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Investigation of biomass and agricultural plastic co-pyrolysis: Effect on biochar yield and properties

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Highlights

- Plastic waste from agriculture and horticulture was co-pyrolyzed with waste biomass
- Low ratios of LDPE plastic were found to have a positive effect on biochar yield
- High ratios of LDPE plastic were found to have negative effect on biochar yield

- Pyrolysis has the potential to valorize mixed biomass with low levels of LDPE plastic

Abstract

Complete separation of mixed plastic and biomass waste is a technically difficult, laborious, expensive and time-consuming process. Hence, co-pyrolysis of these agricultural waste streams with low levels of plastic contamination presents a novel approach for the management of these plastic containing wastes, producing stable forms of carbon with potential use in environmental, agricultural and industrial applications. In this study, spent growing medium along with plastic growing bags, and bean crop residues along with mulching sheets were selected to assess how the presence of plastics would affect the characteristics of the biochars produced. These feedstocks were combined in mass ratios (of plastic in the biomass-plastic mixture) of 0, 0.25, 2.5, 5 and 10%. The resulting feedstock underwent slow pyrolysis in a fixed bed pyrolysis reactor at a temperature of 550 °C to ensure complete conversion of the plastic components of the feedstock. From the results obtained from pyrolysis, low ratios of plastic were found to have a positive impact on biochar yield, while high plastic ratios were found to have negative effect. Higher level of plastic in the feedstock have resulted peculiar functional groups in the biochar, including carboxylate anions, amides and aromatic groups. Biochars produced from spent growing medium along with plastic grow bags (GM biochars) showed no phytotoxic effect, irrespective of the concentration of plastic contamination in the feedstock. Biochars produced from bean crop residues along with mulching sheets (BM biochars) on the other hand showed high level of phytotoxicity (zero germination), irrespective of level of plastic contamination. After washing all BM biochar, very low phytotoxicity levels with no statistically significant effect of plastic contamination were observed, with the exception of 10BM that showed somewhat a reduced germination rate (93%). The results of this study will be beneficial for determining the tolerable level of plastic contamination in managing mixed agricultural

waste biomass and to produce biochars suitable for environmental, agricultural and/or industrial applications.

Keywords

Biochar, Agricultural plastic waste, Spent growing media, Mulching sheets, Plastic grow bags, Co-pyrolysis.

Abbreviations

APW	Agricultural plastic waste
BM	Bean crop residues
BM biochar	Biochar produced through co-pyrolysis of bean crop residues and plastic mulching sheets
GM	Spent growing media
GB	Plastic grow bags
GM biochar	Biochar produced through co-pyrolysis of spent growing media and plastic grow bags
HHV	Higher Heating Value
LDPE	Low-density polyethylene
MS	Mulching sheets
PTE	Potentially Toxic Elements

1. Introduction

With the start of the mass production of plastics in the 1930s, the use of plastic spread into every nook and cranny of the world. Currently, the use of plastics is pivotal for ensuring a resource-efficient economy [1]. The widespread use of plastic became popular amongst the world population due to its favorable qualities such as being lightweight, durability, hydrophobicity, reusability and low cost of production etc. over other alternatives. However, these favorable qualities accelerate plastic accumulation in the environment [2]. By 2015, the world had produced 6300 Mt of plastic waste and the majority of that (79%) had been discarded into landfills or in the natural environment, where they accumulate [1]. With recent developments and the immense increase in agricultural and horticultural production, a substantial amount of plastic waste is being generated through crop farming and protected agricultural activities such as in greenhouses [3–5]. Mulching films, grow bags, greenhouses and tunnel covers, tubes and piping, bale and silage wraps are instances where plastic is heavily used in agriculture. Those agricultural plastic materials are popular among farmers due to their ability to control weed problems, reduce soil moisture evaporation, and the high-quality of crops associated with their application. An increase in the human population, higher demands for food, loss of productive agricultural lands and adverse weather conditions are major challenges for today's farmers [6]. In the EU alone, the plastic industry had a turnover of more than 360 billion euros in 2018 and from the total demand for plastics in the EU, 3.4% was for agricultural purposes [7]. Low density polyethylene (PE-LD) and linear low density polyethylene (PE-LLD) are the most commonly used polymer types in the EU and around the world [1]. From the collected post-consumer plastic waste in the EU, 32.5% is recycled while 24.9% and 42.6% are sent to landfills and energy recovery facilities, respectively [1,2].

Among other agricultural plastic waste, plastic mulching sheets are considered as one key factor for microplastic pollution in agricultural soils [8]. Farmers in some countries incorporate plastic mulching sheets into the soil during tillage practices, and the removal of these mulching sheets/mulching films after use is laborious and time-consuming, leading to the accumulation of residues [5]. These residual plastic materials can adversely impact soil and plant properties. Currently, plastic grow bags are extensively used in greenhouse agriculture and disposal of plastic grow bags filled with spent growing media is a major drawback in greenhouse waste management [3]. Separating plastic wraps from the spent growing medium is laborious and time consuming [9,10]. Even though biodegradable and compostable plastic material exists as alternatives to conventional plastic materials used in agriculture, their cost-effectiveness and long-term use could cause problems for farmers, as a result of weather-induced disintegration and brittleness during long-term use. On the other hand, industrial composting conditions are required for the full degradation of compostable plastic materials and such conditions are lacking in agricultural soils and vary with different environmental factors [11]. Other than the burying or stacking on the same site, other existing practices for mixed agricultural waste management are landfilling, open burning or incineration. There is no doubt that open burning can produce and release a tremendous amount of harmful compounds such as dioxins, furans, CO, and volatile organic compounds amongst others [12]. Having foreign materials such as sand and contamination with agrochemical residues, low thickness (i.e., mulch films), and mixing with other organic materials often constrains the proper waste treatment for agricultural plastics, and makes their management a challenge [13]. Moreover, collection and transportation costs, processing costs, limited capacities for plastic waste recycling are the major obstacles for proper management of agricultural plastic waste [13–15]. Most of the plastic recyclers accept only good quality plastic waste. In the EU, 5% of post-consumer waste is from the agricultural sector. According to Plastics Europe [1], plastic waste recycling rates are 10 times higher when collected separately compared to mixed plastic waste treatments. 52% of collected waste in the EU is mixed waste and only 6% of that is recycled. 57% is used for energy recovery purposes, while 37% is sent to landfills. Although some countries (China, Hong Kong, Malaysia) allow the importation of plastic waste, the transportation of plastic waste between countries is regulated through the Basel convention [5]. Therefore, plastic waste exporting countries have to go through a series of preprocessing options such as removal of contaminants, washing, segregation etc. making waste treatment complex, time-consuming and expensive [5].

Currently, countries that import plastic waste also face environmental problems such as emissions due to improper flue gas filtrations and lack of post-treatments for the flue gases produced [16].

Conventionally, the plastic materials used in agriculture are not biodegradable. Thus, to achieve the destruction of these plastic materials, thermal treatments such as combustion or pyrolysis are ideal [2]. Currently, incineration is mostly used for plastic waste management. Qureshi et al. [16] identified pyrolysis having a lower carbon footprint compared to incineration. As stated above, conventional methods of plastic waste management could result in a myriad of environmental and health problems. Most of the organic materials mixed with agricultural plastic waste (APW) contain a lower amount of plastics [4,17]. Due to the herbaceous nature of the crop residues, it is not easy to separate those materials. In this respect, co-pyrolysis of organic waste (i.e., crop residues and spent growing mediums) mixed and/or associated with plastics seems to be the most viable option to valorize such waste streams due to the complete degradation of plastic materials at higher temperatures [18]. However, this process could introduce contaminants such as PTEs, dioxins, PAHs and VOCs to pyrolysis products. Due to this reasons, International Biochar Initiative (IBI) [19] only allow 2% (w/w) of contaminants (including fossil fuel derived contaminants) in the feedstock material use for the biochar production. Not only that, European Biochar Certificate (EBC) [20] only allows 1% (w/w) of plastic contaminants in feedstock when biochar produced for EBC feed, EBC agro and EBC agro organic class biochars. However, For the EBC material class biochars, feedstock could contain up to 15% (w/w) of plastic content. Moreover, Biochar Quality Mandate (BQM) [21] only allow 0.25% (w/w) of contaminants in feedstock material for biochar production.

Pyrolysis of plastic waste alone to obtain liquid and gas products has been extensively studied over the last couple of years [22]. However, relatively few studies have examined the effect on biochar yield and biochar properties after biomass co-pyrolysis with low levels of plastics

[23,24]. Since the International Biochar Initiative (IBI), Biochar Quality Mandate (BQM) and European Biochar Certificate (EBC) allow for a certain level of contamination in both biochar and their feedstock, it would be interesting to see the effect of low levels of plastic contamination on biochar produced from the co-pyrolysis of agricultural plastic waste and biomass [19,21].

The choice of spent growing medium and bean plant residue was as a result of their common association with plastics and their relatively short life cycles, which means they become waste in just a few months, a year or at most 2 years. On the other hand, mulching sheets used in agriculture identified as a major environment polluter in intense agricultural areas [25]. Bean crop residues selected to represent the herbaceous nature of crop residues and association with mulching sheets with bean crop cultivation. The main objective of this study was to investigate the presence or absence of a positive effect exhibited by low levels of plastic contamination on biomass pyrolysis, and how the effects or (lack thereof) evolve as the plastic to biomass ratio changes and how it effects biochar yield and properties.

2. Materials and methods

2.1. Feedstock supply and biochar production

The feedstocks used for this study are bean crop residues and spent strawberry growing medium, they were mixed with plastic mulching sheets (LDPE), and plastic growbags (LDPE) respectively. The bean crop residues and mulching sheets were obtained from a field in Afsnee, Belgium and the spent strawberry growing medium was obtained from Stockbridge Technology Centre Ltd in the United Kingdom, along with the plastic grow bags (LDPE). Feedstocks (bean crop residue and spent growing medium) were first air-dried and thereafter, dried in an oven for a period of 24 hours at a temperature of 105 °C. Then the samples were ground thoroughly using a Bosch blender and sieved to particle sizes of 0.5 – 2 mm. The ground feedstock was combined with the plastic materials as indicated in Table 1.

The International Biochar Initiative permits 2% of contaminants in the feedstock material (IBI, 2012) while the European Biochar Certificate only allows 1% of contaminants in the feedstock material (EBC, 2020). The Biochar Quality Mandate, which is UK based allows only 0.25% of contaminants in the feedstock (Shackley et al., 2014). Moreover, postconsumer plastic mixed waste collected in Europe has plastic levels within the range of 2-8% (Plastics Europe, 2019). On the other hand, spent grow bags used in this study had plastic levels (as an outer plastic cover/wrap) up to 2.5% (average, on dry weight basis). Regarding the plastic mulching sheets, their plastic content compared to crop residues is highly dependent on the farm size, crop type, weather conditions, etc. Based on all this information, to represent the whole range of low levels of plastic contamination in waste biomass materials, plastic contents in the feedstock material were selected as 0, 0.25, 2.5, 5 and 10% on a dry weight basis

A slow pyrolysis experiment was carried out in a small-scale fixed-bed pyrolysis reactor made up mainly of stainless-steel piping and fittings. The more details of the pyrolysis setup is described in elsewhere [26]. The reactor vessel consisted of a 15 cm^3 stainless-steel pipe made from tapered pipe fittings. The reactor is capable of reaching temperatures of around 1000 °C and the temperatures of the middle of the reactor chamber and oven wall are monitored with the aid of two thermocouples (Figure 1). For the pyrolysis experiments, an oven temperature (T_{oven}) of 550 °C was used as the set temperature. During the pyrolysis experiments, at the maximum average reactor middle temperature (T_{bed}) (532 ± 2.12 °C), the maximum furnace wall temperature ($T_{\text{reactor wall}}$) was 483 ± 3.54 °C. Nitrogen gas (Alphagaz™, ≥ 99,999 %, Air Liquide, Belgium) was used as a carrier gas. The average heating rate of the pyrolysis experiments was 10.42 °C/min and residence time was 30 minutes at the highest treatment temperature. All experiments were carried out in duplicates, with an average sample weight of 7.5±0.5 g per experiment.

Table 1. Produced biochar types and their feedstock composition. (The numbers in front of the "GM" and "BM" abbreviations denote the plastic level in percentage dry weight basis (dwb) included in the feedstock material).

Biochar type	Feedstock Composition (Biomass: Plastic, dwb)	Percentage combination (Biomass: Plastic, dwb)
0GM	Spent growing medium	100: 0
0.25GM	Spent growing medium: Plastic grow bag	99.75: 0.25
2.5GM	Spent growing medium: Plastic grow bag	97.5: 2.5
5GM	Spent growing medium: Plastic grow bag	95: 5
10GM	Spent growing medium: Plastic grow bag	90:10
0BM	Bean crop residue	100:0
0.25BM	Bean crop residue: Plastic mulching Sheet	99.75: 0.25
2.5BM	Bean crop residue: Plastic mulching Sheet	97.5: 2.5
5BM	Bean crop residue: Plastic mulching Sheet	95: 5
10BM	Bean crop residue: Plastic mulching Sheet	90:10

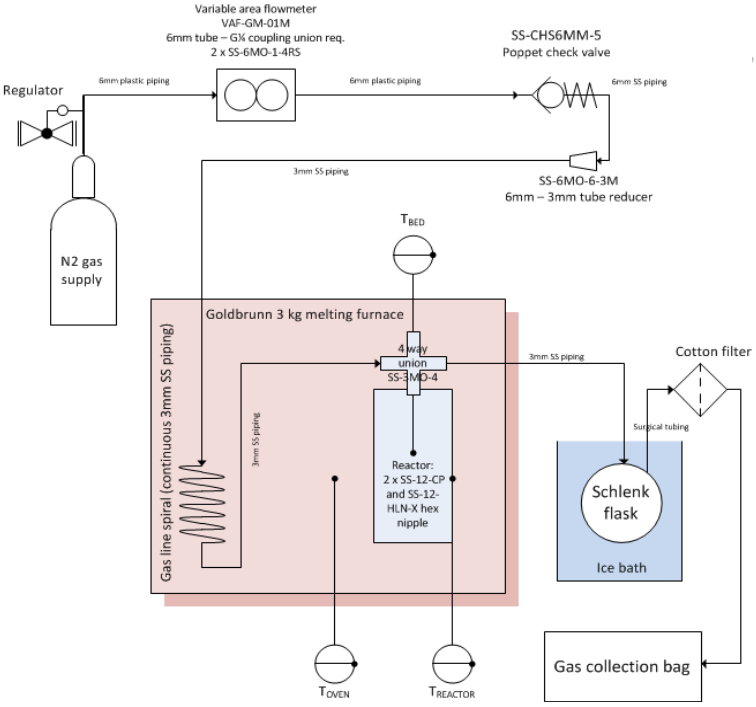

Figure 1. Schematic diagram of the pyrolysis set-up used for the biochar production [26].

2.2. Biochar characterization

2.2.1. Proximate analysis and HHV determination

Proximate analysis was done using an adaptation of the ASTM D1762-84 for biochar described by Enders and Lehmann [27]. The higher heating value was calculated from the fixed carbon (FC), volatile matter (VM) and ash content (ASH), using equation 1 described by Parikh et al. [28]. Values of VM, ASH and FC were used in percentage dry weight basis.

$$\mathrm{HHV\ (MJ/kg)} = 0.3536\mathrm{FC} + 0.1559\mathrm{VM} + 0.078\mathrm{ASH} \qquad \text{(eq. 1)}$$

2.2.2. CHNO analysis

The C, H, N and S composition of the samples were carried out using the Flash 2000 Organic Elemental Analyzer from Thermo Scientific. 2,5-bis (5-tert-butyl-benzoxazol-2-yl)-thiophene (BBOT) was used as a standard material. Oxygen content was calculated by difference on an ash-free basis.

2.2.3. The pH of biochar samples

To determine the pH and EC of the samples, ground biochar was dispersed in deionized water in the ratio of 1:20. Then the pH of the samples was measured with a Fisher Scientific Accumet pH meter after calibration with buffers of pH 4, 7 and 10.

2.2.4. FTIR analysis of biochar

FTIR analysis was performed using a Shimadzu IRAFFINITY-1S Fourier Transform Infrared (FTIR) spectrophotometer with compact dimensions. Infrared spectra with an S/N ratio of 30,000, were obtained in a clean (unmodified) form using a quest attenuated total reflectance (ATR) accessory with a diamond crystal puck. Twenty scans of each sample were performed in duplicates at a spectral range of 400 cm^{-1} to 4000 cm^{-1} and a maximum resolution of 0.5 cm^{-1}.

2.2.5. Nutrients and PTEs of biochar

Total elemental analysis of the GM and BM biochars were carried out using the modified dry ash method described by Enders et al. [29]. Briefly, 0.2 g of sample was weighed into crucibles and then transferred to a furnace. Crucibles were heated from ambient to 500 °C, over 2 hours and were held at this temperature for 8 hours. Thereafter, the furnace was allowed to cool to 175 °C and the furnace door was opened slightly and was further cooled to 30 °C before the samples were taken out. 5 ml of concentrated HNO_3 acid (Chem-Lab, Zedelgem, Belgium) was added to each crucible and was evaporated off at 120 °C on a digestion block. Thereafter, the crucibles were cooled and 1 ml concentrated HNO_3 and 4 ml H_2O_2 (Chem-Lab, Zedelgem, Belgium) were added. The crucibles were placed back on the digestion block and evaporated to dryness at 120 °C. The crucibles were vortexed with deionized water and filtered with Whatman No. 42 qualitative cellulose filter paper and the volume was made up to 50 ml. The total elemental composition of the extract was determined using ICP-OES (Varian Vista MPX, Varian Palo Alto, California, USA).

2.3. Germination assay

The phytotoxicity test method used in this study, which used sand only control, is an adapted version of the EN 16086-2 2011 method, which was developed by Mumme et al. [30] to test biochars used for soil amendments and depict more realistic but worst case scenario effects on seed germination under soil environmental conditions. The procedure involved mixing 29.7g of white quartz sand which was heated treated in a muffle furnace at 550 °C for 6 hours (Sand, white quartz 50-70 mesh particle size, Sigma-Aldrich, Belgium) with 0.3g of biochar, to which 6.6g of deionized water was added. An additional 0.9g of deionized water was added to a filter paper contained in a petri dish. The sand, biochar and deionized water mixture, was spread evenly on the surface of the filter paper and 10 healthy watercress seeds were selected and evenly placed on the surface of the mixture. The petri dishes were covered with a parafilm and placed in a dark incubation chamber at 25 °C at a 50° angle for 3 days. Thereafter, the number of germinated seeds was counted and expressed as germination rate.

2.3.1. Leaching of excess salts

Leaching was done in order to remove the exchangeable trace elements from biochar samples and test the impact of leaching on seed germination. This was done according to the modified version of BS ISO 19730:2008 - extraction procedure of trace elements from soil using ammonium nitrate solution, which was modified by Buss et al. [31] to leach biochar samples. Briefly, ground biochar samples (<2 mm) were suspended in 1 M laboratory-grade NH_4NO_3 (Chem-Lab, Zedelgem, Belgium) solution in a ratio of 1:10, due to the high sorption capacity of biochar. In this regard, 0.5 g of biochar was suspended in 5 ml of NH_4NO_3 (Chem-Lab, Zedelgem, Belgium) solution in 10 ml centrifuge tubes. The mixture was shaken on a benchtop shaker at 150 rpm for 2 hours and subsequently centrifuged for 30 minutes at 3500 rpm. The supernatant was decanted and filtered through Whatman No 1 filter paper. Then the biochar residue was subjected to another round of shaking after dispersion in 25 ml of deionized water for 2 hours in a benchtop shaker at 150 rpm. After this, the biochar-deionized water mixture was again filtered through Whatman No. 1 filter paper and the retained biochar residue was dried overnight in an oven at 55 °C and again subjected to the germination tests as described in the previous section.

2.4. Statistical analysis

A one-way ANOVA test was performed using Minitab 19 statistical software and Tukey’s test was performed for the mean separation.

3. Results and discussion

3.1. Biochar yield

The results of the biochar yields are presented in Figure 2 below. In the GM biochars, there was a slight increase in yield in 0.25GM and 2.5GM (5.3% and 3.4% increase respectively) compared to 0GM. However, biochar yield was decreased by 1.6% and 4.8% in 5GM and 10GM respectively. In BM biochars, when 0.25% MS was incorporated into feedstock, biochar yield increased by 0.5% compared to 0BM. With the increase of plastic level from 2.5% to 10%, biochar yield decreased by 2.2%, 8.9% and 3.3% compared to 0BM. However, no significant difference among BM biochar yields was observed. The average biochar yield of GM biochars and BM biochars were 50±2% and 34±1% respectively. GM feedstock mainly consisted of peat and clay granules.

Degradation of cellulose and hemicellulose occurs in the range of 220-315 °C and 315-400 °C respectively [32]. When pyrolysis temperature exceeds 450 °C, lignin in the feedstock start to degrade. Peat consists mainly of undecomposed organic materials under anaerobic conditions. Thus, peat contains a proportionally higher lignin than cellulose and hemicellulose content when compared to fresh lignocellulosic biomass. Also, having clay granules together with highly stable peat in the feedstock may be the reason for the resulting high biochar yield in GM biochar as clay granules does not become volatilize upon pyrolysis. On the other hand, bean crop residues contain a higher amount of cellulose and hemicellulose which are less thermally stable. Additionally, char yield is governed by the lignin content in the feedstock [32] hence resulting in higher char yields in the peat-based feedstock versus the bean crop waste feedstock.

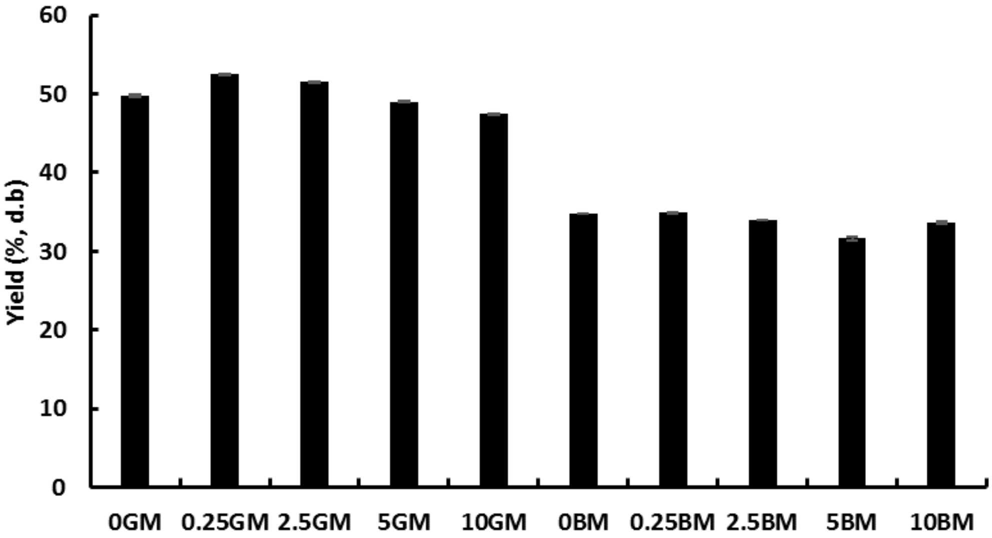

Figure 2. The results of the biochar yields (mean ± SD, n=2)

During slow pyrolysis, plastic (LDPE) degradation occurs in a narrow range of temperature (500-550°C) [33,34]. Both (pure) MS and GB were characterized by higher volatile matter content. The increase in yield was mostly dependent on the biochar formation due to repolymerization reactions in biochars with lower plastic ratios [35]. However, it seems that the char formation due to repolymerization was not able to compensate for yield losses due to the higher volatile matter content in higher plastic level biochars, leading to a decrease in their overall yield. On the other hand, the ash content of the feedstock also contributes to the char yield and both GM and BM feedstocks have higher ash content than the GB and MS plastic materials, whereas GB and MS consist mainly of volatile matter. Therefore, GM and BM are the major determinants of the char yield. This is indicated by the reduction of biochar yield at higher plastic levels (Table 2).

3.2.Proximate analysis and HHV

Results of the proximate analysis and HHV are summarized in Table 2. The proximate analysis gives an idea of the ash, volatile matter and fixed carbon content in the material [27]. The volatile content of the feedstocks was dependent on the major components of the biomass.

Cellulose and hemicellulose-rich BM had a higher volatile matter content than the lignin-rich GM (76.49 ± 2.84% and 59.69 ± 1.78% in BM and GM feedstocks, respectively). Both MS and GM plastic materials mostly consist of volatile matter. The mulching sheets (MS) with a volatile matter content of 96.91 ± 0.14% had the highest volatile matter content, this was followed by that of the growbag with a volatile matter content of 92.47 ± 0.30%. On the other hand, GM feedstock had almost two times more ash content than the BM feedstock material. Both MS and GB had a low amount of ash content (7.15 ± 0.04% and 1.47 ± 0.08 % in GB and MS respectively). Fixed carbon content was high in GM feedstock compared to BM feedstock.

Following the incorporation of GB into GM feedstock material, an increase in the volatile matter content of the GM biochars was observed (Table 2). This trend of increasing VM with increasing plastic content was observed in BM biochars too. This is likely due to the high volatile matter content of the plastic materials (MS and GB). Similar observations were reported by Ro et al. [24]. Following the addition of GB plastic into GM feedstock, the ash content in GM biochars decreased. On the other hand, the addition of MS plastic into BM feedstock showed a slight increase in the ash content with an increase in the plastic content. However, the increase in the ash in BM biochars was not significant. Both MS and GB, being plastics, had a low amount of ash. Thus, the ash content of the biochar was mostly dependent on the GM and BM composition and quantities.

Due to the reduction of the weight portion of the GM and BM in the feedstock mixtures with an increase in plastic content, reduction of ash content in biochars was observed at higher plastic levels in the feedstock. Also, spent growing medium material itself contained 5% of clay granules in its initial growing medium composition. Moreover, none of the feedstock materials used in this study were subjected to cleaning/washing prior to pyrolysis experiments to represent actual field conditions. According to previous studies [5] , those soil-clay-mineral particles form small quantities of high ash solids during pyrolysis and they will remain as solid materials even after pyrolysis in the solid product of pyrolysis (biochar).

Table 2. Volatile matter content, ash content, fixed carbon content and HHV of biochar samples and feedstock materials (average ± standard deviation, n=2 for yield and n=3 for proximate analysis and HHV results)

Sample type	VM	Ash	FC	HHV
	Percentage, dry weight basis			(MJ/kg)
0GM	20.01 ± 1.01	37.96 ± 0.22	42.03 ± 1.23	18.28 ± 0.27
0.25GM	20.10 ± 0.63	37.02 ± 0.84	42.88 ± 0.21	18.58 ± 0.17
2.5GM	20.02 ± 1.13	36.93 ± 0.09	43.05 ± 1.04	18.62 ± 0.19
5GM	21.12 ± 1.00	33.84 ± 2.43	45.03 ± 1.42	19.48 ± 0.64
10GM	22.25 ± 0.08	30.59 ± 2.39	47.16 ± 2.47	20.38 ± 0.84
0BM	26.69 ± 0.86	33.21 ± 0.47	40.10 ± 0.40	18.60 ± 0.01
0.25BM	26.36 ± 0.90	33.82 ± 1.12	39.82 ± 0.22	18.45 ± 0.21
2.5BM	26.28 ± 1.48	34.80 ± 0.26	38.92 ± 1.74	18.13 ± 0.38
5BM	27.36 ± 0.47	35.75 ± 0.49	36.89 ± 0.96	17.59 ± 0.26
10BM	27.59 ± 0.39	34.49 ± 1.22	37.92 ± 1.61	17.98 ± 0.50
GB	92.47 ± 0.30	7.15 ± 0.04	0.38 ± 0.25	nd
MS	96.91 ± 0.14	1.47 ± 0.08	1.62 ± 0.22	nd
GM feedstock	59.69 ± 1.78	20.17 ± 3.01	20.14 ± 1.23	16.59 ± 0.69
BM feedstock	76.49 ± 2.84	11.26 ± 0.29	12.26 ± 2.55	16.35 ± 0.46

Increment of fixed carbon content in GM biochars compared to 0GM was 2% higher in 0.25GM and 2.5GM and 7% and 12% higher in 5GM and 10GM, respectively. BM biochars exhibited an opposite trend, a decrease of the fixed carbon content was observed with an increased level of plastic content in the feedstock. Reduction of fixed carbon content was higher at higher plastic levels compared to low levels of plastic in the feedstock. HHV of feedstock materials and produced biochar materials are presented in Table 2. HHV depicts the energy content in the material and increased with the total carbon content of the material. It is supported by the increase of HHV with the increase of fixed carbon content in biochar samples. Addition of plastic into both GM and BM feedstocks increased the HHV of produced biochars. GM biochars and BM biochars exhibited average an HHV of 19±0.9 MJ/kg and 18±0.4 MJ/kg respectively.

According to Briassoulis et al. [15], materials with an average calorific value of 14 MJ/Kg can be used as a fuel in firing systems.

3.3. CHNO content

The results of the elemental analysis and elemental analysis based molar ratios are summarized in

Table 3 and show a shift in the elemental composition of the feedstock with pyrolysis. From these results, it can be deduced that the GM and BM feedstocks were the major determinant of the elemental composition of the resulting biochars. A general increase in the carbon content of the biochars was expected in pyrolysis, with the GM biochars experiencing a higher carbon content than its BM counterparts. This is more likely due to the high C content in (lignin-rich) GM feedstock than the (holocellullose rich) BM feedstock. An increasing trend similar to that of the carbon content was observed for the fixed carbon content of the feedstock and biochar materials. On the other hand, both MS and GB had an extremely high level of carbon content, 78.36 ± 1.21in GB and 83.29 ± 2.14% in MS, respectively. This is not surprising, since polyethylene consists mainly of carbon and hydrogen. Following the incorporation of plastic into the GM feedstock, an initial bump in the C content of 0.25GM was observed. Afterwards, a decreasing trend in the C content of the other GM biochars was observed. The total C reduction was 8%, 4% and 14% in 2.5GM, 5GM and 10GM, respectively, compared to 0GM. The total H content in the produced biochar materials exhibited an increasing trend in the BM biochars and a decreasing trend for GM biochars. However, an initial bump in the H content was observed in 0.25GM when compared to 0GM. Thereafter, H content decreased by 7%, 3% and 15% in the 2.5GM, 5GM and 10GM, respectively.

Table 3. Results of the elemental analysis of produced biochar samples (average ± standard deviation, n=3)

Sample Name	C (%, d.b)	H (%, d.b)	N (%, d.b)	O (%, d.b)	H/C molar ratio	O/C molar ratio
0GM	51.86 ± 1.68	2.27 ± 0.11	1.38 ± 0.06	6.49 ± 2.83	0.52 ± 0.03	0.09 ± 0.01
0.25GM	52.42 ± 0.89	2.32 ± 0.35	1.33 ± 0.16	6.93 ± 1.14	0.53 ± 0.01	0.10 ± 0.01
2.5GM	47.65 ± 1.29	2.10 ± 0.28	1.23 ± 0.15	12.01 ± 1.21	0.53 ± 0.01	0.19 ± 0.02
5GM	49.59 ± 3.86	2.20 ± 0.17	1.29 ± 0.11	12.92 ± 1.52	0.53 ± 0.03	0.20 ± 0.01
10GM	44.75 ± 4.06	1.93 ± 0.29	1.12 ± 0.13	21.20 ± 1.04	0.52 ± 0.27	0.36 ± 0.34
0BM	46.91 ± 0.62	2.26 ± 0.07	3.97 ± 0.04	13.87 ± 0.61	0.58 ± 0.01	0.22 ± 0.01
0.25BM	47.31 ± 0.89	2.32 ± 0.28	3.98 ± 0.23	12.40 ± 1.39	0.59 ± 0.02	0.20 ± 0.04
2.5BM	45.98 ± 0.29	2.15 ± 0.09	3.83 ± 0.07	13.03 ± 0.25	0.56 ± 0.01	0.21 ± 0.06
5BM	47.74 ± 2.45	2.39 ± 0.44	3.82 ± 0.16	10.04 ± 3.02	0.60 ± 0.04	0.16 ± 0.03
10BM	47.69 ± 1.06	2.48 ± 0.10	3.57 ± 0.08	11.26 ± 1.19	0.62 ± 0.06	0.18 ± 0.04
GB	78.36 ± 1.21	13.66 ± 0.25	-	-	0.01 ± 0.03	-
MS	83.29 ± 2.14	14.32 ± 0.05	-	-	0.01 ± 0.00	-
GM	44,26 ± 0,60	5,41 ± 0,05	1,26 ± 0,06	27,07 ± 0,58	1,47 ± 0,01	0,46 ± 0,02
BP	39.83 ± 2.40	5.78 ± 1.02	3.62 ± 1.02	11.3 ± 2.25	1.09 ± 0.01	0.74 ± 0.02

In BM biochars, a decreasing trend was observed between the oxygen content and an increase in plastic levels. Due to the nitrogen-fixing capacity of the bean plant, the BM feedstock and BM biochars had a higher nitrogen level compared to the GM feedstock and GM biochars. According to the IBI and EBC guidelines, char materials can be categorized as "biochar" when H/C_{org} and O/C molar ratios are lower than the 0.7 and 0.4, respectively. Both H/C and O/C ratios are frequently used to assess the stability of biochar [36,37]. Both BM and GM biochars fulfilled these criteria, indicating the absence of pyrolytic deficiencies, and resulting in an increase in the stability of the biochars compared to their feedstock materials. A slight increase of both H/C and O/C ratios with an increase in plastic levels occurred. Hence, a decrease in the stability of both GM and BM biochars was expected with the increase of plastic levels in the feedstock. Reduction of stability in biochars was well aligned with the reduction of elemental

C content and fixed carbon content and increase of volatile matter content in each biochar type (Table 2).

3.4.Surface functionality of biochar

FTIR spectra of biochar samples are presented in Figure 3. FTIR analyses of produced biochar samples were carried out to identify the changes of surface functionality with an increase in the plastic levels of the feedstock materials.

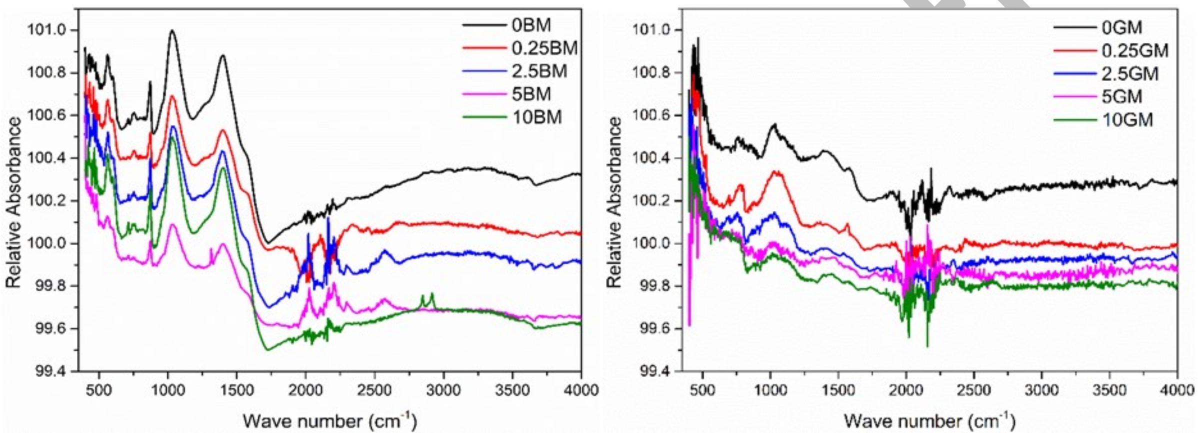

Figure 3. FTIR spectrums of biochar samples (x-axis - wave number (cm^{-1}), y-axis - absorbance).

FTIR spectral analysis of the biochar derived from co-pyrolysis of BM and MS is illustrated in Figure 3. Increase in the intensity of absorbance was observed as the plastic to biomass ratio increased. Alkyl and oxygen-containing functional groups were mostly observed in all biochar samples in the same spectral regions. The first well-resolved peak indicating C=C bending was observed in the absorbance region of 873 cm^{-1} to 871 cm^{-1} indicating the presence of an olefin (alkene) functional group. The most prominent peak was observed in the oxy region of the spectrum, indicating the presence of high levels of oxygen-containing functional groups. This is observed in all biochars in the spectral region of 1031 cm^{-1} (C-O from carbohydrates). Alkyl/alkane functionality representing CH_2 bending is encountered next in all biochar samples between 1404 cm^{-1} and 1413 cm^{-1}.

FTIR analysis of the GM biochars was characterized by the presence of paraffinic, olefinic and oxygen-containing functional groups. Using the intensity of absorbance as a criterion, the oxygen-containing functional groups seemed to be dominant in the biochar samples, as they produced the absorbance with the highest peaks. They were typically observed in the absorbance regions between 1008 cm^{-1} - 1053 cm^{-1}. The olefinic groups appeared to exhibit a somewhat lower level of dominance than the oxy functional groups but a higher level of dominance than the paraffinic groups in samples where all three were present but exhibited a steady decline in intensity and an eventual disappearance as the plastic content in biomass increased. As a result, the peak was barely noticeable in the 5% biochar sample and disappeared completely in the 10% plastic to biomass sample, with no discernable peak. Paraffinic groups were also observed in all biochar samples but had a much lower level of dominance compared to the olefins and oxy functional groups. This is evident in the small peaks produced by their absorbance and these alkanes were typically observed in the absorbance regions from 1415 cm^{-1} to 1429 cm^{-1} [38]. In addition to the paraffinic and oxy functional groups which are common to all biochar samples, the 10% plastic to biomass biochar was found to have developed other functional groups peculiar to that sample, including a C=C group at spectral region 1560 cm^{-1} and a carbonyl functional groups (carboxylate anions and amide vibrations) at the region of 1722 cm^{-1} [38].

Overall, differences in surface functionality started to appear with an increase in the plastic ratio to 2.5% in the feedstock. A carboxylic acid group was observed in 2.5BM along with all other functional groups present in the 2.5GM chars, this was also observed for the 5BM and 10BM chars. No noticeable changes in functional groups were observed from 0GM to 5GM chars, but this changed with the introduction of a higher plastic ratio. The 10GM char was found to have developed other peculiar functional groups, including carboxylate anions, amides and a C=C aromatic bonds.

3.5. Total nutrients, PTEs, and pH

The total macro and micronutrients present in biochar samples are summarized in Table 4. The P, K, S, Ca and Mg are considered as plant macronutrients while Fe, B, Mn, Zn, Cu, and Mo are grouped as plant micronutrients. In GM biochars, K content increased with plastic content in the feedstock while Mg, Ca, S content decreased. For GM biochars, P, Fe and Mn did not show any clear trend with an increase in the levels of plastic in the feedstock. In BM biochars, none of the macro and micronutrients exhibited a clear trend with an increased level of plastic content in the feedstock. Ca content in BM biochars was twice that of the GM biochars. BM biochars had approximately fifty times higher K content than the GM biochars. The Mg content in BM biochars is 3 times higher than that in GM biochars. The P content in BM biochars is 10 times higher than the GM biochars. S content also relatively higher in the BM biochars than the GM biochars. Micronutrients such as Fe, and Mn contents in GM biochars were comparatively higher than the BM biochars. The total nutrients in the two biochar groups differed along feedstock lines. Therefore, BM biochars had higher levels of macronutrients compared to BM biochars and GM biochars had higher levels of micronutrients compared to BM biochars.

The potentially toxic element concentration in both GM and BM biochars and threshold levels stipulated by different international organizations are summarized in

Table 5. In GM biochars, Cd content increased with the plastic level and Zn content decreased with the plastic content. No clear trend could be observed for Co, Cr, Cu and Ni with the increase of the plastic content in the feedstock. In BM biochars, Zn and Co exhibited a decrease

in concentration with an increase in plastic levels. However, in BM biochars, Cd, Cr, Cu and Ni did not show any clear trend with an increased level of plastic in the feedstock. Both GM and BM biochars were within PTEs thresholds stipulated in the IBI guidelines (

Table 5).

However, both BM and GM biochars exceed the permitted Cd concentrations for EBC basic, EBC premium grade, EBC feed, EBC Agrobio, and EBC agro class biochars [37]. However, Cd level in both BM and GM biochars lower than the threshold for EBC material class biochars. Also, the 10BM biochar cannot be graded as EBC premium-grade, EBC feed, EBC Agrobio, EBC agro class biochar due to a higher concentration of Ni. However, Ni content in 10BM biochar is within the threshold limit for EBC material class biochar (

Table 5). The elevated level of Ni may be attributed to the abrasion of the reactor wall components into the biochar. All biochar samples had PTE concentrations within the BQM standard grade threshold levels, except the 10BM biochar (due to higher Ni level). All other biochar types can be graded as BQM high-grade biochars [21].

The pH of biochar samples indicated in Table 4 shows that BM biochars had a comparatively higher pH than GM biochars. Following the addition of plastic into GM feedstock, a slight reduction of the pH was observed up to 2.5% plastic level. That reduction of pH was 2% at 0.25GM and 1% at 2.5GM. Then, there was an increase of pH in 5GM and 10GM biochar types by 5% and 3% compared to 0GM biochar type. There was no significance difference between 5GM and 10GM. Also, no significant difference in pH between 0GM, 0.25GM and 2.5GM biochar types was observed. However, 5GM and 10GM exhibited a significantly higher pH compared to other biochar types. In BM biochars, following the addition of plastic into the feedstock, the pH gradually increased. There was no significant difference between 5BM and 10BM biochar types. Also, no significant difference in the pH between 0BM, 0.25BM and 2.5BM was found. However, 5BM and 10BM exhibited a significantly higher pH compared to other biochar types. Having significantly higher concentrations of K and Ca in BM biochars compared to GM biochars is likely the main reason for having a higher pH in BM biochars compared to GM biochars. The ash contents were also well aligned with the changes in the pH of both biochar samples (Table 2). Having elevated pH levels in biochar samples (especially in BM biochars) can restrict their use in soil and environmental applications. Several studies [39–41] reported the phytotoxicity imposed by highly alkaline biochars due to salt stress created by soluble salts. However, washing can remove the excess salts before applications and improve the agronomic qualities of biochar [42]. The most favorable pH range of a soil amendment is between 5.5 and 6.5. None of the GM and BM biochars had a pH that low. However, these biochars will be suitable in the amelioration of acidic soils and remediation of contaminated soil through the reactions associated with mediating of the soil solution pH [43].

Table 4. Macronutrients, micronutrients and pH of biochar samples (average ± standard deviation, n=2 for macro and micronutrients, n=3 for pH)

Sample Name	Ca (g/kg)	K (g/kg)	Mg (g/kg)	S (g/kg)	P (g/kg)	Fe (g/kg)	Mn (g/kg)	pH (1:20)
0GM	23.18 ± 0.61	2.16 ± 0.06	3.44 ± 0.06	2.62 ± 0.09	0.68 ± 0.07	2.36 ± 0.22	0.15 ± 0.00	8.73 ± 0.03
0.25GM	21.17 ± 0.43	2.35 ± 0.22	3.21 ± 0.12	2.26 ± 0.10	0.86 ± 0.23	2.86 ± 0.46	0.13 ± 0.00	8.55 ± 0.09
2.5GM	20.26 ± 0.46	2.51 ± 0.06	3.06 ± 0.06	2.16 ± 0.04	0.40 ± 0.09	1.32 ± 0.22	0.18 ± 0.01	8.68 ± 0.06
5GM	21.40 ± 0.15	2.77 ± 0.34	3.08 ±0.03	2.39 ± 0.15	1.02 ± 0.32	3.88 ± 1.10	0.16 ± 0.00	9.21 ± 0.01
10GM	20.07 ± 2.71	2.84 ± 0.56	2.79 ± 0.5	1.99 ± 0.16	0.91 ± 0.04	2.95 ± 0.15	0.15 ± 0.03	9.02 ± 0.01
0BM	49.23 ± 0.88	98.72 ± 2.45	9.11 ± 0.19	3.40 ± 0.22	12.15 ± 0.16	0.16 ± 0.05	0.12 ± 0.00	10.17 ± 0.11
0.25BM	45.42 ± 4.23	90.94 ± 8.06	8.49 ± 0.67	3.17 ± 0.35	11.59 ± 1.03	0.19 ± 0.00	0.11 ± 0.01	10.23 ± 0.01
2.5BM	51.84 ± 0.97	102.41 ±2.06	9.55 ± 0.33	3.71 ± 0.10	12.77 ± 0.09	0.23 ± 0.01	0.13 ± 0.00	10.36 ± 0.04
5BM	52.21 ± 1.64	103.11 ± 3.41	9.51 ± 0.21	3.53 ± 0.03	12.31 ± 0.48	0.13 ± 0.03	0.12 ± 0.00	10.57 ± 0.04
10BM	46.24 ± 4.50	88.68 ± 8.68	8.55 ± 0.92	3.39 ± 0.46	10.99 ± 0.77	0.13 ± 0.02	0.11 ± 0.01	10.73 ± 0.01

Table 5. PTEs concentrations in biochar samples (average ± standard deviation, n=2) (Cu and Zn can be categorized as micronutrients too. However, for the comparison purpose, Cu and Zn are included in this table as PTEs)

Sample Name	Zn (g/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)
0GM	0.16 ± 0.00	2.44 ± 0.45	2.31 ± 0.08	7.99 ± 0.32	13.64 ± 1.21	5.87 ± 0.00
0.25GM	0.15 ± 0.01	2.34 ± 0.14	2.02 ± 0.78	11.69 ± 2.16	12.05 ± 0.03	3.99 ± 0.98
2.5GM	0.15 ± 0.01	2.78 ± 0.07	2.43 ± 0.13	4.79 ± 0.14	15.03 ± 0.81	3.94 ± 2.18
5GM	0.13 ± 0.00	2.54 ± 0.16	2.69 ± 0.20	12.69 ± 3.42	17.47 ± 2.20	6.57 ± 0.96
10GM	0.12 ± 0.02	2.78 ± 0.02	1.93 ± 0.07	10.86 ± 0.21	14.45 ± 1.40	4.47 ± 1.62
0BM	0.15 ± 0.01	2.99 ± 0.89	2.44 ± 0.17	12.41 ± 3.84	21.40 ± 2.56	17.04 ± 0.48
0.25BM	0.12 ± 0.01	2.90 ± 0.23	2.14 ± 0.00	10.25 ± 0.19	22.39 ± 0.87	12.59 ± 1.92
2.5BM	0.13 ± 0.01	2.71 ± 0.10	1.90 ± 1.42	14.59 ± 0.37	29.32 ± 1.55	16.50 ± 0.47
5BM	0.13 ± 0.00	2.48 ± 0.08	2.02 ± 0.38	6.96 ± 0.86	24.56 ± 1.41	8.91 ± 0.94
10BM	0.11 ± 0.01	2.83 ± 0.07	1.64 ± 0.87	13.38 ± 1.08	25.22 ± 3.95	42.71 ± 9.89
Guidelines	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
IBI[1]	200 - 7000	1.4 - 39	40 - 150	64 - 1200	63 - 1500	47 -600
EBC basic[2]	400	1.5	-	100	100	50
EBC premium[2]	400	1	-	80	100	30
EBC feed (class 1)[3]	400	1	-	80	100	30
EBC-Agrobio (class 2)[3]	200	0.7	-	70	70	25
EBC- Agro (class 3)[3]	400	1.5	-	90	100	50
EBC material (class 4)[3]	750	5	-	250	250	250
BQM high grade[4]	150	3	-	15	40	10
BQM standard grade[4]	2800	39	-	100	1500	600

[1] Guidelines of International Biochar Initiative [44], [2] European Biochar Certificate (2012) [37], [3]European Biochar Certificate (2020) [20], [4]Biochar Quality Mandate [21].

3.6.Germination assay and leaching of excess salts

Results of the germination assay before and after leaching of excess salts are presented in Figure 4. Cress seeds are frequently used in phytotoxicity assessments due to its rapid growth rate and sensitivity to phytotoxicity. Cress seed germination was observed in all GM biochar amended treatments, but with the BM biochar amended treatments total growth inhibition was observed. Zero germination was observed even after an extended period of 7 days, indicating phytotoxicity of the BM biochar.

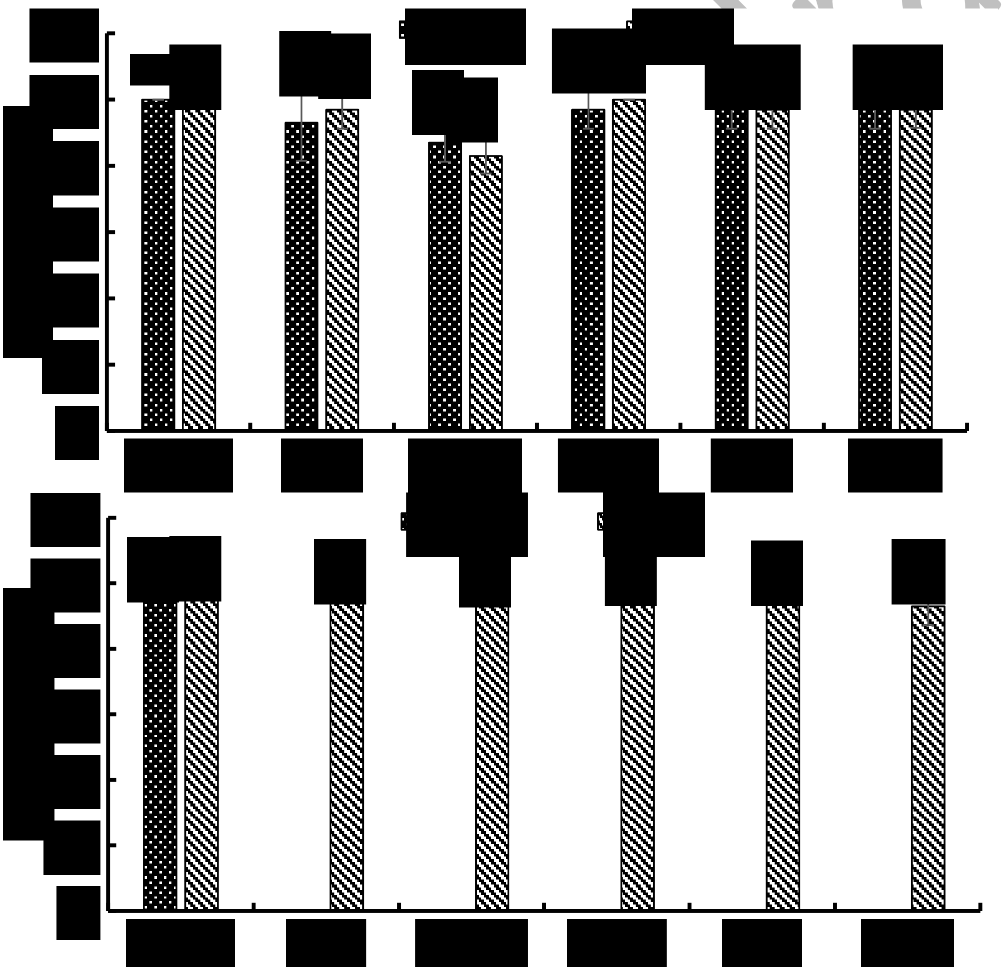

Figure 4. Germination rates of GM and BM biochars before and after leaching with ammonium nitrate (mean ± standard deviation, n=50). Different letters indicate significant difference of germination rate between different biochar types and control (P<0.05).

This may be due to the high alkalinity and presence of higher concentration of Ca and K in BM biochar (Table 4). Presence of K+ and Ca+2 ions could create salt stress on seeds and inhibit the germination [40]. On the other hand, presence of PTEs at high levels could interrupt the seed germination through interrupting the seed metabolism [45]. Both promotion and inhibition of seed germination after mixing with biochar have been reported in previous studies [30,42,46]. However, there was no significant difference between the germination rate of GM biochar types and control treatment before leaching.

Leaching of both BM and GM biochars with 1M ammonium nitrate was carried out to remove all the exchangeable nutrients and PTEs. Compared to other extractants (i.e., ammonium chloride, calcium chloride etc.), ammonium nitrate is less reactive and nitrate as a counter ion does not cause additional complexations with other ions. Also, NH_3 could make complexes with metals and induce additional release of metals [47,48]. Leaching with ammonium nitrate promoted the germination rate in 0GM and 2.5GM biochars by 4% and 3% and inhibited germination by 5% in 0.25GM. BM biochars exhibited a remarkable increase of germination rate after leaching. This may be due to the diminishing of salt stress occurred through alkaline nutrients and toxicities imposed by PTEs. There was no significant difference between the germination rate of all BM biochars and control after leaching, except the 10BM biochar type. Having higher quantity of PTEs in 10BM biochar could be the reason for lower germination rate in 10BM biochar even after the leaching. Even though leaching with ammonium nitrate could remove considerable amount of metals (both nutrients and PTEs), complete removal of metals in exchangeable fraction cannot be assured and the remaining amount of metals on biochar is higher when biochar initially contain those metals in higher concentrations (

Table 5).

4. Conclusions

This study investigated the presence or absence of a positive effect in biomass mixed/associated with low levels of plastic during pyrolysis. Biochar yields of the pyrolysis process were mostly determined by the biomass feedstock with lower contribution from the plastic residues. From the results obtained from the GM pyrolysis, low ratios of GB plastic were found to have a positive effect on char yield, while high plastic ratios were found to have negative effect. High plastic ratios were also observed to have negative effect on BM biochar yields. However, the yield of 10GM biochar was significantly lower compared to the other biochars and no significant difference was found in the yields of the BM biochars. Plastic contamination generally had a positive impact on the volatile matter content of both BM and GM biochars. The fixed carbon content and higher heaving values of the GM biochars increased with plastic contamination while that of the BM biochars decreased. Presence of plastic in feedstock mostly had negative effect on the carbon and hydrogen content of the GM biochars and mostly a positive effect on those of the BM biochars. The GM biochars showed no phytotoxic effect, irrespective of the concentration of plastic contamination in the feedstock. The BM biochar on the other hand showed high level of phytotoxicity (zero germination), irrespective of level of plastic contamination. This was due to high soluble salt content originating from the biomass feedstock and therefore not plastic related. After washing all BM biochar showed very low phytotoxicity level with no statistically significant effect of plastic contamination, with the exception of 10BM that showed somewhat reduced germination rate (93%). In light of these findings, it can be concluded that co-pyrolysis of agricultural waste mixed with low levels of plastic residues shows great potential for the recycling of such waste streams, without the need for laborious, expensive and time-consuming sorting and separation.

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