

## Research Article

# Efficient Heavy Metal Removal from Industrial Wastewater Effluent Using Low-cost Clay Pellets: Case Study of 7-UP Bottling Company

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**Abstract**— Industrial wastewater often contains toxic heavy metals, posing environmental and health risks. This study investigates the efficacy of low-cost clay pellets in removing heavy metals (Pb, Cu, Cd, Zn) from industrial wastewater. Batch adsorption experiments were conducted to evaluate the effects of pH, and temperature. The Clay soil samples collected from “Imiegba” In Etsako East local Government area of Edo State, Benin City, Nigeria were analyzed for their geochemical composition, mineralogical and geotechnical characteristics, x-ray diffraction analysis and index property tests were used to determine the elemental composition, mineralogical nature and geotechnical attributes of the clay. The XRD reveals that quartz (SiO<sub>2</sub>) is the most abundant with an average mean of 48.10% and ranged between 42.83 and 55.78%. Mineralogical analyses reveal kaolinite as the dominant clay mineral with quartz as the dominant non-clay mineral. The geotechnical index test showed that the studied clay particle size distribution is fine-grained with a percentage fine fraction of 99%. The grounded clay samples were later mixed with additive (laterite and limestone) and fired into clay ball pellets. The concentration of some heavy metals, Mn, Cu, Mg, Fe, Zn, Pb, Cd, Cr and Ni, were collected from the discharge outlet pipe of “7-UP Bottling Company in Edo State Benin City”. Samples were analyzed as composite samples and the concentrations of these heavy metals in the effluent were 6.68 mg/l, for Fe, 5.65 mg/l for Zn, 2.23 mg/l for Mn, 2.87 mg/l for Cu, 6.65 for Ni, 1.49 for Cd, 4.53 mg/l for Cr, 1.55 mg/l for Pb. From the different formulations of clay ball pellets after treatments, the study shows that Imiegba clay has a good performance, and proved effective, eco-friendly and economical as an adsorbent for industrial wastewater treatment.

**Keywords**— Clay-pellets, Heavy metals, wastewater-effluent, adsorbent, efficiency

## 1. Introduction

Surface or underground water is one of the environmental materials most exposed to pollution. Large numbers of pollutants are identified in it compared to the number present in its air counterpart. Heavy-metal cations such as Cd<sup>2+</sup>, Cr<sup>3+</sup>, Cr<sup>6+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup> etc., have been identified as the main water pollutants and they are not biodegradable hence accumulate in living organisms thereby causing a variety of disorders, [1]. As a result of intense human activity before now, heavy metal concentration in the environment has increased dramatically. Processes such as chemical, textile and leather industries, metallurgy (ferrous and non-ferrous), electroplating, mining, petroleum refining, fossil fuels and waste burning, all contribute to the problem due to the release into the environment of flue gases, wastewater and wastes from normal activities or accidents, [2]. The water quality in our environment is highly affected

by the discharging of these heavy metals into the water supply. The hazards of these heavy metals are mainly stemmed to their non-degradability and toxicity thereby posing as a pollutant to the environment and imposing health challenges to human life, [3]. The treatment of the wastewater containing these highly toxic heavy metals before discharging into municipal disposal systems is now a great concern for protecting the water in our environment, [4]. Removing these pollutants from water mostly involves their adsorption onto suitable adsorbents. The adsorption technique is effective and practical in the treatment of wastewater containing pollutants owing to its high efficiency, simplicity and the availability of many adsorbents. Activated carbon has been considered one of the most widely used adsorbents for the adsorptive removal of organic compounds and inorganic compounds due to its large specific surface area and high adsorption capacity. Activated carbon is of great importance for contamination control, [5]. However, it is considered a high-cost adsorbent and as such its use as an adsorbent has been constrained, [6].

The Elais-guineensis kernel-activated carbon also known as palm kernel shell has been investigated as an effective adsorbent material for the removal of metals such as copper in wastewater, [7]. The adsorbent capacity of Hevea-brasiliensis seed bark/coat charcoal has been studied for removing toxic metal ions like  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by [8] and it was concluded that the Hevea Brasiliensis bark activated carbon possess the required adsorption capacity and effective adsorbent for the removal of toxic metal ions from an aqueous solution. Following the relatively high cost of materials used as activated carbon for adsorbent applications, a highly available cheap and locally sourced material like clay minerals has been advocated as an effective adsorbent for heavy metal removal. Clay minerals have been noted to be good absorbers of heavy metal ions in solidified water and soil. Clays have been instrumental in many applications such as colloid stabilizers, catalysts, chemical supports, coagulants, sorbents, coatings, cosmetics, moulding and pottery, drilling agents, plastic, construction materials, filling, geological applications, agriculture, etc., [9]. For adsorbent applications for heavy metal removal and other pollutant control, clay minerals have been classified as an effective remediation for contaminated soil, water and other media because of their large surface areas and non-toxic, thus; making them environmentally friendly materials, [10-12]. The adsorption mechanisms that play out in clay minerals have been x-rayed to include; ion exchange, complexation, electrostatic interaction, and bonding, [13, 14]. The clay usually contains bacterial or fungal species, which are significant in assorting the biogeochemical series. As adsorbent materials, clay minerals can adsorb heavy metals in soil and play an important role in the restoration of groundwater.

## 2. Related Work

The use of low-cost pyrrhotite ash/clay-based inorganic membrane for industrial wastewater treatment has been investigated by [15]. The authors concluded based on their findings that the membrane formed using the pyrrhotite ash/clay-based sample is quite efficient for industrial wastewater treatments. The study of the applicability of calcined clay collected from southern Tunisia as an adsorbent bed for heavy metal removal from wastewater has been reported by [16]. The authors suggested that the obtained results can be extended to the industrial usage for cleaner water production in southern Tunisia where there are high rates of industrial effluent discharge to the water system. The use of sand, gravel and a variety of natural clay minerals such as zeolite, diatomite and bentonite as package materials for pollutant removal from wastewater for irrigation purposes in Egypt has been investigated and reported by [17]. Their analysis results were higher than the values stipulated by the Egyptian and international licenses. Still, the treatment of drainage water using the clay sample appeared very feasible. [18], has studied the treatment of industrial effluents using fortified soil-clay column samples and reported that clay samples have high potential for regular and industrial wastewater treatment. The treatment efficiency is directly related to the mineralogical assemblage. Significant improvement in water quality could be achieved if more than

one column is employed. The authors argued that fortified soil clays have the potential to be used to remove contaminants in industrial wastewater. However, the long-term effectiveness of using the sample should be determined by carrying out further pilot-scale studies. The adsorption capacities of different ratios of clay, zeolite and activated carbon mixture in heavy metal removal in wastewater effluent from the pulp and paper industry have been reported by [19]. It was discovered that the mixture with a concentration highly suited for the reduction of heavy metals can be achieved with the 6:3:1 adsorbent ratio at a maximum contact time of 150 minutes. The authors concluded that zeolite/activated carbon-ceramic composite can be well positioned as an alternative adsorbent material for wastewater treatment. A comprehensive review of the application of clay minerals as adsorbents for removing heavy metals from the environment has been carried out by [20]. It was gathered that in addition to the use of clay minerals as adsorbent, it can serve as an ideal catalyst carrier material. The authors revealed that various features of clay minerals can be improved for effective heavy metal removal by modification of clay minerals and this plays very important role in wastewater treatment and soil remediation. This study aims to examine the removal of some heavy metals from industrial effluents using clay pellets by optimizing the treatment conditions.

## 3. Experimental Method

The materials used in this study include clay samples, Wastewater with concentrations of heavy metals, laterite and limestone. Systematic sampling methods were used in collecting the clay sample deposit. The clay samples were collected from freshly exposed surfaces in sealed polythene bags to prevent contamination and loss of moisture and were coded as  $\text{IM}_A$ ,  $\text{IM}_B$ , and  $\text{IM}_C$  respectively. Three samples were collected vertically of each bed from top to bottom in an upward coarsening sequence, the bottom was made up of dark shale of fine grain texture, as a result of high organic content, and the middle was brownish sandy shale because of oxidation and high content of iron, while the top is coarse sandstone of medium grained and are white to yellow coloured. The samples were air-dried, ground to powder with mortar and pestle and sieved with a laboratory sieve. The Wastewater effluent samples were collected from industrial waste sources at 7-UP Bottling Company in Benin City, Edo state Nigeria. These samples were collected and immediately taken to the laboratory for testing. The testing done includes; Mineralogical analysis, Chemical analysis and Geotechnical analysis testing. The Mineralogical analysis was performed to determine the quantitative mineralogical properties of the clay samples using the X-ray diffraction method (Rigaku D/Max-111C X-ray diffractometer Rigaku Int. Corp. Tokyo, Japan). The Chemical analysis was carried out using the XRF technique to determine the elemental abundances of the samples and some trace elements using a phillips PW1606 X-ray Fluorescence Spectrometer. The samples were analyzed for major element oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{k}_2\text{O}$  and  $\text{MnO}$ ) in percentage while Mn, Ni, Co, Cr, and Zn were analyzed in part per million. The Geotechnical test was done to determine the geotechnical properties of clay

samples. The various analyses carried out include the determination of grain size distribution, moisture content, Atterberg limit using Casagrande Instrument (liquid limit, plastic limit and plasticity index), specific gravity, natural moisture content and linear shrinkage. The laboratory analyses were carried out according to British Standard Methods of Testing for soils for civil engineering purposes. (BS 1377: part 2: 1990). The liquid limit, plastic limit and plasticity index of clays are also used extensively, to correlate with engineering behaviour such as compressibility, permeability, compatibility, shrink-swell and shear strength and to specify the end product materials.

### 3.1. Clay Ball Pellets Preparation and Formulation

In the preparations of ball pellets for the experimental investigation, laterite and limestone were used as pore-forming agents which were later mixed with the clay. Four different clay ball pellet formulations were produced from the mixed clay. However, formulation 1 was not mixed with laterite and limestone is as follows.

#### Formulation 1:

- Weigh 100 g of clay.
- Form the clay into pellets without adding any laterite or limestone.

#### Formulation 2:

- Weigh 50 g of clay.
- Weigh 50 g of laterite.
- Mix the clay and laterite thoroughly.
- Form the mixture into clay ball pellets.

#### Formulation 3:

- Weigh 250 g of clay.
- Weigh 200 g of laterite.
- Weigh 50 g of limestone.
- Mix the clay, laterite, and limestone thoroughly.
- Form the mixture into clay ball pellets.

#### Formulation 4:

- Weigh 200 g of clay.
- Weigh 100 g of laterite.
- Weigh 200 g of limestone.
- Mix the clay, laterite, and limestone thoroughly.
- Form the mixture into clay ball pellets.

These clay ball pellets formed are presented in figure 1.



Figure 1. Formulation of the 4 different clay ball pellets with laterite and limestone

### 3.2 Wastewater Treatment Test Experiment

It is known that water does not percolate through clay easily. Clay ball pellets were mixed with laterite and limestone which act as flux and also to aid water percolation. Aside from their functions as a percolation aid, the clay ball additive also acted as an inert media for microbial attachment and growth. Therefore, microorganisms are partially retained in the system as the water passes through. The clay minerals found in the clay samples investigated are kaolinite, Illite and Smectite. Kaolinite is not swelling clay; illite shows intermediate swelling between kaolinite and the swelling clay. Swelling reduces the pore spaces in clay structures, which in turn affects the permeability of solvents. The higher the swelling rate of any clay type when soaked in water, the lower the permeability, laterite and limestone were introduced to the clay to act as additive and reduce the swelling capacity. A small multi-component system experiment was made for the water effluent treatment using the different clay ball pellet formulations as adsorbents. In order to assess the treatment potential of each different clay ball pellet formulation, a litre of the wastewater effluent sample was made to pass through the clay ball pellets in the multi-component system experiment. To test the adsorption capacity between the raw effluent and the treated effluent, the raw effluent (adsorbate) was soaked with the different clay ball pellets (adsorbent) at ambient temperature for 48 hours in which the effluent was made to pass through the different clay ball pellet formulations by gravity flow. The treated effluent was collected from the outlet of the different clay formulations and analyzed for various water characteristics. The result of the raw and treated effluent is shown in Table 5.

### 4. Results and Discussion

#### 4.1 Chemical Analysis of the Clay Samples

Table 1: Geochemical analysis result

Samples	IM <sub>A</sub>	IM <sub>B</sub>	IM <sub>C</sub>	Mean	Range	LAS
Elemental Oxide	(%)	(%)	(%)			(%)
SiO <sub>2</sub>	42.83	45.70	55.78	48.10	42.83-55.78	52.97
Al <sub>2</sub> O <sub>3</sub>	32.21	35.20	35.24	34.22	32.21-35.24	28.42
Fe <sub>2</sub> O <sub>3</sub>	1.04	0.08	0.77	0.63	0.08-1.04	3.65
TiO <sub>2</sub>	0.06	0.05	0.05	0.05	0.05-0.06	1.14
CaO	0.14	0.11	0.04	0.09	0.04-0.11	1.85
P <sub>2</sub> O <sub>5</sub>	0.06	0.01	-	0.04	0.01-0.06	-
K <sub>2</sub> O	1.95	1.60	0.62	1.39	0.62-1.95	0.94
MgO	0.04	0.06	0.05	0.05	0.04-0.06	0.08
Na <sub>2</sub> O	0.36	0.25	0.29	0.30	0.25-0.36	0.05
LOI	12.44	12.40	12.42	12.42	12.40-12.44	10.20
CIA	92.90	94.70	97.40	95.00	92.9-97.40	90.9
CIW	98.50	99.20	99.10	98.9	98.5-99.20	93.7
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	53.70	70.40	70.40	64.83	53.7-70.40	24.9

Table 2. Chemical analysis of the clay samples (trace element concentration in ppm)

Trace elements	IM <sub>A</sub>	IM <sub>B</sub>	IM <sub>C</sub>	LAS
Ba	614.86	662.63	670.62	662.67
Cu	27.26	28.26	28.33	28.36
Cr	115.2	114.20	112.40	100.30
Ni	30.55	31.45	32.55	31.65
Zn	211.46	210.44	209.4	210.39

#### 4.2 Mineralogical Composition of Clay Deposits

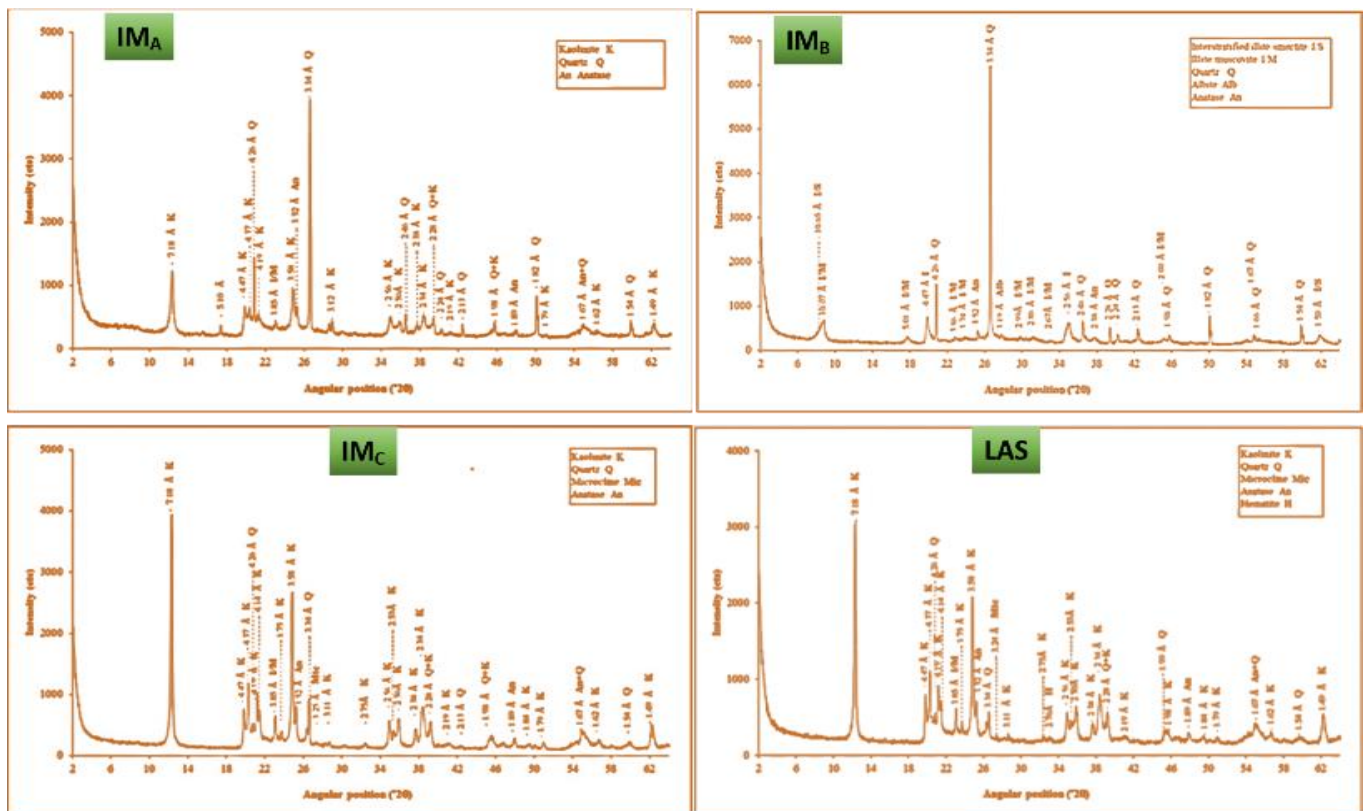


Figure 2: X-ray diffractogram of the Imiegba clay deposit and laterite samples (IM<sub>A</sub>, IM<sub>B</sub>, IM<sub>C</sub> and LAS)

**Table 3.** Mineralogical composition of Clay deposit

Samples	Composition
IM <sub>A</sub>	Kaolinite, Quartz, Anatase
IM <sub>B</sub>	Illite/Smectite, Illite/Muscovite, Quartz, Albite, Anatase
IM <sub>C</sub>	Kaolinite, Quartz, Microcline, Anatase
LAS	Kaolinite, Quartz, Microcline, Anatase, Hematite

IM – Imiegba clay

LAS – Laterite

**4.3 Geotechnical Characteristics**

**Table 4: Geotechnical characteristics of the studied clay samples**

Clay samples	Particle size Distribution			Fine %	Atterberg Limit				Natural moisture content %	Specific Gravity	Swell test
	Clay %	Silt %	Sand %		Liquid limit %	Plastic limit %	Plasticity index %	Linear shrinkage %			
IM <sub>A</sub>	63	36	1	99	56.0	20.19	35.81	11.40	0.10	2.26	100
IM <sub>B</sub>	65	34	1	99	60.0	20.62	39.38	11.86	0.11	2.06	30
IM <sub>C</sub>	58	41	1	99	51.50	15.70	35.80	11.84	0.42	2.12	37

**Table 5: Results of Raw and Treated Industrial Wastewater Effluent Compared to WHO and FEPA (1991) Standards**

Parameters	Raw Effluent	Results After Treated				WHO	FEPA 1992
		Form 1 Clay	Form 2 Clay+LAS	Form 3 Clay+LAS+Lime	Form 4 Clay+LAS+Lime		
pH	5.12	5.06	5.55	5.82	6.1	6.5-8.5	6.9
EC	312	1900	880	1140	2400	100	400
Fe <sup>3+</sup>	6.68	1.69	1.58	1.04	1.74	0.3	20
Zn <sup>2+</sup>	5.65	2.15	1.81	1.74	0.64	5	<1
Mn <sup>2+</sup>	2.23	0.92	0.71	1.85	0.72	0.1	5
Cu <sup>2+</sup>	2.87	1.28	1.36	2.25	0.11	1	<1
Ni <sup>2+</sup>	6.65	3.1	2.88	3.56	1.48	0.05	<1
Cd <sup>2+</sup>	1.49	0.02	0.23	0.09	0.12	0.005	<1
Cr <sup>6+</sup>	4.53	0.65	0.77	0.48	1.43	0.05	<1
Pb <sup>2+</sup>	1.55	0.08	0.54	0.34	0.12	0.04	<1

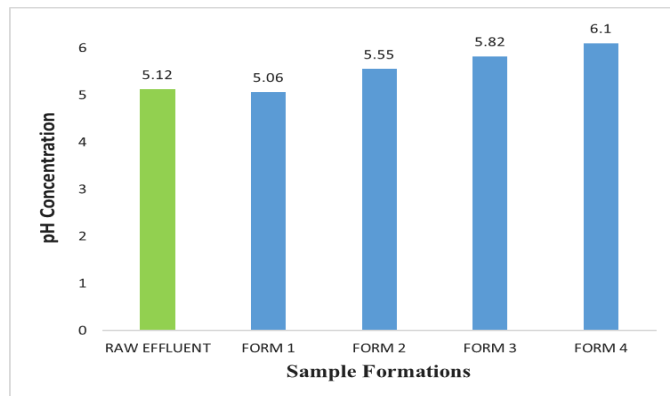
FORM-FORMULATIONS, LAS-LATERITE, LIME-LIMESTONE

**4.4 Treatment of the Industrial Effluent**

**Table 6.** The percentage reduction of the treated wastewater effluent

Parameters	Raw Effluent	Form 1 Clay %	Form 2 Clay+LAS %	Form 3 Clay+LAS+Lime %	Form 4 Clay+LAS+Lime %
Fe <sup>3+</sup>	6.68	74	76	84	73
Zn <sup>2+</sup>	5.65	61	67	69	88
Mn <sup>2+</sup>	2.23	58	68	17	67
Cu <sup>2+</sup>	2.87	55	52	21	96
Ni <sup>2+</sup>	6.65	53	56	46	77
Cd <sup>2+</sup>	1.49	98	84	93	91
Cr <sup>6+</sup>	4.53	85	83	89	68
Pb <sup>2+</sup>	1.55	94	65	78	92

FORM – FORMULATIONS, LAS- LATERITE, LIME- LIMESTONE



**Figure 6.** pH concentration of the wastewater effluent

**Discussions**

Table 1 and 2 present the results of the chemical analysis of the collected clay samples showing the different oxide forms of the major elements contained in the clay samples. The results showed the major element oxide compositions and the calculated Weathering Indices of the clay samples in the study area are shown in Table 1. The results indicate that quartz (SiO<sub>2</sub>) is the most abundant with an average mean of 48.10% and ranged between 42.83 and 55.78%. Table 1 also showed that the major oxides apart from SiO<sub>2</sub>, include Al<sub>2</sub>O<sub>3</sub> with an average mean of 34.22% while TiO<sub>2</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, and N<sub>2</sub>O<sub>5</sub> were present in the clays only in small amounts. Iron as Fe<sub>2</sub>O<sub>3</sub> in the Imiegba clay sample is less than 2% while that of Laterite is greater than 2%. The

values for K<sub>2</sub>O varied from 0.62 to 1.95% of the sample with an average mean of 1.39% and shows the presence of illite. The low amount of MgO and CaO shows the absence of associated carbonate or dolomitization process in the study area. Table 2 presents the result of the chemical analysis showing the different trace elements contained in the clay samples which are expressed in part per million (ppm). This includes Cu, in the range of (27.26 – 28.36), Cr (100.30 – 115.2), Ni (30.55 – 32.55), and Zn (209.4 – 211.46). The concentration amount of Cu and Ni are very low which will not imply any coloration.

The results obtained from the X-ray diffraction analysis are presented in Figure 2 and a summary of the X-ray results of mineralogy is presented in Table 3. The results of the mineralogical composition of the clay revealed that kaolinite, illite, smectite, albite, and anatase are the predominant clay minerals. Other minerals include quartz, microcline, muscovite, and accessory minerals such as hematite. Although quantitative analysis was not carried out, the diffractogram indicates that kaolinite was present in Imiegba clay A and C and also present in the Laterite deposits but only Imiegba clay B was found to contain variable amount of illite/smectite and illite/muscovite which are absent in Imiegba clay deposit A, C and laterite. This could be an indicative that the imiegba clay deposits were deposited at different time during their time of formation.

The results of the basic geotechnical characteristics of the studied clay samples are presented in Table 4. The particle size distribution of the studied clay indicated that the clay is a fine-grained with percentage fine fraction of 99%. The clay is generally light grey to brownish grey in hand specimens and turns brownish on firing. Other physical properties exhibited are liquid limit (55.8%), plasticity index (36.9%), and linear shrinkage (11.7%).

Physical properties, mineralogical, chemical composition and clay pellets formulations were the parameters used for heavy metal treatment from industrial wastewater effluent. Sample treatment was carried out using low-cost clay pellets as a treatment reagent. The results of the raw and treated effluent were compared to the Environmental standards for effluent limitation of the World Health Organization (WHO) and Federal Environmental Protection Agency (FEPA) as shown in Table 5. The results of the raw effluents show that all the heavy metals were higher than the recommended standard, while great reductions from the heavy metals were observed after the effluent was treated with the different clay balls pellet formulations, though not all the treated heavy metals from the waste effluent fall below the WHO and FEPA recommended standard, this could be as a result of the 48hourly of the effluent subjection to the clay balls pellets. The results of the experiment carried out to assess the percentage removal of the pollutants from industrial effluents at different levels of adsorbents are presented in Table 6. The removal efficiency of the treated effluent for all the metal ions was calculated as adsorption percentages as provided by [21, 22].

$$\text{Adsorption}(\%) = \frac{A-B}{A} \times 100 \quad (1)$$

Where A is the concentration of the raw effluent and B is the concentration of the treated heavy metals.

Due to the high concentration of some of the parameters obtained from the industrial effluents which were higher than the WHO, the effluent was treated with clay pellets of different formulations to reduce the concentrations of these parameters to acceptable limits. Pure clay (FORM 1), Clay mixed with laterite (FORM 2), Clay mixed with laterite and limestone (FORM 3) and Clay mixed with laterite and limestone (FORM 4) were utilized for the effluent treatment. The percentage reduction of the effluents is shown in Table 6. A general decrease in the concentration of all the metals was recorded for all the clay pellet formulations in the treated effluent. Similarly, decreases in heavy metal concentration from contaminated solutions after clay treatments have been reported [23]. The clay ball pellets formulation 3 was found to be more effective for the reduction of iron concentration Fe<sup>2+</sup>, concentration from 6.68 - 1.04 mg/l (84% removal). However, the clay ball pellets were generally found to be at its best performance in the effluent treatment. A great reduction in the Cu<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>2+</sup>, and Pb<sup>2+</sup> concentration of the effluent was obtained for all the clay ball pellet formulations used in the treatment. The treatment with clay pellets formulation 4 was found to be the best adsorbent for the removal of Cu<sup>2+</sup> concentration for the effluent with a high reduction from 2.87mg/L – 0.11mg/l (97% removal), while clay pellets formulation 1 was found to be best for the reduction of Cd<sup>2+</sup> concentration from 1.49 – 0.02mg/l (98% removal), clay pellets formulation 3 was also found to be best for the reduction of Cr<sup>2+</sup> concentration from 4.52 – 0.48mg/l (89% removal), and clay pellets formulation 1 was best suited for the reduction of Pb<sup>2+</sup> concentration which reduces from 1.55 to 0,8mg/l (94% removal). Analysis of the effluent also showed clay pellets formulation 4 gave a reasonable reduction of Zn<sup>2+</sup> concentration from 5.65 to 0.65 mg/l (88% removal) and formulation 2 gave the best reduction of Mn<sup>2+</sup> concentration from 2.23 to 0.71mg/l (68% removal), while formulation 4 also gave a better reduction of Ni<sup>2+</sup> concentration from 6.65 to 1.48mg/l (77% removal). The result showed a significant decrease in Fe<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>2+</sup>, and Pb<sup>2+</sup> after treatment with clay ball pellets which were slightly below the WHO and FEPA standards.

The pH of the raw effluent 5.12mg/l was below the WHO and FEPA recommended standard and after treatment, the pH for formulation 1 decreased while formulations 2, 3, and 4 increased as shown in figure 6. The increase in pH for formulations 2, 3, and 4 results from the additives (laterite and limestone). Limestone has the chemical composition of CaCO<sub>3</sub>. When the limestone reacts with water (H<sub>2</sub>O) it forms calcium hydroxide that dissolves in water as a soda and hydrogen gas, leading to an increase in the pH.

## 5. Conclusion and Future Scope

This work studied the use of clay ball pellets to remove heavy metals from industrial waste effluents, and it proved to be a

very viable alternative material for treating industrial wastewater effluents with heavy metals. The removal of the heavy metals from industrial wastewater through the formulations of different clay ball pellets was done for 48 hours of treatment with the effluents and indicated that the heavy metal concentration was favorably adsorbed. The heavy metals and their range of percentage in concentration for heavy metals in industrial wastewater includes; Fe<sup>2+</sup> (73 - 84%), Zn<sup>2+</sup> (61 - 68%), Mn<sup>2+</sup> (17 - 68%), Cu<sup>2+</sup> (21 - 96%), Ni<sup>2+</sup> (46 - 77%), Cd<sup>2+</sup> (84 - 98), Cr<sup>2+</sup> (68 - 89), and Pb<sup>2+</sup> (68 - 94%). The adsorbent materials were found to show good adsorption capacity for all the metal ions under the study with clay formulations 1 and 4 having adsorption capacity for percentage reduction of 56% and 96% for Cu<sup>2+</sup>, 91% and 98% for Cd<sup>2+</sup> and 92% and 94% for Pb<sup>2+</sup>. Formulations 2 and 3 showed a percentage reduction capacity of 76% and 84% for Fe<sup>2+</sup> and 83% - 89% for Cr<sup>2+</sup>. Formulation 4 also gave a better performance of % reduction for Zn<sup>2+</sup> (88%) and Ni<sup>2+</sup> (%), while formulation 2 gave a better % reduction for Mn<sup>2+</sup> (68%). Formulation 3 gave a poor % reduction for Mn<sup>2+</sup>(17%), Cu<sup>2+</sup> (21%) and Ni<sup>2+</sup> (46%) indicating that the ratio of the mixed clay with laterite and limestone is not good enough for heavy metals treatment. The comparison of these results with the WHO and FEPA standards for heavy metal concentrations showed that not all the treated heavy metals concentration meets the FEPA and WHO standards of heavy metals even after treatment. This can be attributed to the short time of 48 hours of wastewater treatment with the sample and hence more time could be given for the treatment to achieve a 100% reduction.

### Conflict of Interest

Authors declare that they do not have any conflict of interest.

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### Authors' Contributions

The first and second authors sourced for the raw materials and performed the various analysis tests. The third and fourth authors contributed to the analysis of data obtained. The fifth and sixth authors drafted the first part of the manuscript subject to review by the seventh author. All authors reviewed and edited the manuscript and approved the final version of the manuscript in accordance to the journal template.

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### References

[1] M. Ahmaruzzaman, "Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals," *Advances in colloid and interface science*, Vol.166, No 1-2, pp. 36-59, 2011.

[2] N. Ng, A.S.A. Keyon, W.A.W. Ibrahim, M.M. Sanagi, Z.A. Sutirman, F.M. Marsin, "Amino-functionalised chrysin as

adsorbent in dispersive micro-solid phase extraction of selected heavy metal ions from stingless bee honey", *Journal of Food Composition and Analysis*, Vol.123, pp. 105561, 2023.

[3] G. Gupta, J. Khan, N.K. Singh, "Application and efficacy of low-cost adsorbents for metal removal from contaminated water", *A review. Materials Today: Proceedings*, Vol. 43, pp. 2958-2964, 2021.

[4] A. Tripathi, M.R. Ranjan, "Heavy metal removal from wastewater using low cost adsorbents", *Journal of Bioremed Biodeg*, Vol. 6, No 6, pp. 315, 2015.

[5] A. Tripathi, M.R. Ranjan, "Heavy metal removal from wastewater using low cost adsorbents", *Journal of Bioremed Biodeg*, Vol. 6, No 6, pp. 315, 2015.

[6] I. Ali, M. Asim, T. A. Khan, "Low cost adsorbents for the removal of organic pollutants from wastewater", *Journal of Environmental Management*, Vol. 113, pp. 170-183, 2012.

[7] M. Ghaedi, N. Mosallanejad, "Removal of heavy metal ions from polluted waters by using of low-cost adsorbents", *Journal of Chemical Health Risks*, Vol. 3, No 1, pp. 07-22, 2013.

[8] N. D. Tumin, A. L. Chuah, Z. Zawani, S. A. Rashid, "Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon", *Journal of Engineering Science and Technology*, Vol.3, No. 2, pp. 180-189, 2008.

[9] D. Abilasha, L. Lisy, "Studies on the adsorption characteristics of Hevea Brasiliensis seed coat charcoal on Cu (II) & Zn (II) Ions", *International Journal of Advanced Science and Research*, Vol. 1, No. 11, pp. 08-12, 2016.

[10] S.C. Aboudi Mana, M.M. Hanafiah, A.J.K. Chowdhury, "Environmental characteristics of clay and clay-based minerals", *Geology, ecology, and landscapes*, Vol.1, No 3, pp. 155-161, 2017.

[11] V. Zotiadiis, A. Argyraki, "Development of innovative environmental applications of attapulgite clay", *Bull. Geol. Soc. Greece*, Vol. 47, No 2, pp. 992-1001, 2013.

[12] M. Vhahangwele, G.W. Mugeru, "The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: Simultaneous sorption of Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions", *J. Environ. Chem. Eng.* Vol. 3, No 4, pp.2416-2425, 2015.

[13] M.K. Uddin, "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade", *Chem. Eng. J.* Vol. 308, pp. 438-462, 2017.

[14] B.O. Otunola, O.O. Ololade, "A review on the application of clay minerals as heavy metal adsorbents for remediation purposes", *Environmental Technology & Innovation*, 100692, 2020.

[15] S. Xie, L. Huang, C. Su, J. Yan, Z. Chen, M. Li, M., ... H. Zhang, "Application of clay minerals as adsorbents for removing heavy metals from the environment", *Green and Smart Mining Engineering*. Vol. 1, pp. 249-261, 2024.

[16] B. Hatimi, J. Mouldar, A. Loudiki, H. Hafdi, M. Joudi, E.M. Daoudi, M. Bakasse, "Low-cost pyrrhotite ash/clay-based inorganic membrane for industrial wastewater treatment", *Journal of Environmental Chemical Engineering*, Vol. 8, No 1, pp. 1-11, 2020.

[17] L. Khalfa, A. Sdiri, M. Bagane, M.L. Cervera, "A calcined clay fixed bed adsorption studies for the removal of heavy metals from aqueous solutions", *Journal of Cleaner Production*, Vol. 278, 123935, 2021.

[18] E.E. ElBastamy, L.A. Ibrahim, A. Ghandour, M. Zelenakova, Z. Vranayova, M. Abu-Hashim, "Efficiency of Natural Clay Mineral Adsorbent Filtration Systems in Wastewater Treatment for Potential Irrigation Purposes", *Sustainability*, Vol. 13, 5738, 2021.

[19] N. A. Oladoja, C.M.A. Ademoroti, I. O. Asia, "Treatment of industrial effluents using fortified soil clay", *Desalination*, Vol. 197, No 1-3, pp. 247-261, 2006.

[20] T. Aprianti, S. Miskah, S. Selpiana, R. Komala, S. Hatina, "Heavy metal ions adsorption from pulp and paper industry wastewater using zeolite/activated carbon-ceramic composite adsorbent", *In AIP Conference Proceedings*, Vol. 2014, No 1, 2018.

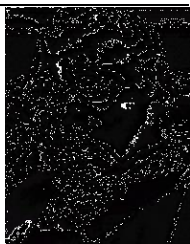
[21] S. Xie, L. Huang, C. Su, J. Yan, Z. Chen, M. Li, H. Zhang,

“Application of clay minerals as adsorbents for removing heavy metals from the environment”, *Green and Smart Mining Engineering*, 2024.

- [22] H. Bahmanpour, R. Habashi, S.M. Hosseini, “Investigating the efficiency of lightweight expanded clay aggregate (LECA) in wastewater treatment of dairy industry”, *Anthropogenic Pollution*, Vol. 1, No 1, pp. 9-17, 2017.
- [23] I. Sreedhar, N.S. Reddy, “Heavy metal removal from industrial effluent using bio-sorbent blends”, *SN Applied Sciences*, Vol. 1, pp. 1-15, 2019.
- [24] E.I. Unuabonah, B.I. Olu-Owolabi, K.O. Adebowale, L.Z. Yang, “Removal of lead and cadmium ions from aqueous solution by polyvinyl alcohol-modified kaolinite clay: a novel nano-clay adsorbent”, *Adsorption Science & Technology*, Vol. 26, No 6, 383-405, 2008.

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