

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, initial concentrations and bed height). The prepared adsorbent was characterized by determining the physicochemical properties, proximate analysis, carbon, Hydrogen, Nitrogen and Sulphur analysis, Fourier Transform-Infra Red, Potentiometric titration. Different dynamic models were 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 mgg^{-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;

1. INTRODUCTION

The exponential increase in the world population as well as increase in industrial activities made environmental pollution an important issue of serious concern. 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 [1].

Among toxic substances exceeding threshold levels are heavy metals and water pollution by heavy metals 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 [2]. When heavy metal concentration in waste water is considerably high, it would endanger public health and the environment if discharged into the environment without adequate treatment [3].

Several methods such as ion exchange, solvent extraction, reverse osmosis, and precipitation have been used for the removal of heavy metals from aqueous solutions but most of these methods are non-economical and have many

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39 disadvantages such as high reagents and energy requirements, generation of toxic sludge of other waste products that
40 also require disposal after treatment [4]. However, adsorption of heavy metals from aqueous solutions is a well
41 established process that has proven very efficient and promising in the removal of contaminants from aqueous
42 effluents where interactions between metal ions and biomass present potential applications for the remediation of
43 metal contaminated waters in various industries [3]. The process of adsorption has an edge over other methods due to
44 its sludge free clean operation and efficient removal of toxic metals even from dilute solution. It is as an innovative
45 principle of using waste to treat waste and will be more efficient because the agricultural by-products used as
46 adsorbents are readily available, affordable, eco-friendly and have high uptake capacity for heavy metals due to the
47 presence of functional groups which can bind metals to effect their removal from effluents making it more cost effective
48 than the use of commercial activated carbon which is expensive. Alternative activated carbon produced from velvet
49 tamarind fruits will be cheap, locally available and could be used to reduce environmental pollution by heavy metals.

50 The release of toxic metals into the environment would be controlled in this way, and so, the process could be used
51 more extensively as an alternative method to the conventional treatment techniques [5].

52 Considerable attention has been devoted to the development of unconventional materials like used agricultural by-
53 products for the removal of heavy metals from waste water [6], since these plant based by-products represent waste
54 resources, and are widely available and environmentally friendly [7]. Various natural adsorbents obtained from
55 agricultural wastes like sun flower stalk, Eucalyptus bark, maize husk, coconut shell, waste tea, rice straw, tree leaves,
56 peanut and walnut husk, palm fruit bunch and African spinach stalk have been tried as raw materials for adsorbents to
57 achieve effective removal of various heavy metals[8][9].

58 Commercial activated carbons have been used for the removal of heavy metals but are imported and expensive. There
59 is a need to look for viable non-conventional low-cost adsorbents as alternative to commercial activated carbon in
60 order to meet the growing demand for cheaper and effective adsorbents. Velvet tamarind is among common fruits
61 produced in Nigeria and large volumes of its non-edible and non useful parts such as the shells constitute
62 environmental problems. These non essential parts of velvet tamarind could be explored for the production of activated
63 carbon.

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

66 2. Materials and Methods

67 2.1 Sample Collection and Preparation

68 The carbonaceous precursor used for preparation of activated carbon is velvet tamarind shells that were obtained as
69 agricultural and forest wastes. Prior to use, samples were washed gently with water to remove mud and other impurities
70 present on the surface and then sundried for one week. The samples shells collected after discarding the fruit pulp, were
71 washed with deionized water, sun dried and then dried in a vacuum oven at 80°C for 24 h, crushed and ground using
72 mortar and pestle. The particles were separated by using a US standard testing sieve (No. 100~No. 200). 100 g of raw

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73 material was impregnated with 100 cm³ of concentrated H₂SO₄ for 12 h. The impregnation was carried out at 70 °C in a
74 hot air oven to achieve well penetration of chemical into the interior of the precursor. The sieved samples were placed in
75 a crucible and heated in a muffle furnace for 60 min at 500°C. Activated carbons produced were cooled in desiccators and
76 rinsed with deionized water until neutral pH was attained and stocked for subsequent heavy metal removal tests and
77 analysis.

78 2.2 Sample Characterization

79 The pH, bulk density, iodine number, specific surface area, chemical composition of the adsorbents, proximate
80 analysis of the activated carbons were determined using standard test [10][11][12][13]. Ultimate analysis (CHNS
81 elemental analysis) of the samples were determined by subjecting them to combustion process (furnace at ca. 1000°C)
82 for 30 min, where carbon was converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of
83 nitrogen and sulphur to sulphur dioxide. The combustion products were swept out of the combustion chamber by inert
84 carrier gas and passed over heated (about 600° C) high purity copper situated at the base of the combustion chamber
85 to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas.
86 The gases were then passed through the absorbent traps in order to leave carbon dioxide, water, nitrogen and sulphur
87 dioxide which were separated and detected using GC and thermal conductivity detection.

89 2.3 Fourier Transform Infrared (FTIR) Spectrometer

90 FTIR analysis was made using IPRrestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). Sample of 0.1 g
91 was mixed with 1 g of KBr, spectroscopy grade (Merk, Darmstadt, Germany), in a mortar. Part of this mix was
92 introduced in a cell connected to a piston of a hydraulic pump giving a compression pressure of 15 kPa / cm². The mix
93 was converted to a solid disc which was placed in an oven at 105°C for 4 h to prevent any interference with any
94 existing water vapor or carbon dioxide molecules. Then it was transferred to the FTIR analyzer and a corresponding
95 spectrum was obtained showing the wave lengths of the different functional groups in the sample which were identified
96 by comparing these values with those in the library.

97 2.4 Preparation of Pb Solution (Simulated Effluent)

98 Standard lead (Pb) stock solution (1000 mgdm⁻³) was prepared by placing 1.578 g Pb(NO₃)₂ in a volumetric flask to
99 which 100 cm³ of deionized water was added. The flask was shaken vigorously to ensure the dissolution of the
100 mixture. The solution was made up to 1000 cm³ mark with deionized water. The working concentrations were prepared
101 from the stock solution by serial dilution. pH adjustment of solutions were made using dilute NaOH and HCl solutions.
102 Deionized water was used to prepare all the solutions. All reagents were of analytical grade.

104 2.5 Fixed Bed Column Experimental Procedure

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a volumetric flask...

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Fixed bed column studies were carried out using a glass column of 30 mm internal diameter and 400 mm length. The activated carbon having 0.425 to 0.600 mm particle size range was used. The activated carbon was packed in the column with a layer of glass wool at the top and bottom. Bed height of 50, 100 and 150 mm were used. The tank containing the heavy metal solution was placed at a higher elevation so that the metal solution could be introduced into the column by gravitational flow. The flow controller helps to regulate the flow rate. Three flow rates (1, 3 and 5 cm³min⁻¹) were used while initial ion concentrations of 50, 100 and 150 mgdm⁻³ were used. The effluent samples were collected at hourly intervals and analyzed for the residual metal concentration using atomic absorption spectrophotometer.

2.6 Dynamic models of Column Adsorption of lead (Pb) onto activated carbon from Velvet Tamarind (*Dialium indum*) Shells

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 behavior 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, 3 and 5 cm³min⁻¹ was calculated from the area under the breakthrough curves as given by the Equation 4 (Ahmad and Hameed, 2010)

$$q_{\text{total}} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} C_{ad} dt \quad (4)$$

where $C_{ad} = C_i - C_e$ (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)

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

139 The mass transfer zone (Zm) is one of the widely used parameters to examine the effects of the column adsorption
140 height. To determine the length of the adsorbent zone in the column, Zm was calculated from Equation 7:

141
$$Z_m(\text{cm}) = Z(t_e - t_b/t_e) \quad (7)$$

142 where, L presents the closed height (cm), t_b is the time (minute) required to reach the breakthrough point or $C_{\text{eff}}/C_o =$
143 0.05 and t_e is the time (minute) required to reach the exhaustion point or $C_{\text{eff}}/C_o = 0.95$ (Apiratikul and Pavasant,
144 2008).

145 3.0 RESULTS AND DISCUSSION

146 The proximate analysis, ultimate analysis and physicochemical properties of activated carbons produced from velvet
147 tamarind shells are presented in Tables 1, 2 and 3

148 **Table 1. Proximate analysis, of the activated carbons prepared from velvet tamarind shells**

149

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

150 Vt = activated carbon from velvet tamarind fruit shells

151

152 3.0 Ultimate Analysis of Activated Carbons from Velvet Tamarind Fruit Shells

Element	Vt
C	75
H	1.2
N	1.8
S	0.8
O	21.5

153

154

155

156

157 **Table 2. Physicochemical Properties of Activated carbons prepared from Velvet Tamarind shells.**

Parameter	Vt
Bulk density (gcm ³)	0.51
Iodine number (mgg ⁻¹)	614.7
Surface area (m ² g ⁻¹)	570
Particle density (gcm ³)	0.72
Porosity (%)	26.4
pH	6.9
Pore Volume	0.13

158

159 **3.1 Proximate and ultimate analysis of activated carbons from velvet tamarind shells**

160 According to [14], ash content is the measurement of the amount of mineral (e.g. Ca, Mg, Si and Fe) in activated
 161 carbon. Ash content obtained in this work was 4.45 for activated carbons prepared from velvet tamarind shells (Table
 162 1). The ash content of this carbon is well below the typical ash content values of 8-12% obtained by [15] and 12%
 163 obtained by [16] but higher than the 3.58 and 4.89 obtained by [17] and [18] for coconut and Bael fruit shell
 164 respectively. Typical ash content of activated carbons is around 5-6 % [19]. A small increase in ash content causes a
 165 decrease in adsorptive properties of activated carbons by reducing the mechanical strength of carbon and affects
 166 adsorptive capacity. The presence of ash has been shown to inhibit surface development [20].

167

168 The value of 78 and 65.05% fixed carbon were obtained from percentage ultimate and proximate analysis of activated
 169 carbon prepared from velvet tamarind fruit shells (Table 1&2). [21] prepared activated carbon from *Euphorbia*
 170 *antiquorum* and obtained 57.94% fixed carbon. [22] reported values ranging from 23.7 to 87.13% within 450 to 950°C.
 171 Carbonization leads to carbon atoms rearrangement into graphitic-like structures and the pyrolytic decomposition of the
 172 precursor and non-carbon species elimination, resulting in a fixed carbonaceous char produced [23]. Also activating
 173 agents act as dehydrating agents and oxidants which also influence the pyrolytic decomposition and prevent the
 174 formation of the tar or ash, hence developing the carbon yield. The combine influence of activation and carbonization
 175 increases carbon yield.

176

177 As reported in Table 3.0, the following: 0.51 g/cm³, 614.7 mg/g, 570 m²/g, 26.4% were obtained as the values of bulk
 178 density, iodine number, surface area and porosity for activated carbon prepared from Velvet Tamarind shells. The
 179 values of bulk density, surface area, and iodine number were similar to the values obtained by [24][26] produced

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180 activated carbon from palm kernel shell and obtained yields of bulk density of 0.5048g/cm³, iodine number of 766.99
181 mgg⁻¹ and 669.75 m²g⁻¹ BET surface area. Bulk density is the weight per unit volume of dry carbon in a packed bed
182 and is 80-85% of the apparent density [27]. Higher density provides greater volume activity and normally indicates
183 better quality activated carbon. [28] in his comparative adsorption studies for the removal of copper (II) from aqueous
184 solution by different adsorbent obtained bulk density values ranging from 0.32 to 0.62 gcm⁻³. Bulk density of 0.48 gcm⁻³
185 was obtained by [21] and is lower than 0.51 gcm⁻² obtained for velvet tamarind shells.

186
187 The iodine number value is an indication of surface area of the activated carbon [29]. Activated carbons with iodine
188 numbers of about 550 mgg⁻¹ can be attractive for waste water treatment from the user's viewpoint [30]. The iodine
189 number values of 614.7 mgg⁻¹ was obtained for activated carbon prepared from velvet tamarind fruits shells (Table
190 3.0). These results were within the range of 608 and 746 mgg⁻¹ obtained by [31]. Analysing the iodine number of
191 activated carbon prepared from palm-oil shell by pyrolysis and steam activation in a fixed bed reactor, [25] obtained
192 maximum value of 766.99 mgg⁻¹ at 750°C. According to [13], each 1.0mg of iodine adsorbed is ideally considered to
193 represent 1.0 m² of activated carbon internal area. Therefore the adsorbents have enough internal surface area for
194 adsorption.

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195 3.2 Surface area of activated carbons from velvet tamarind fruit shells

196 Surface area is the carbon particle area available for adsorption. In general, the larger the effective surface area, the
197 greater is the adsorption capacity. A surface area of the activated carbons used in this study is as reported in Table
198 4.0. The results indicated that the surface area of 570 m²g⁻¹ was obtained for velvet tamarind shells activated carbon.
199 The specific surface area as indicated in Table 4.0 further confirmed the porous nature of the activated carbons.
200 According to [32], an adsorbent with a surface area of 500 m²g⁻¹ and above has a well formed microporous structures
201 suitable for adsorption. According to [31], 95% of the total surface areas of a given adsorbent are micropores. [33]
202 stated that most widely used commercial activated carbon has surface areas of between 600-1000 m²g⁻¹.

203 3.3 pH of activated carbons from velvet tamarind fruit shells

204 The pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. The chemical nature
205 of the carbon surfaces are mostly deduced from the acidity or pH of the carbon. Table 4.0 presented the pH of the
206 activated carbon prepared from velvet tamarind fruits shells as 6.9. The results suggest weakly acidic surface
207 properties. Similar results were obtained by [34]. [20] obtained pH between 6.4 and 7.4 for activated carbon prepared
208 from bagasse.

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209 3.4 Moisture content of activated carbons from velvet tamarind shells

210 Moisture content was measured from loss of water over initial weight of raw materials. Usually moisture content
211 decreases as the temperature increases. As presented in Table 4.0, moisture content of 3.43% was obtained for the
212 activated carbon prepared from Velvet tamarind fruits shells. [25] obtained values between 8.35 to 11.38% for moisture
213 content while [16] obtained 4.33% in their work. The moisture contents of commercial activated carbons ranged
214 between 2- 10 % [33]. The practical limit for the level of moisture content allowed in the activated carbon varies within 3
215 to 6% [6]. The moisture content of 3.43% obtained for the the activated carbon prepared from Velvet tamarind fruits
216 shells activated carbons therefore fall within the practical limit.

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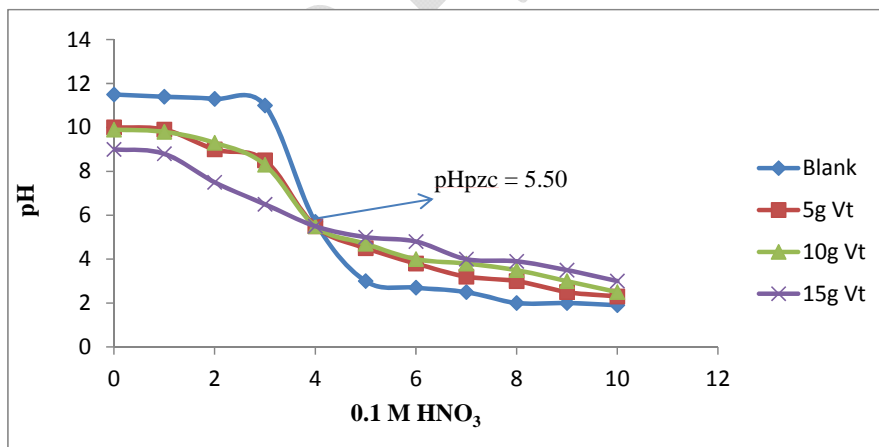
217 3.5 Volatile matter of activated carbons from velvet tamarind shells

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

221 3.6 Potentiometric titration curves of activated carbons from velvet tamarind fruit shells

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

227



229

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

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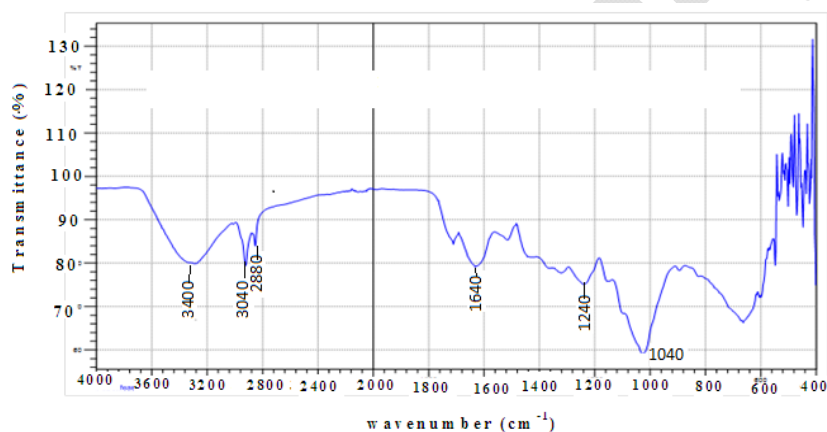
231

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

236 3.7 Fourier transforms infrared spectrometer (FTIR) result of activated carbons from velvet 237 tamarind

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

241



242

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

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

250

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

3.8.1 Effect of bed height

The adsorption of metal ions in the packed bed column is largely dependent on the bed height, which is directly proportional to the quantity of adsorbent in the column. The effect of bed height on breakthrough curve analysis was studied by varying the bed height from 5 cm to 15 cm at increment of 5 cm. The adsorption breakthrough curves were obtained by varying the bed heights at a flow rate of $1\text{ cm}^3/\text{min}$ and an inlet Pb ions concentration of $50\text{ mg}/\text{dm}^3$. The breakthrough curves are presented in Figures 2.0. Faster breakthrough curves were observed for a bed height of 5 cm compared to the bed height of 10 cm and 15 cm.

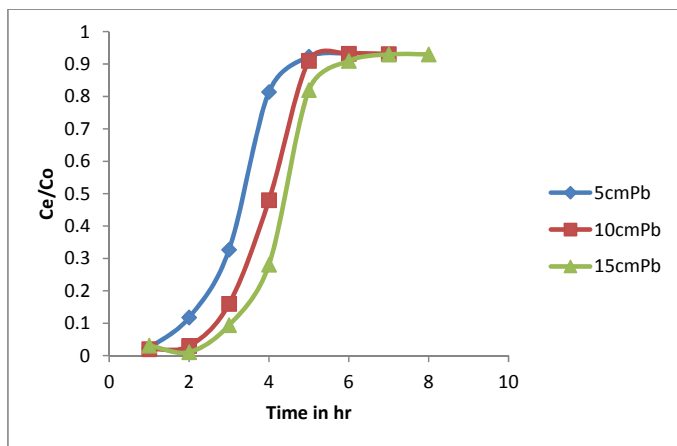


Figure 3.0: Column adsorption of Pb(II) by Activated Carbon from Velvet Tamarind Fruits Shells at different Bed height

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

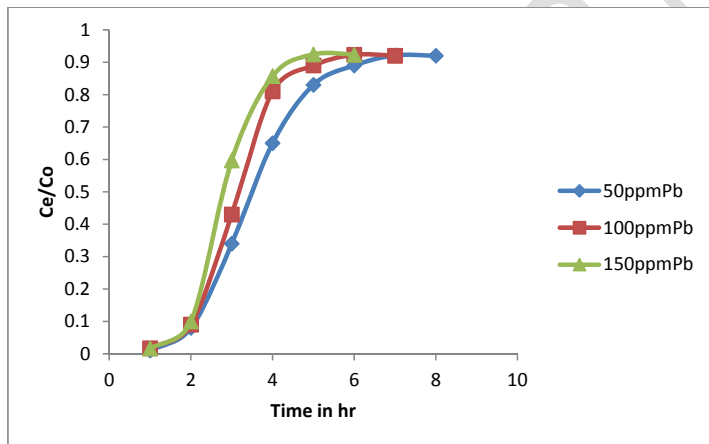
The results indicate that the throughput volume of the aqueous solution increased with increase in bed height, due to the availability of more number of sorption sites [21]. At higher bed depth of 10 cm, adsorbent mass was more residing in the column thereby providing larger service area for binding, fixation, diffusion and permeation of the solute to the

274 adsorbent. Longer bed depth also provided more reaction area and larger volume of influent treatment which translated
275 to higher adsorption capacity.

276
277 The equilibrium sorption capacity decreased with increase in bed height. This shows that at smaller bed height, the
278 effluent adsorbate concentration ratio increased more rapidly than for a higher bed height. Furthermore, the bed is
279 saturated in less time for smaller bed heights. The slope of the S-shape from t_b to t_e decreased as the bed height
280 increased from 5 to 15 cm, indicating the breakthrough curve becomes steeper as the bed height decreased. Also the
281 breakthrough time (t_b) and exhaustion time (t_e) increase with increase in bed depth

282 3.8.2 Effect of Initial Metal Concentration

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



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

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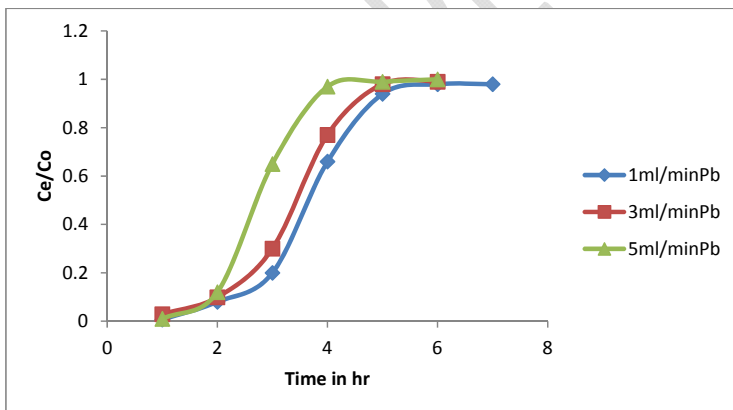
292 It can be seen from the Figure 4.0 that breakthrough curves display three important features: an initial lag period during
293 which effluent metal ions are non-detectable, followed by a rise in concentration, and finally a period of slow increase in
294 effluent level. It was assumed that the breakthrough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

297 increasing the initial metal concentration, the driving forces increases which enhance the rate of metal adsorption and
298 saturates the binding sites more quickly. This is consistent with results of the finding of [35], where the authors found
299 that by increasing inlet adsorbate concentration, the slope of the breakthrough curve increased and the volume treated
300 before carbon regeneration reduced. This behaviour was attributed to the high concentrations which saturated the
301 activated carbon more quickly, thereby decreasing the breakthrough time. It is also clear from Figures 1.0 to 5.0 that all
302 the curves exhibit a characteristic "S" shape which indicates an effective use of adsorbent [36].

303 3.8.3 Effect of flow rate on breakthrough curves

304 The adsorption columns were operated with different flow rates (1, 3 and 5 cm³/min) until no further metal ions removal
305 was observed. The adsorbent bed height and inlet initial metal ions concentration were fixed at 10 cm and 50 mg/dm³,
306 respectively. The breakthrough curve for a column was determined by plotting the ratio of the C_e/C_0 (C_e and C_0 are
307 the metal ions concentration of effluent and influent, respectively) against time, as shown in Figures 1.0 to 5.0
308 respectively. The effect of the flow rate on the adsorption of Cu, Cd, Pb and Ni are shown as breakthrough curves in
309 the figures. It was observed that breakthrough generally occurred faster with higher flow rate. The reason is that at
310 higher flow rate, the rate of mass transfer increased, thus the amount of metal ions adsorbed onto the unit bed height
311 (mass transfer zone) increased [37]. In addition, the adsorption capacity decreases with increase in flow rates due to
312 insufficient residence time of the solute in the column and lack of diffusion of the solute into the pores of the adsorbent,
313 therefore the solute left the column before equilibrium occurred. These results were in agreement with other findings as
314 reported by [38].

315



316

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

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319

320 The column performed well at the lowest flow rate (1cm³/min). Earlier breakthrough and exhaustion times were
321 achieved, when the flow rate was increased from 1 to 5 cm³/min. This was due to a decrease in the residence time,
322 which restricted the contact of metal ions to the adsorbents. Similar results have been found for As (III) removal in a
323 fixed-bed system using modified calcined bauxite and for color removal in a fixed-bed column system using surfactant-
324 modified zeolite [39].

325 3.9 Column Kinetic Study

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

327 3.9.1 Thomas model

329 The model was applied to the experimental data with respect to the initial metals concentration, flow rate and bed
330 height. The kinetic coefficient, kTh and the adsorption capacity of the bed, q_o were determined from the plot of
331 $\ln\left(\frac{C_o}{C_e} - 1\right)$ against t. The results of kTh, R² and q_o are given in Table 4.0. The results showed that the kinetic coefficient
332 kTh is dependent on flow rate, initial ion concentration and bed height. The maximum adsorption capacity q_o and
333 Kinetic coefficient kTh decreased with increase in flow rate but increased with increase in bed height and initial ion
334 concentration. The values of kTh obtained in this work is similar to the ones obtained by [15]. High values of regression
335 coefficients were obtained indicating that the kinetic data conformed well to Thomas model in contrast with the report of
336 [40] but in agreement with the results obtained by [41]. The trend observed with the calculated values of kTh, q_o are in
337 agreement.

338 3.9.2 Yoon and Nelson Model

339 This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate
340 molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the
341 adsorbent [42]. The Yoon and Nelson equation for single component system is expressed as shown in equation 4.3
342 [43]:

$$343 \quad \ln \frac{C_e}{C_o - C_e} = K_y n t - \tau K \quad (4.3)$$

344 Yoon and Nelson model has been used in the study of column adsorption kinetics [42][21]. The values of the Yoon-
345 Nelson parameters (k_{yn} and τ) were determined from the plot of $\ln \frac{C_e}{C_o - C_e}$ versus t at various operating conditions (Table
346 1.0 to 5.0). A plot of $\ln \frac{C_e}{C_o - C_e}$ versus t gives a straight line with slope of K_{yn}, and intercept of -τK. The results showed

347 that the rate constant, K_{yn} increased with increased inlet ions concentration, flow rate and bed height. The time
348 required for 50% breakthrough, τ decreased with increase in flow rate and initial ion concentration. High values of
349 correlation coefficients obtained indicate that Yoon and Nelson model fitted well to the experimental data and can be
350 used to describe the Cd(II), Cu(II), Pb(II) and Ni(II)-Velvet Tamarind shell and Cd(II), Cu(II), Pb(II) and Ni(II) – Sandal
351 fruit shell biosorption system.

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355 **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									
Kyn (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

357 **3.9.3 Lead Uptake in the Column at Different Operating Parameters**

358 This study showed that the sorption uptake capacity of the column Pb 1.73 mg g⁻¹ for velvet tamarind fruit
359 shells activated carbon as shown in Table 5.0. The increased capacity of the column method is largely due to the
360 continuous increased concentration gradient in the interface of the adsorption zone as it passes through the
361 column, whereas the gradient concentration decreases with time in batch systems [44][45]

362
363 A characterisation study on the Velvet Tamarind shells prior to biosorption showed that hydroxyl and carboxylic
364 functional groups were present and might be involved in the removal of metal ions from aqueous solutions by
365 this biosorbent, besides micro precipitation and electrostatic attraction forces. The results obtained by [44] for
366 Ni(II), Cd(II), Zn(II) and Pb(II) ions using H₂SO₄ treated coconut shell suggest that a lower pH of 6 is required for
367 optimal removal of the studied metals, similar to the pH of 6 ± 0.2 used in this study.

368
369 **Table 5.0: Uptake of Pb(II) by activated carbon from Velvet Tamarind Fruit shells at different flow rates**

	Z	Q	C ₀	V _{eff}	q _{total}	q _{e(exp)}	Z _m
	(cm)	(cm ³ min ⁻¹)	(mg dm ⁻³)	(cm ³)	(mg)	(mgg ⁻¹)	(cm)
V _t	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

370

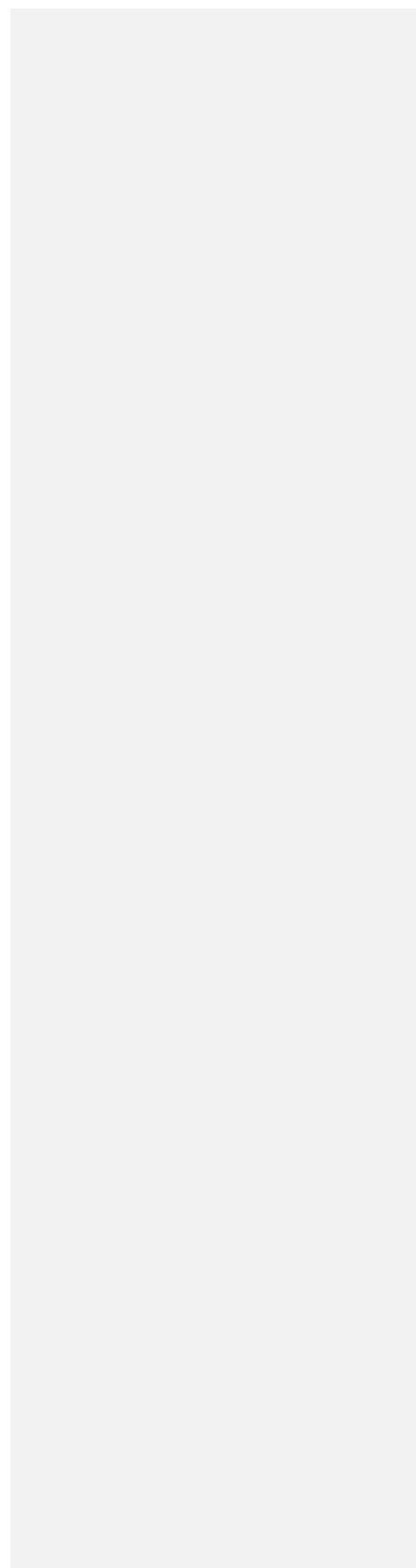
371

372 **4.0 Conclusion**

- 373 i. The experimental data revealed that an increase in bed height and initial metal concentration or a
374 decrease of flow rate enhances the longevity of column performance by increasing both breakthrough
375 time and exhaustion time thereby delaying bed saturation.
- 376 ii. The design of a continuous fixed bed column for removal of metal ions by velvet tamarind and sandal
377 fruit shells activated carbons can be achieved using the BDST, Yoon-Nelson and Thomas models.
- 378 iii. The FTIR analysis results suggested the presence of functional groups such as hydroxyl, carbonyl,
379 carboxyl and amine which could bind the metals and remove them from the solution.
- 380 iv. The values of moisture content, volatile matter, fixed carbon and ash content as obtained from %
381 proximate analysis are 3.43, 27.07, 65.05, 4.45 for activated carbons prepared from velvet tamarind
382 shells.

383 v. Ultimate analysis revealed that activated carbons prepared from velvet tamarind shells contained
384 75% carbon.
385

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386 **5.0 REFERENCES**

387 Oliveira, R. C., Guibal, E. & Garcia, O. (2012). Biosorption and desorption of lanthanum (III) and neodymium(III)
388 in fixed-bed columns with Sargassum sp. Perspectives for separation of rare earth metals.
389 *Biotechnology Progress*, 28(3), 715-722.

390 Ahluwalia, S. S., & Goyal, D. (2005). Removal of heavy metals by waste tea leaves from aqueous solution.
391 *Engineering and Life Science*, 5(9),158- 162.

392 Nouri, J., Mahvi, A. H., Babaei, A. A., Jahed, G. R., & Ahmadpour, E. (2006). Investigation of heavy metals in
393 groundwater *Pakistan Journal of Biological Science*, 9 (3), 377-384

394 Dermibas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous*
395 *Material*, 157(8), 220-229

396 Lazaridis, N. K., Matis, K. A., & Diels, L. (2005). 'Application of flotation to the solid/liquid separation of *Ralstonia*
397 *metallidurans*', 3rd *Eur. Bioremediation Conf.*, TU Crete, Chania,4-7 July.

398 Kuma, A., & Jena, H.M (2015) *Applied Surface Science* 356: 753–761.

399 Abia, A. A., & Asuquo, E. D. (2007). Kinetics of Cd²⁺ and Cr³⁺ Sorption from aqueous solution using
400 mercaptoacetic acid modified and unmodified oil palm fruit fibre (*elaeis*

402 Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, J., & Siemieniowska, T.
403 (2006). Reporting Physisorption data for gas/solid interface with special reference to the determination of
404 surface area and porosity. *Pure and Applied Chemistry*. 57, 603-619.

406 Kahraman, S., Dogan, N., & Erdemoglu, S. (2008). Use of various agricultural wastes for the removal of heavy
407 metal ions. *International Journal of Environmental Pollution*, 34, 275-284.

408 American Society for Testing and Materials. (1996). Standard, Refractories, Carbon and Graphic Products;
409 activated Carbon, ASTM, Philadelphia, PA, 15(01)

410 Ahmedna, M., Johns, M. M., Clarke, S. J., Marshall, W. E., & Rao, R. M. (1997). Potential of agricultural by-
411 product-based activated carbons for use in raw sugar decolourisation. *Journal of the Science of Food*
412 *and Agriculture*, 7(5),117-124.

413 American Society for Testing and Materials. (1986). Standard test method for determination of iodine number of
414 activated carbon. Philadelphia, PA: ASTM Committee on Standards.

415 Al-Quodah, Z., & Shawabkah, R. (2009). Production and characterization of granular activated carbon from
416 activated sludge. *Brazilian Journal of Chemical Engineering*, 26(1), 6-10.

417 Alam, C., Molina-Sabio, M., & Rodriguez-Reinoso, F. (2008). Adsorption of methane into ZnCl₂-activated carbon
418 derived discs. *Microporous and Mesoporous Materials*, 76(15), 185-191

419 Yahaya, N. K. E. M., Abustana, I., Latiff, M. F. I. P. M., Bello, O. S. & Ahmad, M. A. (2011). Fixed-bed column
420 study for Cu (II) removal from aqueous solutions using rice husk based activated carbon. *International*
421 *Journal of Engineering & Technology*, 11(1), 248-252.

422 Maheswari, B. L., Mizon, K. J., Palmer, J. M., Korsch, M. J., Taylor, A.J., & Mahaffey, K.R. (2008). Blood lead
423 changes during pregnancy and postpartum with calcium supplementation. *Environmental Health*
424 *Perspectives*, 112(15), 1499-1507.

425 Mozammel, H. M., Masahiro, O., & Bhattacharya, S. C. (2010). Activated charcoal from coconut shell using
426 ZnCl₂ activation. *Biomass and Bioenergy*, 22(6), 397-400.

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- 427 Gottipati, R., & Susmita, M.(2012). Process optimization of adsorption of Cr(VI) on activated carbons prepared
428 from plant precursors by a two-level full factorial design. *Chemical Engineering Journal*, 160 (1), 99-107.
- 429 Pandey, K. K., Prasad, G., & Singh, V. N. (2014). Use of wollastonite for the treatment of Cu(II) rich effluent.
430 *Water Air and Soil Pollution*, 27, 287-296.
- 431 Valix, M., Cheung, W. H., & McKay, G. (2004). Preparation of activated carbon using low temperature
432 carbonization and physical activation of high ash raw bagasse for acid dye adsorption. *Chemosphere*,
433 56, 493-501
- 434 Satyawali, Y., & Balakrishnan, M. (2009). Wastewater treatment in molasses-based alcohol distilleries for COD
435 and color removal: A review. *Journal of Environmental Management*, 86, 481-497.
- 436
- 437 Lopez, F. A., Perez, C., Sainz, E., & Alonso, M. (1995). Adsorption of Pb (II) on blast furnace sludge, *Journal of*
438 *Chemical Technology*., 62 (2), 200-206.
- 439 Kanan, K., & Sundaram, M. M. (2001). "Kinetics and mechanism of removal of methylene blue by adsorption on
440 various carbons—a comparative study", *Dyes and Pigments*. 51, 25–40.
- 441 Karthikeyan, S., Balasubramanian, R., & Iyer, C. S. P. (2008). Evaluation of the marine algae *Ulva fasciata* and
442 *Sargassum wightii* for the biosorption of Cu(II) from aqueous solutions. *Bioresource Technology*, 98 (2),
443 452-455.
- 444 Vijayaraghavan, K., Padmesh, T. V. N., Palanivelu, K., & Velan, M. (2006). Biosorption of nickel(II) ions onto
445 *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models. *Journal of*
446 *Hazardous Materials*, 133, 304-308.
- 447
- 448 Mohammed, U. M., Binta, M., Mustapha, S., & Idris, M (2016) Removal of Lead and Cobalt from Pharmaceutical
449 Effluent: Efficiency of Activated Coconut Shell and Commercial Activated Carbon. *American Chemical*
450 *Science Journal*, 12(2), 1-8
- 451 Alikarami, M., Abbari, Z., & Mohammadnezhad, S. (2016). Kinetics and thermodynamic studies of copper (II),
452 mercury(II) and chromium(II) adsorption from aqueous solution by peels of banana. *Journal of Basic and*
453 *Applied Scientific Research*, 3(3), 8-15.
- 454 Amuda, O. S., Giwa, A. A., & Bello, I. A. (2007). Removal of heavy metal from industrial wastewater using
455 modified activated coconut shell carbon. *Biochemical Engineering Journal*, 36(23), 174-181.
- 456
- 457 Deheyn, D. D., Gendreu, P., Baldwin, R. J., & Latz, M. I. (2005). Evidence for enhanced bioavailability of trace
458 elements in the marine ecosystem of Deception Island, a volcano in Antarctica. *Marine Environmental*
459 *Research*, 60(4), 1-33.
- 460
- 461 Castro, A., Suarez-Garcia, F., Martinez-Alonso, A., & Tascon, J. M. D. (2008). Activated carbon fibers with a high
462 content of surface functional groups by phosphoric acid activation of PPTA. *Journal of Colloid and*
463 *Interface Science*, 3(61), 307-315.
- 464
- 464 Liu, S., & Liu, J. (2008). Surface modification of coconut shell based activated carbon for the improvement of
465 hydrophobic VOC removal. *Journal of Hazardous Materials*, 192 (2), 683-690.
- 466 Yang, X., & Duri, B. A. (2005). "Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon".
467 *Journal of Colloid Interface Sciences*, 287, 25-34.
- 468 Alothman, Z.A., Habila, M.A & Ali, R. (2011). Preparation of activated carbon using the copyrolysis of agricultural
469 and municipal solid wastes at a low carbonization temperature. In: Proceedings of the international
470 conference on biological and environmental chemistry: 24, 67–72

- 471 Betzy, N. T., & Soney., C. (2015). Cyanide in industrial wastewaters and its removal: A review on biotreatment.
472 *Journal of Hazardous Materials*, 163, 1-11
- 473 Tamura, H., Hamaguchi, T., & Tokura, S. (2003). "Destruction of rigid crystalline structure to prepare chitin
474 solution", *Advances in chitin science*. 7, 84–87.
- 475 Patil, S., Bhole, A., & Natrajan, G. (2006). Scavenging of Ni(II) Metal Ions by Adsorption on PAC and Babhul
476 Bark. *Journal of Environmental Science and Engineering*, 48(3), 203-208.
- 477 Volesky, B. (2005). Advances in biosorption of metals: selection of biomass types. *Microbiology Reviews*, 14,
478 291–302.
- 479 Hrapovic, L., & Rowe, R. K. (2002). Intrinsic degradation of volatile fatty acids in laboratory- compacted clayey
480 soil. *Journal of Contaminant Hydrology*, 58, 221- 242
- 481 Sasikala, S., & Muthuraman, G. (2016) Removal of Heavy Metals from Wastewater Using *Tribulus terrestris*
482 Herbal Plants Powder. *Iranica Journal of Energy and Environment*, 7(1),39-47.
- 483 Baek, K., Song, S., Kang, S., Rhee, Y., Lee, C., Lee, B., Hudson, S., & Hwang, T. (2007). Adsorption kinetics of
484 boron by anion exchange resin in packed column bed. *Journal of Industrial Engineering Chemistry*,
485 13(3), 452-456.
- 486 Kavak, D., & Öztürk, N. (2004). Adsorption of boron from aqueous solution by sepiolite: II. Column studies. II.
487 Illuslrararasi. *Journal of American Chemical Society*, 23(25), 495-500.
- 488 Aksu, Z., Gönen, F., & Demircan Z. (2004). Biosorption of chromium (VI) ions by Mowital®B30H resin
489 immobilized activated sludge in a packed bed: comparison with granular activated carbon. *Process*
490 *Biochemistry*, 38(2),175-186
- 491 Sousa, F. W. (2010). Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed
492 column technology. *Journal of Environmental Management*, 91(8), 1634-1640
- 493 Martín-Lara, M. A., Blázquez, G., Ronda, A., Rodríguez, I.L., & Calero, M. (2012). Multiple biosorption–
494 desorption cycles in a fixed-bed column for Pb(II) removal by acid-treated olive stone. *Journal of*
495 *Industrial and Engineering Chemistry*, 18(3), 1006-1012
- 496
- 497