

Effects of Rice Husk and Rice Straw Hydrochar as Soil Amendment

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Biomass wastes, such as agricultural residues from rice field are generated in a large amount. Hydrothermal carbonization (HTC) treatment can convert biomass wastes into value-added product known as hydrochar, which gained researchers interests for various environmental applications. However, recent studies have shown inconsistent results for the use of hydrochar on crop production and soil improvement. Thus, the aim of this study is to understand the characteristics and potential use of rice husk and rice straw hydrochar as soil amendment. Two types of hydrochar (RHH: rice husk hydrochar, and RSH: rice straw hydrochar) produced using HTC at a pressure of 1.6 MPa, temperature at 160 – 180 °C, and reaction time of 30 min, were used to conduct pot experiment. Nutrients and morphological study of hydrochar and its raw biomass were analyzed. Five treatments (0 % hydrochar as control, 1 % RHH, 10 % RHH, 1 % RSH, and 10 % RSH (w/w)) were applied in commercial garden soil to observe the effects on soil pH and Spinach plant growth. The result from this study shows that HTC have significant effects on the hydrochar properties. The hydrochars have coarser surface and several microstructures formed on the surface. HTC significantly decreased pH, increased moisture content, and altered the nutrient compositions of the biomass. Pot experiment results showed that all hydrochar-amended treatments decreased soil pH below optimal pH of 6.0, which causes the decreased plant biomass by 60 – 67 % compared to control. This shows that these hydrochars are useful as soil amendment for dry degraded soils with pH ≥ 8 . Further research is needed to reveal the mechanisms and potential modification required before using the hydrochar as soil amendment.

1. Introduction

Rice as a staple food for around half of the world's population, generates large amount of biomass wastes of approximately 150 Mt of rice husk and 800 Mt of rice straw annually. Rice straw does not have commercial value, and its direct incorporation into soil causes methane emissions. When burned in fields, rice straw generates greenhouse gasses (GHG) which are harmful to the environment. The husks are considered a waste in the rice mill industry, which are commonly burned, or disposed of in landfills (Cavali et al., 2022). Rice husk are lignocellulosic biomass with hemicellulose, cellulose, and lignin content of 22.0 %, 28.6 %, 19.2 %, and rice straw with 19.7 %, 32.0 %, 13.5 % (Goodman, 2020). These polymers form very stable structure, which makes degradation and separation of the individual cell wall polymers difficult. This scenario boosts the need to manage these wastes using a more environmentally friendly treatment. Hydrothermal carbonization (HTC) is a promising thermochemical treatment which can convert biomass wastes into valuable solid and liquid products. It is an energy efficient and eco-friendly technology as relatively lower temperature is required, and no pre-drying of feedstock is needed as compared to other pre-treatment technologies such pyrolysis or gasification. Hydrolysis reaction is the main mechanism initiating biomass degradation during HTC, as water acts as a solvent, reactant, and catalyst. The solid product is known as hydrochar which have various applications depending on its physicochemical and morphological properties. The parameters that highly influence its properties include type of feedstock and HTC operating conditions such as reaction temperature, pressure, and time (Masoumi et al.,

2021). Recently, there are increasing interests on using hydrochar for environmental remediation and soil improvement as it has desirable properties and can provide direct supply of essential nutrients, improve soil physical and chemical properties. However, the application of hydrochar on crop production shows inconsistent results for various plants, as it could either be productive or counterproductive (Khosravi et al., 2021). A study by Rillig et al. (2010) found increasing concentrations of HTC material is deleterious for plant growth, starting at 10 % addition, however, the fungal symbiont was stimulated at 20 % addition. Another study by Bargmann et al. (2014) found increased shoot dry matter yield of Leek plants in 2 % and 4 % beet root chip-derived hydrochar but decreased by 1 % in 10 % hydrochar treatment. On the other hand, the shoot dry matter of Poplar was increased by 37% in maize silage-derived hydrochar (Amendola et al., 2017). Similarly, dry biomass of Plantain was increased by 60 % in 10 % application rate of beet root chip hydrochar (Salem et al., 2013). This shows that the effects of hydrochar on soil and plant growth is varies depending on the feedstock types, HTC conditions, crop species, type of soil and environmental conditions. Thus, this study aims to assess the potential use of hydrochars derived from rice husk and rice straw as a soil amendment, by analysing its properties and effects on soil and plant growth.

2. Materials and methods

2.1 Materials

Rice husk and rice straw were collected from a local rice mill in Malaysia. Spinach seeds were purchased from Sakata Seed Co., (Japan). Commercial garden soil was purchased from a gardening supplier in Japan. Organic fertilizer with N:P:K ratio of 1:1:1 was purchased from Hanagokoro Co., Ltd. (Japan) and diluted to 1:100 upon application. A digital soil pH meter was purchased from Shinwa Rules Co., Ltd. (Japan).

2.2 Hydrochar production

A pilot-scale, Multipurpose Recycling Machine (MRM) reactor located in Universiti Teknologi Malaysia (Pagoh Campus) was used to perform hydrothermal pretreatment of biomass. 250 kg of rice husks were loaded into the reactor and HTC conditions were operated at a pressure of 1.60 MPa, temperature at 160 – 180 °C and reaction time of 30 min (Wang et al. 2018). The same procedure was repeated for rice straw biomass. The solid products were labelled as rice husk hydrochar (RHH) and rice straw hydrochar (RSH), respectively.

2.3 Hydrochar characterization

Proximate and nutrient analysis was conducted using kjedahl method for Total Nitrogen (TN), gravimetry method for moisture content, potentiometry for pH value (10 % solid in water), titrimetric method for Total Organic Matters (TOM), and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for other nutrients including Phosphorus (P), Potassium (K), Magnesium (Mg), Chromium (Cr), Zinc (Zn), and Boron (B). Surface morphologies were analysed using Field Emission Scanning Electron Microscope (FESEM) JSM-7800F operating at 3 and 5 kV.

2.4 Pot experiment

Pot experiment was conducted in University of Tsukuba from November – December 2022. Five different treatments (0 % hydrochar as control, 1 % RHH, 10 % RHH, 1 % RSH, and 10 % RSH (w/w)) were mixed with 1 kg of soil in 8-inch planting pots. Spinach seedlings with two true leaves were transplanted into each pot. The pots were placed outdoors at a rain-protected area with a minimum of 9 h daylight, for 45 days. The plants were regularly watered to maintain moisture. Organic fertilizers were applied after 14 days, with a 7-days interval. Soil pH were measured at a 5-days interval. At the end of 45 days, Spinach plants were harvested for plant growth measurement. The experiment was conducted in duplicate (Salem et al. 2013).

2.5 Plant growth measurement

Spinach plants were carefully taken out from the soil with the roots and shoots still attached. Plants were gently shaken and soaked in tap water to remove any excess soil from the roots. Plants were washed with distilled water and dabbed with dry tissue to remove excess water. The fresh weight of plants, height of plants, number of leaves, and size of leaves were measured. Spinach plants were dried in the oven at 105 °C for 30 min and 65 °C for 6 h, until constant dry weight was achieved (de Jager et al. 2020). Dry weight of shoots and roots were measured.

3. Results and discussions

3.1 Proximate and nutrient analysis

To assess the potential use of hydrochar as soil amendment, it is important to study the properties which are highly determined by feedstock species and HTC conditions (Zhang et al., 2019). Table 1 shows HTC significantly reduced the pH of both types of hydrochars. Raw rice husk is moderately acidic (5.7) but the pH was greatly reduced to highly acidic (3.5), meanwhile, raw rice straw was neutral to slightly alkaline (7.1) but dramatically decreased to highly acidic (4.0) after HTC process. This reduction in pH values could be due to the reactions involved during HTC including hydrolysis, dehydration, condensation, and polymerization of the lignocellulosic biomass. At low temperature of around 180°C, hemicellulose starts to hydrolyze and produce acidic functional groups including carboxyl and hydroxyl. These organic products may be retained in the hydrochar surface when the solids are not washed, which influences its pH value (Cavali et al., 2022). Rice husk and rice straw are considered as dry biomass (<30 %) with low moisture content of 8.2% and 8.5%, but greatly increased to 41.3 % and 31.8 %, after HTC. This may be due to the presence of water at high temperature and pressure during HTC, which results in the production of hydrochar along with liquid byproduct. After separation of the two HTC products (typically by filtration), hydrochar may adsorb water molecules due to its high surface area and porosity (Islam et al., 2021). It was also observed that both types of hydrochars decreased in Total Organic Matter (TOM) by 18.2 – 27.5% compared to its raw biomass. Macronutrients which are essential for plant growth, such as phosphorus (P), potassium (K) and magnesium (Mg) were slightly decreased after HTC. This may be due to some portions of the inorganic soluble dissolves into liquid byproducts. Micronutrients including zinc (Zn), boron (B), and chromium (Cr) are needed in a much lower concentration in the soil as excessive amount can be toxic to plants. The average concentration of chromium in soils range from 14 to around 70 mg/kg (WHO, 2000). HTC greatly reduced chromium concentration in the rice husk from 80.9 to 3.1 mg/kg, hence, does not introduce toxic levels of the element into the soil.

Table 1: Proximate and nutrient properties of raw biomass and hydrochars

Component	Units	Rice Husk		Rice Straw	
		Raw	RHH	Raw	RSH
pH	-	5.7	3.5	7.1	4.0
Moisture	% (w/w)	8.2	41.3	8.5	31.8
Total Organic Matters	% (w/w)	80.5	58.3	90.9	74.4
Total Nitrogen (TN)	% (w/w)	0.65	0.51	0.76	0.32
Phosphorus (P)	mg/kg	624	518	597	710
Potassium (K)	mg/kg	2,330	1,680	15,900	11,800
Magnesium (Mg)	mg/kg	480	336	699	854
Chromium (Cr)	mg/kg	80.9	3.1	9.5	1.8
Zinc (Zn)	mg/kg	13.0	9.6	30.0	24.0
Boron (B)	mg/kg	3.1	2.6	4.9	3.2

3.2 Morphological study

The micrographs of biomass before and after HTC was obtained using FESEM, as shown in Figure 1 (a, b, c, d). In response to HTC, both types of hydrochar show slightly coarser surface as compared to the smooth character of its raw biomass. The raw rice husk has relatively continuous and flat smooth surface, meanwhile, rough surfaces with several particle formation such as microspheres were formed on the RHH surface. Similarly, raw rice straw has limited porosity and smooth surface, while the RSH have slightly more rugged surface with new filamentous structure formed on the surface. This may be due to partial degradation of easily collapsible polymers such as hemicellulose which dissolve at approximately 180 °C during HTC. These polymers decompose into fragments that lead to a rugged and porous surface on the solid residue and would further melt or form carbonaceous spheres on the surface (Wang et al. 2018) The original structure of raw rice husk and rice straw remained due to the presence of lignin, which requires higher carbonization temperature (>260 °C) during HTC process, as reported previously (Arellano et al. 2016). From the morphological study, it can be concluded that the HTC operating conditions used in this study has negligible effects on lignin, meanwhile, partial decomposition of less recalcitrant structures such as hemicellulose and cellulose had occurred. Thus, the

alteration of biomass structure may favor the use of hydrochar as soil amendment by increasing soil porosity or providing microenvironment for bacterial growth (Thunshirn et al., 2021).

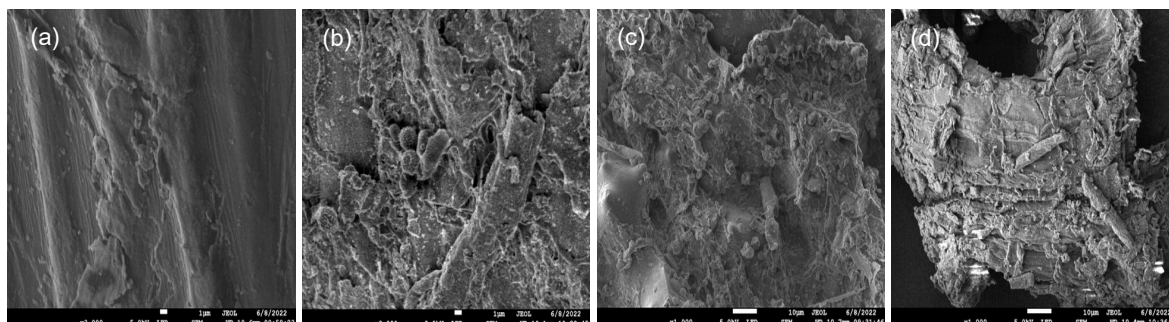


Figure 1: FESEM images of (a) raw rice husk (b) RHH, 3000x magnified; (c) raw rice straw (d) RSH, 1000x magnified

3.3 Effects of hydrochar on soil pH

Soil pH is one of the most important soil parameters due to its influence on nutrient availability, microbial activity, and plant growth (de Jager and Giani, 2021). Figure 2 shows at the beginning of pot experiment, the control treatment had neutral to weakly acidic soil (6.5). 1 % RHH, 10 % RHH, and 1 % RSH treatments decreased pH towards slightly acidic (6.3 – 6.4) but remained in the optimum pH range of Spinach plants (6.0 – 7.5), while the 10 % RSH immediately decreased pH to moderately acidic (5.8). Throughout the experiment, the pH of control soil remained relatively unchanged compared to all hydrochar-amended soil, with 10 % RSH reaching lowest pH (5.3), followed by 10 % RHH (5.4), 1 % RSH (5.5), and 1 % RHH (5.7). Organic fertilizers applied on Day 14 and 28 have significant effects on soil pH as seen from the peak on Day 15 and 35 in all treatments, especially the hydrochar-amended soil. The increase in soil pH may be induced by microbial activities due to nutrients increase. 10 % RSH had the greatest pH increase of 1.0 units (from 5.3 to 6.3), meanwhile, only slight change of 0.3 units (from 6.3 to 6.6) for control. At the end of experiment, higher rates of hydrochar, 10 % RHH and 10 % RSH is more acidic (5.5 and 5.6) compared to lower rates of hydrochar, 1 % RHH and 1 % RSH (6.0 and 5.8). The control treatment maintained its initial soil pH (6.5). This shows that hydrochar highly influence the shifting of soil pH, which is stronger in higher hydrochar rates regardless of the type of feedstock. Change in pH is due to release of nutrients in the soil, which increase the exchange of hydrogen ions, and consequently alter soil pH (Lowenfels and Lewis, 2010). Hydrochar have enhanced concentrations of major cations such as potassium (K^+) and magnesium (Mg^{2+}) leading to higher rates of ion exchanges in the soil. The decrease in soil pH is due to soil response toward the pH of the hydrochar which is strongly acidic in this study (soil: 6.5, RHH: 3.5, RSH: 4.0). As such, RHH and RSH may be more suitable for adjustment of alkaline soil with $pH \geq 8$. Modifications of hydrochars such as lime addition or alkaline washing should be performed prior to using RHH and RSH in acidic soil.

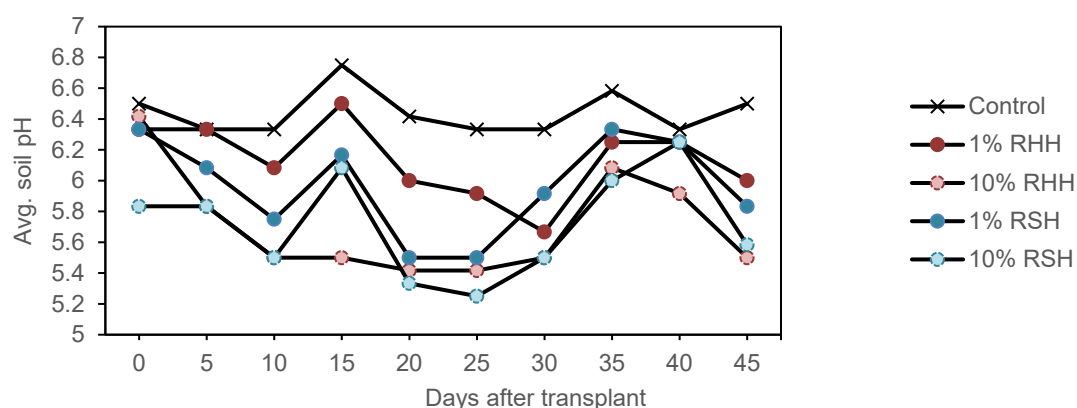


Figure 2: Effects of different treatments on soil pH over 45 days of transplant

3.4 Effects of hydrochar on plant growth

After harvesting, plant biomass and growth were measured. Figure 3 shows all hydrochar-amended treatments, 1 % RHH, 10 % RHH, 1 % RSH and 10 % RSH significantly decreased plant dry biomass by 61.6 %, 66.1 %, 60 % and 66.9 %, compared to control. Figure 4 shows reduced number of leaves and plant height, especially in higher rates of 10% hydrochar, compared to lower rates of 1 % hydrochar. When comparing between the two hydrochars, RSH inhibited the plant growth more than RHH. This shows that effects on plant growth is dependent on the soil pH, type of feedstock and application rates of hydrochar. The reduction in plant growth is due to the highly acidic soil, which can decrease nutrient availability and microbial activity in the soil, leading to poor plant growth (de Jager et al., 2020). Higher rates of hydrochar treatments have more acidic soil compared to lower rates of hydrochar, resulting in decreased plant biomass and growth. However, even at low rates of hydrochar, plant growth was significantly reduced which indicate there may be multiple factors besides soil pH. A study by Farru et al. (2022) found the root growth with higher amount of untreated hydrochar were largely inhibited, which may be due to the presence of phytotoxic compounds such as phenolic compounds or volatile fatty acids (VFAs) formed during HTC process, however, the inhibitory effects were reduced with treated hydrochar. Kalderis et al. (2019) reported that post-treatments of hydrochar such as washing the hydrochar with water or any weakly alkaline solution may be a potential solution to improve pH and reduce toxic byproducts. Additionally, prolonged maturity period of hydrochar in soil may lower its phytotoxicity and bring positive effects on plant growth. A study by Puccini et al. (2018) observed that 4-months aged hydrochar reduced the phytotoxic effects on plants as it has lower concentrations of polyphenols and VFAs which may be due to the partial evaporation of the volatile toxic substances. Another study Bargmann et al. (2014b) found that germination-inhibiting substances in hydrochars were removed 9 weeks after soil incorporation, which may be due to microbial degradation of hydrochar components.

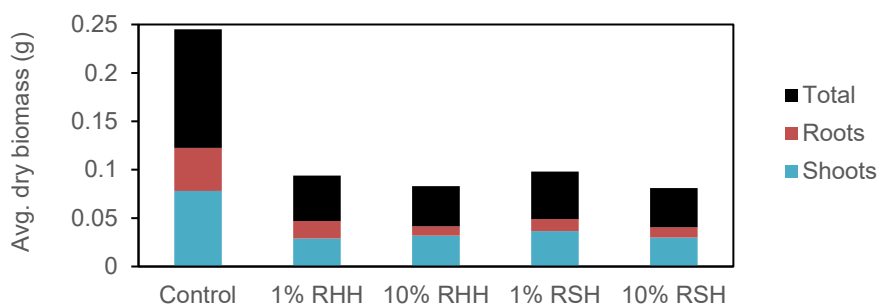


Figure 3: Effects of different treatments on dry biomass of Spinach plants

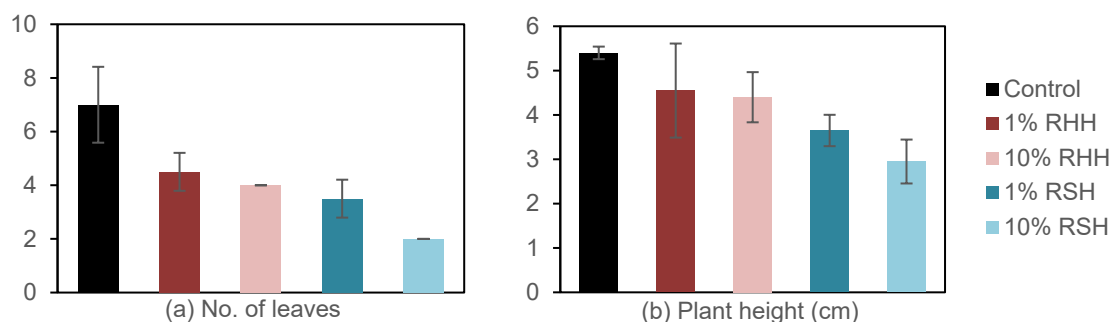


Figure 4: Effects of different treatments on Spinach (a) number of leaves (b) height of plants

4. Conclusions

HTC is a promising technology that can help manage biomass wastes sustainably. Properties of rice husk and rice straw biomass changed by HTC is due to partial degradation of hemicellulose and cellulose polymers. Application of hydrochar decreased soil pH to acidic, which indicates the suitable use for dry degraded soil with $\text{pH} \geq 8$. Hydrochar-amended treatments significantly reduced plant dry biomass especially in 10 % application rates, regardless of the feedstock. Comparing between the two types of hydrochar, RSH decreased plant growth more than RHH. Thus, the effects on plant growth are highly dependent on soil pH, type of feedstock, and application rates of hydrochar. Post-treatments such as washing or aging of hydrochar is highly suggested to

reduce inhibition of plant growth. Further research on soil properties and microbial communities is needed to assess the potential use of hydrochar derived from rice husk and rice straw to improve plant growth.

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