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Treatment of Tannery Effluent from Sharada Industrial Estate in Kano, Nigeria with Porous Clays

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The tannery industry plays a significant role economically, but it negatively hampers the environment by elevating the concentration of pollutants during the tanning process. The geochemical and mineralogical properties of two Nigeria clay samples were studied by Atomic Absorption Spectrophotometer (AAS) and X-ray diffractometer respectively. Clay samples were obtained from Ozanagogo and Otor-Edo in Delta State, coded OZ and OT respectively. Column clay packed with pebbles in a ratio of 1:4 was used for the purification/removal of pollutants using batch method. Results revealed that the pH of the treated effluents increased from 3.7 to 6.9 and 8.2. Turbidity values reduced from 63.00 NTU to 0.2 NTU and 0.5 NTU, while COD values dropped from 877.00 mg/L to 2.71 mg/L and 15 mg/L, and BOD values decreased from 350.00 mg/L to 0.71 mg/L and 5.00 mg/L. A reduction in chloride levels from 2650.00 mg/L to 97 mg/L and 102.00 mg/L was also observed, while treatment of the effluents brought the bacterial count from 1.9×10^8 to nil, using both clay samples. The mineralogical study revealed that kaolinite was the most abundant clay mineral in both clay types, while hematite was the least abundant in both samples. This paper studied the use of locally sourced material (clays) in treating tannery effluent, and compared the values of the treated effluent with WHO, SON and NESREA standards for drinking water. This study has shown that the porous clay method is an effective purification system using cost-effective, locally-sourced materials and a simple decentralized treatment method.

Keywords: Tannery, Clay, Effluent, Treatment, Environment.

1. Introduction

Some of the sources of pollution worldwide are industries. Effluent disposal from industries without treatment is a challenge to developing countries. Effluents that are untreated and discharged directly into rivers or other bodies of water deplete dissolved oxygen (DO) making it unsuitable for man, aquatic organisms and for other beneficial uses (Bernard and Abdul-Qadri, 2017; Zhoe *et. al*., 2022). One of the contributors to environmental pollution is the leather industry. Wastewater from the tannery industries include but are not limited to heavy metals such as iron, lead, zinc, copper, arsenic, chromium, ammonium sulphate, chloride and chromium salts (Bernard and Ogunleye, 2015). Industries located along the coastal areas cause environmental degradation, with water pollution being one of the most pressing challenges of the entire world. The quality of water is important for its suitability for drinking, industrial and domestic uses (Solomon *et. al.*, 2015). Before being discharged into the appropriate channel, effluents should be treated according to the required specification of regulatory bodies for the specified usage (Younas *et. al*., 2022). Effluents from hides and skin treatment contain large amounts of toxic and heavy metals. Tannery effluents are the topmost pollutants as a result of the salts as NaCl, $Ca(OH)_2$, $Cr(SO_4)_3$ and others, used largely in the production process (Selvan *et. al.*, 2023; Lakshmi and Malliga, 2014) with different concentrations of pH and suspended solids which are toxic to animals, plants and other organisms (Abdulnrium *et. al*., 2015; Shaibu and Audu, 2019). Hence, the quality of the effluent needs to be determined and the appropriate treatment method applied to reduce pollutants to acceptable standards (Awad *et. al.*, 2019; Arpit *et. al*., 2023).

The second largest industrial state in Nigeria and largest in Northern Nigeria is Kano State, with privately-owned small and medium industries manufacturing various products ranging from cosmetics, pharmaceuticals, beverages, textile materials, tanned leather, footwear, agricultural products; and state-owned establishments as Sharada and Challawa which contributes to rapidly growing industrialization (Varsha *et. al*., 2017; Doumbi *et. al*., 2022).

This study aimed to examine the pollution level of effluents from Sharada effluent conference point and usage of different porous clays aided with small stone pebbles as a percolating material, to treat tannery effluents and compare its values with World Health Organization standard (WHO, 2018).

2. Materials and Methods

2.1 Sample Collection

The sample was mapped out at the effluent conference discharge point at Sharada Industrial Estate wastewater point, collected and composite samples were used. A 20-liter plastic container with a sinker tied to it was used in sample collection at intervals of 6 hours at depths of 10 cm, 20 cm, 30 cm and 40 cm. Sharada Industrial Estate is located in Kano State, Nigeria and lies between latitude 11°56'0"N – 11°58'0"N and longitude 8°29'0"E – 8°31'0"E of the equator (Shaibu and Audu, 2019). The samples were iced-cooled in coolers and moved to the laboratory for analysis.

2.2 Preparation of Column

Small stone pebbles collected from Orogodo river in Ika South Local Government Area of Delta State, were thoroughly washed under tap water and air dried. Clay was collected from Ozanogogo (OZ) and Otor-Edo (OT) in Delta State, Nigeria. They were air-dried, pulverized with laboratory mortar and sieved with a 0.02 nm-sized filter.

Plastic columns of height 120 cm and diameter 15 cm were setup with glass wool packed at the base of the column to a depth of 5 cm. Carefully, quantities of pebbles and clay were mixed in ratio 1:4 and loaded in the column at 90 cm mark this is to allow for expansion. This was used for both raw and treated effluent samples.

2.3 Determination of Physiochemical Parameters

pH level was measured with HACH pH meter using electronic method HQ 30. Dissolved Oxygen (DO) was determined by alkaline azide modification method on site using HACH, DO meter, while turbidity was analyzed by Nephelometric method using HACH 2100P turbidimeter. Suspended solid was determined by photometer method using HACH DR 2010, and total solids was estimated gravimetrically. Closed reflux titrimetric method was used to determine biochemical oxygen demand (BOD) levels, while direct Nesslerization method was used for the determination of ammonium-nitrogen (NH_4+N) using HACH DR 5000UV – visible spectrophotometer. Total Kjeldahl nitrogen was determined using indophenol colourimetric method (using HACH 5000 spectrophotometer). Nitrate-nitrogen (NO_3-N) was measured by sodium salicylate colourimetric method using DR 4000V spectrophotometer. Chloride determination was carried out by Mohris method, while alkalinity and sulphate were determined by titration methods.

2.3 Determination of Heavy Metals and Mineralogical Composition

Heavy metal concentration was measured by digestive method using Atomic Absorption Spectrophotometer (GBS scientific Model 200A) as described by APHA (2023). Mineralogical analysis was done using 1800 Philips Model X-ray diffractometer, while cation exchange capacity (CEC) was analyzed using the method of Chapman (1965) as described by Oyebiyi *et. al*. (2016).

3. Results and Discussion

The results in table 1 show the mineralogical compositions (in percentage) of both clay types used for this study.

Table 1: Percentage mineralogical composition of clays

Clay Mineral	OZ (Ozanagogo)	OT (Otor-Edo)
Saporite	2.00	4.80
Montmorillonite (Smectite group)	10.30	5.10
Chlorite	1.00	6.10
Iilite	12.40	20.40
Mixed layer	14.40	22.40
Kaolinite	37.40	32.20
Quartz	22.50	8.00
Hematite	0.00	1.00
Total composition	100	100

The analysis of the mineralogical composition shows both OZ and OT are predominantly kaolinite clays. The montmorillonite group (smectite) which is the expanding clay group was more in quantity in OZ clay type than OT and had more adsorbing properties than other types of clay previously studied (Umudi *et. al.*, 2022).

Table 2 shows the geochemical analysis of oxides (in percentage) and cation exchange capacities (CEC) of the clay types used.

Table 2: Result of geochemical analysis and cation exchange capacity of the clay samples.

Clay mineral	OZ	OT
SiO_2	42.12	46.44
Al_2O_3	40.95	36.70
Fe_2O_3	5.89	7.77
Na_2O	1.88	0.88
MgO	1.80	1.83
K_2O	1.70	1.67
TiO_2	0.83	0.99
CaO	3.41	0.31
H_2O	1.42	3.51
CEC (Cmol/kg clay)	77	65

From table 2, the values of Na_2O and TiO_2 are low since the aluminum contents are high which are characteristics of kaolin clays. The CEC with OZ (77 Cmol/kg) and OT (65 Cmol/kg) reveals clay type OZ as a more expanding clay (due to the smectite group) than OT clay type, and thus remove pollutants better (Selvan *et. al*., 2023).

Tannery effluents samples were percolated through a medium of porous clay column fortified with pebbles. The effluents were analyzed before and after treatment, and their characteristics, as well as the percentage reduction for each parameter is shown in table 3.

Table 3: Results from raw and treated wastewater from tannery effluents (sample mean values)

Parameter	Unit	Raw Effluents	Treated Effluents				SON/NESREA Standard	WHO Standard
			OZ	% reduction	OT	% reduction		
pH		3.7	6.9		8.2		7.89	5.10-6.8
Colour	TCU	18.00	0.00	100	3.0	83.33	3.0	0.00
Turbidity	NTU	63.00	0.2	99.68	5.0	92.06	5.0	0.31
TS	mg/L	60.00	24.0	60.00	50.0	16.67	500	10.25
DS	mg/L	62.00	30.2	51.29	0.00	100	0.00	0.00
SS	mg/L	5679.00	0.00	100	0.00	100	0.00	0.00
DO	mg/L	1.30	4.4		3.98		-	-
COD	mg/L	877.00	2.71	99.69	15	98.29	15	3.9
BOD	mg/L	350.00	0.71	99.80	5.00	98.57	5.50	0.87
TKN	mg/L	55.20	0.00	100	0.00	100	0.00	0.00
NH_4^+-N	mg/L	47.20	0.00	100	0.00	100	0.00	0.00
NO_3-N	mg/L	2.70	0.01	99.63	0.01	99.63	0.02	0.00
Cr	mg/L	75.10	0.04	99.95	0.05	99.93	0.05	0.00
Pb	mg/L	0.13	0.00	100	0.01	92.31	0.00	0.00
Cd	mg/L	20.01	0.00	100	0.002	99.99	0.00	0.00
Bacteria count	cfu	1.9×10^8	0.00	100	0.00	100	0.00	0.00
Sulphate	mg/L	650.00	0.00	100	2.00	99.69	1.00	0.00
Chloride	mEq/L	2650.00	97.10	96.34	102.00	96.15	100.00	0.21
Alkalinity	mEq/L	705.00	0.82	99.88	100	85.82	100.00	2.10

Abbreviations: **WHO** – World Health Organization.

SON/NESREA – Standard Organization of Nigeria/National Environment Standard and Regulation Enforcement Agency.

From the analysis, there was complete removal of colour and suspended solids resulting from nitrogenous substances derived from skin and hides during tanning and preservation (Rajesswari, 2015; Hansen *et. al*., 2020). Biochemical oxygen demand (BOD) levels plays a role in the amount of dissolved oxygen available to aerobic bacteria. The BOD values in the effluents were high (350 mg/L), and this is as a result of fleshing in the beam house due to decomposition of organic matters. Treatment of the effluents caused a reduction in BOD levels to 0.71 mg/L for OZ and 5.0 mg/L for OT clay. Chemical oxygen demand (COD) is a measure of oxygen equivalent of the organic matter content of a sample susceptible to oxidation. The COD values were very high (877 mg/L), an influence of chemical and organic load in the effluent, indicating pollution. Since COD values were higher than BOD values, they were polluted by non-oxygen-dependent (anaerobic) bacteria (Ahmed *et. al.* 2022). Post-treated effluent COD levels however dropped to 2.71 mg/L (OZ) and 15 mg/L (OT), both falling within the acceptable limits set by WHO and SON/NESREA respectively. For samples with low COD and BOD values, the DO values are expected to be high (Korpe and Venkateswan, 2022), as DO is essential for the survival of aerobic bacteria involved in the breakdown of components, which could be a spontaneous or gradual process, hence the increase in DO values in both clay types after treatment. Sulphide compounds (salts) usually in tannery are used in treating leather, with the major drawback being its disposal, since it is toxic. Its value of 650 mg/L is high compared to WHO values. Sulphide compounds can cause fish mortality and gives objectionable smell (Tamersit and Bouhidel, 2020). Treatment of the raw effluent with both clay types caused a fall in sulphate levels to within regulatory standards. Most chromium compounds are not biodegradable, some are epithelial irritant and carcinogens. Exposure to chromium may cause lungs, kidney, liver and nervous failure. Chromium value was 75.10mg/L from this work which was higher than the set limit (0.05mg/L) which can cause system damage. It also had values higher than WHO set limits. A reduction in the chromium levels was observed in the effluent after treatment, to levels equal to or lower than the WHO and SON/NESREA set limits. The high value of alkalinity in the pre-treated effluent is due to the addition of slake lime during the process of unhairing the skins and hides. Alkalinity levels reduced when both clay types were used for treatment of the effluents. The high values of chlorides were as a result of high total solids from salts used during preservation and processing. Discharge of untreated effluents into water bodies alters the salinity of ground water; its impurity making it unfit for drinking, industrial and agricultural purposes (Zidani, 2022). Clays have been shown from previous studies (Umudi and Awatefe, 2018) to reduce salinity levels in wastewater. Before treatment they were higher than the WHO standard as shown in table 2 (2650 mg/L) and higher than the values by WHO/SON for drinking and for discharge into waterbodies, as it inhibits fish growth, plant and bacteria in surface water. High concentration of chloride also leads to breakdown of structural cell and leads to poor yield of crops (Saran *et. al.*, 2023; Flores *et. al.*, 2017). A drop-off in chloride levels to acceptable limits was observed after treatment with both clay types.

The values for heavy metals (Cr, Pb and Cd) in the pre-treated effluent were above the standard values, indicating that it was unfit for drinking and domestic purposes, as exposure to high levels of heavy metals have been implicated in many neurological and hepatological disorders, including Parkinson's disease, Alzheimer's disease, multiple sclerosis and muscular dystrophy (Mohod and Dhote, 2013) and found to induce many toxicities such as hepatotoxicity, neurotoxicity, nephrotoxicity, cardiovascular toxicity and skin toxicity, among others (Mitra, 2022).

The reduction in pollution characteristics is due to the mineralogical composition of clays, chemical composition and high surface area of clays.

4. Conclusion

The tannery effluents discharged from Industrial Estate in Sharadu, Kano State, Nigeria are polluted. The mineral composition of the clays used for this study included saponite, smectite group, chlorite, illite, mixed clay, kaolinite and quartz in varying proportions. The result showed that the concentration of the pollution characteristics studied were higher in the raw effluent samples than the set limits by WHO, SON and NESERA. However, after treatment with clays, these reduced to values lower than the set limits. The findings revealed that clay, a low-cost raw material, which is readily available has potential in wastewater purification, a property linked to their mineral composition.

Conflict of interest

The authors declare no conflict of interest.

Authors' Contributions

EQU designed the study. EQU and OFI conducted the experimental work. EQU, OPU, OFI and OD prepared and edited the manuscript.

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