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Potential of Groundnut Shell-Based Activated Charcoal for Laboratory Water Treatment

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Abstract: *Groundnut shell is a readily available agricultural waste that can be used as a low-cost adsorbent for purification of laboratory water. This agricultural waste was used as a precursor for the preparation of activated charcoal using zinc chloride as a chemical activating agent. Biosorption of contaminants with the adsorbent in laboratory water was investigated using standard methods with a view to ascertaining the adsorbent purification efficacy. The physicochemical properties of the laboratory water treated with the test adsorbent and the commercial activated charcoal (control), generally indicated significant ($P<0.05$) decrease in the properties investigated in the adsorbent-treated water when compared with the untreated water. With exception of alkalinity in the entire treated and untreated water samples, with slightly higher values above the permissible limit, other parameters investigated in the water treated with the product fell within the standards for set by regulatory agencies. Generally, the test adsorbent was more effective than the commercial activated charcoal in the adsorption of contaminants in the laboratory water. This research has revealed that groundnut shell-based activated charcoal could be employed as a low-cost alternative adsorbent for decontaminating laboratory water.*

Keywords: *Groundnut shell, activated charcoal, adsorbents, laboratory water, agricultural waste.*

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I. Introduction

Water supplies for laboratory uses are sometimes characterized with high concentrations of contaminants that render them unfit for laboratory experiments. Water, being a universal solvent, dissolves more substances to varying degrees than any other solvent. This is due to the unique polarity and hydrogen bonds of the water molecule [1]. The same unique molecular properties of water account for its ability to react with neutral organic molecules and establish hydrogen bonding with other molecules [1]. For this reason, water quality is crucial in the laboratory because wherever water is required; its purity must be taken into account.

Laboratory water is easily contaminated by chemical solids, gases, vapours and ions that leach from reservoirs, piping lines and containers. These may include sodium and silica from glass, plasticizers and ions from pipes, microbial species and their endotoxins, as well as particulate contaminants [2]. The use of impure water for laboratory analyses can result in compromised experimental results, contaminate reagents, interfere with the analytes of interest and damage analytical equipment [2]. Therefore, the search for solutions to clean contaminated water to be used in the laboratories is becoming urgent to guarantee the reliability of the results being reported.

To overcome this challenge, various methods of water purifications such as electro-coagulation, electro-deionization, ultraviolet oxidation, sedimentation, chemical precipitation, distillation, deionization, coagulation-flocculation and other filtration techniques [1–5] had been applied to decontaminate impure water for laboratory use. However, such treatment methods are faced with one or other drawbacks such as energy, time and labour intensive, expensive to maintain, not environmentally friendly, reintroduction of extracted contaminants as in the case of distillation, filters in filtration unable to remove dissolved material, microbial growth and release of particulates can be a haven from ion exchange beds used in deionization, inability of electro-deionization to remove organics, particles, pyrogens or bacteria and inability of ultraviolet oxidation to remove ions, colloids or particulates [2, 3].

Lately, adsorption of contaminants over activated charcoals has proved to be more preferable in the treatment of impure waters [6–10]. This decontamination technique is becoming acceptable as a result of its versatility, environmental compatibility, relative abundance and low-cost starting materials (sometimes wastes), adsorption of a broad range of pollutants, fast adsorption kinetics, and ease of production [11–13]. Activated charcoals had been used successfully in effluent treatment [14, 15], water purification [11, 16–19], pesticide adsorbent from wastewater [20] and heavy metal sorption from aqueous media [16, 21–26]. They are also applicable for the treatment of poisons [27, 28] and prevention against novel Corona virus (SARS-CoV-2) [13].

Commercial activated charcoals are expensive due to the use of non-renewable and relatively high-cost starting materials such as coal [29, 30]. In developing countries, Nigeria inclusive, where economy plays a very big role, it is better to find relatively low-cost alternative adsorbent for purification of laboratory water. Recently, researchers have tried to produce activated charcoals using renewable, readily available and cheaper precursors which are mainly industrial and agricultural wastes such as bagasse [31], activated sludge [32], rice husk [19, 31, 33], coconut shell [34, 35], sawdust [18, 36, 37], empty palm fruit bunch [38], physic nut waste [24, 39, 40], pruning mulberry shoot [5], bamboo stem [11, 16], chickpea [25] acorn shell [41] and some plant seeds [17, 23]. However, despite extensive scientific researches on the treatment of waters with activated charcoals, to date, no significant study has been conducted on the treatment of laboratory water with groundnut shell-based activated charcoal, hence, this study. This study was aimed at producing activated charcoal from what was hitherto referred to as an agricultural waste. The produced charcoal was used to decontaminate laboratory water. Some parameters that are necessary to determine the quality of the purified water were carried out in order to confirm the effectiveness of the adsorbent.

Groundnut shell is a waste that is largely generated after the edible seeds had been removed. This waste product is usually burnt in an open air causing environmental pollution. Conversion of this cheap and abundant agricultural waste into a useful and value-added product will contribute to solving part of the laboratory water treatment problems and by and large, helps in the management of solid waste which will greatly enhance the aesthetic conditions of the environment.

II. Experimental

Samples' Collection and Preparation

Groundnut shells were collected from the processing plant at Abakaliki, Nigeria. They were transported to the Chemistry Research Unit of the Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria. Extraneous materials were removed and were repeatedly washed with deionized water to remove other impurities and then, sun-dried for 3 days. The dried sample was pulverized and particle sizes of 500 to 600 μm were collected and stored in an air-tight container for further analyses. The water used for adsorption studies was collected from a reservoir tank that supplies water for laboratory uses. Temperature and pH were measured in situ. Commercial activated charcoal (Calgon carbon, F-300) used as a control and other chemicals were of analytical grades and were sourced from BDH Chemicals Limited, UK. Carbonization and activation of the groundnut shell were performed according to our previous study [8] and method of Wang et al. [5].

Fixed Bed Adsorption Studies

The test adsorbent (GAC) and the commercial activated charcoal (CAC) were parked separately into different filtration columns. Through the open ends of the columns, the test water was poured through the cartridges of the columns already packed with the adsorbents. The filterates were collected separately from the other open ends of the columns for physicochemical assay.

Physicochemical Properties of Untreated and Treated Water

Physicochemical properties (pH, temperature, colour, odour, total suspended solids and total dissolved solids, alkalinity, hardness, chemical oxygen demand, biological oxygen demand, turbidity, conductivity, chloride, nitrate, phosphate, sulphate and heavy metal ions) that are essential to determine the quality of water in the untreated water, filtrate from the commercial activated charcoal (FCAC) and filtrate from the groundnut-based activated charcoal (FGAC) were determined accordingly following standard methods [42].

Analytical Method Control

Several batteries of quality control and assurance measures were carried out. All chemicals used were checked for possible trace metal contamination. Double-distilled deionized water was employed for the preparation of all requisite solutions. Samples were carefully handled to avoid cross contamination. All glassware used for analyses were previously soaked in 10% nitric acid (v/v) for 24 hr., washed with detergent, rinsed with double-distilled deionised water and dried in a clean laboratory oven. Standard solutions of the heavy metals in the filtrates and untreated water were prepared in five different concentrations to obtain respective calibration curves. Blanks were prepared and similarly treated as samples to give room for blank correction. Blanks and standard solutions were co-analysed with the analytical samples. Linear ranges were obtained for the target ions with good correlation coefficients ($R^2 \geq 0.9995$). The limits of detection of the elements analysed were determined and were found to be Cd^{2+} (0.002), Ni^{2+} (0.006), Pb^{2+} (0.005), Mn^{2+} (0.030), Fe^{2+} (0.025), Zn^{2+} (0.025), Cu^{2+} (0.015), Cr^{3+} (0.020), and As^{3+} (0.001) mg dm^{-3}. Recovery tests were also performed by spiking a known concentration of the analyte to the samples and results were in the range of 94 –

105%. The precision (relative standard deviation) of 10 replicate determinations of the target ions were calculated; this ranged from 0.76 to 2.66%.

III. Results and Discussion

Properties of Treated and Untreated Water

The results as presented in Table 1 showed the physicochemical properties of untreated water, and water samples treated with the CAC and GAC. The GAC balanced the pH of the untreated water to a reasonable degree after the treatment; and the value was within the approved standards [43–45], thus indicating improvement in the water quality. Similar reports of pH adjustment in contaminated water with activated charcoals had been documented [11, 46]. There were no significant differences ($p = 0.05$) in the temperature before and after the adsorption process. The entire results (Table 1) fell within the minimum and maximum permissible limit [43]. This implies that the adsorbent had no significant effect on the temperature of the water sample.

Total dissolved solids (TDS) measure the amount of dissolved materials in a water sample. TDS in the untreated water was reduced to 63.7% after treatment with the GAC but the efficiency was lower than 70.5% achieved by the CAC. However, it was more effective than activated carbon from bamboo [11], where only 24.3% dissolved solids were removed. High total suspended solids (TSS) in a water sample signifies the presence of impurities, high BOD and NO_3^- due to the microbial oxidation of the suspended organics [47]. The GAC adsorbed more suspended solids from the untreated water compared to the CAC but less effective compared to the adsorbent prepared elsewhere [46].

The values reported in this research for alkalinity in the untreated and treated water samples were higher than the recommended value of 100mg dm^{-3} [43, 44]. However, alkalinity is not considered detrimental to humans but is generally associated with high pH values and hardness [47]. There were no significant differences ($p = 0.05$) in the hardness values obtained in the FCAC and FGAC but statistically differ with the value obtained in untreated water (Table 1). Hard water may form scale in glassware, pipes, and heating apparatus [47] and invalidate experimental results.

Table 1: Results of untreated water, filtrate from water treated with commercial activated charcoal (FCAC) and filtrate from groundnut shell-based activated charcoal (FGAC).

Parameter	**Untreated water**	**FCAC**	**FGAC**	**WHO limit (2003)**	**SON limit (2007)**	**USEPA limit (2012)**
pH	5.52 ± 0.10^c	6.32 ± 0.20^b	6.76 ± 0.30^a	6.5 - 9.5	6.5-8.5	6.5-8.5
Temperature (℃)	25.4 ± 0.30^a	25.2 ± 0.20^a	25.3 ± 0.15^a	20-32	Ambient	NVA
Odour	Odourless	Odourless	Odourless	Unobjectionable	Unobjectionable	3 TON
Colour (TCU)	8.2	2.1	1.8	15	15	15
TDS (mg dm^{-3})	441 ± 6.00^a	130 ± 5.00^c	160 ± 6.00^b	500	500	500
TSS (mg dm^{-3})	120 ± 2.00^a	85.0 ± 4.00^b	44.0 ± 1.04^c	NVA	NVA	NVA
TS (mg dm^{-3})	561 ± 3.20^a	215 ± 2.23^b	208 ± 3.01^c	500	NVA	NVA
Turbidity (NTU)	0.87 ± 0.05^a	0.21 ± 0.10^b	0.16 ± 0.02^b	NVA	5	0.5
Conductivity (µscm^{-1})	882 ± 8.00^a	224 ± 4.00^c	248 ± 7.30^b	1200	1000	NVA
Alkalinity (mg dm^{-3})	154 ± 1.01^a	132 ± 2.30^b	124 ± 2.70^c	100	100	NVA
Hardness (mg dm^{-3})	36.0 ± 2.70^a	19.0 ± 2.00^b	18.5 ± 0.50^b	100	150	NVA
BOD (mg dm^{-3})	544 ± 10.0^a	198 ± 4.00^b	110 ± 5.00^c	NVA	NVA	NVA
COD (mg dm^{-3})	684 ± 9.23^a	200 ± 4.45^b	86.0 ± 3.32^c	NVA	NVA	NVA
NO_3^-(mg dm^{-3})	3.50 ± 0.50^b	3.20 ± 0.10^b	6.40 ± 0.30^a	50	50	10
SO_4^{2--}(mg dm^{-3})	70.1 ± 5.10^a	31.3 ± 2.28^b	22.5 ± 3.11^c	500	100	250
PO_4^{3-} (mg dm^{-3})	350 ± 2.51^a	121 ± 1.78^b	124 ± 2.00^b	NVA	NVA	NVA
Cl^- (mg dm^{-3})	531 ± 14.00^a	44.0 ± 4.00^c	86.0 ± 1.00^b	500	250	250
Cd (mg dm^{-3})	BLD	BLD	BLD	NVA	0.003	0.005
Ni (mg dm^{-3})	0.03 ± 0.00	BLD	BLD	NVA	0.02	0.1
Pb^{2+} (mg dm^{-3})	0.01 ± 0.00	BLD	BLD	0.05	0.01	0.05

Mn (mg dm^{-3})	0.40 ± 0.01^{a}	BLD	0.02 ± 0.00^{b}	0.4	0.2	0.05
Fe^{2+} (mg dm^{-3})	0.92 ± 0.23^{a}	0.77 ± 0.11^{a}	0.83 ± 0.05^{a}	3.0	0.3	0.3
Zn^{2+} (mg dm^{-3})	1.88 ± 0.12^{b}	0.23 ± 0.01^{c}	2.65 ± 1.01^{a}	NVA	3	5
Cu^{2+} (mg dm^{-3})	0.30 ± 0.00^{a}	0.19 ± 0.00^{b}	BLD	NVA	1	1
Cr (mg dm^{-3})	0.25 ± 0.020^{a}	0.09 ± 0.005^{b}	0.02 ± 0.005^{c}	5.0	0.05	0.1
AS^{3+} (mgdm^{-3})	BLD	BLD	BLD	NVA	0.01	0.01

$^{a-c}$means±SD with the same superscript letters within a row are not significantly different ($p = 0.05$); BLD - below limit of detection; NVA – no value available.

Turbidity is a measure of water quality with respect to colloidal and residual suspended matter [46]. Low level of turbidity signifies appreciable purity [47]. The GAC was very effective in lowering the turbidity reading by 81.6% as compared to 64% by the CAC and 68% reduction achieved with granulated activated charcoal in well water [46]. Yet, the test adsorbent was less effective compared to the activated charcoal prepared from waste bamboo stem [11], where 100% removal of turbidity was achieved. Conductivity is directly related to mineral contents of a water sample [47]. The GAC-treated water had lower conductivity measurement compared to untreated water (Table 1). This suggests that the GAC had significant adsorption efficacies on the dissolved ions in the impure water. Results obtained from the FGAC and FCAC were within the acceptable limits [43–45]. The observed reduction was also reflected in the lower values of metallic and non-metallic ions determined in the FCAC, and FGAC (Table 1).

Biochemical oxygen demand (BOD) signifies organic pollution and measures the productivity of water. The higher the value, the more polluted the water sample [47]. The GAC lowered BOD by 79.8% in the impure water compared to 63.6% by the CAC. Similar degree of BOD reduction was observed in the results of Siong et al. [46] and Ademiluyi et al. [11] with 77.3% and 74.8%, respectively in contaminated waters. Chemical oxygen demand (COD) is a measure of the amount of a specified oxidant that reacts with the water sample under controlled condition [46]. Approximately 87.4% reduction was achieved with the GAC as an adsorbing agent. This result had a better COD reduction compared to 77.8% with granulated activated charcoal [46] and 62.2% with bamboo stem activated charcoal [11].

There were significant differences in the mean concentrations of the non-metal ions determined in the water samples. The results of these ions in the filtrates (FCAC and FGAC) showed significant reduction in their concentrations. Water sample high in chloride ions may result in an objectionable salty tast and produce a laxative effect [47]. The chloride content in the untreated water (531 mgdm^{-3}) was higher than maximum permissible level of 500 mgdm^{-3} [43] but the GAC lowered this value by 83.8%. Also, it reduced the sulphate content from 70.10 mgdm^{-3} in the untreated water to 22.5 mgdm^{-3}. The higher the concentrations of nitrate and phosphate of a water sample, the higher the level of pollution [47]. The low values of nitrate and phosphate in the FGAC may not pose serious effect on the results of laboratory investigations. There is a great tendency for bacteriological pollution if the nitrate concentration is above permissible recommended level [47].

Some of the heavy metal ions investigated in the water are carcinogenic, teratogenic, mutagenic, and toxic [47]. Some were found below the limits of detection after the impure water passed through the test adsorbent while there was significant decrease in the concentrations of others with the exception of zinc, which had a higher value in the FGAC. This is expected since $ZnCl_2$ was used as an activating agent, which might have added up to the Zn^{2+} concentration in the FGAC. The reduction of these metal ions in the water after treatment in this study was in tandem with similar reports [7, 16, 23–25, 28].

IV. Conclusion

Activated charcoal was produced from an agricultural waste, groundnut shell, using zinc chloride as an activator. The significant reduction of contaminants below the regulatory limits when the adsorbent was tested with laboratory impure water bares credence to it adsorption prowess in the treatment of contaminated water. This result from this research had made it clear that carbonized biomass, groundnut shell-based activated charcoal could be used to generate reagent grade water for laboratory experiments. In addition, utilization of this biomass for the production of activated charcoal can serve as a better solid waste management option, which will greatly enhance the aesthetic values of our environment.

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