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Ecotoxicological Composition and Potential Treatment with Orthophosphate Modified Rice Husk Activated Carbon of Wastewater Discharge from Local Chemist Shops Within Onitsha Metropolis.

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Abstract-- **The study involved the preparation of orthophosphate-modified rice husk activated carbon and subsequent utilization for the treatment of pharmaceutical wastewater discharge within Onitsha Metropolis. Wastewater from five major pharmaceutical companies was treated with the rice husk activated carbon. The analysis of pharmaceutical wastewater in Onitsha metropolis indicated higher concentrations of essential elements (Mg, Fe, Zn) with an averageof 5.301 mg/L, compared to toxic metals (Pb, Cd, Co) with an average of 0.388 mg/L. Pb (0.954 mg/L) exceeded NAFDAC/NESREA and WHO limits, while Cd (0.124 mg/L) and Zn (2.451 mg/L) fell within acceptable ranges. The concentration hierarchy was Mg > Fe > Zn > Cd > Co > Pb, with activated rice husk demonstrating effective adsorption, particularly for Pb (95.07%) and Fe (86.95%). The bio-indicator plant, tomatoes, accumulated metals, indicating a high potential for biomagnification for Zinc (BAF = 1.014), while iron showed a BAF below one (BAF = 0.715). Hazard quotient evaluations identified significant health risks from lead (HQ = 19.00) and cadmium (HQ = 16.12), with trace metals posing minimal risks (HQ < 1).Correlations showed negative relationships between turbidity and pH (-0.66), while acidity positively correlated (0.53) with pH. The wastewater's pH ranged from 2.01 to 7.36, with an average turbidity of 4.63 NTU. Treatment with rice husk activated carbon reduced pH to 5.68 and turbidity to 4.55 NTU, while fluoride concentrations (8.89 mg/L) were above WHO standards, showing a 95.55% removal post-treatment. However, nitrogen removal was poor (7.58% efficiency). Bacterial colonies decreased significantly post-treatment, showing effective reduction of pathogenic bacteria by orthophosphate modified rice husk activated carbon. Overall, the study underscored the efficiency of rice husk activated carbon in wastewater treatment and the ongoing risks posed by certain heavy metals.**

Keywords--**orthophosphate, pharmaceutical, wastewater, rice husk, bacterial**

I. INTRODUCTION

Wastewater from local chemist shops can contain a variety of potentially harmful chemical compounds, including pharmaceuticals, disinfectants, and other substances. These compounds can pose risks to aquatic life and potentially contaminate drinking water sources if not properly treated (Mamdouh ET AL, 2016). Ecotoxicological assessments are needed to evaluate the impact of these discharges on the environment (Omuku, et al 2024a: Zhao et al, 2020). Various raw materials from animals, minerals, and vegetables can be the source for the production of an activated carbon (Yahya et al., 2015). Previous researchers reported on the modification of natural materials and some of the agricultural waste materials as an activated carbon, e.g., bagasse fly ash (Gupta et al., 2002), rice husk (Masoud et al., 2012), poplar leaf powders (Abbas, 2013), orange peel (Ali and Abdel-Satar, 2017) and sugarcane bagasse (Razi et al., 2018). Agricultural wastes are lignocellulosic materials containing the basic structural components of hemicellulose, lignin and cellulose (Karaboyaci et al., 2017: Fatemeh, et al 2024: Anwer et al, 2023).

This study investigated the ecotoxicological composition of wastewater discharged from local chemist shops in Onitsha metropolis and explored the potential of using orthophosphate-modified rice husk activated carbon (OP-RHAC) for treatment (Vinneeta, et al, 2017: Idris et al, 2013). The research analyzed the types and concentrations of pollutants in the wastewater, assess the toxicity of these pollutants, and evaluated the effectiveness of OP-RHAC in removing these pollutants. Rice husks, an agricultural waste product, would be converted into activated carbon by heating the rice husk in a controlled environment to create a porous structure with a high surface area.

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The activated carbon would be treated with orthophosphate, which could enhance its ability to remove certain pollutants, particularly heavy metals (Daifullah et al, 2003). The OP-RHAC would be used to filter the wastewater, removing pollutants through adsorption. The effectiveness of OP-RHAC in removing different pollutants would be assessed by analyzing the treated wastewater and comparing it to the untreated wastewater (Onwumelu et al 2016: Omuku, et al, 2016). The research significantly provided valuable information about the types and concentrations of pollutants present in wastewater from local chemist shops and their potential impact on the environment. Rice husk is a readily available and low-cost material, making OP-RHAC a potentially cost-effective solution for wastewater treatment, especially in developing countries (Onwumelu, 2012). Utilizing agricultural waste like rice husk promotes waste reduction and resource optimization, contributing to a more sustainable approach to wastewater management (El-Nemr et al, 2005: Rhman, et al, 1997). By reducing the toxicity of wastewater released to the environment, the research served to help protect public health and the environment (Omuku, et al, 2024a: Omuku et al, 2024b). This study is important because it addressed a real-world problem of wastewater pollution from local chemist shops, which could have significant environmental and public health implications. By adopting the use of OP-RHAC, the research aimedat identifing a sustainable and cost-effective solution for treating this type of wastewater (Rhman et al, 1997: Khalil, et al, 1994).

II. Materials And Methods

The rice husk was obtained from local mills and was washed several times with distilled water followed by filtration. 25 g of the rice husk was heated gradually at the temperature rate of 50^oC/15mins, in a stainless-steel pipe furnace tube up 500^oC (carbonization), in the second step, the temperature of the furnace tube was raised to 900^oC for an hour. The rice husk was removed and placed into desiccator to cool. After cooling the carbonized rice husk were crushed into granules with the aid of a pulverizing machine for activation. 5% orthophosphoric acid was prepared for the activation of the rice husk. The prepared acid solution was poured into the carbonized rice husk in a pot, stirred, and placed on electric hot plate at temperature of 80^0C with continuous stirring until it dries up. The dried activated rice husk was allowed to cool and thereafter washed severally with distilled water until a neutral pH of 7.0 was obtained. The washed activated rice husk was filtered and dried in an oven at temperature of 105^0C for 8hours, thereafter; the activated rice husk was sieve with 0.02mm mesh size. The sieve was stored in a container for the pharmaceutical wastewater treatment. American Public Health Association, APHA standard method was used in the evaluation of the physiochemical parameters of the untreated and the treated pharmaceutical wastewater.

III. Results And Discussion.

The results of the trace and heavy metal analysis of the pharmaceutical shops wastewater effluents for both untreated and treated wastewater samples are presented in Table 1.

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Table 1:
Concentration of Trace and Heavy Metals in the Untreated Pharmaceutical Wastewater Effluents (mg/L)

Samples	**Co**	**Mg**	**Zn Pb**	**Cd**	**Fe**	
A	0.111±0.01	0.52±1.03	3.895±0.530.335±0.000.90±0.050.87±3.50			
B	0.094±0.03	0.795±0.22	3.501±0.48	0.150±0.01	0.413±0.18	5.578±2.25
C	0.073±0.01	9.18±1.44	1.982±0.77	0.103±0.01	0.059±0.10	4.237±1.90
D	0.063±0.02	7.394±1.19	0.221±0.15	1.900±0.12	0.021±0.03	0.838±0.45
E	0.096±0.15	1.364±2.50	2.658±0.32	2.283±0.35	0.037±0.06	8.547±3.08
TOTAL	0.437	38.266	12.257	4.771	0.620	29.074
	0.087	**7.653**	**2.451**	**0.954**	**0.124**	**5.815**

Values are means of triplicate readings: Maximum permissible limit by NAFDAC and National Environmental Standards and Regulations Enforcement Agency NESREA in mg/L: Cd (0.1 to 0.2), Co (0.01), Zn (100). WHO: Pb (0.01), Cd (0.005)

The observed tread in the mean metal concentration in mg/l was Mg > Fe > Zn > Pb > Cd > Co as shown on Table 1. The essential elements (Mg, Fe, Zn) occurred at higher concentration (average 5.301 mg/L) than the toxic metals (Pb, Cd. Co) with mean value of 0.388mg/L.Vineeta et al 2027 evaluated the metal load of pharmaceutical industrial wastewater where they reporte concentrations of Co, Cd, Pb, Zn and Fe respectively as 0.087, 0.124, 0.954, 2.451 and 1.90 mg/L which were comparatively lower that the values obtain for this research. The concentrations of Mg were relatively higher than all other metals of interest in all pharmaceutical wastewater samples.

Sagar and Pratap 2012 reported concentration of Fe with a mean value 6 - 20 mg/L pharmaceutical wastewater which I higher than the value of 5.8 mg/L obtained in this research, but lower than 1.9 mg recorded by Vineeta et al 2017. The mean concentration of Pb (0.954mg/L) was above the maximum permissible limit (MPL) of NAFDAC/NESREA (0.01mg/L). the average Cadmium and zinc concentrations (0.124mg/L and 2.451mg/L respectively) in the pharmaceutical wastewater effluents were within the MPL of NAFDAC/NESREA (0.1 to 0.02mg/L and 100mg/L respectively). The mean concentration of lead in the samples (0.954mg/L) exceeded the MPL of World Health Organisation (WHO) of 0.01mg/L.

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Table 2:
Concentration of Heavy Metals in the Treated Pharmaceutical Wastewater Effluents mg/L

Samples	**Co**	**Mg**	**Zn**	**Pb**	**Cd**	**Fe**
A	0.031±0.01	6.100±1.30	0.550±0.05	0.151 ±0.00	0.064±0.55	0.455±0.05
B	0.015±0.03	1.944±0.52	0.391±0.03	0.038±0.01	0.131±0.08	2.378±1.25
C	0.071±0.04	0.913±0.14	0.071±0.01	0.004 ±0.01	0.027±0.00	0.306±0.09
D	0.032±0.02	0.969±0.05	0.087±0.05	0.014±0.12	0.010±0.03	0.337±0.05
E	0.089±0.05	1.545±0.50	0.234±0.02	0.030±0.05	0.029±0.06	0.318±0.08
TOTAL	0.238	11.471	1.333	0.237	0.261	3.794
MEAN	**0.048**	**2.294**	**0.267**	**0.047**	**0.052**	**0.759**

The variations in the mean concentration of metals (mg/l) in the treated pharmaceutical wastewater effluents showed Mg > Fe > Zn > Cd > Co > Pb in Table 4.2.The results revealed the absorption capacity of the activated rice husk for the removal of the metal contaminants in the pharmaceutical wastewater effluents.

The removal efficiency of the metals in the pharmaceutical wastewater effluents were Mg (70.03%) > Fe (86.95%) > Zn (89.11%) > Cd (58.06%) > Co (44.83%) > Pb (95.07%). The results showed that the activated carbon from rice husk had the greatest adsorption capacity of 95.07% for lead while the least adsorption capacity was recorded for Cobalt with a value of 44.83%.

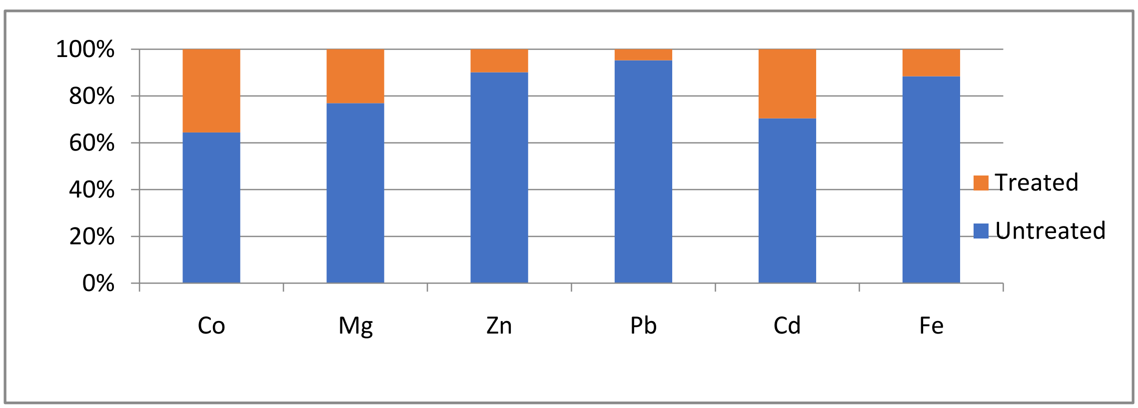

Figure 1 : Comparison in the Concentration of Metals in Treated and Untreated fast Food Wastewater Effluents.

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Heavy metal concentrations in a tomato plant species(Control) free from the pharmacuetical waste water effluents and a tomato specie planted along the drainage system of the pharmaceutical waste water effluent were determined and the differences in results of the concentration of metal in the plant specie (tomato plant) in the control and the one located on the pathway of the pharmaceutical drainage system are presented in Table 2.

Table 4.4:
Metal Concentrations in the Tomato plant species in Mg/L.

Samples	Co	Mg	Zn	Pb	Cd	Fe
A	0.062±0.01	6.100±1.30	0.550±0.05	0.151 ±0.00	1.64±0.55	0.455±0.05
B	0.011 ±0.03	1.944±0.52	0.391±0.03	0.038±0.01	0.131±0.08	2.378±1.25
C	0.091±0.04	0.913±0.14	0.071±0.01	0.004 ±0.01	0.027±0.00	0.306±0.09
D	0.232±0.02	0.969±0.05	0.087±0.05	0.014±0.12	0.031±0.03	0.337±0.05
E	0.099±0.05	1.545±0.50	0.234±0.02	0.030±0.05	0.059±0.06	0.318±0.08
TOTAL	0.468	11.471	1.333	0.237	1.888	3.794
MEAN	0.094	2.294	0.267	0.047	0.378	0.759
BAF	0.924	0.851	1.014	0.760	0.806	0.715
HQ	2.305	0.008	0.101	19.000	16.120	0.694
HQr	**-**	**5.463**	**0.110**	**3.876**	**2.640**	**0.264**

$BAF = \frac{\text{Conc in plant}}{\text{Conc in Wastewater sample}}$ *(McMullen et al, 2024).* $HQ = \frac{\text{Conc of POI in wastewater in mg/l}}{\text{RfD in mg/l}}$ *(Kassim et al, 2022): WHO RfD in Mg/l :(Co=O.4, Mg=100, Zn=10, Pb=0.04, Cd=0.05, Fe=1.03) (Akhtar et al., 2022), HQr = HQ of previous research from Literature (Ugwu et al, 2024)*

The concentrations of the metals (mg/L) in the bio-indicator plant, tomato specie, revealed a trend Fe > Mg > Zn > Co > Cd > Pb with average trace metal concentrations (Fe, Mg, and Zn = 5.878 mg/l) greater than the mean heavy metal concentrations (Co, Cd, and Pb = 0.138 mg/l) as shown in Table 2. The results of the bio-indicator plant (Table 4.4) showed that the test plant (tomato plant), was absorbing and retaining more of Zinc metal concentration than it was eliminating it, as the bioaccumulation factor (BAF) for Zinc metal was greater than one (BAF > 1, BAF = 1.014). There was possibility of biomagnification of Zinc metal in the bio-indicator plant as the BAF was greater than one.

This work revealed the advantages of consumption of tomato fruits produced within Onitsha metropolis as the effects of biomagnification of zinc up the ecosystem would be beneficial to man considering the fact that zinc metal in the body supports enzyme functions, aid metabilism and other body immune system. The mean iron concentration (11.211 mg/L) in the bio-indicator was relatively high but the BAF was less than one, an indication that the bioindicator plant, tomato plant was eliminating iron at a faster rate than it was absorbing it (BAF = 0.715). The observed trend in the BAF was Zn > Co > Mg > Cd > Pb > Fe. Interestingly, iron with highest mean concentration had the least bioaccumulation factor.

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A review of the results of the hazard quotient evaluation for the pharmaceutical wastewater effluents (Table 4.4) implicated Pb and Cd with a HQ of above 10 (high potential health risks possibility) and the observed trend given as Pb (HQ = 19.00) > Cd (HQ = 16.12) > Co (HQ = 2.31) > Fe (HQ = 0.694) > Zn (HQ = 0.10) > Mg (HQ = 0.008). The Mg hazard quotient (0.008) obtained from this study was lower compare to the value (5.463) recorded by Ugwu *et al*, 2024. The HQ for Zn (0.101) and Fe (0.294) were in agreement with their respective values (Zn = 0.110 and Fe = 0.264) reported by Ugwu *et al*, 2024 while HQ for Pb (19.00) and Cd (16.12) were higher than the level recorded for Pb (3.876) and Cd (2.64). The analytical results showed that there was high health risk associated with exposure to lead metal concentration (HQ of Lead = 19.00) from the pharmaceutical wastewater effluents from Onitsha metropolis. The heavy metal concentrations (Pb, Cd and Co) possessed potential health risks associated with exposure to the pharmaceutical wastewater effluents from Onitsha metropolis. The trace metal concentrations, Mg, Zn and Fe with HQ values of 0.008, 0.101 and 0.694 respectively indicated minimal health risks associated with the exposure to the wastewater effluents from the Fast food companies as their HQ was less than one.

Notably, cobalt exceeded the maximum permissible limit set by NAFDAC/NESREA. Correlation coefficients between metal concentrations indicated various relationships, with negative correlations suggesting that as one metal concentration increases, another decreases. For instance, Cobalt showed a strong positive correlation with Lead (0.414) and a negative correlation with Magnesium (-0.528). **Adsorption Efficiency**: Activated carbon derived from rice husk demonstrated significant removal efficiencies for metals, particularly Fe (95.07%) and Cd (58.06%). Cobalt had the lowest adsorption capacity (44.83%). **Bio-indicator Plant Study**: The tomato plant exhibited a bioaccumulation factor (BAF) for Zinc greater than one, indicating potential biomagnification. The mean iron concentration in the plant was high, but the BAF was less than one, suggesting it was eliminating iron faster than absorbing it. **Health Risk Assessment**: Hazard quotient evaluations revealed that lead (HQ = 19.00) and cadmium (HQ = 16.12) posed significant health risks, while trace metals like magnesium and zinc indicated minimal risks.

Table 3:
Result of the Paired t-test

Heavy Metals	T-statistics	p-value
Cobalt	-0.136	0.898
Magnesium	2.977	0.041
Zinc	3.821	0.019
Lead	1.895	0.131
Cadmium	-0.515	0.633
Iron	3.990	0.016

Metals with **p-values less than 0.05** show statistically significant differences between untreated and treated samples, therefore Magnesium, Zinc and iron showed a significant reduction in concentration after treatment. Whereas metals with **p-value greater than 0.05** do not show statistically significant differences. Based on this parameter, the result above clearly reviews that Cobalt, Lead and Cadmium did not show statistically significant difference between treated and untreated samples, therefore, this analysis suggests that the treatment was effective for reducing certain metals like Mg, Zn and Fe while other metals like Co, Pb and Cd, the treatment process was less effective.

The strength of the linear relationship between treated and untreated samples were measured and their association were computed.

Visual Representation of the Correlation Result

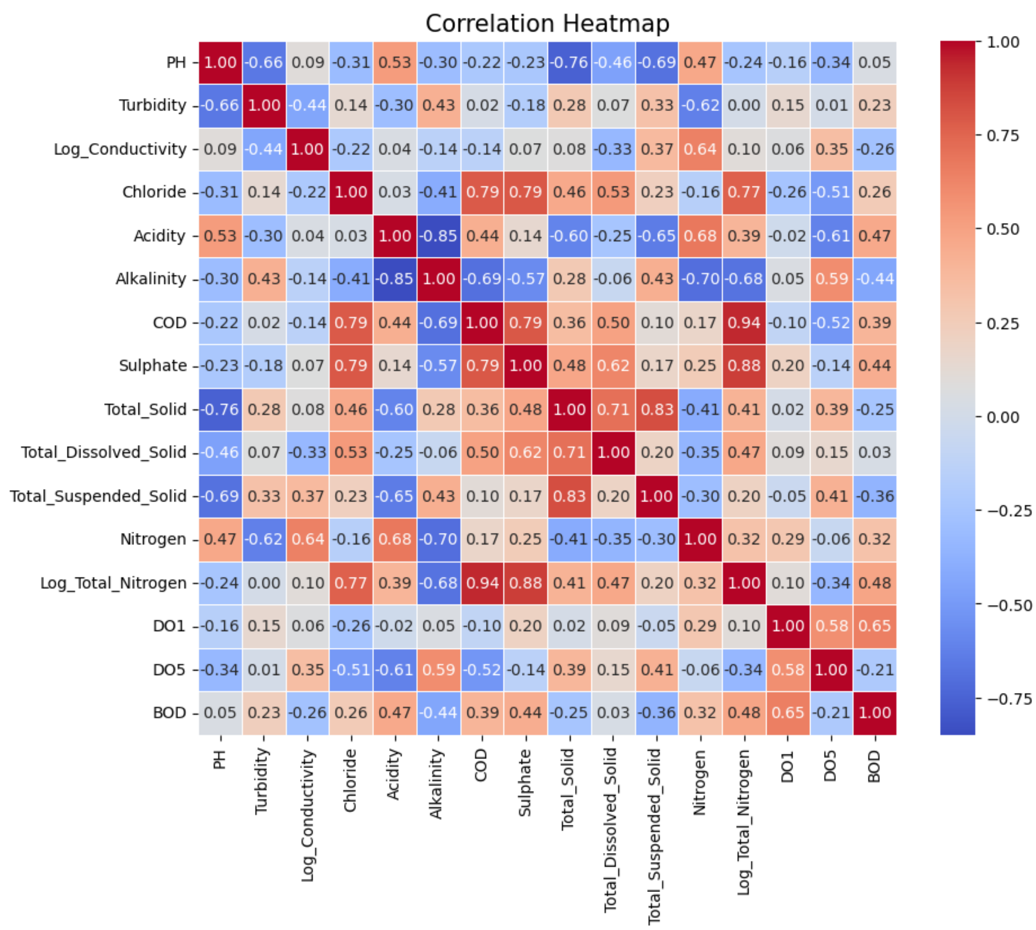

Figure 1: Results of the Visual Heatmap of the Correlation Analysis of the Metals

Correlation of pH with other parameters:

Turbidity: Negative correlation (-0.66). Moderate relationship, suggesting a positive change in pH result to a fairly decrease in Turbidity.

Chloride: Low negative correlation (-0.31), indicated that as pH increases, Chloride concentration tends to decrease slightly (Figure 1). It could suggest that pH is unrelated to ionic concentration.

Acidity: Moderate positive correlation (0.53). As expected, higher acidity corresponds with moderate pH values.

COD: Low negative correlation (-0.22). Higher pH levels are associated with lower Chemical Oxygen Demand, which may indicate less organic matter breakdown at higher pH levels.

Total_Solid: Strong Negative correlation (-0.76). This suggests a relationship where higher pH is associated with lower levels of suspended solids in the water.

Log_Total_Nitrogen: Weak negative correlation (-0.23). There's a slight tendency for Total Nitrogen to decrease as pH increases, but not strongly.

DO1: Weak negative correlation (-0.16). Minimal relationship between pH and dissolved oxygen at day 1.

DO_5: Negative but weak correlation (-0.34). Small decrease in dissolved oxygen after 5 days with increasing pH levels.

BOD: Very weak positive correlation (0.05). Biological Oxygen Demand shows little or no relationship with pH changes.

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Correlation of Turbidity with other parameters:

Log_Conductivity: Weak negative correlation (-0.44). Changes in turbidity and conductivity show little to no association.

Chloride: Weak positive correlation (0.14). Low correlation, suggesting that chloride concentration and turbidity do not significantly affect each other.

Log_Total_Nitrogen: Zero correlation (0.00). This suggests that turbidity is somewhat not associated with nitrogen levels, potentially indicating particulate nitrogen not being a part of the turbidity.

COD: Weak positive correlation (0.02). This indicates that higher turbidity is not associated with higher Chemical Oxygen Demand.

Total_Solid: Weak positive correlation (0.28). The turbidity of the water has little or no impact on the presences of Solid.

Acidity: Weak negative correlation (-0.30). A slight tendency for more acidic water to be less turbid.

DO1: Low positive correlation (0.15). Suggests that turbid water tends to have little dissolved oxygen levels on day 1.

DO_5: Low positive correlation (0.01). Similarly, turbidity has little or no associated with dissolved oxygen after 5 days.

BOD: Low positive correlation (0.23). High turbidity tcorrelates slightly with Biological Oxygen Demand, indicating a minimal organic load in turbid waters.

Table 4:
Results of pH, Turbidity and Conductivity for Untreated Pharmaceutical Wastewater

SAMPLE	PH	TURBIDITY (NTU)	ELETRICAL CONDUCTIVITY (us/cm)
A	2.01	3.33	32.40
B	3.54	7.29	1.15
C	5.07	3.45	7.51
D	5.06	5.38	6.90
E	7.36	3.72	31.70
Total	23.04	23.17	79.73
Mean	4.61	4.63	15.95

The pH of the pharmaceutical wastewater occurred at a range of 2.01 - 7.36 (Table 4.5), which was lower than the value 7.2 - 8.12 reported by Fatemeh *et al* 2024 for Zahedan Urban wastewater but aggreed with value 5.9 as published by Idris *et al 2*013 for pharmaceutical effluent from River Gorax in Niger State. The pH of the wastewater was indicative of the acidic nature of the pharmaceutical wastewater which mean pH of 4.61.

The turbidity of 3.33 - 7.29 NTU was lower than the amount 28.78 NTU and 16.6 22 NTU published in the research work by Idris et al 2013, and Fatemeh 2024 respectively. The average turbidity was 4.63 NTU while the mean electrical conductivity was 15.95 us/cm. The electrical conductivities of the pharmaceutical wastewater had a range of 1 - 32 us/cmwhich was in agreement with the value (16.73 us/cm) report by Idris et al 2013 for pharmaceutical wastewater effluent from River Gorax in Minna , Niger State.

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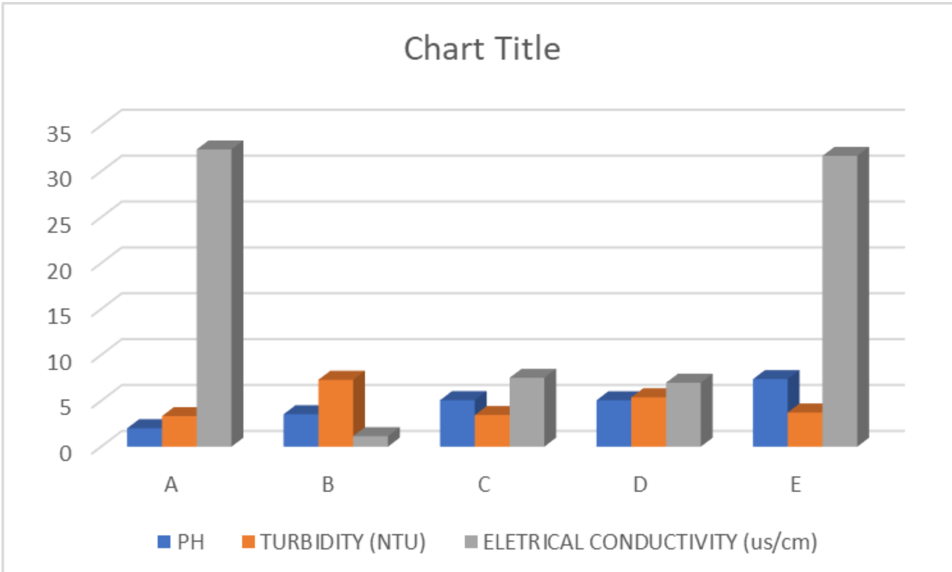

Figure 2: Variation in the pH, Turbidity and Electrical Conductivity of the Untreated Pharmaceutical Wastewater.

The variation in the pH, turbidity and electrical conductivity of the pharmaceutical wastewater is presented in figure 2. There was no observable trend in the levels of the 3 parameters, but electrical conductivity was significantly high in all the samples comparative to turbidity. In all the samples, electrical conductivity was relatively higher than turbidity except in sample B.

Table 5:
Results of pH, Turbidity and Conductivity for Treated Pharmaceutical Wastewater.

SAMPLE	PH	TURBIDITY (NTU)	ELETRICAL (us/cm)	CONDUCTIVITY
A	2.14	9.70	7.20	
B	5.11	6.82	5.07	
C	7.24	2.46	1.89	
D	7.31	2.18	9.62	
E	6.58	1.60	48.70	
Total	28.38	22.76	72.48	
Mean	5.68	4.55	14.50	
% Removal	23	8	9.09	

The results of the pH, Turbidity and Electrical Conductivity for the treated pharmaceutical wastewater effluent is represented in table 5. The rice husk activated carbon used in the treatment of the pharmaceutical wastewater significantly reduced the acidic level from pH of 4.61 to 5.68, with 23% reduction capacity.

The turbidity level was reduced from 4.63 NTU to 4.55 NTU (8% removal efficiency) while the electrical conductivity decreased from 15.95 to 14.50 us/cm with a percentage removal efficiency of 9.09%.

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Table 6:
Physico- Chemical Results for Untreated Sample

Sample	FLUORIDE	ACIDITY	ALKALINITY	TS	TDS	TSS	NO3	NO2	%N2	TOTAL N2
A	9.01	21.60	40.00	13.02	5.00	8.02	8.61	6.02	1.34	15.97
B	6.96	65.00	20.00	6.74	4.74	2.00	10.08	9.06	1.12	20.26
C	6.79	80.00	22.00	7.84	5.72	2.12	8.22	6.60	1.45	16.70
D	10.77	90.00	18.00	5.02	1.52	3.50	10.35	8.80	1.62	20.77
E	11.40	75.00	24.00	5.90	2.32	3.58	10.64	8.32	1.74	20.70
SUM	44.93	331.6	124	38.52	19.3	19.22	47.9	38.8	7.27	94.4
MEAN	8.98	66.32	24.80	7.70	3.86	3.84	9.58	7.76	1.45	18.88

The results of the untreated pharmaceutical wastewater recorded 8.89 mg/L mean value for fluoride concentration in the pharmaceutical wastewater which was above the recommended minimum standard (1.0 - 1.5 mg/L) by WHO for fluoride in pharmaceutical wastewater. The average acidity and alkalinity values were 66.32 mg/L and 24.80 mg/L respectively, which were lower than the values 170 - 200 mg/L published for pharmaceutical wastewater by Anwer et al 2023.

The TSS and TDS for pharmaceutical Effluent of River Gorax in Niger State were 29.67 mg/L and 193 mg/L respectively as reported by Idris et al 2013 which wer ve higher than the amount (3.84 and 3.86 mg/L recorded in this work. The nitrate and nitrite concentrations in the pharmaceutical wastewater were 9.58 mg/L and 7.76 mg/L, where they occurred at higher amount than the values reported for wastewater sludge (0.36 to 0.50 mg/L for Nitrate, and 0.46 - 0.54 for nitrite), Fatemem **et al**, 2024 , and also higher than the level (0.29 - 0.56 for nitrate) recorded by Anwer et al 2023 for pharmaceutical wastewater.

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Table 7:
Physico- Chemical Results for Treated Sample

Sample	FLUORIDE	ACIDITY	ALKALINITY	TS	TDS	TSS	NITRATE	NITRITE	% N2	TOTAL N2
A	0.26	40	56	7.1	2.48	4.62	0.23	1.78	1.23	3.24
B	0.46	30	64	7.06	2.08	4.98	0.38	0.79	0.84	2
C	0.38	45	46	4.48	3.5	0.98	0.3	0.99	1.29	2.57
D	0.46	80	24	3.16	1.64	1.52	0.33	1.37	1.57	3.27
E	0.52	70	26	2.34	0.72	1.62	0.52	1.20	1.79	3.52
Total	2.08	265	216	24.14	10.42	13.72	1.76	6.13	6.72	14.6
Mean	0.42	53	43.2	4.83	2.08	2.74	0.35	1.23	1.34	2.92

The results of the physio-chemical parameters of the treated pharmaceutical wastewater is represented on table 7. The rice husk activated carbon showed high removal efficiency for wastewater with high concentrations fluorides which is evident in the high removal efficiency of 95.55% recorded for the fluoride as 8.89 mg/L of fluoride was observed for the untreated wastewater, while the treated wastewater recorded a value of 0.42 mg/L. The performance of rice husk for the treatment of wastewater containing high percentage Nitrogen was very low as only 7.58% removal efficiency for percentage nitrogen was observed.

The trend observed in the removal efficiency for the physiochemical parameter was Nitrate (96.35%) > Fluoride (95.55%) > total Nitrogen (84.28%) > nitrite (84.15%) > TDS (46.11%) > TS (37.27%) > TSS (28.65%) > acidity (20.08%) > %N2 (7.58%). It was observed that the rice husk was not good for the treatment of wastewater with high alkalinity, as the value of the alkalinity increases after treatment from 24.80 mg/L to 43.2 mg/L with a percentage increase of 74.19%.

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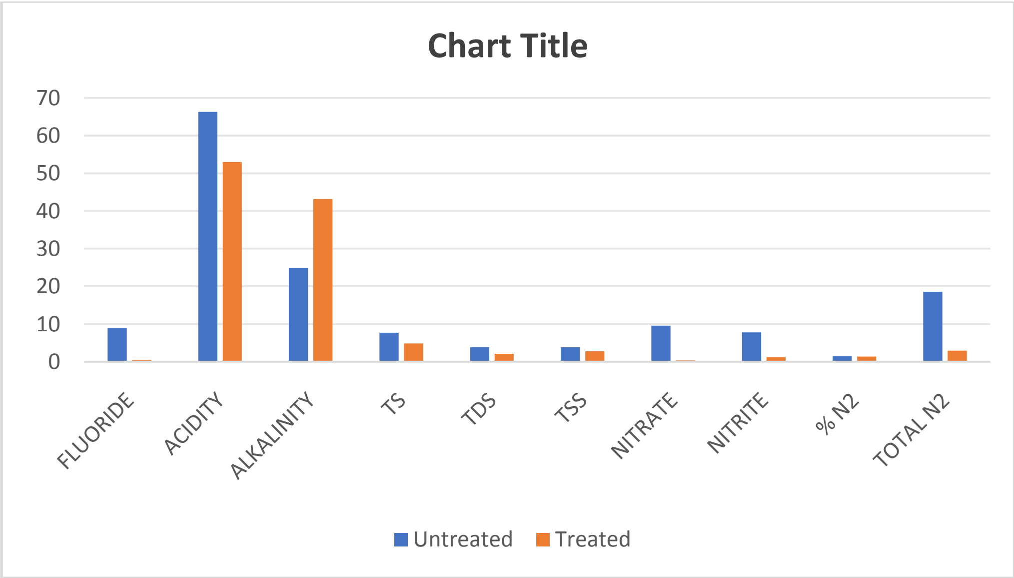

Figure 2 : Physicochemical parameters concentrations in both Untreated and Treated samples.

The figure 4.10 showed that the rice husk activated carbon performed well in the treatment of pharmaceutical wastewater especially for removal of fluorides, nitrates, nitrites, and total nitrogen from the wastewater.It performance was relatively low for treating wastewater with high TS, TSS.

It was further observed that rice husk activated carbon can not be used for the treatment of wastewater with high level of alkalinity, as the level of alkalinity was discovered to increased from 24.80 mg/L to 43.2 mg/L after treatment.

Table 8:
Results of Physico- Chemical Results for Untreated Pharmaceutical Wastewater

Sample	Chloride	Sulphate	COD	DO_1	DO_5	BOD
A	195	164	178	190	133	114
B	263	159	238	177	54	246
C	134	138	197	200	110	179
D	152	128	243	198	73	249
E	173	145	160	214	92	243
TOTAL	917	734	1016	979	462	1031
MEAN	183	146	203	195	92	206

The average chloride concentration for the pharmaceutical wastewater was 183 mg/L (Table 4.9) which was lower than the amount (200 mg/L reported by Anwer et al, 2023 for pharmaceutical wastewater. The 183 mg/L reported for this research was lower than WHo standard value of 250 mg/L for wastewater. The mean value of Sulphate in the pharmaceutical wastewater was 146 mg/L which agreed to the amount (118 - 156 mg/L) published by Hossan et al, 2024. The COD of 203 mg/L recorded in the pharmaceutical wastewater was in agreement to the values (141 - 201 mg/L and 135 - 316 mg/L) respectively published by Fatemeh et al 2024, and Anwer et al 2023 for pharmaceutical wastewater.

The COD of 203 mg/L found in this research was below the amount (323 - 571 mg/L) recorded by Olusegun et al, 2021 for pharmaceutical wastewater and also lower than the values (287 - 515 mg/L) published by Hossan et al 2024. significant decrease was noticed from DO_1 to DO_5, from average value of 195 to 92 mg/L representing 52.82% reduction in DO within 5 days. The DO was relatively high comare to the values (1.38 - 2.26 mg/L and 1.6 - 3.2 mg/L) respectively recorded by Olusegun et al 2021 and Hossan et al, 2024 for pharmaceutical wastewate. The BOD for the pharmaceutical wastewater was 206 mg/L which was in line with the amount published by Hossan et al. 2024, but lower than the amount (323 - 571 mg/L) recorded by Olusegun et al, 2021.

Table 4.10:
Results of Physico- Chemical Results for Treated Pharmaceutical Wastewater

Sample	Chloride	Sulphate	COD	DO_1	DO_5	BOD
A	68	80.65	23.20	142.80	214.40	250
B	124	65.01	30.40	95.60	85.60	138.4
C	99	112.75	44	120.80	215.20	228.4
D	93	77.36	90.67	74.40	109.60	153.2
E	92	105.34	23.20	110	176	198
TOTAL	476	441.11	211.47	543.6	800.8	968
MEAN	95.2	88.22	42.30	108.72	160.16	193.6

The results of the physiochemical parameter of the treated pharmaceutical wastewater is represented in Table 4.10. The treated wastewater had 95.2 mg/L Chloride concentration as against 183 mg/L recorded for untreated samples.

The BOD of both the untreated and treated pharmaceutical wastewater had values (206 mg/L and 193.6 mg/L which were higher than the minimum threshold limit established by FEPA.

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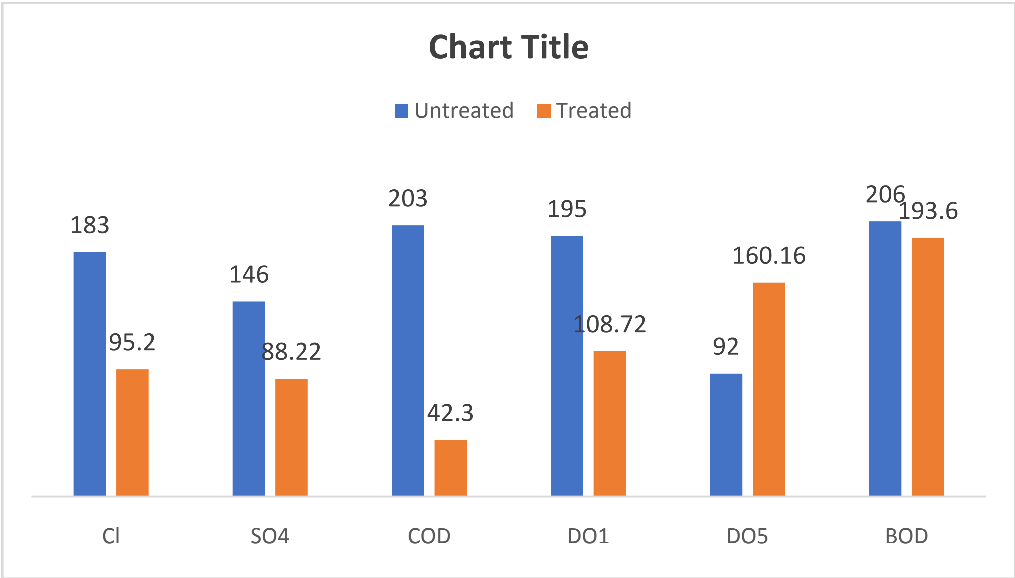

Figure 3: Removal Efficiency of the Rice husk for the Untreated and Treated Pharmaceutical Wastewater

The results of efficiency of the rice husk in the treatment of the pharmaceutical wastewater is represented in figure 3. The observed trend in the percentage reduction of the physiochemical parameters was COD (79.16%) > Chloride (48%) > DO1 (44%) > sulphate (40%) > BOD (6%) > DO5 (-42.6%).

It was observed that rice husk activated carbon was not effective for treatment of wastewater with high DO5 as the DO5 increased after treatment from 92 mg/L to 160.16 mg/L. Rice husk showed excellent treatment capacity for the treatment of pharmaceutical wastewater with high COD.

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Table1 9:
Table showing Total Bacteria count (Cfuml-^{1}) and Total *coliform* count (Cfuml-^{1}) and coliform distribution of treated and untreated waste water samples

	UNTREATED					TREATED				
Samples	**Total Bacteria count (Cfuml-^{1})**		**Total*coliform* count (Cfuml-^{1})**		***Coliform* distribution**	**Total Bacteria count (Cfuml-^{1})**		**Total*coliform* count (Cfuml-^{1})**		***Coliform* distribution**
	No. of Bacterial colonies on plate	**Total Bacterial Count (cfuml-^{1})**	**No. of *coliform* colonies on plate**	**Total *coliform* count (Cfuml-^{1})**		**No. of Bacterial colonies on plate**	**Total Bacterial Count (cfuml-^{1})**	**No. of *coliform* colonies on plate**	**Total *coliform* count (Cfuml-^{1})**	
A	174	1.74 x10^{5}	30	3.0 x10^{4}	*Escherichia coli Klebsiella pneumoniae*	80	8.0x10^{4}	NG	NG	NG
B	75	7.5x10^{4}	42	4.2x10^{4}	*Escherichia coli Klebsiella pneumonia*	58	5.8x10^{4}	NG	NG	NG
C	275	2.75x10^{5}	64	6.4x10^{5}	*Enterobacter aerogenes Proteus mirabilis*	90	9.0x10^{4}	39	3.9 x10^{4}	*Enterobacter Aerogenes*
D	173	1.73x10^{5}	33	3.3 x10^{4}	*Enterobacter aerogenes*	67	6.7x10^{4}	NG	NG	NG
E	112	1.12 x10^{5}	79	7.9.x10^{4}	*Escherichia coli Proteus mirabilis Enterobacter aerogenes*	87	8.7x10^{4}	51	5.1 x10^{4}	*Proteus mirabilis Enterobacter aerogenes*

The number of bacterial colonies on the plate for samples A and E for the untreated wastewater samples had a range of 75 - 275 on the plates. The total bacteria count equivalent to the product of the number of colony and the dilution factor (1000) used in the dilution of the wastewater effluent before the biological test (number of colony multiply by 1000). The total number of Coliform colony for sample A was 174 giving a total coliform count of 174000 CFU/ml (Table 4.11). Table 9 revealed a coliform distribution of *Citrobacter freundii, Escherichia coli, and Klebsiella pneumoniae*for the untreated waste water. There was a reduction in the number of bacterial colony to80 with total bacterial count of 80000 CFU/ml in the treated wastewater effluent for sample A. This showed that the orthophosphate modified rice husk activated carbon was a good adsorbent in the removal of some pathogenic bacteria in the wastewater effluents with removal efficiency of 54%.

The total coliform count of Sample B was 42000 CFU/ml for the untreated wastewater sample which was greatly reduced to near zero coliform count (recorded as no visible growth) in the treated fast food wastewater effluents. This showed the high adsorption capacity of the orthophosphate acid modified rice husk activated carbon for the treatment of wastewater sample polluted with *Enterobacter aerogenes and Escherichia coli.*

Generally, in all the fast food wastewater effluents analysed there was appreciable reduction in both the total bacteria count and the total coliform count between the treated and untreated wastewater effluents, and indication of the capacity of the activated carbon to serve as a good agent for treated of fast food effluent contaminated with microbiological pollutants.

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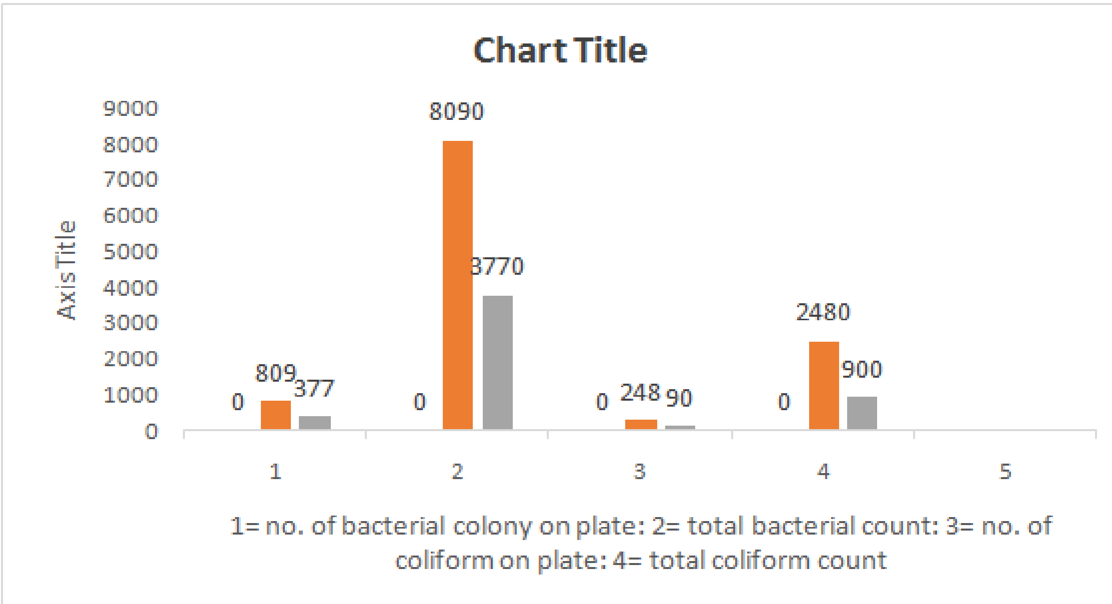

Figure 3: Microbes Variation in the Untreated and the Treated Pharmaceutical Wastewater.

The figure 3 showed that the number of bacterial count on the plate decreased from 809 to 377 after treatment of the wastewater with the rice husk orthophosphate modified activated carbon with 53.4% removal efficiency. The number of coliforms on the plate significantly reduced from 248 to 90 revealing percentage removal of 63.7%. The total bacterial count decreased from 809000 CFU/ml to 377000 CFU/ml with efficiency of 53.3% while the total coliform count reduced from 248000 CFU/ml to 90000 CFU/ml.

IV. Contribution To Knowledge

Pharmaceutical wastewater in Onitsha showed higher essential elements (Mg, Fe, Zn) at 5.301 mg/L vs. toxic metals (Pb, Cd, Co) at 0.388 mg/L. Lead (Pb) exceeded NAFDAC/NESREA and WHO limits, while Cd (0.124 mg/L) and Zn (2.451 mg/L) were acceptable. Treated wastewater showed metal concentration ranking: Mg > Fe > Zn > Cd > Co > Pb. Activated rice husk efficiently removed metals; highest removal for Pb (95.07%) and least for Co (44.83%).Hazard quotient (HQ) revealed health risks from Pb and Cd; trace metals posed minimal risk. Turbidity negatively correlated with pH; increased pH linked to lower organic breakdown and suspended solids.

Treated pH, turbidity, and conductivity decreased significantly. Rice husk activated carbon effectively reduced fluoride and nitrates but poorly treated nitrogen. Bacterial counts significantly reduced post-treatment, indicating effective pathogen removal.

V. Conclusion

The analysis of pharmaceutical wastewater in Onitsha metropolis demonstrated significantly higher concentrations of essential elements such as magnesium (Mg), iron (Fe), and zinc (Zn) compared to toxic metals like lead (Pb), cadmium (Cd), and cobalt (Co). The study found Pb levels surpassed acceptable limits, indicating health risks, while Cd and Zn levels were within safe ranges. The effective use of activated rice husk carbon for treating wastewater resulted in considerable reductions in toxic metals and improved water quality. However, while trace metals posed lower risks, the presence of Pb and Cd highlighted potential health hazards for consumers. Correlations between metal concentrations and various water quality indicators were observed, along with significant decreases in bacteria after treatment. Overall, the study emphasizes the efficiency of rice husk activated carbon in wastewater treatment and the ongoing risks posed by certain heavy metals.

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