SUSTAINABLE UTILIZATION OF RICE HUSK ACTIVATED CHARCOAL THROUGH PHYTOREMEDIATION

ABSTRACT

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

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

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 worming [1].

The conventional municipal waste management approches 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 ideal 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 potential for developing new markets for rice husk based activated carbon because of its relative 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–

1500m^2/g) [4,5] and a high affinity for organic compounds, chlorine, lead, unpleasant tastes and odour in 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 colured, 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.

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

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

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

2. EXPERIMENTAL DETAILS

2.1. Sample Collection and Treatment

The waste material (rice husk) was collected from rice mill beside Eke market, Afikpo, Nigeria. Extraneous materials were removed and repeatedly washed with tap water to remove impurities and then sun dried.

The dried samples were grounded followed by sieving with 60 mesh size sieve and was finally stored in air tight containers prior to carbonization.

All chemicals used were of analytical grade and deionized water was employed for the preparation of all requisite solutions.

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^{O}C for 24hrs. The mixture was carbonized using muffle furnance at 450^{O}C 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^{O}C for 1hr.

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, 100cm^{3} of the effluent from 7UP bottling company was poured through the column. The filterates were collected separately and labelled accordingly.

2.4. Physicochemical Assay

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

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 ($P \leq 0.05$) using SPSS 2008 version 15.0 package.

3. RESULTS AND DISCUSSION

3.1. Table of Results

Results of untreated effluent, effluent treated with commercial activated carbon (ECAC) and effluent treated with rice husk-based activated charcoal (ERAC) in comparism with the international standards for 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
pH	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 (^{O}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})	$561\pm0.6.2^{a}$	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^{c}	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^{c}	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}	BDL^{b}	NA	0.1	0.05
Fe (mgl^{-1})	0.92 ± 0.02^{a}	0.77 ± 0.06^{b}	0.62 ± 0.11^{c}	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

Note: NA = Not Available; BDL = Below Detection Limit.
Values followed by the same superscript alphabets in the same row are not significantly different but those followed by different alphabets are significantly different using Duncan's multiple range test at P = .05

3.2. Discussion

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

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) recorded 25.4^0C, 25.2^0C and 25.3^OC respectively. All the results fell below the permissible limits of waste water to be discharged into sewer and stream (see table).

Intrestingly, the offensive odour and pale yellow colour of the untreated effluent were removed with the help of the absobent 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.

Sample with high TSS possesses high BOD [24] and NO_3^- due to microbial oxidation of the suspended organics [23]. Suspended solids act directly on fish in water, thereby reducing their growth rate, prevent successful development of fish eggs and larvae, clog fish gills and modify aquatic natural environment [25]. TSS of 32.0mg/L in filtrate obtained from RAC was below that of untreated effluent of 120mg/L and far below the regulatory limit of 400mg/L and 1000mg/L for maximum contaminant limit of effluent to be discharge into stream and sewer respectively. TSS indicates the presence of suspended material such as clay, silt, finely divided organic materials, planktons and other inorganic materials and signifies appreciable purity [19]. BOD signifies organic pollution and measures the productivity of a water. The lower the BOD, the purer the water [26]. Taking these two parameters into account, the filterate that passed through RAC, TSS to be 32.0mg/L and BOD to be 145mg/L. These low values denote that the filterate from RAC was pure. COD with BOD on the other hand are indices of organic pollution. Nearly all organic compounds are 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 present 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

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

The mean concentrations of NO_3^-, SO_4^{2-} and Cl^- of the untreated effluent were 3.50mg/L, 70.1mg/L and 531mg/L respectively while the filterate treated with RAC were 2.30mg/L, 2.0mg/l and 5.8mg/l respectively. The low levels of these anions give credence to the prohibition of microbial growth. Chloride concentrations above 250 mg/L in drinking water may cause corrosion in the distribution system [28]. High concentrations of chloride ions may also result in an objectionable salty taste. High chloride water may also produce a laxative effect. The chloride content in the untreated effluent (531mg/L) was above limits for discharge into drinking water and sewer but lower than maximum limit for effluent to be discharge into drinking water. Sulphate is a substance that is often found in drinking water. Health concerns regarding sulphate in drinking water have been raised because of reports of diarrhea associated with the ingestion of water containing high levels of sulphate [29], such water is not also good for industrial applications because it may form a hard scale in boilers and heat exchangers. There is no cause for alarm since RAC was able to reduce the sulphate content from 70.1mg/L (untreated effluent) to 2.0mg/L. High concentrations of nitrate in water result in eutrophication (excessive increase in population of microbiota). The higher the concentration of this anion in water bodies, the higher the level of pollution [26,27].

Heavy metals, some of which are carcinogenic (e.g. As), terratogenic (e.g. Pb), mutagenic (e.g. Cd, Ni, Cu, Pb) and toxic (e.g. Pb, Cd) [27] were reduced below the regulatory bodies' standards of effluent to be discharged into drinking water, stream and sewer. For instance, Pb and Zn were below detectable limit from the raw effluent with the aid of RAC. When the concentrations of iron and manganese are above regulatory limit, they may cause brown and black stains on laundry, plumbing fixtures and sinks [27]. The values recorded in the FRAC may not pose health hazard. The uptake of chromium by this test adsorbent was excellent compared to that of CAC and the value was far below maximum permissible limits in 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 quantitiy of lignins increases, and this is observed when the plant's organs are young [6]. No wonder why RAC had excellent adsorption properties becuase it was prepared from plant that matured and harvested after four months of planting.

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 econonically promising material. Hence, its utilization as an adsorbent in waste water treatment should be encouraged.

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