1	SUSTAINABLE UTILIZATION OF RICE HUSK ACTIVATED CHARCOAL THROUGH
2	PHYTOREMEDIATION
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5	

7 ABSTRACT

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8 The performance of rice husk-based activated carbon prepared by carbonization and chemical activation 9 with zinc chloride was tested with effluent from 7UP Bottling Company, Ngwo, Enugu State, Nigeria, using 10 standard protocols. The result indicated a significant (P<0.05) increase in the pH and temperature of rice 11 husk-based activated carbon treated effluent compared to control with no significant (P>0.05) difference. 12 Overall, the result revealed that there was a general significant (P < 0.05) decrease in the total hardness, 13 alkanility, chemical oxygen demand, biological oxygen demand, nitrate, total dissolved solid, total 14 suspended solid, total solid, sulphate, nitrate, chloride, and metals in rice husk acivated carbon treated 15 filtrate when compared to the untreated. Although, values of physicochemical parameters obtained in 16 filtrate from rice husk-based activated carbon were generally lower than that of commercial, the difference 17 were not statistically significant (P>0.05). The results showed that waste water treated with rice husk 18 activated carbon met the international standards for maximum limits of effluent discharge to sewage, 19 stream and drinking water. The study therefore recommends the use of rice husk-based activated carbon 20 as an efficient and environmental friendly water treament option.

21 **Keywords:** Activated carbon, Rice husk, Effluent, Adsorption, Environmental pollution, Waste management.

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23 **1. INTRODUCTION**

Rice husk is produced as a by-product during rice milling. It surrounds the paddy grain. It is being dumped into environment where burning is taking place, thereby increasing air pollution. The fermented husks in the open field also generate methane among other gases that are contributing to the global warming [1].

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The conventional municipal waste management approaches such as open dumping, sanitary land fill and incineration, are no longer efficient and effective to the growing solid waste problem worldwide [2]. The new idea is to turn waste materials into useful products. The principle is to convert waste liabilities into profitable assets. Present world consensus is on the rapid introduction of environmentally compatible energy and technology systems [1] whereby, wastes undergo recycling into useful products. There is a potential for developing new markets for rice husk based activated carbon because of its relative

33 availability.

Activated carbon is produced by the controlled thermalization of carbonaceous material, normally wood, coal, coconut shells or peat [3]. This activation produces a porous material with a large surface area (500– 36 1500m²/g) [4,5] and a high affinity for organic compounds, chlorine, lead, unpleasant tastes and odour in
 37 effluent or coloured substances from gas or liquid streams [3,6] by the mechanism of adsorption [7,8].

Activated charcoal is now applicable in many fields of operation, particularly in its employment on a commercial scale for a number of purposes, for example, effluent treatment, pollution control, water purification, fertilizer, heavy metal adsorbent, food and pharmarceutical industries and medically for removal of poison [9,10,11].

Effluent from various chemical process industries contains toxic substances in appreciable amounts and exhibit high chemical oxygen demand (COD), are highly coloured, hot and alkaline, containing high amounts of dissolved solids [12]. Adsorption on activated charcoal of these contaminants in waste water treatment has been found to be superior compared to other chemical and physical methods such as distillation, filtration, reverse osmosis, deionization, and others [13] in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity of design.

48 The need to monitor, control and clean up waste water is becoming more important as a result of health 49 risk posed to man and his environment. Although, the toxicity of the effluent has been known for many 50 years, public awareness and sensitivity, combined with increasing and stiffer pollution control regulations, 51 have made the search for the solution to the problem most urgent. However, commercially available 52 activated carbons are still expensive due to the use of non-renewable and relatively high-cost starting 53 material such as coal, which is unjustified in pollution control applications [14,15]. In a country where 54 economy plays a very big role, it is better to find out relatively low-cost adsorbents to be used in this 55 countryside. Activated charcoal is therefore the answer since it has now been recognized as an effective 56 and economic method for the removal of pollutants from the environment [16].

57 In recent years, many researchers have tried to produce activated charcoals for removal of various 58 pollutants using renewable and cheaper precursors which were mainly industrial and agricultural 59 byproducts. In the same line of action, this research focuses on utilization of rice husk (hitherto term waste) 60 generated from the rice milling industry as a raw material for the production of activated charcoal via 61 carbonization and chemical activation. The performance of the prepared activated charcoal as an 62 adsorbent was tested on contaminants present in waste water collected from 7up Bottling Company.

63 Conversion of this cheap and abundant agricultural waste into activated carbon will serve many purposes. 64 First, unwanted agricultural waste is converted to useful, value-added adsorbents and second, the use of 65 agricultural by-products represents a potential source of adsorbents which will contribute to solving part of 66 the wastewater treatment problem [17], and finally, it will help in reducing the heap-log of this waste from 67 causing environmental hazards, which will greatly enhance the aesthetic values of our environment.

68

69 2. EXPERIMENTAL DETAILS

70 **2.1. Sample Collection and Treatment**

71 The waste material (rice husk) was collected from rice mill beside Eke market, Afikpo, Nigeria. Extraneous

72 materials were removed and repeatedly washed with tap water to remove impurities and then sun dried.

- 73 The dried samples were grounded followed by sieving with 60 mesh size sieve and was finally stored in air
- 74 tight containers prior to carbonization.
- All chemicals used were of analytical grade and deionized water was employed for the preparation of allrequisite solutions.

77 **2.2. Carbonization and Activation**

The raw material was impregnated with 1.0moldm⁻³ zinc chloride at the weight ratio of 1:1 for 1hr and dried at 105^oC for 24hrs. The mixture was carbonized using muffle furnance at 450^oC for 4hr after which it was removed and cooled in ice water bath; excess water was drained out and allowed to stand at room temperature. The residual activation reagent and surface ash was removed from the sample by using 0.10moldm⁻³ hydrochloric acid and rinsed with deionized water to remove residual acid. Washing was completed when the pH of 7 was ascertained. It was then dried in an oven at 110^oC for 1hr.

84 **2.3. Adsorption Studies**

The rice husk-based carbon (RAC) prepared and the commercial activated carbon (CAC) were parked separately into different columns with two open ends. One end of the columns was closed with cotton wool to prevent the adsorbents from flowing out. The columns were mounted vertically with the open ends upward. Through the open ends of the columns, 100cm³ of the effluent from 7UP bottling company was poured through the column. The filterates were collected separately and labelled accordingly.

90 **2.4. Physicochemical Assay**

91 The physicochemical properties of each filtrate and that of untreated effluent that are essential to 92 determine the quality of water were analysed separately as per the standard methods [18,19].

93 **2.5. Data Analysis**

Three independent experiments were performed on each filtrate and raw effluent. A one-way analysis of variance (ANOVA) was used to analyze the difference between experimental groups. Means were compared by the Duncan' multiple range test and significance was established at 5% level (P≤0.05) using SPSS 2008 version 15.0 package.

98

99 **3. RESULTS AND DISCUSSION**

100 **3.1. Table of Results**

101 Results of untreated effluent, effluent treated with commercial activated carbon (ECAC) and effluent 102 treated with rice husk-based activated charcoal (ERAC) in comparism with the international standards for 103 maximum limits of effluent discharge to sewer [20], stream [21] and drinking water [22].

Parameter	Untreated Effluent	ECAC	ERAC	Discharge to sewer	Discharge to stream	Discharge to drinking water
Odour	Offensive	Odourless	Odourless	NA	NA	NA
Colour	Pale yellow	Colourless	Colourless	NA	NA	NA
рН	5.52±0.14 ^c	6.32±0.09 ^a	6.29±0.20 ^b	6.0-10.0	6.5-8.5	6.5-8.5
Temperature (⁰ C)	25.4±0.15 ^ª	25.2±0.03 ^b	25.3±1.00 ^c	44	32.5	NA
TDS (mgl ⁻¹)	441±3.13 ^a	130±2.10 ^c	175±1.08 ^b	NA	500	NA
TSS (mgl⁻¹)	120±1.70 ^a	85.0±0.97 ^b	32.0±1.01 ^c	1000	400	NA
TS (mgl ⁻¹)	561±0.6.2 ^a	215±5.40 ^b	177±4.40 ^c	NA	NA	500
Alkalinity (mgl ⁻¹)	154±1.27 ^a	132±0.79 ^b	110±1.10 ^c	2500	NA	NA
Hardness (mgl ⁻¹)	36.0±0.65 ^a	19.0±0.47 ^b	16.0±0.50 ^c	NA	NA	NA
COD (mgl ⁻¹)	544±1.06 ^a	198±2.33 ^b	145±1.90 ^c	8	20	NA
BOD (mgl ⁻¹)	79.0±0.05 ^a	23.0±0.61 ^b	12.0±1.21 [°]	NA	NA	NA
NO_3^{-} (mgl ⁻¹)	3.50±050 ^b	4.20±0.13 ^a	2.30±0.37 ^c	400	NA	NA
SO ₄ ²⁻ (mgl ⁻¹)	70.1±7.50 ^a	31.3±2.23 ^b	26.0±3.81 [°]	1000	NA	400
Cl⁻ (mgl⁻¹)	531.0±4.0 ^a	44.0±2.16 ^c	5.80±1.01 ^b	400	1(free Cl ₂)	600
Pb (mgl ⁻¹)	0.01±0.00 ^a	0.01±0.00 ^b	BDL⁵	NA	0.1	0.05
Fe (mgl⁻¹)	0.92±0.02 ^a	0.77±0.06 ^b	0.62±0.11 [°]	1.5	1	1
Zn (mgl⁻¹)	1.88±0.07 ^a	0.23±0.00 ^c	0.73±0.03 ^b	NA	1	15
Cu (mgl ⁻¹)	0.30±0.03 ^a	0.19±0.00 ^c	0.21±0.00 ^b	50	1	1.5
Cr (mgl ⁻¹)	0.25±0.01 ^a	0.15±0.02 ^b	0.02±0.01 ^c	50	1	NA
As (mgl⁻¹)	BDL	BDL	BDL	NA	1	NA

104 Note: NA = Not Available; BDL = Below Detection Limit.

105 Values followed by the same superscript alphabets in the same row are not significantly different but those

106 followed by different alphabets are significantly different using Duncan's multiple range test at P = .05

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108 **3.2. Discussion**

109 The pH of untreated waste water indicated acidic. pH is an idex of acidity or alkalinity of a substance. The 110 pH of treated sample increased and was within the range of 6.5 to 9.5 given by international standards of 111 waste water discharge into drinking water, stream and sewer, thus, indicating improvement in the water 112 quality.

- 113 The temperature of the untreated effluent, effluent treated with commercial activated carbon (CAC) and
- filtrate obtained from effluent that passed through rice husk-based activated carbon (FRAC) measured to
- 115 be 25.4°C, 25.2°C and 25.3°C respectively. All fell below the permissible limits of waste water to be
- 116 discharged into sewer and stream (see table).
- 117 Interestingly, the offensive odour and pale yellow colour of the untreated effluent were removed with the 118 aid of the absorbent prepared (RAC) and that of CAC.
- The total dissolved solid (TDS) of untreated effluent was 441mg/l. TDS contains dissolved materials such as carbonates, chloride, sodium, potassium, magnesium sulphates and other ions. TDS value of 175mg/L for RAC treated filterate in this study was below the recommended value and far below that of untreated effluent. It is a known fact that water sample with very high TDS and Cl⁻ concentrations is not useful for bathing, drinking and for industrial applications; such water is expected to have high osmotic potential, thereby making the sample to be potential irritant of the skin [23]. As far as the value obtained with RAC is concern, there is no cause for alarm.
- 126 Sample with high TSS possesses high BOD [24] and NO₃ due to microbial oxidation of the suspended 127 organics [23]. Suspended solids act directly on fish in water, thereby reducing their growth rate, prevent 128 successful development of fish eggs and larvae, clog fish gills and modify aquatic natural environment 129 [25]. TSS of 32.0mg/L in filtrate obtained from RAC was below that of untreated effluent of 120mg/L and 130 far below the regulatory limit of 400mg/L and 1000mg/L for maximum contaminant limit of effluent to be 131 discharge into stream and sewer respectively. TSS indicates the presence of suspended material such as 132 clay, silt, finely divided organic materials, planktons and other inorganic materials and signifies appreciable 133 purity [19]. BOD signifies organic pollution and measures the productivity of a water. The lower the BOD, 134 the purer the water [26]. Taking these two parameters into account, the filterate that passed through RAC, 135 TSS to be 32.0mg/L and BOD to be 145mg/L. These low values denote that the filterate from RAC was 136 pure. COD with BOD on the other hand are indices of organic pollution. Nearly all organic compounds are
- 137 oxidized in the COD test, it is therefore expected that the values of COD are higher than that of BOD.
- Water medium with extreme alkalinity cannot support aquatic lives. In addition, the presence of alkalis in waste water influences the toxicity of inorganic pollutants [26]. The values reported in this research for untreated effluent (154mg/L), FCAC (132mg/L) and FRAC (110mg/L) were far below maximum limit of 2500mg/L recommended for effluent to be discharged into sewer. Alkalinity is not considered detrimental to humans but is generally associated with high pH values, hardness and excess dissolved solids and may also have an unpleasant taste [23,25]
- The hardness of the untreated effluent reveals that there were presence of dissolved salts of metals like calcium, magnesium and iron while the treated samples were low, which is an indication of soft water. Concentrations of calcium and magnesium are important contributors to water hardness.There was no significant difference between the hardness of FRAC (16.0mg/L) and that of FCAC (19.0mg/L), but were lower than that of untreated effluent (36.0mg/L). There was appreciable reduction of the effluent hardness after passing through RAC. The reduction in the hardness from this investigation was lower compared to activated carbon prepared by Ajiwe et al [27] from *Pterocarpus santalinoides*, which put hardness at

151 30mg/L. Hard water may not have health effect but may form scale in boilers, water heaters, pipes and152 cooking utensils [26].

The mean concentrations of NO₃, SO₄² and Cl⁻ of the untreated effluent were 3.50mg/L, 70.1mg/L and 153 154 531mg/L respectively while the filterate treated with RAC were 2.30mg/L, 2.0mg/l and 5.8mg/l respectively. 155 The low levels of these anions give credence to the prohibition of microbial growth. Chloride 156 concentrations above 250 mg/L in drinking water may cause corrosion in the distribution system [28]. High 157 concentrations of chloride ions may also result in an objectionable salty taste. High chloride water may 158 also produce a laxative effect. The chloride content in the untreated effluent (531mg/L) was above limits 159 for discharge into drinking water and sewer but lower than maximum limit for effluent to be discharged into 160 drinking water. Sulphate is a substance that is often found in drinking water. Health concerns regarding 161 sulphate in drinking water have been raised because of reports of diarrhea associated with the ingestion of 162 water containing high levels of sulphate [29], such water is not also good for industrial applications 163 because it may form a hard scale in boilers and heat exchangers. There is no cause for alarm since RAC 164 was able to reduce the sulphate content from 70.1mg/L (untreated effluent) to 2.0mg/L. High 165 concentrations of nitrate in water result in eutrophication (excessive increase in population of microbiota). 166 The higher the concentration of this anion in water bodies, the higher the level of pollution [26,27].

167 Heavy metals, some of which are carcinogenic (e.g. As), terratogenic (e.g. Pb), mutagenic (e.g. Cd, Ni, 168 Cu, Pb) and toxic (e.g. Pb, Cd) [27] were reduced below the regulatory bodies' standards of effluent to be 169 discharged into drinking water, stream and sewer. For instance, Pb and Zn were below detectable limit 170 from the raw effluent with the aid of RAC. When the concentrations of iron and manganese are above 171 regulatory limit, they may cause brown and black stains on laundry, plumbing fixtures and sinks [27]. The 172 values recorded in the FRAC may not pose health hazard. The uptake of chromium by this test adsorbent 173 was excellent compared to that of CAC and the value was far below maximum permissible limits in 174 accordance with international standards [30,31].

Generally, RAC adsorbed the pollutants in the effluent beyond the limit set aside by the regulatory authorities. The adsorption efficiencies of activated charcoal are modified by lignin, a non-carbohydrate constituent. The adsorption ability of plant increases as the quantity of lignins increases, and this is observed when the plant's organs are young [6]. No wonder why RAC had excellent adsorption properties because it was prepared from plant **a** that **is** matured and harvested after four months of planting.

180

181 4. CONCLUSION

Considering the chemical indicators for pollution in water, all the parameters tested in FRAC were far below the maximum desirable level when compared with the international standards for effluent discharge. This study has revealed that rice husk is a good and cheap agricultural residue precursor for the production of activated charcoal, thus, representing an economically promising material. Hence, its utilization as an adsorbent in waste water treatment should be encouraged.

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