Furthermore, physicochemical properties such as bulk density, pH, pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ), proximate analysis, compositions and morphologies of the biochars were further analyzed using different techniques, including SEM-EDX, XPS, TGA and FTIR. The engineered biochar with the highest surface area had a bulk density of 0.34  $\text{g}/\text{cm}^3$ , a slightly acidic pH of 6.21 and  $\text{pH}_{\text{pzc}}$  of 6.9. This biochar had low moisture content of 5.69 wt% but a high ash content of 26.61 wt%. The major component of the biochar was fixed carbon at 55.03 wt% which is in agreement with the SEM-EDX and XPS analysis. These results indicated the engineered biochar derived from grass jelly tree may be suitable for adsorption of organic and inorganic pollutants.

**Keywords:** Engineered biochar; Grass jelly tree; Pyrolysis; Modification; Surface area

## Introduction

Biochars are used as low-cost adsorbents for removal of a wide range of organic and inorganic compounds from aqueous solutions. Porous biochars have presented a good adsorption capacity for many pollutants such as heavy metals (Zhao *et al.*, 2019), dyes (Praveen *et al.*, 2022), herbicides

(Binh and Nguyen, 2020), and antibiotics (Stylianou *et al.*, 2021). To improve the adsorption capacity, biochars are frequently modified through physical and/or chemical techniques that endow the biochar with desirable properties (e.g., higher porosity and introduction of surface functional groups). Physical

<sup>1</sup> Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, 40002, Thailand. E-mail: nyuvarat@kku.ac.th

<sup>2</sup> Department of Educational Research and Evaluation, Faculty of Education, Chaiyaphum Rajabhat University, 36000, Thailand.

<sup>3</sup> Department of Mechanical Engineering, The project to establish the Faculty of Engineering and Industrial Technology, Chaiyaphum Rajabhat University, 36000, Thailand. E-mail: pla.supattra.cpru@gmail.com

<sup>4</sup> Biodiversity and Environmental Management Division, International College, Khon Kaen University, Khon Kaen, 40002, Thailand.

\* Corresponding author

modification techniques include ball milling, microwave treatment and magnetic modification whereas chemical techniques comprise oxidizing modification, chemical impregnation/coating and clay coating (Panahi *et al.*, 2020). Various chemical agents such as  $H_2SO_4$ ,  $H_3PO_4$ , KOH, NaOH and  $ZnCl_2$ , have been proposed. Among these,  $H_3PO_4$  and  $ZnCl_2$  treatments has several advantages such as low corrosion to the equipment, relatively low pyrolysis temperature, inexpensive, high biochar yield and minor pollution to the environment (Liu *et al.*, 2020; Zakaria *et al.*, 2022).

Biochars can be produced from a wide variety of biomasses including agricultural and forest residues (Petrova *et al.*, 2023), animal manure (Liao *et al.*, 2022), marine and aquatic organisms (Nguyen *et al.*, 2022) and industrial waste (Wang *et al.*, 2020a). Examples of biomass feedstocks for biochar production are rice husk, corn straw, bagasse, switch grass, soybean stalk, olive pomace, orange waste, pine and oak wood or bark, paper sludge and sewage sludge (Sri Shalini *et al.*, 2021). Converting industrial wastes into biochar contributes to both environmental protection and waste management.

Grass jelly is a popular dessert component in Asian cuisines. One dessert company in Thailand has a grass jelly production capacity of around 2,000 tons per year, which also generates large amounts of grass jelly tree waste after the production process. This waste is disposed of in landfills, resulting in the need for large storage volumes. So, the conversion of this waste into value-added products would be an attractive waste management approach. To the best of our knowledge, no research has been carried out on the production and characterization of biochar from grass jelly tree waste.

The objective of this study was to produce and characterize a new biochar that was prepared from an industrial bio-waste (grass jelly tree waste). The pyrolysis temperature was optimized in order to obtain a high porosity and specific surface area. To further increase the porosity, the biochar was impregnated with  $H_3PO_4$  and  $ZnCl_2$ . Characterization of the engineered biochar was done by  $N_2$  adsorption-desorption, FTIR spectroscopy, SEM-EDX, XPS, TGA, proximate analysis, bulk density, pH and  $pH_{pzc}$ .

## Materials and Methods

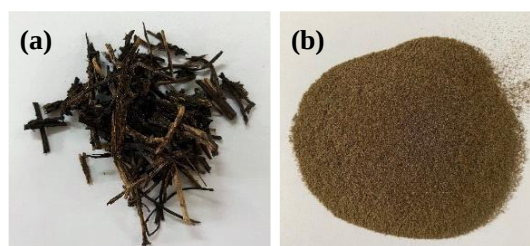
### Materials and Reagents

The dried grass jelly tree waste (Figure 1 (a)), the waste from dessert production, was obtained from Siam Dessert Co., Ltd. All reagents, i.e.,  $H_3PO_4$  (QR c),  $ZnCl_2$  (KEMAUS), NaCl (RCI

Labscan), NaOH (LOBA CHEMIE) and HCl (RCI Labscan), were of AR grade.

### Preparation of biochar and engineered biochar

The dried grass jelly tree waste without any treatment was ground into powdered form and sieved through mesh no. 80 (180  $\mu m$ ) (Figure 1 (b)). Then, 50 g of this sample was loaded into a cylindrical stainless steel fixed bed reactor of 30 cm length and 5 cm diameter. The reactor was placed inside an in-house developed electric furnace connected to a temperature and heating control system. Pyrolysis was done at three temperatures (500, 600 and 700 C) with a fixed residence time of 1 h in  $N_2$  atmosphere. The resulting biochars were named BC500, BC600 and BC700, respectively. The biochar yield was calculated by the ratio between biochar mass after pyrolysis and biomass mass before pyrolysis.



**Figure 1.** Dried grass jelly tree waste (a) in original form and (b) after ground and sieved

Next, the obtained biochar was soaked in 30 wt% activator solution ( $H_3PO_4$  or  $ZnCl_2$ ) at room temperature for 24 hrs using chemical weight ratio between biochar:activator of 1:3. These experimental conditions were the same as generally reported in literature (Wang *et al.*, 2020b; Jabar *et al.*, 2022). The treated sample was washed with distilled water and dried at 120 C. Finally, the resulting engineered biochar was placed in a sealed container until characterization.

### Characterization of engineered biochar

The engineered biochars were characterized for their textural porosity, proximate analysis, bulk density, pH,  $pH_{pzc}$  at the point of zero charge ( $pH_{pzc}$ ), surface functional groups, thermal decomposition profile, composition and surface morphology.

The  $N_2$  adsorption-desorption isotherms of the biochars were determined by a surface area and pore analyzer (ASAP2460 Micromeritics) at -196 C. The specific surface area ( $S_{BET}$ ) and the average pore diameter ( $D_{avg}$ ) were found from Brunauer-

Emmett-Teller (BET) method. The total pore volume ( $V_{\text{total}}$ ) was obtained by converting the  $N_2$  adsorption capacity at a  $P/P^0$  of 0.99 into volume. The micropore volume ( $V_{\text{mic}}$ ) was calculated by Dubinin-Radushkevich (DR) method.

Proximate analysis including moisture, ash content and volatile matter was performed by the international standard procedure (ASTM D1762-84 Standard Test Method for Chemical Analysis of Wood Charcoal). Fixed carbon (% dry basis) was calculated using the equation  $100 - \text{ash} (\% \text{ dry basis}) - \text{volatile matter} (\% \text{ dry basis})$ . The weight to volume ratio as the bulk density was determined according to ASTM D2854-09.

The pH value of the engineered biochar was measured by adding 1 g biochar into 100 mL distilled water. The suspension was heated to 90°C and kept stirring for 20 min. After cooling down to room temperature, the pH of the slurry was measured using a pH meter (Starter 3100 OHAUS). The  $pH_{\text{pzc}}$  of the engineered biochar was determined by pH-drift method. Here, 0.1 g biochar was mixed with 50 mL of a 0.01 M NaCl solution of different pH between 3-11 adjusted with 0.1 M HCl or NaOH solutions. The final pH value was recorded after 24 h of contact time. The  $pH_{\text{pzc}}$  was identified as the pH value at the intersection of a measured curve with the  $pH_{\text{final}} = pH_{\text{initial}}$  line.

The functional groups available on raw grass jelly trees and engineered biochar surface were detected using Fourier transform infrared spectroscopy (FTIR; ALPHA II Bruker). The spectra were scanned from 4000 to 550  $\text{cm}^{-1}$ . The morphology and surface elemental composition of the biochars were examined using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX; Helios NanoLab G3 CX FEI). In addition, X-ray photoelectron spectroscopy (XPS; AXIS Ultra DLD Kratos) measurements were carried out to determine the elemental composition and chemical state on the biochar surface. Thermal stability and decomposition behavior of engineered biochar were investigated using a thermogravimetric analyzer (TGA) with a heating rate of 10°C/min to 800°C under nitrogen or air flow of 60 mL/min.

## Results and Discussion

### Characteristics of biochar

The grass jelly tree biochar yield was 42.07, 39.06 and 38.01 wt% at a pyrolysis temperature of 500, 600 and 700°C, respectively. The decrease in yield with temperature was ascribed to the rapid and comprehensive decomposition of lignocellulosic components at higher temperatures. Table 1

presents the surface area and pore properties of biochar. The BET surface area of the grass jelly tree biochars increased when increasing pyrolysis temperature. As the pyrolysis temperature increases, pore blocking substances are driven off or are thermally cracked, thus increasing the accessible surface area. The surface areas of the biochar were in the range of 2.32-5.67  $\text{m}^2/\text{g}$ , which was comparable to other biochars. For example, Rafiq *et al.* (2016) measured a surface area and average pore diameter between 3.17-4.58  $\text{m}^2/\text{g}$  and 6.30-10.6 nm, respectively, for corn stover biochars. Wystalska *et al.* (2023) also reported low specific surface area of 0.93-2.91  $\text{m}^2/\text{g}$  for biochar from sunflower hull pellets. To improve the porosity, the grass jelly tree biochar was modified with  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$ .

**Table 1. Porous properties of biochars at different pyrolysis temperatures**

| Sample | $S_{\text{BET}}$<br>( $\text{m}^2/\text{g}$ ) | $V_{\text{mic}}$<br>( $\text{cm}^3/\text{g}$ ) | $V_{\text{total}}$<br>( $\text{cm}^3/\text{g}$ ) | $D_{\text{avg}}$<br>(nm) |
|--------|-----------------------------------------------|------------------------------------------------|--------------------------------------------------|--------------------------|
| BC500  | 2.32                                          | 0.001<br>(17%)                                 | 0.006                                            | 11.30                    |
| BC600  | 2.56                                          | 0.001<br>(14%)                                 | 0.007                                            | 11.17                    |
| BC700  | 5.67                                          | 0.003<br>(30%)                                 | 0.010                                            | 7.19                     |

### Physicochemical characterization of engineered biochar

The  $N_2$  adsorption-desorption isotherms of the engineered biochars are shown in Figure 2 and Table 2 summarizes the textural parameters. In the low pressure region at  $P/P^0 < 0.2$ , the  $N_2$  adsorption increased rapidly with increasing pressure, which is indicative of the presence of micropores. However, at  $P/P^0 > 0.4$ , the isotherms were IUPAC type IV with the presence of a hysteresis loop. This indicated the abundance of mesopores, which was supported by the large fraction of mesopore volume of 40-62% and 56-86% of total volume for  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$  treatment (Table 2), respectively. The quick increase in the adsorbed  $N_2$  for this type of isotherm after the plateau could be due to capillary condensation, suggesting that adsorption occurred only on the external surface.

As seen in Table 2, treatment with both  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$  led to an increase in biochar surface area. The maximum surface area of 111  $\text{m}^2/\text{g}$  was obtained for BC700 with  $\text{H}_3\text{PO}_4$  treatment. The higher surface area after  $\text{H}_3\text{PO}_4$  modification was possibly due to the addition or insertion of the  $\text{H}_3\text{PO}_4$  groups that lead to swelling within the precursor matrix. After removal of the acid by

washing with water, the matrix was left in a swollen state, resulting in a porous structure (Wang and Liu, 2023). This engineered biochar had surface area comparable to chemical treatment biomass-based biochar reported in literature. For example, Zhao *et al.* (2021) found that the surface area of pulp sludge-derived biochar increased from 78 to 100 m<sup>2</sup>/g after modification with ZnCl<sub>2</sub>. Chen *et al.*, (2019) prepared biochar from alfalfa and then improved the surface area by activation with nitric acid pickling and reheating. Finally, they used this biochar as adsorbent for removal of *p*-nitrophenol. The resulting pickling-reheating activated alfalfa biochar had a specific surface area of 120 m<sup>2</sup>/g. Liu *et al.* (2023) prepared biochar by pyrolysis of septic tank sludge, modified with KOH and then pyrolyzed again. The resulting modified biochar with surface area between 77-85 m<sup>2</sup>/g was used as adsorbent for phosphate adsorption. Wood powder biochar treated with H<sub>3</sub>PO<sub>4</sub> (surface area 118 m<sup>2</sup>/g) was also used to adsorbed methylene blue pigment (Liu *et al.*, 2020). This suggested that the engineered biochar obtained from grass jelly tree with moderate surface area is feasible to use as adsorbent.

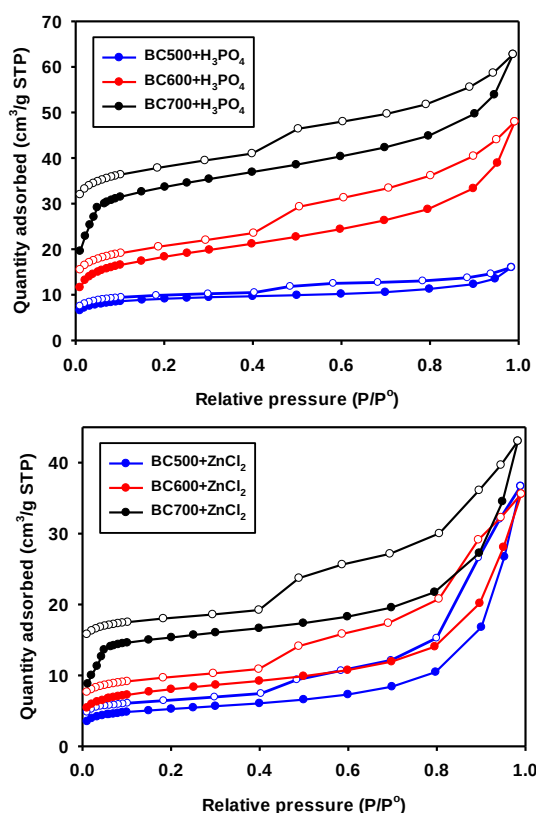


Figure 2. Nitrogen gas adsorption-desorption isotherms of biochar treated with (a) H<sub>3</sub>PO<sub>4</sub> and (b) ZnCl<sub>2</sub>

The proximate analysis together with bulk density, pH and pH<sub>pzc</sub> of the engineered biochar obtained at optimal conditions (i.e., treatment of BC700 with H<sub>3</sub>PO<sub>4</sub>) are presented in Table 3. The proximate analysis confirmed that the moisture content (5.69%) and volatile matter (18.36%) were according to the recommended values suggested from the standard specification of powdered activated carbon (i.e., max. 15% and max. 25% for moisture content and volatile matter, respectively (Hanum *et al.*, 2017)). However, the ash content (26.61%) was higher than the standard (max. 10% (Hanum *et al.*, 2017)). A high ash content is undesirable because it reduces the mechanical strength and adsorption capacity of biochar (Hanum *et al.*, 2017). The engineered biochar had a fixed carbon content of 55.03% while the standard for activated carbon requires at least 65% (Hanum *et al.*, 2017). Nevertheless, the produced engineered biochar still exhibited a carbon-rich material.

Table 2. Effect of different treatment reagents on engineered biochar texture

| Sample                                       | S <sub>BET</sub><br>(m <sup>2</sup> /g) | V <sub>mic</sub><br>(cm <sup>3</sup> /g) | V <sub>total</sub><br>(cm <sup>3</sup> /g) | D <sub>avg</sub><br>(nm) |
|----------------------------------------------|-----------------------------------------|------------------------------------------|--------------------------------------------|--------------------------|
| <b>H<sub>3</sub>PO<sub>4</sub> treatment</b> |                                         |                                          |                                            |                          |
| BC500                                        | 30                                      | 0.014<br>(56%)                           | 0.025                                      | 3.28                     |
| BC600                                        | 63                                      | 0.028<br>(38%)                           | 0.074                                      | 4.73                     |
| BC700                                        | 111                                     | 0.058<br>(60%)                           | 0.097                                      | 3.49                     |
| <b>ZnCl<sub>2</sub> treatment</b>            |                                         |                                          |                                            |                          |
| BC500                                        | 18                                      | 0.008<br>(14%)                           | 0.057                                      | 12.71                    |
| BC600                                        | 27                                      | 0.012<br>(22%)                           | 0.055                                      | 8.04                     |
| BC700                                        | 50                                      | 0.029<br>(44%)                           | 0.066                                      | 5.30                     |

Table 3. Main characteristics of the engineered biochar obtained at optimum conditions (treatment of BC700 with H<sub>3</sub>PO<sub>4</sub>)

| Parameter                         | Value |
|-----------------------------------|-------|
| Proximate analysis (wt%)          |       |
| Moisture                          | 5.69  |
| Ash (dry basis)                   | 26.61 |
| Fixed carbon (dry basis)          | 55.03 |
| Volatile matter (dry basis)       | 18.36 |
| Bulk density (g/cm <sup>3</sup> ) | 0.34  |
| pH                                | 6.21  |
| pH <sub>pzc</sub>                 | 6.90  |

The bulk density of the engineered biochar was  $0.34 \text{ g/cm}^3$  which is in accordance with the standard for activated carbon. This standard established the values in the range of  $0.2\text{--}0.6 \text{ g/cm}^3$  (Ademiluyi and Nze, 2016).

The pH value of the engineered biochar was 6.21. The acidity of the biochar was likely influenced by the acid treatment. The pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) is the pH value at which the net total surface charge of biochar is zero. Figure 3 shows the plot obtained using the pH drift method. The  $\text{pH}_{\text{pzc}}$  value of the engineered biochar was 6.9. When the pH value of a solution that contained adsorbate ( $\text{pH}_{\text{solution}}$ ) is below the  $\text{pH}_{\text{pzc}}$ , the surface charge of biochar is positive. This favors the adsorption of anionic species such as congo red or methyl orange dyes. In contrast, the surface charge of biochar is negative when  $\text{pH}_{\text{solution}} > \text{pH}_{\text{pzc}}$ , at which the adsorption of cationic forms such as methylene blue dyes, malachite green dyes or cationic metal ions (copper(II), zinc(II), nickel(II), lead(II), cadmium(II)) is favored.

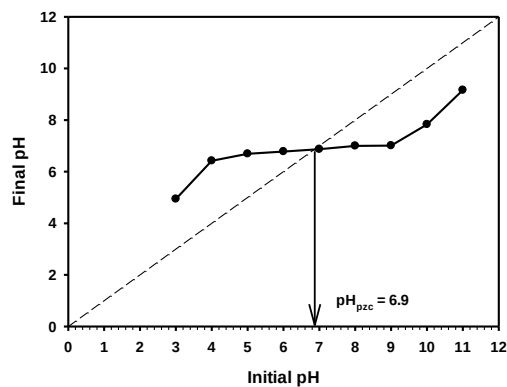


Figure 3.  $\text{pH}_{\text{pzc}}$  of engineered biochar obtained at optimum conditions

The SEM-EDX analysis provided qualitative morphological and elemental information (Figure 4). The engineered biochar contained rough and irregular structures with pores. The EDX analysis confirmed that carbon was the dominant element (60.8 wt%), followed by oxygen (25.2 wt%). Small amounts of Fe, P, Si, Ca and Cl were also found.

The surface elemental composition and chemical state of the engineered biochar was measured by XPS. Figure 5 shows the XPS spectra of C 1s and O 1s and Table 4 presents the quantified results. In Figure 5 (a) the peak at 282.5 eV corresponded to carbide. Carbon-hydrogen bonds

(C-H) were found at 283.4 eV and different carbon-carbon bonds (C-C/C=C) can be found at 284.9 eV (Saeed *et al.*, 2021; Zhang *et al.*, 2023). At 286.4 eV, carbon was bound to oxygen (C-O) (Joseph *et al.*, 2010) and the presence of O-C=O groups was confirmed by the peak at 287.6 eV. Carbon formed a double bond with oxygen (C=O) at 288.9 eV (Joseph *et al.*, 2010).

The O 1s peaks revealed oxygen containing groups, with the existence of C=O, C-O, -OH and O-C=O at 531.0, 532.2, 533.1 and 534.6 eV (Saeed *et al.*, 2021), respectively, as shown in Figure 5 (b). The binding energy at 529.7 eV can be attributed to metal oxides in biochar (Anthonysamy *et al.*, 2022; Papadopoulou *et al.*, 2023; Zhang *et al.*, 2023).

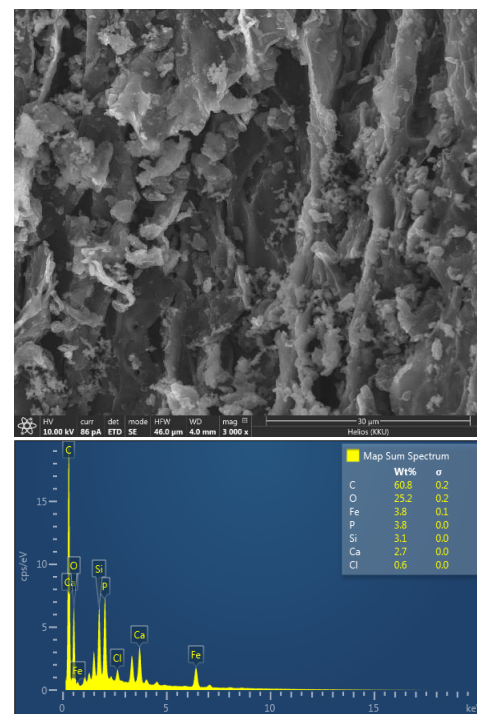
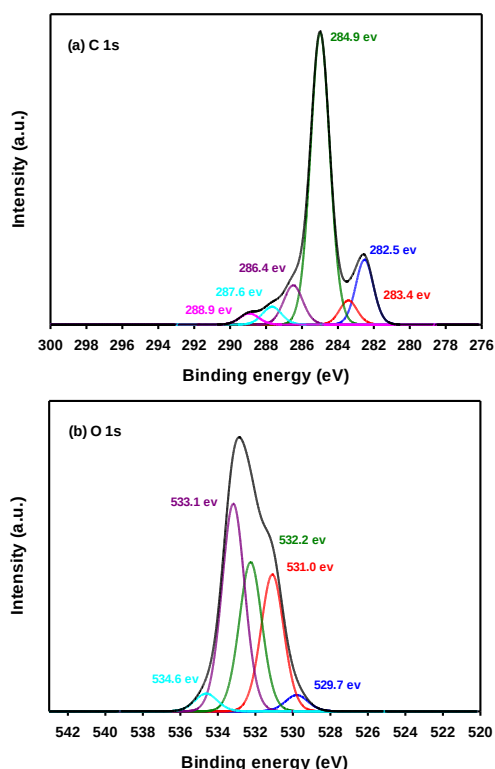


Figure 4. SEM-EDX analysis of engineered biochar obtained at optimum conditions

Table 4. Atomic concentration of the XPS measurement for engineered biochar

| Electron shell | %     |
|----------------|-------|
| C 1s           | 62.57 |
| O 1s           | 25.52 |
| Si 2p          | 7.85  |
| N 1s           | 2.78  |
| Al 2p          | 0.91  |
| P 2p           | 0.37  |



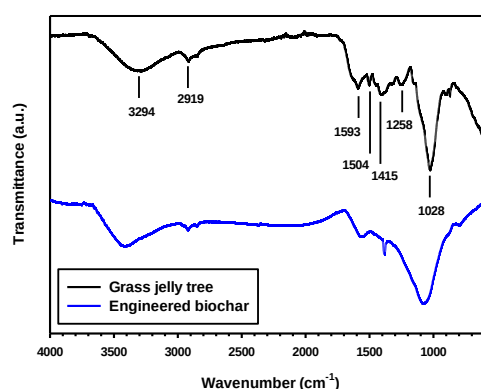
**Figure 5.** XPS spectrum of engineered biochar obtained at optimum conditions (a) C peak and (b) O peak

As shown in Table 4, the C and O contents of the engineered biochar as measured by XPS were 62.57 and 25.52%, respectively, which are in agreement with EDX results. This confirmed that the engineered biochar contained mainly carbon. The surface O/C atomic ratio was calculated to evaluate the surface oxidation degree and hydrophilicity of the biochar (Tan *et al.*, 2020). The ratio of engineered biochar obtained at optimum conditions was 0.41, which indicates a high hydrophilicity that is advantageous for adsorption (Gao *et al.*, 2022).

Moreover, the O/C ratio is often used as indicator of biochar stability. The biochars with O/C ratio < 0.2 are highly stable (half-life exceeding 1000 years), O/C ratio 0.2-0.6 are moderately stable (half-life 100–1000 years) and O/C ratio > 0.6 are relatively unstable (half-life less than 100 years) (Ippolito *et al.*, 2020). Therefore, the obtained engineered biochar from this study exhibits a moderately stable character.

Figure 6 illustrates the FTIR spectra of raw grass jelly tree and engineered biochar obtained at optimum conditions. The FTIR spectral band assignments are listed in detail in Table 5. The feedstock spectrum was dominated by the broad

peak at 3294  $\text{cm}^{-1}$  corresponding to hydroxyl group (-OH) stretching and strong hydrogen bonding (Komnitsas and Zaharaki, 2016). The aliphatic C-H stretching vibrations appeared at 2919  $\text{cm}^{-1}$  and suggested the presence of hemicellulose and cellulose (Elnour *et al.*, 2019). A band at 1593  $\text{cm}^{-1}$  was assigned to C=C stretching vibrations (Arshad *et al.*, 2019). The peaks at 1504 and 1415  $\text{cm}^{-1}$  were assigned to aromatic C-C and -COOH (Chen *et al.*, 2019), respectively, were also observed. The band at 1258  $\text{cm}^{-1}$  was attributed to C-O vibrations in acetyl groups (Li *et al.*, 2016). The aliphatic C-O-C group vibration at 1028  $\text{cm}^{-1}$  was attributed to the presence of cellulose (Cui *et al.*, 2019). The peaks at 1504 and 1258  $\text{cm}^{-1}$  disappeared in the engineered biochar, possibly due to pyrolysis and chemical treatment.



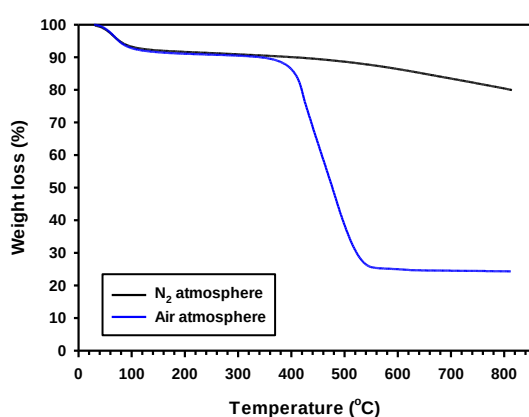
**Figure 6.** FTIR spectra of raw grass jelly tree and engineered biochar obtained at optimum conditions

**Table 5.** FTIR spectra band assignments for grass jelly tree and engineered biochar

| Band ( $\text{cm}^{-1}$ ) | Assignment                      |
|---------------------------|---------------------------------|
| 3294                      | Hydroxyl group (-OH) stretching |
| 2919                      | Aliphatic C-H stretch           |
| 1593                      | C=C stretching                  |
| 1504                      | Aromatic C-C                    |
| 1415                      | -COOH                           |
| 1258                      | C-O in acetyl group             |
| 1028                      | Aliphatic C-O-C                 |

The TGA curves of the engineered biochar obtained at optimum conditions are shown in Figure 7. This experiment was carried out under nitrogen atmosphere to study pyrolytic performance and thermal stability of biochar while oxidative stability was studied in air atmosphere. The weight loss at temperatures up to 120°C for both atmospheres was due to moisture loss. Under

nitrogen atmosphere, the major weight loss took place between 450 and 800°C after a minor weight loss from 200 to 400°C. This means that the engineered biochar was thermally stable in a nitrogen atmosphere up to a temperature of 450°C with a residual mass of 80%. In the air atmosphere, the weight loss between 200 and 540°C involved devolatilization while biochar combustion took place between 400 and 720°C (Petrova *et al.*, 2023). The residual mass around 24% was possibly due to incomplete combustion and partial presence of inorganic species and was similar to the ash content (Table 3).



**Figure 7. TGA curves of the engineered biochar obtained at optimum conditions**

## Conclusions

This study has shown that it is feasible to prepare engineered biochar from solid waste of dessert industry, grass jelly tree waste. The pristine biochars were prepared at 500, 600 and 700°C and  $H_3PO_4$  and  $ZnCl_2$  were used to improve their porosity. Compared to the pristine biochars, the engineered biochars showed higher surface area and pore volume. The highest surface area of 111 m<sup>2</sup>/g with an average pore size of 3.49 nm was obtained by  $H_3PO_4$  modification of BC700. The acid treatment resulted in a biochar with pH 6.21 and pH<sub>pzc</sub> 6.90. SEM analysis showed the distribution of pores on engineered biochar structure. The main elements in engineered biochar contained carbon (C) and oxygen (O) which were studied by EDX and XPS analyses. TGA result revealed that engineered biochar exhibited thermal stability in both N<sub>2</sub> and air atmospheres.

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