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Research Article

Enhanced Biochar Production via Co-Pyrolysis of Biomass Residual with Plastic Waste after Recycling Process

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Biomass pyrolysis for oil production results in biochar byproduct, whose characteristics can be improved by the reuse of waste plastics. While the plastic recycling process leads to a large amount of plastic waste that cannot be reused, this underutilized feedstock holds the potential for coprocessing with biomass, thereby increasing the likelihood of producing valuable biochar products. This study sought to evaluate how the inclusion of plastic waste influences the pyrolysis of biomass residue. To this end, sawdust and hardwood biomass were chosen as materials to investigate how the presence of plastics might alter the properties of the resulting chars. Synergies were observed among the biomass components, particularly in samples with higher lignin content from hardwood biomass, which resulted in increased biochar yields. The results showed that a 20% blend of plastic waste with wood at 300°C produced a solid char with a yield of 40% by weight. Co-pyrolysis of the biochar derived from blends of 20 wt. % PP with both sawdust and hardwood resulted in significant enhancement of various properties of the resulting biochar, including surface area, carbon content, hydrophobicity, and aromaticity. This enhancement had a favorable effect on the carbon content and calorific values of the biochar. These enhanced properties significantly contributed to the biochar's capacity for sorbing substances like various heavy metals. It can be proved that this result showed the importance of the energy content of biochar and its potential use for renewable applications. The beneficial combined effect seen in the plastic blends can be credited to the interaction between the biomass and polymer components, resulting in the production of fewer volatile products at higher temperatures. It can be suggested that biochar from biowaste and plastic waste not only reduces environmental impact but also converts it into a valuable and eco-friendly product.

1. Introduction

Population and technological innovation changes have increased the production of plastics over the last few decades. Global plastics production was estimated to be 391 million metric tons in 2021, which generated plastic waste of approximately 464 million tons [1]. Plastic pollution has emerged as an excessive threat to ecological concerns due to its high resistance to biodegradation processes. Mechanical recycling and incineration are employed to treat plastic waste. However, their efficiency and performance have restrictions that lead to economic growth, energy conversion,

and quality recycling of plastics [2]. In addition, the recycling process creates microplastics in the environment. The majority of these particles are <10μm in size and and, therefore, environmentally significant concentrations of microplastics are observed. Instead of being deemed waste, nonrecyclable plastics or microplastic can be regarded as a crucial resource for generating alternative energy and valuable chemical products through thermochemical conversion processes.

The thermochemical conversion process provides the potential to convert plastic wastes into value-added petrochemicals. Moreover, the thermochemical processing of plastic waste is a potential solution for municipal solid waste (MSW) disposal and serves as a good option for recovering fuels and chemicals [3, 4] which is economically feasible [5]. One of the approaches to thermochemical conversions is pyrolysis. Pyrolysis has gained increasing attention as an economical technology for processing a wide range of feedstocks into energy and petrochemicals [6, 7]. Pyrolysis is the process of thermal degradation of organic matter without oxygen [8]. The pyrolysis process conditions influence the physicochemical properties, quality, and yields of products [9]. The process parameters are the key input variables that determine and enhance the value and amount of the final pyrolyzed products [9].

Because of the versatility and cost-efficiency of pyrolysis, most studies have focused primarily on the conversion of liquids via pyrolysis, often neglecting the solid-phase pyrolytic byproduct, which possesses significant potential as a valuable, flammable resource. Biochar is known as the solid produced via the pyrolysis process and has functions in various applications ranging from energy and electricity generation to improving soil properties [10–12]. Biochar is also a promising additive to activated carbon, which has high porosity and excellent adsorption capabilities [13]. Compared to liquid and gaseous products, biochar needs only the slightest pretreatment. The quantity and quality of biochar produced in pyrolysis are affected by the feedstock types and several other factors. A slow pyrolysis process with a long residence time and slow heating rate provides the maximized yield of biochar [13–15]. About 30% of biochar was produced through slow pyrolysis, with up to 95% carbon purity [13, 15].

Agricultural practices involve operations that generate significant byproducts, which can lead to environmental issues, generate smoke, and cause adverse effects on human health. Converting agricultural byproducts into biochar is an alternative approach to increasing their value and utilizing them for various purposes. Wood processing results in various sizes of woody branches as byproducts. Woody materials are waste lignocellulosic materials obtained from wood processing and they have considerable potential for conversion into a carbon source that can be applied for waste management. Pyrolysis of wood has been previously reported and the yields of the gases, pyrolysis char, and pyrolysis oils were observed to be in the ranges 17–38 wt%, 30–52 wt%, and 30–45 wt%, respectively [16]. The yield of pyrolysis char obtained from the pyrolysis of sewage sludge and sawdust was 48.0% [17]. Soil properties could be improved by applying sawdust biochar for soil amendment [18]. More than that, coprocessing biomass with waste plastics and municipal waste components is an important approach to waste management and it enhances product' quality. Investigations have enabled appreciation of the adaptability of biochar as a material which has been applied for many purposes, such as removing undesirable contamination from water and pollution prevention [19, 20].

The pursuit of blending carbon-based material from biomass and plastic waste has become attractive. The combination of biomass and plastics via a thermochemical process is advantageous because organic matter derived from biomass helps decrease the negative effects of pyrolysis oil. Also, the hydrogen-rich components from waste plastic improve the quantity and quality of pyrolysis oil through synergetic interaction between plastic and biomass. Moreover, co-pyrolysis leads to less need for hydrogen consumption for the pyrolysis oil produced. Furthermore, using biomass and plastic waste as raw material gives another resource to the process chain to produce biofuels [21]. Because of the plastic degradation, hydrogen donation occurs with hydrogen being transferred from the plastic polymer chain to radicals formed from biomass [22]. There is evidence that show the improvement of biochar when blended with plastic compared to biomass biochar alone. Biochar product provides high consistency in an oxidation environment, with the improved moment of identical amounts of biochar throughout oxidation. This suggests that the biochar quality was enhanced through co-pyrolysis with no significant decrease in biochar yield, resulting from an increase in heavy aromatics and efficient volatile depletion [22].

Although there is increasing research on the production of fuels from plastic waste through the thermochemical conversion process, there is little knowledge on the quality of charcoal produced from biomass residues-microplastic waste, which is retrieved directly from the plastic recycling process. Feedstock types were selected with the overarching purpose of valorizing plastic wastes into value-added biochar products. Wood waste is generated at a million tons in a year and was therefore of particular interest. The effect of plastic blending on cochairing via co-pyrolysis is unknown. This study aims to investigate the co-pyrolysis process of microplastic recycling waste polypropylene (PP), sawdust, and hardwood biomass to produce biochar composite and to characterize physic-chemical, structural, and surface properties.

2. Materials and Methods

2.1. Materials. Sawdust and hardwood biomass were chosen as a biomass feedstock. The sawdust (1-2 cm pieces) was obtained as a byproduct of woodworking operations. Hardwood biomass, which was around 5–10 cm in dimension, was used as received from a nearby agricultural zone in Chaiyaphum Province, Thailand. Polypropylene (PP) waste was used as a representative of aromatic plastic polymer waste (dimension <2 mm). PP waste was obtained as a waste material after the process of recycling plastics from Thaweerat-Plastic Company, Chaiyaphum Province. The

ultimate analysis was carried out in accordance with ASTM D5291 to determine the carbon (C), hydrogen (H), and oxygen (O) content. In addition, the high heating values of both dry sawdust and hardwood biomass were measured using ASTM E711, yielding values of 18.26 MJ/kg and 18.55 MJ/kg, respectively. Detailed information regarding the composition of the biomass can be found in the supporting materials. All raw materials used and obtained products are shown in Figure 1.

2.2. Co-Pyrolysis Plastic Waste with Biomass. The preparation of hardwood–plastic biochar and sawdust–plastic biochar via co-pyrolysis, biomass residues (hardwood and sawdust), and plastic wastes was conducted in a cylindrical reactor (dimension 300 mm, length 60 cm, maximum capacity 5 kg, stainless-steel). The stainless-steel reactor controlled the release of gaseous products via a pressure gauge, a pressure relief valve, and a needle valve. The reactor (Figure 2) was heated externally by liquid propane gas flame to the required operation condition at a heating rate of 5°C min^{-1}. A thermocouple, linked to data logging software, was utilized to oversee and record temperature variations. The thermocouple voltage was then measured and recorded by data logging software, allowing for precise monitoring of temperature changes over time in the production process. In a standard trial, the stainless-steel reactor was filled with a combined total of 1 kg of material, consisting of biomass mixed with PP microplastic waste. In the 80 : 20 ratio experiments, there were 800 g of biomass and 200 g of either sawdust or hardwood biomass. The stainless-steel reactor was tightly sealed and subjected to pyrolysis at three different temperatures (with the completed reaction taking place at 300°C, 400°C, and 500°C). The resulting products from the pyrolysis process were directed into a condenser for the collection of liquid products. Noncondensable gas was collected by means of a Teflon gas bag affixed to the liquid collection flask's outlet. At the end of the slow co-pyrolysis process, the obtained biochar remained in the pyrolyzer and was kept for further physical and chemical analysis.

2.3. Yield of Product. The percentages of product/yield of product phases were determined based on mass percentages on a dry basis. This calculation was derived from precise weight measurements taken after the completion of the reaction. This approach ensured an accurate assessment of the yield of each phase of the products. The yield of the each product phase was calculated through the following formulas:

$$\text{Liquid yield: Liquid (wt. \%)} = \frac{\text{mass of liquid (g)}}{\text{mass of dry biomass (g)} + \text{mass of plastic (g)}} \times 100, \quad (1)$$

$$\text{Residue (Char) yield: Residue (char) (wt. \%)} = \frac{\text{mass of residue (g)}}{\text{mass of dry biomass (g)} + \text{mass of plastic (g)}} \times 100, \quad (2)$$

$$\text{Gas yield: Gas (wt. \%)} = 100\% - (\text{liquid} + \text{residue}). \quad (3)$$

2.4. Assessing the Moisture, Volatile, Ash Content, and Fixed Carbon. The moisture content of the material was assessed following the guidelines outlined in EN ISO 18134-3 [23], utilizing the indirect drying method [24]. A 1 g sample of the material under examination was subjected to a 90 min drying process in a laboratory oven equipped with forced air circulation and precise temperature control, set at 105°C. Subsequently, the dried samples were placed in a desiccator to cool and were then weighed on an analytical balance with a precision of ±0.0001 g. Moisture content measurements were carried out on finely ground samples with particles smaller than 0.2 mm in size. The moisture content of the biochar samples was assessed utilizing the following formula:

$$\text{Moisture content} = \frac{w_i - w_d}{w_d} \times 100\%, \quad (4)$$

where w_i represents the initial weight of the sample and w_d represents the weight after drying.

The volatile matter (VM) content [23] of the sample materials was assessed in accordance with ASTM D 1762-84, utilizing a sequential muffle procedure based on an oven dry-weight basis. The volatile matter content percentage was obtained by measuring the weight loss and employing a mass balance method. This entailed subtracting the weight loss due to moisture from the total weight loss of the test sample.

$$\text{Volatile matter (\%)} = \left(M_{\text{biochar}} - M_c\right) \times 100, \quad (5)$$

where M_{biochar} represents the initial dry mass of the biochar and MC is the dry mass of the remaining carbonized biochar after heating.

The ash content of the raw material [23], hardwood–plastic, and sawdust–plastic biochar was examined through a process of dry combustion of the carbonized biochar/stalk residue, in accordance with ASTM D 1762-84. The procedure involved several steps:

(a) Samples were initially dried at 105°C for a period of 12 h in an oven

(b) 2.0 grams of the dried samples were placed into a preweighed crucible

(c) Crucible and sample were placed into an oven set at a constant temperature of 750°C overnight

(d) Temperature was allowed to gradually decrease to around 250°C or lower before removing the samples

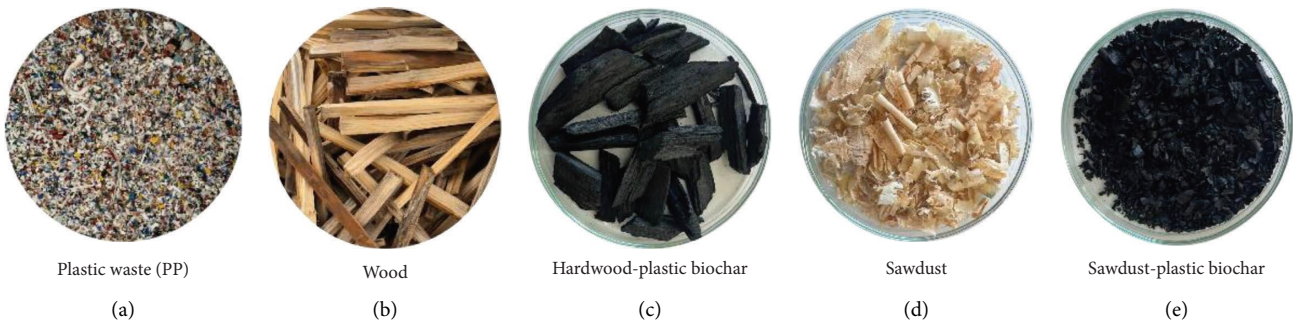

Figure 1: (a) Plastic waste, (b) wood, (c) hardwood–plastic biochar, (d) sawdust, and (e) sawdust–plastic biochar.

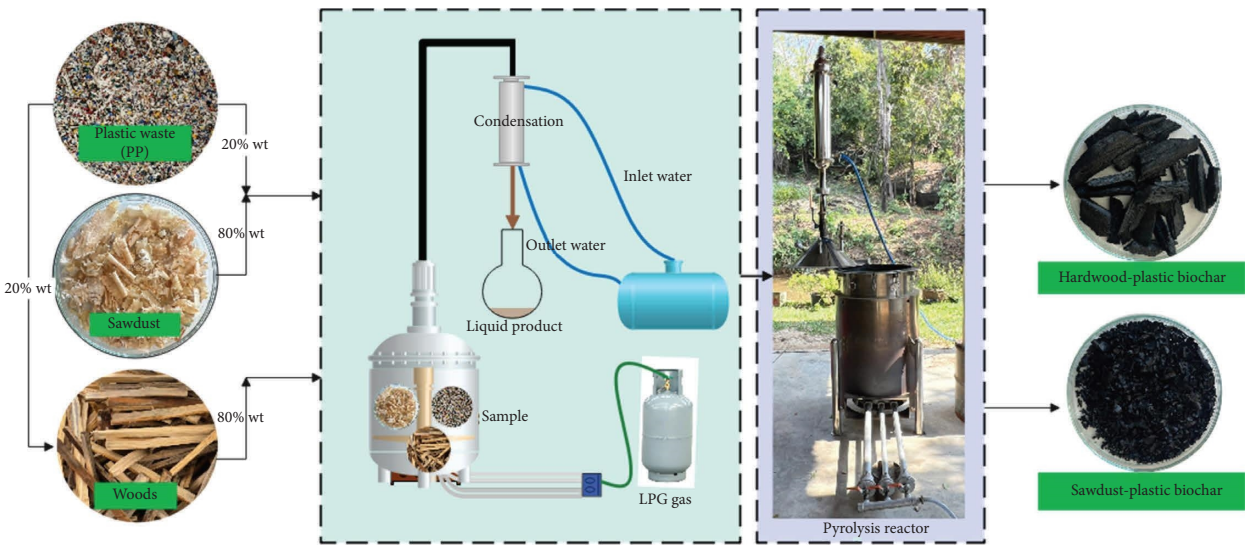

Figure 2: Pyrolysis process for the production of hardwood–plastic and sawdust–plastic biochars.

(e) Samples were placed into desiccators for adsorbing the moisture content

(f) The resulting ash in the crucible was weighed

(g) The ash content was subsequently computed as the percentage of the remaining residue following the dry oxidation process at 600°C, as determined by the following equation:

$$\text{Ash\%} = \frac{\text{weight}_{\text{crucibleplusash}} - \text{weight}_{\text{crucible}}}{\text{oven-dried weight}_{\text{sample}}}. \quad (6)$$

Fixed carbon [25] in the biochar was calculated as follows:

$$\text{Fixed carbon (FC) (\%)} = (100 - \text{\%VM} - \text{\%ash}). \quad (7)$$

2.5. The pH of Biochar Samples. The pH of the biochar was examined as follows. First, ground biochar was mixed with deionized water of a ratio of 1 part biochar to 20 parts waters. Subsequently, the pH of the resulting mixtures was determined with a Fisher Scientific Accumet pH meter. Prior to obtaining measurements, the pH meter was calibrated using buffer solutions of known pH values: 4, 7, and 10. This calibration step guarantees precise pH readings for the biochar-water mixture.

2.6. Characterization of Quantification of Unreacted Plastic in Biochar. Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical method utilized to assess the composition of a substance by detecting its absorption, reflection, or emission of infrared light. This technique proves highly versatile and offers crucial insights into the chemical makeup and arrangement of diverse materials across a broad spectrum of scientific and industrial fields. It enables the identification of functional groups within biochar products. The FTIR spectra were captured using a Bruker (INVENIOR®) FTIR spectrometer, covering wavelengths from 4000 to 600 cm^{-1}.

2.7. Methodology of Elemental Analysis, Carbon, and Energy Recoveries. The analysis of elemental composition, encompassing carbon, hydrogen, nitrogen, and sulfur content, for both the biomass feedstock and the resulting products, was outsourced to Suranaree University of Technology in Thailand. The oxygen content was calculated

as the remaining percentage after the other elements were determined. This comprehensive analysis provided valuable insights into the chemical makeup of the materials studied.

$$\mathrm{O}\,(\mathrm{wt\%}) = 100\text{-}\mathrm{C}\text{-}\mathrm{H}\text{-}\mathrm{N}\text{-}\mathrm{S}\,(\mathrm{wt\%}). \tag{8}$$

The higher heating values (HHV) of the biomass was determined using the Dulong formula. This formula incorporates the weight percentages of carbon (C), hydrogen (H), and nitrogen (N) present in the samples. The HHV represents the maximum amount of energy that can be obtained when a substance is completely combusted. This calculation is important for understanding the potential energy content of the biomass and plastic waste.

$$\mathrm{HHV}\left(\mathrm{MJ\,kg^{-1}}\right) = 0.3383\mathrm{C} + 1.422\left(\mathrm{H}\text{-}\left(\frac{\mathrm{O}}{8}\right)\right). \tag{9}$$

Energy recovery in each product phase will be calculated as follows:

$$\text{Energy recovery }(\%) = \frac{\text{HHV product }(\%) \times \text{mass of product }(\%)}{\text{HHV of feedstock }(\%)}. \tag{10}$$

2.8. Synergistic Effects. The degree of interactive synergistic effects between biomass and plastics was assessed through the calculation of biochar yield. Theoretical outcomes were calculated by comparing the experimental char produced during the co-pyrolysis process with the char obtained from each feedstock using the following equation.

$$\text{Synergistic effect} = Y_{\text{char}} - \left(X_{\text{biomass}} \times Y_{\text{biomass}} + \left(1 - X_{\text{biomass}}\right) \times Y_{\text{plastic}}\right), \tag{11}$$

where Y_{char} represents the char yield attained during the experiment, X_{biomass} denotes the mass fraction of biomass (sawdust and hardwood), Y_{biomass} represents the char yield of pure biomass, and Y_{plastic} is the char yield of pure plastic. When synergistic effects >0, there is a positive correlation between both reactants and the total yield of co-pyrolysis was higher than when the two reactants were conducted independently. In contrast, when synergistic effects <0, the total yield of co-pyrolysis was lower than when the two reactants were conducted individually

2.9. The Surface and Total Pore Volume. The physical properties of specific surface area, pore volume, and pore size distribution were analyzed via a specialized surface area and pore volume distribution analyzer (Bell Sorp mini, TriStar II Plus Version 3.00, Norcross, GA, USA). To assess these properties, the BET (Brunauer–Emmett–Teller) method was used to determine the specific surface area, while the BJH (Barrett–Joyner–Halenda) approach was applied to ascertain the total pore volume and pore diameters of the sample materials. In addition, nitrogen adsorption and desorption isotherms were examined across a range of relative pressures (P/P_0). The adsorption isotherms were studied from 0.1 to 0.99, and the desorption isotherms were analyzed from 0.96 to 0.99. This detailed analysis provides crucial information about the porosity and surface characteristics of the materials under study.

2.10. Surface Morphology Analysis via SEM. The examination of surface morphology, in conjunction with elemental analysis, encompassed a comprehensive study conducted before and after the process co-pyrolysis. This investigation employed a cutting-edge Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDX) system, with a specific focus on the sophisticated model SEM-TM4000Plus developed by HITACHI, ensuring a comprehensive analysis of the specimens at a microscopic level.

3. Results

3.1. Effect of Waste Plastic Contents on Pyrolysis Product Yields at Difference Temperatures. Microplastic waste (PP) was coprocessed with 20 wt. % weight loading of sawdust and hardwood biomass at 300°C, 400°C, and 500°C for 60 min. Mass yields were determined on an ash-free basis (DAF%) according to total feedstock. The increased temperature affected the product yields. In general, an increase in pyrolysis temperature led to a decrease in biochar production (Figure 3). At higher temperatures, volatile matter contents was decreased undertaking secondary reactions into liquid and gas phases. There was also a significant mass loss with the residual biochar production after the pyrolysis process at higher temperatures. In contrast, the plastic co-pyrolysis showed a positive effect on biochar yields relative to the pyrolysis of biomass alone at the same conditions. Similar effects were reported by Adeniyi et al. [26]; the thermochemical coconversion is preferred for the conversion of individual material leading to enhancing the yield of the biochar. Co-pyrolysis with hardwood biomass showed the most significant impact, biochar yield increased from 36% for pure hardwood to 40% for 20 wt% plastic blends at 300°C. On the addition of 20 wt% plastic in sawdust, the biochar yield increased slightly from 28% for raw sawdust biochar to 32% for 20% wt plastic blend at 300°C. At increased temperatures, biochar yield decreased from 21% to 40% from 500°C to 300°C for the 20 wt% plastic in hardwood biomass and from 23% at 300°C to 32% at 500°C for sawdust.

Hardwood biomass yielded more biochar in comparison to sawdust as it contained more lignin. Biomass with more composition of cellulose and hemicellulose seems to generate more volatiles during processing and leads to liquid and gas products. Furthermore, with the larger particle size of hardwood biomass, it is not heated sufficiently quickly. The small particle size of sawdust enables it to ultimately be decomposed because of diffusion-controlled processes and results in higher rates of decomposition [27].

Temperature also had a significant effect on gas products. The gas yield experienced similar changes as those of liquid pyrolysis yield. Gas yield increased from 38% to 40% from 300°C to 400°C and rose further to 43% at 500°C for raw sawdust biochar. No significant changes in biochar products were found via plastic co-pyrolysis compared to biochar obtained from pure biomass. The gas products found from the 20 wt% plastic were slightly changed compared to pure hardwood and pure sawdust at the same conditions.

The blending of biomass and plastic for coprocessing does not significantly affect the yield of liquid pyrolysis at 300°C; liquid yields produced from co-pyrolysis with 20 wt% plastic blends were slightly different to those of biochar produced from individual biomass; a slight yield decrease of 1.0–2.0% was found for sawdust and hardwood biomass, respectively. In contrast, a temperature of 500°C maximized the liquid yield. Liquid yield increased with increasing temperature, which increased from 32% to 43% from 300°C to 500°C for the 20 wt% plastic in hardwood and from 33% to 40% from 500°C to 300°C for the 20 wt% plastic in sawdust. Plastic co-pyrolysis also showed an improvement in overall liquid yields relative to the pyrolysis of individual biomass at the same conditions. This was mostly due to the interaction between biomass and plastics which plays a significant part in enhancing the breakdown of plastic as an increased temperature.

3.2. Synergistic Effect. An experimental outcome resulting from interactions between two substances with greater effects than the sum of their individual effects is called a synergistic effect. With the blending of plastic to biomass, an increasing synergistic effect in the pyrolysis process at temperatures from 300°C to 500°C was observed, ranging from 1.8% to 18% for sawdust and from 0% to 19% for hardwood biomass (Figure 4). This showed that there was some interaction between biomass and plastic. At 500°C, the synergism reached a maximum of 18% and 19% for the 20 wt % plastic in hardwood and sawdust biomass, respectively, which demonstrated that the synergy effect between biomass and plastic was strongest at higher temperature. This suggests that there is a potential interaction between the biomass residues and the plastic wastes where the biomass could synergistically help the decomposition of plastic. It therefore seems likely that the plastic increases thermal benefits as a hydrogen donor, transferring hydrogen from the plastic polymer chain to radicals produced from biomass [28]. Co-pyrolysis of biomass with plastic polymers led to changes in the carbon, oxygen, and hydrogen balance of feedstock, which we suggest, served to improve the properties of the decomposition of plastic [29].

3.3. Obtained Biochar Composition. The elemental yields using experiment biomass from hardwood and sawdust with 20% PP blend at different temperatures from 300°C, 400°C, and 500°C for 60 minutes are shown in Figure 5. A substantial increase in the carbon content was found for all biochars with the combination of plastic blend as compared to those of biochar alone (a modest increase from 64.8% to 84.4% for hardwood and an increase from 64.5% to 84.4% for sawdust). A slow pyrolysis process involves the cracking of C and functional groups on the biomass surface, including –OH, aliphatic C–O, and aliphatic C–H groups [30]. Plastic coprocessing could be effective in changing the biomass's quantity of carbon, oxygen, and hydrogen resulting in significant changes in the effects of polymer degradation [31]. This is likely due to the radical degradation process of biomass via the rapidity of the decomposition of natural macromolecules which have lower thermal stability than plastics [32]. Increasing the pyrolysis temperature from 300 to 400°C resulted in increased carbon content. In contrast, when the temperature further rose to 400 and 500°C, there was only a small carbon content reduction. Higher temperatures caused the carbon content, ash content, surface area, and pore volume to change [33]. This suggests the decomposition of the oxygenated bonds to atomic hydrogen and oxygen [34]. The sawdust biochar produced from the plastic co-pyrolysis had a slightly lower amount of carbon as compared to the biochar produced from wood.

Figure 6 presents the high heating values (HHV) of biochar samples. HHV increased from 18.1 MJ kg^{-1} for sawdust biomass to 24.8 MJ kg^{-1} for pure sawdust biochar and increased from 18.5 MJ kg^{-1} for hardwood biomass to 24.0 MJ kg^{-1} for hardwood biochar at 300°C. This happened because pyrolysis temperature can promote the HHV in biomass [35]. With the plastic waste blending, the addition of plastics resulted in increasing total biochar carbon content, decreasing nitrogen, and enhanced HHV, leading to many beneficial biochar properties in comparison to the pure biomass biochar at the same reaction temperature. The energy of biomass with plastic blend chars tended to be relatively high from 26.4 to 32 MJ kg^{-1} for hardwood–plastic biochar at 300°C and from 24 to 30 MJ kg^{-1} for sawdust biochar at 300°C (Figure 5). No significant differences of HHV were found at higher temperatures for sawdust biochars. The HHV of biochar was slightly decreased at the higher reaction temperature. The highest HHV (32 MJ kg^{-1}) was found in biochar produced from of 20 wt. % plastic blends with hardwood at 300°C. This suggest that the co-pyrolysis of plastic with biomass mainly contributed to an increase in the biochar product and the most significant impact was observed at 300°C. It is noteworthy that the addition of plastic blending provided the greatest influences on proximate and ultimate investigation effects at 400°C, at which PP waste breakdown was completed. At higher temperatures, the yield is greater, as the components were more effectively broken down into gas and ash.

In order to determine the effective outcome, the energy recovery was assessed according to biochar yield, elemental composition, and HHV found (Figure 7). Plastic co-pyrolysis resulted in the highest energy recovery for

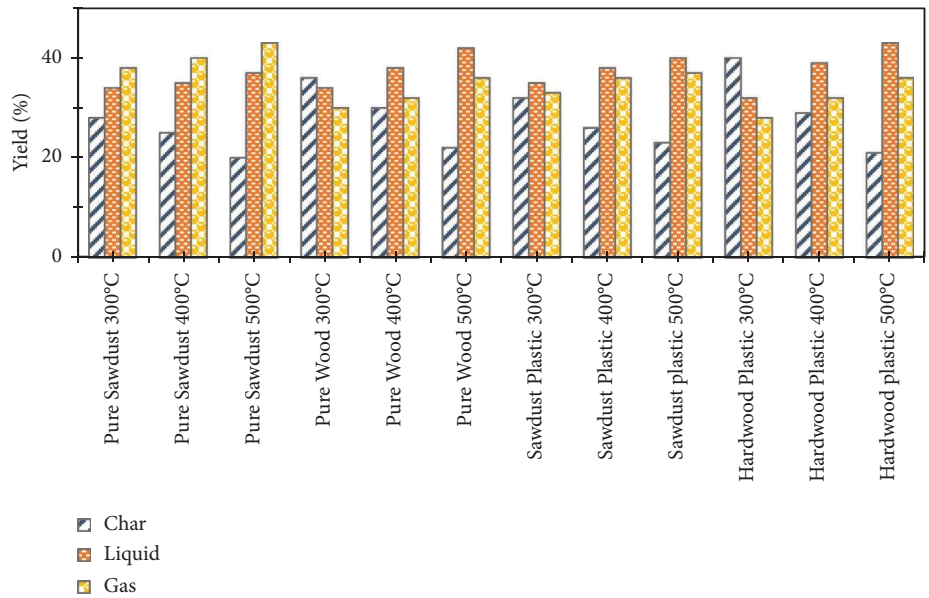

Figure 3: Product yields from plastic co-pyrolysis with of hardwood and sawdust.

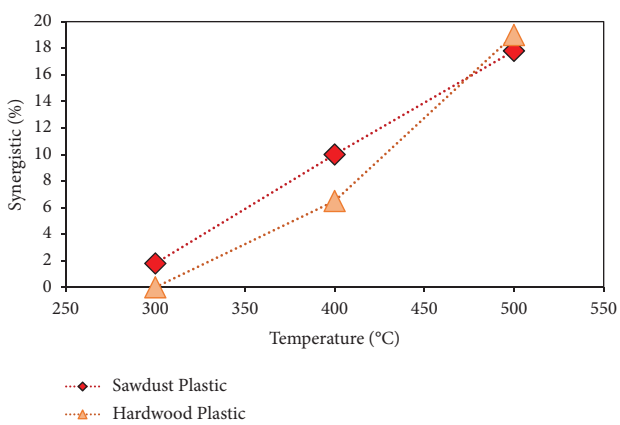

Figure 4: Synergistic effects on biochar yields from plastic co-pyrolysis with biomass.

sawdust at 300°C (70%). This value was higher than the energy recovery in pure biomass biochar (increasing from 42% for pure sawdust char and 37% for pure hardwood char). In contrast, the lowest energy conversion (50%) was found when the temperature was increased to 500°C, suggesting that biochar productivity decreased in co-pyrolysis at an increased pyrolysis temperature.

One method of evaluating the suitability of biochars to be used in various biofuel forms is to study the elemental ratios of H/C and O/C via a Van Krevelen diagram (Figure 8.). Compared to the pure biomass, much lower H/C and O/C ratios were found in biochar, which demonstrated that there were significant structural changes of biomass along with the dehydration reactions occurred throughout the decomposition process. The O/C ratio for individual biomass biochar (both sawdust and hardwood) was quite low, ranking between 0.14 and 0.23 for pure sawdust biochar and between 0.13 and 0.20 for pure hardwood biochar, and the O/C ratio tended to decrease at higher pyrolysis temperature. The reduction in O/C resulted in a beneficial carbonization process because hydrophilic functional groups from biomass structures were decreased [36]. In contrast, the O/C ratio of plastic waste with sawdust biochar first increases slightly from 300 to 400°C and then decreases from 400 to 500°C.

An increasing trend (similar to that found for H/C), both pure biomass biochars decreased as the temperature increased (0.72–0.52 for pure sawdust biochar and 0.78–0.50 for pure hardwood char). A decrease in the H/C generally shows advanced structural stability in biochar. As the future deoxygenation and dehydrogenation reaction occurred during pyrolysis process, the atomic H/C and O/C ratio of carbon products reduced, resulting in the growth of carbonized material [37]. The reduction of atomic ratio of H/C and O/C biochar was found at higher pyrolysis temperatures, suggesting that aromaticity and polarity in biochars enhanced homogeneity via dehydration and decarboxylation reactions.

The positions of the H/C and O/C of most solid fuels produced showed the similarity of the region of coal and anthracite. The biochar obtained may be considered for use as a solid biofuel with comparable quality to coal and anthracite. Anthracite is the highest quality of coal that is exposed to the highest grade of metamorphism [38]. Anthracite has a high carbon content and mostly has the highest HHV of all types of coal [39].

3.4. The Specific Surface Area, Pore Volume, and Pore Size Distribution of Sawdust–Plastic Biochar and Hardwood–Plastic Biochar. Biochar can be incorporated into wastewater treatment systems to enhance the removal of pollutants. It is important to note that while biochar is a valuable tool for pollution mitigation, its effectiveness can vary depending on factors such as feedstock type, pyrolysis conditions, and application methods. In addition, site-

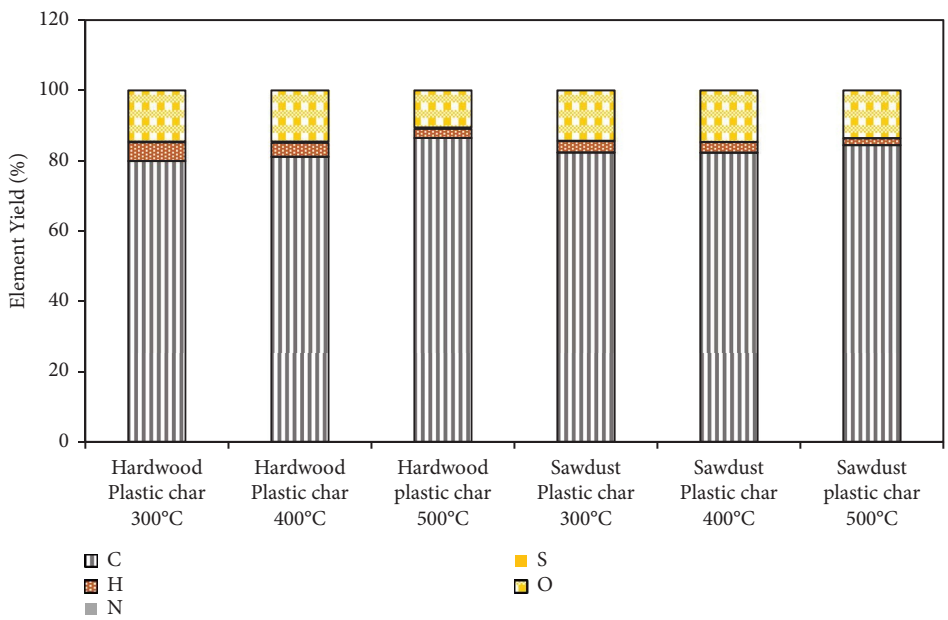

Figure 5: Elemental composition of hardwood–plastic and sawdust–plastic biochars.

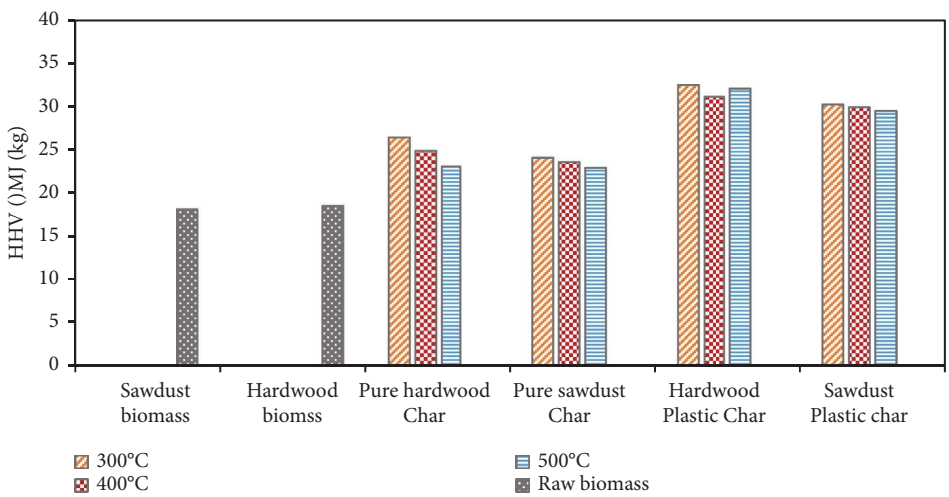

Figure 6: Heating value of hardwood–plastic and sawdust–plastic biochars.

specific conditions and contaminant types will influence the optimal use of biochar in pollution management strategies. Therefore, the specific surface area, pore volume, and pore size distribution of sawdust–plastic biochar and hardwood–plastic biochar have been explored to break down inorganic and organic pollutants for water and wastewater treatment. Table 1 presents the specific surface area, pore volume, and pore size distribution of sawdust–plastic biochar and hardwood–plastic biochar obtained. It can be concluded that the sawdust–plastic and hardwood–plastic biochar at 500°C had the highest specific surface area of about 0.67 $m^2\ g^{-1}$ and 42.47 $m^2\ g^{-1}$ followed by 400°C and 300°C, respectively. In other words, the structure changed with the following temperature along with porosity and pore volume. Total pore volume and average pore diameter are also followed by the results of specific surface area, indicating that the properties of plastic biochar obtained can be modified using different manufacturing techniques to suit the purpose for which it is being used. As mentioned above results, it can be summarized that increasing pyrolysis temperature from 300°C to 500°C caused changes in the physical surface structure of biochar such as surface area, total pore volume, and porosity. The physical transformation could involve the gradual breakdown of hemicelluloses, cellulose, and lignin, accompanied by the formation of channel-like structures throughout the pyrolysis process [40]. In addition, at elevated temperatures, the materials produced were breakdown products of aliphatic alkyl and ester groups, as well as the aromatic lignin, which can contribute to an increased surface area [41, 42]. These

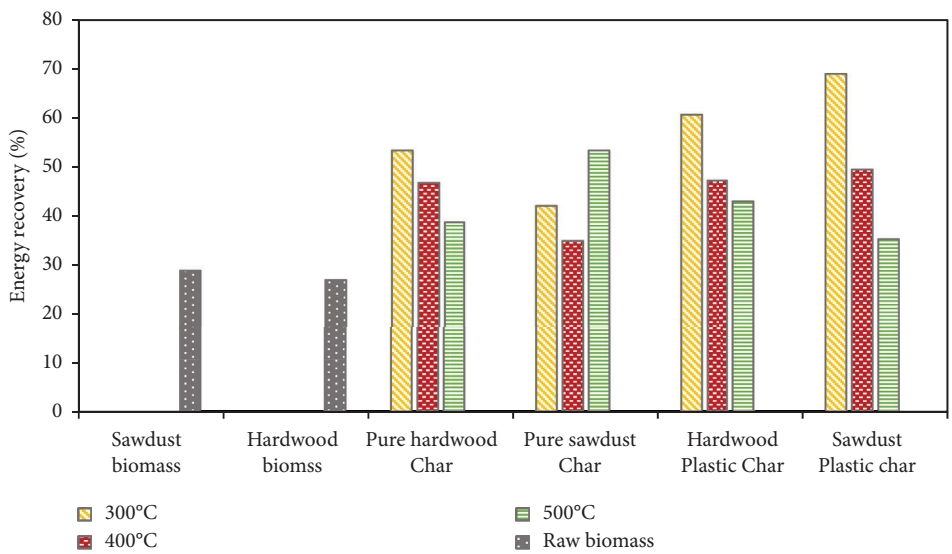

Figure 7: The energy recovery in the hardwood–plastic and sawdust–plastic biochars.

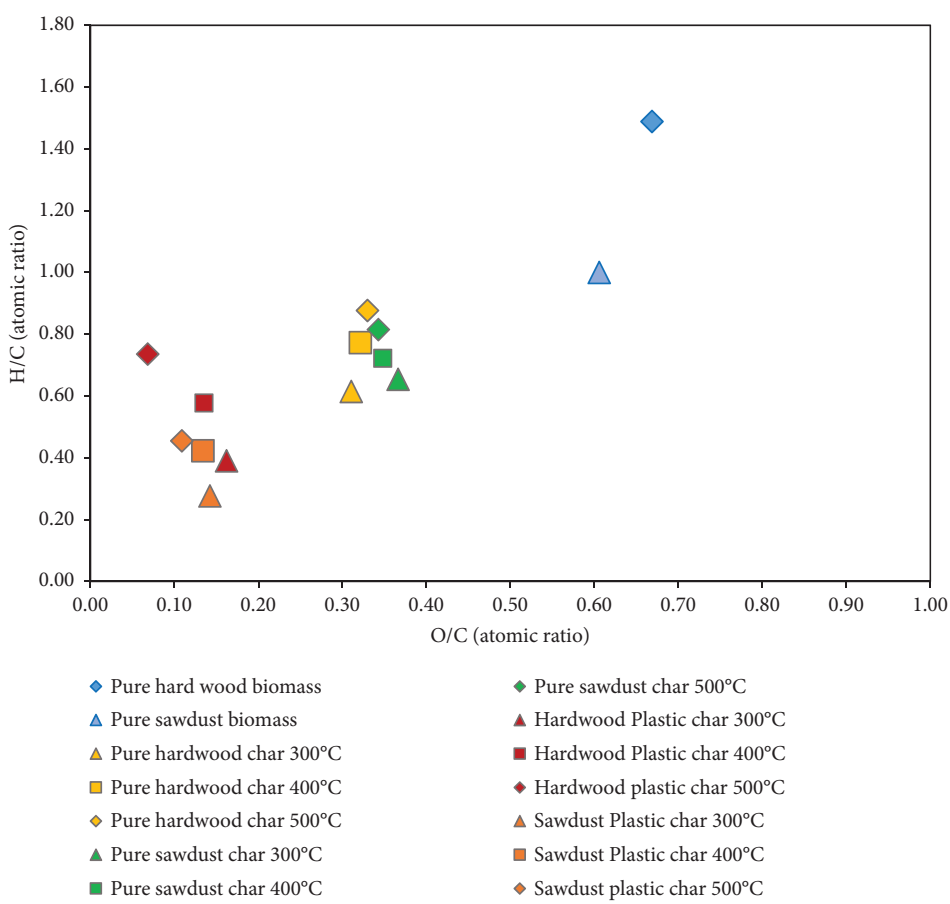

Figure 8: Van Krevelen diagram with H : C and O : C molar ratio.

materials can affect an escalation in pore volume from 0.0018 to 0.0049 $m^2\ g^{-1}$ and the rise in specific surface area from 0.30 to 0.67 $m^2\ g^{-1}$, as the pyrolysis temperature increases from 300 to 500°C in sawdust–plastic biochar obtained [43]. The hardwood–plastic biochar obtained was also similar to the biochar obtained from sawdust–plastic. This indicates

Table 1: The specific surface area, pore volume, and pore size distribution of sawdust–plastic biochar and hardwood–plastic biochar.

Sample	Pyrolysis temperature (°C)	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore dimension (nm)
Sawdust–plastic biochar	300	0.30	0.0018	22.08
	400	0.35	0.0040	24.08
	500	0.67	0.0049	56.05
Hardwood–plastic biochar	300	11.97	0.0130	11.53
	400	16.67	0.0500	21.53
	500	42.47	0.1100	26.64

that higher pyrolysis temperatures lead to greater devolatilization [44] of material, resulting in the generation of additional pore volume and an expanded surface area, enhancing its adsorption capabilities.

3.5. SEM Images of Obtained Sawdust–Plastic Biochar and Hardwood–Plastic Biochar. The morphology of obtained sawdust–plastic biochar and hardwood–plastic biochar was analyzed via SEM-EDX as presented in Figures 9 and 10. Figures 9(a)–9(c) are SEM images of hardwood–plastic biochar at 300°C, 400°C, and 500°C pyrolysis temperature for 1 h. The structure of hardwood–plastic biochar at 300°C (Figure 9(a)) had a porosity distribution with a small pore (11.53–26.64 nm, Table 1) at the surface. Hardwood–plastic biochar at 400°C had conspicuous porosity (Figure 9(b), pores size of about 11.53 nm). However, hardwood–plastic biochar at 500°C, when materials are subjected to high temperatures, can lead to a breakdown in porosity or a decrease in porosity as shown in Figure 9(c) (average pore dimension of about 26.64 nm).

In terms of sawdust–plastic biochar, it can be seen that after pyrolysis for 1 h, the structure at 300°C (Figure 10(a)) had a porosity distribution with plastic cover on the surface. This covering might block the existing holes and cavities in the biochar by plastic waste (PP). While sawdust–plastic biochar at 400°C (Figure 10(b)) had a large pore size diameter of about 22.08 nm, it displayed an amorphous/unstructured, disorganized structure with irregularly shaped voids, a result of the dehydration and devolatilization of cellulose through varying temperature. Sawdust–plastic biochar at 500°C showed the biggest of average pore dimensions (56.05 nm). It can be seen at high temperatures that the surface was smoother; however, it still had no established pores due to its low specific surface areas; this might be due to small pores that can crack and form a large average pore size diameter [45] and might occur because of a more uniform composition or a processing method that resulted in a smoother texture. It is also possible that the material underwent a pyrolysis process that led to this smoother surface with a difference in specific surface area and pore volume. It can be concluded that the alternative raw materials selected and the control of activation parameters, such as temperature, time, and method, are crucial in determining the surface structures of activated materials. These factors support tailoring the development of the pore and surface area to meet specific requirements for several applications, such as adsorption for water and wastewater treatment, catalysis for industry plants, and energy storage.

3.6. Physical Characteristics of Materials Used as Obtained Biochar. The experiment involved analyzing moisture content, ash content, volatile matter, and fixed carbon yields in biomass derived from a blend of sawdust and wood, along with a 20% plastic (PP) mixture. The pyrolysis was performed at different temperatures such as 300°C, 400°C, and 500°C for 60 minutes, and the results are summarized in Table 2. Higher moisture content in the biomass leads to significant energy losses during biochar production. Biomass with moisture levels below 10% is considered optimal, as excessive moisture hinders its ability to generate biofuel. It was found that raising the pyrolysis temperature resulted in a decrease in the moisture content of the biochar. Co-pyrolysis with plastic resulted in a decrease in overall moisture compared to biomass alone, and this effect was more pronounced at higher temperatures. For biochar derived from sawdust, the moisture content ranged from 3.64% to 1.58% across temperatures from 300°C to 500°C. In terms of hardwood raw material, the moisture content ranged from 1.30% to 0.34% within the same temperature range. The biochar with the lowest moisture content was found at 500°C, while the maximum moisture content was recorded at 300°C.

Ash content denotes the portion of a material that comprises nonvolatile and noncombustible elements [46]. The output of plastic into the feedstock exhibited a minor decrease in ash content as temperature increased, registering between 8.60% and 5.96% for sawdust-derived biochar and from 9.87% to 3.33% for hardwood-derived biochar across the temperature choice of 300–500°C. Wood, being predominantly organic and composed of cellulose fibers with an extremely volatile content, generates less residual ash after pyrolysis. Coprocessing the biomass with a plastic blend was noted to significantly diminish ash content. Yields dropped from 8.60% for pure sawdust char to 4.05% with a 20 wt% plastic blend at 300°C, and similar trends were observed at 400 and 500°C. This aligns with findings from Mota-Panizio et al. [47], where ash levels diminished with an increasing proportion of biomass in the composite/mixture. This is advantageous as high ash content can lead to equipment malfunction and slag formation. Co-pyrolysis of biomass residues with plastics led to decreased ash contents compared to pure biomass residues at the same temperature. This corresponds with the study by Oh and Seo [48], who found that co-pyrolysis using rice straw composited with plastics such as PP, PE, or PS improved various properties of the resulting biochar, including surface area, carbon content,

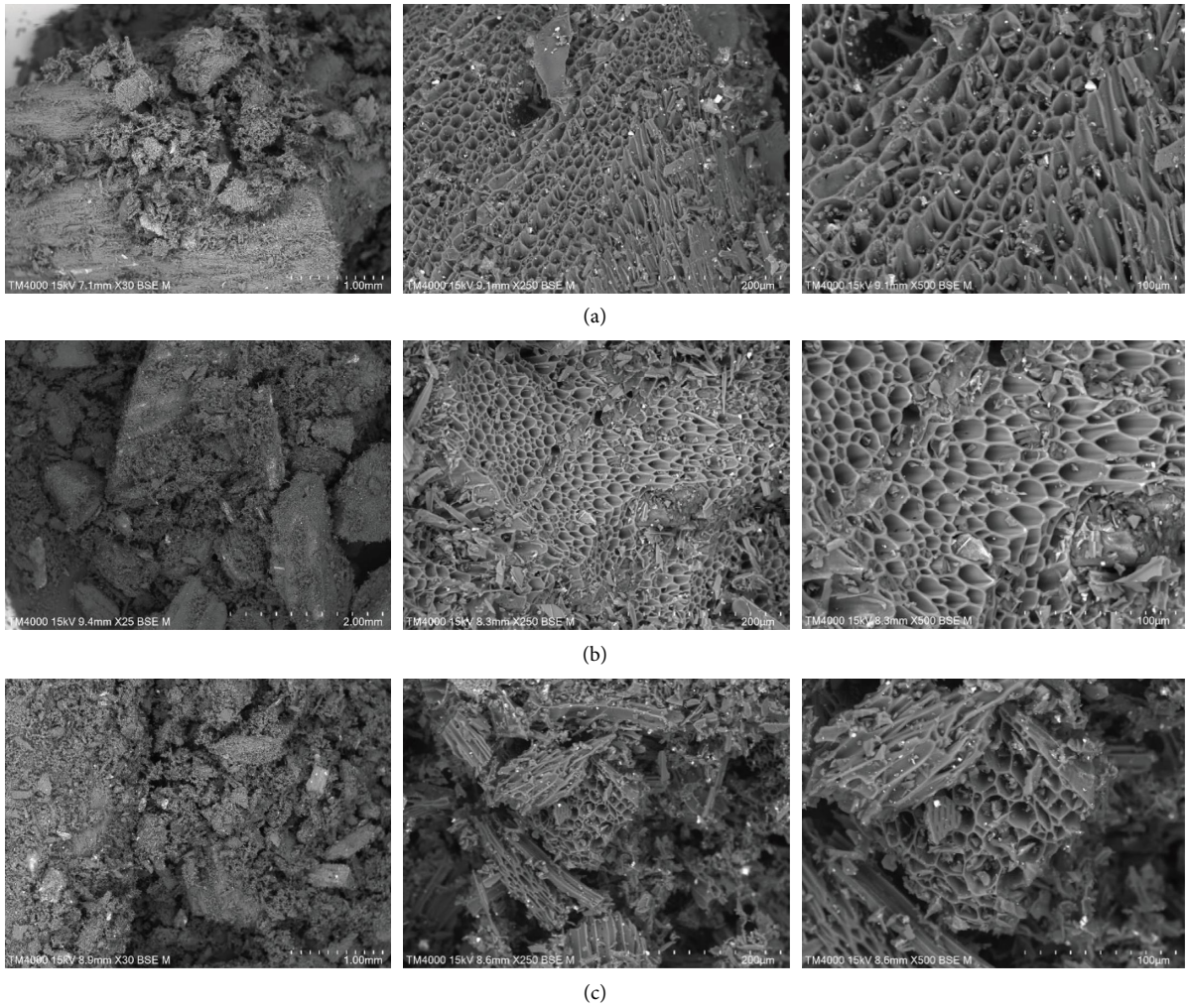

Figure 9: Scanning electron microscopy image of (a) hardwood–plastic biochar 300°C, (b) hardwood–plastic biochar 400°C, and (c) hardwood–plastic biochar 500°C at X30, X200, and X500, respectively.

hydrophobicity, and aromaticity. These enhanced properties significantly contributed to the biochar's capacity for sorbing substances like Pb and 2,4-dinitrotoluene.

The biochar derived from both sawdust wood and hardwood biomass blended with plastic primarily comprised volatile matter. As anticipated, the volatile content decreased with rising pyrolysis temperatures. Pure hardwood biochar exhibited the highest volatile matter content (38%) at 300°C. A similar trend was observed for pure sawdust biochar, which displayed volatile matter contents of 38%, 23%, and 19% at 300°C, 400°C, and 500°C, respectively. The beneficial combined effect seen in the plastic blends can be credited to the interaction between the biomass and polymer components, resulting in the production of fewer volatile products at higher temperatures. Possible sorption mechanisms were identified including plastic electron donor-acceptor interactions and hydrophobic sorption [48]. Thus, the enhancement of the interactions of plastic and biochar can be explained by two possible mechanisms. First, carbon residues from polymers may increase the hydrophobicity. Second, the increased carbon content and aromaticity that results from pyrolysis can enhance possible interactions between plastic and biochar.

The temperature plays the important role to increase the biochar properties. This finding aligns with Zhao et al.' observations of the production of biochar derived from apple tree branches [49], where an elevated pyrolysis temperature resulted in a decline in the content of volatile matter (by 60.8–14.9%). This indicates that elevated temperatures encourage the further breakdown of volatile components into smaller, low-molecular-weight liquids and gases, rather than their conversion into biochar. Higher temperatures can lead to the removal of hydroxyl groups through dehydration and cause the thermal degradation (organic polymers break down) of cellulose and lignin. This phenomenon occurs in various natural processes, such as combustion, pyrolysis, or during industrial processes like the production of biochar [50]. During the initial stages of pyrolysis (up to 250°C), biochars underwent transformations involving oligosaccharides. As the temperature rose to 290°C, phenols and furans emerged. Beyond this threshold, the primary components of the biochar shifted to alkyl furans, benzenoid aromatics, and

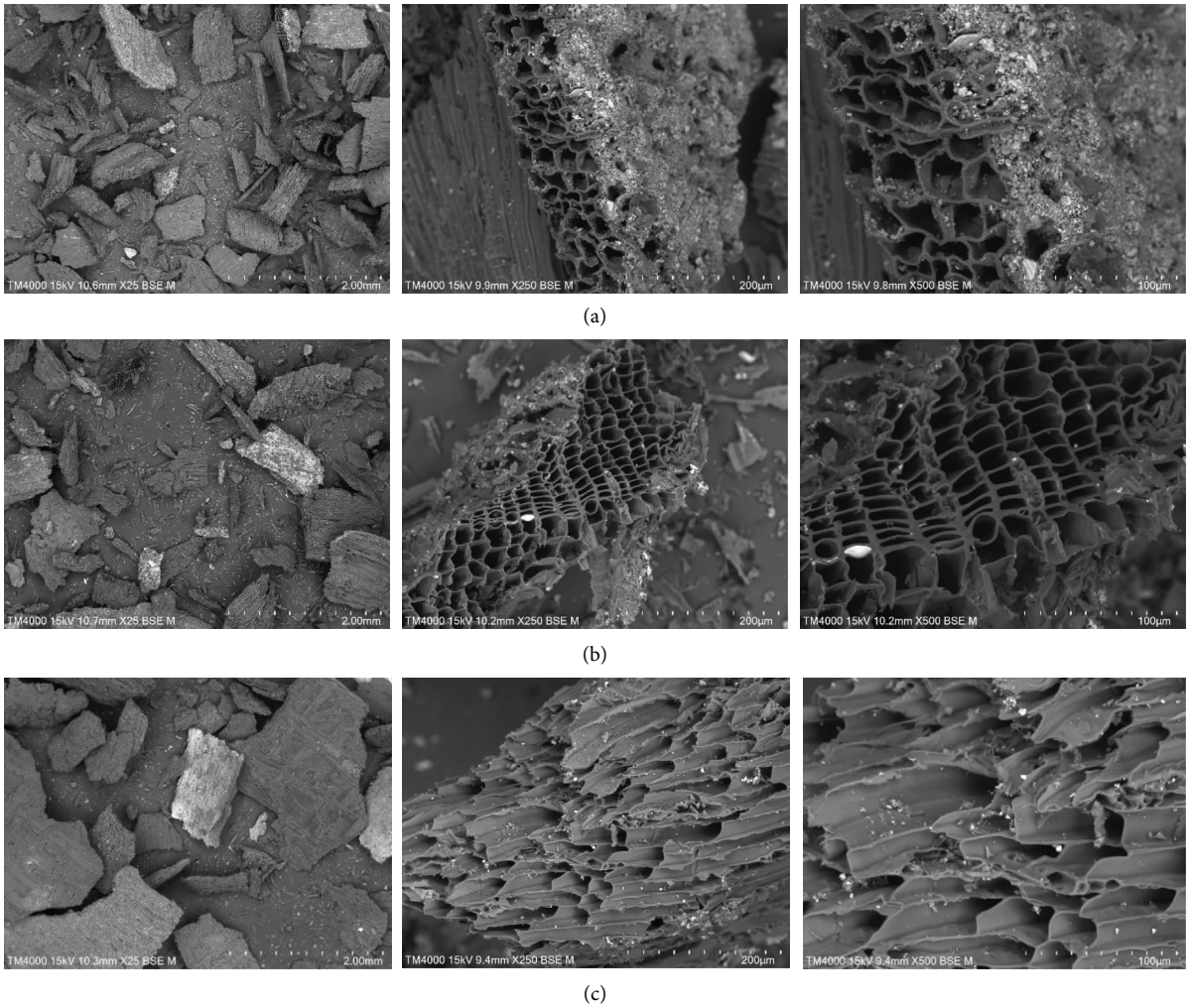

Figure 10: Scanning electron microscopy image of (a) sawdust–plastic biochar 300°C, (b) sawdust–plastic biochar 400°C, and (c) sawdust–plastic biochar 500°C.

Table 2: Ash content, moisture, volatile, and fixed carbon of materials used and obtained biochar.

Sample	Pyrolysis temperature (°C)	Ash content (%)	Moisture (%)	Volatile matter (%)	FC (%)
Pure sawdust char	300	8.60	6.17	38	57.7
	400	7.05	4.34	23	69.5
	500	5.96	2.68	19	70.1
Pure hardwood char	300	3.33	5.25	39	53.4
	400	5.90	4.67	25	69.0
	500	9.87	2.15	21	75.0
Sawdust–plastic char	300	4.05	3.64	30	64.0
	400	4.64	2.78	22	70.4
	500	5.26	1.58	12	80.7
Hardwood–plastic char	300	2.04	1.30	32	68.0
	400	3.90	0.70	25	74.1
	500	4.38	0.34	14	84.6

condensed aromatics. A greater volatile matter content can contribute to enhancing the stability of the biochar [51]. The content of volatile matter also influences soil nitrogen transformations and plant growth [52].

An elevated fixed carbon content in plant-based biomass is a sign of a greater presence of lignin [53]. Biochar production tends to be more efficient from lignin-rich biomass compared to biomass rich in cellulose and hemicellulose content [54]. A significant rise in fixed carbon content was evident in the biochars derived from sawdust when compared to those from hardwood biomass. Specifically, at 300°C and 400°C, the fixed carbon content rose from 57.5% to 69.5% and 53.4% to 69.0%, respectively. However, the highest fixed carbon content (75%) was recorded in hardwood biochar at 500°C. An increased fixed carbon content indicates a more intense carbonization process at elevated temperatures, leading to a higher concentration of carbon within aromatic structures. As previously mentioned, the impact of varying pyrolysis temperatures (300°C, 400°C, and 500°C) was explored in changes in the physicochemical properties of hardwood and sawdust–plastic biochar was characterized by a general decrease in moisture and volatile content, along with a rise in ash and residual carbon content. These alterations were notably influenced by the pyrolysis temperature [55].

The incorporation of plastic into the biomass blend resulted in an overall fixed carbon relative to the pure biochar at the same conditions. The most significant impact was observed for co-pyrolysis with plastic, with a substantial increase in fixed carbon from 70.1% to 80.7% for sawdust at 500°C and from 75.0% to 84.6% for wood at 500°C. These results suggest that the radical interactions of plastic and biomass contributed to the positive synergistic effect during pyrolysis reaction.

3.7. The pH of Obtained Biochar. Due to their pH levels, biochar may have limitations in their application in soil and environmental contexts. The pH values of the biochar samples are recorded in Table 3, revealing that biochar produced at higher temperatures tended to exhibit relatively higher pH levels compared to that produced at lower temperatures. This suggests that at elevated temperatures, acidic functional groups (–COOH) may diminish, while the emergence of basic functional groups could be a contributing factor. Upon introducing plastic into biomass feedstocks, a slight decrease in pH was observed in comparison to biochar derived solely from biomass. Notably, no significant difference in pH was observed between sawdust and wood biomass. The pH range of the biochar samples fell between 8.2 and 9.6. These pH levels could be suitable for improving acidic soils and remediating contaminated soil, as they are associated with the adjustment of soil solution pH.

3.8. Identification of Major Functional Groups in Obtained Biochar. The infrared spectra of the obtained biochar derived from the blend of biomass residues with plastic at various temperatures are depicted in Figure 11. Notably, the FTIR spectra of sawdust–plastic biochar and hardwood–plastic biochar derived at different temperatures closely resemble those generated from biomass residues alone. This suggests that plastics can be effectively coprocessed with biomass residues through pyrolysis, with plastics undergoing substantial breakdown. Moreover, it is revealed that the obtained biochar at lower pyrolysis temperatures exhibits higher intensity peaks compared to those obtained at higher temperatures. This implies that as the temperature increases during the pyrolysis process, the valorization (the organic material undergoes a series of chemical reactions) of the various compounds comprising the material takes place. These reactions lead to the breakdown and transformation of the compounds present in the material. When organic materials are subjected to pyrolysis (heating in the absence of oxygen), a complex series of chemical reactions occur. These reactions lead to the breakdown of the organic molecules present in the material, resulting in the formation of a wide range of compounds. The magnitude of these peaks shows a noticeable reduction in the char obtained from the co-pyrolysis of plastic and biomass residues. Specifically, the peak at 2958 and 2918 cm^{-1} is attributed to the alkyl groups, including -CH3- and -CH2-, present in the pure microplastic biochar. These groups undergo degradation with rising pyrolysis temperature. In addition, the absorbance related to the C=C bond of alkanes at 1458 cm^{-1} is present, indicating the presence of long aliphatic chains. However, it can be seen that these peaks become rarely distinguishable in the FTIR spectra at higher temperatures, indicating a preference for polymer chain breaking, and almost vanish in the pyrolyzed biomass materials at 550°C [56]. The robust absorption bands observed at 1600 cm^{-1} are attributed to the carboxylic -OH group. It can be seen that the peak also weakens due to increasing temperature during the pyrolysis, suggesting the removal of polar groups. This result is consistent with biochar exhibiting decreased polarity and increased aromaticity [57]. In addition, other peaks showing strong absorption bands around 1020 cm^{-1} and 870 cm^{-1} are attributed to the stretching vibrations in FTIR spectra of the C-H bonds in aromatic rings from sawdust [58], and these

Table 3: pH of biochar sample.

Sample	Pyrolysis temperature (°C)	pH
Pure sawdust char	300	8.7
	400	9.2
	500	9.4
Pure hardwood char	300	8.6
	400	9.4
	500	9.6
Sawdust–plastic char	300	8.4
	400	9.0
	500	9.2
Hardwood–plastic char	300	8.2
	400	9.2
	500	9.5

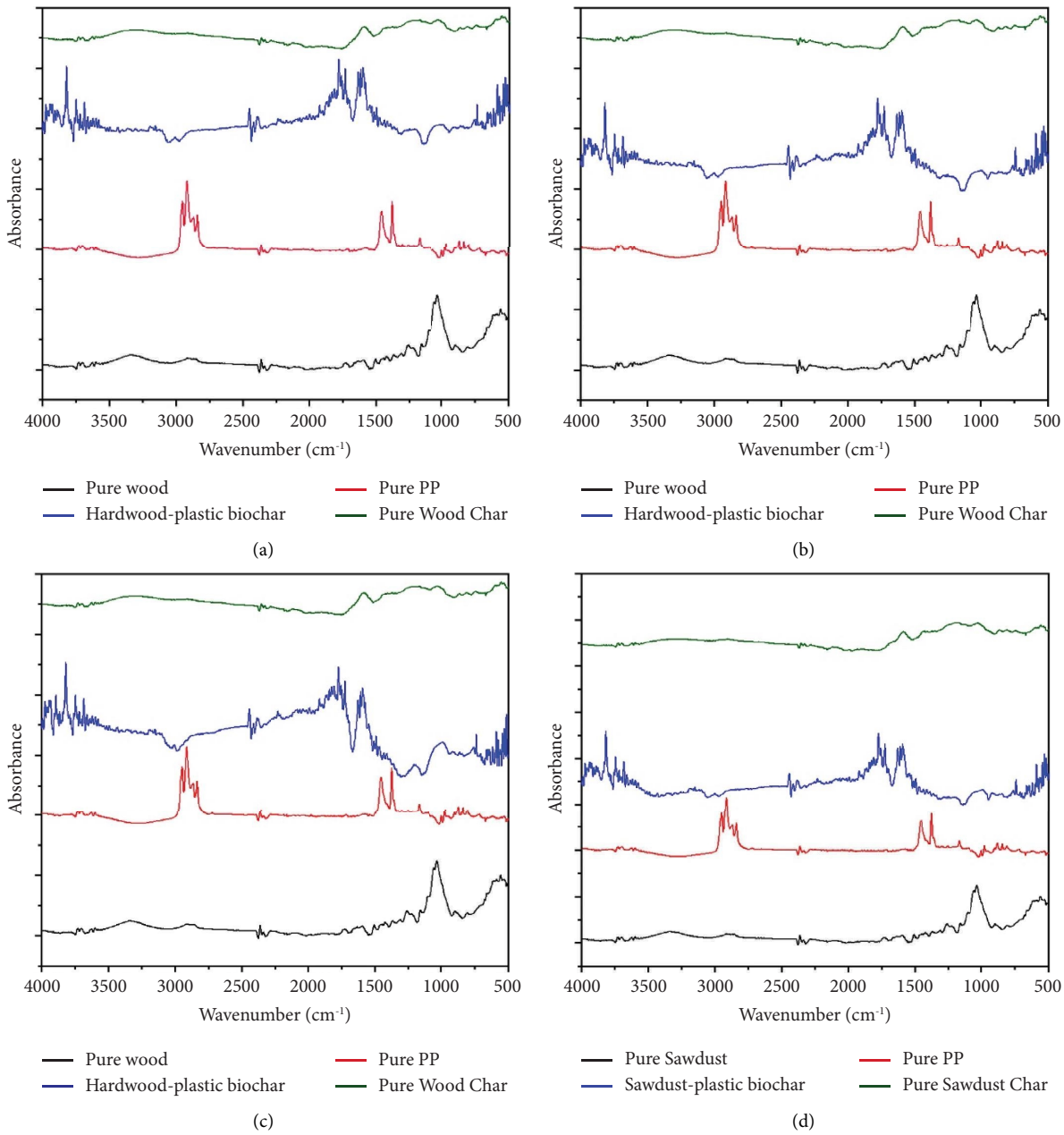

Figure 11: Continued.

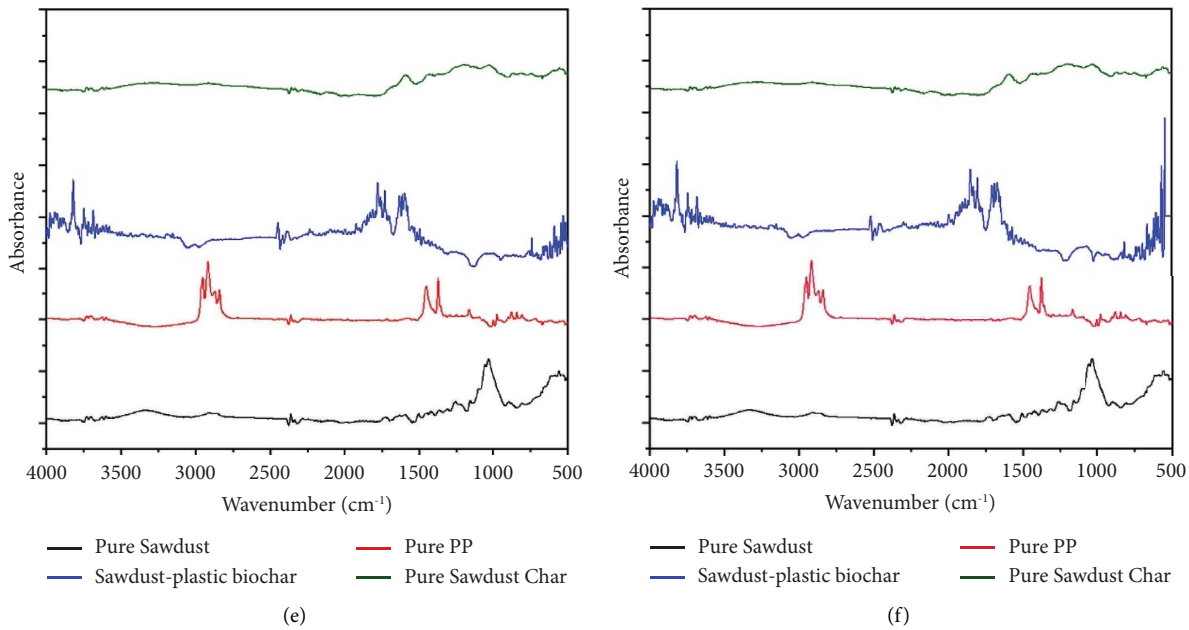

Figure 11: Comparison of functional groups of material used and obtained; (a) hardwood, pure PP, hardwood–plastic biochar, and pure wood char at 300°C, (b) hardwood, pure PP, hardwood–plastic biochar, and pure wood char at 400°C, (c) hardwood, pure PP, hardwood–plastic biochar, and pure wood char at 500°C, (d) sawdust, pure PP, sawdust–plastic biochar, and pure sawdust char at 300°C, (e) sawdust, pure PP, sawdust–plastic biochar, and pure sawdust char at 400°C, and (f) sawdust, pure PP, sawdust–plastic biochar, and pure sawdust char at 500°C.

also diminish in intensity with increasing temperature (300°C–500°C) of pyrolysis [59].

4. Conclusions

The recycling of plastic leads to a substantial generation of microplastic waste, which persists widely in the environment without being reutilized. This study evaluated the impact of such microplastic waste on the pyrolysis of biomass residues. The biochar's yields and physicochemical properties were predominantly affected by the pyrolysis temperature and the incorporation of plastic blends. At 300°C, the maximum biochar yields were 40 wt% for plastic–hardwood and 30 wt % for plastic–sawdust. As the temperature increased, biochar yields decreased. In addition, the introduction of plastic into the feedstock further reduced biochar yields at 400 and 500°C. Co-pyrolysis exhibited a positive effect on the conversion of waste plastics and biomass residues through biochar, enhancing both the efficiency and effectiveness of the process. This led to improved biochar properties from the specific feedstock. The presence of plastic generally led to an increase in the volatile matter content in both hardwood and sawdust biochar materials. This suggests that the introduction of plastics during the pyrolysis process resulted in higher levels of volatile organic compounds and other substances that are easily vaporized at relatively low temperatures. Moreover, the fixed carbon content and higher heating values of these biochars also increased with the addition of plastic. Biochar derived from hardwood exhibited superior physicochemical properties compared to that from sawdust biomass. Both types of biochar demonstrated excellent adsorbent characteristics, making them valuable for removing numerous contaminants from water, wastewater, air, and soil (soil structure, water retention, and nutrient availability). The utilization of biochar derived from biowaste not only reduces environmental biowaste but also transforms it into an environmentally friendly and valuable product.

Data Availability

No data were used to support the findings of this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this manuscript.

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