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(RESEARCH ARTICLE)

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The use of locally formulated green de-oiler in oil field effluent water treatment

Charles Monday ^{1,*}, Joseph Ajienka ², and Benson Evbuomwan ^{3,4}

¹ Center for Gas, Refining and Petrochemicals, University of Port Harcourt, Nigeria.

² Department of Petroleum and Gas Engineering, University of Port Harcourt, Nigeria.

³ Department of Chemical Engineering, University of Port Harcourt, Nigeria.

⁴ Godwin Igwe Chair in Gas, Refining & Petroleums, University of Port Harcourt, Nigeria.

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Abstract

The purpose of this research was to examine the feasibility of treating refining wastewater with activated carbon made from plantain peels. Physiochemical analysis was conducted on the activated carbon to determine its properties, and the results showed that it was suitable for use in water treatment. The effluent water was also analyzed for its TDS, TSS, metals, phenols, oil and grease, and TPH content, which were found to be above the maximum recommended levels. The efficacy of activated carbon at various doses for wastewater treatment was then investigated. Results showed that as the dosage of activated carbon increased, the absorption of metallic ions such as lead, nickel, zinc, iron, cadmium, and copper increased. As the amount was increased, both the total dissolved solids and the total dispersed solids were found to have diminished. Furthermore, the study found that the pH level of the treated water fluctuated at different levels of adsorbent dosage, but the 30g dosage gave the standard level of the treated water. In conclusion, this study demonstrates that activated carbon produced from plantain peels can be effectively used for the purification of refinery effluent water. The use of activated carbon can significantly reduce the levels of TDS, TSS, metals, phenols, oil and grease, and TPH in the effluent water. Based on the findings, treating industrial effluent with activated carbon may be a viable long-term option.

Keywords: Refinery Wastewater; Adsorption; Plantain Peel; Activated Carbon; Physiochemical Analysis Introduction

1 Introduction

The procedures carried out in petroleum refineries, which separate unrefined oil into its different components (such as petroleum motor spirit, automotive gas oil, naphtha, heavy gas oil, etc.), are the source of the effluent known as "refinery wastewater" [1]. The effluents have a devastating effect on the aquatic environment. Effluent from refineries varies in makeup depending on the grade of the petroleum they process. Conditions of operation also play a role [2]. The wastewater generated by crude oil refining facility is substantial. The volume of these effluents is roughly 0.4%-1.6% of the petroleum oil handled [3]. Some of this water may exist with crude in the formation or used in the pre-treatment process alongside the petroleum oil. Water that comes into touch with unrefined oil will be tainted due to the oil's concentration of refractory molecules and organic contaminants. The other processes in the refinery can also produce wastewater, such as turnaround repair, wash-offs from containers, tanks, and drainage units; unintentional releases from working units; condensed steam pump-around; etc. [4, 5].

Wastewater treatment, whether for reprocessing or disposal, is subject to regulations aimed at ensuring a pollutantfree atmosphere and secure operation of industries that handle petroleum oil [6]. Untreated effluent has the potential to reduce the levels of life-sustaining dissolved oxygen (DO) in adjacent water bodies [7]. Dissolved and dispersed particles, oil and fat, aromatics, and other harmful substances are the primary components of refining effluent. Effluent

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^{*} Corresponding author: Charles Ahuruezenma Monday

contains a variety of hydrocarbons, but paraffin (which includes benzene (C_6H_6), toluene (C_7H_8), and xylene (C_8H_{10})) is one of the three most common types. It is known that Naphthenic acid in effluent is toxic, and it is also known that heavy metals are hazardous at certain amounts. The best chance of success in the fight against these contaminants would be to employ a combination of physical, pharmacological, and biological remediation strategies. Methods of treatment are selected in accordance with treatment goals, types of contaminants to be removed, budgetary constraints, and legal mandates [8].

Heavy metals found in wastewaters from refineries and other businesses are a major reason for worry due to the harmful impacts they have on the ecosystem. Heavy metals aren't biodegradable and can create a variety of issues in the environment and in biological organisms. As a result, research efforts are focused on employing low-priced adsorbents that have been shown to possess impressive pollutant-binding capacities. Adsorption, using the metal binding powers of different agricultural refuse such as yucca husk, tree bark, ground almond husk, saw dust, and others, has garnered attention as a possible innovative technique for the removal of heavy metals from waste streams.

Many nations, Nigeria included, have set up environmental security organisations. For instance, in Nigeria, we have a government agency whose job it is to ensure compliance with environmental laws (NESREA). Its responsibilities include, but are not limited to, enacting and carrying out the laws delegated to it by an authorizing authority. In addition, it prevents the release of toxic substances into the ecosystem and water sources like waterways, lakes, and oceans by treating industrial pollutants. As a result, numerous studies have investigated the efficiency of various methods for eliminating heavy metals, including ion exchange, reverse osmosis, chemical precipitation, electro-dialysis, electrolytic extraction, and coagulation. However, many of these options are either unaffordable or ineffective. However, adsorption, with activated carbon as the most prevalent technique, has been shown to be a possibly effective option.

Activated carbon is a porous type of carbon that has been manufactured or treated to create a high degree of permeability. Due to its high porosity and large surface area, it is an excellent adsorbent for a wide variety of heavy metals in both liquid and gaseous phases [9]. Activated carbon made from agricultural waste is appealing because of its potential for use in the reduction of toxic metals and its cheap production cost, and the fact that it can be produced locally in poor nations.

The low quality of effluents is directly responsible for the deterioration of lakes, rivers, streams, and other waters that are exposed to them. Discharge volume, chemical and microbiological concentration/composition of effluents, and the number of organisms present all contribute to the likelihood that contaminated wastewater effluents will have a negative impact on the quality of receiving water bodies [10]. Discharge characteristics (such as the concentration of potentially harmful compounds like heavy metals and organo-chlorines, as well as suspended particles and organic matter) and receiving water characteristics interact to determine the outcome [11]. Because of the ideal circumstances present in eutrophied water networks, toxin-producing cyanobacteria may flourish there. Toxins produced by these microbes have been related to a variety of diseases in animals, including chronic diarrhea, liver failure, nervous system malfunction, cutaneous irritation, and even liver cancer [12, 13]. Anyone who swims, paddles, or otherwise interacts with water, as well as anyone who comes into contact with water, is at risk of becoming ill. The health of aquatic environments that are exposed to sewage effluents may be affected by a variety of variables.

Low liquid oxygen levels have numerous detrimental effects on fish, including but not limited to: increased susceptibility to disease; delayed development; reduced moving ability; changed eating and migration behavior; and, in the worst cases, quick mortality. Species composition could change as a result of persistently low liquid oxygen levels [14,15]. Physical harm can also be caused to approaching aquatic areas by wastewater discharge that is not properly managed. All aquatic organisms have very particular climate needs and tastes. Warming seas could threaten the survival of many aquatic creatures. Typically, warmer than entering water bodies, effluents can aid in thermal improvement [14], blocking sunshine (which lowers photosynthesis), bodily hurting fish, and harmful impacts from contaminants related to suspended particulates are all indirect environmental effects of releasing suspended solids into recipient rivers. Bioaccumulation and bio-magnification of pollutants in untreated sewage effluent poses risks to ecosystems and human health. Through a process known as bioaccumulation, chemicals initially present in dilute fluids can build up to toxic levels within the tissues of animals and plants. These compounds are extremely resistant to breakdown in the digestive tract and have a very long molecule half-life [16, 17]. It's possible that as pollutants move up the food chain from prey to predator, they'll become exponentially more concentrated due to bio-magnification [16]. Some compounds found in wastewater can cause worry even in minute concentrations due to bioaccumulation and bio-magnification processes. Some examples include mercury and other heavy metals, as well as organo-chlorine herbicides. Chronic bioaccumulates (such as dangerous substances in the ecosystem) still come largely from city waste, in addition to industrial releases and air pollution. Plant and animal life on land can also be poisoned by toxins in wastewater that flows into receiving water bodies.

The process of identifying and isolating bacterium pollutants in effluent can be time-consuming, labour-intensive, and costly. Due to the importance of accurately assessing the potential for illness in effluent, indicator organisms are always used. [18]. Wastewater that has been contaminated presents a serious threat because of the existence of pathogens. They develop subtly, spread quickly, remain unnoticed for longer, and are harder to cure [19].

The peels of plantain contain a number of different molecular components, including cellulose, hemicellulose, pectin, amino active groups, hydroxyl groups, and carboxyl groups, all of which have the ability to attach to and draw substances or ions from biomass. The capability of plantain shells to collect these ions was investigated as part of an effort to locate low-cost materials with absorption properties that could be utilized for reducing the impact of heavy metals associated with refinery effluents in aquatic systems. Only the fruit of the plantain is consumed, while the plantain's shells are thrown away as refuse and permitted to disintegrate hence one of the goals of this research is to introduce a waste-to-wealth concept.

It has been determined that adsorption is one of most efficient technique for removing biological pollutants from water [20]. Adsorption is widely regarded as the most practical, efficient, cost-effective, competitive, and straightforward method for cleaning up a wide range of organic and inorganic contaminants. This study lays the groundwork for commercial production of activated plantain peel carbon (APPC) which can then be evaluated for remediation of other contaminants in industrial wastewaters.

Activating agents can be made from a diverse assortment of molecular substances; some examples of these substances are acids, artificial salts, organic salts, and bases. Other examples include boric acid, calcium hydroxide, calcium phosphate, chlorine, cyanides, dolomite, ferric chloride, magnesium chloride, phosphoric acid, nitric acid, potassium trioxocarbonate(v)acid, magnesium sulphate, potassium sulphide, potassium thiocyanate, sodium hydroxide, sodium phosphate, sodium sulphate, sulphur, sulphur dioxide, sulfuric acid, and zinc chloride [21].

2 Materials and Methods

2.1 Research Design

2.1.1 Sampling, Classification, and Processing

The Rumuosi-Choba region served as the source for the plantain peel (PP) samples. The gathered plantain skins were rinsed twice, once with regular faucet water and once with purified water, to get rid of any remaining grease, grime, grit, or sodium (Figure 1). The samples were sun-dried after being desiccated at 100 degrees Celsius for 24 hours. The PP was dried and then ground to a thinner consistency. The plantain variety, Musa paradisiacal, was identified in Choba, Nigeria, in the Department of Crop and Soil Science at the University of Port Harcourt.

2.1.2 Reagents Used and Carbonization

Activation of the carbonized banana involved the use of sodium hydroxide (NaOH). The new sample is weighed in clean silicon crucibles and then heated in an air - tight furnace at 350°C for 1 hour to complete the carbonization process.

Raw plantain peel $\overline{350^{\circ}C, 1hour}$ C + CO₂(carbonization). (1)

Carbonized plantain peel is shown in Figure 2.

2.1.3 Activation

Two crucibles containing exactly 2.00 grammes of carbonized plantain skin were weighed using the top pan scale depicted in Figure 3.4 below, and the contents of each crucible were combined with 2 cm3 of 0.5M NaOH before being heated to 750 degrees Celsius for five minutes. Every activated sample was desiccated in 110°C kiln for 6 hours after being filtered through Whatman No. 1 filter paper and rinsed with de-ionized water until the pH was between 6 and 7.

Carbonized – plantain peel $\overline{750^{\circ}C}$, AA, 5minutes AC + CO2 (Activation) (2)

A is the activating agent and AC is the activated charcoal (Figure 3).

2.2 Characterization Studies

2.2.1 Material Dryness and Wetness Analysis

Mass of fresh plantain skin samples were repeated after they had been dried in an oven at 105 degrees Celsius for three hours, cooled in a dehydrator, and then dried again [22].

2.2.2 Quantifying the Amount of Ash

A plantain skin sample was weighted in crucibles that had been fired in a furnace to around 500 degrees Celsius, then chilled in a desiccator. A kiln was used to heat the crucibles holding the desiccated material to a temperature of 700 degrees Celsius. After 3 hours, the crucible was taken out and set aside to chill before being measured and the plantain skin content assessed.

2.2.3 Determination of pH

The activated plantain skin sample was mixed with 1% (w/v) deionized water to create a solution. The pH of the activated carbon was measured after 2 hours.

2.2.4 Bulk density

The dynisco device was used to make this determination.

2.3 Density of Carbonized Material

A measuring sphere with a volume of 100 cm^3 was cleaned and desiccated. The amount of water was reported to be twenty millimetres. The amount of the carbonized water after being moved to the measuring container (4.0 g) was noted. After making sure there were no air pockets, capacity was measured.

Volume of water displaced (cm³) = Final volume – Initial volume (V_b-V_a)

Bulk density
$$\binom{\text{kg}}{\text{m3}} = \frac{\text{Mass of Carbonized}}{\text{Volume of Water Displaced}}$$
 (3)

2.4 The Removal of Physiochemical Properties of Effluent Wastewater and Its Effect on Adsorbent Dosage

We used adsorbent amounts of 10g, 15g, 20g, 25g, and 30g to determine the adsorption efficiencies of activated carbon of plantain skin on the selected physiochemical characteristics of the refinery effluent water sample as in Figure 4. Each type of absorbent was put as a filled bed after being individually measured. Filtrate was gathered from the bottom of the compacted bed after the discharge water was permitted to run through it. Using Whitman filter paper, we were able to isolate the absorbent from the adsorbate solution. The physiochemical properties of the collected filtered samples were analyzed in order to evaluate the effectiveness of the adsorption technique.



Figure 1 Plantain Peel sample

Figure 2 Carbonized plantain peel



Figure 3 Activated Charcoal

Figure 4 Effluent water sample

3 Results

3.1 Physiochemical Properties

The data below shows the result obtained from the analysis of the activated carbon.

Table 1 Activated charcoal's physiological and molecular characteristics

Parameter	Level		
рН	6.74		
Bulk Density (kg/m)	2.66		
Ash Content (%)	1.80		
Moisture Content (%)	2.15		
Dry Matter (%)	2.13		

3.2 Effluent Water from Refineries: A Physiochemical study

Table 2 Physiochemical Analysis Result of Raw Effluent Water

S/N	Parameter	Result	Standard*
1	pH	5.03	6.5 - 8.5
2	Biological Oxygen demand (mg/l)	18.21	10 max
3	Temperature (°C)	28.90	25 - 30
4	PAH (mg/l)	25.30	< 10max
5	Total Petroleum Hydrocarbon (mg/l)	22.14	10max
6	Nickel (mg/l)	1.804	0.07max
7	Lead (mg/l)	1.50	0.05max
8	Cadmium (mg/l)	0.502	0.10max
9	Total iron (mg/l	1.590	1.0max
10	Zinc (mg/l)	1.640	1.0max
11	Copper (mg/l)	0.957	1.5max

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12	Conductivity (µs/cm)	744.18	1000max		
13	Total Dissolve Solid (TDS) (mg/l)	370.92	2000max		
14	Salinity (mg/l)	351.60	600max		
15	Dissolved Oxygen (mg/l)	19.50	10max		
16	Total Dissolved Solid (mg/l)	28.72	30max		
17	Turbidity (NTU)	18.90	15max		
18	Phenol (mg/l)	0.620	0.10max		
19	Oil and Grease (mg/l)	15.50	10max		
*Environmental Guidelines and Standards for Petroleum Industries in Nigeria [23]					

Table 3 Physiochemical Analysis Result of Raw Effluent Water Treatment with Varying Adsorbent Dosages

S/N	Parameter	Test Method	10g	15g	20g	25g	30g
1	рН	APHA 4500HB	5.41	5.47	5.80	5.46	6.67
2	Biological Oxygen demand (mg/l)	APHA 5210D	15.0	12.16	9.66	7.59	6.48
3	Temperature (°C)	APHA 4500T	28.50	28.30	27.40	27.40	27.40
4	PAH (mg/l)	APHA 3111B	23.52	14.60	12.14	9.33	8.70
5	Total Petroleum Hydrocarbon (mg/l)	APHA 3111B	18.06	15.10	11.40	9.50	8.10
6	Nickel (mg/l)	APHA 3111B	1.002	0.550	0.360	0.063	0.059
7	Lead (mg/l)	APHA 3111B	1.14	0.119	0.108	0.071	0.0442
8	Cadmium (mg/l)	APHA 3111B	0.331	0.270	0.211	0.077	0.058
9	Total iron (mg/l	APHA 3111B	1.088	0.740	0.652	0.610	0.454
10	Zinc (mg/l)	APHA 3111B	1.351	0.718	0.559	0.403	0.293
11	Copper (mg/l)	APHA 3111B	0.718	0.585	0.397	0.302	0.288
12	Conductivity (µs/cm)	APHA 2510B	687.50	610.53	378.19	298.10	211.58
13	Total Dissolve Solid (TDS) (mg/l)	APHA 2510B	343.60	298.40	191.40	146.50	142.15
14	Salinity (mg/l)	APHA 4500B	310.82	280.50	220.11	201.80	149.70
15	Dissolved Oxygen (mg/l)	APHA 5210D	17.19	14.60	11.20	9.69	8.47
16	Total Suspended Solid (mg/l)	APHA 5210D	25.04	19.48	16.30	15.01	12.45
17	Turbidity (NTU)	APHA 2130B	17.80	16.06	12.91	10.50	9.86
18	Phenol (mg/l)	APHA 3111B	0.58	0.513	0.350	0.251	0.141
19	Oil and Grease (mg/l)	APHA 3111B	13.94	11.04	9.65	9.12	8.84



Figure 5 Treated effluent sample from varying adsorbent dosage.

 Table 4
 Effect of Adsorbent Dosage on Adsorption Percentage

Dosage (g)	Nickel (%)	Lead	Cadmium	Iron	Zinc	Copper	РАН	Phenol	ТРНС
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
10	44.457	24.000	34.064	31.572	33.659	24.974	26.798	6.452	18.428
15	69.512	92.067	46.215	53.459	54.878	38.871	42.292	17.258	31.798
20	80.044	92.800	57.968	58.994	60.244	58.516	52.016	43.548	48.509
25	96.508	95.267	84.661	61.635	62.805	68.443	63.123	59.516	57.091
30	96.729	97.053	88.446	71.447	72.317	69.906	65.613	77.258	63.415





3.3 Model Development for Physiochemical Parameters

Table 5 Models for theoretical determination of the components' concentration using the same adsorbent.

S/N	Metal Component	Model Developed	R ² Value
1	Nickel	$y = 0.0023x^2 - 0.1376x + 2.145$	0.9861
3	Cadmium	y = -0.0148x + 0.485	0.9596
4	Iron	$y = -0.528 \ln(x) + 2.2526$	0.9413
5	Zinc	$y = 0.003x^2 - 0.1685x + 2.6862$	0.9681
6	Copper	$y = 0.001x^2 - 0.0609x + 1.247$	0.9852

7	рН	y = 0.0502x + 4.758	0.5594		
8	Oil and Grease	y = -0.4288x + 22.002	0.9654		
9	ТРН	y = -0.5144x + 22.68	0.9668		
10	Phenol	y = -0.0228x + 0.823	0.9882		
11	BOD	y = -0.4288x + 22.002	0.9654		
12	Turbidity	y = -0.4322x + 18.822	0.9765		
13	TDS	y = -11.096x + 446.33	0.9159		
14	TSS	y = -0.593x + 29.462	0.9295		
X = dosage of adsorbent; y= adsorbed metal ion					

4 Discussion

The results above are discussed below explicitly on the behaviour of each parameter with the dosage of the adsorbent.

4.1 Adsorbent Physiochemical Characteristics

From Table 1, in the physiochemical analysis of the activated carbon, the pH (6.74) shows that it is slightly below the neutrality level (7.0). The bulk density (2.66%), ash content (1.80%), moisture content (2.5%), dry matter (2.13%) and the iodine value (25.38%). The percentages of wetness and dry materials in the ash are also significantly lower than the utmost allowed. Table 2 shows physiochemical content of effluent water sample against EGASPIN standard.

4.2 Metal Adsorption: The Role of Adsorbent Dose

Table 4 and Figure 6 display the content of lead (Pb) and nickel both in the raw water and at each dosage treatment. The initial lead content in the water was (1.5mg/l), the adsorbent dosage of 30g, 25g, 20g, 15g and 10g shows that as the dosage increases, the absorption of the Pb content also increases. At the adsorbent dosage of 30g, the Pb content (0.0442) is below the maximum (0.05) level. Similarly, the nickel absorption increases as the dosage increased and at 30g (maximum dosage) the initial nickel in level (1.08ng/l) was reduced to 0.059mg/l which is below the maximum level (0.07mg/l).

Also, the initial content of cadmium at dosages of 30g and 25g gave below the maximum content (0.1mg/l) of cadmium. But for iron with the maximum recommended content of 1.0mg/l dosage of 30g(0.454), 25g(0.61mg/l), 20g(0.652) and 15g(0.74mg/l) gave the required output of iron.

For zinc, the concentration level is obtained from adsorbent dosage of 30g(0.293mg/l), 25g(0.43mg/l), are below the maximum but the dosage of 20g gave exactly the maximum level of zinc. Copper was adsorbed more amongst all the metals when compared with the required recommended concentration. All adsorbent dosage gave concentration level below the maximum amount of copper required, after treatment of refinery effluent water.

4.3 Total Suspended Solids and Total Dissolved Solids in Refinery Wastewater as Affected by Dosage of Adsorbent

Each and every absorbent level produced a concentration that was lower than the highest concentration of both total dissolved solid and total suspended solid. In both cases, the 30g dosage of adsorbent gave the minimum concentration. For TSS (30g = 12.45mg/l less than the maximum 30mg/l) TDS (30g = 142.15mg/l less than the maximum 2000mg/l)

4.4 TPH and Phenol Concentrations in Refinery Wastewater as a Function of Adsorbent Dose

The TPH which is the total petroleum hydrocarbon has a maximum adsorption with adsorbent dosage of 30g and 25g. The concentrations of these dosages are slightly below the maximum concentration level (10mg/l). All adsorbent dosage could not adsorb phenol below the maximum level.

4.5 Refinery Wastewater Biological Oxygen Demand (BOD) and Turbidity as Affected by Adsorbent Dose

It was discovered that as the quantity of the adsorbent increased, there was a decrease in the biological oxygen demand (BOD), which refers to the amount of dissolved oxygen that aerobic biological organisms require in order to decompose organic material that is present in the wastewater sample. Similarly, the turbidity which was caused by particles

suspended in the effluent water reduced as the adsorbent dosage increases. The treated water product is clearer and scatters less light at 30g dosage of adsorbent (see Figure 5).

4.6 pH Change Due to Adsorbent Dosage

The pH of the effluent water at the different dosage of adsorbent varies. At 30g dosage, the pH scale value was increased from its original value 5.03 to 6.67 and at 25g dosage, it was reduced to 5.46 and raised again at 20g to 5.80 and lowered at 15g and 10g to 5.47 and 5.41 respectively. Therefore, at 30g, it tends towards neutrality and at other dosage it tends towards acidity again.

4.7 The Impact of Adsorbent Concentration on Oil and Grease Concentration

The oil and grease adsorption increases as the adsorbent dosage was increased. At 30g:52.2% of the oil and grease was adsorbed, at 25g:56.6%, 20g:68.3%, 15g:84.9% and 10g:94.2% of oil and grease was absorbed. Therefore, the oil and grease adsorption are dependent on the quantity of adsorbent used in the treatment process.

4.8 Component Modeling in Development

The Table 4 contain information about the set of models developed using Microsoft Excel 365 to analyze the concentration of various components at different adsorbent dosages. The R-squared value is a statistical measure of how well the data fits into the model. Values closer to 0 suggest a poorer match, while values closer to 1 show a flawless fit.

In this case, the R-squared values for all the components are greater than or equal to 0.9 but less than 1. This suggests that the models developed have a good fit to the data, but not a perfect fit. A high R-squared value indicates that the model explains a large portion of the variability in the data. Therefore, a value of 0.9 or above indicates that the models explain a high percentage of the variability.

However, the pH component has an R-squared value of 0.5594, which is lower than the other components. This suggests that the model for the pH component does not fit the data as well as the models for the other components. It is possible that other factors not included in the model may be influencing the pH measurements, which could explain the lower R-squared value.

5 Conclusion

In conclusion, the quality of the models that were developed involves analyzing the concentration of various components at various amounts. It was found that while the majority of the models have a decent fit to the data, there is one component (pH) where the fit is not as robust as in the other components.

According to the findings of the research, the sample contained a concentration of metals that was significantly greater than what is customary prior to discharge or re-use, depending on the circumstances; this was the case before the treatment was carried out. Following the application of the absorbent in the form of plantain skins, the concentration of the vast majority of the metals was brought down to acceptable levels, as determined by the regulating agencies. This activated carbon was used for the purification of the refinery effluent water at different dosage. Treated water was collected from each treatment process at varying dosage and subjected to another physiochemical analysis and the results were recorded. The metallic (lead, nickel, zinc, iron, cadmium, and copper) absorption increased as the dosage of the adsorbent increased. When the quantity of the adsorbent is increased, there is also an increase in the amount of total dissolved solids and total dispersed solids that are absorbed. The pH level in the water treated by the adsorbent experienced a fluctuating change as the amount of the adsorbent was increased, but the standard pH level was achieved with 30g.

Compliance with ethical standards

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Disclosure of conflict of interest

There are no conflicts of interest.

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