



Ballast Water Treatment Using Modified Cow-Dung and Plantain Peels NanoBiochars



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ABSTRACT: Ballast water treatment is a crucial aspect of environmental protection, aiming to minimize the transfer of non-indigenous species. In this study, Biochar Klin pyrolyzer, was used to prepare the nanobiochars from cow-dung and plantain peels followed by ball-milling, and centrifugation. The nanobiochars were subjected to acidic and alkaline treatments and then characterized for their physico-chemical properties, as well as the ballast water using prescribed standard methods. The pre-treatment analysis of the ballast water sample revealed a pH of 9.2, chloride ion concentration of 68.7 mg/L (well below the WHO standard of 250 mg/L), nitrate concentration of 5.6 mg/L (above the WHO standard of 3.2 mg/L), and sulphate concentration of 3.2 mg/L (below the WHO standard of 250 mg/L). The BOD and COD levels were 28.6 mg/L and 54.2 mg/L, respectively, both significantly exceeding the WHO standard of 10 mg/L. Post-treatment examination revealed that the modified plantain peel biochar effectively reduced the concentration of pollutants (Lead (Pb^{2+}) from 0.314mg/L to 0.104mg/L, Cadmium (Cd^{2+}) from 0.028mg/L to 0.025mg/L) and microbial organisms (coliforms from 2.1cfu/mL to 1.1cfu/mL) thereby demonstrating its potential as a sustainable and cost-effective treatment solution. Activated adsorbent's larger surface area and nanoporous structure significantly enhanced its adsorption capacity.

KEYWORDS: Ballast water, Ballast water treatment, Cow dung adsorbent, Plantain peel adsorbent.

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I. INTRODUCTION

80% of goods worldwide are transported by ships. Navigation has increased due to the demand for more vessels as cargo volumes rise (Golovan, 2023). Ships take in water for buoyancy at one port and release it at another while unloading cargo. Ballast water is the process that involves bringing in and letting out seawater to keep a vessel stable and maneuverable (Baeva *et al.*, 2017). Safe ship operations depend on effective ballast water management, which lessens hull stress from choppy seas or variations in cargo weight, fuel, and water (Lakshmi *et al.*, 2020). Ballast water discharge presents serious risks to the environment since it may introduce heavy metals, dangerous viruses, and non-native species into marine ecosystems, resulting in major harm to the environment as well as financial losses (Kurniawan *et al.*, 2022). This comprises decreased production from fisheries, loss of biodiversity as a result of invading species and threats to public health from dangerous viruses. Marine species may accumulate heavy metals in ballast water, which could have a detrimental impact on their survival and general well-being (Kurniawan *et al.*, 2022). Sealife and people who eat seafood may be harmed by heavy metals in the water (Feng *et al.*, 2017; Jacqueline *et al.*, 2019). These metals can harm humans' kidneys and cause cancer, among other major health problems (Sayinli *et al.*, 2022). Because of its variety of sources and low cost, biochar

a carbon-rich byproduct of burning biomass is prized (Wang *et al.*, 2021). It is an efficient, reasonably priced adsorbent for eliminating heavy metal contaminants from water due to its high porosity, broad surface area, and functional groups (Wang *et al.*, 2021). Cow dung biochar and plantain peel biochar are a potential solution for treating ballast water since they effectively discharge organic pollutants and heavy metals, among other benefits (Iwuozor *et al.*, 2021; Suarez-Vazquez *et al.*, 2021; Fan *et al.*, 2023). Because of its porous nature, biochar can absorb and immobilize heavy metals, lowering the amount that plants absorb and that people and animals would subsequently ingest (Medyńska-Juraszek *et al.*, 2020). Biochar from waste biomass is an inexpensive, easy-to-use, and environmentally acceptable solution for treating ballast water (Iwuozor *et al.*, 2024). Nanobiochars creation for use in water treatment applications encourages the recycling of waste, supporting sustainable practices and the circular economy (Kumar *et al.*, 2021). As a result, nanobiochar made from cow dung and plantain peel has a lot of potential to help with environmental issues related to ballast water discharge. The study therefore underscores the cost effectiveness and sustainability of an ultrafiltration technique using nanobiochars from modified cow-dung and plantain peels in addressing the challenges of ballast water disposal.

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II. MATERIALS AND METHODS

The ballast water was sourced from the Ballast Tank (MV African Spirit) from Lagos Port to Bayelsa, Nigeria, MV African Spirit (2169 gross tonnage was built in 1983, Flag: Stad Norway). The vessel took off from Lagos Port on the 20th of March 2023, while ballasting and berthed at the canal in Awele 3D offshore for a seismic operation between Delta and Bayelsa. The water sample is designated BWAA. The cow dung was obtained from the Odo Eran Abattoir, Bariga Lagos, and plantain peels the Canteen at the Faculty of Science, University of Lagos. Hexamethylene Tetramine, Hydrazine Sulphate, Barium Chloride, Potassium Iodide, Sulphuric acid, Acetic acid, Phosphoric acid was obtained from Sigma-Aldrich and Merck, Germany. Ballast Water Sample Collection Before being used, the ballast water sample was collected in plastic containers that had been cleaned using non-ionic detergent, tap water, and de-ionized water. For the sample containers were filled for the sampling process, it was rinsed three times and washed with sample water. Prior to analysis, the material was stored at about 4°C. in a refrigerator.

A. Characterization Ballast Water

The following common physicochemical characteristics were used to evaluate the ballast water sample's quality: pH and electrical conductivity using the laboratory calibrated pH and electrical conductivity meters (APHA. (2005). Total dissolved solids were determined using the TDS meter. Through the use of laboratory gravimetric analysis, the total suspended solids were ascertained. Separating the two solids was crucial for the assessment since the water contains both suspended and dissolved solids. Total Solids, alkalinity, acidity, Biochemical Oxygen Demand (BOD), turbidity, total Phosphorus were determined using standard methods (Nwigwe & Kiyokazu, 2023). Total Nitrogen was determined using a UV/VIS spectrophotometer, the Bicarbonates and Carbonates were determined using Phenolphthalein and methyl orange were used as markers when titrating the sample against standard sulfuric acid (H_2SO_4) to quantify the amount of carbonate and bicarbonate ions present (APHA. (2005). Sulphate was determined using the Gravimetric Technique with Residue Principle Ignition (Nwigwe & Kiyokazu, 2023). [Chloride was done using titrimetric (Nwigwe & Kiyokazu, 2023). The Chemical Oxygen Demand was done as prescribed by (Geerdink *et al.*, 2017). Heavy Metals Determination: Lead, Copper, Iron, and other heavy metals were identified using AAS in the water sample. Specific metal standards in the metals' linear range were utilized to calibrate the Atomic Absorption Spectrophotometer (AAS, Unicom 969). The samples were examined for eight heavy metals, specifically Mg, Cu, Fe, As, Cr, Cd, Zn, and Pb, using

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established procedures (Tolian *et al.*, 2020). The microbial activities in the water were determined using the Most Probable Number (MPN) presumptive test to estimate coliform bacilli, while the plate count approach was used to estimate total heterotrophic bacteria (THB). Each 3-MPN tube of Tryptic Soy broth was inoculated with 1 mL of the sample, and the tubes were then incubated at 30°C for up to 48 hours (Erkmen, 2021). The tubes were checked for dense growth (turbidity) and color change after incubation. For every dilution, the quantity of positive tubes was specified. Phenotypic testing and selective/differential agar media were used to confirm each positive tube. For confirmation, the plate was streaked with MPN tubes that were presumed to be positive on MYP agar. The Petri plates spent a full day at 35°C. The Petri plates were checked for typical colony formation after incubation (Erkmen, 2021).

B. Preparation of Cow Dung Biochar

Using a shredder, the feedstock was taken from the abattoir, dried, and chopped into little pieces. These waste materials were shredded and put into a Biochar Klin pyrolyzer, which was then lit. Using an infrared thermometer, the pyrolyzer's temperature was monitored to be 500 °C and allowed to char for one hour and thirty minutes. The biochars were then subjected to ball-milling and centrifugation to nanosized the chars into fine powder sieved using a 65µm sieve.

C. Preparation of Plantain Peel Biochar

The plantain peels were collected after being separated from the plantain itself. These peels were dried and reduced into smaller pieces and then taken through pyrolysis (in a Biochar Klin pyrolyzer) to produce the biochar. The pyrolyzer's temperature was 500 °C for one hour and thirty minutes of charring, monitored using an infrared thermometer. The biochar was then subjected to treatment as earlier reported.

D. Characterization of Nanobiochar

The nanobiochars were characterized in terms of the percentage yield obtained as the weight difference between the pre- and post-pyrolyzed. pH determination of the nanobiochars was carried out using the pH meter, which was calibrated using buffers 4 and 7 standards (APHA. 2005). Metal content of the biochar was determined using methods as described by the Jones, (1990), and Chamarty, (2001). The Sodium and Potassium contents were determined using a Flame Photometer. The conductivity of the biochars were determined by using the conductivity meter in a ratio of biochar to water of 1:10.

E. Modification of the Nanobiochar

An appropriate amount of washed cow dung biochar was weighed, and a concentration of sulfuric acid (H_2SO_4) (Chen *et al.*, 2015; Vithanage *et al.*, 2015; Özer &

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İmamoğlu, 2022) was used to modify the biochar. Similarly, an appropriate amount of washed plantain peel biochar was weighed, and a concentration of potassium hydroxide (KOH) (Chen *et al.*, 2015; Vithanage *et al.*, 2015; Özer & İmamoğlu, 2022) was used to modify the biochar.

F. Characterization of the Modified NanoBiochars
The morphological makeup of the biochars were examined using a scanning electron microscope (SEM) both before and after alteration. The biochars were scanned at 400–4000 cm⁻¹ using FTIR to examine changes in its functional groups both before and after alteration. An element analyzer identified the primary components of biochars both before and after alteration. To examine the biochars' physical characteristics, such as its orientation and crystal structure.

G. Treatment of the Ballast Water

Ultra-Filtration Technique: Sand, filter paper, cotton wool, and charcoal make up the filter medium in the ultrafiltration apparatus, which is built with a plastic container (Eniola, & Sizirici, 2023). As the water flows through the filter medium due to gravity, it is treated by passage of the water through the layers of the filtration bed. Figure 1 shows the schematic diagram of the ultrafiltration set-up.

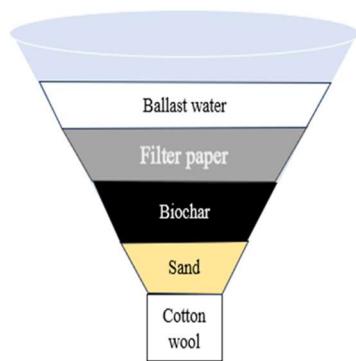


Figure 1 Schematic diagram of the Ultra Filtration Set-up

III. RESULTS AND DISCUSSION

Untreated ballast water is a major vector for introducing non-native species into new habitats. These invaders can outcompete sea food species, disrupt food webs and reduce

biodiversity. This not only threatens the sustainability of commercial fisheries but also affects the availability and safety of seafood for human consumption (Perkowski & Bialoweic 2021). Physiochemical analyses were done on untreated ballast water, and the treated ballast water. The samples were designated as: Untreated ballast water as: BWAA, Ballast water treated with cow dung be denoted as BWBb, Ballast water treated with modified cow dung be denoted as BWCc, Ballast water treated with plantain peel be denoted as BWDD, Ballast water treated with modified plantain peel be denoted as BWEE, Ballast water treated with activated charcoal be denoted as BWFF. Table 1 shows the physiochemical analysis of the samples.

Pre-treatment analysis of the ballast water sample BWAA showed pH 9.2, Chloride ion of 68.7 mg/L against the WHO standard and NSDWQ of 250 mg/L, Nitrate concentration of 5.6 mg/L with a WHO standard of 3.2 mg/L and NSDWQ of 50 mg/L, Sulphate concentration of 3.2 mg/L against the WHO standard of 250 mg/L and NSDWQ of 100 mg/L. The BOD and COD showed 28.6 mg/L and 54.2 mg/L which is way higher than the WHO standard of 10 mg/L. This shows that water is not fit for consumption. After treatment analysis of sample BWAA, the pH of samples BWBb, BWCc, BWDD, BWEE, and BWFF were 9.1, 4.3, 9.7, 8.5 and 6.5 respectively. This showed that the sample BWFF is in accordance with the WHO standard and NSDWQ of 6.5-8.5. BOD and COD of all 5 samples were higher than the required standard of 10 mg/L, this calls for serious concerns on the discharge of the treated water into the water bodies and it makes it unsafe for consumption. The Nitrates, Phosphates and Sulphates of the 5 samples BWBb, BWCc, BWDD, BWEE, BWFF showed that they were within range with the WHO standard and NSDWQ limit, indicating that sample BWFF, had a better concentration than samples BWBb, BWCc, BWDD, BWEE. Compared to unmodified biochar, the treated biochar and the activated charcoal exhibited substantially larger surface area and porous structure (Saadallah *et al.*, 2022). The increased surface area and porosity of activated charcoal significantly boost its ability to adsorb a variety of organic, inorganic, and microbiological contaminants present in ballast water.

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Table 1: Shows the physiochemical analysis conducted on all 6 samples (BWAa, BWBb, BWCc, BWDd, BWEe and BWFf)

Parameters	BWAa	BWBb	BWCc	BWDd	BWEe	BWFf	WHO STANDARD 2015 Limit	NIGERIAN STANDAD FOR DRINKING WATER QUALITY 2015 Limit
Appearance	Clear with suspended particles	Clear with suspended particles	Clear with suspended particles	Clear with suspended particles	Clear with suspended particles	Clear	Clear Colorless Liquid	Clear Colorless Liquid
Odor	Objectionable	Objectionable	Objectionable	Objectionable	Objectionable	Objectionable	Odorless	Unobjectionable
Turbidity	14	7.5	7.8	7.6	8	5.2	NTU 30 max	5
pH @28°C	9.2	9.1	4.3	9.7	8.5	6.5	6.5-8.5	6.5-8.5
Conductivity (mS/cm)	248	8.99	8.09	8.69	8.3	7.89	2500	1000
Salinity (mg/L)	564	106	106	201	126	126	1000	NS
Total Solid (mg/L)	2690	1558	1568	1812	1875	1340	1500	NS
Total Dissolved Solid (mg/L)	1876	899	972	675	872	896	2000	500
Acidity (mg/L)	1.2	2.3	5.2	2.82	2.4	1.2	NS	NS
Alkalinity (mg/L)	5.2	4.9	1.4	6.23	4.8	1.4	NS	NS
Total Hardness (mg/L)	122.4	76.6	53.6	154.20	73.4	33.7	200	150
Calcium Hardness (mg/L)	86.7	54.5	38.4	96.72	48.7	21.6	200	150
Chloride ion (Cl ⁻) (mg/L)	68.7	2.7	2.5	30.2	28.8	2.4	250	250
Nitrate (NO ₃ ⁻) (mg/L)	5.6	3.8	1.4	2.6	2.6	1.2	50	50
Sulphate (SO ₄ ²⁻) (mg/L)	3.2	6.2	12.4	3.4	2.6	3.2	250	100
Phosphate (PO ₄ ³⁻) (mg/L)	0.002	0.003	0.001	0.003	0.002	0.002	0.03	NS
BOD (mg/L)	28.6	15.5	12.6	21.34	18.6	12.2	10	NS
COD (mg/L)	54.2	35.4	25.3	34.42	32.4	24.3	10	NS

NS= No Standard, mg/L = milligram per liter, mS/cm = millisiemens per centimeter

A. Results from the Heavy metals test conducted on the Ballast Water

Heavy metals such as Iron, Lead, Cadmium and Copper are toxic pollutants commonly found in ballast water due to contamination from industrial activities and ship operations. These metals can accumulate in marine organisms, posing risks to ecosystems and human health through seafood consumption. Assessing heavy metal concentrations in ballast water is essential to evaluate pollution levels and the effectiveness of treatments methods in meeting environmental standards (David & Verling 2013; Kumar *et al.*, 2020). Table 2 shows the heavy metal analysis conducted on the samples.

The untreated ballast water BWAa, had iron content higher than the required WHO and NSDWQ standard,

which indicates a high level of iron contained in the water. For samples BWBb, BWCc, BWd, BWEe and BWFf there was decreasing progression in the levels of iron across these samples and in line with the WHO limit of 0.3 (mg/L), with BWFf having the lowest. A high iron percentage taints clothing and kitchenware and negatively alters the color, flavor, and odor of water (Kumar *et al.*, 2017). The analysis showed that untreated ballast water contained elevated levels of iron (0.434 mg/L), lead (0.314 mg/L), Cadmium (0.028 mg/L), and copper (0.302 mg/L). Treatments with cowdung, modified cow dung, plantain peel, modified plantain peel, and activated charcoal reduced these concentrations, with modified cow dung achieving the greatest reductions.

Table 2 shows the heavy metal analysis conducted on all 6 samples (BWAa, BWBb, BWCc, BWd, BWEe and BWff)

Heavy Metals	BWAa (mg/L)	BWBb (mg/L)	BWCc (mg/L)	BWDd (mg/L)	BWEe (mg/L)	BWff (mg/L)	WHO STANDARD (2015) (mg/L)	NIGERIAN STANDARD FOR DRINKING WATER QUALITY (2015) (mg/L)
Iron (Fe ²⁺)	0.434	0.142	0.132	0.242	0.232	0.124	0.3	0.3
Lead (Pb ²⁺)	0.314	0.102	0.094	0.124	0.104	0.064	0.1	0.01
Cadmium (Cd ²⁺)	0.028	0.024	0.022	0.022	0.025	0.020	<0.1	0.003
Copper (Cu ²⁺)	0.302	0.152	0.142	0.296	0.276	0.132	0.3	1

The amount of time the water has been left stagnant in the pipes can also significantly raise the copper concentration in the water, bringing it up to several micrograms per liter (Shelmani *et al.*, 2024). After treatments, the samples BWBb, BWCc, BWd, BWEe and BWff showed a lower concentration of copper as compared to the WHO standard limit of 0.3 mg/L. However, lead and cadmium levels in all samples exceeded the safe limits set by WHO (0.01 mg/L for lead and 0.003 mg/L for cadmium) and the Nigeria Standard for Drinking Water Quality, indicating significant health risks. Iron levels in some samples also exceeded aesthetic limits but pose less health risk, while copper levels remained within safe limits. Despite reductions, the treated ballast water is not safe for human consumption due to toxic heavy metal concentrations, especially lead and cadmium.

Table 3 Microbiological characteristics of ballast water

Parameter	BWAa	BWBb	BWCc	BWDd	BWEe	BWff	WHO STANDARD (2015)	NIGERIAN STANDARD FOR DRINKING WATER QUALITY (2015)
Total Bacteria Count (cfu/ml)	2.2 × 10 ³	1.1 × 10 ²	1.1 × 10 ²	2.1 × 10 ²	2.1 × 10 ²	1.1 × 10 ²	1.0 × 10 ²	0
Total Coliform (cfu/ml)	2.1	1.1	1.1	1.1	1.1	1.0	0.0	10

Cfu= Colony-forming unit

The microbial tests showed that untreated ballast water had a total bacteria count of 2.2×10^3 and total coliforms of 2.1. The treatments using cow dung, modified cow dung, plantain peel, modified plantain peel, and activated charcoal significantly reduced bacterial loads to between 1.1×10^2 and 2.1×10^2 , with coliform levels around 1.0 - 1.1. The absence of this group of organisms is necessary for optimal water quality. According to WHO and Nigerian Standard for Drinking Water Quality (NSDWQ), drinking water must have no detectable coliforms in 100 mL samples

Further advanced treatment is necessary to meet drinking water standards.

B. Results of the Microbial Analysis conducted on the Ballast Water

Analyzing the microbial content of the ballast water is essential to determine contamination levels and to assess how effectively treatment methods comply with international standards such as those established by the International Maritime Organization (IMO). These microbial contaminants can include harmful pathogens that affect aquatic organisms and human health (Kumar *et al.*, 2020).

Table 3 shows the microbiological characteristics of ballast water.

to be considered safe. Although the treatments lowered microbial counts, coliform bacteria were still present, indicating the water is not safe for human consumption without further treatment. These findings

suggest that while the tested materials effectively reduce microbial contamination in ballast water, helping meet environmental discharge standards, they do not meet potable water standards.

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C. Fourier Transform Infrared Analysis (FTIR) of the Biochar

The biochars were scanned using a transmission method, with 32 scans and a resolution range of 4000-650 cm^{-1} . Figures 2-5 show the different spectral analysis of cow dung biochar.

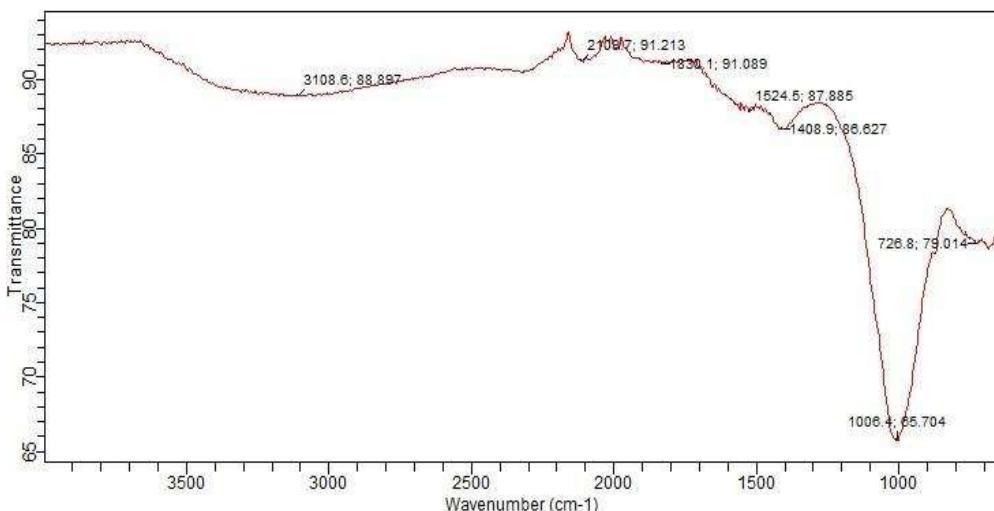


Figure 2 Cow dung biochar (Unmodified)

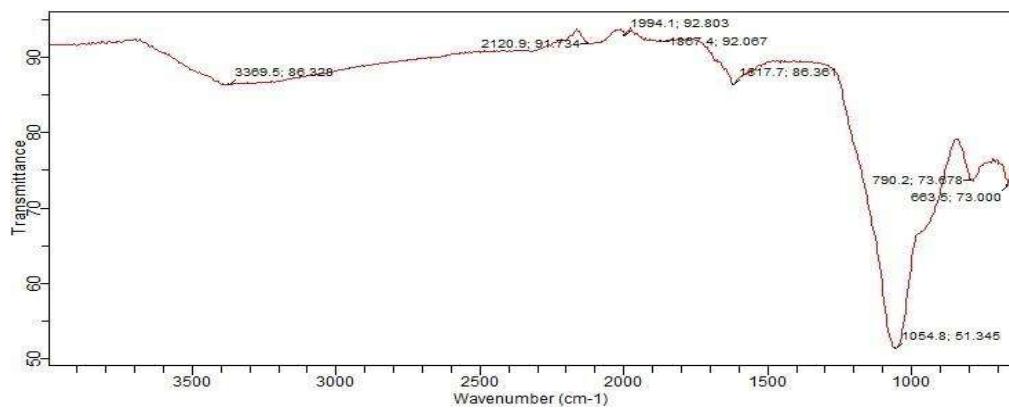


Figure 3 Cow dung biochar (modified)

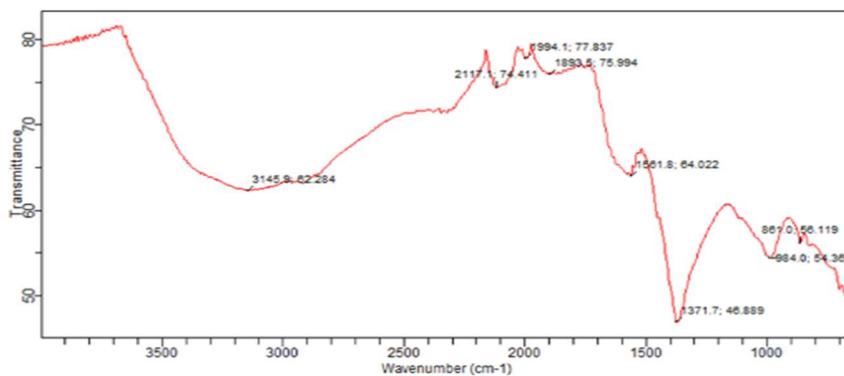


Figure 4 Plantain peel biochar (Unmodified)

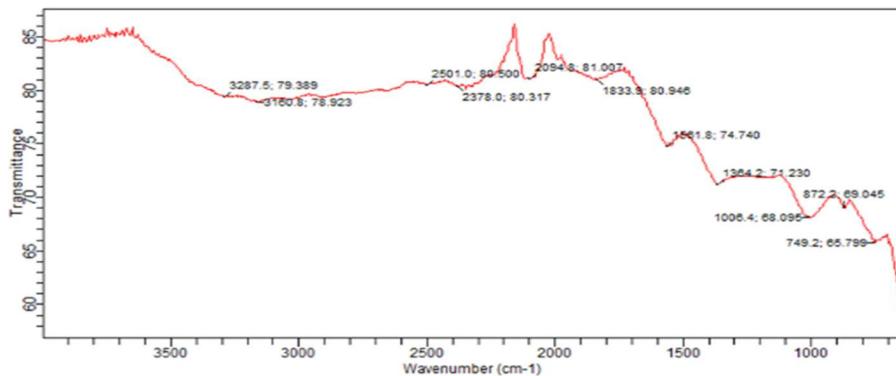


Figure 5 Plantain peel biochar (modified)

Figure 2: The spectral analysis of the cow dung biochar revealed the presence of various functional groups. Peaks at 3108 cm^{-1} , 1524 cm^{-1} , and 726 cm^{-1} indicate aromatic rings and alkenes, suggesting lignin-derived structures. The absorption at 2109 cm^{-1} points to alkynes or nitriles, likely formed due to high-temperature processing. A carbonyl peak at 1836 cm^{-1} suggests the presence of anhydrides or conjugated ketones. Additionally, peaks at 1408 cm^{-1} and 1006 cm^{-1} indicate oxygen-containing groups such as alcohols, ethers, carboxylic acids, or phenols. These functional groups influence the biochar's chemical behavior, enhancing its adsorption capacity in water treatment and contributing to carbon sequestration (Sarfaraz *et al.*, 2020). Figure 3: The FTIR spectrum analysis reveals various functional groups present in the modified cow dung biochar. The broad peak at 3369 cm^{-1} suggests hydroxyl groups, indicating the presence of alcohols, phenols, or adsorbed water. The peak at 2120 cm^{-1} indicates the presence of alkynes or nitriles, likely formed during pyrolysis. Peaks at 1994 cm^{-1} and 1867 cm^{-1} , although unusual for simple carbonyl stretching, may correspond to overtones or combination bands related to carbonyl groups in diverse environments. The 1817 cm^{-1} peak suggests $\text{C}=\text{O}$ stretching, hinting at anhydrides, esters, or ketones. The absorption at 1054 cm^{-1} is associated with $\text{C}-\text{O}$ stretching, indicating alcohols, ethers, or esters from the breakdown of cellulose, hemicellulose, or lignin. Peaks at 790 cm^{-1} and 663 cm^{-1} reflect $\text{C}-\text{H}$ out-of-plane bending, suggesting aromatic ring structures. These functional groups contribute to the biochar's complex structure, imparting both hydrophilic and hydrophobic characteristics that influence its adsorption capabilities and interactions in various applications. Figure 4: The peak at 3145.90 cm^{-1} corresponds to $\text{C}-\text{H}$ stretching in alkenes, indicating the presence of carbon-carbon double bonds. Peaks at 2117.10 cm^{-1} , 1994.10 cm^{-1} , and

1893.50 cm^{-1} suggest $\text{C}\equiv\text{C}$ stretching, characteristic of alkynes. The absorption at 1561.80 cm^{-1} corresponds to $\text{C}=\text{C}$ stretching in conjugated alkenes and aromatic structures, indicating a system of delocalized double bonds. The 1371.70 cm^{-1} peak represents bending vibrations of methyl or methylene groups. Additionally, peaks at 984.00 cm^{-1} and 861.00 cm^{-1} are linked to $\text{C}-\text{H}$ bending vibrations in aromatic rings, specifically meta-substituted benzene structures. These functional groups confirm the presence of alkenes, alkynes, and aromatic compounds in the biochar structure. Figure 5: The FTIR spectrum indicates the biochar's complex structure with both hydrophilic and hydrophobic properties. The peak at 3287.50 cm^{-1} corresponds to $\text{O}-\text{H}$ stretching, suggesting the presence of hydroxyl groups from alcohols or phenols. The absorption at 3160.80 cm^{-1} indicates $\text{N}-\text{H}$ stretching, characteristic of amine or amide groups. Peaks at 2501.00 cm^{-1} and 1833.90 cm^{-1} are linked to carbonyl ($\text{C}=\text{O}$) stretching, likely from aldehydes, ketones, carboxylic acids, esters, or amides. The 2378.00 cm^{-1} peak suggests the presence of cyanide ($\text{C}\equiv\text{N}$), while 2094.80 cm^{-1} corresponds to $\text{C}\equiv\text{C}$ stretching, confirming the presence of alkynes. The 1561.80 cm^{-1} peak indicates $\text{C}=\text{C}$ stretching in conjugated alkenes and aromatic compounds. Additional peaks at 1364.20 cm^{-1} , 1006.40 cm^{-1} , 872.20 cm^{-1} , and 749.20 cm^{-1} suggest the presence of methyl groups and aromatic structures. These findings confirm that the modified biochar contains a variety of functional groups, enhancing its potential for various applications.

D. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopic (EDS) Analysis of the Biochars

The biochars fibers' shape and elemental content have been examined using energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy

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(SEM). They both give information on the elemental composition of the biochar, micro-structure information and chemical composition (Wan *et al.*,

2018). Figures 6-9 shows the SEM analysis of samples.

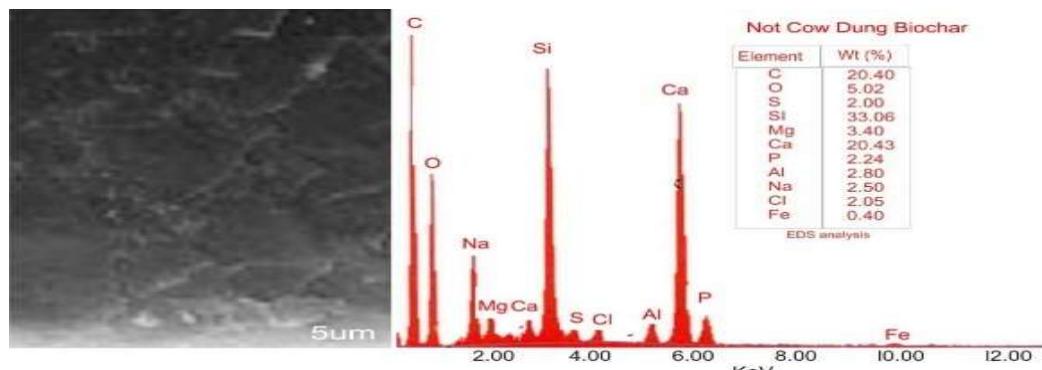


Figure 6 SEM for Unmodified Cow dung Biochar

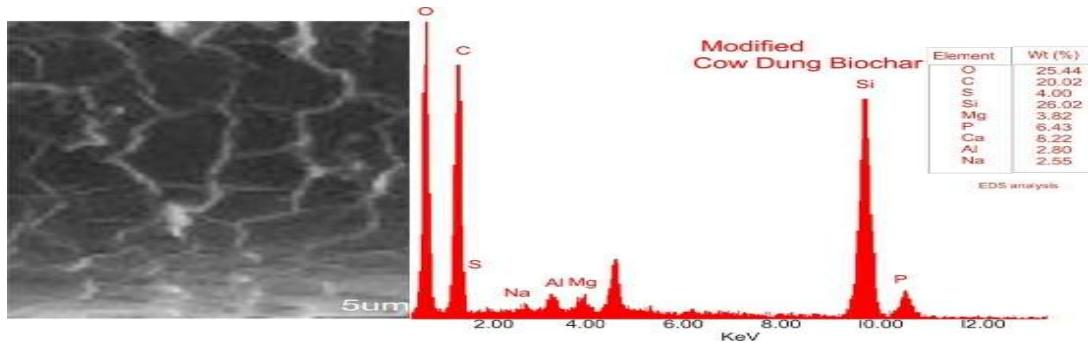


Figure 7 SEM for Modified Cow dung Biochar

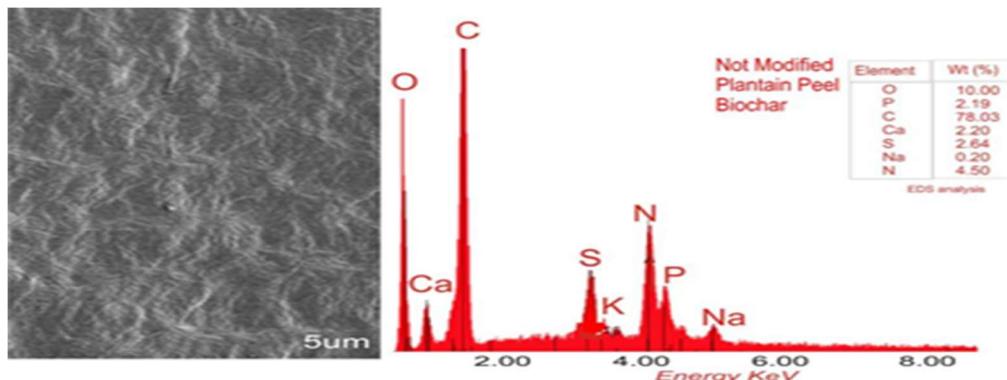


Figure 8 SEM for Unmodified Plantain peel Biochar

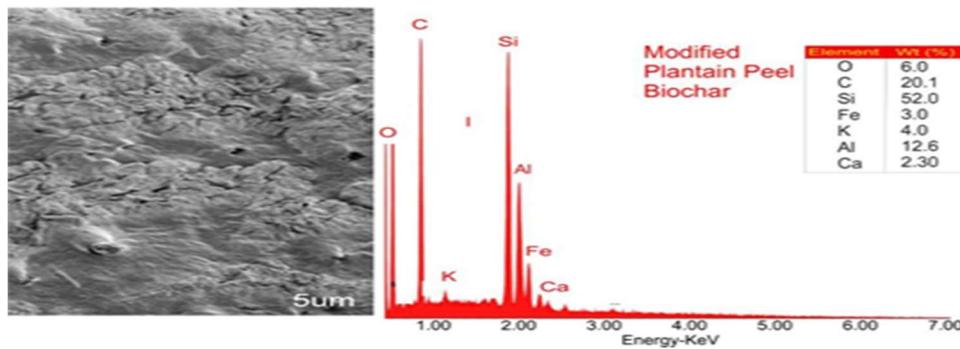


Figure 9 SEM for Modified Plantain peel Biochar

In Figure 6, the microstructure and elemental composition of cow dung fibers were analyzed using SEM and EDS. SEM images revealed a honeycomb-like, layered matrix with strong bonding properties. EDS analysis identified key elements in unmodified cow dung biochar, including high silicon (33.06%), carbon (20.40%), and calcium (20.43%), along with oxygen, sulfur, magnesium, phosphorus, aluminum, sodium, chlorine, and iron. The high silicon content suggests strong adsorption potential for removing contaminants from ballast water (Gupta *et al.*, 2016), while calcium and magnesium could help neutralize acidity (Surendrakumar *et al.*, 2022). Additionally, phosphorus and other nutrients may support microbial growth for biological treatment (Gupta *et al.*, 2016), and carbon content could serve as an energy source for microorganisms in biofilters (Singh *et al.*, 2024). These findings highlight the potential of cow dung biochar in environmental applications. Figure 7: SEM analysis reveals that sulfur modification enhances the biochar's surface area, pore volume, and porous structure. EDS analysis of sulfur-treated biochar shows notable compositional changes, including an increase in sulfur (from 2.00% to 4.00%) and oxygen (from 5.02% to 25.44%), indicating successful incorporation of sulfur-containing functional groups. A slight decrease in carbon (from 20.40% to 20.02%) suggests oxidation of carbon-based structures, while phosphorus increased (from 2.24% to 6.43%) and calcium decreased (from 20.43% to 8.22%), likely due to mineral redistribution. These modifications enhance biochar's potential for ballast water treatment by improving heavy metal adsorption, pH buffering, and

microbial support, making it more effective for filtration and pollutant removal (Gupta, 2023). Figure 8 and Figure 9: The elemental composition of plantain peel biochar before and after modification with Potassium Hydroxide (KOH) highlights its improved potential for ballast water treatment. EDS analysis shows a significant reduction in carbon (78.03% to 20.10%) and oxygen (10.00% to 6.00%), indicating structural modifications that lower microbial activity and limit unwanted chemical reactions. The removal of sulfur, phosphorus, and nitrogen suggests reduced nutrient availability, while increased silicon (52.00%), iron (3.00%), potassium (4.00%), and aluminum (12.60%) enhance heavy metal adsorption, ion exchange, and pH buffering. These modifications make the biochar more effective for water purification, improving pollutant removal and adsorption efficiency

E. X-ray Diffraction (XRD) Analysis of the Biochars
 Certain crystalline peaks are visible in the XRD pattern, and these correspond to particular mineral compounds that are present in the biochar. The degree of crystallinity in the biochar is indicated by the XRD peaks' sharpness and intensity. Crystallinity is higher in biochars with more prominent and smaller peaks. Biochars with softer, wider peaks, on the other hand, appear to have a more amorphous structure (Ekuya Lombolu *et al.*, 2022). Figures 10-13 show the XRD for different samples.

Phase name	Formula	Figure of merit	Phase reg. detail	Space Group	DB Card Number
Kalsilite	K0.95 (Al Si O4)	1.323	Si/M/PDF-4 Minerals 2024)	159 : P31c	01-090-8761
Biphosphammite, syn	H2 (N H4) (P O4)	1.962	Si/M/PDF-4 Minerals 2024)	122 : I-42d	04-007-7071
Edenite	Na Ca2 Mg5 Al Si7 O22 (O...	1.901	Si/M/PDF-4 Minerals 2024)	12 : C12/m1	00-023-1405
Urea, syn	C H4 N2 O	1.938	Si/M/PDF-4 Minerals 2024)	113 : P-421m	00-008-0822
Graphite	C	2.579	Si/M/PDF-4 Minerals 2024)	147 : P-3	00-001-0640
Silicon Oxide	Si O2	1.668	Si/M/PDF-4 Minerals 2024)	62 : Pmcn	00-035-0063

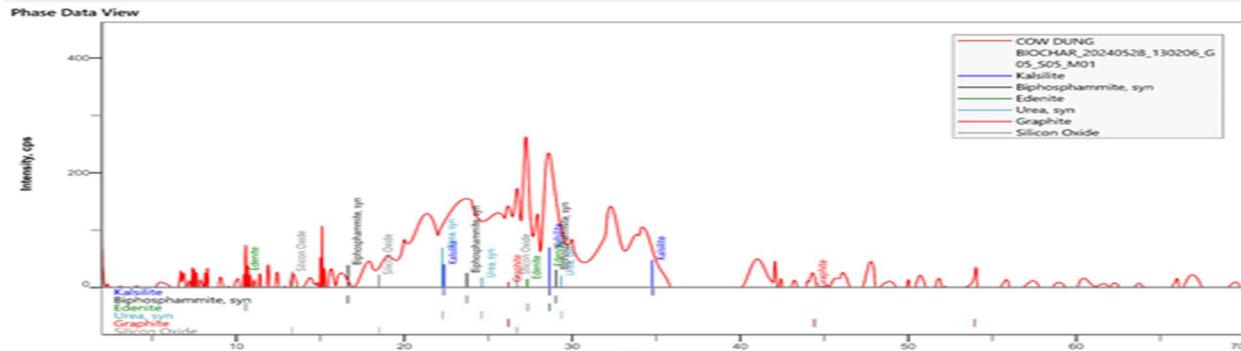


Figure 10. XRD for Unmodified cow dung biochar

Phase name	Formula	Figure of merit	Phase reg. detail	Space Group	DB Card Number
Kalsilite	K0.95 (Al Si O4)	1.323	Si/M/PDF-4 Minerals 2024)	159 : P31c	01-090-8761
Biphosphammite, syn	H2 (N H4) (P O4)	1.962	Si/M/PDF-4 Minerals 2024)	122 : I-42d	04-007-7071
Edenite	Na Ca2 Mg5 Al Si7 O22 (O...	1.901	Si/M/PDF-4 Minerals 2024)	12 : C12/m1	00-023-1405
Urea, syn	C H4 N2 O	1.938	Si/M/PDF-4 Minerals 2024)	113 : P-421m	00-008-0822
Graphite	C	2.579	Si/M/PDF-4 Minerals 2024)	147 : P-3	00-001-0640
Silicon Oxide	Si O2	1.668	Si/M/PDF-4 Minerals 2024)	62 : Pmcn	00-035-0063

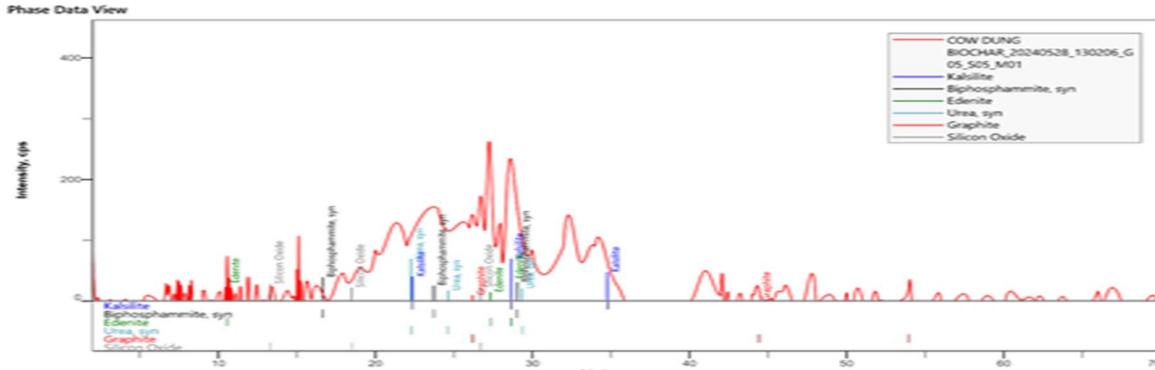


Figure 11 XRD for modified cow dung biochar

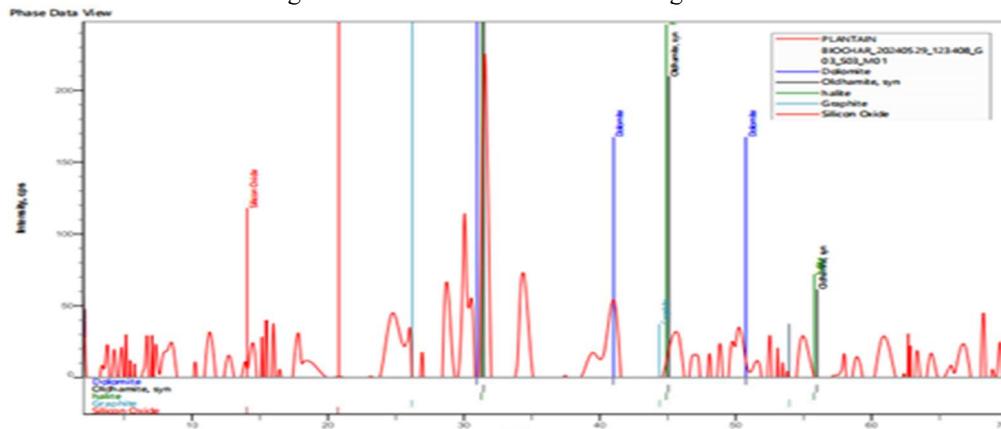


Figure 12 XRD for Unmodified Plantain peel biochar

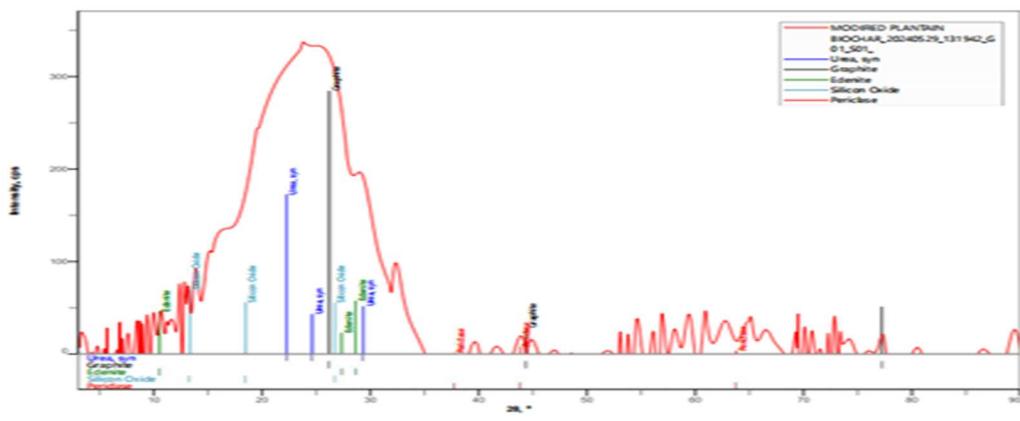


Figure 13 XRD for Modified Plantain peel biochar

Figure 10: The XRD analysis reveals that cow dung biochar contains a diverse mineral composition, enhancing its suitability for ballast water treatment. Kalsilite (37%) contributes to its high cation exchange capacity, aiding in heavy metal adsorption. Biphosphammite (19%) and urea (20%) provide essential nutrients that support microbial growth for biological treatment. Edenite (4.7%) helps regulate pH, while graphite (16%) enhances adsorption of organic pollutants and serves as a microbial support material. Silicon oxide (3.3%) further reinforces its adsorptive and catalytic properties. These crystalline phases, identified through peak analysis and cross-referenced with standard XRD databases, confirm the biochar's multifunctionality for cost-effective ballast water treatment (Cong *et al.*, 2021, Yameen *et al.*, 2024) Figure 11: The graph shows that sulfuric acid modification enhances the adsorption capacity of cow dung biochar by increasing its surface area and microporosity. The dominant mineral, aluminopyracmonite (38%), effectively adsorbs heavy metals and pollutants. Coesite (18.5%) suggests structural changes that improve micropore formation, while urea (25%) introduces nitrogen-containing compounds beneficial for microbial activity in biological treatment. Edenite (3%) aids in pH regulation, and graphite (15.6%) enhances adsorption of organic pollutants and microbial immobilization. These modifications make the biochar a cost-effective material for comprehensive ballast water treatment (Ekman *et al.*, 2023). Figure 12: The XRD graph shows the mineral composition of the unmodified plantain peel biochar, highlighting its potential for water treatment. Dolomite (33.6%) enhances pH

buffering, cation exchange, and porosity. Oldhamite (16%) contributes to sulfur content, influencing microbial activity. Halite (20.6%) aids in adsorption and ion exchange but introduces salinity concerns. Graphite (15.6%) increases porosity, adsorption capacity, and structural integrity while influencing electrochemical properties. Silicon oxide improves chemical stability and pH buffering, ensuring prolonged effectiveness in water treatment. These properties make the biochar a promising material for contaminant removal and water purification. Figure 13: The modified plantain peel biochar contains several key minerals, each contributing to its water treatment potential. Urea (66.6%) releases nitrogen, supporting beneficial bacteria for ballast water bioremediation and aiding pH buffering. Graphite (25.7%) increases surface area, adsorption capacity, and electrochemical properties, enhancing structural integrity. Edenite (3.26%) helps balance pH in acidic ballast water and increases surface reactivity. Silicon oxide (3.79%) improves chemical stability and aids in pH buffering. Periclaste enhances adsorption through coagulation and exhibits antimicrobial properties, further supporting its role in water treatment.

IV. CONCLUSION

The analysis of ballast water treatment using modified cow dung adsorbents and modified plantain peel adsorbents indicates varying degrees of effectiveness across different treatment methods. The pre-treatment analysis of the ballast water sample BWAa revealed a pH of 9.2, chloride ion concentration of 68.7 mg/L (well below the WHO [43] standard of 250 mg/L), nitrate concentration of 5.6 mg/L (above the WHO

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[43] standard of 3.2 mg/L), and sulphate concentration of 3.2 mg/L (below the WHO [43] standard of 250 mg/L). The BOD and COD levels were 28.6 mg/L and 54.2 mg/L, respectively, both significantly exceeding the WHO standard of 10 mg/L. All treated samples showed BOD and COD levels higher than the WHO standard of 10 mg/L, raising concerns about the discharge of treated water into natural water bodies, nitrate, phosphate, and sulphate levels in samples BWBb, BWCc, BWDd, BWEe, and BWFF were within the WHO standard limits. Notably, sample BWFF exhibited the most favorable results compared to BWBb, BWCc, BWDd and BWEe. The treatment of ballast water with modified biochars proved to be the most effective method because of the nanoporous nature. Their superior treatment capability is attributed to its significantly larger surface area and highly porous structure compared to unmodified biochar. This enhanced surface area and porosity substantially improve its adsorption capacity for various organic, inorganic, and microbiological contaminants found in ballast water.

AUTHOR CONTRIBUTIONS

L.O Ekebafe: Supervision, Conceptualization, and Methodology. **F.O Onyeama:** Writing – Original draft, Writing – Review & Editing. **F.E Jegede:** Writing – Review & Editing. **D.K Obodo:** Software and Validation, Writing – Review and Editing.

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