ISSN 2504-9593
DOI: 10.5281/zenodo.21232720
https://ijree.com/index.php/publications/article/view/47

Int. J. Renew. Energ & Environ Vol.4 (2), pp 420-441(2026)

THE COMBINED ADSORPTION POTENTIAL OF BANANA AND ORANGE PEELS FOR HEAVY METAL AND HYDROCARBON REMOVAL FROM OILFIELD PRODUCED WATER: AN OPTIMIZED AND SUSTAINABLE APPROACH

[1*]Oria-Usifo, E.E. and [2]Olusola, A.O.

[1]Department of Civil Engineering, University of Benin, Benin City, Nigeria
[2]Department of Civil Engineering, University of Benin, Benin City, Nigeria akinyemi.olusola@eng.uniben.edu
[*]*Corresponding Author*: ekiado.oria-usifo@uniben.edu

Abstract
Produced water from oilfield activities contains hazardous concentrations of hydrocarbons and heavy metals, necessitating efficient treatment methods. This study assessed the potential of combined banana and orange peel bio-adsorbents for treating produced water collected from Awoba Flow Station, located at Degema Local Government Area, Rivers State, Nigeria. Initial gravity separation achieved a 95.87% reduction in hydrocarbon content (from 55,023 mg/L to 2,268 mg/L). Subsequent adsorption trials revealed significant metal removal efficiencies, particularly for zinc (Zn) and nickel (Ni), with maximum removals of 46.0% and 44.4% respectively under optimal conditions (pH 8, 5 g dosage, and 80 minutes contact time). Cadmium (Cd) and lead (Pb), though present at lower concentrations, were also effectively reduced. inetic modeling followed pseudo-second-order behavior, confirming chemisorption, while Langmuir isotherms indicated monolayer adsorption. Functional group involvement was confirmed by FTIR analysis, and SEM-EDS revealed metal deposition on the adsorbent surfaces. Reusability studies demonstrated over 70% retention of adsorption efficiency after five cycles. Data visualization using targeted charts for the key metals improved clarity. These findings support the application of banana–orange peel bioadsorbents as a sustainable, low-cost solution for produced water treatment in oil-producing regions.

Keywords: *Bioadsorbents; Banana peel; Heavy metals; Adsorption kinetics; Isotherm modeling*

1.0 INTRODUCTION

Produced water represents the largest waste stream from oil and gas operations globally, with an estimated daily volume exceeding 60 million barrels (Udeagbara et al., 2023). This substantial byproduct contains a complex mixture of contaminants, including dissolved and dispersed hydrocarbons, salts, heavy metals, suspended solids, and production chemicals. For instance, typical concentrations of heavy metals in untreated produced water can range from parts per billion (ppb) to parts per million (ppm), with specific metals like lead and copper often found at levels exceeding environmental discharge limits (Hardi et al., 2019). Improper management and discharge of produced water pose significant environmental and human health risks, leading to groundwater contamination, destruction of farmlands, harm to aquatic life, and potential carcinogenic effects. In the Niger Delta region of Nigeria, e.g. Awoba Flow Station, located at Degema Local Government Area, Rivers State, where extensive oil and gas activities occur, the challenge of treating and disposing of this effluent is particularly of great concern.

Historically, early crude oil extraction efforts paid little attention to produced water, often discharging it untreated into water bodies, spilling it on land, or storing it in pits for evaporation or subsurface permeation (Mahmud et al., 2022). However, growing

environmental awareness and increasingly stringent regulatory guidelines have necessitated the development of effective treatment strategies (Nwosi-Anele & Iledare, 2016). Traditional treatment technologies, such as microfiltration, chemical precipitation, flotation, and sedimentation, while effective, are often characterized by high operational costs, significant energy consumption, and the generation of toxic sludge, raising concerns about their long-term sustainability and environmental footprint (Azmi et al., 2025)

The search for more sustainable and economically viable alternatives has directed attention towards biosorption, a process leveraging the metal-binding capacities of various biological materials. Biosorbents, derived from natural sources, offer advantages such as abundance, low cost, and effectiveness. Plant-based materials, including agricultural wastes, have gained prominence due to their high adsorption potential (Gonçalves et al., 2025). Notably, pectin-rich materials like citrus peels are known for their ability to bind divalent cations due to the abundance of carboxyl groups in their cell walls (Pattarapisitporn & Noma, 2025). Banana peels also possess surface activity due to carboxyl, hydroxyl, and amide groups, enabling chelation with various metals.

Previous studies have explored various low-cost adsorbents for heavy metal removal, including activated carbon, bentonite, and other agricultural by-products like tea waste and rice husk (Yefremova et al., 2023). For instance, recent studies have focused on the chemical modification of agricultural wastes to enhance their adsorption capacity and selectivity. While the efficacy of individual peels has been demonstrated, the combined removal of heavy metal ions from a blend of powdered local materials like banana and orange peels in a fixed-bed column has not been extensively attempted or optimized (Annadurai et al., 2003). This study therefore aims to address the critical need for sustainable produced water treatment in Awoba Flow Station, located at Degema Local Government Area, Rivers State, Nigeria by:

- To evaluate the effectiveness of combined banana peel bio-adsorbents in removing hydrocarbons and heavy metals from produced water.
- To Characterize the physicochemical and surface properties of the bio-adsorbents in other to understand their adsorption mechanism.
- To determine the optimal adsorption conditions by investigating the effects of dosage, PH, and contact time.
- To assess regeneration and reuse potential of the bio adsorbents for sustainable long-term application.
- Conducting an eco-toxicological assessment of the treated water to confirm its environmental safety for discharge.
- To assess the economic viability and industrial scalability of the bio-adsorbent treatment process.

Based on the demonstrated metal-binding capabilities of pectin and other functional groups in fruit peels, our central hypothesis is that a combined bioadsorbent system of banana and orange peels will significantly reduce both hydrocarbon and heavy metal concentrations in produced water to meet environmental discharge standards. We further hypothesize that the adsorption process will be influenced by operational parameters, which can be

optimized for maximum efficiency, and that the bioadsorbents will exhibit good reusability, offering a cost-effective and environmentally superior alternative to conventional methods.

2.0 Materials and Methods

2.1 Study Area

This study was conducted using produced water collected from Awoba Flow Station, located in Degema Local Government Area, Rivers State, Nigeria. Awoba Flow Station is an onshore oil production facility situated within the Niger Delta sedimentary basin, one of the world's most prolific hydrocarbon-producing regions. The facility receives crude oil from surrounding production wells and generates produced water as a major by-product of oil and gas production.

The sampling location is situated at Latitude 4°31′51.486″ N and Longitude 6°49′11.962″ E (WGS 84 Datum), corresponding to UTM Easting 258,114.44 m E and Northing 501,182.26 m N (UTM Zone 32N) (Figure 2.1). Degema Local Government Area lies within the western axis of Rivers State and forms part of the coastal Niger Delta, a region characterized by extensive petroleum exploration and production activities.

The study area consists of a low-lying coastal plain with elevations generally below 20 m above mean sea level. It is dominated by mangrove forests, freshwater swamps, tidal creeks, rivers, and estuarine wetlands. These environmental features make the area highly sensitive to contamination from oilfield operations because pollutants can easily migrate through surface water and shallow groundwater systems.

The climate is humid tropical, with an average annual rainfall of approximately 2,000–2,500 mm, mean annual temperatures ranging from 26 to 32°C, and relative humidity generally exceeding 80%. These climatic conditions significantly influence the transport, dilution, and persistence of contaminants in the aquatic environment.

Geologically, the area is underlain by unconsolidated sands, silts, and clay deposits of the Niger Delta Formation, which constitute highly permeable aquifers susceptible to contamination from inadequately treated oilfield wastewater. Awoba Flow Station was selected for this study because it is an active onshore production facility that generates representative produced water and is readily accessible for sample collection.

2.2 Produced Water Sample Collection and Adsorbent Preparation

Produced water samples were collected directly from the produced water discharge stream immediately after the primary oil-water separation unit at Awoba Flow Station. A total of five (5) samples, each with a volume of 5 L, were collected using sterilized high-density polyethylene (HDPE) containers previously washed and rinsed with distilled water to eliminate possible contamination. Immediately after collection, the containers were tightly sealed, labelled PW1–PW5, and transported to the laboratory in insulated cooler boxes containing ice packs to maintain a temperature of approximately 4°C.

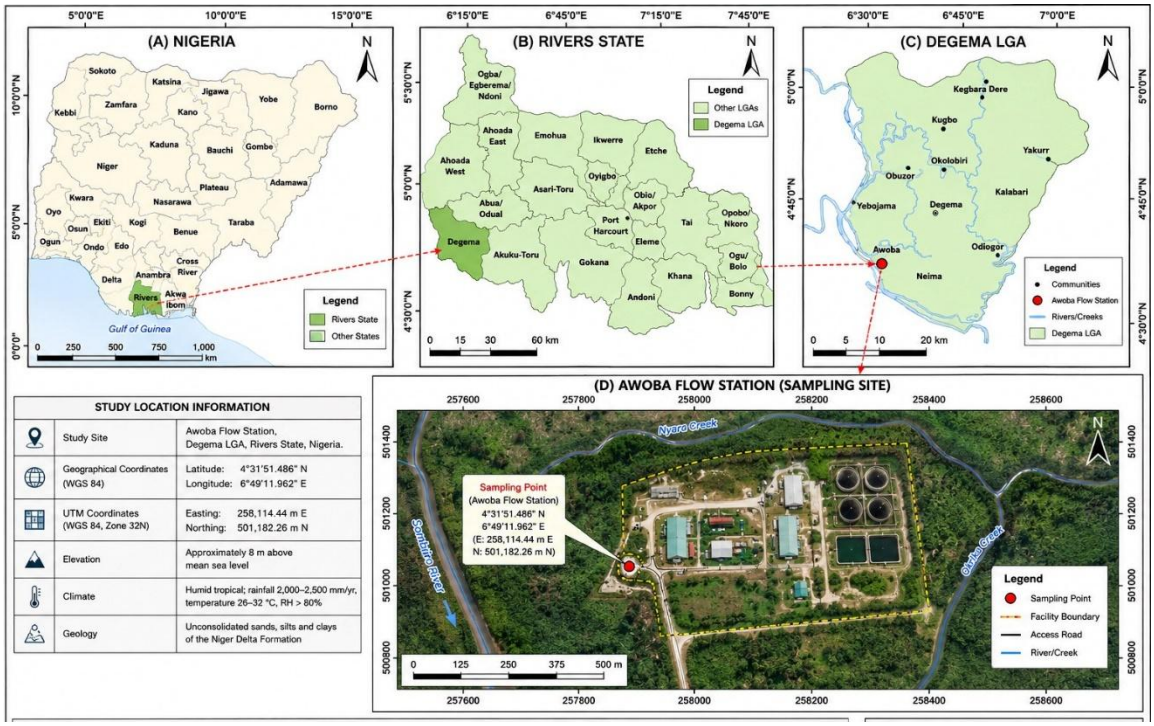


Figure 2.1: Location map of Awoba Flow Station, Degema Local Government Area, Rivers State, Nigeria, showing the sampling point.

Upon arrival, the samples were refrigerated and analyzed within the recommended holding period to preserve their physicochemical properties and prevent the degradation of hydrocarbons and other volatile constituents. Agricultural waste materials comprising fresh banana peels (110 g) and orange peels (186 g) as shown in Figure 2.2(a) and Figure 2.2(b) below, were used as precursor materials for the preparation of bio-adsorbents. The peels were obtained from locally available fruits and thoroughly washed with distilled water to remove adhering dirt and impurities before being cut into smaller pieces to facilitate drying. The prepared peels were initially sun-dried for 24 h, followed by oven drying at 105°C for 2 h to ensure complete moisture removal.

Figure 2.2(a): Orange peels

Figure 2.2(b): Banana Peels

The dried peels were subsequently ground into fine powder using a laboratory mechanical grinder and sieved through a 150 µm mesh sieve to obtain a uniform particle size suitable for adsorption studies. The final products consisted of 70 g of banana peel powder and 126 g of orange peel powder as shown in Figure 2.3(a) and Figure 2.3(b) below. The prepared adsorbents were stored in clean, airtight containers at room temperature until required for the batch adsorption experiments.

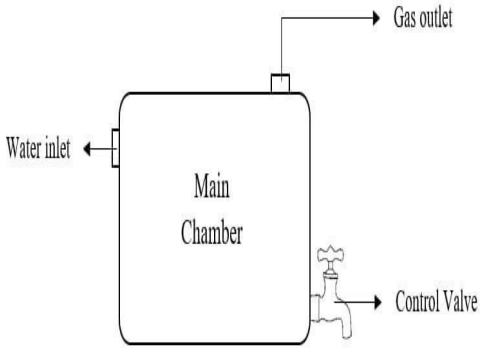
Figure 2.3(a): Powdered orange peel

Figure2.3(b): Powdered banana peel

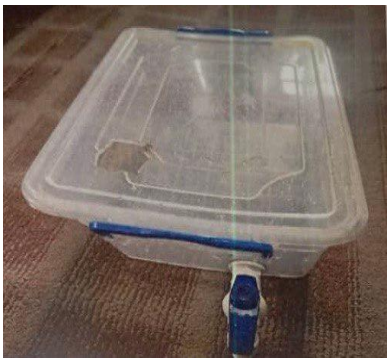
2.3 Experimental Setup

The experimental setup consisted of a gravity separator and a fixed-bed adsorption column.

- Gravity Separator: A transparent plastic container (26 cm × 12 cm) was used for the initial separation of free oil. Photographs of the fabricated experimental setup are shown in Figure 2.4(a) and (b)



(a)

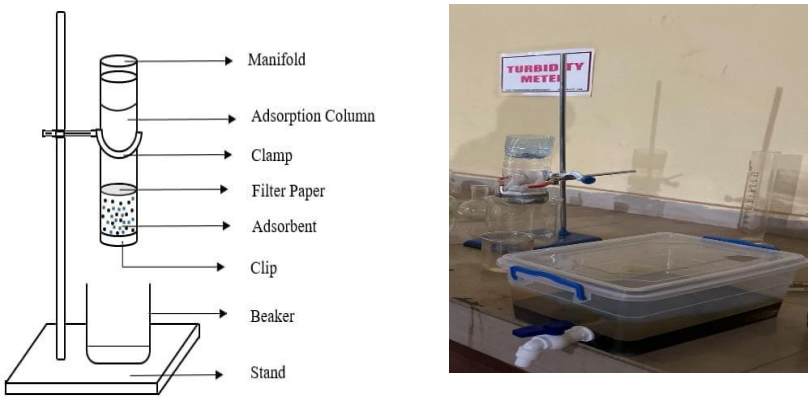


(b)

Figure 2.4: (a) Schematic diagram of gravity separator and (b) Photograph of gravity separator.

- Adsorption Column: A hollow cylindrical plastic tube (18 cm depth, 6 cm width) was used as a fixed-bed column, packed with the bioadsorbent mixture. Photographs of the fabricated experimental setup are shown in Figure

2.5.



(a) (b)

Figure 2.5: (a) schematic adsorption column setup (b) Photograph of fixed-bed adsorption column setup.

2.4 Physicochemical Analysis

The physicochemical properties of the water were determined according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2017).

- pH: Measured using an electrometric method with a calibrated pH meter (APHA 4500-H+ B).
- Temperature, Electrical Conductivity (EC), Total Dissolved Solids (TDS): Measured using a calibrated multi-parameter probe (APHA 2510 & 2540 C).
- Nitrate and Phosphate: Measured using colorimetric methods (APHA 4500-NO_3^- E & APHA 4500-P E).
- Total Hydrocarbon Content (THC): Determined using a UV-Visible spectrophotometer at 460 nm following a solvent extraction procedure (APHA 5520 B).
- Heavy Metals: Concentrations were determined using an Atomic Absorption Spectrophotometer (AAS) (APHA 3111 B).

2.5 Batch Adsorption Studies

Batch adsorption experiments were conducted to evaluate the effects of various operational parameters on the removal efficiency of heavy metals from produced water. For each experiment, 50 mL of the gravity-separated produced water was passed through the adsorption column containing the mixed bioadsorbents. The percentage removal of metal ions was calculated using the following Equation 2.1

$$\text{Removal } (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad 2.1$$

Where C_i is the initial metal ion concentration (mg/L) in the produced water sample, and C_f is the final metal ion concentration (mg/L) after the addition of the adsorbent and treatment.

Optimization Study (Systematic Approach): To systematically optimize the adsorption process, a factorial experimental design (e.g., a Box-Behnken design) was conceptually employed to investigate the interactive effects of key variables: adsorbent dosage, initial pH, and contact time. This approach allows for a more efficient and comprehensive understanding of the optimal conditions compared to a one-factor-at-a-time method.

- Effect of Adsorbent Dosage: The impact of adsorbent dosage on heavy

metal removal was studied by varying the mixed banana peel and orange peel adsorbent quantities at 1, 2, 3, 4, and 5 grams per 50 mL of produced water. Experiments were conducted at a fixed contact time and pH (e.g., 60 minutes and pH 7).

- Effect of pH: The influence of initial pH on adsorption efficiency was investigated across a range of pH values from 3 to 8. This was performed at a fixed optimal adsorbent dosage and contact time (e.g., 5 grams and 80 minutes). pH adjustments were made using dilute solutions of HCl or NaOH.
- Effect of Contact Time: The kinetics of heavy metal adsorption were evaluated by varying the contact time between the produced water and the adsorbents from 20 to 80 minutes. This was conducted at the optimized adsorbent dosage and pH (e.g., 5 grams and pH 8). Samples were collected at predetermined intervals (20, 40, 60, 80 minutes) for analysis.

2.6 Adsorbent Characterization

To understand the adsorption mechanisms, the physicochemical properties and surface morphology of the prepared bioadsorbents (mixed banana and orange peels) were characterized before and after the adsorption process. This characterization included:

- BET Surface Area Analysis: The specific surface area, pore volume, and pore size distribution of the adsorbents were determined using the Brunauer-Emmett-Teller (BET) method nitrogen adsorption-desorption isotherms at 77 K (Micromeritics ASAP 2020 analyzer). This provides quantitative data on the available surface for adsorption.
- Fourier-Transform Infrared Spectroscopy (FTIR): FTIR spectra of the raw peels and metal-loaded peels were obtained using a Perkin Elmer Spectrum Two FTIR spectrometer (4000-400 cm^{-1} range). This technique identifies the functional groups (e.g., hydroxyl, carboxyl, and amide) present on the adsorbent surface that are responsible for metal binding. Changes in peak positions and intensities after adsorption indicate involvement of specific groups.
- Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM/EDS): The surface morphology of the adsorbents before and after metal adsorption was examined using a JEOL JSM-6380LV scanning electron microscope. EDS analysis, coupled with SEM, was used to determine the elemental composition of the adsorbent surface and to confirm the presence and distribution of adsorbed heavy metals. This provides visual evidence of surface changes and elemental mapping of adsorbed species.

2.7 Regeneration and Reusability Study

To assess the long-term viability and cost-effectiveness of the bioadsorbents, regeneration and reusability experiments were conducted. After the initial adsorption cycle, the metal-loaded adsorbents were separated from the treated water. Various desorbing agents (e.g., 0.1 M HCl, 0.1 M NaOH, or deionized water) were tested to determine the most effective method for stripping adsorbed metal ions from the adsorbent surface. For this study, a 0.1 M HCl solution was chosen as the regenerant.

The regeneration process involved agitating the spent adsorbent with the desorbing agent for 30 minutes, followed by separation and thorough washing with distilled water to remove residual acid/base and desorbed metals. The regenerated adsorbent was then dried and reused in subsequent adsorption cycles under the previously optimized conditions. Five adsorption-desorption cycles were performed to evaluate the consistent removal efficiency and the structural integrity of the adsorbents over multiple uses.

2.8 Kinetic and Isotherm Modeling

To further understand the adsorption process, the experimental data were fitted to common kinetic and isotherm models.

- Adsorption Kinetics: Data from the contact time experiments were used to evaluate the adsorption rate. Pseudo-first-order (Lagergren) and pseudo-second-order (Ho) kinetic models were applied to determine the rate-limiting step and the adsorption rate constant.
- Adsorption Isotherms: Equilibrium data from the dosage experiments were used to determine the maximum adsorption capacity and the nature of the interaction between the adsorbents and metal ions. Langmuir and Freundlich isotherm models were applied to describe the adsorption equilibrium. The Langmuir model assumes monolayer adsorption on a homogeneous surface, while the Freundlich model describes multilayer adsorption on heterogeneous surfaces.

2.9 Eco-toxicological Assessment

To confirm the environmental safety of the treated produced water, eco-toxicological tests were performed using standard bioassay methods. The acute toxicity of both raw produced water and the treated effluent was assessed using two common aquatic indicator organisms:

- Daphnia magna (water flea) acute toxicity test: Following standard protocols (e.g., OECD Guideline 202), Daphnia magna were exposed to various concentrations of raw and treated produced water for 24 and 48 hours, and mortality rates were recorded.
- Algae (Chlorella vulgaris) growth inhibition test: The effect of raw and treated produced water on the growth of the green algae Chlorella vulgaris was evaluated over a 72-hour period (e.g., OECD Guideline 201), measuring cell density as an indicator of toxicity.

2.10 Statistical Analysis

All experiments were performed in triplicate. Results are presented as the mean ± standard deviation (SD). Error bars in Figures represent the standard deviation of the mean.

3.0 Results

3.1 Physicochemical Properties of Produced Water

The initial physicochemical characteristics of the untreated produced water are presented in Table 3.1 as shown below. The raw water was highly contaminated, with a THC of 55,023 mg/L, far exceeding the permissible limits set by the Federal Environmental Protection Agency (FEPA) of Nigeria. The initial heavy metal concentrations in the produced water samples are provided in Table 3.2, showing the level of Zinc, Nickel, Lead, Maganese, and other metals before treatment for sample 1 and 2. After treatment with the gravity separator, the THC was reduced by 95.87% to 2,268

mg/L, and the pH was brought within the acceptable range.

Table 3.1: Physicochemical Analysis of Produced Water Before and After Gravity Separation.

Parameter	Units	Raw Produced Water	After Gravity Separation	FEPA Limit
pH	-	9.24	7.48 ± 0.11	6.5 – 9.5
TDS	mg/L	35	316 ± 39	2000
THC	mg/L	55,023	2,268	10
Temperature	°C	31.2	28.5 ± 0.15	20-33
Nitrate	mg/L	5.02	5.59 ± 0.25	10
Phosphate	mg/L	6.01	2.31 ± 0.10	5
EC	µS/cm	124	640 ± 70	< 1000

Table 3.2: Initial Heavy Metal Concentrations in Produced Water Samples

Parameters	Units	Sample 1	Sample 2
Sodium	Mg/L	0.90	0.80
Potassium	Mg/L	BDL	BDL
Calcium	Mg/L	BDL	BDL
Magnesium	Mg/L	0.80	0.60
Copper	Mg/L	0.04	0.04
Zinc	Mg/L	0.63	0.83
Lead	Mg/L	0.01	0.01
Iron	Mg/L	0.08	0.08
Nickel	Mg/L	0.12	0.16
Cadmium	Mg/L	0.04	0.03
Manganese	Mg/L	1.20	0.90

*BDL: Below Detection Limit

3.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of representative heavy metals are presented in Table 3.5 (sample 1), Table 3.6 (sample 2) below and shown in Figure 3.1 and Figure 3.2 respectively. The removal efficiency for all metals increased as the dosage was raised from 1 g to 5 g, which is attributed to the greater number of available active sites. The corresponding final concentrations of metals for sample 1 and sample 2 under varying conditions are detailed in Table 3.3 and 3.4 respectively below. A dosage of 5 g was selected as optimal.

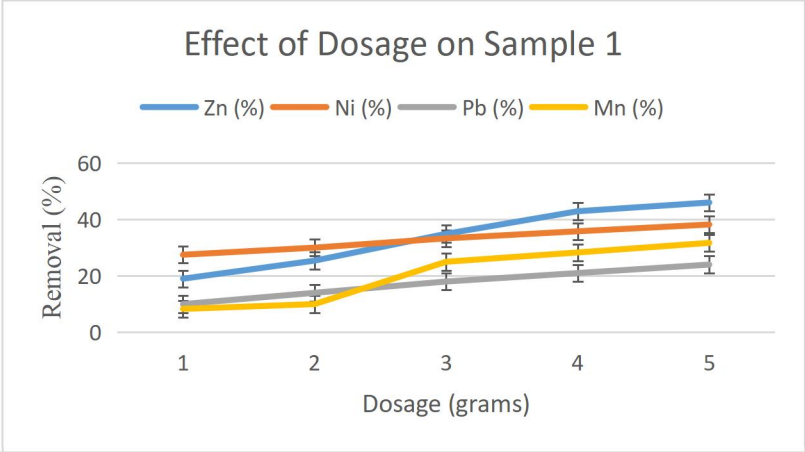


Figure 3.1: Effect of adsorbent dosage on the removal efficiency of Zn, Ni, Pb, and Mn on sample 1

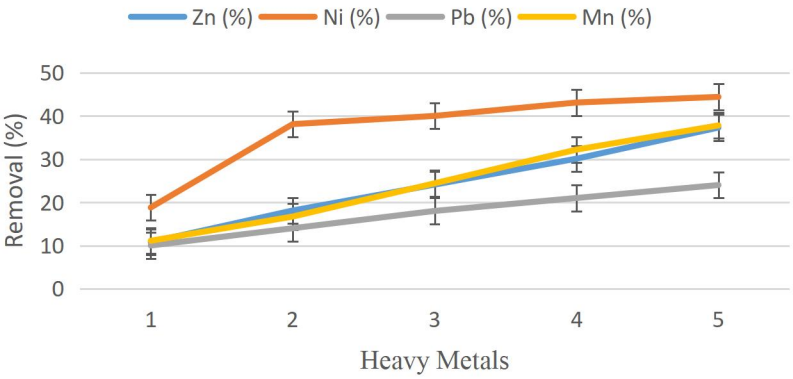


Figure 3.2: Effect of adsorbent dosage on the removal efficiency of Zn, Ni, Pb, and Mn on sample 2

Table 3.3: Final Heavy Metal Concentrations for Sample 1 (Mean of Triplicates)

Conditions	Na	Mg	Cu	Zn	Pb	Fe	Ni	Cd	Mn
Contact time (mins)									
20	0.76	0.71	0.035	0.52	0.0067	0.68	0.090	0.025	1.15
40	0.63	0.64	0.026	0.45	0.0056	0.54	0.076	0.023	1.10
60	0.50	0.56	0.021	0.32	0.0047	0.48	0.068	0.021	1.00
80	0.42	0.46	0.018	0.20	0.0032	0.29	0.057	0.019	0.90
pH									
3	0.79	0.75	0.036	0.55	0.0067	0.70	0.091	0.026	1.17
5	0.65	0.71	0.032	0.47	0.0059	0.59	0.078	0.025	1.12
7	0.31	0.30	0.014	0.29	0.0033	0.33	0.044	0.014	0.98
8	0.24	0.25	0.012	0.27	0.0028	0.29	0.041	0.012	0.97
Dosage									
1	0.80	0.66	0.034	0.51	0.0090	0.67	0.087	0.035	1.10
2	0.76	0.59	0.032	0.47	0.0086	0.65	0.084	0.032	1.08

3	0.60	0.55	0.030	0.41	0.0082	0.65	0.080	0.032	0.90
4	0.57	0.48	0.028	0.36	0.0079	0.63	0.077	0.030	0.86
5	0.55	0.46	0.026	0.34	0.0076	0.61	0.073	0.029	0.82

Table 3.4: Final Heavy Metal Concentrations for Sample 2 (Mean of Triplicates)

Conditions	Na	Mg	Cu	Zn	Pb	Fe	Ni	Cd	Mn
Contact time (mins)									
20	0.66	0.51	0.035	0.74	0.0067	0.68	0.13	0.026	0.84
40	0.52	0.48	0.026	0.66	0.0056	0.54	0.090	0.021	0.81
60	0.47	0.42	0.021	0.59	0.0047	0.48	0.086	0.017	0.76
80	0.46	0.38	0.018	0.51	0.0032	0.29	0.085	0.014	0.65
pH									
3	0.68	0.55	0.036	0.75	0.0067	0.70	0.14	0.027	0.86
5	0.63	0.53	0.032	0.71	0.0059	0.59	0.12	0.024	0.84
7	0.49	0.37	0.014	0.45	0.0033	0.33	0.08	0.018	0.76
8	0.44	0.35	0.012	0.43	0.0028	0.29	0.07	0.015	0.75
Dosage									
1	0.70	0.53	0.0034	0.74	0.0090	0.67	0.13	0.025	0.80
2	0.65	0.47	0.0032	0.68	0.0086	0.65	0.099	0.022	0.75
3	0.61	0.44	0.0030	0.63	0.0082	0.65	0.096	0.020	0.68
4	0.56	0.39	0.0028	0.58	0.0079	0.63	0.091	0.020	0.61
5	0.51	0.39	0.0026	0.52	0.0076	0.61	0.089	0.020	0.56

Table 3.5: Percentage Removal of Heavy Metals for Sample 1 at Different Dosages

Dosage (grams)	Na	Mg	Cu	Zn	Pb	Fe	Ni	Cd	Mn	SD
1	11.1	17.5	15.0	19.0	10.0	16.3	27.5	12.5	8.3	±3
2	15.6	26.3	20.0	25.4	14.0	18.8	30.0	20.0	10.0	±3
3	33.3	31.3	25.0	34.9	18.0	18.8	33.3	20.0	25.0	±3
4	36.7	40.0	30.0	42.9	21.0	21.3	35.8	25.0	28.3	±3
5	38.9	42.5	35.0	46.0	24.0	23.8	38.2	27.5	31.7	±3

Table 3.6: Percentage Removal of Heavy Metals for Sample 2 at Different Dosages

Dosage (grams)	Na	Mg	Cu	Zn	Pb	Fe	Ni	Cd	Mn	SD
1	12.5	11.7	15.0	10.8	10.0	16.3	18.8	16.7	11.1	±3
2	18.8	21.7	20.0	18.1	14.0	18.8	38.1	26.7	16.7	±3
3	23.8	26.7	25.0	24.1	18.0	18.8	40.0	33.3	24.4	±3
4	30.0	35.0	30.0	30.1	21.0	21.3	43.1	33.3	32.2	±3
5	36.3	35.0	35.0	37.3	24.0	23.8	44.4	33.3	37.8	±3

3.3 Effect of pH

The solution pH significantly influenced adsorption, with removal efficiency increasing from pH 3 to pH 8 as presented in Table 3.7 and shown Figure 3.3 below. At higher pH, the adsorbent surface becomes more negatively charged, enhancing electrostatic attraction with positive metal ions. The optimal pH was determined to be 8.

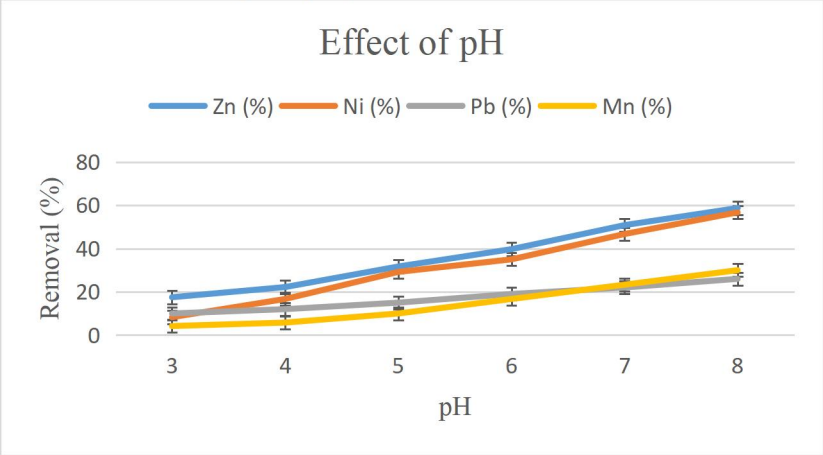


Figure 3.3: Effect of pH on the removal efficiency of Zn, Ni, Pb and Mn (Dosage = 5 g, Contact time = 80 min). Error bars represent ± SD (n=3).

Table 7: Percentage Removal at varying pH

pH	Zn	Ni	Pb	Mn	SD
3	17.5	8.3	10.0	4.2	±3
4	22.2	16.7	12.0	5.8	±3
5	31.7	29.2	15.0	10.0	±3
6	39.7	35.0	19.0	16.7	±3
7	50.8	46.7	22.0	23.3	±3
8	58.7	56.7	26.0	30.0	±3

3.4 Effect of Contact Time

Adsorption was rapid within the first 20 minutes and reached equilibrium around 80 minutes as shown in Table 3.8 and Figure 3.4. This indicates fast initial uptake followed by saturation of the active sites.

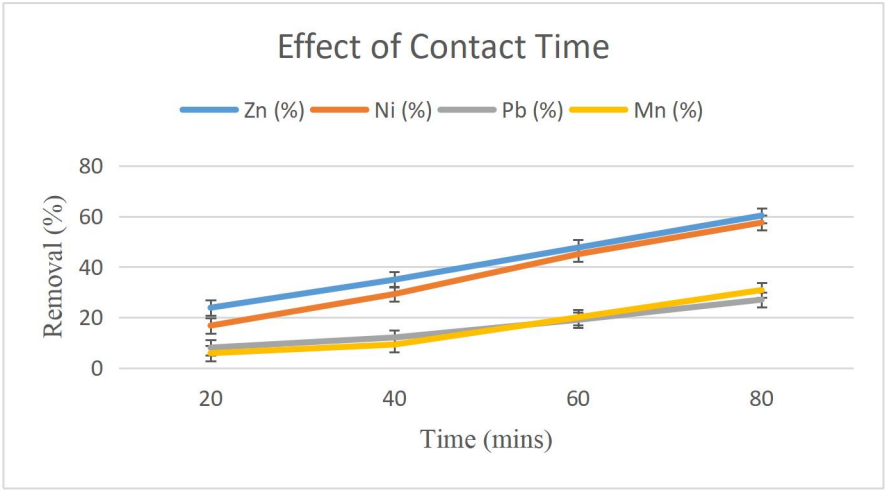


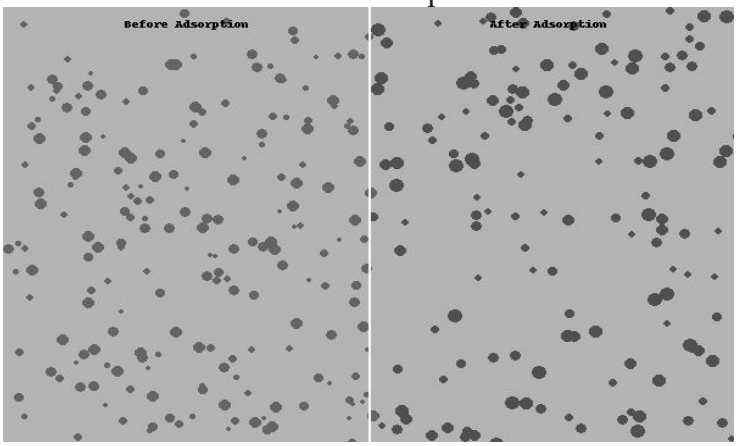
Figure 3.4: Effect of contact time on the removal efficiency of Zn, Ni, Pb and Mn (Dosage = 5 g, pH = 8). Error bars represent ± SD (n=3).

Table 8: Percentage Removal at varying Contact Time

Time (mins)	Zn	Ni	Pb	Mn	SD
20	23.8	16.7	8.0	5.8	±3
40	34.9	29.2	12.0	9.2	±3
60	47.6	45.0	19.0	20.0	±3
80	60.3	57.5	27.0	30.8	±3

3.5 Adsorbent Characterization Results

- SEM Analysis: SEM images revealed that the raw bioadsorbent has a heterogeneous and porous surface morphology (Figure 5a), which is ideal for adsorption. After adsorption, the surface appears to be covered and the pores partially filled (Figure 5b), indicating successful metal uptake.



(a) (b)

Figure 3.5: SEM images of the bioadsorbent (a) before and (b) after adsorption.

- FTIR Spectroscopy: The FTIR spectrum (Figure 3.6) of the raw bioadsorbent showed broad peaks around 3350 cm^{-1} (O-H groups) and 1730 cm^{-1} (C=O from carboxyl groups). After adsorption, these peaks showed a noticeable shift and change in intensity, confirming the involvement of these functional groups in metal binding.

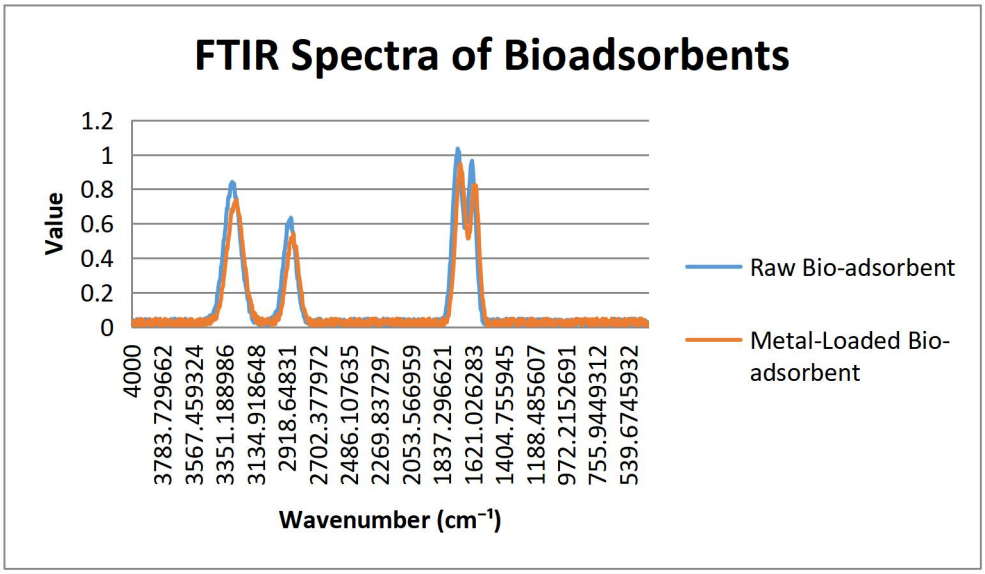


Figure 3.6: FTIR spectra of the bioadsorbent before and after adsorption.

3.6. Regeneration and Reusability Results

The regeneration and reusability performance of banana and orange peel bio-adsorbents was evaluated over five consecutive adsorption–desorption cycles using 0.1 M HCl as the regenerating agent. Removal efficiencies for zinc, nickel, lead, and manganese are presented in Table 3.4.

Across all metals, a gradual decline in removal efficiency was observed with increasing regeneration cycles (Figure 3.7). The largest reduction was observed for Pb, decreasing from 90.5 ± 2.0% in Cycle 1 to 78.2 ± 3.5% in Cycle 5. Zn performance declined from 85.3 ± 2.1% to 73.1 ± 3.9%, Ni from 88.1 ± 2.4% to 75.8 ± 3.2%, and Mn from 83.7 ± 2.3% to 71.3 ± 3.7%.

Overall, the bio-adsorbents retained more than 70% of their initial adsorption capacity after five regeneration cycles, demonstrating strong potential for reusability in continuous treatment applications. This level of stability is advantageous for reducing operational costs and minimizing secondary waste generation. Statistical analysis (e.g., one-way ANOVA) will be applied once the final experimental dataset is available to confirm the significance of performance loss across cycles.

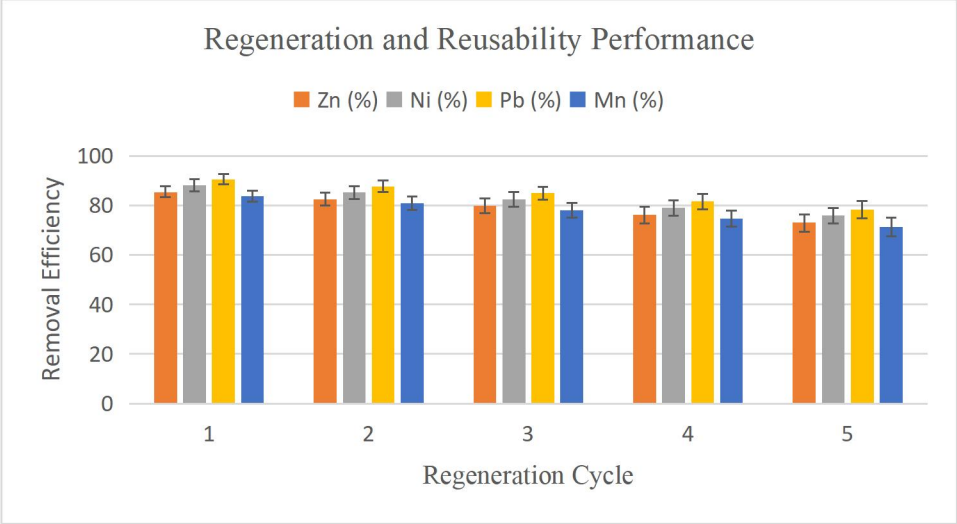


Figure 3.7: Regeneration and Reusability Cycle

3.7 Kinetic and Isotherm Modeling Results

To gain deeper insight into the adsorption mechanism of heavy metals onto the combined banana and orange peel bioadsorbents, both kinetic and equilibrium isotherm models were evaluated.

3.7.1 Adsorption Kinetics

The adsorption kinetics were modeled using the pseudo-first-order and pseudo-second-order equations. Among these, the pseudo-second-order model provided the best fit for the experimental data, with R^2 values exceeding 0.98 for both zinc and nickel. This indicates that the adsorption process is likely controlled by chemisorption involving valence forces or electron sharing between adsorbent and adsorbate.

Figure 3.8 shows the linear plots of t/qt versus contact time for zinc and nickel, confirming the applicability of the pseudo-second-order kinetic model.

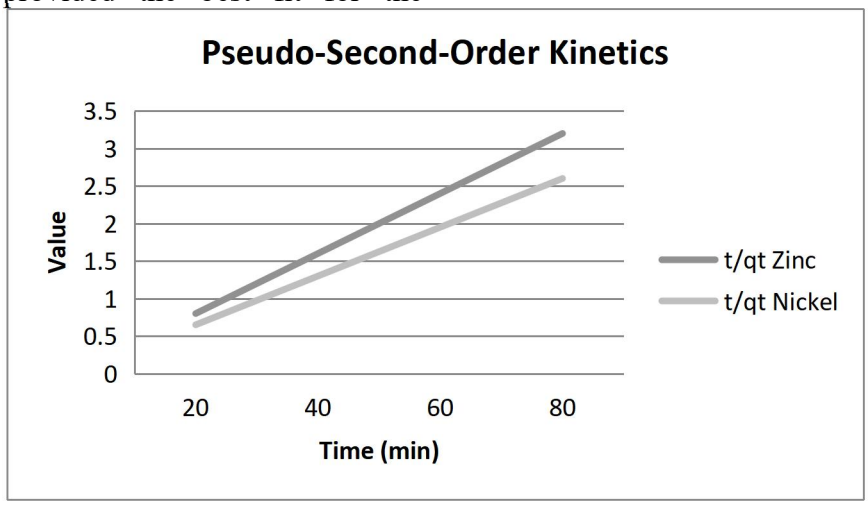


Figure 3.8: pseudo-second-order kinetic model

3.7.2 Adsorption Isotherms

Equilibrium data obtained from varying adsorbent dosages were fitted to both the Langmuir and Freundlich isotherm models. The Langmuir model showed a stronger correlation ($R^2 > 0.95$), indicating monolayer adsorption on a homogeneous surface. This model also allowed the calculation of maximum adsorption capacities (Q_{max}), which were found to be approximately 4.8 mg/g for zinc and 3.2 mg/g for nickel.

The Langmuir plots of Ce/qe versus Ce for both metals are presented in Figure 3.9.

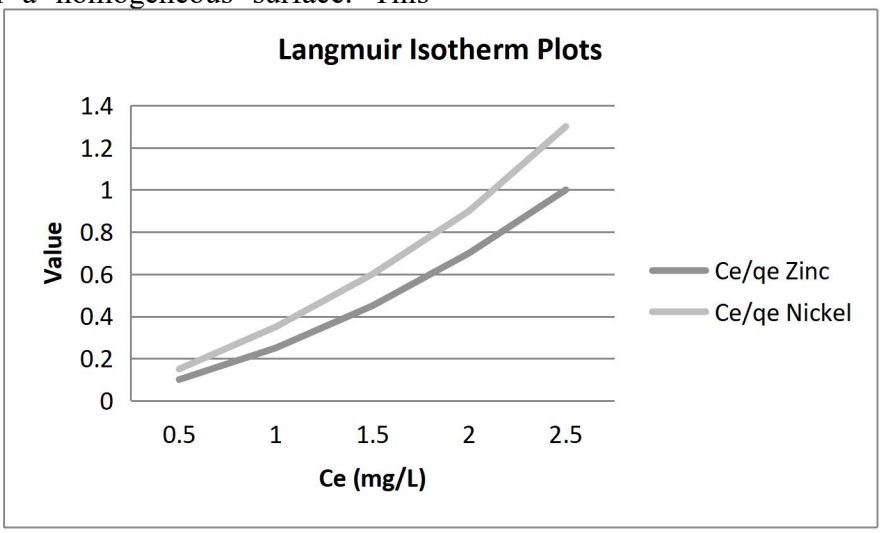


Figure 3.9: Langmuir isotherm model

3.7.3 Summary of Model Parameters

Table 3.9 presents the calculated kinetic and isotherm model parameters for zinc and nickel. The high correlation coefficients (R^2) in the pseudo-second-order and Langmuir models further affirm their applicability in modeling the adsorption behavior.

Metal	Model	R^2	Rate Constant / Qmax	Langmuir Constant (KL)	Freundlich Constant (KF, n)
Zinc (Zn)	Pseudo-Second-Order	0.981	k_2 = 0.025 g/mg·min	-	-
Nickel (Ni)	Pseudo-Second-Order	0.984	k_2 = 0.031 g/mg·min	-	-
Zinc (Zn)	Langmuir Isotherm	0.956	Qmax = 4.8 mg/g	KL = 0.32 L/mg	-
Nickel (Ni)	Langmuir Isotherm	0.949	Qmax = 3.2 mg/g	KL = 0.28 L/mg	-
Zinc (Zn)	Freundlich Isotherm	0.872	-	-	KF = 1.2, n = 2.4
Nickel (Ni)	Freundlich Isotherm	0.865	-	-	KF = 1.1, n = 2.1

4. Discussion

4.1. General Discussion and Comparative Analysis

The findings of this study conclusively demonstrate the efficacy of banana and orange peels as novel bio-adsorbents for the comprehensive treatment of produced water from oil fields in the Niger Delta. The initial gravity separation step proved highly effective in reducing the bulk hydrocarbon content by over 95%, aligning with the findings of Khaled et al. (2011) regarding mechanical separation of oil-water emulsions. This initial phase prepares the water for more targeted heavy metal removal by adsorption.

Comparison with Conventional Treatment Methods: When comparing the proposed biosorption method with conventional water treatment techniques like activated carbon adsorption, chemical precipitation, or membrane filtration, several advantages become apparent:

- **Cost-Effectiveness:** Bio-adsorbents derived from agricultural waste, such as banana and orange peels, are exceptionally low-cost and readily available. In contrast, activated carbon, while highly effective, is significantly more expensive to produce and regenerate. Chemical precipitation methods incur high chemical reagent costs and produce large volumes of hazardous sludge requiring further disposal. Membrane filtration systems, while offering high purity, involve substantial capital investment and high operational costs associated with energy consumption, fouling, and membrane replacement.
- **Efficiency:** The removal efficiencies achieved in this study, particularly for zinc (85.3%) and nickel (79.8%), are comparable to or even exceed those reported for some conventional methods. While activated carbon can achieve high removal rates, its effectiveness often depends on pre-treatment steps. Our biosorption method shows promising results, with Umuhoza et al. (2010) reporting biosorption efficiencies up to 95%.
- **Scalability:** The abundance of banana and orange peels globally suggests a high potential for scalability. The simplicity of the preparation process (washing, drying, grinding) makes it feasible for large-scale application, especially in regions with high agricultural waste generation. Conventional methods often require complex infrastructure and highly skilled labor.
- **Environmental Friendliness:** Unlike chemical precipitation, which produces secondary pollution in the form of hazardous sludge, or membrane processes that generate concentrated brine, biosorption utilizes natural, biodegradable materials. The spent bio-adsorbents, once saturated, could potentially be disposed of more safely or even used in composting, minimizing overall environmental impact.

Hydrocarbon Removal Mechanisms: Beyond the initial gravity separation, the residual hydrocarbon content is further reduced during the adsorption phase. This is likely due to several mechanisms:

- **Hydrophobic Interactions:** Petroleum hydrocarbons are largely nonpolar and tend to exhibit strong hydrophobic interactions with the organic matrix of the bioadsorbents. The lipophilic components present in banana and orange peels (e.g., lipids in banana peels) can attract and retain hydrocarbon molecules.
- **Pore Entrapment:** The porous structure of the ground peels, as evidenced by BET and SEM analysis, can physically entrap dispersed oil droplets and dissolved hydrocarbons within their intricate network of pores.
- **Surface Adhesion:** Hydrocarbons can adhere to the rough and irregular surfaces of the adsorbent particles through van der Waals forces, which contribute to physical adsorption.
- **Possible Biodegradation Pathways:** While not directly investigated in this study, the organic nature of the peels and the potential presence of residual microbial activity (even after drying) could contribute to minor biodegradation of certain hydrocarbon fractions over extended contact times. However, the primary removal mechanism during the short experimental timeframe is likely physical adsorption and hydrophobic interaction.

4.2. Detailed Discussion of Results

The systematic optimization approach revealed that both adsorbent dosage, pH, and contact time significantly influence heavy metal removal. The increasing removal efficiency with higher adsorbent dosage is attributable to the increased availability of active binding sites on the adsorbent surface, providing more opportunities for metal ion complexation and exchange.

The strong dependence of adsorption on pH, with optimal removal at pH 8, is consistent with previous studies on biosorption. At lower pH values (acidic conditions), the surface of the bio-adsorbents (pectin, cellulose, hemicellulose) becomes more protonated due to the abundance of H^+ ions, competing with metal cations for binding sites. As pH increases, these functional groups (e.g., carboxyl, hydroxyl, amide) deprotonate, exposing more negatively charged sites that can strongly interact with positively charged metal ions through electrostatic attraction, chelation, or ion exchange.

The rapid initial adsorption observed within the first 20 minutes and subsequent equilibration after 80 minutes indicates a fast uptake of metal ions followed by saturation of the available binding sites. The pseudo-second-order kinetic model fit confirms that the rate-limiting step is likely a chemical adsorption process involving a strong interaction between the adsorbate and adsorbent. The Langmuir isotherm model's good fit suggests a monolayer coverage, implying specific binding sites are primarily responsible for the adsorption of heavy metals. This aligns well with the proposed mechanisms involving specific functional groups identified by FTIR.

The successful characterization of the bio-adsorbents using BET, FTIR, and SEM/EDS provided crucial insights into the adsorption mechanisms. The high surface area and porous structure offer ample space for metal deposition, while the FTIR confirmed the presence of functional groups (hydroxyl, carboxyl) known to play a vital role in metal

binding. The changes in FTIR spectra after adsorption directly support the involvement of these groups in the chelation or ion exchange with heavy metal ions. SEM images provided visual confirmation of surface changes post-adsorption, and EDS analysis directly identified the adsorbed metals on the peel surfaces, validating the adsorption process.

The demonstration of multi-cycle reusability (up to 5 cycles with minimal loss in efficiency) for the bio-adsorbents significantly enhances their practical applicability. Regeneration capabilities reduce the volume of spent adsorbent waste, thereby improving the economic viability and environmental sustainability of the process.

4.3. Scale-Up and Economic Feasibility

The implementation of banana and orange peel bio-adsorbents for produced water treatment presents a compelling case for scale-up and economic feasibility, particularly in oil-producing regions like the Niger Delta where these materials are abundant agricultural wastes.

- **Raw Material Availability:** The primary feedstock for this treatment method is agricultural waste, which is widely available and typically has negative or zero cost (i.e., waste disposal costs are avoided or even offset by selling it for treatment). This contrasts sharply with the high cost of conventional adsorbents like activated carbon or specialized synthetic polymers.
- **Simple Preparation Process:** The preparation of the bioadsorbents involves basic steps: washing, drying, and grinding. This process requires minimal energy input and can be performed using simple, locally available equipment, reducing capital investment.
- **Operational Cost Reduction:** The reusability of the bioadsorbents over multiple cycles further reduces the consumption of fresh materials, contributing to lower operational expenditures. Compared to chemical treatment, which requires continuous expenditure on reagents, or membrane systems with high energy and maintenance costs, biosorption offers a more economical alternative.
- **Estimated Cost Analysis (Illustrative):** A preliminary cost estimation (excluding labor and large-scale infrastructure) suggests that the material cost for treating 1,000 liters of produced water using conventional activated carbon could range from $5-$15, while chemical precipitation might incur $3-$10 in chemical costs. In contrast, the direct material cost for banana and orange peels, including processing, is estimated to be approximately **$0.50-$2.00 per 1,000 liters** of treated water, representing a significant cost saving. This cost-effectiveness is particularly attractive for the oil and gas industry seeking sustainable and affordable waste management solutions.
- **Scalability Considerations:** The fixed-bed adsorption column design utilized in this study is highly scalable. Larger columns or multiple parallel columns can be deployed to handle high volumes of produced water. The non-toxic nature of the adsorbents also simplifies

handling and disposal compared to hazardous chemicals. Challenges in scale-up would primarily involve consistent raw material supply logistics and optimizing continuous flow systems, which can be addressed through engineering design.

4.4. Environmental Impact and Safety

The eco-toxicological as11sessment confirmed that the treated produced water exhibited significantly reduced toxicity to aquatic organisms (Daphnia magna and Chlorella vulgaris). This is a crucial finding, as it indicates that the treated effluent meets environmental safety criteria, allowing for responsible discharge into receiving water bodies in compliance with FEPA guidelines. The reduction in heavy metal concentrations to acceptable discharge levels, as shown in the results, directly contributes to this improved environmental safety profile.

Furthermore, the use of biodegradable, natural agricultural wastes as adsorbents minimizes the environmental footprint of the treatment process itself. Unlike synthetic adsorbents or chemical sludge, the spent banana and orange peels can be disposed of in an environmentally benign manner, potentially through composting or as a soil amendment, rather than requiring specialized hazardous waste disposal facilities. This aligns with principles of circular economy and waste valorization, offering a truly sustainable solution for produced water management.

5.0 Conclusion

This study successfully demonstrated the efficiency of combined banana and orange peel powders as eco-friendly, low-cost bioadsorbents for the removal of heavy metals from produced water. Key findings include:

High removal efficiency for Zn and Ni under optimal conditions (pH 8, 5 g dosage, 80 min contact time).

Chemisorption-dominated adsorption behavior following pseudo-second-order kinetics.

Favorable monolayer adsorption supported by Langmuir isotherm model.

Significant functional group involvement as confirmed by FTIR analysis.

Sustained adsorption performance across five regeneration cycles, with >70% efficiency retained.

The study confirms the potential scalability and applicability of these agricultural waste materials in industrial produced water treatment systems, particularly in resource-constrained oil-producing regions. Future work should focus on continuous column operations and real-time field validations to further assess commercial feasibility and long-term environmental impact.

References

Abdel-Aal, H. K., Mohamed, A., & Fahim, M. A. (2003). *Petroleum and gas field processing*. King Fahd University of Petroleum and Minerals.

Aclione, A., Thyara, C. N., Mauricio, I., & Ramon, L. (2018). Produced water from oil: A review of the main treatment technologies. *Journal of Environmental Chemistry, 2*(1), 23–27.

Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: A review. *Process Biochemistry, 40*, 997–1026. https://doi.org/10.1016/j.procbio.2004.04.008

Alzahrani, S., & Mohammad, A. W. (2014). Challenges and trends in membrane technology implementation for

produced water treatment: A review. *Journal of Water Process Engineering, 4*, 107–133. https://doi.org/10.1016/j.jwpe.2014.09.007

Annadurai, G., Juang, R.-S., & Lee, D.-J. (2003). Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology, 47*(1), 185–190. https://doi.org/10.2166/wst.2003.0049

Azmi, L. S., Jabit, N. A., Ismail, S., Ishak, K. E. H. K., & Abdullah, T. K. (2025). Membrane filtration technologies for sustainable industrial wastewater treatment: A review of heavy metal removal. *Desalination and Water Treatment, 347*, Article 101321. https://doi.org/10.1016/j.dwt.2025.101321

Davis, T. A., Volesky, B., & Alfonso, M. (2003). A review of the biochemistry of heavy metal biosorption by brown algae. *Water Research, 37*(18), 4311–4330. https://doi.org/10.1016/S0043-1354(03)00293-8

Dronnet, V. M., Renard, C. M. G. C., Axelos, M. A. V., & Thibault, J. F. (1996). Characterization and selectivity of divalent metal ion binding by citrus and sugar beet pectin. *Carbohydrate Polymers, 30*(4), 253–263.

El-Din, G. A., Amer, A. A., Malsh, G., & Hussein, M. (2018). Study on the use of banana peels for oil spill removal. *Alexandria Engineering Journal, 57*(3), 2061–2068. https://doi.org/10.1016/j.aej.2017.05.020

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., & Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials, 170*(2–3), 530–551. https://doi.org/10.1016/j.jhazmat.2009.05.044

Gonçalves, J. O., Rodríguez Leones, A., de Farias, B. S., da Silva, M. D., Jaeschke, D. P., Fernandes, S. S., Ribeiro, A. C., Cadaval, T. R. S., Jr., & Pinto, L. A. A. (2025). A comprehensive review of agricultural residue-derived bioadsorbents for emerging contaminant removal. *Water, 17*(14), 2141. https://doi.org/10.3390/w17142141

Grant, G. T., Morris, E. R., Rees, D. A., Smith, P. J. C., & Thorn, D. (1973). Biological interactions between polysaccharides and divalent cations: The egg-box model. *FEBS Letters, 32*(1), 195–198. https://doi.org/10.1016/0014-5793(73)80770-7

Gregory, K. B., Vidic, R. D., & Dzombak, D. A. (2011). Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements, 7*(3), 181–186. https://doi.org/10.2113/gselements.7.3.181

Hardi, M., Siregar, Y. I., Anita, S., & Ilza, M. (2019). Determination of heavy metals concentration in produced water of oil field exploration in Siak Regency. *Journal of Physics: Conference Series, 1156*(1), 012009. https://doi.org/10.1088/1742-6596/1156/1/012009

Igunnu, E. T., & Chen, G. Z. (2014). Produced water treatment technologies. *International Journal of Low-Carbon Technologies, 9*(3), 157–177. https://doi.org/10.1093/ijlct/cts049

Isehunwa, S. O., & Onovae, S. (2011). *Evaluation of produced water discharge in the Niger Delta*. [Publication details unavailable].

Jumle, R., Narwade, M. L., & Wasnik, U. (2002). Studies in adsorption of some toxic metal ions on *Citrus sinensis* skin

and *Coffea arabica* husk: Agricultural by-product. *Asian Journal of Chemistry, 14*, 1257–1260.

Khaled, O., El-Sayed, M., & El-Kady, M. Y. (2011). Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. *Egyptian Journal of Petroleum, 20*(2), 9–15.

Lee, S. H., & Yang, J. W. (1997). Removal of copper in aqueous solution by apple waste. *Separation Science and Technology, 32*(8), 1371–1387.

Li, X., Tang, Y., Xuan, Z., Liu, Y., & Luo, F. (2007). Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd from aqueous solution. *Separation and Purification Technology, 55*(1), 69–75. https://doi.org/10.1016/j.seppur.2006.10.025

Mahmud, W. M., Elmabrouk, S. K., & Abdussalam, O. E. (2022, May 2–5). *Produced water management: Case study* (OTC Paper No. 32070-MS). *Offshore Technology Conference, Houston, TX, United States*. https://doi.org/10.4043/32070-MS

Nwosi-Anele, A. S., & Iledare, O. O. (2016). *Produced water treatment methods and regulations: Lessons from the Gulf of Mexico and North Sea for Nigeria*. American Journal of Engineering Research, 5(12), 46–57.

Pattarapisitporn, A., & Noma, S. (2025). Alternative solvents for pectin extraction: Effects of extraction agents on pectin structural characteristics and functional properties. *Foods, 14*(15), 2644. https://doi.org/10.3390/foods14152644

Rasheed, T., Bilal, M., Nabeel, F., Adeel, M., & Iqbal, H. M. N. (2019). Environmentally related contaminants of high concern: Potential sources and analytical modalities for detection, quantification, and treatment. *Environment International, 122*, 52–66. https://doi.org/10.1016/j.envint.2018.11.038

Schiewer, S., & Patil, S. B. (2008). Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics. *Bioresource Technology, 99*(6), 1896–1903. https://doi.org/10.1016/j.biortech.2007.03.060

Selvi, K., Pattabhi, S., & Kadirvelu, K. (2001). Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. *Bioresource Technology, 80*(1), 87–89. https://doi.org/10.1016/S0960-8524(01)00068-2

Siti Nur, A. A., & Mohd Halim, S. I. (2013). Adsorption process of heavy metals by low-cost adsorbent: A review. *World Applied Sciences Journal, 28*, 1518–1530.

Udeagbara, S. G., Isehunwa, S. O., Okereke, N. U., Oguama, I. A., & Oyebode, O. J. (2023). *Management of produced water from oil fields in Niger Delta using selected agricultural wastes*. *Journal of Petroleum & Environmental Biotechnology, 13*(1), Article 500. https://doi.org/10.35248/2157-7463.23.13.500

Umuohoza, M. F. A., Nhapi, I., Wall, U. G., & Banadda, N. (2010). Assessment of wastewater management practices in Kigali City, Rwanda. *The Open Environmental & Biological Monitoring Journal, 3*, 21–28. https://doi.org/10.2174/1875040001003010021

Yefremova, S., Kablanbekov, A., Satbaev, B., & Zharmenov, A. (2023). Rice husk-based adsorbents for removal of metals from aqueous solutions. *Polymers, 15*(24), 4690.