

Changes in Structural and Chemical Properties of Rice Husk Biochar Co-pyrolysed with Eppawala Rock Phosphate under Different Temperatures

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ABSTRACT: *Although properties of rice husk biochar (RHB) can be changed by altering pyrolysis temperature, they still remain as a poor-quality soil amendment. We hypothesised that addition of phosphate rock powder during the pyrolysis process will enhance structural and chemical properties of RHB. This experiment was conducted to determine the effect of temperature on properties of RHB co-pyrolysed with Eppawala Rock Phosphate (ERP). Rice husk was slow-pyrolysed at 350 °C, 500 °C and 650 °C, with and without 4.2% ERP (w/w), and produced six different types of RHB. Scanning electron micrographs showed an improved pore structure in RHB with increasing pyrolysis temperature, however co-pyrolysis with ERP did not show any further improvements. Raman spectroscopy provided evidence for increased aromatisation with the increase in temperature and formation of $-PCH_3$ (sp^2 bond) in RHB co-pyrolysed with ERP at 350 °C. Iodine number in RHB increased by 140 mg/g when the temperature increased from 350 °C to 650 °C, however it has increased more in the presence of ERP at 350 °C. The pH, EC, and available nutrients (P, K and Mg) in RHB increased with increasing temperature. Addition of ERP increased available P by 3-fold at all temperatures and K by 13% in RHB under 500 °C. We conclude that chemical properties of RHB can be improved by co-pyrolysing rice husk with ERP. When all characteristics were assessed together, biochar pyrolysed at 500 °C appears to be the most suitable soil amendment to improve soil fertility among conditions tested.*

Keywords: *Available nutrients, Eppawala rock phosphate, pyrolysis, rice husk biochar, structural properties*

INTRODUCTION

Rice husk is an agricultural waste which accounts for 20% of the grain weight (Takita, 1987). Hence in Sri Lanka, about 0.5 million metric tons of rice husk is generated annually based on rice production statistics of the Central Bank of Sri Lanka (Anon, 2017). It has been used to generate bioenergy in rice milling plants, as a bedding material in poultry farms and as a soil amendment in different forms in agricultural lands to increase soil fertility and crop productivity (Siavoshi *et al.*, 2011). Rice husk is also used as a raw material during composting and rice husk ash is directly applied to improve the fertility status of soil (Badar and Qureshi, 2014; Priyadharshini and Seran, 2009). Production of biochar from rice husk

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and applying them into paddy fields, is another way of utilizing the beneficial structural and chemical properties of rice husk effectively (Pratiwi and Shinogi, 2016).

Biochar is a carbonaceous material produced by pyrolysing biomass under zero or limited oxygen condition to obtain a higher porous structure with a large surface area and enhanced adsorption capacity (Lehmann, 2007). According to previous studies, its inherent physical and chemical characteristics depend on the quality of the raw material used and pyrolysis environment (Lehmann, 2007; Enders *et al.*, 2012). Rice husk biochar (RHB) is a material which inherently composed of a poor porous structure due to presence of high amount of silica. Previous studies have tried to improve the porous structure by chemical means and applying high temperatures, around 600 °C during pyrolysis (Oh and Park, 2002; Ahiduzzaman and Islam, 2016). Few studies have attempted to improve the structural properties of biochar, by compositing it with a mineral matrix. For example, Rawal *et al.* (2016) have used iron sulphate clay slurry to pre-treat bamboo biochar and found that clay promotes biomass degradation. Moreover, clay develops high pore volume at low pyrolysis temperatures (250 °C) and low pore volume at higher temperatures while condensing aromatic, acidic and phenolic carbon species. However, only a few studies have researched the changes in structural and chemical properties of rice husk biochar co-pyrolysed with mineral matter.

Eppawala Rock Phosphate (ERP) is a less soluble fertilizer, produced in Sri Lanka, contains a mixture of more soluble and less soluble phosphate composite with ferruginous and aluminous complexes, with a P₂O₅ content of 30% on average (Dahanayake *et al.*, 1995). Due to its low water solubility and very slow release of P resulted this fertilizer to be recommended mainly as a direct applying fertilizer for perennial crops. Solubility of the phosphate rocks (RP) could be enhanced by treating with acids such as sulphuric and phosphoric (Bolan *et al.*, 1990) or by mixing with acidic materials (Rathnayake *et al.*, 1993). Another technique to enhance P availability in rock phosphates (RP) is heat treatment (Mgaidi *et al.*, 2004). Albeit lower temperature than standard heat treatment, the heat generated during the pyrolysis process could be used to change properties of phosphate rocks and increase availability of P. There is no published literature on pyrolysing rock phosphate together with biomass to improve the availability of P. Moreover, it is beneficial to enhance chemical and physical properties within RHB to suit specific agricultural purposes prior to application. Specifically, the properties that are favourable for soil fertility improvement includes, its surface area, porosity and adsorption properties (Downie *et al.*, 2009) and plant available nutrient contents (Enders *et al.*, 2012; Ippolitto *et al.*, 2015).

Therefore, it was hypothesised that mixing of ERP with rice husk prior to the pyrolysis process would improve nutrient availability and structural properties of RHB. This study was carried out with the objective of determining the changes in structural and chemical characteristics of RHB when rice husk was co-pyrolysed with ERP under different temperatures.

METHODOLOGY

Preparation of biochar

Rice husk discarded from rice mills was taken as the feedstock in preparing biochar. Dried rice husk was sieved using a 0.5 mm mesh sieve and material remained on the sieve

(particles >0.5 mm) was used for pyrolysis. A metal container was fully packed to minimize O₂ content inside, with 120±1 g of rice husk with or without 5 g of ERP and tightly closed. The container was placed inside a muffle furnace with an exhaust pipe and heated to prepare biochar at three different temperatures (350 °C, 500 °C and 650 °C) with a rate of heating of 10 °C/min). While feedstock at 350 °C took about 2 hours to complete pyrolysis, feedstock at 500 °C and 650 °C completed pyrolysis process in about 25 minutes after reaching the temperature. All RHB types had a conversion ratio of 38- 47%.

Determination of structural properties

Rice husk biochar pyrolysed under above temperatures were imaged after gold coating at 60 kV electron beam using a fully automated Scanning Electron Microscope (VEGA3 SEM, TESCAN). Raman mapping was conducted using BRUKER SENTERRA Raman Microscope Spectrometer. Samples were mounted on glass slides and pressed with a spatula to make a flat surface. Four different places of each sample were analysed at laser power of 10 mW and at a resolution ~9 -15 cm⁻¹. Fourier Transformed Infrared (FTIR) spectroscopy analysis was done for finely ground (<0.05 mm) biochar samples using the diffuse reflectance accessory in a Nicolet (IS50) IR spectrophotometer. Absorbance spectra were obtained at 650 - 4000 cm⁻¹. The spectral analysis was performed using OriginPro 8.6 software. Iodine number was determined according to the standard ASTM D4607-94 method described in Lori *et al.* (2008). The sample was pounded and sieved through 2 mm sieve and three sub samples were used from each treatment. The iodine adsorption number (I) was calculated by multiplying the volume of I₂ adsorbed into biochar (C) by a conversion factor (f), as indicated below

$$I = C \times f \quad \dots\dots\dots(1)$$

$$f = \frac{MW \times N \times V}{W \times B} \quad \dots\dots\dots(2)$$

$$C = B - R \quad \dots\dots\dots(3)$$

where, MW is the molecular weight of I₂ (g/mol), N is the normality of I₂ (mol/dm³), V is the volume of I₂ (ml), W is the weight of the biochar sample (g), B is the blank reading (ml) and R is the burette reading of the sample (ml).

Determination of chemical properties

Three sub-samples were drawn from each biochar type after air-drying and following analyses were performed. The pH and electrical conductivity were measured according to Guarena *et al.* (2015) in a mixture of biochar and distilled water at 1:20 ratio. Sample was shaken for 1.5 hours in an orbital shaker and the pH was measured using EUTECH pH 510 pH meter and electrical conductivity was measured using EUTECH CON 2700 conductivity meter. Available phosphorous (P) content was determined as described by Kuo (1996) by extracting P with Mehlich-3 extractant and determining the intensity of the blue colour developed by Murphy and Riley (1962) method at 880 nm wave length using the double beam UV visible spectrophotometer (SHIMADZU UV-1601). Exchangeable potassium (K), magnesium (Mg), and calcium (Ca) were extracted as described by Enders *et al.* (2012). Potassium content in the extracts was measured using flame photometer (JENWAY PFP7) while Mg and Ca contents were measured using AGILENT 200 atomic absorption spectrophotometer. Total P, K, Mg, and Ca were determined using the modified dry ashing

method as explained by Enders *et al.* (2012). Total C and N were analysed in finely ground samples (<250 µm) using the SKALAR Primacs^{SCN-100} Carbon/Nitrogen analyser.

Statistical analysis

Since biochar with and without ERP were not prepared in replicates, three sub samples from each biochar type were used as pseudo-replicates. Therefore, standard error of the pseudo-replicates in each analysis was reported.

RESULTS & DISCUSSION

Changes in structural properties

Scanning electron micrographs were used to visualise the surface pore structure of biochar. Rice husk biochar has a complex porous structure made of inter connected tube-like structures and mesopores and micropores (Figure 1). Pore structure of rice husk biochar contains more cracks and enlarged pores with higher pyrolysis temperatures with or without the ERP addition. ERP addition showed a clearer image of tube-like structures compared to rice husk biochar than without ERP.

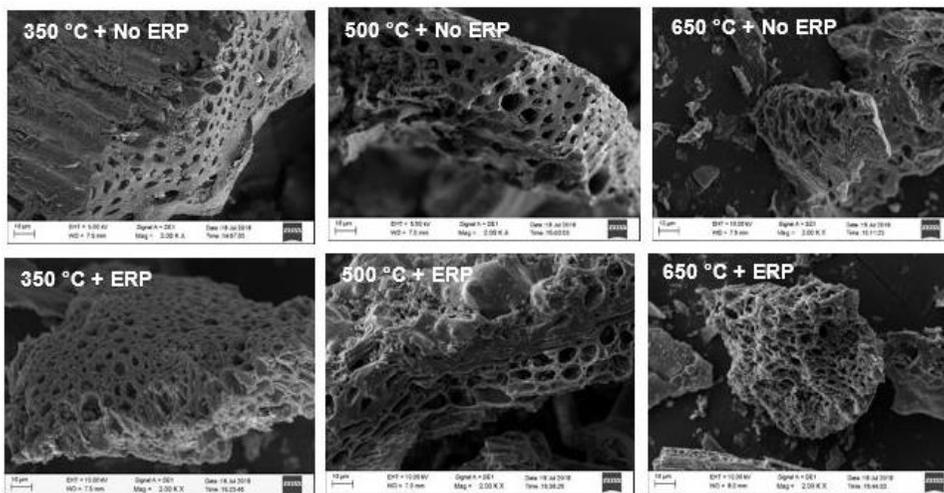


Figure 1. Scanning electron micrographs of rice husk biochar produced at different pyrolysis temperatures with and without ERP with a magnification of x 2.00 K

Mesopores and macropores are produced due to cracks in walls of adjacent micropores at high temperatures (Phuong *et al.*, 2016). Liou and Wu (2009) observed the formation of surface vesicles as a result of the release of volatile compounds inside the matrix during the pyrolysis process softening the cellular component. This could be the reason for the peeled off appearance on outer epidermis of RHB or having clear cuts on the surfaces and some surface folds due to silica deposited on outer epidermis.

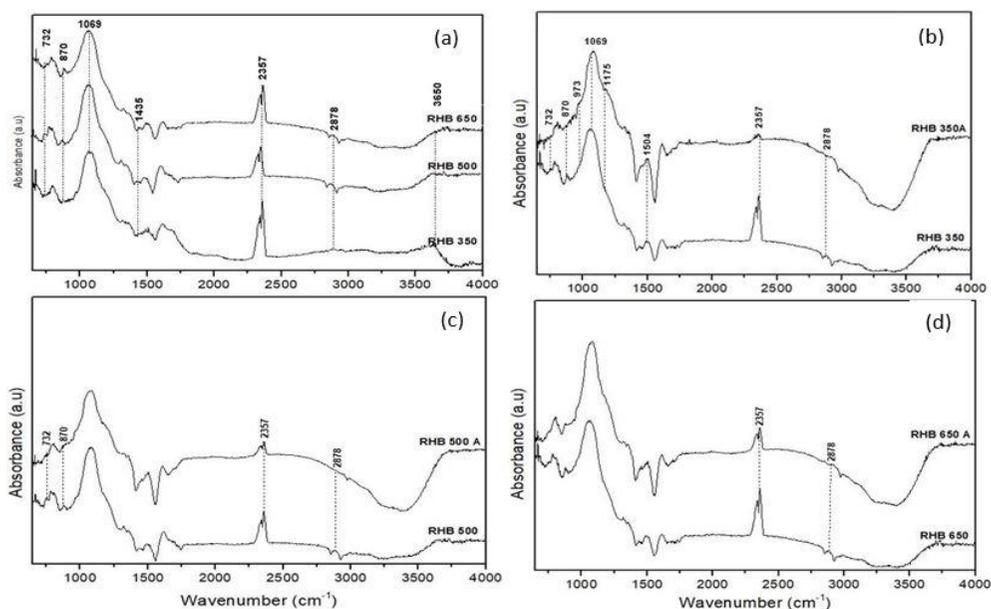


Figure 2. FTIR spectra (a) Comparison of three pyrolysis temperatures of RHB without ERP (b) comparison of RH pyrolysed with and without adding ERP at 350 °C (c) at 500 °C (d) at 650 °C. Addition of ERP is designated by the letter (A)

The FTIR analysis revealed that RHB pyrolysed at all three temperatures had few characteristic peaks within the observed 4000 – 650 cm^{-1} region (Figure 2). Peaks at 1069 cm^{-1} , 2357 cm^{-1} and vibrations around 3650 cm^{-1} corresponding to Si-O-C bend or organic siloxane/ silicone, -C-O-O stretch and O-H stretching vibrations, respectively, were common to all three pyrolysis conditions. Rice husk contains very high amount of silica showed by very strong, prominent symmetric and asymmetric stretching bands around 1070 cm^{-1} appear at all three temperatures. These peaks represent the Si-O bonds which are also observed in rice straw biochar around 1100 cm^{-1} by Yakout (2015).

Peaks that visible at higher temperatures were $-\text{CH}_3$ rocking vibration at 870 cm^{-1} , C-H (aldehyde) weak stretching at 2878 cm^{-1} and bands at 732 cm^{-1} and 1435 cm^{-1} which corresponds to $-(\text{CH}_2)_3$ rocking vibrations and asymmetric CH_3 deformation vibration ($=\text{CHOH}$). An increase in aromatic C-H out of plane deformations at 781 cm^{-1} , 885 cm^{-1} were observed by Zhao *et al.* (2017) with increasing pyrolysis temperature in biochar made from apple tree branches. Yakout (2015) has observed that there is an increase in intensities of the peaks around 2920 and 2850 cm^{-1} with temperature up to 750 °C that shows the prevalence of some aliphatic species on biochar. Similarly, Lee *et al.* (2017) observed an aliphatic CH deformation at 1420 – 1470 cm^{-1} with the increase in carbonization temperature. Further they suggested that pyrolysing for a short time period below 400–500 °C could results more aromatic compounds around 1600 cm^{-1} and 750 to 885 cm^{-1} . Aromatic compounds are more stable and therefore, when biochar rich in aromatic compounds is applied in to soil, nutrients embedded into such carbon structures will only be available slowly to plants (Wang *et al.*, 2015). Moreover, application of biochar with enriched aromatic carbon could be incorporated into more protected intra aggregation and organo-mineral compounds ultimately contributing to higher C sequestration (Kimetu and Lehmann, 2010). Biochar pyrolysed at higher temperature result more recalcitrant characters

with the increase in aromatic compounds (Jindo *et al.*, 2014). Characteristic peaks around 1600 cm^{-1} and 1490 cm^{-1} (Figure 2) disappeared with the increase in pyrolysis temperature. Lee *et al.* (2017) also observed that, bonds appeared around 1600 cm^{-1} at low temperatures disappeared with the increase in carbonisation temperature due to the loss of cellulose and lignin content in raw rice husk at higher pyrolysis temperatures. Aromatic C=C and C=O stretching of conjugated ketones and quinones were responsible for the peaks around 1600 cm^{-1} and their intensity decreases with the increase in pyrolysis temperature may be due to degradation of phenolic and carboxylic compounds in lignin (Zhao *et al.*, 2017).

Peak intensity of $-\text{CO}_2$ (2357 cm^{-1}) has reduced at higher pyrolysis temperatures compared to $350\text{ }^\circ\text{C}$. It was observed that the prominent peak appeared at 2350 cm^{-1} is responsible for the C–O bond which resulted due to the presence of ketene in rice husk biochar. This is prominent even in rice straw biochar at 2300 cm^{-1} as explained by Yakout (2015). The presence of oxygen containing functional groups are important in sorption of heavy metals on the biochar surface by forming strong complexes (Sun *et al.*, 2014; Ahmad *et al.*, 2014) and make them less bioavailable.

Addition of ERP resulted disappearance of some prominent stretching vibrations in RHB (Figure 2). Stretches at 732 cm^{-1} , 870 cm^{-1} , 2357 cm^{-1} , and 2878 cm^{-1} were disappeared or lowered their intensities in the presence of ERP. It has been observed that mineral incorporation prior to pyrolysis could enhance the release of oxygenated compounds including humics and phenolics from biochar (Kleber *et al.*, 2015). Certain new peaks were formed as a result of the ERP incorporation during pyrolysis which showed by wave numbers 973 cm^{-1} and 1175 cm^{-1} . According to Bekiaris *et al.* (2016) weak stretch at 975 cm^{-1} represented tribasic calcium phosphates and 1160 cm^{-1} corresponded to amorphous dibasic calcium phosphate. Since the chemical formula of the main constituent of ERP, apatite, is $(\text{Ca}_5(\text{PO}_4)_3.\text{OH},\text{F},\text{Cl})$, the observed stretches at 973 and 1175 cm^{-1} could be due to the reactions between ERP and carbon structure of rice husk biochar.

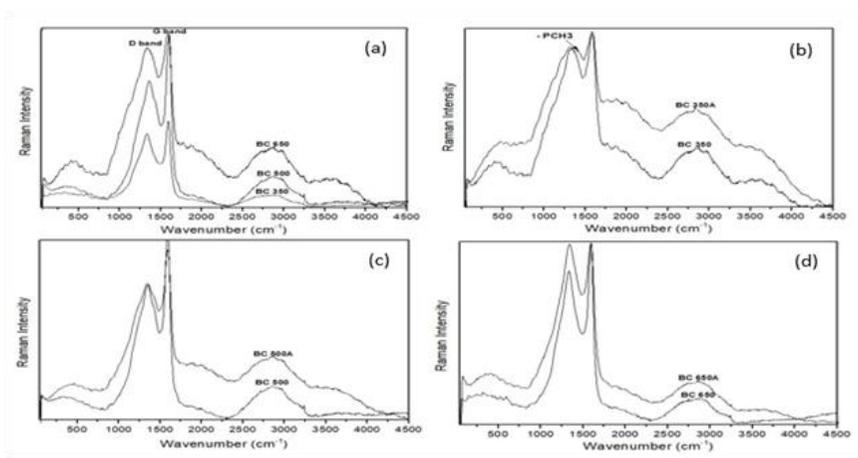


Figure 3. Raman spectroscopy (a) Comparison of three pyrolysis temperatures of RHB (b) Comparison of RH pyrolysed with and without adding ERP at $350\text{ }^\circ\text{C}$ (c) at $500\text{ }^\circ\text{C}$ (d) at $650\text{ }^\circ\text{C}$. Addition of ERP designated by the letter (A)

Raman Spectroscopy is an indicator for the presence of aromatic carbon in a carbonized material (Zhao *et al.*, 2013). Increase in pyrolysis temperature has a substantial impact on

aromatisation which depicts through the formation of G and D bands on Raman spectroscopy of rice husk biochar (Figure 3). The G band observed at 1590 cm^{-1} represent the presence of sp^2 carbon (double bonds) in the graphitic matrix (Wang *et al.*, 2011; Zhao *et al.*, 2013) while D band indicates the addition of ERP has not influenced the aromatisation.

Iodine number gives an idea about micropore structure and the surface area of produced rice husk biochar as these properties correlates to the I_2 adsorbent capacity (Itodo *et al.*, 2010). Iodine number of rice husk biochar produced, increased from 53 mg/g to 193 mg/g (without ERP) and from 62 mg/g to 175 mg/g (with ERP) as the pyrolysis temperature increased from $350\text{ }^\circ\text{C}$ to $650\text{ }^\circ\text{C}$ (Figure 4). Addition of ERP during pyrolysis slightly reduced the iodine number in RHB at higher temperatures ($500\text{ }^\circ\text{C}$ and $650\text{ }^\circ\text{C}$), however increased at $350\text{ }^\circ\text{C}$. Increase in iodine number with the increase in pyrolysis temperature is a common feature observed in many studies (Itodo *et al.*, 2010; Phuong *et al.*, 2016). Powar and Gangil (2015) observed that, iodine number in activated carbon prepared with soybean has increased from 167.7 to 288.78 mg/g when pyrolysis temperatures increased from $450\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$.

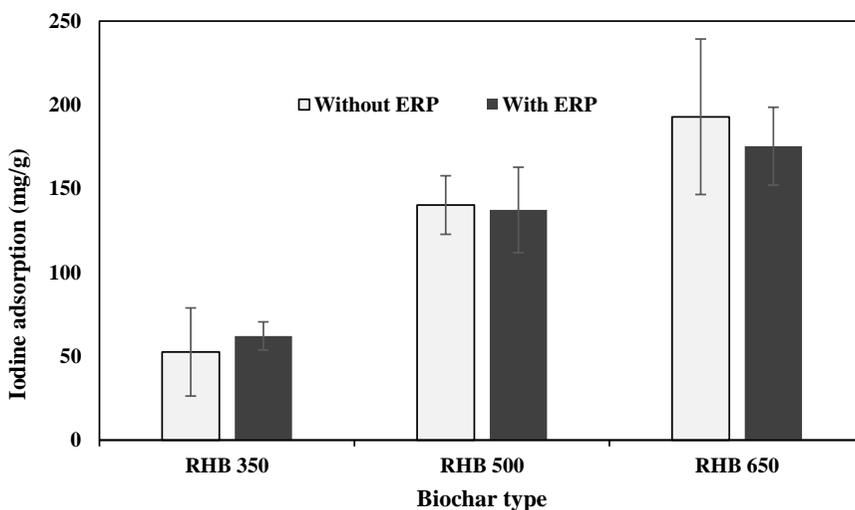


Figure 4. Variation in iodine number in rice husk biochar samples made with and without ERP at different pyrolysis temperatures

Rice husk contains high ash content in which the main component is silica. Liou and Wu (2009) observed that the absence of silica would improve the pore structure in rice husk biochar. High Si rich ash content could have resulted the low surface area or the low iodine adsorption capacity in the RHB prepared by us. Ahiduzzaman and Islam (2016) also observed few pores on the surface topography of rice husk biochar due to high Si contents in the rice husk.

Changes in chemical properties

The pH ranged from 7.48 to 9.38 (Table 1) in all produced biochar at different pyrolysis temperatures. It varied from a slightly alkaline pH to an alkaline pH with the increase in temperature both in the presence and absence of ERP. The lowest pH (7.48) observed in RHB produced at $350\text{ }^\circ\text{C}$ while the highest (9.38) was at $650\text{ }^\circ\text{C}$ (Table 1). Anđın and Şensöz (2014) also observed an increase in pH with increasing pyrolysis temperature. The pH in

RHB increases due to increase in ash content. Moreover, the minerals in the organic matrix degrade into inorganic salts at temperatures higher than 350 °C (Claoston *et al.*, 2014). Presence of ERP during pyrolysis process did not significantly influence pH of the produced RHB.

Table1. Some chemical properties of RHB prepared under different pyrolysis temperatures. Presence of ERP indicated with letter A. Results are given as mean \pm standard error ($n = 3$)

| Parameter | Biochar type | | | | | |
|----------------------|--------------------|--------------------|--------------------|---------------------|--------------------|--------------------|
| | RHB 350 | RHB 500 | RHB 650 | RHB 350A | RHB 500A | RHB 650A |
| pH | 7.48 ± 0.04 | 9.11 ± 0.01 | 9.38 ± 0.02 | 7.63 ± 0.01 | 9.06 ± 0.01 | 9.36 ± 0.08 |
| EC (S/m) | 0.01 ± 0.00 | 0.05 ± 0.00 | 0.06 ± 0.00 | 0.009 ± 0.00 | 0.04 ± 0.00 | 0.06 ± 0.00 |
| Available P (mg/kg) | 256 ± 4 | 472 ± 25 | 518 ± 27 | 829 ± 85 | 1364 ± 96 | 1456 ± 53 |
| Available K (mg/kg) | 5366 ± 187 | 6525 ± 548 | 7469 ± 197 | 4722 ± 227 | 7384 ± 239 | 7598 ± 340 |
| Available Mg (mg/kg) | 150 ± 13 | 247 ± 14 | 300 ± 5 | 113 ± 19 | 347 ± 24 | 277 ± 10 |
| Total P (%) | 0.22 ± 0.01 | 0.29 ± 0.01 | 0.19 ± 0.00 | 0.35 ± 0.01 | 0.46 ± 0.01 | 0.43 ± 0.03 |
| Total K (%) | 0.57 ± 0.03 | 0.69 ± 0.03 | 0.75 ± 0.04 | 0.54 ± 0.04 | 0.72 ± 0.04 | 0.79 ± 0.01 |
| Total Mg (%) | 0.11 ± 0.00 | 0.12 ± 0.00 | 0.07 ± 0.01 | 0.05 ± 0.00 | 0.13 ± 0.01 | 0.06 ± 0.01 |
| Total C (%) | 45.4 ± 1.6 | 47.8 ± 1.5 | 50.0 ± 0.8 | 48.4 ± 0.1 | 45.4 ± 0.7 | 48.2 ± 0.9 |
| Total N (%) | 0.51 ± 0.03 | 0.56 ± 0.09 | 0.37 ± 0.01 | 0.48 ± 0.00 | 0.44 ± 0.02 | 0.33 ± 0.01 |

Electrical conductivity (EC) of rice husk biochar ranged from 0.0108 to 0.0624 S/m. Addition of ERP has slightly reduced the EC of RHB in all three temperatures in comparison to RHB without ERP. Electrical conductivity increased with the increase in pyrolysis temperature and this may be due to increase in surface ash content which is responsible for the increase in mobility of potassium (K^+) ion in biochar at high pyrolysis temperature (Claoston *et al.*, 2014; Yargicoglu *et al.*, 2015). This possibility was supported by the increase in available K content observed with the increase in pyrolysis temperature. Available P and K increased with increasing pyrolysis temperature from 350 °C to 650 °C. Berecha *et al.* (2015) also observed similar results in their experiment using coffee husk and corn cob biochar where available P content and exchangeable cation contents increased when pyrolysis temperatures increased from 350 °C to 500 °C. In general, slow pyrolysis of feedstock produces biochar with higher available P and Mg (Ippolito *et al.*, 2015). Available P content in this study increased from 256 mg/kg to 518 mg/kg in RHB without ERP and from 829 mg/kg to 1456 mg/kg with ERP (Table1). Co-pyrolysis of rice husk with ERP has increased the available P contents in the resultant RHB by 180 to 210% depending on the temperature. Moreover, it was observed that in RHB without ERP, the available magnesium (Mg) content has increased by two-fold when the pyrolysis temperature increases from 350 °C to 650 °C.

The higher cation concentrations at higher temperatures are due to hydrolysis of carbonates and bicarbonates of base cation in feedstock material (Berecha *et al.*, 2015). This trend was not observed with ERP added RHB but a substantially higher Mg levels were resulted at 500 °C and 650 °C temperatures (Table 1). The quantity of available nutrients from the total varied with the type of nutrient. The available P content as a% of the total P content in RHB increased with increasing pyrolysis temperature from 11% at 350 °C to 28% at 650 °C without ERP and from 23% to 33% when co-pyrolysed with ERP. However, the total P content increased with the increase in pyrolysis temperature from 350 °C to 500 °C but decreased slightly after that. Knicker (2007) observed that P in organic compounds get volatilized at around 750 °C and could be the reason for lowering of total P content in RHB made at 650 °C.

Total K content is very much similar to that of available K in each pyrolysis temperatures. It showed that, total K in RHB will be readily available once it is applied in to soil. This is not observed with total P and Mg, may be these nutrients are highly bound with the organic matrix of biochar. Ippolito *et al.* (2015) reported K is present in biochar in water soluble form, and that the availability could be ranged from 3.5 – 100% of total K content in it.

Total C content which ranged from 45 - 50% has not varied with the pyrolysis temperature or even with the addition of ERP. Comparatively low total C contents in RHB would be due to the presence of silica like minerals in the feedstock (Ippolito *et al.*, 2015). Total N content was slightly higher in RHB made without ERP. Total N content was high (0.55%) at lower temperatures (<500 °C) but low (0.37%) at 650 °C. Similar observations were made in RHB with ERP addition where it had around 0.48% of total N at lower temperatures and 0.33% at 650 °C. According to Ippolito *et al.* (2015), decrease in TN at higher temperature could be due to loss of N containing aliphatic amino chains by volatilization and the maximum N content in biochar could be obtained at temperatures around 300-400 °C. Effect of pyrolysis temperature on total nutrient content differ with the residence time of the process which allows the reactions to take place whereas slow pyrolysis could concentrate more nutrient compared to fast pyrolysis (Gaskin *et al.*, 2008).

CONCLUSIONS

The present study confirms the previous findings that pyrolysis temperature has a strong impact on changing structural and some chemical properties in RHB. With the increase in pyrolysis temperature, the I₂ number was increased by 270% suggesting a large improvement in the micropore structure and surface area of the RHB. However, incorporation of ERP did not improved the pore structure as suggested from SEM images. Spectroscopic analysis confirmed that the impact on aromatisation, drop in certain aliphatic and -CO₂ compounds and enhanced microporosity with increasing pyrolysis temperatures. Incorporation of ERP during the pyrolysis process increased the phosphorous availability in RHB by 3-fold at all temperatures in addition to small but substantial improvements in exchangeable K and Mg contents, particularly at 500 °C. The improvement in different properties of RHB was temperature dependent where structural properties were better at 650 °C while chemical properties were better at 500 °C. Co-pyrolysis of rice husk with ERP improved P availability in RHB but had only marginal effect in structural properties of RHB. Findings of this study suggest that the optimum temperature at which RHB should be produced is highly dependent in its application. Future research needs are to analyse the economy of the energy usage before recommending the best pyrolysis temperature for a given application.

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REFERENCES

- Ahiduzzaman, M. and Sadrul Islam, A. (2016). Preparation of porous bio-char and activated carbon from rice husk by leaching ash and chemical activation. SpringerPlus. *5(1)*, 1248.
- Ahmad, M., Rajapaksha, A., Lim, J., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. and Ok, Y. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*. *99*, 19-33.
- Angin, D. and Şensöz, S. (2014). Effect of pyrolysis temperature on chemical and surface properties of biochar of rapeseed (*Brassica napus* L.). *Int. J. Phytoremediat.* *16*, 684-693.
- Anon. (2017). The Annual Report of the Central Bank of Sri Lanka for the Year 2017. Central Bank of Sri Lanka, Colombo, Sri Lanka. pp. 42-81.
- Badar, R. and Qureshi, S. (2014). Composted Rice Husk Improves the Growth and Biochemical Parameters of Sunflower. *Plants. J. Bot.* *2014*, 1-6.
- Bekiaris, G., Peltre, C., Jensen, L. and Bruun, S. (2016). Using FTIR-photoacoustic spectroscopy for phosphorus speciation analysis of biochars. *Spectrochim Acta A Mol. Biomol. Spectrosc.* *168*, 29-36.
- Berecha, G., Dume, B. and Tulu, S. (2015). Characterization of Biochar Produced at Different Temperatures and its Effect on Acidic Nitosol of Jimma, Southwest Ethiopia. *Int. J. Soil Sci.* *10*, 63-73.
- Bolan, N., Hedley, M., Harrison, R. and Braithwaite, A. (1990). Influence of manufacturing variables on characteristics and the agronomic value of partially acidulated phosphate fertilizers. *Fert. Res.* *26*, 119-138.
- Claoston, N., Samsuri, A., Ahmad Husni, M. and MohdAmran, M. (2014). Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste. Manage. Res.* *32*, 331-339.
- Dahanayake, K., Ratnayake, M. and Sunil, P. (1995). Potential of *Eppawala* apatite as a directly applied low-cost fertilizer for rice production in Sri Lanka. *Fert. Res.* *41*, 145-150.
- Downie, A., Munroe, P. and Crosky, A. (2009). Characteristics of biochar- physical and structural properties. pp.13-29. In: Lehmann, J. and Joseph, S. (Ed.), *Biochar for Environmental Management: Science and technology*. Earthscan, New York, USA.

- Enders, A., Hanley, K., Whitman, T., Joseph, S. and Lehmann, J. (2012). Characterization of biochar to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* *114*, 644-653.
- Gaskin, J., Steiner, C., Harris, K., Das, K. and Bibens, B. (2008). Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans.Am. Soc. Agric.Biol. Eng.* *51*, 2061-2069.
- Guerena, D., Lehmann, J., Thies, J., Enders, A., Karanja, N. and Neufeldt, H. (2015). Partitioning the contributions of biochar properties to enhanced biological nitrogen fixation in common bean (*Phaseolus vulgaris*). *Biol Fertil Soils*, *51*, 479-491.
- Ippolito, J.A. Spokas, K.A. Novak, J.M. Lentz, R.D. and Cantrell, K.B. (2015). Biochar elemental composition and factors influencing nutrient retention. pp.139-163. In: Lehmann, J. and Joseph, S. (Ed.), *Biochar for Environmental Management: Science and technology*. Earthscan, New York, USA.
- Itodo, A., Abdulrahman, F., Hassan, L., Maigandi, S. and Itodo, H. (2010). Application of methylene blue and iodine adsorption in the measurement of specific surface area by four acid and salt treated activated carbons. *New York Sci. J.* *3*, 25-33.
- Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. and Sonoki, T. (2014). Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences*, *11*, 6613-6621.
- Kimetu, J. and Lehmann, J. (2010). Stability and stabilisation of biochar and green manure in soil with different organic carbon contents. *Aust. J. Soil Res.* *48*, 577-585.
- Kleber, M. Hockaday, W. and Nico, P.S. (2015). Characteristics of biochar: macro-molecular properties. pp.111-132. In: Lehmann, J. and Joseph, S. (Ed.) *Biochar for environmental management: Science and technology*. Earthscan.
- Knicker, H. (2007). How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochemistry* *85*, 91-118.
- Kuo, S. (1996). Phosphorus. pp. 869-919. In: Sparks, D.L. (Ed.). *Methods of Soil Analysis: Part 3*, SSSA Book Series No. 5, SSSA and ASA, Madison.
- Lee, M., Park, J. and Chung, J. (2017). Adsorption of Pb(II) and Cu(II) by ginkgo-leaf-derived biochar produced under various carbonization temperatures and times. *Int. J. Environ. Res. Public Health.* *14*, 1528.
- Lehmann, J. (2007). Bio-energy in the black. *Front. Eco. Environ.* *5*, 381-387.
- Liou, T. and Wu, S. (2009). Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions. *J. Hazard. Mater.* *171*, 693-703.
- Lori, J., Lawal, A. and Ekanem, E. (2008). Adsorption characteristics of active carbons from pyrolysis of bagasse, sorghum and millet straws in ortho phosphoric acid. *J. Environ. Sci. Technol.* *1(3)*, 124-134.

Mgaidi, A., Brahim, F., Oulahna, D., Nzihou, A. and Maaoui, M. (2004). Chemical and structural changes of raw phosphate during heat treatment. *High Temp. Mater. Processes.* 23, 185-194.

Murphy, J. and Riley, J. (1962). A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27, 31-36.

Oh, G. and Park, C. (2002). Preparation and characteristics of rice-straw-based porous carbons with high adsorption capacity. *Fuel*, 81, 327-336.

Phuong, D., Miyanishi, T., kayama, T. and Kose, R. (2016). Pore characteristics and adsorption capacities of biochars derived from rice residues as affected by variety and pyrolysis temperature. *Am. J. Innov. Res. Appl. Sci.* 2, 179-189.

Powar, R. and Gangil, S. (2015). Effect of temperature on iodine value and total carbon contain in bio-char produced from soybean stalk in continuous feed reactor. *Int. J. Agric. Eng.* 8, 26-30.

Pratiwi, E. and Shinogi, Y. (2016). Rice husk biochar application to paddy soil and its effects on soil physical properties, plant growth, and methane emission. *Paddy Water Environ.* 14, 521-532.

Priyadharshini, J. and Seran, T.H. (2009). Paddy husk ash as a source of potassium for growth and yield of cowpea (*Vigna unguiculata* L.). *J Agric. Sci.* 4, 67-72.

Rathnayake, M., Kumaragamage, D. and Dahanayake, K. (1993). A comparison of citric acid solubility of commercially available Eppawala Rock Phosphate and selectively mined primary apatite crystals after mixing with peat. *Trop. Agric. Res.* 5, 69-76.

Rawal, A., Joseph, S., Hook, J., Chia, C., Munroe, P., Donne, S., Lin, Y., Phelan, D., Mitchell, D., Pace, B., Horvat, J. and Webber, J. (2016). Mineral–biochar composites: Molecular structure and porosity. *Environ. Sci. Tech.* 50, 7706-7714.

Siavoshi, M., Laware, S. and L. Laware, S. (2011). Effect of organic fertilizer on growth and yield components in rice (*Oryza sativa* L.). *J. Agric. Sci.* 3,217-224.

Sun, J., Lian, F., Liu, Z., Zhu, L. and Song, Z. (2014). Biochars derived from various crop straws: Characterization and Cd (II) removal potential. *Ecotoxicol. Environ. Saf.* 106, 226-231.

Takita T. (1987). Difference of proportion of hull weight to whole grain between Indica and Japonica rice. *Japan J. Breed.* 37, 212-215.

Wang, J., Xiong, Z. and Kuzyakov, Y. (2015). Biochar stability in soil: meta-analysis of decomposition and priming effects. *GCB Bioenergy.* 8, 512-523.

Wang, S., Alva, A., Li, Y. and Zhang, M. (2011). A rapid technique for prediction of nutrient release from polymer coated controlled release fertilizers. *Open J. Soil Sci.* 01, 40-44.

Yakout, S. (2015). Monitoring the changes of chemical properties of rice straw-derived biochars modified by different oxidizing agents and their adsorptive performance for organics. *Biorem. J.* *19*, 171-182.

Yargicoglu, E., Sadasivam, B., Reddy, K. and Spokas, K. (2015). Physical and chemical characterization of waste wood derived biochars. *Waste Manage.* *36*, 256-268.

Zhao, L., Cao, X., Mašek, O. and Zimmerman, A. (2013). Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. *J. Hazard. Mater.* *256-257*, 1-9.

Zhao, S., Ta, N. and Wang, X. (2017). Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies.* *10*, 1293.