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<td>Author(s)</td>
<td>Chanaka Udayanga, Withanage Don; Veksha, Andrei; Giannis, Apostolos; Chang, Victor W.-C.; Lim, Teik-Thye</td>
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PHYSICOCHEMICAL TRANSFORMATION OF HEAVY METALS IN SLUDGE-BIOCHAR PRODUCED BY PYROLYSIS TREATMENT

W.D. CHANAKA UDAYANGA*, ANDREI VEKSHA°, APOSTOLOS GIANNIS°, VICTOR W.-C. CHANG** AND TEIK-THYE LIM***

*Nanyang Environment & Water Research Institute, Interdisciplinary Graduate School, Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141
°Residues & Resource Reclamation Centre, Nanyang Technological University, 1 Cleantech Loop, CleanTech One, Singapore 637141
**School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798
***Department of Civil Engineering, Monash University, VIC 3800, Australia

SUMMARY: Biochars (BCs) were produced by pyrolysis of dry sewage sludge (DSS) in order to stabilize the heavy metals (HMs). The physicochemical transformations of HMs were studied during pyrolysis at different temperatures (500-700 °C) in a fixed bed reactor. The produced BCs and DSS were introduced into combustion process at 950 °C. The HMs (Cu, Cr, Zn, Ni, As and Mn) were monitored to determine the influence of pyrolysis in terms of enrichment and leachability. Volatilisation tendencies of HMs (except for As) in pyrolysis process were minimal, while the leaching properties of the BCs were lower compared to DSS (except for Zn). After combustion of BCs and DSS, the produced ashes presented comparable HMs leaching and retention characteristics, except for As that had higher retention in the final ash coming from the direct combustion of DSS.

1. INTRODUCTION

Disposal of sewage sludge (SS) has taken considerable attention with modern environmental regulations which limit the use of conventional methods such as sanitary landfilling, fertilizer use etc. Many advantages over conventional handling of SS have driven rapid increase of the use of thermal technologies (Samolada and Zabaniotou, 2014; Cieślik et al., 2015). However, there are still many uncertainties, for instance, the fate of HMs during thermal processing. Among many thermal processes, pyrolysis has been identified as a promising method to retain HMs within the final matrix (BCs) with significant reduction of leaching (Devi and Saroha, 2014).

Recent studies in DSS pyrolysis have showed that pyrolysis could convert the vulnerable HMs leaching fraction to more stable fractions (Shao et al., 2015; Li et al., 2016). On the other hand, during incineration of SS, depending on the metal existing fraction, fate of the metals may vary (Liu et al., 2010). Hence, the conversion of HMs into more stable fractions could effectively change the volatilization and leaching of HMs. In this study, the influence of pyrolysis on HMs fate was investigated by introducing the DSS and BCs to combustion process. Six targeted HMs (Cu, Cr, Zn, Mn, Ni and As) were monitored to investigate the enrichment and leachability
characteristics.

2. MATERIAL AND METHODS

2.1 Material preparation

Anaerobically digested and mechanically dewatered SS was collected from Ulu Pandan water reclamation plant, Singapore. Prior to experiment, SS was dried at 105 °C in an oven at least for 24 h. DSS with particle sizes between 0.25-1.18 mm was prepared using ASTM standard sieves and stored in glass bottles in dry conditions.

2.2 Pyrolysis and combustion

Pyrolysis of DSS was conducted in a fixed bed vertical quartz reactor (Fig. 1).

Figure 1. Experimental setup.

50(±1) g of DSS were placed in the reactor and heated to the desired temperature at 10 °C.min⁻¹ maintaining N₂ purging at 500 mL.min⁻¹. Desired temperature was maintained for 1 h. Pyrolysis products (BCs) produced at temperatures of 500, 600 and 700 °C were labelled as BC500, BC600 and BC700, respectively. BC recovery yield was calculated as the ratio of produced BC weight to the weight of the DSS used.

Combustion of DSS and BC samples were carried out in a muffle furnace with a vent. The samples were placed in the furnace and heated to 950 °C at a ramping of 5 °C.min⁻¹ and maintained for 120 min at 950 °C. Ash sample from DSS, BC500, BC600 and BC700 labelled as ADSS, ABC500, ABC600 and ABC700, respectively. Yields of ash was calculated as the ratio of weight of the ash produced to the weight of the sample used.

2.3 Physicochemical characterization

Moisture and ash contents of samples were measured according to ASTM E1756-95 and ASTM D3174-02 respectively. pH values of the DSS, BCs and ashes were determined based on 1:10 (W/W) DI water suspension of samples after agitating for 24 h at 10 rpm.

Elemental analysis (CHNS) of samples was conducted using Vario EL cube (Elementar). Atomic H/C, O/C and (O+N)/C were calculated using elemental analysis results to determine the degree of aromaticity and polarity of DSS and BCs.
2.4 Relative enrichment and leaching of HMs

HMs concentration of the samples was measured by microwave digesting 0.1 g of sample with a mixture of HNO₃ and H₂O₂ (9:1) at 175 ± 5 °C. Digested samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS Thermo Fisher Scientific iCAP Q). Partitioning of HMs in the BCs and ashes were quantified using relative enrichment factor (REᵢ) as defined in equation (1).

\[
REᵢ = \frac{c_{RC}Y_{BC}}{c_{DSS}} \text{ or } \frac{c_{ASH}Y_{ASH}}{c_{DSS}}
\]

Where, CDSS, CBC and CASH represent the concentration of HMs in DSS, BCs and ashes while YBC and Yash represent the yield of BCs and ashes with respective to DSS used. REᵢ value which is close to 1 is a clear indication of enrichment of HMs with very low volatility, while lower values are indications of volatilization of HMs.

For the determination of HMs leaching characteristics (based on TCLP), 1:20 (W/W) suspension of extraction fluid 01 (pH~5) used (30 rpm for 18 h), after pre-investigation of sample pH (US-EPA, 1992). Filtered extractions, analysed using ICP-MS (Thermo Fisher Scientific iCAP Q). Fluctuations of HMs leaching in BCs and ashes with respective to DSS were quantified using relative leaching factor (RLᵢ) as defined in equation (2).

\[
RLᵢ = \frac{L_{DSS}}{L_{BC}} \text{ or } \frac{L_{DSS}}{L_{ASH}}
\]

Where L_DSS, L_BC and L_Ash represents the leaching of DSS, BCs and ashes, respectively. Positive RLᵢ indicates lower leaching compared to DSS while negative RLᵢ indicates higher leaching compared to DSS.

3. RESULTS AND DISCUSSION

3.1 Recoveries of BC and ash and physicochemical properties

Yields of BCs, ashes and ultimate ashes are presented in Fig. 2. With the increase of pyrolysis temperature, the yield of BCs produced decreased, as a result of feedstock decomposition and secondary reactions which may favour at higher temperatures(Shao et al., 2008). On the contrary, the yield of ash increased for the BCs generated at higher temperature. Even though BC and ash shown different yields, the ultimate ash amount generated with respective to DSS were similar indicating similar decomposition.
Table 1 presents the physical and elemental characterization of DSS and BCs on dry basis. Moisture content of the original sludge was around 83%. Ash contents of the BCs have doubled with compare to DSS.

Table 1. Physical and elemental composition of DSS and BCs (on dry basis)

<table>
<thead>
<tr>
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<th>Proximate (%)</th>
<th>Ultimate (%)</th>
<th>Molar ratios</th>
<th>pH</th>
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<tr>
<td></td>
<td>Ash</td>
<td>CB</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>DSS</td>
<td>24.9</td>
<td>75.1</td>
<td>37.5</td>
<td>5.6</td>
</tr>
<tr>
<td>BC500</td>
<td>50.7</td>
<td>49.3</td>
<td>32.0</td>
<td>2.0</td>
</tr>
<tr>
<td>BC600</td>
<td>54.2</td>
<td>45.8</td>
<td>32.7</td>
<td>1.5</td>
</tr>
<tr>
<td>BC700</td>
<td>57.0</td>
<td>43</td>
<td>33.0</td>
<td>1.2</td>
</tr>
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</table>

Combustible (CB) = 100 - Ash%; O = 100 - (C%+H%+N%+S%+Ash%)

At higher pyrolysis temperature, elemental compositions of BCs have decreased while keeping constant value for S%, whereas C% in BCs indicating an increasing trend with pyrolysis temperature as a result of losing H and O in higher temperature (Zielińska et al., 2015).

Molar ratios of BCs were lower than that of the DSS and trend was to decrease further with the carbonization temperature. Aromatic characteristics of the BCs were improved as the decreased of H/C ratio (Jin et al., 2016b, Zielińska et al., 2015). Dehydration of DSS in higher temperature made O/C and (O+N)/C ratios to decrease making less polar and hydrophobic surfaces on the BCs produced, also the removal of acidic functional groups from the surface attributed to pH changes in the produced BCs by enhancing the alkaline properties (Zielińska et al., 2015, Cantrell et al., 2012). CHNS analysis for ashes relieved that the intensities for each element were below the detection limit of the machine, indicating complete oxidization of DSS and BCs in the combustion process.

3.2 Relative enrichment and leaching of HMs

Fig. 3 presents the RE, for the BCs (a) and ashes (b). RE, for the HMs in BCs seems to be in the range of 0.8-1.2 except for As, implying higher retention of HMs in the pyrolysis process. In the case of ashes, for all the HMs (except for As in ADSS and Mn in all ashes) RE, have shown lower values irrespective of different RE, of BCs. Similar RE, for these HMs indicate similar fate irrespective of the pyrolysis treatment prior to combustion. As is known to volatilize at lower temperature (~200 °C) with the existence of organic compounds upon its chemical species (Van Wesenbeeck et al., 2014), hence, RE, of As had indicated lower value compare to other HMs in pyrolysis process. Higher RE, for As in direct combustion of DSS may be due to the ability of gas compounds of As to react with Fe, K, Na, Ca, Al and Mg compounds to make stable arsenates compound in oxidizing environments (Zhou et al., 2017).

Fig. 4 presents the RL, for the BCs (a) and ashes (b). In the case of BCs, positive RL, values were observed indicating lower leaching compare to DSS except for Zn, which had shown significant fluctuation in the leaching over the experimental temperature range. This ability of BCs to reduce leaching is previously reported by many researchers irrespective of the enrichment of the HMs (He et al., 2010, Devi and Saroha, 2014) and it is noted that this may due to the fact that BCs have higher pH as well as due to adsorptive capability with higher surface area. Also, the conversion of vulnerable fractions of HMs into more stable forms affected these changes (Jin et al., 2016a, Devi and Saroha, 2014). On the other hand, the ashes generated from DSS and BCs have shown similar RL, values irrespective of their leaching characteristics of the feedstock (except for As in ADSS) confirming the similar properties of HMs
compounds formed in ashes irrespective of the pyrolysis process. This lower RL value (except for Cu and As) for ashes may be attributed to the fact of existence of lower concentrations of HMs in ashes with volatilization and also with formation of more stable compounds as the pH of all the ashes were around 8 reducing the effect of pH on the HMs leaching.

![Image](image1.png)

**Figure 4.** TCLP leaching factors of BCs (a) and ashes (b).

4. CONCLUSION

Effect of stabilization of HMs via pyrolysis process was analysed by applying the produced BCs to combustion process. In this study, it is concluded that ultimate leaching and evaporation characteristics of HMs in final ashes were not significantly different from combustion process irrespective of prior pyrolysis process which had changed the stability of the HMs by enriching with lower leaching characteristics, except for As which tend to react with organic compounds and evaporate in pyrolysis process.
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REFERENCES


