

1 **CONVERSION OF SOLID WASTE TO ACTIVATED CARBON TO IMPROVE LANDFILL SUSTAINABILITY**

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8 **Abstract**

9 Landfills' heterogeneous composites waste were evaluated as precursors for generation
10 of activated carbon (AC). A single step chemical activation process was applied involving
11 irradiation with microwave energy and impregnation with KOH. The average percentage
12 yield of AC from active landfill precursor was higher than that from closed landfill for all
13 depths sampled. Increase in impregnation ratio and irradiation power decreased the
14 average percentage yield for both landfill precursors (Active: 38.1 to 33.1%) (Closed
15 42.1: to 33.3%). The optimum pH range for adsorption of methylene blue was pH 6-7,
16 while adsorption increased with increase in temperature over the range 30 to 50°C.
17 Carbonyl and hydroxyl groups were the major functional groups on the surface of AC.
18 The properties of the AC are potentially suitable for the removal of cationic dyes and
19 pollutants. AC generated from the landfill composite were comparable to that from some
20 other biomass being managed through AC generation. This is the first report to
21 demonstrate the possible reuse of landfill composite as AC. The reuse option of landfill
22 composite could provide a means of sustainable management of landfilled municipal
23 waste.

24 **Keywords: Adsorption capacity, Activated carbon, Landfill composites, Microwave**
25 **heating**

26 **Introduction**

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

38 Recently, biomass wastes which are major constituents of some landfills have
39 been identified as potential precursor for the production of activated carbon (AC)
40 (Alslaibi *et al.*, 2014, Septhupathi *et al.*, 2015). A wide range of solid waste has been
41 shown to be suitable for the production of AC, including plants (Tang *et al.*, 2012,
42 Islama *et al.*, 2017), wood and sawdust (Fu and Hameed, 2012, Ali *et al.*, 2012) and
43 industrial sludge (Fu *et al.*, 2013). Synthetic materials and papers have also been used
44 as a precursor for the production of mesoporous activated carbon (Song *et al.*, 2016,
45 Nahil and Williams, 2012). Most developing countries have a high percentage of
46 organic matter in their waste stream, ranging from 40 to 85% of the total waste, which
47 is disposed mainly in the landfills (Hoornweg and Bhada-Tata, 2012). The International
48 Panel on Climate Change (IPPC, 2006) estimates that organic waste constitutes 89 –

49 92% of waste generated in sub-Saharan Africa. Active and old (closed) landfills in
50 Africa could therefore be a reservoir of potential precursor for AC. To the best of our
51 knowledge, there are no published reports on the potential use of landfill composite
52 waste as precursor for the production of AC.

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

58 **Materials and methods**

59 *Sampling sites*

60 Active and closed landfill sites (Olusosun and Abule Egba landfills respectively) located
61 in the western and northern areas of Lagos, Nigeria, were used for this study. Both
62 landfills have proximity to major commercial centres of the state. The closed landfill
63 had received waste for 25 years and was closed in 2009. The active landfill has been
64 in operation since 1992. Waste is disposed at both landfills with no pre-disposal
65 treatment. Manual sorting of recyclable wastes are carried out at both landfill sites
66 while organic or non-recyclable wastes are left to decompose. As at 2012, the
67 composition of the landfill waste was evaluated as: vegetable 45%, paper 10%, glass
68 5%, plastic 15%, metal 5%, textile 4%, fine 8% and putrescible 8% (LAWMA, 2012)

69 *Sampling*

70 The landfill sites were systematically gridded into seven cells according to RCRA
71 USEPA guidelines (USEPA, 2002a). A total of three samples were obtained from the
72 top layer of each of the cell at upper (0-15cm), mid (16-35cm) and low (36-50cm)

73 depths. Approximately 500 g of sample was collected from each sampling point and
74 stored in disinfected plastic containers.

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

82 Sampling Profile

83 Sampling for this research was designed to evaluate the suitability of the first receptor
84 layer (between 5 and 30 cm) of the landfills which reflect the early changes in the
85 composition of the landfill waste. A Shallow landfill sampling covering the whole
86 expand of the landfill was used to reveal the spatial-temporal nature of waste
87 components within this landfill layer. A deeper depth in situ sampling was not
88 considered because the intended use of the landfill component is for an ex situ
89 conversion process which will be least affected by the immediate in situ conditions at
90 the landfill. International Panel on Climate Change (IPCC) recommends the evaluation
91 of the first layer landfill components for countries that lack data on the types and
92 properties of solid waste before disposal like the sampled sites. A linear trend in the
93 degraded components of waste and the sampling depth was observed in both active
94 and closed landfills: with increasing depth the degraded component progressively
95 decreased from 55.8% (w/w) to 43.5% (w/w) for active landfill, while the closed landfill
96 degraded component increased from 58.6% (w/w) to 82.9% (w/w). The degraded
97 component was higher in the closed landfill compared to the active landfill across the

98 depth. The less degraded had no definite trend with depth. A detailed waste
99 component characterization across the sampling depth has previously been reported
100 by Adelopo et al. (2017a).

101 *Precursor characterization*

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

106 *Microwave modification*

107 A domestic microwave (LG Intellowave, model no. MB-382W/03) was modified for the
108 activation process. The oven had a frequency rating of 2.5 GHz, regulators to control
109 the exposure time between 1 to 60 min, and power wattage settings of 90, 180, 360,
110 600 and 800W. A quartz tube with internal diameter of 4cm and length 28cm was run
111 vertically through the microwave area, with gas inlet and outlet at each end to pass gas
112 from the bottom of the microwave to the top outlet duct.

113 *Activation preparation*

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

123 were the major process parameters, which ranged from 600 to 800W and 10 minutes
124 respectively.

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

$$129 \quad \% \text{ yield} = \frac{(\text{weight of precursor before activation} - \text{weight of precursor after activation})}{\text{Weight of precursor before activation}} \times 100 \quad \text{Eq. (1)}$$

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

134 *Adsorption by AC*

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

$$143 \quad q_e = \frac{(C_o - C_e)V}{W} \quad \text{Eq. (2)}$$

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

148 The experimental procedure described above was modified to investigate the
149 effect of adsorbent dosage (10, 25 and 50mg), pH and temperature. The pH effect on

150 adsorption capacity was evaluated by adjusting the pH of the solution to 2-3 or 11-12,
151 through the addition of 5% HCl or 0.1M of KOH respectively. The temperature effect on
152 adsorption capacity was determined by varying the temperature in the Labline orbit
153 environ shaker (model 3527) at 23°C, 30°C and 50°C. Adsorption capacity of the
154 activated carbon at any other time, (Q_t), during the analysis was determined according
155 to Eq. 2.

156 *Characterization of AC*

157 Morphologies of AC samples were evaluated by Scanning Electron Microscopy (SEM),
158 using a Carl Zeiss EVO HD15 instrument set at an accelerating voltage of 20 keV.

159 Fourier transform-infrared (FTIR) spectroscopy was run on Bruker Alpha Attenuated
160 Total Reflection-FTIR spectrophotometer with a frequency range of 4000–400 cm^{-1} .

161 Background correction of the spectrum was carried out prior to every measurement.

162 The surface area and pore structure parameters of AC were obtained by nitrogen
163 adsorption at 77.5 K using a Micromeritics Gemini 2365 surface area analyzer.

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165 **Result and Discussion**

166 *Activation conditions, % yield*

167 Table 1 presents the activation conditions for each precursor, together with the
168 associated yield and reproducibility for the AC produced. Reproducibility was assessed
169 to determine whether the heterogeneous nature of the precursor affected the AC yield
170 and its adsorption properties. At the same activation condition of 600 W and
171 impregnation ratio of 1:1, the average yields of samples from active landfill were higher
172 than from closed landfill for all sampling depths (upper, 23.8% and 19.3%; mid, 52.4%
173 and 34.7%; lower, 35.7% and 27.0%). More degraded samples of the active landfill

174 showed better reproducibility of percentage yield (up to 18% RPD) compared to those
 175 more degraded sample of the closed landfill (up to 30% RPD).

Table 1 : AC yield, reproducibility and adsorption capacity with depth

Samples		Reproducibility				pH
Samples names		% yield ^a	RPD %yield of sample 1 and 2	% uptake of MB	Adsorption capacity ^b (mg/g)	
AMD Upper	1	23.8		87	43.6	6.2
	2	23.8	0	84.5	42.4	6.3
AMD Mid	1	57.1		66.5	33.3	6.4
	2	47.6	18	82.5	41.3	6.5
AMD Lower	1	47.6		86	43	6.7
	2	23.8	17	87	43.4	7.1
CMD Upper	1	30.8		77	38.3	6.7
	2	7.7	30	59	29.5	6.8
CMD Mid	1	30.8		76.5	38.4	6.7
	2	38.5	5	83.5	41.9	6.9
CMD Lower	1	38.5		87.5	43.6	6.2
	2	15.4	21	88	43.9	6.5
ALD upper		57.1		86	43	6.4
ALD Mid		47.6		65	32	6.4
ALD Lower		47.6		32	16	6.4
CLD upper		34.6		87	43	6.4
CLD mid		15.4		51	26	6.9
CLD lower		23.8		78	39	6.8

^a activation conditions: power, 600W; impregnation ratio, 1:1; duration, 10mins

^b adsorption capacity at 23°C, absorbent weight =50mg RPD: Relative Percent difference

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

181 composite) is fairly reproducible. Similar compositional trend of precursor may have
182 influence the reproducibility.

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184 Effect of irradiation power

185 The closed landfill yield of AC progressively decreased from 42.9% to 33.3% with
186 increased irradiation power, while the active landfill precursors also had the lowest
187 yield at the highest irradiation power (Table 2). The relatively low yields at 800 W may
188 be attributed to increased gasification of precursor. During the activation process at
189 800 W, intense build-up of gaseous components within the reaction cavity was
190 observed within the 1-5 seconds of exposure to microwave radiation. The process of
191 precursor degradation, volatilization and decomposition is known to increase with rising
192 microwave power (Foo and Hameed, 2012)

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Table 2. AC yield with variations in wattage and impregnation ratio

Samples	Ma/Ms	Microwave power (W)	% yield	pH
ALD upper	1:1	360	38.1	6.6
ALD upper	1:1	600	57.1	6.4
ALD Upper	1:1	800	33.3	6.4
CLD upper	1:1	360	42.9	6.5
CLD upper	1:1	600	34.6	6.4
CLD upper	1:1	800	33.3	6.3
ALD upper	0.5:1		47.6 ^a	6.2
ALDupper	1:1		57.1	6.4
ALD upper	2:1		33.3	6.4
ALD upper	0.5:1		14.3	6.4
CLD upper	0.5:1		28.6	6.3
CLD upper	1:1	a	42.9	6.4
CLD upper	2:1		47.6	6.2
CLD upper	0.5 : 1		28.6	6.5
CMD upper	0.5:1		38.1	6.3
CMD upper	1:1		19	6.7
AMD upper	0.5:1		42.9	6.2
AMD upper	1:1		23.8	6.2

^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

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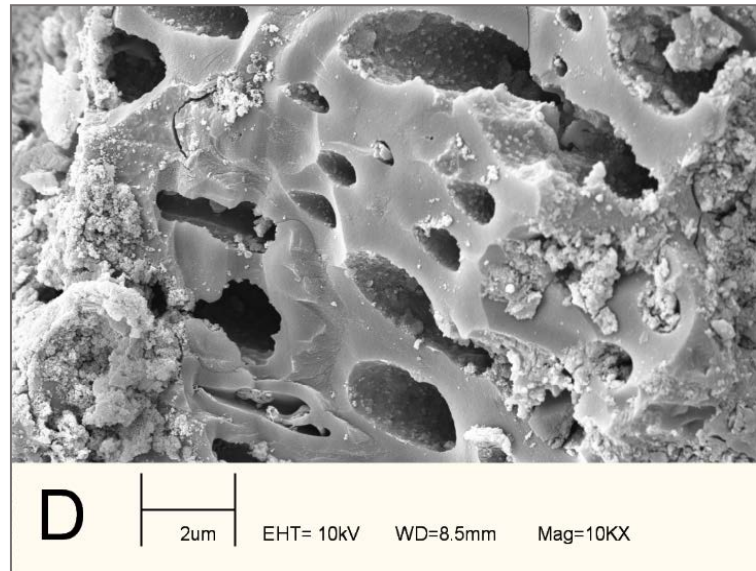
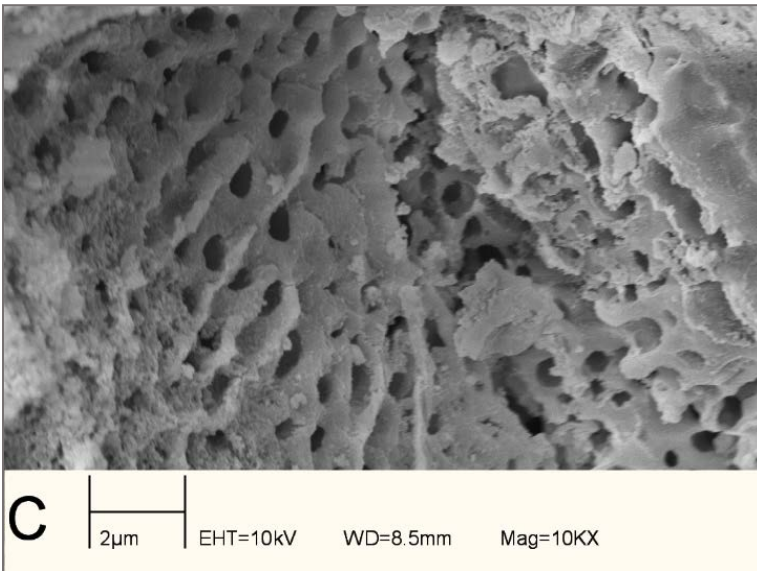
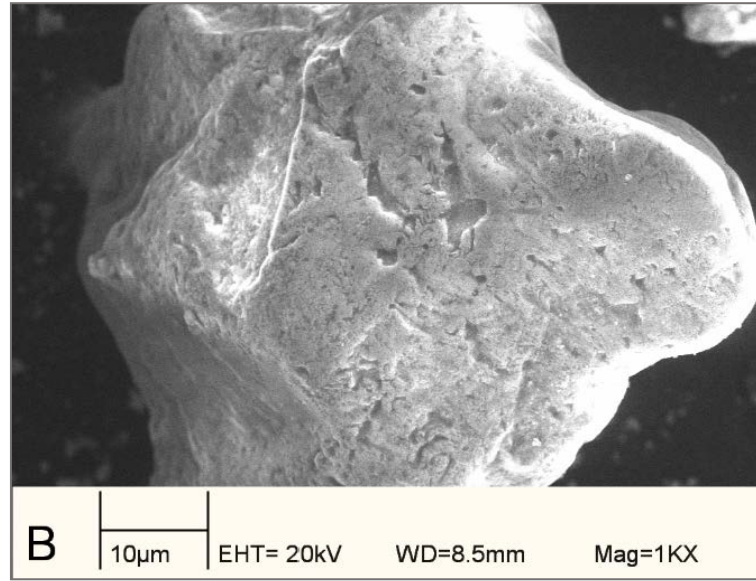
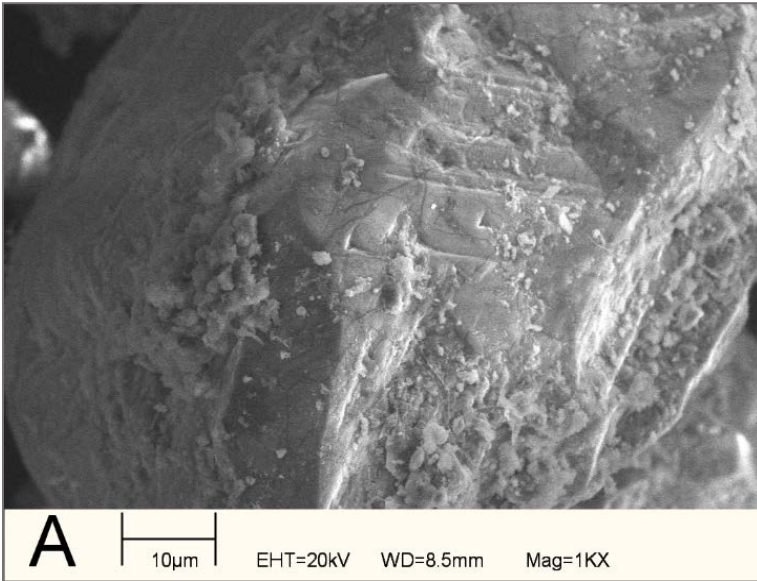
222 Activating agent impregnation ratio is an important parameter in a chemical
223 activation process which influences both quantity and quality of the AC produced
224 (Njoku *et al.*, 2014; Ferrera-Lorenzo *et al.*, 2014). A ratio of 0.5:1 was observed to be
225 more suitable than 1:1 for more degraded sample, with yield enhancement from 19 to
226 38% and from 24 to 43% for the closed and active landfills respectively (Table 2). This
227 suggests that the degraded nature of precursor, with increased surface area absorbed
228 more activating agent. Conversely, for less degraded sample of both landfill, increase
229 in impregnation ratio from 0.5:1 to 1:1 led to increase in percentage AC yield (active
230 47.6 to 57.1 %, closed 28.6 to 42.9%) (Table 2). Similarly, Foo and Hameed (2012a)
231 observed that an increasing ratio of activation chemical reagent from 0.25- 1.25 for
232 Mangosteen peel precursor increased yield of AC from 76.03 to 88.01%.

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234 Characterization of AC

235 Scanning electron microscopy (SEM)

236 Typical SEM micrographs of precursors and obtained AC revealed distinct differences
237 in surface area caused by microwave activation, with well-defined porosity distributed
238 across the surface area of AC (Figure 1). The relationship between the nature of the
239 pore formation and adsorption capacity could not be inferred from the
240 microphotographs. An adsorption study on the AC was therefore carried out using MB.



242 **Figure 1: SEM of typical precursor and its AC.**
243 A and C: precursor and AC of less degraded active landfill lower sample
244 B and D: precursor and AC of more degraded active land lower sample

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250 Adsorption studies

251 Effect of adsorbent quantity

252 Figure 2 shows the absorption capacity at 23°C of AC produced from precursor

253 samples of each landfill. The adsorption capacities of the AC generally decreased with

254 increase in weight of AC; 36 – 190 mg/g for 10 mg, 59-82mg/g for 25mg and 38- 45

255 mg/g for 50mg of the adsorbent. The decrease in adsorption capacity of AC could be

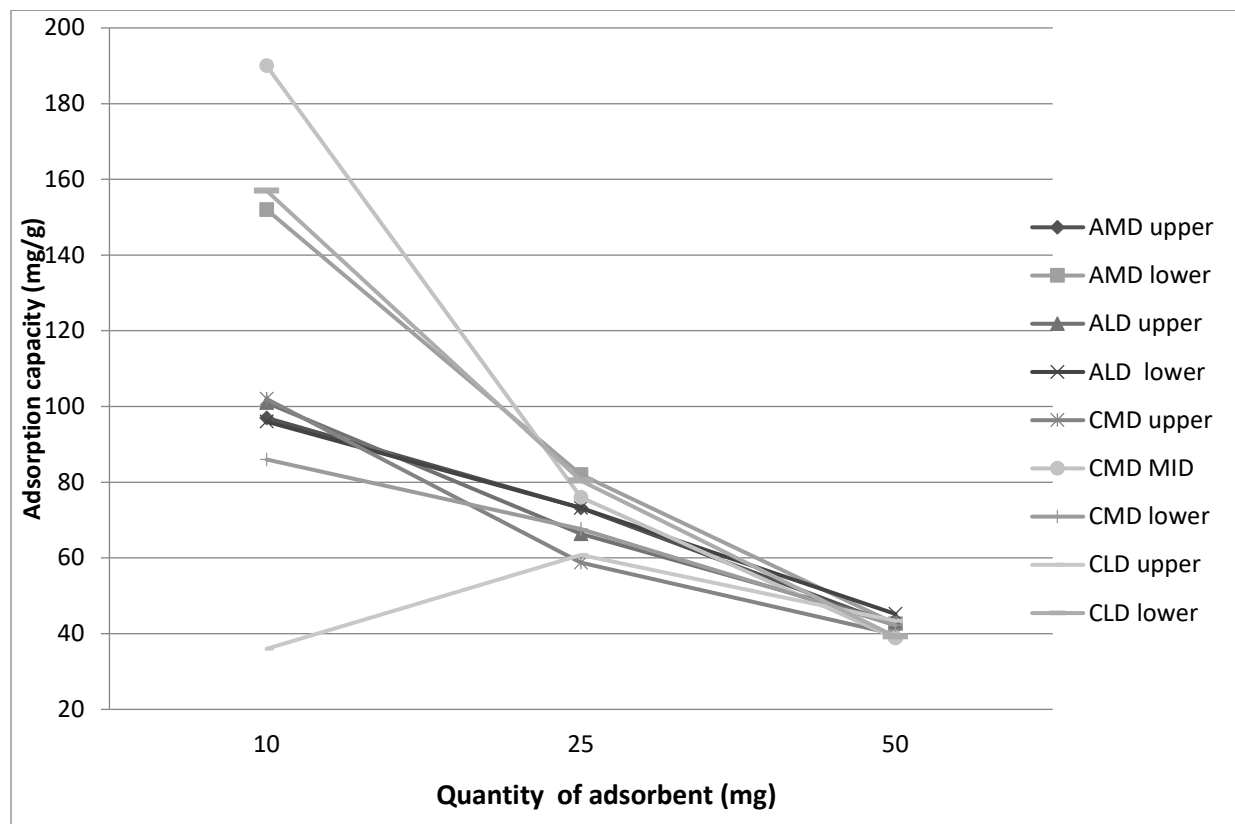
256 due to the splitting effect in the flux (concentration gradient) between the adsorbate

257 and adsorbent (Beekaroo and Mudhoo 2011). As the quantity of adsorbent increased

258 from 10g to 50mg with MB concentration kept constant at 25mg/l, there would be an

259 increase in the number of surface sites of adsorbent available for the adsorbate

260 adhesion leading to lower number of adsorbate molecule per site.



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262 **Figure 2: Effect of Quantity of adsorbent on methylene blue adsorption capacity**
263 **of adsorbent.**
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Adsorption capacity of AC with depth of precursor sampling

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.

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Table 3: Comparison of the maximum adsorption capacities of MB onto different biogenic waste adsorbents.

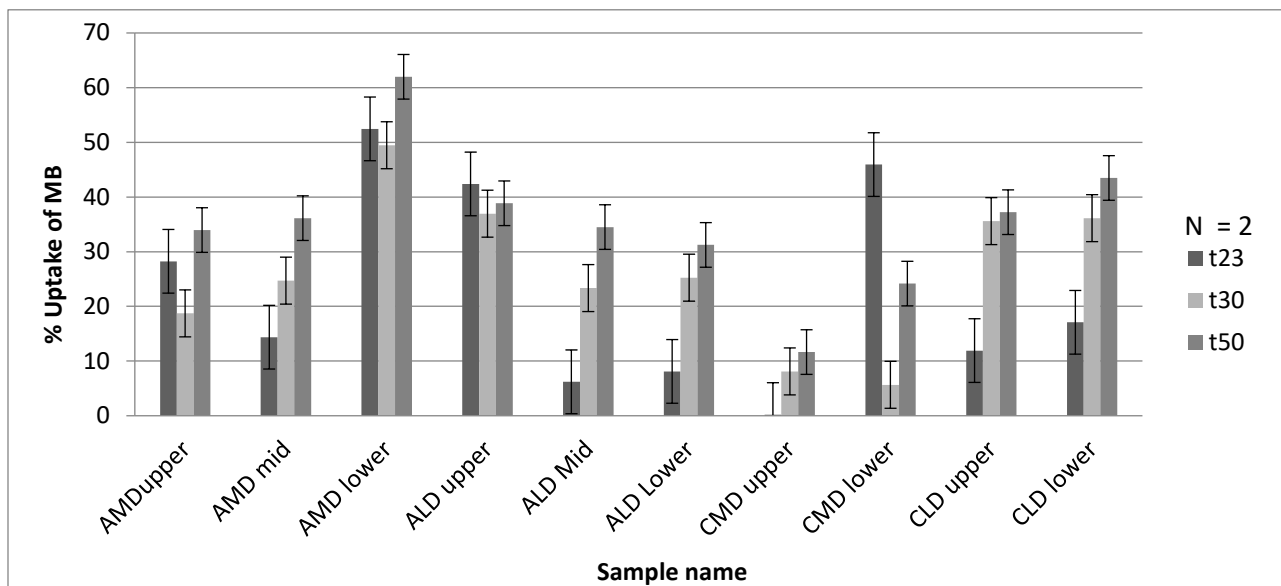
Adsorbents	Adsorption capacity (mg/g)	ref.
Coconut husk based activated carbon	66	Prauchner and Rodríguez-Reinoso, (2012)
Tea waste	85.16	Uddin <i>et al.</i> (2009)
Activated carbon from oil palm wood	90.9	Tamai <i>et al.</i> (1996)
black lignin liquor	92.51	Fu <i>et al.</i> (2013)
Mangosteen peel	345	Foo and Hameed (2012a)
This study: closed landfill composite activated carbon	More degraded	152
closed landfill composite activated carbon	less degraded	101

active landfill composite activated carbon	More degraded	190
	less degraded	157

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303 *Temperature effect on adsorption*

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



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315 **Figure 3: Effect of temperature on the uptake of MB (methylene blue)**

316 N, Number of sample, t23, temperature at 23°C; t30, temperature at 30°C;
317 t50, temperature at 50°C.

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319 *pH effect on adsorption*

320 The percentage uptake of MB onto the activated carbons was affected by solution pH.

321 For all the AC investigated (6 samples), uptake of MB was found to be optimal at a

322 solution pH within the range 6-7 (Figure 4). This is similar to the observation made by

323 Gercel *et al.* (2007) and Karago *et al.* (2008) who observed an optimum adsorption of

324 MB at the pH of 6 for AC produced from *Euphorbia rigida* and Sunflower oil cake

325 respectively. Solution pH and ionic strength are known to be major factors influencing

326 the adsorption process in solution (Foo and Hameed, 2012; Njoku *et al.*, 2014).

327 Solution pH effect on adsorption capacity is controlled by the electrostatic interactions

328 between charged surface of adsorbents and the adsorbates present in the solution

329 (Foo and Hameed, 2012, Karago *et al.* (2008), Moreno-Castilla, 2004).

330 In acidic medium, the AC would be neutral with –COOH groups while the MB would

331 carry a positive charge and thus compete with H⁺ for AC sites. At neutral pH, the AC

332 would become more negatively charged and consequently MB cation uptake on the

333 adsorption site would increase. In the basic medium, the drop in adsorption capacity

334 could have been due to electrostatic repulsion between OH⁻ in the medium and the -

335 COO⁻ surface functional group of the adsorbent. At pH 11-12, the adsorption capacity

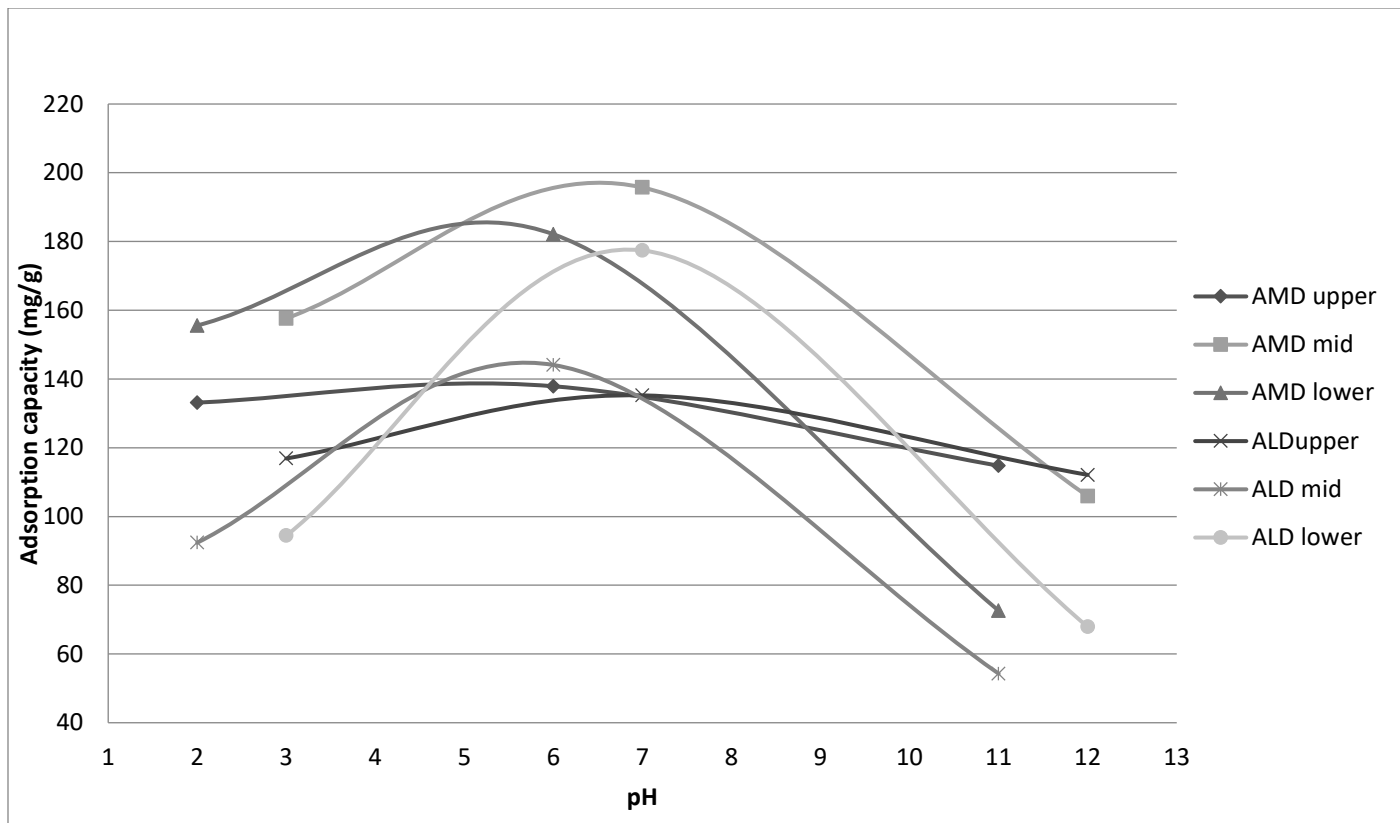
336 of AC of more degraded active landfill precursor progressively decrease with depth

337 from 114 mg/g -upper, 106mg/g-mid to 73mg/g –lower (Figure 4). There was no clear

338 trend in MB adsorption with pH in relation with depth of sampling for other AC samples.

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342 **Figure 4: Effect of pH on the adsorption capacity of AC**

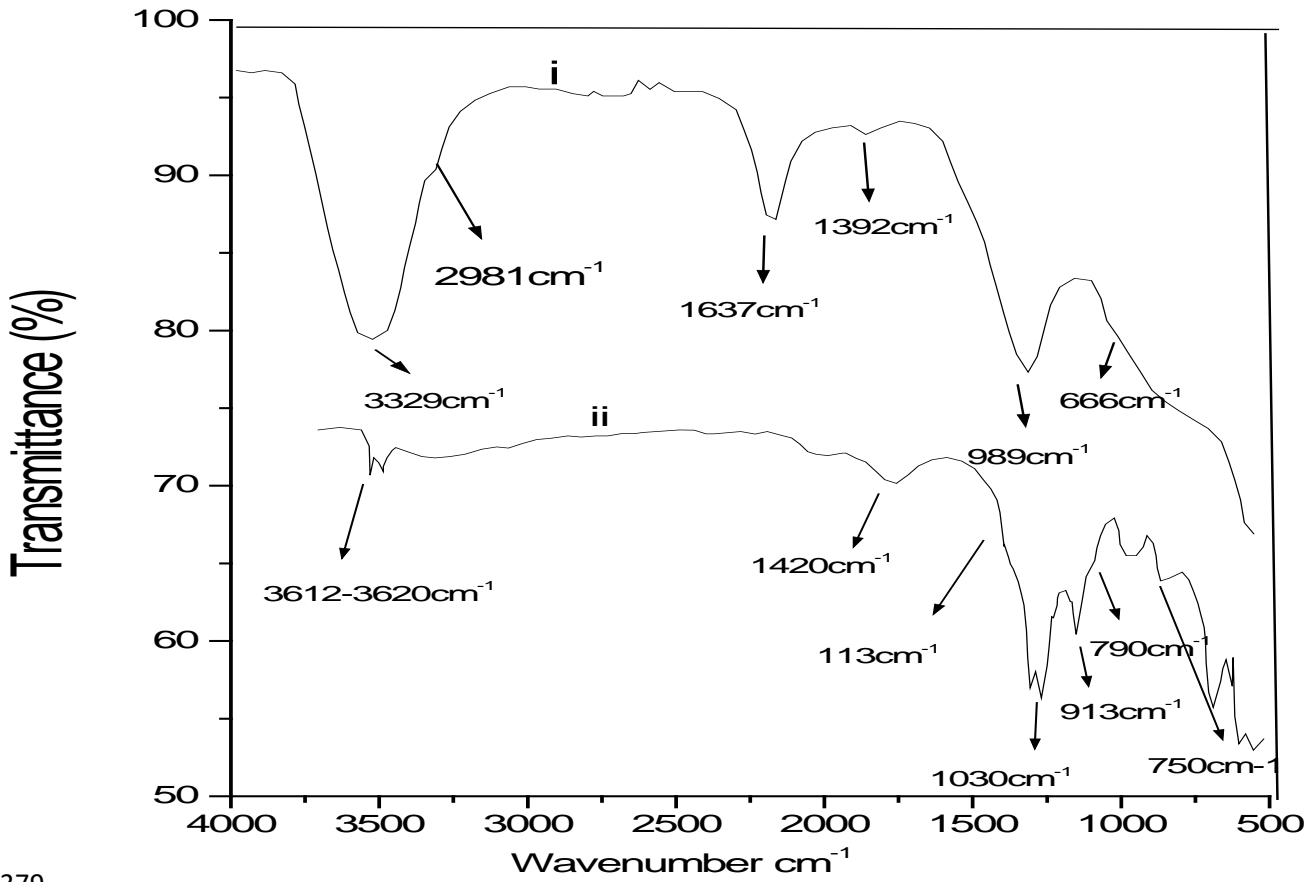
343 A total of 42 FTIR spectra of AC samples were analyzed to investigate the nature of
 344 functional groups common to the ACs. Major peaks located at 3320-3380, 1635-1694,
 345 990-998, 770-779 and 699cm⁻¹ were prominent in most (8 of 12) of the AC samples.
 346 The peak at 3320-3380cm⁻¹ was identified as stretching vibration of hydroxyl group
 347 from alcohol or phenol (Ferrera-Lorenzo *et al.*, 2014, Karago *et al.*, 2008,). The
 348 carboxyl group represented by the 1635-1694cm⁻¹ peak was attributed C=C stretching
 349 vibration of olefins groups (Karago *et al.*, 2008, Tran et el.,2017), while the peaks at
 350 990-998, 779, and 699cm⁻¹ were ascribed to C-H out of plane bending of aliphatic
 351 groups (Karago *et al.*, 2008, Suhas et al. 2007).

352 The FTIR spectra of the AC of both landfills showed significant changes in
 353 functional groups when compared to spectra of their respective precursors (Figure 5).

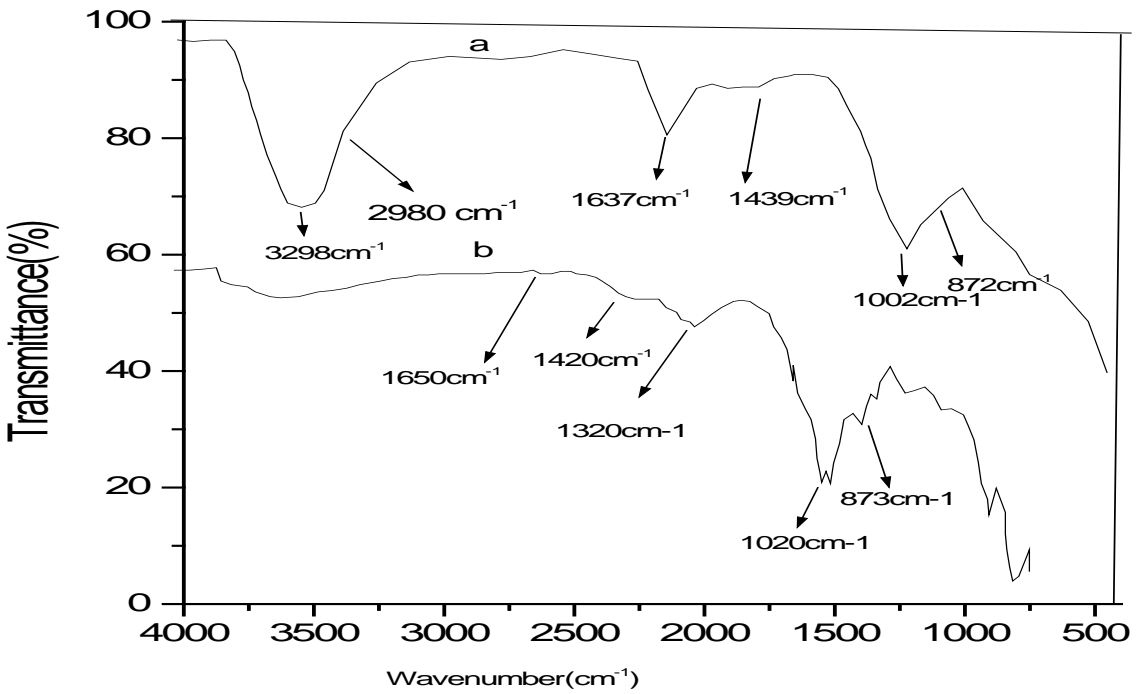
354 Prominent peaks at 3690 and 3619 cm^{-1} for the active landfill precursor, attributed to O–
355 H vibration of clayey materials (possibly Si-OH), was absent in all AC samples of the
356 landfill (Adelopo *et al.*, 2017). This could be attributed to dehydroxylation of the OH group
357 during activation. OH vibration of clayey material is known to become less stable with
358 increase in temperature and can be oxidized to a carboxylic or aldehyde (Suhas *et al.*,
359 2007).

360 The intense peaks at around 1030–3 and 1000–9 cm^{-1} attributed to silica, clay
361 minerals (Si–O–Si and Si–O stretching vibration), which were present in the precursors
362 of both landfill, is completely absent in AC of low and mid layers of the active landfill
363 but not for the upper layer (Adelopo *et al.*, 2017). In most (60%) of the closed landfill
364 AC, however, these peaks were retained but were less intense. This suggests that the
365 source of these peaks in AC differs for each landfill. The AC peaks for active landfill
366 sample could be mainly from clay mineral (Si-OH), which is quite soluble in alkali
367 solvent and less resistant to heat, while those of the AC from closed landfill could be
368 largely due to Si-O-Si stretching of silica, which is more stable to heat. A very weak
369 aliphatic methyl peak at 2980-4 cm^{-1} was found in 95% of AC samples from the closed
370 landfill, but was absent in most AC of the active landfill. Other peaks at 1558- 1560
371 cm^{-1} were ascribed to C-O groups conjugated with aromatic rings (Foo *et al.*, 2013).
372 The peaks at 1440-12 cm^{-1} were attributed to C–O–H in-plane bending of carboxylic
373 carbon (Suhas *et al.*, 2007) while those at 1340-1395 cm^{-1} were ascribed to conjugated
374 moieties of oxygen functional group of C=O stretching and C-O stretching in carboxylic
375 group (Ji *et al.*, 2007). The peaks located at 1165 and 874 cm^{-1} , attributed to C–O and
376 C–H vibrations (Liou, 2010), were found in AC from both landfill types but were more
377 prominent in the closed landfill than the active landfill.

378



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380

381 **Figure 5: Typical spectra of AC and precursor.** (i) Active landfill AC, (ii) active
 382 landfill precursor, (a) closed landfill AC, (b) closed landfill precursor.

383

384 *Brunauer–Emmett–Teller (BET) surface analysis*

385 For both closed and active landfills, the surface area of AC from more degraded
386 precursor samples increase with increase in depth of sampling (closed landfill, 72.53 to
387 132.51 m²/g; active landfill, 34.02, to 105.15 m²/g), whereas that from less degraded
388 precursors had no definite depth relationship (see Table 4). The surface area of AC
389 from more degraded closed landfill samples followed the same trend as the adsorption
390 capacity of MB, i.e an increased with increase in depth of landfill sampling.

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

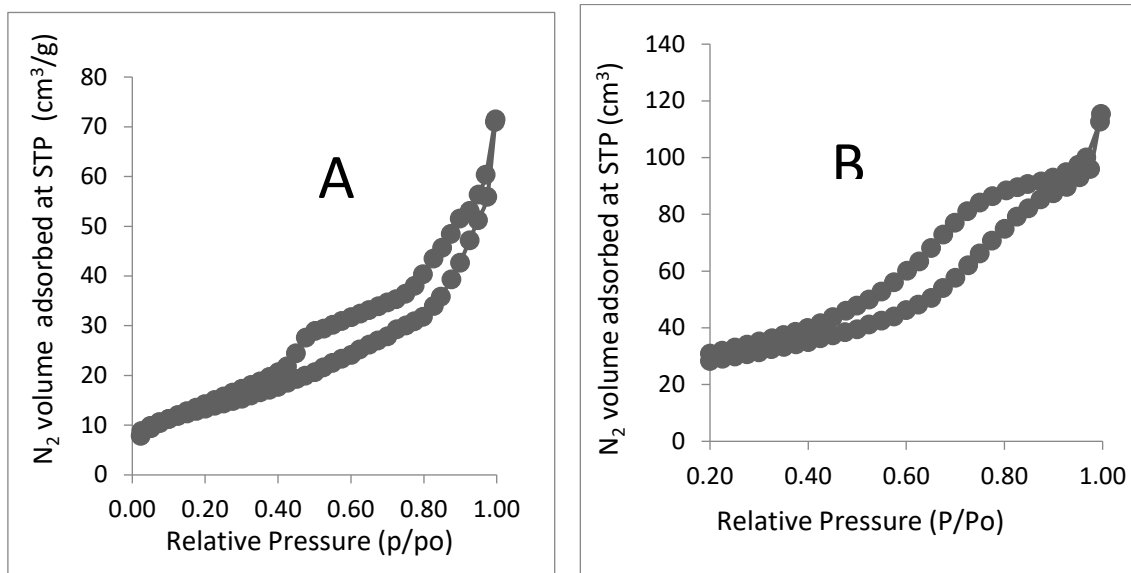
Sample	BET surface area (m ² /g)	Pore surface area(m ² /g)
CMDupper	72.53	5.8
CMD mid	86.07	3.85
CMD lower	132.51	5.19
AMD upper	34.02	7.49
AMDmid	38.08	1.38
AMD lower	105.15	ND
ALD upper	51.64	0.87

ALD lower	92.89	11.33
CLD upper	31.75	2.58
CLD mid	89.33	4.59

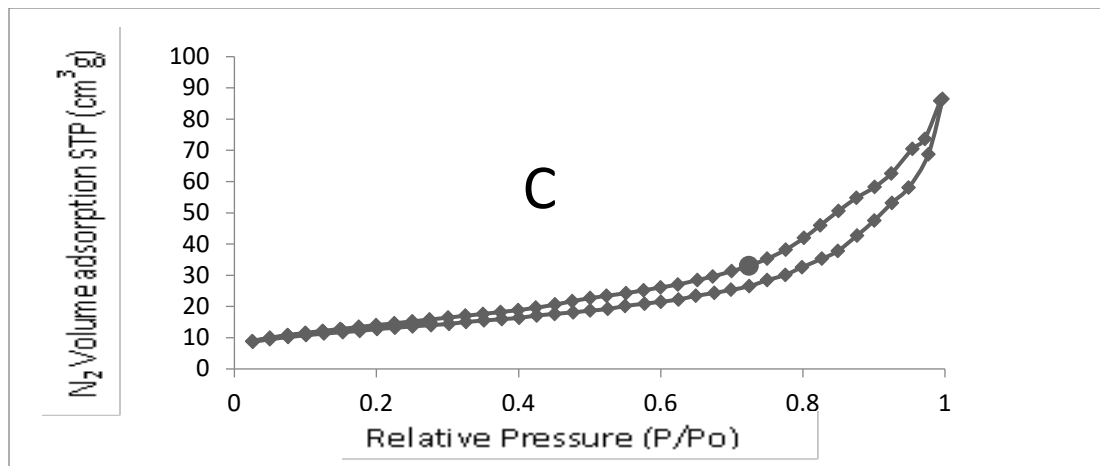
395 *ND: not determined

396 A further study of the pore distribution in three selected samples revealed the distribution
 397 of pore sizes, with most pores diameters of the AC within the range 2-5nm. This indicate
 398 that the ACs were principally mesopores. The ACs had average pore volumes of 0.160,
 399 0.126 and 0.102 cm³.

400 N₂ adsorption isotherms for AC samples are shown in Figure 6. The plots show that N₂
 401 adsorption follows type II (Figures 6a and 6b) and type III (Figure 6c) IUPAC
 402 adsorption



403



404

405 **Figure 6 : N₂ adsorption isotherms of AC from samples:** (A) AC of closed landfill
 406 more degraded lower depth (B) AC of active landfill more degraded upper depth; (C)
 407 AC of active landfill less degraded sample upper depth.

408 Type II and III adsorption processes conform to the Freundlich adsorption model of
 409 unrestricted multilayer adsorption with the adsorbate-adsorbate interaction playing the
 410 major role (Sing *et al.*, 1985). The hysteresis has a type H4 loop, which is attributed to
 411 narrow slit-like pores (Sing *et al.*, 1985). The large Langmuir areas of AC (636, 466.1,
 412 361.8 m²/g) further strength the adsorption potential of the activated carbon. Hu *et al.*
 413 (2001) observed adsorption isothermal of type I and II for the AC from coconut shells
 414 as the ratio of activating agent impregnation increased.

415 Effect of degradation

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

423

424 Process scale-up potential

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

437

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

446

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

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456 **Conclusion**

457 These research findings provide essential information on the potential use of municipal
458 landfill composite as a precursor for AC generation and its MB adsorption capacity. The
459 % yields of AC of between 7.7 - 57.1 % were mainly influenced by the type of landfill
460 (active or closed), composite nature (more or less degraded), and activation parameters
461 (wattage power and impregnation ratio). Carbonyl and hydroxyl groups were the major
462 functional groups on the surface of AC. With an adsorption capacity of 34 – 190 mg/g for
463 MB and Langmuir surface area of 361.8 -636m²/g, the AC could be used to adsorb a
464 range of cationic dyes and pollutants. The properties of AC generated from the landfill
465 composite are comparable with AC from some other biomass, such as oil palm stone
466 and black liquor lignin, which have been identified as having potential of being
467 sustainably managed by conversion to AC (Tamai *et al.* 1996; Fu *et al.*, 2013)

- 468 • The landfill composites from both active and closed landfills represents a novel source
469 of precursor for AC production and a new reuse option for landfill composite. It creates
470 an opportunity for an integrated landfill resource management in which the AC
471 generated could be deployed as landfill liner and/or leachate pond adsorbent.
- 472 • The adsorption capacity of the landfill composite AC suggests that its reuse as a daily
473 landfill covering would curtail organic and inorganic mass transfer within the landfill
474 layers via leaching. This could reduce the substantial cost of daily landfill covering, as
475 well as the amount of virgin soil applied. The cost of daily landfill covering is estimated
476 as 50% of the operational cost of municipal landfills (Johannessen and Boyer, 1997).
- 477 • The depth of both landfill composites significantly influenced both the adsorption
478 capacity and surface area of the generated activated carbon, while age difference did
479 not have a definite influence. A new research finding indicating a relationship between
480 depth of landfill composite and the quality of AC produced. A limitation of the presently

481 reported results, as with most landfill parameters, is that they are dependent on the
482 type of waste disposed, climatic condition and the landfill management practice. It is
483 therefore difficult to generalize the findings for all landfill types.

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

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