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HYDROGEOCHEMISTRY AND ADSORPTION STUDY OF HEAVY METALS FROM JOS WASTEWATER TREATMENT PLANT, NORTH-CENTRAL NIGERIA

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Abstract

The present research focuses on the hydrogeochemistry and adsorption study of heavy metals from the Jos wastewater treatment plant. Ten (10) samples were collected from the Nabor-Gwong Wastewater Treatment Plant in Jos and treated with rice husk ash as adsorbent. The study aimed to determine the levels of some heavy metals (Mg, Mn, Co, Ni, Cd, Pb, Cr and Cu) in wastewater and their comparison with levels of heavy metals in the treated water after treatment with rice husk ash while the water quality index and pollution indices of wastewater and treated water were also compared. The levels of heavy metals in wastewater, treated water and rice husk ash were analysed using Atomic Absorption Spectrometry. The concentrations of heavy metals were subjected to ANOVA and Spearman's correlation analysis. The results indicated that the concentrations of heavy metals in wastewater such as Mg (0.202-0.427 mg/L), Mn (0.217-0.750 mg/L), Co (0.119-0.222 mg/L), Ni (0.117-1.099 mg/L), Cd (0.426-1.704 mg/L), Pb (0.067-1.566 mg/L), Cr (0.925-2.559 mg/L) and Cu (0.965-2.270 mg/L) were higher than WHO permissible limits for drinking water, background values and Nigerian Standard for Drinking Water Quality (NSDWQ). Treated water shows that Mn, Cu and Pb except for samples I to III fall within WHO permissible limits, background values and NSDWQ while the concentrations of Ni, Cd and Cr exceed WHO permissible limits in the treated water. The heavy metals in the wastewater were reduced significantly after treatment and the average percentage reduction is in the order of Mn (93.00) > Mg (89.71) > Pb (88.46) > Cu (84.94) > Cr (82.60) > Co (75.21) > Ni (72.28) > Cd (67.86) which attest to adsorbent effects of rice husk ash. However, other treatment methods or pH modification of rice husk ash may be necessary for metals which exceed permissible limits in treated water.

1.0 INTRODUCTION

Anthropogenic wastewater is wastewater that has been affected in quality due to human influence and comprises liquid waste from domestic, agricultural and industrial activities. The liquid wastewater is eventually discharged into nearby streams leading to surface and underground water contaminations and soils [1] [2]. The quality of soil, water and aquatic life depends on the level of heavy metals in surface and underground water [3] [4] [5]. The heavy metals in soils and the level of water pollution can be a threat to living organisms and adversely affect their lives negatively [6]

Industrialisation contributes to the discharging of huge concentrations of metals along with anthropogenic wastewater [7]. The contaminants in

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the water can be removed through precipitation, ionic exchange, oxidation, osmosis and ultrafiltration [8]. Biological materials like seaweeds, moulds and other agro residues have been used by several authors for the adsorption of heavy metals [9] [10]. Adsorption is a friendly method of reducing heavy metals in wastewater [11] [12] and activated carbon along with other ash from biomaterials have been used as adsorbents [13] [14]. The physical adsorption methods are found to be very useful and are therefore widely used in wastewater treatment [15].

The physical adsorption methods using activated carbon, zeolites, or clay-based materials are discouraged due to their high cost. Rice husk ash has been found to be the most effective and cheapest treatment method for the adsorption of heavy metals [16] due to the surface area, pore sizes, structural characteristics, adsorption capability and simple regeneration [7].

The porous structure and chemical stability of rice husk are also very advantageous to work as a good adsorbent since it can easily be transformed into rice husk ash which contains activated carbon [17]. Rice husk ash predominantly contains silica, and its nature depends on the burning temperature. The rice husk ash produced at the moderate temperature of 600–700 °C usually remains amorphous, while further heating makes it crystalline [18]. When the physical adsorption occurs on the silica surface, the interactions between the adsorbent molecule and the hydroxyl group of adsorbate become dominant [19].

The water quality index (WQI) is used to estimate the overall quality of water based on heavy metals [20] while the suitability of water for drinking is determined by the Organisation's permissible standards. The Pollution load index (PLI) and Nemerow pollution index (*PN*) indicate the extent of pollution in an environment and its potential impact on an area.

The research on hydrogeochemistry and adsorption study of heavy metals from the Jos wastewater treatment plant, in North-Central Nigeria has not been reported. Therefore, there is a need to study the level of heavy metals in wastewater and the implications of treating the wastewater with rice husk ash. The study aimed to determine the levels of some heavy metals (Mg, Mn, Co, Ni, Cd, Pb, Cr and Cu) in wastewater and their comparison with levels of heavy metals in the treated water using rice husk ash as adsorbent while the water quality index and pollution indices of wastewater and treated water were also compared.

An outline of the Geology of the area is reported by [21] and constitutes part of the Basement Complex in northcentral Nigeria which includes: migmatite and early rhyolite that are Precambrian to Lower Paleozoic in age while Aegerine granite, Neil Valley granite porphyry and Jos biotite granite are Jurassic in age of Younger Granite Complexes as shown in Figure 1. Basic dyke of younger age have been identified cross-cutting the Migmatite. The detailed geology of part of Jos-Plateau, northcentral Nigeria was reported by [22].

The geochemical characteristics of crystalline rocks, soils and stream sediments on the Jos Plateau in northcentral Nigeria indicate high concentrations of heavy metals that were higher than the background reference values, threshold limits and permissible limits [23]. Depending on the rock units, climatic conditions and topography within the locality, heavy metals in the rocks, soils and stream sediments can be weathered, leached and transported into nearby streams thereby contaminating the surface water and groundwater [24].

The Geogenic source of water and soil contaminations are due to geological activities like weathering, volcanism and mineralization depending on the mobility characteristics of minerals in the rocks which can contribute to heavy metals in the wastewater [25]. The anthropogenic sources of water and soil contaminations are due to human activities like mining, fossil fuel combustion, waste disposal, agricultural practices and industrial activities [26] which can also contribute to heavy metals in the wastewater.

2.0 METHODOLOGY

2.1 Sample Collection

The study area is located in the Nabor-Gwong Treatment Plant of Plateau State Water-board, Jos Plateau on latitudes $9^{o}54^{I}30^{II}$ to $9^{o}58^{I}00^{II}$ N and longitudes $8^{o}52^{I}30^{II}$ to $8^{o}56^{I}30^{II}$ E. A total of ten (10) wastewater samples were collected from ten (10) different locations of Plateau State Water-board in Nabor-Gwong Treatment Plant, Jos-North Local Government Area as shown in Figure 2 using plastic sample bottles. The sample bottles were rinsed twice before wastewater samples were collected. Rice Husk samples were collected from three (3) rice mills at Wallum, Zambang, and Dadin-kowa of Langtang-South Local Government Area in Plateau State and were mixed to obtain a homogenous sample of Rice Husk.

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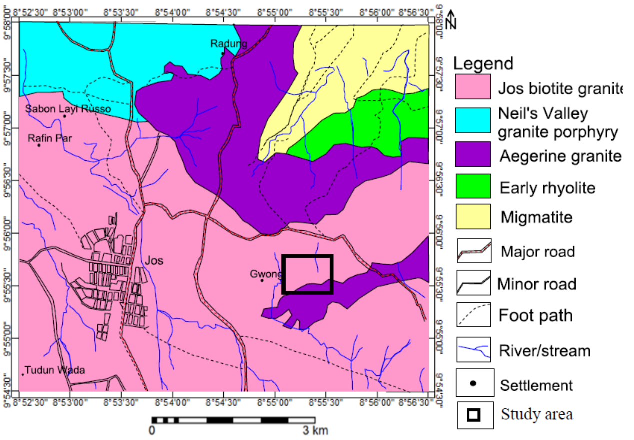

Figure 1: Geological map of the study area

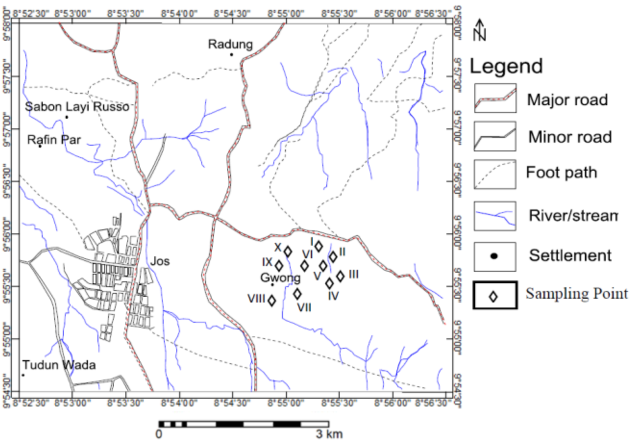

Figure 2: Location map of the study area with the sampling points

2.2 Laboratory Analysis

The Rice Husks were washed with distilled water followed by filtration using Whatmam-110mm filter paper and funnel and dried at 105°C. The dried Rice Husk was taken to the oven for three (3) hours at 300°C. About 90g of the dried mass of the sample (Rice Husk) was weighed on a digital weighing balance. The dried mass was fed into a muffle furnace and calcined at 750°C for two (2) hours. The calcined Rice Husk is referred to as Rice Husk Ash (RHA).

The Rice Husk ash of 2 g was weighed on a weighing balance and put into the beaker containing 200 mL of wastewater. It was mixed properly for 1 hour under stirring and the wastewater was allowed to be adsorbed into the Rice Husk Ash for 24 hours and then filtered into a conical flask using a filter paper and funnel. This was done repeatedly for the ten (10) samples of wastewater.

The pH of the rice husk ash, wastewater and treated water was determined using a digital pH meter. The ten (10) wastewater samples, ten (10) treated water samples and one (1) sample of Rice Husk Ash were taken to the Department of Chemistry, Abubakar Tafawa Balewa University (ATBU) Bauchi State for digestion and heavy metal analyses using AA320N Model of Atomic Absorption Spectrophotometer.

The digestion of the samples was carried out by the addition of 30.00 mL of concentrated Hydrochloric acid (HCl), 10.00mL of Nitric acid (HNO3), and 10.00mL of Perchloric acid (HClO4) to the samples and was heated at 80°C until brown fumes of nitric acid. The procedure for digestion was carried out according to [27]. After cooling, distilled water was added and filtered using What-man filter paper number 1. The resulting solution is called digest which was used for AAS analyses.

2.3 Statistical Analysis

The concentrations of heavy metals obtained from geochemical analysis of wastewater and treated water were subjected to statistical analyses such as ANOVA and Spearman's rho correlation analysis.

Percentage removal of heavy metals

The percentage removal of heavy metals from wastewater was computed as shown below [27]:
percentage removal of heavy metals=

$$\frac{(C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where, C_0 is heavy metal concentration in wastewater and C_t is heavy metal concentration in treated water after using rice husk ash as adsorbent.

2.4 Estimation of Pollution Indices

Heavy metal pollution index

The water quality index (WQI) estimates the suitability of water using the concentrations of heavy metals after [28] [29] as shown below.

$$WQI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \quad (2)$$

Where, Wi is the weightage of the 'i'th heavy metal, n is the number of heavy metals and Qi is the sub index of the 'i'th heavy metal.

$$Wi = \frac{K}{Si} \quad (3)$$

Where, K is the proportionality constant, Si is the standard permissible limit in water.

The sub index, Qi, [30] is calculated by

$$\sum_{i=1}^{n} \frac{(Mi - li)}{Si - li)} \times 100 \quad (4)$$

Where, Mi is concentration of heavy metals obtained in the current study, li is the ideal value of the 'i'th heavy metal based on international limits for drinking water and Si is the standard value of 'i'th heavy metal.

Contamination factor
Contamination Factor (CF) is the degree of pollution [31]:

$$CF = \frac{Chemical\ contaminant\ of\ interest}{Background\ value\ using\ WHO\ standard} \quad (5)$$

Degree of contamination
This is the sum of all chemical contaminants in the area of study [32]:

$$C_{Deg} = \sum(CF) = CF_1 + CF_2 + CF_3 + \text{-----} + CF_n \quad (6)$$

Modified degree of contamination
This is the average effect of all chemical contaminants of interest [32]:

$$mC_{Deg} = \frac{1}{n}\sum(CF) \quad (7)$$

Pollution load index
PLI is the geometric mean of CF value to the *n*th number of chemical contaminants of interest, it is given as [33]:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (8)$$

Where, *n* is the sum total of chemical contaminants.

Nemerow pollution index
It is the complete effect of chemical constituents and given as [33]:

$$P_N = \sqrt{\frac{\overline{CF}^2 + CF_{max}^2}{2}} \quad (9)$$

Where, P_N is the nemerow pollution index, $\overline{CF}^2$ is arithmetic mean of contamination factor of all chemical contaminants, CF_{max}^2 is the maximum contamination factor among all chemical contaminants.

3.0 RESULTS AND DISCUSSION
The results of the pH of rice husk ash, wastewater and treated water samples (Table 1). The value of heavy metal concentrations of rice husk is presented in Table 2. The heavy metal concentration of wastewater and treated water is presented in Table 3, the percentage reduction of each metal after using rice husk ash as an adsorbent is presented in Table 4 while Spearman's rho correlation analysis of heavy metals is presented in Table 5.

The pH value of rice husk is 7.67 and the wastewater 6.30 - 6.90 which indicated weak acid, while the treated water ranged from 7.02 - 7.97 which is relatively neutral as shown in Table 1. Rice husk ash has Mg value of 0.013 mg/L, Mn of 0.019 mg/L, Co value of 0.030 mg/L, Ni of 0.059 mg/L, Cd value of 0.188 mg/L, Pb of 0.004 mg/L, Cr value of 0.184 mg/L and Cu of 0.512 mg/L (Table 2).

Wastewater samples have Mg values ranging from 0.202 - 0.427 mg/L, Mn of 0.217 - 0.750 mg/L, Co of 0.119 - 0.222 mg/L, Ni value of 0.117 - 1.099 mg/L, Cd value of 0.426 - 1.704 mg/L, Pb value of 0.067 - 1.566 mg/L, Cr value of 0.925 - 2.559 mg/L and Cu value of 0.965 - 2.270 mg/L (Table 3). Treated water samples have Mg of 0.013 to 0.067 mg/L, Mn value of 0.013 to 0.049 mg/L, Co value of 0.012 to 0.084 mg/L, Ni value of 0.026 to 0.110 mg/L, Cd of 0.113 to 0.422 mg/L, Pb of 0.001 to 0.117 mg/L, Cr value of 0.054 to 0.725 mg/L and Cu of 0.075 to 0.579 mg/L (Table 3).

Table 1: pH values of rice husk, wastewater and treated water.

Samples		pH
Untreated water	I	6.30
	II	6.42
	III	6.46
	IV	6.90
	V	6.74
	VI	6.71
	VII	6.35
	VIII	6.49
	IX	6.78
	X	6.50
Treated water	I	7.54
	II	7.83
	III	7.97
	IV	7.29
	V	7.08
	VI	7.02
	VII	7.20
	VIII	7.15
	IX	7.32
	X	7.45
Rice Husk Ash		7.67

Table 2: Heavy metals concentration (mg/L) of Rice Husk Ash

Heavy metals	Mg	Mn	Co	Ni	Cd	Pb	Cr	Cu
Concentrations	0.013	0.019	0.030	0.059	0.188	0.004	0.184	0.512

Table 3: Heavy metals values (mg/L) in treated water and wastewater samples in comparison with permissible limit [34], background values [35] [36] [37] and standards [38]

Group	Mg	Mn	Co	Ni	Cd	Pb	Cr	Cu
I (Wastewater)	$0.42750^{r} \pm 0.000500$	$0.40150^{k} \pm 0.000500$	$0.11950^{j} \pm 0.000500$	$0.11750^{f} \pm 0.000500$	$0.92050^{f} \pm 0.000500$	$1.56650^{e} \pm 0.000500$	$1.29150^{a} \pm 0.000500$	$1.71350^{a} \pm 0.000500$

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I (Treated water)	0.01750^{b} ± 0.000500	0.04950^{h} ± 0.000500	0.01150^{a} ± 0.000500	0.04950^{g} ± 0.000500	0.42300^{c} ± 0.001000	0.05250^{f} ± 0.000500	0.24950^{b} ± 0.000500	0.40450^{b} ± 0.000500
II (Wastewater)	0.40450^{o} ± 0.000500	0.40050^{k} ± 0.000500	0.13050^{k} ± 0.000500	0.13450^{h} ± 0.000500	0.65350^{e} ± 0.000500	0.10750^{d} ± 0.000500	2.38850^{c} ± 0.000500	1.75250^{c} ± 0.000500
II (Treated water)	0.01350^{a} ± 0.000500	0.04450^{g} ± 0.000500	0.08500^{l} ± 0.001000	0.08150^{i} ± 0.000500	0.31050^{g} ± 0.000500	0.07850^{g} ± 0.000500	0.09700^{d} ± 0.001000	0.30200^{d} ± 0.001000
III (Wastewater)	0.41550^{q} ± 0.000500	0.43200^{l} ± 0.001000	0.12950^{k} ± 0.000500	0.14150^{j} ± 0.000500	0.67950^{h} ± 0.000500	0.79100^{h} ± 0.001000	1.92450^{e} ± 0.000500	1.72750^{e} ± 0.000500
III (Treated water)	0.02500^{d} ± 0.001000	0.03150^{e} ± 0.000500	0.03950^{g} ± 0.000500	0.04450^{e} ± 0.000500	0.12150^{b} ± 0.001500	0.11800^{i} ± 0.001000	0.19800^{f} ± 0.001000	0.57950^{f} ± 0.000500
IV (Wastewater)	0.20250^{i} ± 0.000500	0.21750^{j} ± 0.000500	0.22300^{p} ± 0.001000	1.09800^{k} ± 0.001000	1.70500^{l} ± 0.001000	0.06800^{j} ± 0.001000	0.92600^{g} ± 0.001000	2.27200^{g} ± 0.002000
IV (Treated water)	0.02500^{d} ± .001000	0.03400^{f} ± .001000	0.03650^{f} ± 0.000500	0.05900^{l} ± 0.001000	0.28350^{j} ± 0.001500	0.00100^{k} ± 0.000000	0.05500^{h} ± 0.001000	0.14150^{h} ± 0.000500
V (Wastewater)	0.21200^{j} ± 0.001000	0.75100^{q} ± 0.001000	0.15350^{n} ± 0.000500	0.14400^{m} ± 0.001000	0.57650^{k} ± 0.000500	0.10700^{d} ± 0.001000	2.56000^{i} ± 0.001000	1.99700^{i} ± 0.001000
V (Treated water)	0.06750^{g} ± 0.000500	0.01400^{a} ± 0.001000	0.04150^{gh} ± 0.000500	0.11150^{n} ± 0.001500	0.25850^{l} ± 0.000500	0.00850^{bc} ± 0.000500	0.47350^{j} ± 0.001500	0.07650^{j} ± 0.001500
VI (Wastewater)	0.22650^{k} ± 0.000500	0.75650^{r} ± 0.000500	0.19700^{o} ± 0.001000	0.50850^{o} ± 0.000500	0.42750^{c} ± 0.001500	1.01700^{l} ± 0.001000	2.24800^{k} ± 0.001000	0.96650^{k} ± 0.001500
VI (Treated water)	0.03400^{e} ± 0.001000	0.02900^{d} ± 0.001000	0.02800^{d} ± 0.001000	0.02650^{c} ± 0.000500	0.13150^{b} ± 0.018500	0.00750^{ab} ± 0.000500	0.72600^{l} ± 0.001000	0.12200^{l} ± 0.001000
VII (Wastewater)	0.31100^{m} ± 0.001000	0.52250^{n} ± 0.000500	0.13150^{kl} ± 0.001500	0.18850^{p} ± 0.000500	0.52200^{d} ± 0.001000	0.19150^{m} ± 0.001500	1.21800^{m} ± 0.001000	1.55250^{m} ± 0.001500
VII (Treated water)	0.02250^{c} ± 0.001500	0.02200^{c} ± 0.001000	0.01850^{b} ± 0.000500	0.03850^{d} ± 0.000500	0.13200^{b} ± 0.001000	0.00650^{ab} ± 0.000500	0.08750^{n} ± 0.000500	0.15100^{n} ± 0.001000
VIII (Wastewater)	0.41250^{p} ± 0.000500	0.61100^{p} ± 0.001000	0.15200^{n} ± 0.001000	0.24400^{q} ± 0.001000	0.66300^{e} ± 0.001000	0.22200^{n} ± 0.001000	1.55150^{o} ± 0.000500	1.64250^{o} ± 0.000500
VIII (Treated water)	0.01950^{b} ± 0.000500	0.02750^{d} ± 0.000500	0.03400^{e} ± 0.001000	0.04300^{e} ± 0.001000	0.18100^{m} ± 0.001000	0.00850^{bc} ± 0.000500	0.33800^{p} ± 0.001000	0.21100^{p} ± 0.001000
IX (Wastewater)	0.27400^{l} ± 0.001000	0.49800^{m} ± 0.001000	0.14350^{m} ± 0.000500	0.32300^{r} ± 0.001000	0.49750^{n} ± 0.001500	0.31200^{o} ± 0.001000	1.32950^{q} ± 0.000500	1.70200^{q} ± 0.001000
IX (Treated water)	0.02250^{c} ± 0.000500	0.03350^{ef} ± 0.000500	0.02550^{c} ± 0.000500	0.03950^{d} ± 0.000500	0.21050^{o} ± 0.000500	0.00550^{a} ± 0.000500	0.07550^{r} ± 0.000500	0.16800^{r} ± 0.001000
X (Wastewater)	0.35550^{n} ± 0.000500	0.59100^{o} ± 0.001000	0.13350^{l} ± 0.000500	0.41600^{s} ± 0.001000	0.52050^{d} ± 0.000500	0.12550^{p} ± 0.000500	1.28450^{s} ± 0.000500	1.49800^{s} ± 0.001000
X (Treated water)	0.04300^{f} ± 0.001000	0.01850^{b} ± 0.000500	0.04250^{h} ± 0.000500	0.02850^{c} ± 0.000500	0.14800^{p} ± 0.001000	0.00850^{bc} ± 0.000500	0.63150^{t} ± 0.001500	0.32100^{t} ± 0.001000
WHO	NGV	0.40000(H)^{k} ± 0.000000	NGV*	0.01000^{a} ± 0.000000	0.00300^{a} ± 0.000000	0.01000^{c} ± 0.000000	0.05000^{u} ± 0.000000	2.00000^{u} ± 0.000000
Background values	NGV	NGV	NGV	0.07000^{t} ± 0.000000	0.00300^{a} ± 0.000000	0.01000^{c} ± 0.000000	0.05000^{u} ± 0.000000	2.00000^{u} ± 0.000000
NSDWQ	0.20000^{h} ± 0.000000	0.20000^{i} ± 0.000000	NGV	0.02000^{b} ± 0.000000	0.00300^{a} ± 0.000000	0.01000^{c} ± 0.000000	0.05000^{u} ± 0.000000	1.00000^{v} ± 0.000000

NGV = No health-based guideline value **NGV*** = No Guideline, **H** = Health Based Value. Values represent mean (of 2 replicates) ± SEM. Values carrying different superscripts are significantly different at $p < 0.05$.

Table 4: Percentage (%) reduction of each heavy metal in the treated water sample

Sample number	Mg	Mn	Co	Ni	Cd	Pb	Cr	Cu
I	96.02	87.81	89.92	58.12	54.18	96.62	80.71	76.43
II	96.78	89.03	35.38	39.30	52.53	27.78	95.90	82.82
III	93.74	92.81	69.77	69.01	82.33	85.19	89.76	66.47

IV	88.12	83.87	83.78	94.72	83.45	98.51	94.16	93.79
V	68.25	98.27	73.20	23.08	55.29	92.45	81.56	96.25
VI	85.40	96.30	86.22	94.88	73.47	99.31	67.74	87.46
VII	93.23	95.98	85.39	79.79	74.86	96.82	92.77	90.20
VIII	95.39	95.57	78.15	82.72	72.81	95.93	78.14	87.21
IX	92.00	93.39	81.82	87.89	57.92	98.39	94.28	90.07
X	88.17	96.95	68.42	93.25	71.73	93.60	50.94	78.65
Average % reduction	89.71	93.00	75.21	72.28	67.86	88.46	82.60	84.94

3.1 Heavy Metal concentrations in Wastewater and Treated Water

The pH value of wastewater samples was acidic as values indicated (6.30 - 6.90) portraying weak acid treated it becomes neutral ranged values of 7.02 - 7.97 while the pH of the rice husk ash is neutral with a value of 7.67 (Table 1). The pH value of 6.30-6.90 in the wastewater is lower than the pH value of 7.02 - 7.97 in the treated water. The slight increase in pH of the treated water (7.02 -7.97) could be attributed to the pH of the rice husk ash (7.67) which acts as a neutralizer during the adsorption process [18].

The value of heavy metals in the rice husk ash sample as presented in Table 2 has Mg value of 0.013 mg/L, Mn value of 0.019 mg/L, Co value of 0.030 mg/L, Ni value of 0.059 mg/L, Cd value of 0.188 mg/L, Pb value of 0.004 mg/L, Cr value of 0.184 mg/L and Cu value of 0.512 mg/L which might have been incorporated into the rice husk ash through soil contaminations as suggested by [1]. The result is also similar to the heavy metal compositions along rivers from central Nigeria as reported in [39] [40].

The heavy metals in wastewater as presented in Table 3 were greater than permissible limits [34], background values [35] [36] [37] and standards [38] but when treated with Rice Husk ash, the concentration of heavy metals reduced and some metals such as Mn, Cu and Pb (except sample III) fall within [34] permissible limit, background values [35] [36] [37] and NSDWQ standards [38] while Ni, Cd and Cr in the treated water exceeded WHO [34] permissible limits (Table 3). The lower values of heavy metals in the treated water compared to wastewater could be attributed to the effect of rice husk ash as an adsorbent.

The Mg value in the treated water ranged from 0.013 to 0.067 mg/L and was lower than the Mg value of 0.202 to 0.427 mg/L in the wastewater. The Mn value in the treated water ranged from 0.013 to 0.049 mg/L which was lower than Mn of 0.217 to 0.750 mg/L in the wastewater. Similarly, the Co value in the treated water ranged from 0.012 to 0.084 mg/L and was lower than the Co value of 0.119 to 0.222 mg/L in the wastewater. The lower values of Mg, Mn and Co in the treated water compared to their corresponding values in the wastewater (Table 3) can be associated with the efficiency of rice husk ash as an adsorbent. The values of Ni, Cd, Pb, Cr and Cu in the treated water are lower than the values of Ni, Cd, Pb, Cr and Cu obtained from the wastewater (Table 3) which attests to the role of rice husk ash as an absorbent in heavy metal separation of wastewater.

Statistical analysis of heavy metals concentrations in wastewater and treated water using ANOVA indicates that the values of heavy metals such as Mg, Mn, Co, Ni, Cd, Pb, Cr and Cu have significant values of 0.000 which are significantly lower than WHO/NSDWQ permissible limits at $p < 0.05$ (Table 3). The average percentage reduction of each metal in the treated water (Table 4) is in the order of Mn (93.00) > Mg (89.71) > Pb (88.46) > Cu (84.94) > Cr (82.60) > Co (75.21) > Ni (72.28) > Cd (67.86).

The reduction of metals in the treated water compared to wastewater could be associated with adsorption [41] [42] [43]. Several researches have shown that low-cost agro-residue can effectively be used to purify wastewater [44] [45]. The rice husk ash has proven to be effective in purifying wastewater as affirmed by the current research in the Jos treatment plant since heavy metals like Mn, Cu and Pb in the treated water fall within the acceptable limit. The result of this finding is supported by [10] at Kigali City, Rwanda investigating the adsorption of metals using rice husks as adsorbents. Similarly, this finding is supported by [11] who evaluates the adsorption of metals using agricultural wastes in Egypt. Heavy metals such as Ni, Cd and Cr whose concentrations exceeded WHO permissible limits have low percentage reductions (Table 4) and are required in extremely low concentrations in drinking water according to WHO and NSDWQ permissible limits (Table 3). According to the classification orders defined by the International Agency for Research on Cancer (IARC), Ni, Cd, Cr and Pb are classified as potential carcinogenic metals. Meanwhile, Zn, Mn, Al, and Cu are appointed as non-carcinogenic metals [46] [47].

Spearman's rho correlation coefficients showed significant ($\rho < 0.01$ and $\rho < 0.05$) positive correlations among most heavy metals as presented in

Table 5. This suggests a consistent pattern of occurrence and potentially being adsorbed together during treatment with rice hush ash. Strong correlations were observed between these heavy metals: Co–Ni (0.886), Cr–Mg (0.812), Cr–Co (0.855), Cd–Ni (0.818), Pb–Mn (0.789) and Cd-Cr (0.794). The highly positive correlations (ρ > 0.7) suggest strong co-occurrence and possibly being adsorbed together during treatment with adsorbent.

Moderate correlations were observed between these heavy metals: Pb-Cd (0.647), Mg–Co (0.728), Ni–Cr (0.727) and Mn–Ni (0.698). The moderate positive correlations (ρ = 0.5–0.7) suggest a shared and moderate probability of being adsorbed together while the weak positive correlations (ρ < 0.5) were observed between these heavy metals**:** Cu–Ni (0.434), Cu–Co (0.348) and Mg-Cu (0.331) which **s**uggest occasional co-occurrence and the lesser tendency of being adsorbed together.

The adsorption mechanism in the study area includes combined pyrolysis/activation processes and surface modification [16]. The activation methods involve the oxidation of surface functional groups with nitric acid to promote the formation of carboxylic acids [27] and this procedure was adopted during the digestion of rice husk ash in the study area. Rice husks functionalized with nitric acids act as reversible ion exchangers during the adsorption of heavy metals from wastewater of the Jos treatment plant.

The efficiency and kinetics of adsorption of heavy metal (Ni) onto carbonized and uncarbonized palm kernel chaff was reported by [48] and the best rate of adsorption and the adsorption capacity was observed from the carbonized sample. This is similar to the present study where Ni was reduced by an average of 72.28% through adsorption using rice hush ash.

Table 5: Spearman's correlation of heavy metals in the wastewater and treated water

			Mg	Mn	Co	Ni	Cd	Pb	Cr	Cu
Spearman's rho correlations	Mg	Correlation Coefficient	1.000	.589**	.728**	.650**	.762**	.697**	.812**	.331*
		Sig. (2-tailed)	.	.000	.000	.000	.000	.000	.000	.025
		N	46	46	46	46	46	46	46	46
	Mn	Correlation Coefficient	.589**	1.000	.607**	.698**	.589**	.789**	.605**	.690**
		Sig. (2-tailed)	.000	.	.000	.000	.000	.000	.000	.000
		N	46	46	46	46	46	46	46	46
	Co	Correlation Coefficient	.728**	.607**	1.000	.886**	.823**	.663**	.855**	.348*
		Sig. (2-tailed)	.000	.000	.	.000	.000	.000	.000	.018
		N	46	46	46	46	46	46	46	46
	Ni	Correlation Coefficient	.650**	.698**	.886**	1.000	.818**	.704**	.727**	.434**
		Sig. (2-tailed)	.000	.000	.000	.	.000	.000	.000	.003
		N	46	46	46	46	46	46	46	46
	Cd	Correlation Coefficient	.762**	.589**	.823**	.818**	1.000	.647**	.794**	.403**
		Sig. (2-tailed)	.000	.000	.000	.000	.	.000	.000	.005
		N	46	46	46	46	46	46	46	46
	Pb	Correlation Coefficient	.697**	.789**	.663**	.704**	.647**	1.000	.692**	.579**
		Sig. (2-tailed)	.000	.000	.000	.000	.000	.	.000	.000
		N	46	46	46	46	46	46	46	46
	Cr	Correlation Coefficient	.812**	.605**	.855**	.727**	.794**	.692**	1.000	.330*
		Sig. (2-tailed)	.000	.000	.000	.000	.000	.000	.	.025
		N	46	46	46	46	46	46	46	46
	Cu	Correlation Coefficient	.331*	.690**	.348*	.434**	.403**	.579**	.330*	1.000
		Sig. (2-tailed)	.025	.000	.018	.003	.005	.000	.025	.
		N	46	46	46	46	46	46	46	46
**. Correlation is significant at the 0.01 level (2-tailed).										
*. Correlation is significant at the 0.05 level (2-tailed).										

3.2 Heavy Metal Pollution Index and Contamination

In wastewater samples as presented in Table 6, the degree of contamination (CDeg) ranges from 220.16 to 610.755, the modified degree of contamination (mCDeg) ranges from 36.69 to 101.79, the pollution load index (PLI) ranges from 42,393 to 956,758 and Nemerow pollution index (*PN*) ranges from 9.79 to 18.30. In treated water samples presented in Table 7, the degree of contamination (CDeg) ranges from 46.716 to 152.012, the modified degree of contamination (mCDeg) ranges from 7.79 to 25.34, pollution load index (PLI) ranges from 0.005 to 14.00 and Nemerow pollution index (*PN*) ranges from 4.83 to 9.11.

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The PLI values of the wastewater ranged from 42,393 to 956,758 and indicate extremely high pollution according to the PLI level of pollution [41]. The PLI values of treated water ranged from 0.005 to 14.00 and indicate that samples I to III have PLI values of 5.62 to 14.00 which suggests extremely high pollution (3 < PLI) while samples IV to X have PLI values of 0.005 to 0.35 which suggests no pollution (PLI <1) according to PLI level of pollution [41]. The low PLI values of 0.005 to 0.35 in samples IV to X attest to the effectiveness of rice husk ash as an adsorbent in the study area.

The Nemerow pollution index (*PN*) in wastewater presented in Table 6 ranged from 9.79 to 18.30 and can be classified as heavily polluted (*PN*>7) in accordance with *the PN* classification of pollution level [42]. *PN* was classified into four (4) categories namely: unpolluted (*PN* < 1), slightly (1 ≤ *PN* < 2.5), moderately (2.5 ≤ *PN* < 7) and heavily polluted (*PN* > 7) according to [42]. The Nemerow pollution index (*PN*) in treated water as presented in Table 7 ranged from 4.83 to 9.11 and can be classified into two namely: moderately (2.5 ≤ *PN* < 7) and heavily polluted (*PN* > 7). The lower *PN* values of 4.83 to 9.11 in the treated water than the *P*N values of 9.79 to 18.30 in wastewater attest to the capacity of rice husk ash in the removal of heavy metals from wastewater. The disparities in pollution indices (PLI and *PN*) could be attributed to different rates of adsorption of heavy metals.

Table 6: Contamination factor, degree of contamination, modified contamination, PLI and *PN*

Wastewater	Mn	Cu	Ni	Cd	Pb	Cr	degC	modC	PLI	*PN*
I	1.34	0.857	1.67	307	165.60	25.82	502.287	83.72	491,571	13.98
II	1.34	0.876	1.93	217.67	10.8	47.76	280.376	46.73	42,393	11.50
III	1.44	0.864	2.03	226.33	79	38.48	348.144	58.02	289,617	11.92
IV	0.72	1.135	15.70	568	6.7	18.50	610.755	101.79	150,546	18.30
V	2.50	0.999	2.04	192.33	10.6	51.18	259.649	43.27	88,600	10.85
VI	2.52	0.483	7.26	142	101.8	44.94	299.003	49.83	956,758	9.79
VII	1.74	0.776	2.69	173.67	19	24.34	222.216	37.04	48,620	10.26
VIII	2.03	0.812	3.47	220.67	22.1	31.02	280.102	46.68	144,214	11.56
IX	1.66	0.851	4.60	166.33	31.1	26.58	231.121	38.52	148,912	10.12
X	1.97	0.750	5.93	173.33	12.5	25.68	220.16	36.69	81,247	10.25

Table 7: Contamination factor, degree of contamination, modified contamination, PLI and *PN*

Treated water	Mn	Ni	Cd	Pb	Cr	Cu	degC	ModC	PLI	*PN*
I	0.16	0.70	140.67	5.30	4.98	0.202	152.012	25.34	14.00	9.11
II	0.15	1.17	103.33	7.80	1.96	0.151	114.561	19.09	6.98	7.82
III	0.10	0.63	40.00	11.70	3.94	0.290	56.66	9.44	5.62	4.97
IV	0.12	0.83	94.00	0.10	1.08	0.071	96.201	16.03	0.012	7.42
V	0.04	1.57	86.00	0.80	9.44	0.038	97.888	16.31	0.26	7.15
VI	0.09	0.37	37.67	0.70	14.50	0.061	53.391	8.90	0.13	4.83
VII	0.07	0.54	43.67	0.60	1.76	0.076	46.716	7.79	0.022	5.07
VIII	0.09	0.60	60.00	0.90	6.78	0.105	68.475	11.41	0.35	5.98
IX	0.11	0.06	70.00	0.50	1.52	0.085	72.275	12.05	0.005	6.41
X	0.06	0.40	49.00	0.80	12.60	0.160	63.02	10.50	0.32	5.45

3.3 Water Quality Index (WQI)

The WQI contents of wastewater presented in Table 8 ranged from 100 to 56,800.00 and can be classified into three (3) categories namely: poor, very poor and unfit for consumption according to the classification of [49]. The WQI contents of treated water (Table 9) ranged from -25.5 to 14067 and this indicates five (5) categories of water quality namely: excellent (WQI < 50), good (50 < WQI ≤ 100), poor (100 < WQI ≤ 200), very poor (200 < WQI ≤ 300) and unfit for consumption (WQI > 300) according to the classification of [44]. The current result of this research is supported by [50] [51] on rivers from India.

The WQI values of some of the treated water samples fall in the excellent and good water quality which shows that some of the water samples are safe for industrial and domestic purposes while the wastewater samples are poor (unfit to drink), very poor (unfit to drink) and water unfit for consumption. This finding is supported by [20] in the Ifite Ogwari area, Southeastern Nigeria where some surface water samples are fit to drink and in the Ekosodin area, southern Nigeria where surface water samples have heavy metals such as Mn, Cu, Cr and Cd that were slightly higher than WHO allowable values [52] and unfit to drink.

Table 8: Water quality index for wastewater

Wastewater	Mn	Ni	Cd	Pb	Cr	Cu
I	151.00	585.00	30,700.00	16,560.00	2,582.00	114.80

II	150.50	675.00	21,767.00	1,080.00	4,776.00	114.40
III	165.50	710.00	22,633.00	7,900.00	3,848.00	115.30
IV	58.50	5,495.00	56,800.00	670.00	1,850.00	153.10
V	325.00	715.00	19,233.00	1,060.00	5,118.00	134.30
VI	328.00	2,540.00	14,200.00	10,180.00	4,494.00	63.10
VII	211.00	940.00	17,367.00	1,900.00	2,434.00	103.50
VIII	255.00	1,215.00	22,067.00	2,210.00	3,102.00	108.60
IX	199.50	1,610.00	16,633.00	3,110.00	2,658.00	113.90
X	245.00	2,075.00	17,333.00	1,250.00	2,568.00	99.90

Table 9: Water quality Index for treated water

Treated Sample	Mn	Ni	Cd	Pb	Cr	Cu
I	-25.50	245.00	14067.00	530.00	498.00	24.41
II	-28.00	410.00	10333.00	780.00	196.00	17.31
III	-34.50	220.00	4000.00	1170.00	394.00	36.48
IV	-32.50	290.00	9400.00	10.00	108.00	6.27
V	-43.50	550.00	8600.00	80.00	944.00	1.72
VI	-36.00	130.00	3767.00	70.00	1450.00	4.90
VII	39.50	190.00	4367.00	60.00	176.00	7.03
VIII	-36.50	210.00	6000.00	90.00	678.00	11.03
IX	-33.50	195.00	7000.00	50.00	152.00	8.21
X	-41.00	140.00	4900.00	80.00	1260.00	18.62

4.0 CONCLUSION

Most heavy metals showed a significant reduction in treated water samples compared to their corresponding wastewater values. The average percentage reductions are in the order of Mn (93.00) > Mg (89.71) >Pb (88.46) > Cu (84.94) > Cr (82.60) > Co (75.21) > Ni (72.28) > Cd (67.86) indicating the effectiveness of rice husk ash as an adsorbent.

The water quality index of treated water indicates excellent, good, poor, very poor and unfit for consumption. The treated water samples with excellent and good water quality index are safe for industrial and domestic purposes.

Spearman's correlation revealed strong positive relationships between most metal pairs, indicating a consistent pattern of occurrence and possible interactions which suggest that heavy metals were adsorbed together during the treatment process with rice husk ash.

The concentrations of Mn, Cu and Pb in the treated water fall below WHO/NSDWQ standards for drinking water while metals like Ni, Cd and Cr exhibited concentrations exceeding WHO/NSDWQ limits in several treated water samples. However, other treatment methods or pH modification of rice husk ash may be necessary, particularly for metals like Ni, Cd and Cr which exceeded permissible limits in treated water samples.

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