INTRODUCTION

Biochar is commonly defined as charred organic matter produced with the intent to deliberately apply to soils to sequester carbon thus mitigating the global-warming effects (Lehmann and Joseph, 2009). It is more stable than non-charred biomass due to its condensed aromatic nature, especially when pyrolysed at high temperature and hence is difficult for microorganisms to degrade (Lehmann et al., 2009; Shackley and Sohi, 2010). The principle of using biochar for carbon (C) sequestration is related to the role of soils in the C cycle. Soil emit about of 60 Gt of C per year mainly as a result of microbial decomposition and respiration of soil organic matter and biomass in the soil system. Biochar amendment soil is considered as carbon negative as it sequester organic carbon in vegetative biomass that would otherwise be released into the atmosphere as carbon dioxide (Spokas, 2010).
Thus through biochar the organic carbon is moved to a more slowly cycling reservoir (biochar) potentially for centuries (Yargicoglu et al., 2014). This forms the basis behind biochar’s possible carbon negativity and hence its potential for climate change mitigation (Verheijen, 2010). In addition to this, it is widely used for the improvement of soil fertility, plant growth, decontamination of soil and water etc. (Jindo et al., 2012). The most essential indicator of biochar quality is its high adsorption and cation exchange capacities, pH and low levels of mobile matter and high aromatic carbon content (Glaser et al., 2002; Liang et al., 2006; McClellan et al., 2007; McLaughlin et al., 2009) and this quality is more dependent on the feedstock characteristics. The diverse range of biochar application depends on its physicochemical properties, which are governed by the pyrolysis conditions and the original feedstock (Enders et al., 2012). Biochar is created through pyrolysis of the plant material thereby potentially increasing its recalcitrance with respect to the original plant material (Coumaravel et al., 2011). The high temperatures used in pyrolysis can induce polymerization of the molecules within the feedstocks, whereby larger molecules are also produced (including both aromatic and aliphatic compounds), as well as the thermal decomposition of some components of the feedstocks into smaller molecules (Shenbagavalli and Mahimairaja, 2012). Thus, Feedstock along with pyrolysis conditions is the most important factor controlling the properties of the resulting biochar (Lehmann and Joseph, 2009). Numerous studies like that of Sjostrom (1993), Demirbas (2004), Winsley (2007) Amonette and Joseph (2009), Antal and Gronly, 2003, Lua et al., (2004), Martinez et al.,(2006), Gonzalez et al., (2009) etc. have demonstrated the role of these two factors on the characteristic behavior and fate of biochars in soil. Hence, detailed information about the complete production process is a key factor in defining the most suitable application of biochars to soil. Research regarding the physical and chemical properties of biochars has responded to increased interest in biochar amendments for environmental applications (Yargicoglu et al., 2014). Thus Biochar characterization study helps to develop biochar property information and their effects that can be differentiated from each other. In this study, traditionally prepared six biochars using various materials are characterized to provide further insight on the effects of production processes and feedstock type on relevant physicochemical properties of biochars in order to assess their suitability as a better soil amendment from a climate change mitigation perspective.

EXPERIMENTAL

Six different feed stocks of cow dung, coconut husk, coconut shell, rice husk, rubber seed shell, *Eichhornia* weed plant were selected for the preparation of biochars. Raw feedstocks were collected from local environment and dried properly under natural conditions. After drying, the materials were cut into desirable size. Slow pyrolysis process by simple mound kiln method referred by FAO (1983) was adopted for pyrolysis of dried feed stock. The prepared biochar is then crushed and sieved through 2mm sieve.

Characterization

The biochar thus prepared was subjected to further physical and chemical characterization. Biochar characterization was done according to the method described by Ahmedna et al. (1998). The bulk density was determined according to Masulili (2010). Biochar pH was measured according to Ahmedna et al. (1998). The biochar percent ash content (wt/wt) was determined by dry combustion at 760°C in air for 6 hrs using a laboratory muffle furnace (Novak et al., 2007). The nutrient content N, P and K were determined as per Masulili, (2010). Energy-dispersive spectroscopy (EDS) was used to quantify the major elemental distribution of the chars. Scanning electron microscopic (SEM) images of the chars were obtained for morphological features analysis. Solid-state Nuclear Magnetic Resonance (NMR) spectral pattern (IISC, Bangalore) of the biochar was obtained to understand the distribution and presence of C functional groups in various chars.
RESULTS AND DISCUSSION
The properties of biochars produced from various feed stocks are shown in Table 1.

Chemical Characteristics
It is seen that all chars are alkaline in nature as the pH ranges from 7.5 to 9.7. Biochar from coconut shell is highly alkaline (9.7) followed by Eichhornia biochar (9.6). Chan and Xu (2009) reviewed biochar pH values from a wide variety of feedstocks and found a mean of pH 8.1 in a total range of pH 6.2-9.6. Considering the very large heterogeneity of its properties, biochar pH values are relatively homogeneous, i.e. they are largely neutral to basic. Application of biochar in acidic soils helps to increase pH (Rodríguez et al., 2009; Masulli, 2010) therefore it is reasonable that the soil treated with biochar in high concentration can reduce acidity. Such ability is related to the liming value of the biochar. This result indicates that biochar could be used as a substitute for lime materials to increase the pH of acidic soils (Prabha et al., 2013). The CEC values varied between 14.9 and 11.2. Eichhornia biochar had a highest CEC whereas biochar from the shells of rubber seed produced lowest value (11.2). Maximum moisture content was seen in the cow dung char whereas it was minimum in rubber seed shell. The bulk density (BD) values varied significantly between the biochars and the maximum value was noted in coconut shell biochar (0.88g/cm³) whereas the least value is noted in Eichhornia (0.80). The nutrient values fluctuated widely between the samples. Maximum N, P and K values were noted in Eichhornia biochar followed by cow dung and coconut husk biochar. In the rubber seed shell and rice husk chars, the nutrient status was comparatively low. Different feedstocks used to prepare biochar contain various amounts of ash, and it represents a greater proportion of the overall material present. Maximum ash content was produced by cow dung char followed by Eichhornia. Earlier reports shows that feedstock like grain husk, grass or fodders and manures like cow dung have very high ash content (Ravindran et al., 1995) whereas woody material have less ash content. Wood contains less ash (<1%) than straw and other crop residues (up to 24%), which also contain more silica (Raveendran et al., 1995). Manures produce high-ash biochars, with ash contents up to 45% (Koutcheiko et al., 2007). The different properties of those biochars seem to be associated with the nature of the chemical constituents in the feedstock biomass. Brown, 2009; Chan and Xu, 2009; Hammes et al., (2006) have confirmed that the different nature of biochar products are typically influenced by wide range of factors including different types of materials being used or feedstock quality and also different charring condition. Chan et al. (2007) showed that biochar made from manure like cow dung will have a higher nutrient content than biochar made from wood materials. According to Sukartono et al., (2011) the nutrient of the cow dung biochar is derived from the fodder biomass which was fed by the animal and this implies the fact that the basic biochar characteristics are of the basic biomass features.

Elemental Composition
The Figure 1 and Table 2 represent the distribution of various elements in different biochars. The C concentration varies between 15.9 and 26.9 % by weight. This difference can be explained on the basis of variation of ash content. This is an important observation as biochars are commonly regarded as OC-rich materials. Presence of Si was noted only in rice husk, coconut shell and Eichhornia biochars. Amorphous Si is of particular interest as it is typically in the form of phytoliths that contain and protect plant C from degradation (Wilding, 1967; Krull et al., 2003; Smith and White, 2004; Parr and Sullivan, 2005; Parr, 2006). Two factors, mainly feedstock and process conditions control the amount and distribution of mineral matter in the biochar.

<table>
<thead>
<tr>
<th>Table 1. Characteristics of Different Biochars</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Eichhornia</td>
</tr>
</tbody>
</table>
Characterization of Selected Biochars to Determine their Suitability as a Soil Amendment from a Climate change Mitigation Perspective

<table>
<thead>
<tr>
<th>Biochar</th>
<th>pH</th>
<th>CEC</th>
<th>BD</th>
<th>P</th>
<th>K</th>
<th>Ash content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cow dung</td>
<td>8.9</td>
<td>13.6</td>
<td>13.9</td>
<td>0.78</td>
<td>0.73</td>
<td>0.57</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>7.5</td>
<td>11.3</td>
<td>8.2</td>
<td>0.81</td>
<td>0.35</td>
<td>0.26</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>9.7</td>
<td>14.2</td>
<td>7.6</td>
<td>0.88</td>
<td>0.34</td>
<td>0.10</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>7.9</td>
<td>11.2</td>
<td>6.5</td>
<td>0.81</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>Rice husk</td>
<td>7.3</td>
<td>12.6</td>
<td>6.9</td>
<td>0.86</td>
<td>0.32</td>
<td>0.12</td>
</tr>
</tbody>
</table>

\[ pH \ p < 0.01; \ CEC \ p < 0.01; \ BD \ p < 0.05; \ P \ p < 0.01; \ K \ p < 0.01; \ Ash \ content \ p < 0.01 \]

Figure 1. EDS spectra showing Elemental Concentration of different Biochars
C Functional Groups

The 13C NMR spectral pattern of various biochar (Figure 6.5) revealed prominent peaks between 120-130 and 180-190 ppm. These peaks indicate that most of this biochar is distributed in aromatic structures. In 0-50ppm, weak signals represent the low occurrence of aliphatic structures. This speculation has merit because the high pyrolysis temperature explains the lack or low occurrence of alkyl C (0-50 ppm), as volatile material such as oils, fatty acids, and alkyl alcohols would be lost (Antal and Gronli, 2003). Carboxyl-containing structures were present in the NMR spectra possibly because of their structural decomposition resistance during pyrolysis.
NMR spectra indicate that these biochars are composed of a mixture of organic structural groups reflecting the chemistry of the feedstock and reactions occurring during both pyrolysis and after pyrolysis on exposure of the biochar to oxygen and water (Schmidt and Noack, 2000: Novotny et al., 2007).

**Morphological Features**

Scanning electron microscopy (SEM) is a potential technique for studying morphology and surface properties. SEM analysis has been especially used to evaluate the structural variations in biochar particles after different thermal treatments and SEM images are very useful to obtain accurate details about pore structure of biochars (Ozcimen and Mericboyu, 2010). Some surface properties of biochar samples such as porosity, total pore volume and surface area are presented in Table 3. It can be seen that porosity values of biochar samples change from 0.13 to 0.17 (%), total pore volume values are in the range of 0.67-14.68 (m³/g), 0.12-0.18 (m³), respectively.

**Table 2. Elemental Concentration (weight %) of various Biochars**

<table>
<thead>
<tr>
<th>Biochar</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>O</th>
<th>Mg</th>
<th>P</th>
<th>Ca</th>
<th>Na</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>15.9</td>
<td>0.23</td>
<td>18.96</td>
<td>0.43</td>
<td>64.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>26.7</td>
<td>-</td>
<td>-</td>
<td>0.96</td>
<td>71.84</td>
<td>0.08</td>
<td>0.09</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>26.9</td>
<td>-</td>
<td>0.05</td>
<td>0.38</td>
<td>72.09</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>0.11</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Cow dung</td>
<td>23.1</td>
<td>0.04</td>
<td>-</td>
<td>0.20</td>
<td>72.39</td>
<td>0.11</td>
<td>0.04</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>26.5</td>
<td>5.37</td>
<td>-</td>
<td>-</td>
<td>70.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><em>Eichhornia</em></td>
<td>23.4</td>
<td>1.90</td>
<td>7.61</td>
<td>32.69</td>
<td>18.15</td>
<td>1.62</td>
<td>-</td>
<td>9.16</td>
<td>1.62</td>
<td>28.61</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3. Porosity of Different Biochars**

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Porosity (%)</th>
<th>Total Pore Volume (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Eichhornia</em></td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Cow dung</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>Rubber seed shell</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>Rice husk</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

**Rubber Seed shell**
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Rice husk

Cow dung

Eichhornia
The SEM analysis (Figure 3) shows the presence of micro-pores with a surface area of 750 - 1360 m²/g and a volume of 0.2-0.5 cm³/g and macro-pores with a surface area of 51 – 138 m²/g and a volume of 0.6-1.0 per g. Here the maximum porosity was achieved by coconut shell followed by coconut husk and Eichhornia. Coconut husk and Eichhornia biochars provided maximum pore volume. All these biochars are prepared under considerable temperature ranges of 350-400°C and this high temperature generally causes greater condensation of aromatic structures (Chan et al., 2007). Hence these chars expected to be more resistant to chemical oxidation and microbial degradation. Therefore a longer half life in soil environment than soil organic matter was also expected. NMR spectra reveals the presence of recalcitrant aromatic C functional group in all biochars prepared and this recalcitrance would be a desirable property if the primary goal was to remove atmospheric CO₂ and sequester carbon in soil for millennia (Harris et al., 1966). The ash content and residue of biochars contains different proportions of carbonates of alkali and alkaline earth metals, amounts of silica, heavy metals, sesquioxides, phosphates and small amounts of organic and inorganic N (Sharma et al., 1968) as observed in EDS spectra and this explains the preferable variation in the pH and CEC of different chars. The SEM images show the variations in the porous structure of morphology. These variations will result in different capacity to adsorb soluble inorganic matter, gases and inorganic nutrient and habitat suitability for microbes to colonize, grow and reproduce, particularly for bacteria (Sainju et al., 2006). The positive effect of biochar on SOC levels was expected due to their high carbon content and this content varies between biochars as observed in the elemental analysis and is greatly dependent on the feedstock properties.
The structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behaviour, function and fate in soils. Thus the characteristic features of the prepared biochars revealed their chemical, physical and morphological features. It can be inferred that certain factors like the nature of feed stock, pyrolysis temperature etc. determine these characteristic features and hence make every biochar distinct from each other. Based on these qualities, the nature of biochar on application to soil also differs. The fate of the biochar in the soil to a larger extent is determined by these basic characteristic features.

CONCLUSION

The data presented in the work showed that the type of feed stock strongly influenced the physicochemical properties of the biochar since there was no variation for the pyrolysing temperature. The structural and chemical composition of biochar is highly heterogeneous, with the exception of pH, which is typically > 7. Present study shows that the biochar derived from wet land weed Eichhornia plant and coconut shell were more suitable for soil application from a climate change mitigation perspective by considering the presence of aromatic carbon and also Si in addition to other soil fertility favouring parameters. Some properties are pervasive throughout all biochars, including the high C content and degree of aromaticity, partially explaining the high levels of biochar’s inherent recalcitrance. Nevertheless, the exact structural and chemical composition, including surface chemistry, is dependent on a combination of the feedstock type used. Dissimilarities in properties between different biochar products emphasize the need for a case-by-case evaluation of each biochar product prior to its incorporation into soil at a specific site.

REFERENCES


Rodriguez L, Salazar P, Preston TR. (2009). Effect of biochar and biodigester effluent on growth of...


