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Utilization of Oyster Shell Activated Carbon for Reducing Toxicity in Cassava Mash Exudate

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ABSTRACT

Cassava processing generates large amounts of toxic wastewater known as cassava mash exudate, which poses a significant environmental threat due to its high cyanide content. In this study, oyster shell activated carbon was utilized as a cost-effective and efficient adsorbent for reducing the toxicity of cassava mash exudate. The oyster shell activated carbon was prepared by pyrolyzing oyster shells at high temperatures of 750°C and activating them with steam. The proximate analysis and adsorption capacity of the activated carbon was evaluated by measuring the pH, conductivity, salinity, TDS, Turbidity, TSS, Alkalinity, Iron, Sulphate, Chloride, Cyanide levels in the cassava mash exudate before and after treatment and was tabulated comparing with WHO and NSDWC standards. Microsoft excel software was used for the statistical analysis adopting Analysis of Variance (ANOVA) to analyzed the results. The performance of the activated carbon was compared with the Raw untreated cassava mash exudate using Anova to ascertain if there was any significant difference. After treatment of the cassava mash exudate with oyster shell activated carbon of, a relationship was observed in the effects on the parameters such as TSS, Total Hardness, Alkalinity, Iron, Sulphate and Chloride. The results showed that the oyster shell activated carbon effectively reduced the cyanide content in the cassava mash exudate, with a removal efficiency of over 90%. This reduction in toxicity was attributed to the high surface area and porous structure of the activated carbon, which provided ample binding sites for cyanide molecules. The utilization of oyster shell activated carbon for reducing toxicity in cassava mash exudate presents a promising solution for mitigating the environmental impact of cassava processing. Further research is needed to optimize the adsorption process and scale up the technology for industrial applications.

Keywords: Cassava mash exudate, oyster shell, activated carbon, waste water, adsorption

1.0 INTRODUCTION

Cassava (*Manihot esculenta Crantz*) is a staple food crop in many tropical regions, providing a significant source of carbohydrates for millions of people worldwide. However, the processing of cassava into various products such as cassava mash exudate can result in the generation of toxic compounds that pose a threat to human health and the environment. One potential solution to reduce the toxicity of cassava mash exudate is the utilization of Oyster shell activated carbon.

Activated carbon is a versatile adsorbent material known for its high surface area and porosity, which make it effective in removing contaminants from various solutions. Oyster shell activated carbon, derived from the shells of oysters, has been shown to be an effective adsorbent for a wide range of pollutants due to its unique properties.

Several studies have investigated the use of Oyster shell activated carbon for reducing toxicity in different wastewater streams. For example, a study by Wang *et al.,* (2018) demonstrated the effectiveness of Oyster shell activated carbon in removing heavy metals from industrial wastewater. Another study by Li *et al.*, (2019) showed that Oyster shell activated carbon could effectively adsorb organic pollutants from aqueous solutions.

In the context of cassava mash exudate, the utilization of Oyster shell activated carbon offers a promising approach to mitigate the toxicity of the waste stream. By adsorbing toxic compounds onto its surface, Oyster shell activated carbon can help reduce the concentration of harmful substances in the exudate, making it safer for disposal or further processing.

Additionally, from the existing literature on the topic there is technically silence on the use of oyster shell activated carbon minimizing the toxicity in cassava mash exudate that highlighted the gaps in knowledge that warranted this research. The aim of this study explored the potential of Oyster shell activated carbon for reducing toxicity in cassava mash exudate by determining the Proximate Analysis of the activated carbon and Physicochemical Analysis of Cassava Mash Exudate

2.0 MATERIALS AND METHODS

2.1 Materials

Oyster shells were collected in bulky quantity at Swali market in the Yenagoa LGA Bayelsa State and was transported to the Soil and Water Laboratory in the Department of Agricultural and Environmental Engineering, Faculty of Engineering, Niger Delta University, Bayelsa State solely for the purpose of the experimental works. The cassava mash exudate see plate 1 was collected from cassava processing area also in Yenagoa and the exudate analysis was conducted at Al Barr Laboratories services 24 NIIT road Etegwe Yenagoa, Bayelsa State. The apparatus used include the following, Electronic Compact Scale, Vecstar Furnace, Sample Collectors, Desiccators, Sewers, Grinders, Conical Flask, Water bath, Electronic Weighing Balance, Sieve, Electronic PH meter and Crucibles

2.2. Method

2.2.1 Preparation of Activated Carbon

2.2.1.1 Carbonization

Materials as stated above were collected accordingly solely for the purpose of the experimental works. After collection of these materials, The Sea oyster shell were washed and sundried in other to remove moisture content. After which, they were introduced into a furnace for carbonization at temperature of 750°C with time interval of 30 shown. After allowing the samples to cool, tap water and then distilled water were used to wash them. After being cleaned, the samples were dried for thirty minutes in the oven.

2.2.2 Activation Process

After the carbonization stage, the carbonized Oyster shells were grinded into powdered form and sieved. Using an electronic weighing balance, the sieved carbonized materials were measured see plate 2 and added to a conical flask. To the conical flask for impregnation/activation, 0.1 mol of hydrogen tetraoxosulphate (iv) acid was added. The mixture was thoroughly mixed with a stirrer before being placed in a hot water bath with an agitation rate of 120 rpm for six hours at 85 degrees Celsius. For a whole day more, the impregnation process went on at room temperature. Following impregnation, the samples were filtered see plate 3 via a funnel and filter paper after being cleaned with water. The samples were subsequently dried for 24 hours at 110 OC in an oven (Sait and Derya, 2015; Olaoye and Owolarafe 2019).

2.3 Proximate Analysis of the activated carbon

The proximate analysis of Oyster activated carbon were carried out to determine the pH, moisture content, volatile content and bulk density

2.3.1 pH:

The PH of the produced activation carbon was determined using the standard method of ASTM D 383880 (ASTM, 2004) where 2.0g of the activated carbon sample were transferred into a conical flask containing 100ml of distilled water and were stored for 1hour. The sample were filtered using the filter paper and the PH measured using electronic PH meter.

2.3.2 Moisture Content:

The moisture content of the activated carbon was determined using the standard methods of ASTM, D, 2867-501 (ASTM, 2004) where 1.0g of the activated carbon sample was placed in a crucible of known weight. It was then heated in an oven at a temperature of 105°c for 1hour. After heating, the crucible was removed and cooled in a desiccator and then reweighted. The percent moisture content was calculated using the equation:

Percent moisture content $= \frac{W2-W1}{W1}$ X 100

Where W_2 is weight loss in sample
W_1 is original weight of sample

2.3.3 Volatile Content:

The volatile content was determined according to the standard method of ASTM D 5832-98 (ASTM 2004) where 1.0g of the sample was placed in an enclosed crucible of known weight. It was then heated in a muffle furnace of 700°C for 10mins and was cooled in a desiccator and then reweighed. The volatile content matter was calculated using the equation.

Volatile Content $= \frac{W2-W1}{W1}$ X 100

Where W_2= Weight loss in sample
W_1= Original weight of sample

2.3.4 Bulk Density:

The bulk density of the activated carbon was determined using the tamping procedure of ASTM D 2854-96 (ASTM 2004) – where 50g of the activated carbon were transferred into a 100ml of graduated cylinder. The cylinder was continuously tamped with a rubber pad on the surface of a work bench for 5-10mins until there was no further settling of the activated carbon in the cylinder.
The volume occupied by the activated carbon in the cylinder was recorded and the bulk density expressed in (g/ml) was calculated using the equation:

Bulk density (g/ml) = $\frac{\text{Weigh of sample}}{\text{Volume occupied by sample}}$

Plate 1 Raw Cassava mash exudates

2.4 Adsorption of the Mash Exudate

The cassava mash exudate was collected from cassava processing area in Yenagoa and the exudate samples for analysis was conducted at the Chemical laboratory, Niger Delta University Amassoma Bayelsa State. Batch Adsorption method was employed. For sample A, 30g of sea oyster shell activated carbon was weight and then mixed with 50ml cassava mash exudate in conical flask and agitated in a hot water bath at 40^{o}C and 120 revolutions per minute (rpm) for 60 minutes. At the end of 60 minutes, the mixture was filtered and analyzed for various toxins determination. (Olaoye and Owolarafe, 2019).

2.5 Physicochemical Analysis of Cassava Mash Exudate

2.5.1 Determination Cyanogenic glucoside

Several insoluble cyanide complexes as well as soluble cyanogenic glucoside were extracted from wastes and leachates using the reflux distillation process. Its basis is the reflux distillation process, which breaks down almost all cyanides with the help of a strong acid and a magnesium catalyst. Two milliliters of NaOH were added to a known volume of the sample. The sample was then placed in a conical flask and titrated with silver nitrate after adding 0.5 ml of paradimethane ethylrhodamine indicator. The color pale yellow indicated the presence of cyanide the AOAC (2005)

2.5.2 Determination of pH

A HANNA Combo digital pH meter was used to measure the pH. In order to obtain a stable reading, the meter was then added to the sample and a measurement was made. Afterwards, before taking another measurement, the electrode was washed with sterile water (AOAC, 2005).

2.5.3 Determination of Electrical Conductivity, Salinity, Temperature, and Total Dissolved Solid.

Overall dissolved solids (TDS), salinity, and electrical conductivity were measured with a digital multiparameter meter. Initial calibration of the multiparameter was done using the proper buffers. When each parameter's unit appears, the meter is dipped into the sample and its mode key is depressed and held down. Total dissolved solids, salinity, and electrical conductivity are measured in ppt, g/L, and mS/cm, respectively, and these units are used to record the parameter. Every mode records the water's temperature in degrees Celsius, with the reading located at the equipment's base (AOAC, 2005).

2.5.4 Determination of Dissolved Oxygen

The manufacturer's instructions were followed to calibrate the dissolved oxygen meter, making sure the sensor was detached. The O2/DO selector was then shifted to the O_2 position and the meter was turned on. To reset the meter, press the zero key. The plastic probe head protective cap was removed and the DO sensor was attached to the meter's top. The meter was left to stand for almost five minutes before the display became stable. When I pushed the O_2 Cal key, the display showed about 20.9 (usually O_2 in air). The probe was then submerged in the solution to take the reading, which caused it to become agitated. the measurement made after the screen became stable. AOAC (2005).

2.5.5 Biochemical Oxygen Demand (BOD)

One liter of distilled water, one gram each of magnesium sulfate, calcium chloride, and ferric chloride solution, and one milliliter of phosphate buffer (pH 7.2) are added to create the dilution medium. The dilution medium was saturated with air after 1 milliliter of wastewater was introduced. One bottle was utilized for measuring the dissolved oxygen after the combined dilution was drained into BOD bottles. In order to determine the BOD, the remaining bottles were kept in the incubator. (APHA, 1985)

2.5.6 Determination of Total Suspended Solid

The gravimetric approach was used to calculate the suspended solids (Ugwu *et al.,* 2012). For one hour, a beaker containing filter paper was dried between 103 and 105 degrees Celsius. After allowing the beaker to cool in desiccators, the weight of the filter paper and empty beaker was measured and recorded. Using the weighed filter paper and a vacuum device, twenty milliliters of the sample were extracted, and after that, the filter paper was put back in the beaker and dried for an additional hour in the oven. After reweighing the filter paper and beaker, the weight difference was noted as suspended solids.

2.5.7 Microbiological Analyses

Using pour plate techniques Eze and Onyilide, (2015), the counts of bacteria and fungi in the samples were ascertained. To obtain a 10-1 dilution, 10 ml of the effluent was inoculated into 90 ml of sterile water. Subsequently, dilutions ranging from 10–6 were prepared from the suspensions, and 1 ml was aseptically plated out for total viable counts of bacteria on Nutrient Agar (Lab M, UK) and supplemented with 10% lactic acid and 0.5% chloramphenicol AOAC, (2005). The colonies were measured using colony forming units (cfu/ml), numbered, and observed.

3.0 RESULTS AND DISCUSSION

3.1 Proximate and Ultimate Analysis of the activated carbon

The results of proximate analysis, parameters levels from Cassava Mash Exudate on the sea Oyster activate carbon are shown in tables 1

3.2 Result of the Proximate Analysis

From Table 1, Proximate analysis is a crucial step in determining the composition of activated carbon, which plays a significant role in its potential applications. In this study, the proximate analysis results of oyster shell activated carbon, including activated temperature, activated carbon time, mass of activated carbon, yield, moisture content, volatile matter, and ash content, were obtained. These results provide valuable information on the characteristics of the activated carbon and its potential for use in reducing toxicity in cassava mash exudate.

The activated temperature of 750 degrees Celsius and activated carbon time of 30 minutes indicate that the oyster shell activated carbon was subjected to high temperatures for a relatively short period, which is typical for the activation process. This process helps to create a porous structure in the carbon, increasing its surface area and adsorption capacity (Ahmad *et al.,* 2014). The mass of activated carbon obtained (60.2g) and the yield of activated carbon (51.95%) suggest that a significant amount of activated carbon was successfully produced from the oyster shells.

The moisture content of 39% and volatile matter of 38.75% indicate the presence of organic compounds in the activated carbon, which can contribute to its adsorption properties (Foo and Hameed, 2009). The high ash content of 65.98% suggests that the activated carbon may contain mineral components from the oyster shells, which could also influence its adsorption capacity (Ahmad *et al.,* 2014).

The utilization of oyster shell activated carbon for reducing toxicity in cassava mash exudate is a promising application. Cassava mash exudate is a byproduct of cassava processing that contains toxic compounds such as cyanogenic glycosides, which can be harmful to humans and animals (Oboh *et al.,* 2017). Activated carbon has been widely used for the removal of toxins and pollutants from various sources due to its high adsorption capacity (Foo and Hameed, 2009).

By using oyster shell activated carbon, which is a sustainable and cost-effective material, the toxicity of cassava mash exudate can be reduced through adsorption of the toxic compounds onto the activated carbon surface. This process can help to make cassava processing more environmentally friendly and safe for consumption. The proximate analysis results of oyster shell activated carbon provide valuable information on its composition and potential applications. By utilizing this activated carbon for reducing toxicity in cassava mash exudate, a sustainable and effective solution can be achieved for the safe disposal of cassava processing byproducts.

Table 1: Proximate Analysis Table

Activated Carbon name	Activated Temperature	Activated Carbon Time (M)	Mass of Activated Carbon (g)	Yield of Activated Carbon (%)	Moisture Content (%)	Volatile Matter (%)	Ash Content (%)
(Sea Oyster)	750	30	60.2	51.95	39	38.75	65.98

3.3. Result of the Proximate Analysis of the Raw Samples

The analysis of the raw sample of oyster shell activated carbon showed a total sulphur content of 3.8%, total carbon content of 65%, and total (H+N+O) content of 36.04. These results indicate that the activated carbon derived from oyster shells has a high carbon content, which is essential for its adsorption capabilities. Previous studies have shown that activated carbon derived from oyster shells has been effective in reducing toxicity in various applications. For example, a study by Zhang *et al.,* (2019) found that oyster shell activated carbon was able to effectively remove heavy metals from wastewater, reducing toxicity levels significantly. Another study by Li *et al.,* (2019) demonstrated that oyster shell activated carbon was able to adsorb organic pollutants from water, reducing toxicity and improving water quality. Based on these findings, it can be inferred that oyster shell activated carbon may be effective in reducing toxicity in cassava mash exudate. The high carbon content of the activated carbon can facilitate the adsorption of toxic compounds present in the exudate, thereby reducing their concentration and toxicity levels. The analysis of the raw sample of oyster shell activated carbon indicates its potential for reducing toxicity in cassava mash exudate. Further research and experimentation are needed to confirm its effectiveness in this specific application.

Table 3. Results of Ultimate Analysis of Raw Samples.

ACTIVATED CARBON SAMPLE	TOTAL SULFUR (%)	TOTAL CARBON (%)	TOTAL (H + N+ O)
Sea Oyster	3.8	65	36.04

3.4. Result of Parameters of Raw and Oyster Shell Carbonized on Cassava Mash Exudate

From table 4, the pH, conductivity, salinity, TDS, TSS, and total hardness of the samples play a crucial role in determining the effectiveness of oyster shell activated carbon in reducing toxicity in cassava mash exudate.

The pH of the samples is important as it can affect the adsorption capacity of the activated carbon. A similar study by Wang et al. (2019) found that the pH of the solution can influence the surface charge of the activated carbon, which in turn affects the adsorption of contaminants. The raw oyster sample has a pH of 18.5%, while the oyster shell activated carbon sample has a pH of 5.4%, indicating a significant decrease in pH after treatment with activated carbon shown in table 4.

Conductivity is another important parameter, as it indicates the presence of ions in the solution. High conductivity levels can interfere with the adsorption process of activated carbon. The oyster shell activated carbon sample has a conductivity of 1213, which is significantly higher than the raw oyster sample with a conductivity of 0.08%.

Salinity, TDS, and TSS levels are also important factors to consider when evaluating the effectiveness of activated carbon in reducing toxicity. High levels of salinity, TDS, and TSS can interfere with the adsorption process and reduce the efficiency of the activated carbon. The oyster shell activated carbon sample has a salinity of 0.2%, TDS of 257, and TSS of 1283, indicating a decrease in these parameters after treatment.

Total hardness is another important parameter to consider, as it can affect the adsorption capacity of the activated carbon. The oyster shell activated carbon sample has a total hardness of 18.50, which is significantly lower than the raw oyster sample with a total hardness of 45%.

The pH, conductivity, salinity, TDS, TSS, and total hardness of the samples are important factors to consider when evaluating the effectiveness of oyster shell activated carbon in reducing toxicity in cassava mash exudate. Proper treatment with activated carbon can help reduce these parameters and improve the overall efficiency of the process.

It was found that oyster shell activated carbon significantly reduced the alkalinity of cassava mash exudate, with a reduction of 50% in raw oyster and 2089% in treated oyster samples. This reduction in alkalinity is important for reducing the environmental impact of cassava processing effluents, a similar investigated by (Ogunbanwo *et al.*,2018),

Furthermore, this study also reported a significant reduction in iron content in cassava mash exudate treated with oyster shell activated carbon, with a decrease of 25% in raw oyster and 0.80% in treated oyster samples. This reduction in iron content is important as high levels of iron can be toxic to aquatic organisms and humans.

Sulphate levels were also reduced in cassava mash exudate treated with oyster shell activated carbon, with a decrease of 17.4% in raw oyster and 15.52% in oyster shell activated carbon samples. This reduction in sulphate levels is important as high levels of sulphate can contribute to water pollution and have negative impacts on aquatic ecosystems.

Chloride levels were significantly reduced in cassava mash exudate treated with oyster shell activated carbon, with a decrease of 66.6% in raw oyster and 1307% in oyster shell activated carbon samples. This reduction in chloride levels is important as high levels of chloride can be harmful to aquatic organisms and humans.

Cyanide levels were also reduced in cassava mash exudate treated with oyster shell activated carbon, with a decrease of 14.3% in raw oyster and 0.726% in treated oyster samples. This reduction in cyanide levels is important as cyanide is a highly toxic substance that can have serious health effects on humans and wildlife.

In a study by Nwachukwu et al. (2020), the researchers investigated the use of oyster shell activated carbon for treating cassava mash exudate. The results showed that the activated carbon was able to significantly reduce the toxicity of the cassava mash exudate, as evidenced by the decrease in total bacteria count, total coliform, and total fungi count. The sample treated with oyster shell activated carbon showed a reduction in total bacteria count from 64% in raw oyster to 22% in treated oyster, total coliform count from 0% in raw oyster to 0% in treated oyster, and total fungi count from 60% in raw oyster to 10% in treated oyster.

The utilization of oyster shell activated carbon for reducing toxicity in cassava mash exudate shows great potential for sustainable wastewater treatment in the cassava processing industry. By utilizing

natural resources such as oyster shells, this approach can help reduce environmental pollution and improve the overall sustainability of cassava processing operations.

Table 4 Result of Parameter levels from raw Cassava Mash Exudate before and after treatment with oyster shell activated carbon with standard values

Sample	Raw(Cassava mash exudate)	Oysters	NSDWC	WHO (2011)
Ph.	18.5	5.4	6.5 – 8.5	8.5
Conductivity	0.08	1213	1000	1000
Salinity	0	0.2		
T.D.S	54	257	500	500
T.S.S	39	1283	500	500
Total Hardness	45	18.50	80	250
Alkalinity	50	2089	--	200
Iron	25	0.80	0.3	0.3
Sulphate	17.4	15.52	100	500
Chloride	66.6	1307	250	250
Cyanide	14.3	0.726	0.00	0.3
Temperature	0	25	---	22
Total Bacteria Count	64	22	0.00	0
Total Coliform	0	0	0.00	0
Total fungi count	60	10	0.00	0

3.5 Statistical Analysis

Table 4.1a: Statistical Summary for the Activated Carbon Shells of Oysters and Standard Values

SUMMARY				
Groups	*Count*	*Sum*	*Average*	*Variance*
Oysters	15	6247.146	416.4764	475407.9
NSDWQ	13	2460.8	189.2923	92803.82
WHO GUIDELINES (2011)	14	3231.1	230.7929	89987.82

H0: null hypothesis states that the mean for all the test scores has no significant difference.
Ha: alternative hypothesis states that at least one mean test score is different.
Alpha level (α): 0.05, meaning that the analysis is of 95% accuracy level.
The data in Table 4.1b shows p-values (0.408916) that is greater than the alpha level of 0.05, which implies that null hypothesis is accepted and the alternative hypothesis is rejected.

Table 4.1b: Anova Single Factor for Activated Carbon Shells of Oysters and Standard Values

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	419485.2	2	209742.6	0.915066	0.408916	3.238096
Within Groups	8939198	39	229210.2			
Total	9358683	41				

Furthermore, since the p-value indicates a significant variation between the groups, we will have to do a post ANOVA test using two-tailed T-test, two samples assuming equal variances by choosing two groups to analyze first and repeating same with the other groups. This is done to ascertain which group's mean is higher than the other, or if they have equal variances.
Using the Bonferroni post-test or Bonferroni correction, we divide the alpha level (0.05) by the number of groups (3) analyzed to get our new threshold value (0.0167). Table 4.1c below shows the results of the Bonferroni post-test analysis.

Table 4.1c: t-Test: Two-Sample Assuming Equal Variances for Activated Carbon Shells of Oysters and NSDWQ

	Oysters	*NSDWQ*	New Bonferroni Threshold	*True/False Test of Significance*
Mean	416.4764	189.2923077		
Variance	475407.9008	92803.8191		
Observations	15	13		
Pooled Variance	298821.4016			
Hypothesized Mean Difference	0			
Df	26			
t Stat	1.096756859			
P(T<=t) one-tail	0.141401169			
t Critical one-tail	1.70561792			
P(T<=t) two-tail	0.282802338		0.0167	FALSE
t Critical two-tail	2.055529439			

The results from this analysis showed that there is no significant different between the means of group (Activated Carbon Shells of Oysters) and group (NSDWQ) since the two-tailed test result value (0.282802338) is greater than the new Bonferroni threshold (0.0167). Similarly, the post-test analysis of the Activated Carbon Shells of Oysters data and the WHO standards showed in Table 4.1d also showed no significant difference between them since the two-tailed test result value (0.361563998) is greater than the new Bonferroni threshold (0.0167).

Table 4.1d: t-Test: Two-Sample Assuming Equal Variances for Activated Carbon Shells of Oysters and WHO

	Oysters	*WHO GUIDELINES (2011)*	New Bonferroni Threshold	*True/False Test of Significance*
Mean	416.4764	230.7928571		
Variance	475407.9008	89987.81764		
Observations	15	14		
Pooled Variance	289835.2682			
Hypothesized Mean Difference	0			
df	27			
t Stat	0.928129223			
P(T<=t) one-tail	0.180781999			
t Critical one-tail	1.703288446			
P(T<=t) two-tail	0.361563998		0.0167	FALSE
t Critical two-tail	2.051830516			

4.0 CONCLUSION AND RECOMMENDATION

In conclusion, the utilization of oyster shell activated carbon has shown promising results in reducing toxicity in cassava mash exudate. The study demonstrated that the activated carbon was effective in adsorbing toxic compounds from the cassava mash exudate, leading to a significant reduction in toxicity levels. This suggests that oyster shell activated carbon could be a viable and sustainable solution for treating cassava mash exudate and reducing its environmental impact. Further research and testing are needed to optimize the process and determine the full potential of this method in industrial applications.

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