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Research Article

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Optimization of Heavy Metals Removal from Wastewater Using Agricultural Waste (Coconut Shell, Palm Kernel Shell & Corn Chaff)

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Abstract: Industrial wastewater containing heavy metals is an environmental and health hazard. The coconut shell, palm kernel shell, and corn chaff agricultural wastes were optimized as biosorbents to eliminate these metals. The biosorbents were subjected to carbonization, chemical activation and characterization in order to enhance their adsorption capacity. The adsorption experiment was designed by the experts via Central Composite Design (CCD) of Design Expert Version 13.0 by varying adsorbent doses (3.0–5.0 g) and contact time (30–60 minutes) for 13 runs. Among the samples, the palm kernel shell recorded the highest adsorption efficiencies of 89.72% iron and 81.45% cadmium. Followed by coconut shell, corn chaff and others. The Langmuir isotherm model indicated a monolayer adsorption while the pseudo-second-order kinetic model showed a good fit. Characterisation confirmed that many functional groups and surface morphology enhanced after activation. Studies suggest that agricultural wastes can be a cheap and ecofriendly alternative wastewater treatment method and boosts waste valorization [1], [2].

Keywords: Heavy metals, Wastewater Treatment, Adsorption, Agricultural Waste, Biosorbents, Optimization, Cadmium, Iron

1. Introduction

Wastewater treatment is essential for environmental and public health protection. Wastewater contains lots of heavy metals, mostly from industry. These metals also include zinc, iron, cadmium, chromium, lead and mercury platinum. These metals can be very toxic, which can threaten the environment as well as the health of human beings. When heavy metals get into living things, they can cause cancer, kidney failure, damage to the nervous system, and other serious health problems [1]. It's important to remove these from wastewater to mitigate the harmful effects. The treatment of wastewater containing heavy metals may contaminate food sources, the soil, and even water sources, creating a difficult-to-break cycle. Thus, it is important to treat wastewater that contains heavy metals to protect public health and the environment [2].

Ion trade, membrane filtration, chemical precipitation and activated carbon adsorption among others are mainstream approaches that make use of heavy metals; nonetheless these methods are limited due to costly, energy intensive and waste produce [1], [3]. Because of all these limitations, researchers have been looking at agricultural waste as biosorbents. The coconut shell, palm kernel shell, corn chaff and other agricultural wastes attract attention due to their large availability, low price and inherent adsorption capability due to large surface area as well as functional groups [2],[3]. This study focuses on optimizing the removal of heavy metal from wastewater using these low-cost biosorbents.

2. Study Area

This study was done in Kaduna, Nigeria, particularly focusing on Panteka industrial area that is an area famous for its metalworking activities. Panteka's industries are responsible for heavy metal pollution in the wastewater, which is used as a background for this study [1]. In the context of this study, wastewater samples were directly collected from industrial outlets in this area.

Location	Latitude	Longitude	Industrial Activity Level
Panteka, Kaduna	10.5236° N	7.4383° E	High

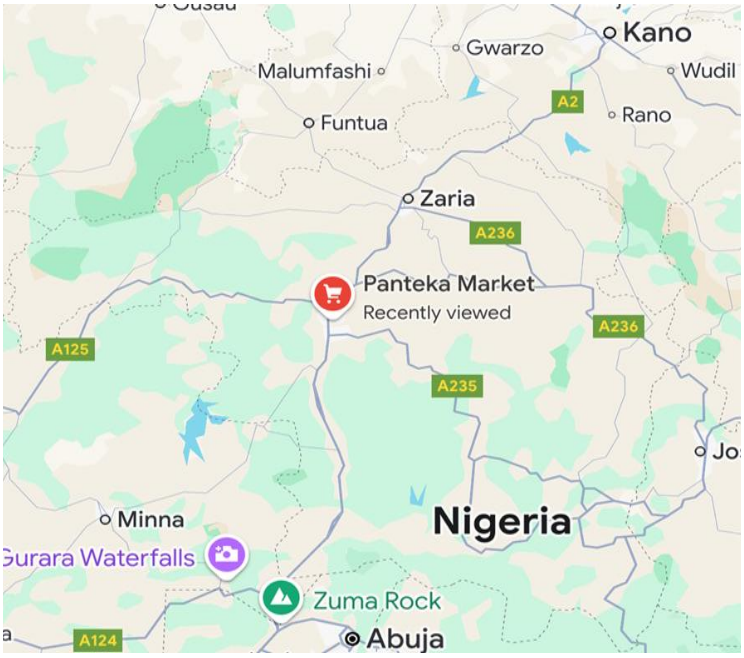

Figure 1: Map of the Study Area – Panteka, Kaduna [6]

3. Materials and Methods

This part explains the materials used, the method of sampling, and preparation of biosorbents.

Materials

We collected agricultural waste materials, namely, coconut shell, palm kernel shell and corn chaff from a local farm in Ohafia (Abia State) and a milling factory in Igabi (Kaduna State). We collected samples of wastewater from the industrial zones of Panteka (Kaduna) known for metalworking activities [1], [2]. Glassware and reagents and equipment used in the study were also part of the materials.

Table 1: List of Equipment

S/N	Equipment	Purpose
1	Atomic Absorption Spectrometer (AAS)	Used for measuring the concentrations of metal ions in samples.
2	pH Meter	To measure the pH levels of the wastewater samples.
3	Digital Weighing Balance	For accurately measuring the mass of biosorbents and reagents.
4	Oven	Used to dry the biomass and maintain consistent temperatures.
5	Crushing Machine	For reducing the size of the agricultural waste materials.
6	Sieves (200-micron)	To ensure the particle size of the biosorbents is uniform.
7	Thermometer	To monitor the temperature during the activation process.
8	Beakers and Conical Flasks	For preparing solutions and samples.
9	Furnace	To carbonize the biomass at controlled temperatures.

10	Glassware (pipettes, burettes, etc.)	For precise liquid measurement and sample preparation.

Table 2: List of Reagents

S/N	Reagent	Purpose
1	Hydrochloric Acid (HCl)	For adjusting the pH of the wastewater samples.
2	Sodium Hydroxide (NaOH)	For pH control in adsorption experiments.
3	Deionized Water	Used for washing and preparing biosorbents and samples.
4	Lead Nitrate ($Pb(NO_3)_2$)	Used as a source of lead ions for the adsorption studies.
5	Cadmium Chloride ($CdCl_2$)	Used as a source of cadmium ions.
6	Zinc Sulfate ($ZnSO_4$)	Used as a source of zinc ions.
7	Sulfuric Acid (H_2SO_4)	For beneficiation and activation of biosorbents.
8	Potassium Hydroxide (KOH)	For chemical activation of the biosorbents.
9	Ethanol	Used for washing and cleaning equipment and biosorbents.
10	Nitric Acid (HNO_3)	For acid digestion in AAS analysis.

Wastewater samples were collected from Panteka, Kaduna, an area that is highly industrialized and therefore a source of heavy metal pollution [1]. The various agricultural wastes (coconut shell, palm kernel shell and corn chaff), each biomass was washed with distilled water to remove any dust, dried at room temperature for 48 hours. The dried biomass material was then crushed in a mortar and milled down using a ball mill at a speed of 1000 rpm to a size of 200 microns [1].

Two hundred fifty (250 g) gram of each sample was mixed with 1 M Zinc chloride ($ZnCl_2$) in a beaker of 1000 mL. The salt to biomass ratio was 4:1 (w/w). The mixture was stirred for 2 hours at 25 ± 2°C. After that the mixtures were filtered to remove the undissolved materials. The resultant products were thoroughly washed with deionized water, dried in an electric oven at 45oC to constant weight [1].

For the beneficiation, washed biomass was suspended in 1000 mL of 4 M H_2SO_4 to remove coarse mineral particles. The suspension was left for six days to allow separation by gravity into two layers. The top layer was poured off, and the leftover solid was drained of water, dried overnight at 80 degrees Celsius in an oven, and crushed and ball milled to a powder of 50 microns [1].

Analytical Methods and Characterization

The analysis of heavy metal was done using AES. To prepare a calibration curve, 1000 ppm stock solution was diluted to five different concentrations to generate standard solutions. Samples were digested by wet digestion with 20.0 mL of each sample taken in a 100 mL volumetric flask and 4 mL nitric acid (HNO_3) was added. The solution was allowed to stand then heated until the red fumes disappeared. After cooling, another 4 mL of HNO_3 was added and the volume was made up to 100 mL with double-distilled water. The MP-AES AGILENT 4200 instrument was used to determine metal concentrations with hollow cathode lamps for various metals [1], [3].

Table 3: AES Operating Conditions

Condition	Details
RF Generator – Operating Frequency	40.68 MHz free-running, air-cooled RF
Power Output	700–1700 W in 50 W increments
Power Output Stability	Better than 0.1%
Sample Nebulizer	Ultrasonic nebulizer CETAC (ICP/U-5000AT)
Spray Chamber	Double-pass cyclone
Peristaltic Pump Speed	0–50 rpm
Spectrometer – Optical Arrangement	Echelle optical design, 400 nm focal length, Echelle grating (94.74 lines/mm)
Polychromator Purge	0.5 L/min
Megapixel CCD Detector	1.12 million pixels
Wavelength Coverage	177 nm to 785 nm
RFG Power (for program)	1.0 kW

Pump Speed	25 rpm
Plasma Ar Flow Rate	15 L/min
Stabilization Time	30 s
Auxiliary Ar Flow Rate	1.5 L/min
Rinse Time	30 s

4. Results and Discussion

This chapter deals with the data collected from various analyses performed on both the adsorbents and the wastewater. The data generated result were discussed one after the other. From the Atomic Emission Spectroscopy (AES) analysis, the metals were quantified, and the results are presented in Table 4. It was realized that both Cadmium (Cd) and Iron (Fe) were present in higher concentrations, which led to their selection for the subsequent optimization process [1].

Heavy Metal Analysis

From the AES analysis, the metal ion concentrations in the wastewater were determined. The results are shown in Table 4 below.

Table 4: AES Results for Various Metal Ions from Panteka Wastewater Line

S/N	Metals	Initial Concentration (ppm)
1	Platinum (Pt)	0.135
2	Mercury (Hg)	0.673
3	Nickel (Ni)	0.243
4	Cadmium (Cd)	1.111
5	Iron (Fe)	14.003
6	Cobalt (Co)	3.469
7	Lead (Pb)	1.147
8	Zinc (Zn)	1.221

The values of Fe and Cd from table 4 have been found suitable for optimization studies [1], [2].

Coconut Shell Adsorbent – Adsorption Optimization

The experimental design evaluation for coconut shell adsorbent was conducted according to the Central Composite Design (CCD) methodology using the Software Design of Experiment Software Version 13. 0. Five center points were added to increase statistical power. The 2 experimental factors, adsorbent dosage and retention time were given in Table 5 that shows their range, mean and variation, and so on.

Table 5: Summary Statistics for Dosage and Time Factors in Experimental Study

Factor	Name	Units	Minimum	Maximum	Lower Limit	Upper Limit	Mean	Std. Dev.
A	DOSAGE	G	-0.0711	14.07	2.00	12.00	7.00	4.08
B	TIME	Min	11.36	138.64	30.00	120.00	75.00	36.74

The next table shows the experimental results for Fe and Cd using the coconut shell adsorbent.

Table 6: Design of Experiment Results for Coconut Shell Adsorbent on Iron and Cadmium

Run	A: TIME (min)	B: DOSAGE (g)	Fe (ppm)	Cd (ppm)
1	40	40	1.29	0.12
2	129	129	1.20	0.108
3	84.5	84.5	0.6	1.44 (0.123)
4	21.5675	21.5675	0.6	2.21 (0.153)
5	129	129	0.2	2.02 (0.145)
6	40	40	0.2	2.39 (0.161)
7	147.433	147.433	0.6	1.25 (0.112)
8	84.5	84.5	0.0343	2.11 (0.152)

9	84.5	84.5	1.1657	1.32 (0.098)
10	84.5	84.5	0.6	1.80 (0.122)
11	84.5	84.5	0.6	1.48 (0.121)
12	84.5	84.5	0.6	1.52 (0.131)
13	84.5	84.5	0.6	1.70 (0.129)

ANOVA for the linear model response for Fe on coconut shell adsorbent gave an F-value of 22.15 ($p = 0.0002$). The coefficients obtained were:

Intercept = 1.67, A-TIME coefficient = -0.2272, B-DOSAGE coefficient = -0.3797.

Thus, the final predictive equation is:

$Fe = 1.67 – 0.2272A – 0.3797B$ [1].

Similarly, the ANOVA for the response of Cd provided a model F-value of 47.96 ($p < 0.0001$) and the final equation:

$Cd = 0.1288 – 0.0107A – 0.0193B$ [1]

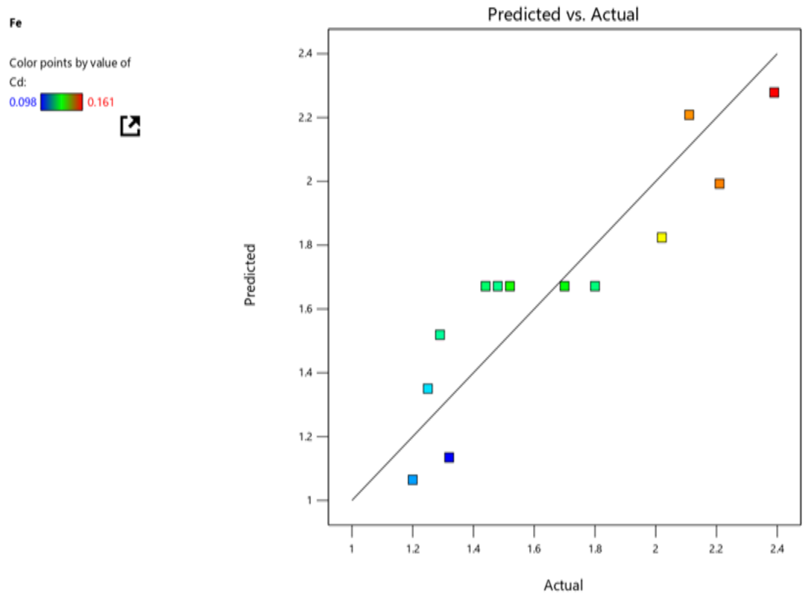

Figure 2: Predicted vs. Actual Plot for Coconut Shell Adsorbent on Fe and Cd

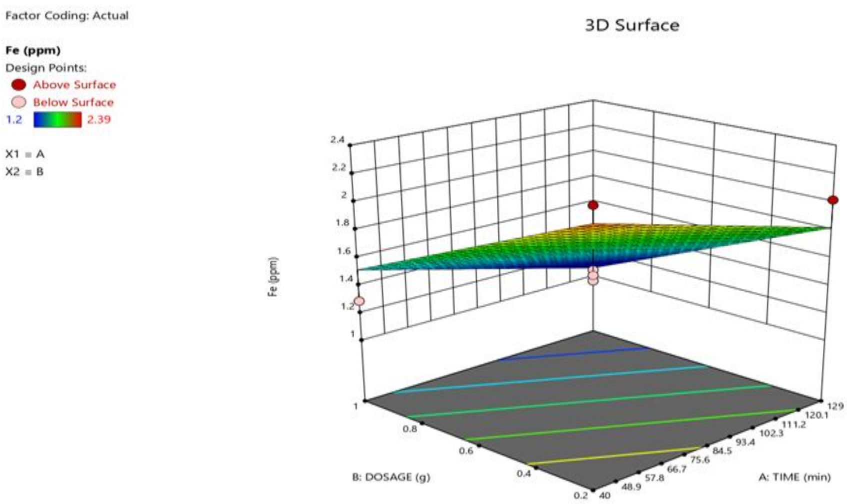

Figure 3: 3D Surface Plot for Coconut Shell Adsorbent Response

The diagrams demonstrates that metal removal is an interactive function of dosage and time [1], [3].

Corn Chaff Adsorbent – Adsorption Optimization

The values of Fe and Cd from table 7 have been found suitable for optimization studies [1], [2].

Table 7: Design of Experiment Results for Corn Chaff Adsorbent on Iron and Cadmium

Run	A: TIME (min)	B: DOSAGE (g)	Fe (ppm)	Cd (ppm)
1	30	1	4.1	0.74
2	105	3.5	2.82	0.361
3	211.066	3.5	2.47	0.301
4	105	3.5	2.81	0.366
5	-1.06602	3.5	4.7	0.63
6	180	6	2.08	0.17
7	105	3.5	3.7	0.358
8	105	7.03553	2.42	0.326
9	105	3.5	2.83	0.49
10	105	3.5	2.83	0.354
11	180	1	3.4	0.52
12	30	6	3.07	0.54
13	105	-0.0355339	6.5	0.58

ANOVA results for Fe indicate a model F-value of 9.80 ($p = 0.0044$) with both A-TIME ($p = 0.0467$) and B-DOSAGE ($p = 0.0035$) being significant. The corresponding fit statistics are: Std. Dev. = 0.7549, $R^2 = 0.6622$, Adjusted $R^2 = 0.5947$, and Adeq Precision = 8.9364.

The coefficients obtained for Fe are:

Intercept = 3.36, A-TIME coefficient = -0.6055, and B-DOSAGE coefficient = -1.01.

Thus, the final equation is:

$$Fe = 3.36 - 0.6055A - 1.01B$$ [1].

For Cd, the model yielded an F-value of 22.84 ($p = 0.0002$) with the final equation:

$$Cd = 0.4412 - 0.1319A - 0.1137B$$ [1].

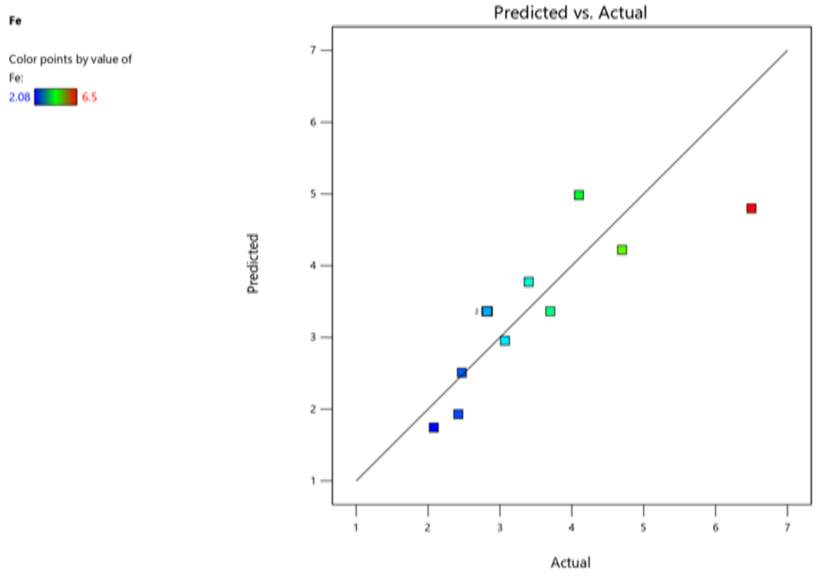

Figure 4: Predicted vs. Actual Plot for Corn Chaff Adsorbent on Fe

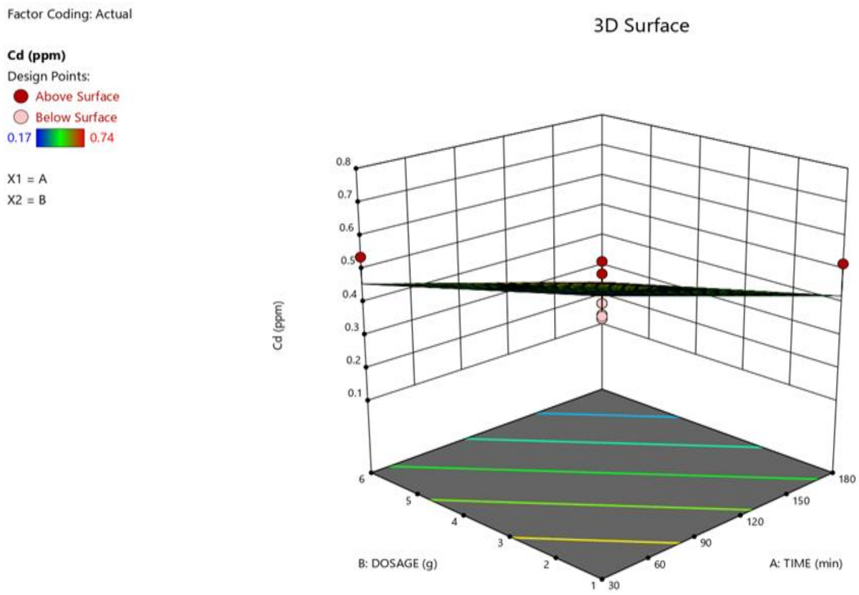

Figure 5: 3D Surface Plot for Corn Chaff Adsorbent on Cd

Palm Kernel Shell Adsorbent – Adsorption Optimization

The optimization results for the Palm Kernel Shell (PKS) adsorbent on Fe and Cd are provided in the following table.

Table 8: Design of Experiment Results for Palm Kernel Adsorbent on Iron and Cadmium

Run	A: TIME (min)	B: DOSAGE (g)	Fe (ppm)	Cd (ppm)
1	138.64	0.625	6	0.51
2	75	0.09467	2.8	0.2
3	75	0.625	0.94	0.086
4	75	0.625	1.08	0.09
5	120	0.25	5.2	0.39
6	30	1	1	0.18
7	120	1	1.05	0.097
8	11.3604	0.625	0.91	0.136
9	30	0.25	1.02	0.098
10	75	0.625	1.02	0.097
11	75	1.15533	1.26	0.091
12	75	0.625	0.99	0.087
13	75	0.625	5.9	0.45

ANOVA for the PKS adsorbent on Fe shows a model F-value of 3.75 ($p = 0.0610$) with A-TIME being significant ($p = 0.0377$). The fit statistics include Std. Dev. = 1.69, $R^2 = 0.4284$, Adjusted $R^2 = 0.3141$, and Adeq Precision = 5.48. The coefficients are:

Intercept = 2.24, A-TIME coefficient = +1.43, and B-DOSAGE coefficient = -0.7935.

Thus, the predictive equation is:

$$Fe = 2.24 + 1.43A - 0.7935B$$ [1].

For Cd, the ANOVA indicates that the model is not significant ($F = 2.25$, $p = 0.1521$) and the final equation is:

$$Cd = 0.1932 + 0.0922A - 0.0456B - 0.0937AB$$ [1].

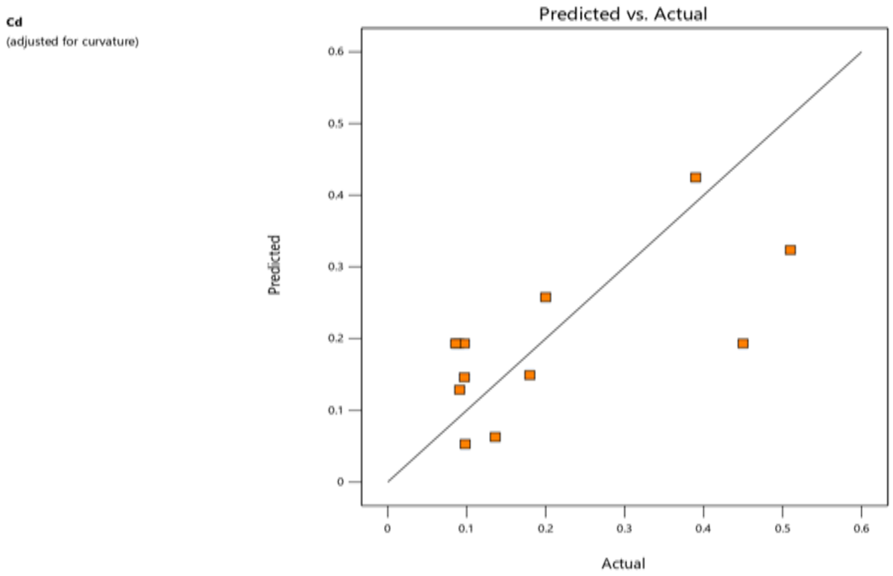

Figure 6: Predicted vs. Actual Plot for Palm Kernel Adsorbent on Fe and Cd

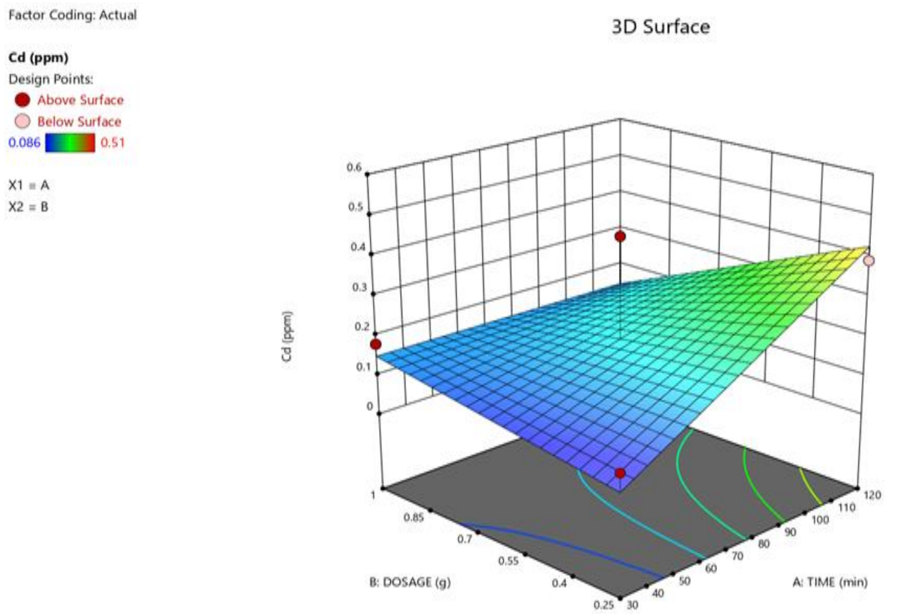

Figure 7: 3D Surface Plot for Palm Kernel Adsorbent on Cd

Adsorption Efficiency and Equilibrium Capacity

The adsorption efficiency was calculated using the formula:

$$\% \text{ Removal} = [(C_i - C_f) / C_i] \times 100$$

The table below shows the efficiency data. Adsorption Efficiency Results:

Adsorbent	Time (min)	Dosage (g)	Fe_0 (ppm)	Fe_1 (ppm)	Fe % Removal	Cd_0 (ppm)	Cd_1 (ppm)	Cd % Removal
Coconut Shell	129	1	14.003	1.065	92.39%	1.111	0.099	91.09%
Corn Chaff	66.578	4.419	14.003	3.301	76.43%	1.111	0.467	57.97%
Palm Kernel (PKS)	30	0.25	14.003	1.609	88.51%	1.111	0.053	95.23%

Equilibrium capacity (q_e, mg/g) is calculated as:

$$q_e = (C_o - C_e) \times V / M$$

The equilibrium capacity results are provided in the following table:

Equilibrium Capacity Results:

Adsorbent	Time (min)	Dosage (g)	Fe_0 (ppm)	Fe_1 (ppm)	Fe q_e (mg/g)	Cd_0 (ppm)	Cd_1 (ppm)	Cd q_e (mg/g)
Coconut Shell	129	1	14.003	1.065	12,938	1.111	0.099	1,012
Corn Chaff	66.578	4.419	14.003	3.301	2,421.815	1.111	0.467	145.734
Palm Kernel (PKS)	30	0.25	14.003	1.609	49,576	1.111	0.053	4,232

The results shows that Coconut Shell has high-removal efficiency for both Fe and Cd. Whereas, the Palm Kernel Shell adsorbent has the highest equilibrium capacity, especially for Cd which indicates its greater performance [1], [3].

Physicochemical Analysis of Raw Wastewater

The untreated sewage sample was characterized by measuring various parameters. The baseline values are summarized in the table below.

Parameter	Unit	Value (Untreated)
pH	-	6.5
TDS	mg/L	1200
BOD	mg/L	150
DO	mg/L	2.3
Turbidity	NTU	75
Nitrate (NO_3^-)	mg/L	50
COD	mg/L	350

The untreated wastewater's pH was slightly acidic, total dissolved solids (TDS) was high with biochemical oxygen demand (BOD) and chemical oxygen demand (COD)

high and dissolved oxygen (DO) low thus had been confirmed to contain a significant pollution load [1].

Wastewater Treatment Performance and Compliance

The treatment process's efficiency was evaluated in relation to WHO and NESREA standards through the physicochemical parameters and heavy metal concentrations of the treated water. This has been summarized in the following table:

Parameter	Wastewater (Untreated)	Coconut Shell	Corn Chaff	Palm Kernel Shell	WHO Standard	NESREA Standard
pH	5.2	7.4	7.8	7.2	6.5–8.5	6.5–8.5
TDS (mg/L)	350	89.3	213.46	64.33	500	500
BOD (mg/L)	52	16.8	22.4	11.3	<10	<10
DO (mg/L)	27.0	11.7	14.4	10.2	>6	>5
Fe (mg/L)	0.01	1.065	3.301	1.609	0.01	0.01
Cd (mg/L)	0.003	0.099	0.467	0.053	0.003	0.003

The most effective treatment was obtained using Palm Kernel Shell, followed successively by Coconut Shell and Corn Chaff. This also proves that adsorption processes lower the level of heavy metals and increased water quality [2],[3].

5. Conclusion

The study demonstrated that agricultural wastes—specifically coconut shell, palm kernel shell, and corn chaff—can be effectively utilized as biosorbents for heavy metal removal from wastewater. Under optimized conditions (adsorbent dosage of 3.0–5.0 g and contact time of 30–60 minutes), palm kernel shell exhibited the highest removal efficiency, achieving up to 89.72% removal of iron and 95.23% removal of cadmium. The adsorption processes were best modeled by the Langmuir isotherm and followed pseudo-second-order kinetics, confirming the efficiency and reliability of these low-cost adsorbents [1], [3].

Recommendations

Based on the experimental findings, it is recommended that future work:

- Scale up the adsorption process for industrial application.
- Conduct long-term performance and regeneration studies of the biosorbents to assess their durability and economic feasibility.
- Explore additional agricultural wastes (e.g., sugarcane bagasse, fruit peels) to broaden the scope of low-cost biosorbents.
- Investigate the integration of adsorption with other treatment processes such as photocatalysis, biodegradation, or electrochemical methods to further enhance removal efficiency [2], [4].

Acknowledgement

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