

Adsorption Performance of Packed Bed Column for the Removal of Lead (II) using Velvet Tamarind (*Dialium indum*) Shells

ABSTRACT

The removal of Pb ions by activated carbons prepared from velvet tamarind (*Dialium indum*) shells was studied to investigate its uptake potentials using Column sorption at different operating conditions (Flow rates, different initial concentrations, and bed height). The prepared adsorbent was characterized by determining the physicochemical properties, proximate analysis, CHNS analysis, FT-IR, Potentiometric titration. Different dynamic models was used to describe the sorption processes. The FTIR analysis results suggested the presence of functional groups such as hydroxyl, carbonyl, carboxyl and amine which could bind the metals and remove them from the solution. The values of moisture content, volatile matter, fixed carbon and ash content as obtained from % proximate analysis are 3.43, 27.07, 65.05, 4.45 for activated carbons prepared from velvet tamarind shells. Ultimate analysis revealed that activated carbons prepared from velvet tamarind shells contained 75% carbon. The surface area and Iodine Number of activated carbon from velvet tamarind shell are $570 \text{ m}^2/\text{g}^{-1}$ and $614.7 \text{ mg}/\text{g}^{-1}$, respectively. The column experimental data revealed that an increase in bed height and initial metal concentration or a decrease of flow rate enhances the longevity of column performance by increasing both breakthrough time and exhaustion time thereby delaying bed saturation. Low ash content and high surface areas are indication of good mechanical strength and microporosity of the activated carbons prepared from this precursor. The activated carbons are inexpensive and appeared to be effective and can be explore for future commercial application for environmental sustainability.

Key words: Adsorbent, Velvet tamarind, adsorption, Pollution, Lead

1.0 INTRODUCTION

The geometrical increase in the world population as well as increase in industrial activities has made environmental pollution an important issue of serious concern (Singh *et al.*, 2006). Gaseous, liquid and solid wastes emanates from these activities. Earth's surface is made up of 70% water which is the most valuable natural resource existing on our planet without which life becomes impossible. Although this fact is widely recognized, pollution of water resources is a common problem being faced today. Lakes, rivers and oceans are being overwhelmed with many toxic contaminants (Oliveira *et al.*, 2012). Among toxic substances exceeding threshold levels are heavy metals (Zeng *et al.*, 2004).

Heavy metal pollution occurs directly by effluent discharge from industries such as textiles, dyes, leather tanning, electroplating, metal finishing, refineries, mine water and waste treatment plants and indirectly by the contaminants that enter the water supply from soils/ground water systems and from the atmosphere via rain water. The presence of these toxic substances in an undesirable level in wastewaters makes their removal to receive much attention (Ahluwalia and Goyal, 2005). When heavy metal concentration in waste water is

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1. INTRODUCTION
2. MATERIALS AND METHODS
3. RESULTS AND DISCUSSION

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[1] not (Singh *et al.*, 2006)

Standardize throughout the text.

36 considerably high, it would endanger public health and the environment if discharged into the environment
37 without adequate treatment (Nouri *et al.*, 2006).

38 Several methods such as ion exchange, solvent extraction, reverse osmosis, and precipitation have been used
39 for the removal of heavy metals from aqueous solutions but most of these methods are non-economical and
40 have many disadvantages such as high reagents and energy requirements, generation of toxic sludge of other
41 waste products that also require disposal after treatment (Dermibas, 2008). However, adsorption of heavy
42 metals from aqueous solutions is a relatively new process that has proven very efficient and promising in the
43 removal of contaminants from aqueous effluents where interactions between metal ions and biomass present
44 potential applications for the remediation of metal contaminated waters in various industries (Nouri *et al.*,
45 2006). The process of adsorption has an edge over other methods due to its sludge free clean operation and
46 efficient removal of toxic metals even from dilute solution. It is as an innovative principle of using waste to
47 treat waste and will be more efficient because the agricultural by-products used as adsorbents are readily
48 available, affordable, eco-friendly and have high uptake capacity for heavy metals due to the presence of
49 functional groups which can bind metals to effect their removal from effluents making it more cost effective
50 than the use of commercial activated carbon which is expensive. Alternative activated carbon produced from
51 velvet tamarind fruits will be cheap, locally available and could be used to reduce environmental pollution by
52 heavy metals.

53 The release of toxic metals into the environment would be controlled in this way, and so, the process could
54 be used more extensively as an alternative method to the conventional treatment techniques (Lazaridis *et al.*,
55 2005).

56 Considerable attention has been devoted to the development of unconventional materials like used
57 agricultural by-products for the removal of heavy metals from waste water (Kuma and Jena, 2015), since
58 these plant based by-products represent waste resources, and are widely available and environmentally
59 friendly (Abia and Asuquo, 2007). Various natural adsorbents obtained from agricultural wastes like sun
60 flower stalk, Eucalyptus bark, maize husk, coconut shell, waste tea, rice straw, tree leaves, peanut and walnut
61 husk, palm fruit bunch and African spinach stalk have been tried as raw materials for adsorbents to achieve
62 effective removal of various heavy metals (Sing *et al.*, 2006; Kahraman *et al.*, 2008).

63 Commercial activated carbons have been used for the removal of heavy metals but are imported and
64 expensive. There is a need to look for viable non-conventional low-cost adsorbents as alternative to

65 commercial activated carbon in order to meet the growing demand for cheaper and effective adsorbents.
66 Velvet tamarind is among common fruits produced in Nigeria and large volumes of its non-edible and non
67 useful parts such as the shells constitute environmental problems. These non essential parts of velvet
68 tamarind could be explored for the production of activated carbon.

69 The aim of this study is to prepare, characterize and assess the heavy metal adsorption potentials of activated
70 carbons produced from velvet tamarind.

71 **2.0 Materials and methods**

72 **2.1 Sample Collection and Preparation**

73 The carbonaceous precursor used for preparation of activated carbon is velvet tamarind shells that were
74 obtained as agricultural and forest wastes. Prior to use, samples were washed gently with water to remove
75 mud and other impurities present on the surface and then sundried for one week. The samples shells collected
76 after discarding the fruit pulp, were washed with deionized water, sun dried and then dried in a vacuum oven
77 at 80°C for 24 h, crushed and ground using mortar and pestle. The particles were separated by using a US
78 standard testing sieve (No. 100~No. 200). 100 g of raw material was impregnated with 100 cm³ of
79 concentrated H₂SO₄ for 12 hours. The impregnation was carried out at 70 °C in a hot air oven to achieve well
80 penetration of chemical into the interior of the precursor. The sieved samples were placed in a crucible and
81 heated in a muffle furnace for 60 minutes at 500°C. Activated carbons produced were cooled in desiccators
82 and rinsed with deionized water until neutral pH was attained and stocked for subsequent heavy metal
83 removal tests and analysis.

84 **2.2 Sample Characterization**

85 The pH, bulk density, iodine number, specific surface area, chemical composition of the adsorbents,
86 Proximate analysis of the activated carbons were determined using standard test (ASTM, 1996, Ahmedna *et*
87 *al*, 1997, ASTM D 4607-86, 1986, Al-Quodah and Shawabkah, 2009, ASTM D2867 –96). Ultimate
88 Analysis (CHNS elemental analysis) of the samples were determined by subjecting them to combustion
89 process (furnace at ca. 1000°C) for 30 minutes, where carbon was converted to carbon dioxide; hydrogen to
90 water; nitrogen to nitrogen gas/oxides of nitrogen and sulphur to sulphur dioxide. The combustion products
91 were swept out of the combustion chamber by inert carrier gas and passed over heated (about 600° C) high
92 purity copper situated at the base of the combustion chamber to remove any oxygen not consumed in the
93 initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases were then passed through

94 the absorbent traps in order to leave carbon dioxide, water, nitrogen and sulphur dioxide which were
95 separated and detected using GC and thermal conductivity detection.

97 2.3 Fourier Transform Infrared (FTIR) Spectrometer

98 FTIR analysis was made using IPRestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan).
99 Sample of 0.1 g was mixed with 1 g of KBr, spectroscopy grade (Merk, Darmstadt, Germany), in a mortar.
100 Part of this mix was introduced in a cell connected to a piston of a hydraulic pump giving a compression
101 pressure of 15 kPa / cm⁻². The mix was converted to a solid disc which was placed in an oven at 105°C for 4
102 hours to prevent any interference with any existing water vapor or carbon dioxide molecules. Then it was
103 transferred to the FTIR analyzer and a corresponding spectrum was obtained showing the wave lengths of the
104 different functional groups in the sample which were identified by comparing these values with those in the
105 library.

106 2.4 Preparation of Pb Solution (Simulated Effluent)

107 Standard Lead (Pb) stock solution (1000 mg /dm⁻³) were prepared by placing 1.578 g Pb(NO₃)₂ in a
108 volumetric flasks to which 100 cm³ of deionized water was added. The flasks were shaken vigorously to
109 ensure the dissolution of the mixture. The solution was made up to 1000 cm³ mark with deionized water.
110 The working concentrations were prepared from the stock solution by serial dilution. pH adjustment of
111 solutions were made using dilute NaOH and HCl solutions. Deionized water was used to prepare all the
112 solutions. All reagents were of analytical grade.

114 2.5 Fixed Bed Column Experimental Procedure

115 Fixed bed column studies were carried out using a glass column of 30 mm internal diameter and 400 mm
116 length. The activated carbon having 0.425 mm to 0.600 mm particle size range was used. The activated
117 carbon was packed in the column with a layer of glass wool at the top and bottom. Bed height of 50 mm, 100
118 mm and 150 mm were used. The tank containing the heavy metal solution was placed at a higher elevation
119 so that the metal solution could be introduced into the column by gravitational flow. The flow controller
120 helps to regulate the flow rate. Three flow rates (1, 3 and 5 cm³ /min⁻¹) were used while initial ion
121 concentrations of 50, 100 and 150 mg /dm⁻³ were used. The effluent samples were collected at hourly
122 intervals and analyzed for the residual metal concentration using atomic absorption spectrophotometer.

2.6 Dynamic Models

For the successful design of a column adsorption process, it is important to predict the concentration-time profile or breakthrough curve for effluent parameters. A number of mathematical models have been developed for use in the design of continuous fixed bed sorption columns. In this work, the Bed Depth Service Time (BDST), Thomas and Yoon-Nelson models were used in predicting the behaviour of the breakthrough curve because of their effectiveness. The model's equations are presented in Equations 1 to 3:

$$\text{BDST} = t = \frac{N_0}{C_0 F} Z - \frac{1}{K a C_0} \ln \left(\frac{C_0}{C_B} \right) - 1 \quad (1)$$

$$\text{Thomas} = \ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{K t h q_0 M}{Q} - K t h C_0 t \quad (2)$$

$$\text{Yoon-Nelson} = \ln \left(\frac{C_t}{C_0 - C_t} \right) = K y n t - \tau K y n \quad (3)$$

The maximum column capacity, q_{total} (mg) for a bed height of 10.00 cm, initial metal concentration of 50.00 mg/dm³ and flow rates of 1.00, 3.00 and 5.00 cm³/min⁻¹ was calculated from the area under the breakthrough curves as given by the Equation 4 (Ahmad and Hameed, 2010)

$$q_{\text{total}} = \frac{Q A}{1000} = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} C a d t \quad (4)$$

where $C a d = C_i - C_e$ (mg l⁻¹), $t = \text{total}$ is the total flow time (min), Q is the flow rate (cm min⁻¹) and A is the area under the breakthrough curve (cm²).

The equilibrium uptake ($q_{e(\text{exp})}$), i.e. the amount of the metals adsorbed (mg) per unit dry weight of adsorbent (mgg⁻¹) in the column, was calculated from Equation 5 (Martin-Lara *et al.*, 2012):

$$q_{e(\text{exp})} = \frac{q_{\text{total}}}{W} \quad (5)$$

where W is the total dry weight of Velvet tamarind shell in the column (g).

The total volume treated, V_{eff} (cm³) was calculated from Equation 6 (Futalan *et al.*, 2011)

$$V_{\text{eff}} (\text{cm}^3) = Q t_{\text{total}} \quad (6)$$

The Mass Transfer Zone (Zm) is one of the widely used parameters to examine the effects of the column adsorption height. To determine the length of the adsorbent zone in the column, Z_m was calculated from

Equation (7):

$$Z_m(\text{cm}) = Z(t_e - t_b/t_e) \quad (7)$$

where, L presents the closed height (cm), t_b is the time (minute) required to reach the breakthrough point or $C_{\text{eff}}/C_0 = 0.05$ and t_e is the time (minute) required to reach the exhaustion point or $C_{\text{eff}}/C_0 = 0.95$ (Apiratikul and Pavasant, 2008).

3.0 RESULTS AND DISCUSSION

The Proximate Analysis, Ultimate Analysis and physicochemical properties of activated carbons produced from velvet tamarind shells are presented in Tables 1.0, 2.0 and 3.0

Table 1.0: Proximate Analysis, of the Activated Carbons Prepared from Velvet Tamarind Shells

Property	Vt
Moisture	3.43
Volatile Matter	27.07
Fixed carbon	65.05
Ash	4.45

Key : Vt = activated carbon from velvet tamarind fruit shells

Table 2.0: Ultimate Analysis of Activated Carbons from Velvet Tamarind Shells in Comparison with other Commercial Activated Carbons

Element	Vt	Cs
C	75	56.48
H	1.2	2.56
N	1.8	0.61
S	0.8	0.23
O	21.5	40.12

Cs = activated carbon from coconut shell (Yusup *et al.*, 2010)

Table 3.0: Physicochemical Properties of Activated carbons prepared from Velvet Tamarind shells.

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Standardize for other tables.

Parameter	Vt
Bulk density (g/cm ³)	0.51
Iodine number (mg/g)	614.7
Surface area (m ² /g)	570
Particle density (g/cm ³)	0.72
Porosity (%)	26.4
pH	6.9
Pore Volume	0.13

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168

169 | 3.1 Proximate Analysis of Activated Carbons from Velvet Tamarind Shells

170 | According to Alam *et al.* (2008), Ash content is the measurement of the amount of mineral (e.g. Ca, Mg, Si
171 | and Fe) in activated carbon. Ash content obtained in this work was 4.45 for activated carbons prepared from
172 | Velvet Tamarind shells (Table 1.0). The ash content of this carbon is well below the typical ash content
173 | values of 8-12% obtained by Yahaya *et al.* (2011) and 12% obtained by Maheswari *et al.* (2008) but higher
174 | than the 3.58 and 4.89 obtained by Mozammel *et al.* (2010) and Gottipati (2012) for coconut and Bael fruit
175 | shell respectively. Typical ash content of activated carbons is around 5 – 6 % (Pandey *et al.*, 2014). A small
176 | increase in ash content causes a decrease in adsorptive properties of activated carbons by reducing the
177 | mechanical strength of carbon and affects adsorptive capacity. The presence of ash has been shown to inhibit
178 | surface development (Valix *et al.*, 2004).

179

180 | The value of 78% and 65.05% fixed carbon were obtained from percentage ultimate and proximate analysis
181 | of activated carbon prepared from Velvet Tamarind fruit shells (Tables 1.0 and 2.0). Satyawali (2009)
182 | prepared activated carbon from *Euphorbia antiquorum* and obtained 57.94% fixed carbon. Lopez *et al.*
183 | (1995) reported values ranging from 23.7 to 87.13 within 450 to 950°C. Carbonization leads to carbon atoms
184 | rearrangement into graphitic-like structures and the pyrolytic decomposition of the precursor and non-carbon
185 | species elimination, resulting in a fixed carbonaceous char produced (Kanan and Sundaram, 2001). Also
186 | activating agents act as dehydrating agents and oxidants which also influence the pyrolytic decomposition

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187 and prevent the formation of the tar or ash, hence developing the carbon yield. The combine influence of
188 activation and carbonization increases carbon yield.

189
190 As reported in Table 3.0, the following; 0.51 g/cm³, 614.7 mg/g, 570 m²/g and, 26.4% were obtained as the
191 values of bulk density, iodine number, surface area and porosity for activated carbon prepared from Velvet
192 Tamarind shells. The values of bulk density, surface area, and iodine number were similar to the values
193 obtained by Karthikeyan *et al.* (2008). Vijayaraghavan *et al.* (2006) produced activated carbon from palm
194 kernel shell and obtained yields of bulk density of 0.5048 g/cm³, iodine number of 766.99 mg/g and 669.75
195 m²/g BET surface area. Bulk density is the weight per unit volume of dry carbon in a packed bed and is 80-
196 85% of the apparent density (Mohammed *et al.*, 2016). Higher density provides greater volume activity and
197 normally indicates better quality activated carbon. Alikarami *et al.*(2016) in his comparative adsorption
198 studies for the removal of copper (II) from aqueous solution by different adsorbent obtained bulk density
199 values ranging from 0.32 to 0.62. Bulk density of 0.48 g/cm³ was obtained by Satyawali, (2009) and is lower
200 than 0.51 g/cm² obtained for velvet tamarind shells.

201
202 The iodine number value is an indication of surface area of the activated carbon (Amuda *et al.*, 2007).
203 Activated carbons with iodine numbers of about 550mg/g can be attractive for waste water treatment from
204 the user's viewpoint (Deheyn *et al.*, 2005).The iodine number values of 614.7 mg/g was obtained for
205 activated carbon prepared from velvet tamarind fruits shells (Table 3.0). These results were within the range
206 of 608 and 746 mg/g obtained by Castro *et al.* (2008). Analysing the Iodine number of activated carbon
207 prepared from palm-oil shell by pyrolysis and steam activation in a fixed bed reactor, Vijayaraghavan *et al.*
208 (2006) obtained maximum value of 766.99 mg/g at 750°C. According to Al-Quodah and Shawabkah (2009),
209 each 1.0mg of iodine adsorbed is ideally considered to represent 1.0 m² of activated carbon internal area.
210 Therefore the adsorbents have enough internal surface area for adsorption.

211 3.2 Surface Area of Activated Carbons from Velvet Tamarind and Sandal Fruit Shells

212 Surface area is the carbon particle area available for adsorption. In general, the larger the effective surface
213 area, the greater is the adsorption capacity. A surface area of the activated carbons used in this study is as
214 reported in Table 4.0. The results indicated that the surface area of 570 m²/g was obtained for velvet tamarind
215 shells activated carbon. The specific surface area as indicated in Table 4.0 further confirmed the porous

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216 nature of the activated carbons. According to Liu and Liu (2008), an adsorbent with a surface area of 500
217 m²/g and above has a well formed microporous structures suitable for adsorption. According to Castro *et al.*
218 (2008), 95% of the total surface areas of a given adsorbent are micropores. Yang and Duri (2005) stated that
219 most widely used commercial activated carbon has surface areas of between 600-1000 m²/g.

220 **3.3 pH of Activated Carbons from Velvet Tamarind Fruit Shells**

221 The pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. The
222 chemical nature of the carbon surfaces are mostly deduced from the acidity or pH of the carbon. Table 4.0
223 presented the pH of the activated carbon prepared from velvet tamarind fruits shells as 6.9. The results
224 suggest weakly acidic surface properties. Similar results were obtained by Allothman *et al.* (2011). Valix *et*
225 *al.* (2004) obtained pH between 6.4 and 7.4 for activated carbon prepared from bagasse.

226 **3.4 Moisture content of activated carbons from Velvet Tamarind Shells**

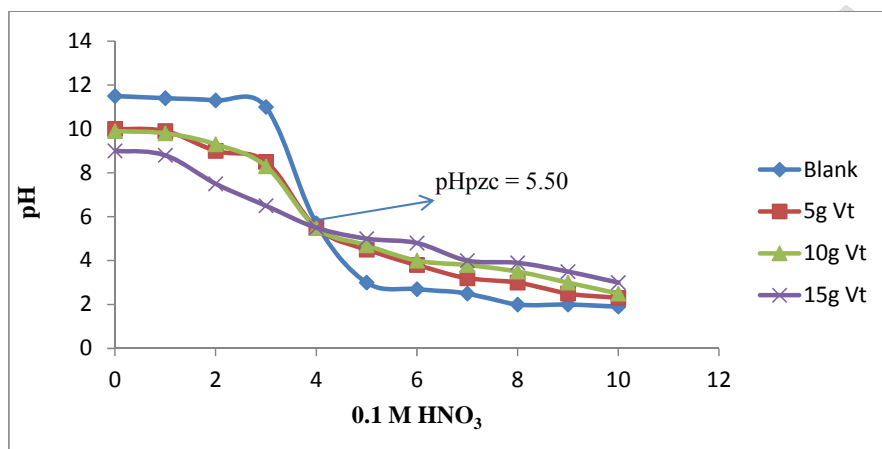
227 Moisture content was measured from loss of water over initial weight of raw materials. Usually moisture
228 content decreases as the temperature increases. As presented in Table 4.0, moisture content of 3.43% was
229 obtained for the activated carbon prepared from Velvet tamarind fruits shells. Vijayaraghavan *et al.* (2006)
230 obtained values between 8.35 to 11.38% for moisture content while Maheswari *et al.* (2008) obtained 4.33%
231 in their work. The moisture contents of commercial activated carbons ranged between 2- 10 % (Yang and
232 Duri, 2005). The practical limit for the level of moisture content allowed in the activated carbon varies within
233 3 to 6% (Kuma and Jena, 2015). The moisture content of 3.43% obtained for the the activated carbon
234 prepared from Velvet tamarind fruits shells activated carbons therefore fall within the practical limit.

235 **3.5 Volatile matter of activated carbons from velvet tamarind shells**

236 The values of volatile matter of 27.07% (Table 1.0) was obtained for Velvet tamarind fruit shells activated
237 carbons. Lou *et al.* (1999) studied chars prepared from oil palm waste and obtained % volatile matter ranging
238 from 74.86 to 4.08% between 450 to 950°C.

239 **3.6 Potentiometric titration curves of activated carbons from velvet tamarind fruit shells**

240 Figures 1.0 indicate the result of Potentiometric curves of the activated carbons investigated to determine the
241 Point of Zero Charge on the surface of the adsorbent. The point of zero charge (PZC) is an adsorption
242 phenomenon which describes the condition when the electrical charge density on a surface is zero. The
243 common intersection point of the titration curves with the blank is the pH at PZC (pH_{PZC}). From the curves
244 (Figure 1.0), the pH_{PZC} for activated carbon prepared from velvet tamarind shells were identified as 5.50.
245



246

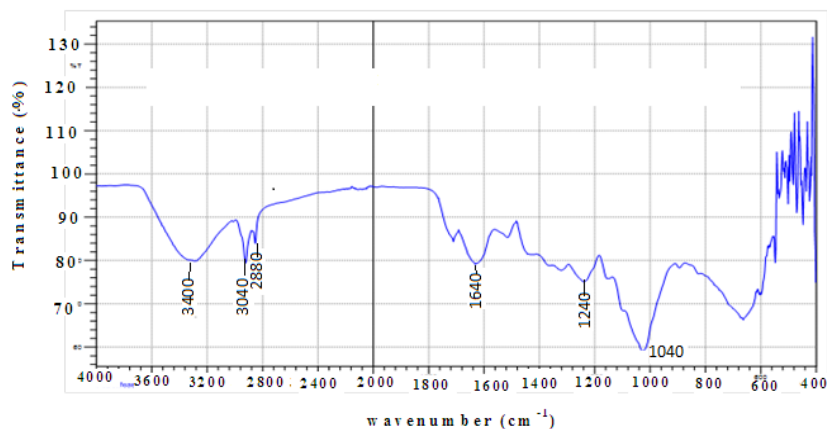
247 **Figure 1.0: Potentiometric Titration Curves of Activated Carbon from Velvet Tamarind Shell**

248

249 The titration curve of Velvet tamarind shells is a bit steep. This indicates a moderate capacity of the shells to
250 take up protons (buffering capacity). Therefore, the capacity to take up cationic metals by ionic exchange is
251 probably also moderate. Any pH above $pH(pzc)$ provide a negatively charged surface favourable for
252 adsorption of cationic heavy metals from the solution.

253 3.7 Fourier transforms infrared spectrometer (FTIR) result of activated carbons from velvet 254 tamarind

255 The FTIR spectral of activated carbons prepared from velvet tamarind fruit shells were used to determine the
256 vibration frequency changes in the functional groups on the surface which facilitates the adsorption of metal
257 ions. The spectra of the activated carbons were measured within the range of $400 - 4000\text{cm}^{-1}$ wave number
258 as shown in Figures 2.0.



260

261 **Figure 2.0: FTIR Spectrum of Activated carbon prepared from Velvet Tamarind Shell**

262 The FTIR analysis result (Figure 2.0) suggest the presence of such functional groups as the carboxylic acid
 263 or alcoholic O-H bond stretching which may overlap with amine (N-H) bond stretching at peaks between
 264 3250-3400 cm^{-1} ; possible C=O bond of carbonyl or amide groups within 1640-1670 cm^{-1} ; C-O and O-H bond
 265 stretching of alcohol and ethers at 1000-1260 cm^{-1} of the finger-print region (Gimba et al, 2001). The
 266 important parameters that influence and determine the adsorption of metal ions from aqueous solutions are
 267 the carbon-oxygen functional groups present on the carbon surface and the pH of the solution (Bansal and
 268 Goyal, 2005).

269

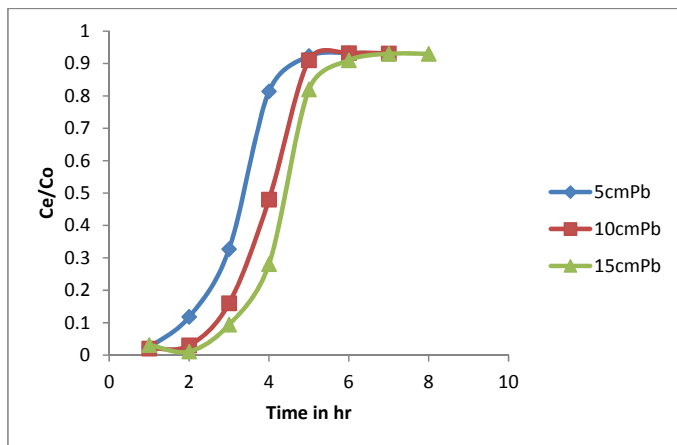
270 **3.8 Column Adsorption Studies of Lead (Pb) on Activated carbon Prepared from Velvet Tamarind**

271 **Shells**

272 **3.8.1 Effect of bed height**

273 The adsorption of metal ions in the packed bed column is largely dependent on the bed height, which is
 274 directly proportional to the quantity of adsorbent in the column. The effect of bed height on breakthrough
 275 curve analysis was studied by varying the bed height from 5 cm to 15 cm at increment of 5cm. The
 276 adsorption breakthrough curves were obtained by varying the bed heights at a flow rate of $1\text{cm}^3/\text{min}$ and an

277 inlet Pb ions concentration of 50 mg/dm^3 . The breakthrough curves are presented in Figures 2.0. Faster
278 breakthrough curves were observed for a bed height of 5 cm compared to the bed height of 10 cm and 15 cm.



279
280 **Figure 3.0: Column adsorption of Pb(II) by Activated Carbon from Velvet Tamarind Fruits Shells**
281 **at different Bed height**

282
283 As depicted by Figure 3.0, the breakthrough time varied with bed height. Steeper breakthrough curves were
284 achieved with a decrease in bed depth. The breakthrough time decreased with a decreasing bed depth from 15
285 to 5 cm, as binding sites were restricted at low bed depths. At low bed depth, the metal ions do not have
286 enough time to diffuse into the surface of the adsorbents, and a reduction in breakthrough time occurs.
287 Conversely, with an increase in bed depth, the residence time of metal ions solution inside the column was
288 increased, allowing the metal ions to diffuse deeper into the adsorbents.

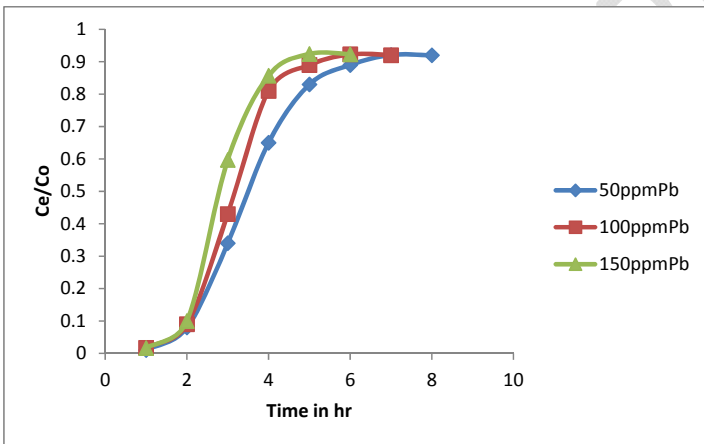
289
290 The results indicate that the throughput volume of the aqueous solution increased with increase in bed height,
291 due to the availability of more number of sorption sites (Satyawali, 2009). At higher bed depth of 10 cm,
292 adsorbent mass was more residing in the column thereby providing larger service area for binding, fixation,
293 diffusion and permeation of the solute to the adsorbent. Longer bed depth also provided more reaction area
294 and larger volume of influent treatment which translated to higher adsorption capacity.

295
296 The equilibrium sorption capacity decreased with increase in bed height. This shows that at smaller bed
297 height, the effluent adsorbate concentration ratio increased more rapidly than for a higher bed height.

298 Furthermore, the bed is saturated in less time for smaller bed heights. The slope of the S-shape from t_b to t_e
299 decreased as the bed height increased from 5 to 15 cm, indicating the breakthrough curve becomes steeper as
300 the bed height decreased. Also the breakthrough time (t_b) and exhaustion time (t_e) increase with increase in
301 bed depth

302 3.8.2 Effect of Initial Metal Concentration

303 A Series of column experiments with different metals concentrations namely, 50, 100 and 150 ppm were
304 conducted to investigate the effect of initial metal concentration on the performance of the fixed-bed
305 operation. Figure 3.0 presented the breakthrough curves for the adsorption of Pb onto Velvet tamarind fruit
306 shells activated carbon at various initial metal concentrations.



308 **Figure 4.0: Column adsorption of Pb(II) by Activated Carbon from Velvet Tamarind Fruit shells at**
309 **different Initial Concentration.**

312 It can be seen from the Figure 4.0 that breakthrough curves display three important features: an initial lag
313 period during which effluent metal ions are non-detectable, followed by a rise in concentration, and finally a
314 period of slow increase in effluent level. It was assumed that the breakthrough metal-concentration would be
315 5% of the influent concentration. It is evident that by increasing initial metal concentration, the slope of the
316 breakthrough curve increased and became much steeper, hence reducing the volume which can be treated
317 before breakthrough occurred. This is due to the fact that by increasing the initial metal concentration, the

318 driving forces increases which enhance the rate of metal adsorption and saturates the binding sites more
319 quickly. This is consistent with results of the finding of Betzy and Soney (2015), where the authors found
320 that by increasing inlet adsorbate concentration, the slope of the breakthrough curve increased and the
321 volume treated before carbon regeneration reduced. This behaviour was attributed to the high concentrations
322 which saturated the activated carbon more quickly, thereby decreasing the breakthrough time. It is also clear
323 from Figures 1.0 to 5.0 that all the curves exhibit a characteristic “S” shape which indicates an effective use
324 of adsorbent (Tamura, 2003)

325 **3.8.3 Effect of flow rate on breakthrough curves**

326 The adsorption columns were operated with different flow rates (1, 3 and 5 cm³/min) until no further metal
327 ions removal was observed. The adsorbent bed height and inlet initial metal ions concentration were fixed at
328 10 cm and 50 mg/dm³, respectively. The breakthrough curve for a column was determined by plotting the
329 ratio of the C_e/C_0 (C_e and C_0 are the metal ions concentration of effluent and influent, respectively) against
330 time, as shown in Figures 1.0 to 5.0 respectively. The effect of the flow rate on the adsorption of Cu, Cd, Pb
331 and Ni are shown as breakthrough curves in the figures. It was observed that breakthrough generally
332 occurred faster with higher flow rate. The reason is that at higher flow rate, the rate of mass transfer
333 increased, thus the amount of metal ions adsorbed onto the unit bed height (mass transfer zone) increased
334 (Patil *et al.*, 2006). In addition, the adsorption capacity decreases with increase in flow rates due to
335 insufficient residence time of the solute in the column and lack of diffusion of the solute into the pores of the
336 adsorbent, therefore the solute left the column before equilibrium occurred. These results were in agreement
337 with other findings as reported by Volesky (2005).

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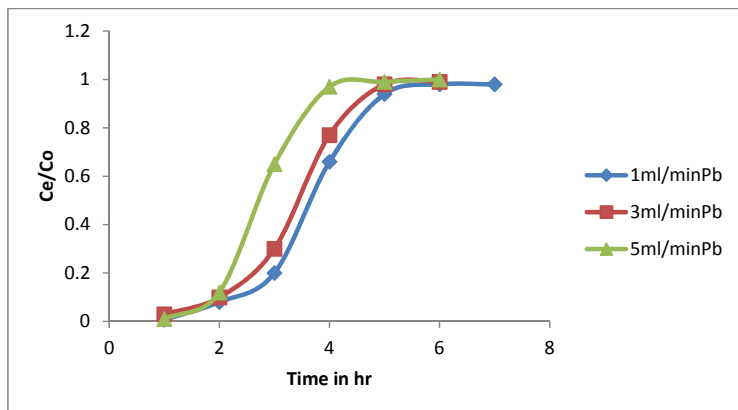


Figure 5.0: Column adsorption of Pb(II) by Activated Carbon from Velvet Tamarind Fruits Shell Activated Carbon at different Flow rate.

The column performed well at the lowest flow rate (1cm³/min). Earlier breakthrough and exhaustion times were achieved, when the flow rate was increased from 1 to 5 cm³/min. This was due to a decrease in the residence time, which restricted the contact of metal ions to the adsorbents. Similar results have been found for As (III) removal in a fixed-bed system using modified calcined bauxite and for color removal in a fixed-bed column system using surfactant-modified zeolite (Hrapovic and Rowe, 2002).

3.9 Column Kinetic Study

Three models (Thomas model, Yoon-Nelson and BDST models) were used to analyze the column performance.

3.9.1 Thomas model

The model was applied to the experimental data with respect to the initial metals concentration, flow rate and bed height. The kinetic coefficient, k_{Th} and the adsorption capacity of the bed, q₀ were determined from the

plot of $\ln\left(\frac{C_0}{C_e} - 1\right)$ against t. The results of k_{Th}, R² and q₀ are given in Table 4.0. The results showed that the

kinetic coefficient k_{Th} is dependent on flow rate, initial ion concentration and bed height. The maximum

357 adsorption capacity q_0 and Kinetic coefficient k_{Th} decreased with increase in flow rate but increased with
358 increase in bed height and initial ion concentration. The values of k_{Th} obtained in this work is similar to the
359 ones obtained by Yaya (2011). High values of regression coefficients were obtained indicating that the
360 kinetic data conformed well to Thomas model in contrast with the report of Sasikala and Muthuraman (2016)
361 but in agreement with the results obtained by Baek *et al.* (2007). The trend observed with the calculated
362 values of k_{Th} , q_0 are in agreement.

363 3.9.2 Yoon and Nelson Model

364 This model is based on the assumption that the rate of decrease in the probability of adsorption for each
365 adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate
366 breakthrough on the adsorbent (Kavak and Öztürk, 2004). The Yoon and Nelson equation for single
367 component system is expressed as shown in equation 4.3 (Aksu *et al.*, 2004):

$$368 \quad \ln \frac{C_e}{C_0 - C_e} = K_{ynt} - \tau K \quad (4.3)$$

369 Yoon and Nelson model has been used in the study of column adsorption kinetics (Kavak and Öztürk, 2004,
370 Satyawali, 2009). The values of the Yoon-Nelson parameters (k_{yn} and τ) were determined from the plot of
371 $\ln \frac{C_e}{C_0 - C_e}$ versus t at various operating conditions (Table 1.0 to 5.0). A plot of $\ln \frac{C_e}{C_0 - C_e}$ versus t gives a
372 straight line with slope of K_{yn} , and intercept of $-\tau K$. The results showed that the rate constant, K_{yn} increased
373 with increased inlet ions concentration, flow rate and bed height. The time required for 50% breakthrough, τ
374 decreased with increase in flow rate and initial ion concentration. High values of correlation coefficients
375 obtained indicate that Yoon and Nelson model fitted well to the experimental data and can be used to
376 describe the Cd(II), Cu(II), Pb(II) and Ni(II)-Velvet Tamarind shell and Cd(II), Cu(II), Pb(II) and Ni(II) –
377 Sandal fruit shell biosorption system.

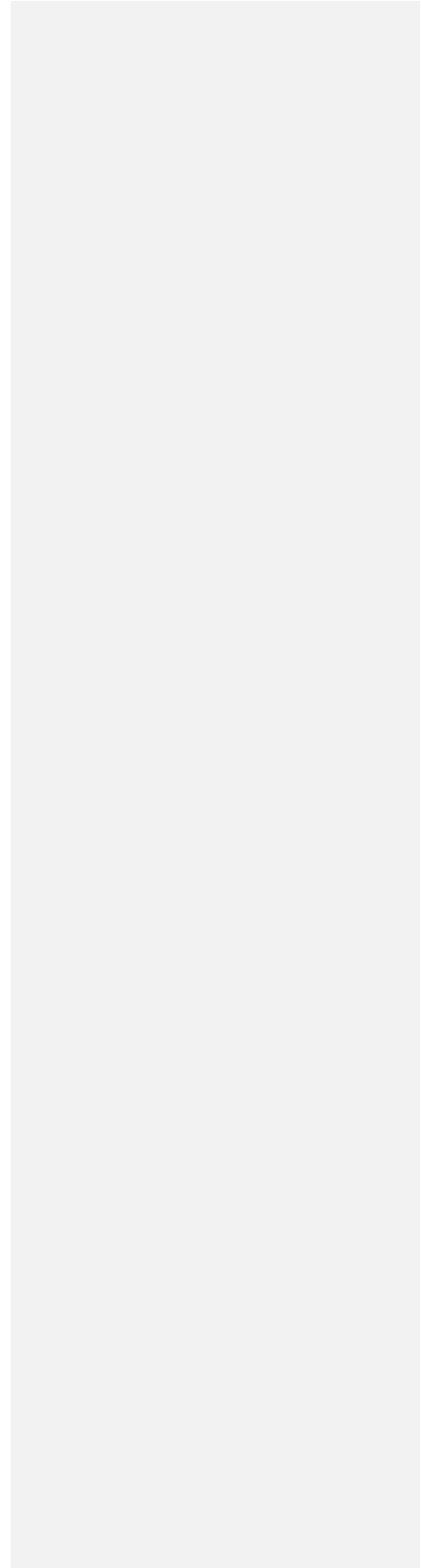
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383 **Table 4.0: Column kinetic parameters for Pb ions adsorption on activated carbon from Velvet tamarind fruit Shells**

	Initial ion concentration(mg/dm ³)			Flow rates in cm ³ /min			Bed height (cm)		
	50	100	150	1	3	5	5	10	15
Thomas K _{Th} (cm ³ /min/mg) X10 ⁻³	2.40	7.20	2.30	0.34	0.38	0.64	0.24	0.42	0.42
q _o (mg/g)	1.20	1.93	2.80	0.71	0.38	2.10	1.00	1.20	1.80
R ²	0.98	0.97	0.95	0.98	0.99	0.98	0.96	0.95	0.99
Yoon & Nelson K _{yn} (min ⁻¹) X10 ⁻²	1.00	1.40	2.00	1.60	2.00	2.50	1.90	1.90	3.10
τ̄ (min)	251.00	205.00	125.00	173.00	167.00	126.00	125.00	150.00	194.00
R ²	0.95	0.99	0.94	0.97	0.99	0.94	0.97	0.99	0.97

385 **3.9.3 Lead Uptake in the Column at Different Operating Parameters**

386 This study showed that the sorption uptake capacity of the column Pb 1.73 mg g⁻¹ for velvet tamarind
387 fruit shells activated carbon as shown in Table 5.0. The increased capacity of the column method is
388 largely due to the continuous increased concentration gradient in the interface of the adsorption zone
389 as it passes through the column, whereas the gradient concentration decreases with time in batch
390 systems (Sousa, 2010; Martin-Lara *et al.*, 2012).

391
392 A characterisation study on the Velvet Tamarind shells prior to biosorption showed that hydroxyl and
393 carboxylic functional groups were present and might be involved in the removal of metal ions from
394 aqueous solutions by this biosorbent, besides micro precipitation and electrostatic attraction forces.
395 The results obtained by Sousa (2010) for Ni(II), Cd(II), Zn(II) and Pb(II) ions using H₂SO₄ treated
396 coconut shell suggest that a lower pH of 6 is required for optimal removal of the studied metals,
397 similar to the pH of 6 ± 0.2 used in this study.

398 **Table 5.0: Uptake of Pb(II) by activated carbon from Velvet Tamarind Fruit shells at different**
399 **flow rates**

	Z (cm)	Q (cm ³ min ⁻¹)	C ₀ (mg dm ⁻³)	V _{eff} (cm ³)	q _{total} (mg)	q _{e(exp)} (mgg ⁻¹)	Z _m (cm)
Vt	10.00	1.00	50.00	1191.00	1.79	1.73	6.40
	10.00	3.00	50.00	882.00	0.44	1.64	7.95
	10.00	5.00	50.00	300.00	0.30	0.54	5.50

400

401

402 **4.0 Conclusion**

403 i. The experimental data revealed that an increase in bed height and initial metal concentration
404 or a decrease of flow rate enhances the longevity of column performance by increasing both
405 breakthrough time and exhaustion time thereby delaying bed saturation.

- 406 ii. The design of a continuous fixed bed column for removal of metal ions by velvet tamarind
407 and sandal fruit shells activated carbons can be achieved using the BDST, Yoon-Nelson and
408 Thomas models.
- 409 iii. The FTIR analysis results suggested the presence of functional groups such as hydroxyl,
410 carbonyl, carboxyl and amine which could bind the metals and remove them from the
411 solution.
- 412 iv. The values of moisture content, volatile matter, fixed carbon and ash content as obtained
413 from % proximate analysis are 3.43, 27.07, 65.05, 4.45 for activated carbons prepared from
414 velvet tamarind shells.
- 415 v. Ultimate analysis revealed that activated carbons prepared from velvet tamarind shells
416 contained 75% carbon.
- 417

418

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Comment [R15]: References should be corrected according to instructions for authors.
All references need to be corrected.

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