CONVERSION OF SOLID WASTE TO ACTIVATED CARBON TO IMPROVE LANDFILL SUSTAINABILITY

A.O. Adelopo1*, P. I. Haris3, B. Alo2, K. Huddersman3, and R. O. Jenkins3

1Department of Works and Physical Planning, University of Lagos, Lagos, Nigeria
2Department of Chemistry, University of Lagos, Lagos, Nigeria
3Faculty of Health and Life Sciences, De Montfort University, The Gateway, Leicester LE1 9BH, UK

* Corresponding Author: aadelopo@unilag.edu.ng

Abstract

Landfills’ heterogeneous composites waste were evaluated as precursors for generation of activated carbon (AC). A single step chemical activation process was applied involving irradiation with microwave energy and impregnation with KOH. The average percentage yield of AC from active landfill precursor was higher than that from closed landfill for all depths sampled. Increase in impregnation ratio and irradiation power decreased the average percentage yield for both landfill precursors (Active: 38.1 to 33.1%) (Closed: 42.1: to 33.3%). The optimum pH range for adsorption of methylene blue was pH 6-7, while adsorption increased with increase in temperature over the range 30 to 50°C. Carbonyl and hydroxyl groups were the major functional groups on the surface of AC. The properties of the AC are potentially suitable for the removal of cationic dyes and pollutants. AC generated from the landfill composite were comparable to that from some other biomass being managed through AC generation. This is the first report to demonstrate the possible reuse of landfill composite as AC. The reuse option of landfill composite could provide a means of sustainable management of landfilled municipal waste.
Keywords: Adsorption capacity, Activated carbon, Landfill composites, Microwave heating

Introduction

Landfill remains a major means of solid waste management despite concerted efforts at reducing over reliance on this method of final waste disposal. There are hundreds of thousands of active, closed or abandoned landfills worldwide, with around 100,000 in the U.S., >150,000 in Europe and an overwhelming majority in developing countries (Butt et al., 2014). Sustainable management of the huge tonnage of landfill waste to prevent immediate and future environmental pollution remains a significant and pressing challenge. Reuse and recovery of landfill composite via enhanced mining of landfill sites has been suggested as an alternative option to reduce negative environmental impact (Kaartinen et al., 2013; Jain et al., 2014). Typically, 50 – 60% of excavated landfill waste are fine and intermediate components with limited reused options (Jain et al., 2014).

Recently, biomass wastes which are major constituents of some landfills have been identified as potential precursor for the production of activated carbon (AC) (Alslaibi et al., 2014, Septhupathi et al., 2015). A wide range of solid waste has been shown to be suitable for the production of AC, including plants (Tang et al., 2012, Islama et al., 2017), wood and sawdust (Fu and Hameed, 2012, Ali et al., 2012) and industrial sludge (Fu et al., 2013). Synthetic materials and papers have also been used as a precursor for the production of mesoporous activated carbon (Song et al., 2016, Nahil and Williams, 2012). Most developing countries have a high percentage of organic matter in their waste stream, ranging from 40 to 85% of the total waste, which is disposed mainly in the landfills (Hoornweg and Bhada-Tata, 2012). The International Panel on Climate Change (IPPC, 2006) estimates that organic waste constitutes 89 –
92% of waste generated in sub-Saharan Africa. Active and old (closed) landfills in Africa could therefore be a reservoir of potential precursor for AC. To the best of our knowledge, there are no published reports on the potential use of landfill composite waste as precursor for the production of AC.

The aim of the work presented here was to assess active and closed landfill composites as precursors for the production of AC in a single step chemical activation process involving KOH and microwave heating. A further aim was to evaluate the quality of AC produced with regards to the particle size and depth of precursor used, its chemical functionalities and adsorption mechanism for methylene blue.

Materials and methods

Sampling sites
Active and closed landfill sites (Olusosun and Abule Egba landfills respectively) located in the western and northern areas of Lagos, Nigeria, were used for this study. Both landfills have proximity to major commercial centres of the state. The closed landfill had received waste for 25 years and was closed in 2009. The active landfill has been in operation since 1992. Waste is disposed at both landfills with no pre-disposal treatment. Manual sorting of recyclable wastes are carried out at both landfill sites while organic or non-recyclable wastes are left to decompose. As at 2012, the composition of the landfill waste was evaluated as: vegetable 45%, paper 10%, glass 5%, plastic 15%, metal 5%, textile 4%, fine 8% and putrescible 8% (LAWMA, 2012)

Sampling
The landfill sites were systematically gridded into seven cells according to RCRA USEPA guidelines (USEPA, 2002a). A total of three samples were obtained from the top layer of each of the cell at upper (0-15cm), mid (16-35cm) and low (36-50cm)
depths. Approximately 500 g of sample was collected from each sampling point and stored in disinfected plastic containers.

Samples were dried in an oven at 105°C to a constant weight. The dried samples were separated by size and physical properties into composites of less degraded and more degraded components (more degraded <6.3mm, less degraded > 6.3mm). Each composite sample was crushed and homogenised using a ball-mill to obtain representative samples excluding metals. The composite were identified by landfill type, size and depth: Active landfill (A); closed landfill (C); more degraded (MD); less degraded (LD); upper depth (upper); mid depth (mid); lower depth (lower).

Sampling Profile

Sampling for this research was designed to evaluate the suitability of the first receptor layer (between 5 and 30 cm) of the landfills which reflect the early changes in the composition of the landfill waste. A Shallow landfill sampling covering the whole expand of the landfill was used to reveal the spatial-temporal nature of waste components within this landfill layer. A deeper depth in situ sampling was not considered because the intended use of the landfill component is for an ex situ conversion process which will be least affected by the immediate in situ conditions at the landfill. International Panel on Climate Change (IPCC) recommends the evaluation of the first layer landfill components for countries that lack data on the types and properties of solid waste before disposal like the sampled sites. A linear trend in the degraded components of waste and the sampling depth was observed in both active and closed landfills: with increasing depth the degraded component progressively decreased from 55.8% (w/w) to 43.5% (w/w) for active landfill, while the closed landfill degraded component increased from 58.6% (w/w) to 82.9% (w/w). The degraded component was higher in the closed landfill compared to the active landfill across the
depth. The less degraded had no definite trend with depth. A detailed waste component characterization across the sampling depth has previously been reported by Adelopo et al. (2017a).

**Precursor characterization**

The elemental and chemical characterization of the precursors had been carried-out using Scanning Electron Microscope/Energy-Dispersive X-ray spectroscopy SEM/EDX, Fourier transform-infrared (FTIR) spectroscopy and proximate analysis as reported in Adelopo et al. (2017b).

**Microwave modification**

A domestic microwave (LG Intellowave, model no. MB-382W/03) was modified for the activation process. The oven had a frequency rating of 2.5 GHz, regulators to control the exposure time between 1 to 60 min, and power wattage settings of 90, 180, 360, 600 and 800W. A quartz tube with internal diameter of 4cm and length 28cm was run vertically through the microwave area, with gas inlet and outlet at each end to pass gas from the bottom of the microwave to the top outlet duct.

**Activation preparation**

Samples were further homogenized using a mortar and pestle to an average particle size of 0.25mm. An aliquot (5g) of sample was impregnated with 5g of KOH dissolved in 10ml of distilled water. The mixture was agitated using a stirrer at 80 rpm for 1 hour, then dried in an oven at 105°C for 24 hours to attain a constant weight. An aliquot (2g) of the mixture was loaded into a sample holder (combustion tube) in the reactor fixed within the microwave cavity. Pure nitrogen gas (99.5%) was passed through the microwave cavity at a flow rate of 15cm³/sec for 1 minute to purge the oxygen, then the sample was irradiated for 10 minutes under the stream of nitrogen gas. The sample was allowed to cool while under nitrogen gas flow. Power input and the radiation time
were the major process parameters, which ranged from 600 to 800W and 10 minutes respectively.

The activated samples were washed with 5% HCl and then continuously washed with distilled water until the pH was within a neutral range (6-7). The activated sample was then dried in the oven at 105°C to a constant weight. The % yield was determined as:

\[
\text{% yield} = \left(\frac{\text{weight of precursor before activation} - \text{weight of precursor after activation}}{\text{weight of precursor before activation}}\right) \times 100
\]  

The reproducibility of yield was evaluated through duplicate activation of the precursor and the relative percentage difference (RPD) determined.

**Adsorption by AC**

Assessment of the adsorption capacity of AC samples was carried out using methylene blue (MB). A 25mg/l solution of MB in distilled water prepared from a 100mg/l stock solution. An aliquot (10ml) of the 25mg/l MB solution was added to 10mg of activated carbon. The mixture was agitated in a shaking water bath (Brunswick C76) at 200 rpm for two hours at 23°C. Supernatant solution (2ml) was removed by pipette after the solution was allowed to settle and MB concentration in the supernatant was determined by measuring absorbance at 664nm. The amount of adsorbed MB at equilibrium, \( q_e \) (mg/g), was calculated by:

\[
q_e = \left(\frac{C_0 - C_e}{W}\right)V \quad \text{Eq. (2)}
\]

Where \( C_0 \) and \( C_e \) (mg/l) is the initial and final concentrations of MB (mg/l) before and after equilibrium, respectively. \( V \) is the volume of the solution (l), and \( W \) is the mass of dry adsorbent used (g).

The experimental procedure described above was modified to investigate the effect of adsorbent dosage (10, 25 and 50mg), pH and temperature. The pH effect on
adsorption capacity was evaluated by adjusting the pH of the solution to 2-3 or 11-12, through the addition of 5% HCl or 0.1M of KOH respectively. The temperature effect on adsorption capacity was determined by varying the temperature in the Labline orbit environ shaker (model 3527) at 23°C, 30°C and 50°C. Adsorption capacity of the activated carbon at any other time, \( q_t \), during the analysis was determined according to Eq. 2.

**Characterization of AC**

Morphologies of AC samples were evaluated by Scanning Electron Microscopy (SEM), using a Carl Zeiss EVO HD15 instrument set at an accelerating voltage of 20 keV. Fourier transform-infrared (FTIR) spectroscopy was run on Bruker Alpha Attenuated Total Reflection-FTIR spectrophotometer with a frequency range of 4000–400 cm\(^{-1}\). Background correction of the spectrum was carried out prior to every measurement. The surface area and pore structure parameters of AC were obtained by nitrogen adsorption at 77.5 K using a Micromeritics Gemini 2365 surface area analyzer.

**Result and Discussion**

**Activation conditions, % yield**

Table 1 presents the activation conditions for each precursor, together with the associated yield and reproducibility for the AC produced. Reproducibility was assessed to determine whether the heterogeneous nature of the precursor affected the AC yield and its adsorption properties. At the same activation condition of 600 W and impregnation ratio of 1:1, the average yields of samples from active landfill were higher than from closed landfill for all sampling depths (upper, 23.8% and 19.3%; mid, 52.4% and 34.7%; lower, 35.7% and 27.0%). More degraded samples of the active landfill
showed better reproducibility of percentage yield (up to 18% RPD) compared to those more degraded sample of the closed landfill (up to 30% RPD).

For both active and closed landfills, the percentage yield did not show a definitive trend with depth. The pH of samples from both landfills samples were within the same narrow range, pH 6.2 - 7.1. These data indicated that under the same set of activation parameters the percentage yield of AC from the heterogeneous precursor used (landfill

<table>
<thead>
<tr>
<th>Samples names</th>
<th>% yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>RPD % yield of sample 1 and 2</th>
<th>% uptake of MB</th>
<th>Adsorption capacity&lt;sup&gt;b&lt;/sup&gt; (mg/g)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMD Upper</td>
<td>23.8</td>
<td>87</td>
<td>43.6</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>23.8</td>
<td>0</td>
<td>42.4</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>AMD Mid</td>
<td>57.1</td>
<td>66.5</td>
<td>33.3</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>47.6</td>
<td>18</td>
<td>82.5</td>
<td>41.3</td>
<td>6.5</td>
</tr>
<tr>
<td>AMD Lower</td>
<td>47.6</td>
<td>86</td>
<td>43</td>
<td>6.7</td>
<td>7.1</td>
</tr>
<tr>
<td>CMD Upper</td>
<td>30.8</td>
<td>77</td>
<td>38.3</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>50</td>
<td>29.5</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>CMD Mid</td>
<td>30.8</td>
<td>76.5</td>
<td>38.4</td>
<td>6.7</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>38.5</td>
<td>83.5</td>
<td>41.9</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>CMD Lower</td>
<td>38.5</td>
<td>87.5</td>
<td>43.6</td>
<td>6.2</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>15.4</td>
<td>88</td>
<td>43.9</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>ALD upper</td>
<td>57.1</td>
<td>86</td>
<td>43</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>ALD Mid</td>
<td>47.6</td>
<td>65</td>
<td>32</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>ALD Lower</td>
<td>47.6</td>
<td>32</td>
<td>16</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>CLD upper</td>
<td>34.6</td>
<td>87</td>
<td>43</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>CLD mid</td>
<td>15.4</td>
<td>51</td>
<td>26</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>CLD lower</td>
<td>23.8</td>
<td>78</td>
<td>39</td>
<td>6.8</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> activation conditions: power, 600W; impregnation ratio, 1:1; duration, 10mins
<sup>b</sup> adsorption capacity at 23°C, absorbent weight =50mg RPD: Relative Percent difference
composite) is fairly reproducible. Similar compositional trend of precursor may have influence the reproducibility.

Effect of irradiation power

The closed landfill yield of AC progressively decreased from 42.9% to 33.3% with increased irradiation power, while the active landfill precursors also had the lowest yield at the highest irradiation power (Table 2). The relatively low yields at 800 W may be attributed to increased gasification of precursor. During the activation process at 800 W, intense build-up of gaseous components within the reaction cavity was observed within the 1-5 seconds of exposure to microwave radiation. The process of precursor degradation, volatilization and decomposition is known to increase with rising microwave power (Foo and Hameed, 2012).
Table 2. AC yield with variations in wattage and impregnation ratio

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ma/Ms</th>
<th>Microwave power (W)</th>
<th>% yield</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD upper</td>
<td>1:1</td>
<td>360</td>
<td>38.1</td>
<td>6.6</td>
</tr>
<tr>
<td>ALD upper</td>
<td>1:1</td>
<td>600</td>
<td>57.1</td>
<td>6.4</td>
</tr>
<tr>
<td>ALD Upper</td>
<td>1:1</td>
<td>800</td>
<td>33.3</td>
<td>6.4</td>
</tr>
<tr>
<td>CLD upper</td>
<td>1:1</td>
<td>360</td>
<td>42.9</td>
<td>6.5</td>
</tr>
<tr>
<td>CLD upper</td>
<td>1:1</td>
<td>600</td>
<td>34.6</td>
<td>6.4</td>
</tr>
<tr>
<td>CLD upper</td>
<td>1:1</td>
<td>800</td>
<td>33.3</td>
<td>6.3</td>
</tr>
<tr>
<td>ALD upper</td>
<td>0.5:1</td>
<td></td>
<td>47.6\textsuperscript{a}</td>
<td>6.2</td>
</tr>
<tr>
<td>ALD upper</td>
<td>1:1</td>
<td></td>
<td>57.1</td>
<td>6.4</td>
</tr>
<tr>
<td>ALD upper</td>
<td>2:1</td>
<td></td>
<td>33.3</td>
<td>6.4</td>
</tr>
<tr>
<td>ALD upper</td>
<td>0.5:1</td>
<td></td>
<td>14.3</td>
<td>6.4</td>
</tr>
<tr>
<td>CLD upper</td>
<td>0.5:1</td>
<td></td>
<td>28.6</td>
<td>6.3</td>
</tr>
<tr>
<td>CLD upper</td>
<td>1:1</td>
<td></td>
<td>42.9</td>
<td>6.4</td>
</tr>
<tr>
<td>CLD upper</td>
<td>2:1</td>
<td></td>
<td>47.6\textsuperscript{a}</td>
<td>6.2</td>
</tr>
<tr>
<td>CLD upper</td>
<td>0.5:1</td>
<td></td>
<td>28.6</td>
<td>6.5</td>
</tr>
<tr>
<td>CMD upper</td>
<td>0.5:1</td>
<td></td>
<td>38.1</td>
<td>6.3</td>
</tr>
<tr>
<td>CMD upper</td>
<td>1:1</td>
<td></td>
<td>19</td>
<td>6.7</td>
</tr>
<tr>
<td>AMD upper</td>
<td>0.5:1</td>
<td></td>
<td>42.9</td>
<td>6.2</td>
</tr>
<tr>
<td>AMD upper</td>
<td>1:1</td>
<td></td>
<td>23.8</td>
<td>6.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} activation conditions: power, 600W; impregnation ratio, 1:1; duration, 10mins, C = closed landfill, MD = more degraded, A = active landfill, LD = less degraded, upper = upper depth, mid = mid depth, lower = lower depth
Activating agent impregnation ratio is an important parameter in a chemical activation process which influences both quantity and quality of the AC produced (Njoku et al., 2014; Ferrera-Lorenzo et al., 2014). A ratio of 0.5:1 was observed to be more suitable than 1:1 for more degraded sample, with yield enhancement from 19 to 38% and from 24 to 43% for the closed and active landfills respectively (Table 2). This suggests that the degraded nature of precursor, with increased surface area absorbed more activating agent. Conversely, for less degraded sample of both landfill, increase in impregnation ratio from 0.5:1 to 1:1 led to increase in percentage AC yield (active 47.6 to 57.1 %, closed 28.6 to 42.9%) (Table 2). Similarly, Foo and Hameed (2012a) observed that an increasing ratio of activation chemical reagent from 0.25- 1.25 for Mangosteen peel precursor increased yield of AC from 76.03 to 88.01%.

Characterization of AC

Scanning electron microscopy (SEM)

Typical SEM micrographs of precursors and obtained AC revealed distinct differences in surface area caused by microwave activation, with well-defined porosity distributed across the surface area of AC (Figure 1). The relationship between the nature of the pore formation and adsorption capacity could not be inferred from the microphotographs. An adsorption study on the AC was therefore carried out using MB.
Figure 1: SEM of typical precursor and its AC.
A and C: precursor and AC of less degraded active landfill lower sample
B and D: precursor and AC of more degraded active land lower sample
Adsorption studies

Effect of adsorbent quantity

Figure 2 shows the absorption capacity at 23°C of AC produced from precursor samples of each landfill. The adsorption capacities of the AC generally decreased with increase in weight of AC; 36 – 190 mg/g for 10 mg, 59-82mg/g for 25mg and 38- 45 mg/g for 50mg of the adsorbent. The decrease in adsorption capacity of AC could be due to the splitting effect in the flux (concentration gradient) between the adsorbate and adsorbent (Beekaroo and Mudhoo 2011). As the quantity of adsorbent increased from 10g to 50mg with MB concentration kept constant at 25mg/l, there would be an increase in the number of surface sites of adsorbent available for the adsorbate adhesion leading to lower number of adsorbate molecule per site.

Figure 2: Effect of Quantity of adsorbent on methylene blue adsorption capacity of absorbent.
The adsorption capacity of AC produced from less degraded active landfill decreased with depth (upper, 43mg/g; mid, 32mg/g; lower, 16mg/g), while that of the AC from more degraded precursor of closed landfill increases with depth (upper, 35mg/g; mid, 39mg/g; lower, 42mg/g), at 23°C using 50mg absorbent (Figure 2). This trend may reflect the elemental content of carbon in the precursor. The adsorption capability of 9 out of 12 of the AC followed the same trend as reported for elemental content of carbon in the elemental characterization studies of the precursors by Adelopo et al. (2017), i.e. active degraded, upper > mid > lower; closed degraded, lower > upper > mid. For both landfills, the average adsorption capacity AC from more degraded precursors was higher than that of AC from less degraded precursors (active landfill 42 and 30mg/g respectively; closed landfill 41 and 36mg/g respectively). This may be due to higher fixed carbon content in the more degraded samples than the less degraded samples; fixed carbon of a biomass represents the carbon content available for fuel and energy conversion (García et al., 2013).

Table 3 compares the optimum absorption capacity of the landfill precursor AC with AC generated from other biogenic waste. The optimum adsorption capacity of AC generated from both landfill using MB were higher than values reported for AC from oil palm and tea waste.
### Table 3: Comparison of the maximum adsorption capacities of MB onto different biogenic waste adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tea waste</td>
<td>85.16</td>
<td>Uddin et al. (2009)</td>
</tr>
<tr>
<td>Activated carbon from oil palm wood</td>
<td>90.9</td>
<td>Tamai et al. (1996)</td>
</tr>
<tr>
<td>black lignin liqour</td>
<td>92.51</td>
<td>Fu et al. (2013)</td>
</tr>
<tr>
<td>Mangosteen peel</td>
<td>345</td>
<td>Foo and Hameed (2012a)</td>
</tr>
<tr>
<td><strong>This study:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>closed landfill composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>activated carbon</td>
<td>More degraded</td>
<td>152</td>
</tr>
<tr>
<td>closed landfill composite</td>
<td>less degraded</td>
<td>101</td>
</tr>
<tr>
<td>activated carbon</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Temperature effect on adsorption

There was an increase in the percentage uptake of MB with increase in temperature from 30 to 50°C for all AC samples tested (Figure 3). However, only 60% of the AC samples indicated an increase in the percentage uptake of MB with increase in temperature from 23 to 30°C. The AC from more degraded precursor of active landfill (upper and lower layer) showed higher uptake of MB at 23°C than at 30°C. ANOVA statistical analysis was used to investigate if there was a significant difference in percentage MB uptake at each of the three temperatures: 23, 30 and 50°C. Taking landfill type (closed and active) and sample nature (more degraded and less degraded) as fixed factors, ANOVA analysis showed that there was no significant statistical difference ($p > 0.2$) in percentage MB uptake at each of the temperatures.

Figure 3: Effect of temperature on the uptake of MB (methylene blue)
N, Number of sample, t23, temperature at 23°C; t30, temperature at 30°C; t50, temperature at 50°C.

\textit{pH effect on adsorption}

The percentage uptake of MB onto the activated carbons was affected by solution pH. For all the AC investigated (6 samples), uptake of MB was found to be optimal at a solution pH within the range 6-7 (Figure 4). This is similar to the observation made by Gercel \textit{et al.} (2007) and Karago \textit{et al.} (2008) who observed an optimum adsorption of MB at the pH of 6 for AC produced from \textit{Euphorbia rigida} and Sunflower oil cake respectively. Solution pH and ionic strength are known to be major factors influencing the adsorption process in solution (Foo and Hameed, 2012; Njoku \textit{et al.}, 2014). Solution pH effect on adsorption capacity is controlled by the electrostatic interactions between charged surface of adsorbents and the adsorbates present in the solution (Foo and Hameed, 2012, Karago \textit{et al.} (2008), Moreno-Castilla, 2004).

In acidic medium, the AC would be neutral with –COOH groups while the MB would carry a positive charge and thus compete with H\textsuperscript{+} for AC sites. At neutral pH, the AC would become more negatively charged and consequently MB cation uptake on the adsorption site would increase. In the basic medium, the drop in adsorption capacity could have been due to electrostatic repulsion between OH\textsuperscript{−} in the medium and the -COO\textsuperscript{−} surface functional group of the adsorbent. At pH 11-12, the adsorption capacity of AC of more degraded active landfill precursor progressively decrease with depth from 114 mg/g -upper, 106mg/g-mid to 73mg/g –lower (Figure 4). There was no clear trend in MB adsorption with pH in relation with depth of sampling for other AC samples.
A total of 42 FTIR spectra of AC samples were analyzed to investigate the nature of functional groups common to the ACs. Major peaks located at 3320-3380, 1635-1694, 990-998, 770-779 and 699 cm\(^{-1}\) were prominent in most (8 of 12) of the AC samples. The peak at 3320-3380 cm\(^{-1}\) was identified as stretching vibration of hydroxyl group from alcohol or phenol (Ferrera-Lerenzo et al., 2014, Karago et al., 2008,). The carboxyl group represented by the 1635-1694 cm\(^{-1}\) peak was attributed C=C stretching vibration of olefins groups (Karago et al., 2008, Tran et al., 2017), while the peaks at 990-998, 779, and 699 cm\(^{-1}\) were ascribed to C-H out of plane bending of aliphatic groups (Karago et al., 2008, Suhas et al. 2007).

The FTIR spectra of the AC of both landfills showed significant changes in functional groups when compared to spectra of their respective precursors (Figure 5).
Prominent peaks at 3690 and 3619 cm\(^{-1}\) for the active landfill precursor, attributed to O–H vibration of clayey materials (possibly Si-OH), was absent in all AC samples of the landfill (Adelopo et al., 2017). This could be attributed to dehydroxylation of the OH group during activation. OH vibration of clayey material is known to become less stable with increase in temperature and can be oxidized to a carboxylic or aldehyde (Suhas et al., 2007).

The intense peaks at around 1030–3 and 1000–9 cm\(^{-1}\) attributed to silica, clay minerals (Si–O–Si and Si–O stretching vibration), which were present in the precursors of both landfill, is completely absent in AC of low and mid layers of the active landfill but not for the upper layer (Adelopo et al., 2017). In most (60%) of the closed landfill AC, however, these peaks were retained but were less intense. This suggests that the source of these peaks in AC differs for each landfill. The AC peaks for active landfill sample could be mainly from clay mineral (Si-OH), which is quite soluble in alkali solvent and less resistant to heat, while those of the AC from closed landfill could be largely due to Si-O-Si stretching of silica, which is more stable to heat. A very weak aliphatic methyl peak at 2980-4 cm\(^{-1}\) was found in 95% of AC samples from the closed landfill, but was absent in most AC of the active landfill. Other peaks at 1558- 1560 cm\(^{-1}\) were ascribed to C-O groups conjugated with aromatic rings (Foo et al., 2013). The peaks at 1440-12cm\(^{-1}\) were attributed to C–O–H in-plane bending of carboxylic carbon (Suhas et al., 2007) while those at 1340-1395cm\(^{-1}\) were ascribed to conjugated moieties of oxygen functional group of C=O stretching and C-O stretching in carboxylic group (Ji et al.,2007). The peaks located at 1165 and 874cm\(^{-1}\), attributed to C–O and C–H vibrations (Liou, 2010), were found in AC from both landfill types but were more prominent in the closed landfill than the active landfill.
Figure 5: Typical spectra of AC and precursor. (i) Active landfill AC, (ii) active landfill precursor, (a) closed landfill AC, (b) closed landfill precursor.
**Brunauer–Emmett–Teller (BET) surface analysis**

For both closed and active landfills, the surface area of AC from more degraded precursor samples increase with increase in depth of sampling (closed landfill, 72.53 to 132.51 m²/g; active landfill, 34.02, to 105.15 m²/g), whereas that from less degraded precursors had no definite depth relationship (see Table 4). The surface area of AC from more degraded closed landfill samples followed the same trend as the adsorption capacity of MB, i.e an increased with increase in depth of landfill sampling.

---

**Table 4: BET determined surface and pore surface areas of AC**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMD upper</td>
<td>72.53</td>
<td>5.8</td>
</tr>
<tr>
<td>CMD mid</td>
<td>86.07</td>
<td>3.85</td>
</tr>
<tr>
<td>CMD lower</td>
<td>132.51</td>
<td>5.19</td>
</tr>
<tr>
<td>AMD upper</td>
<td>34.02</td>
<td>7.49</td>
</tr>
<tr>
<td>AMD mid</td>
<td>38.08</td>
<td>1.38</td>
</tr>
<tr>
<td>AMD lower</td>
<td>105.15</td>
<td>ND</td>
</tr>
<tr>
<td>ALD upper</td>
<td>51.64</td>
<td>0.87</td>
</tr>
</tbody>
</table>
A further study of the pore distribution in three selected samples revealed the distribution of pore sizes, with most pores diameters of the AC within the range 2-5nm. This indicate that the ACs were principally mesopores. The ACs had average pore volumes of 0.160, 0.126 and 0.102 cm$^3$.

N$_2$ adsorption isotherms for AC samples are shown in Figure 6. The plots show that N$_2$ adsorption follows type II (Figures 6a and 6b) and type III (Figure 6c) IUPAC adsorption.
Figure 6: N\textsubscript{2} adsorption isotherms of AC from samples: (A) AC of closed landfill more degraded lower depth (B) AC of active landfill more degraded upper depth; (C) AC of active landfill less degraded sample upper depth.

Type II and III adsorption processes conform to the Freundlich adsorption model of unrestricted multilayer adsorption with the adsorbate-adsorbate interaction playing the major role (Sing et al., 1985). The hysteresis has a type H4 loop, which is attributed to narrow slit-like pores (Sing et al., 1985). The large Langmuir areas of AC (636, 466.1, 361.8 m\textsuperscript{2}/g) further strength the adsorption potential of the activated carbon. Hu et al. (2001) observed adsorption isothermal of type I and II for the AC from coconut shells as the ratio of activating agent impregnation increased.

Effect of degradation

A similar trend was observed in the properties of AC of more degraded precursors of both landfills compared to their less degraded precursors. AC from the more degraded samples had higher adsorption capacity and BET surface area than that from the less degraded samples (see Tables 1 and 4). Also, at equilibrium, the isothermal adsorption of MB onto AC for all degraded precursor conformed to the Fredulich’s model regardless of the landfill type. This could indicate the effect of degradation between the precursor used (less degraded vs more degraded) and the nature of the constituent waste.
Process scale-up potential

The potential scale up of activation process from landfill composite, could be conceptually considered a possibility with the robust reviews of economic, social and technological enhancement in landfill mining provided by pervious research. Frandegard et al., 2013, Danthurebandara et al., 2015, and Zhou et al., 2015, had identified and evaluated cost effective technologies preferred in harnessing the landfilled component which is the first challenge in the landfill activated carbon generation. According to Maria et al., 2013, a mechanical sorter having 2-3 dimensional outlets and near infrared selector scan can separate an average of 71,000 tonnes of landfilled municipal waste per year with 98% ferrous recovery potential. The screening process of the landfill composite waste for activated carbon could be modified in line with this preferred technology. The cost point here is inherent to all process of landfill mining for ex situ purpose.

Crushing and homogenizing of precursor is a major step in precursor treatment for all activation precursor types (Njoku et al. 2014, Islama et al., 2017). In this case, granular activation agent could be introduced during crushing at known ratio. High and low speed crusher have been successfully deployed by previous work for different landfill waste (Sua-iam and Makul, 2013, Shen et al., 2013). Similar crusher with desired mesh size could be suitable. On this basis, the process may not require any specialized equipment apart from the routine equipment used in activation process. However, an upgrade of some parts may be required.

Microwave energy source may be the major challenge for the scale–up process. Large scale application of microwave energy is quite limited due to the complexity of electromagnetic waves reflection and absorption in the microwave unit (Motasemi and Afzal 2013). Despite it numerous advantages, a full-scale application of the microwave-assisted activation processes is still been studied, and is a focus for our on-going research.
Conclusion

These research findings provide essential information on the potential use of municipal landfill composite as a precursor for AC generation and its MB adsorption capacity. The % yields of AC of between 7.7 - 57.1 % were mainly influenced by the type of landfill (active or closed), composite nature (more or less degraded), and activation parameters (wattage power and impregnation ratio). Carbonyl and hydroxyl groups were the major functional groups on the surface of AC. With an adsorption capacity of 34 – 190 mg/g for MB and Langmuir surface area of 361.8 -636m²/g, the AC could be used to adsorb a range of cationic dyes and pollutants. The properties of AC generated from the landfill composite are comparable with AC from some other biomass, such as oil palm stone and black liquor lignin, which have been identified as having potential of being sustainably managed by conversion to AC (Tamai et al. 1996; Fu et al., 2013)

• The landfill composites from both active and closed landfills represents a novel source of precursor for AC production and a new reuse option for landfill composite. It creates an opportunity for an integrated landfill resource management in which the AC generated could be deployed as landfill liner and/or leachate pond adsorbent.

• The adsorption capacity of the landfill composite AC suggests that its reuse as a daily landfill covering would curtail organic and inorganic mass transfer within the landfill layers via leaching. This could reduce the substantial cost of daily landfill covering, as well as the amount of virgin soil applied. The cost of daily landfill covering is estimated as 50% of the operational cost of municipal landfills (Johannessen and Boyer, 1997).

• The depth of both landfill composites significantly influenced both the adsorption capacity and surface area of the generated activated carbon, while age difference did not have a definite influence. A new research finding indicating a relationship between depth of landfill composite and the quality of AC produced. A limitation of the presently
reported results, as with most landfill parameters, is that they are dependent on the
type of waste disposed, climatic condition and the landfill management practice. It is
therefore difficult to generalize the findings for all landfill types.

- Further research on deep sampling, robust landfill mining strategy and activation
  conditions is required for this concept to have utility at the field-scale level.

References

Adelopo AO, Haris PI, Alo B, Huddersman K., Jenkins RO, (2017a) Seasonal variations
in moisture content and the distribution of total organic carbon in landfill composites:


