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Low cost adsorbent to reduce pollutants in Owa-Adlidinma, influence of oil flow station Southern Nigeria

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Abstract
The capacity of kaolin clays from UR (Udophori) OZ (Ozanagogo) and AU(Auchi) for removal of pollutants from wastewater and run-off at Owa-Alidinma. X-ray diffractometer, ultraviolet /visible spectrophotometer and Atomic Absorption spectrophotometer were used for analysis of clays and pollutant. Percolation rate studies and performance efficiency was carried out to choose the best combination ratio of pebble/clay ratio (1:3) was found suitable using batch and continuous columns treatment methods using standard methods of analysis Oz clay type gave the best result from the four continuous treatment cloums. The batch and continues treatment were tried. Oz clay type gave the best result for the reduction of pollutants using the four continuous columns, for batch treatment turbidity (5.16-17.67%) Biological Oxygen Demand (BOD) (4.11-14.93%), Chemical Oxygen Demand (COD) (7.16-15.75%), phosphorous (5.33-15.78%), Nitrates (4.00-9.70%), Iron (Fe) (21.00-26.00%), Chromium (Cr) (30.00-16.12%), Copper (Cu) (15.00-24.49%) and Zinc (Zn) (6.20-13.40%) reduction, while for continuous column treatment, BOD (89.73-95.54%), COD (86.50-90.35%), phosphate (77.10-84.82%), Fe (86.50-91.00%), Cr and Zn not detected, Cu (94.78-96.10%) respectively. Final effluent characteristics were found to be comparable with World Health O,rganisation (WHO), Standard Organisation Nigeria (SON) and National Environmental Standard and Regulation Enforcement Agency (NESREA) standards for various purposes. This method is low energy consuming, easy to manipulate and can alleviate the problem of fresh water shortage in these areas and access to potable water

Keywords: Adsorption clay, Low cost, Oil station, Pollutants

1. Introduction

Water is essential for all socio-economic development and for maintaining healthy ecosystems. Water is vital to life, it is a transport medium, participant, solvent and catalyst in nearly all chemical reactions. The mammoth demand for clean water has always been met by tapping ground (borehole) water from its ciquifers, but the sudden realization that the supply is not inexhaustible has awakened researchers to device sustainable means of water/waste water treatment for reuse (Zohre et al, 2021). This have resulted in varying treatment processes to cater for its water needs. Different types of materials have been used in on-site wastewater treatment in percolator systems “Koba yashi et al 2017) like slag, ground stones, sand and straws (Pawar et al, 2016) (Ahamd, et al, 2018) but these processes are expensive.

Heavy metals are toxic even at low concentrations resulting in accumulative poisoning, destroy liver, cancer and brain damage when found above the tolerance level (Tingting et al., 2021; Meena et al., 2023) that the removal of Cd(11), Pb(11), Hg(11) and Cu(11) and Zn(11) is depended on concentration, Ph, contact time and type of adsorbent.

Nitrate consuming from water or through plant in food chain may increase risk of thyroid disease, diabetics and certain types of cancers, people with heart or lung diseases, certain inherited enzyme defects may be more sensitive to the toxic effects of nitrates than healthy individuals (Tian et al, 2019), (Rezvani et al, 2021). Nitrates which are also a limiting factor to Eutrophication if present above the normal level, can causes algae bloom (Shalyari et al, 2019). This deprives the water body of dissolved oxygen which affects aquatic organisms (Badeenzhad et al, 2019).

A lot of research has be done on wide varieties of low cost sorbent Zeolite, bentonite. In order to assuage the scourge resulting from lack of adequate and sustainable potable water, developing countries require the use of high-performance, low cost, simple low energy consuming decentralized wastewater treatment technology to control pollution in the environment and alleviate escalating water shortage caused by water pollution. The chemist views the clay as catalyst, adsorbent, filter and are fine grain size with platey shape with its peculiarities of the crystal structure give it opportunity for adsorbing ions in a variety of ways (Umudi, 2021).

Heavy metals are potential health and environmentally hazardous materials that are toxic at low concentrations. Accumulative poisoning, destroying vital organs when found above the tolerance level. Other pollutants can disrupt the natural ecosystem i.e. depletion of oxygen, additional nutrients to the water body (Umudi, 2022). Presently, chemical precipitation, extraction, reverse osmosis are been used for pollutant removal. Adsorption with clays is economical, simple and friendly with the environment (Cui et al, 2020). It is a simple decentralized wastewater purifying system with smooth stone pebbles to improve soil (clay) permeability which have restricted it's us as percolating medium.

Recent study informs us about materials used to reduce parameter. (pollutants) in water/waste water (Neswir, 2016). Bentonite clay is a potential low-cost adsorbent of such using adsorption system. Zeolite is also an adsorbent gaining attention in environmented protection and sustainability (Mohammed, 2019). Bentonite is more absorbing because the size of colloidal particles is very small with high ion surface capacity. Severl studies have been applied to absorption of inorganic elements such as Cd2+ Pb2+, Cu2+, Mn2+, Ni2+ and Fe (its used in BOD and COD removal have been modelled) (Dare Jeh, N, et, al 2016). There is also information about the adsorption of heavy metal ions from water and waste water using various nanostructured adsorbents as kaolinites, montrmorillonit and bentonites carbon nanotubes (Vijay, et al, 2019; Minglin et al., 2021). However numerous workers have done research for the removal of these pollutants and various clays and modified clays have been used extensively for this purpose (Niraman, and Bernad, 2023). But all identified adsorbent materials are not able to remove pollutants after certain concentration and contaminants are left behind to create other environment issues and have low cost of operation.

This study uses a purifying column system of stone pebbles/clay for the removal of pollutants, using batch and continuous treatment method. This study Owa-Alidinma in Ika North East Local Government area of Delta State in Nigeria latitudes in Agbor. It lies within latitude 5, 45N of the equator and between longtitudes 5o31i and 6o 141 East of the Greenwich mendian. North by Edo State and Ika South Local Government Area. Aniocha North and South Local Government Area. Eastern boundary. It lies between Orogodo and Namiah rivers both flows into the coast and dictate the social economic lives of the people characterized by undulating lowlands, sand, loamy soil for agricultural purpose.

2.0 Material and methods

2.1 Sample collection and preparation

Three locally available adsorbents kaolin clays were collected from different locations in Nigeria-Agbor (Ozanogogo), Uduophori (Bomadi) and Auchi (Edo State) and were coded as OZ, U and AU respectively, fig 1 map of Delta State showing Owa-Alidima in Ika North East they were air dried, Pu verized using pestle in the laboratory mortar. The powdered samples were sieved weighed and Ozanogogo latitude 61-8o-61 10oN and longitude61-6o- include longitude and 61 17oE of Delta State.

Uduophi in Bomadi Local Government Area is on coordinates of latitude 5o 101o1N and 5, 55o oE longitude and Auchi in Edo State. 71 41 07104N1 and 61 29.1828o6 clays analysis was done using a PW 1800 automated powder diffraction equipped with a Cu-K & radiation source. The diffraction patters were obtained with the aid of a computer, 20, d-values and peak intensities yielded by the powder patterns were used to identify the minerals. Small stone pebbles were collected from Oviorie-Ovu river site from dredging sites in

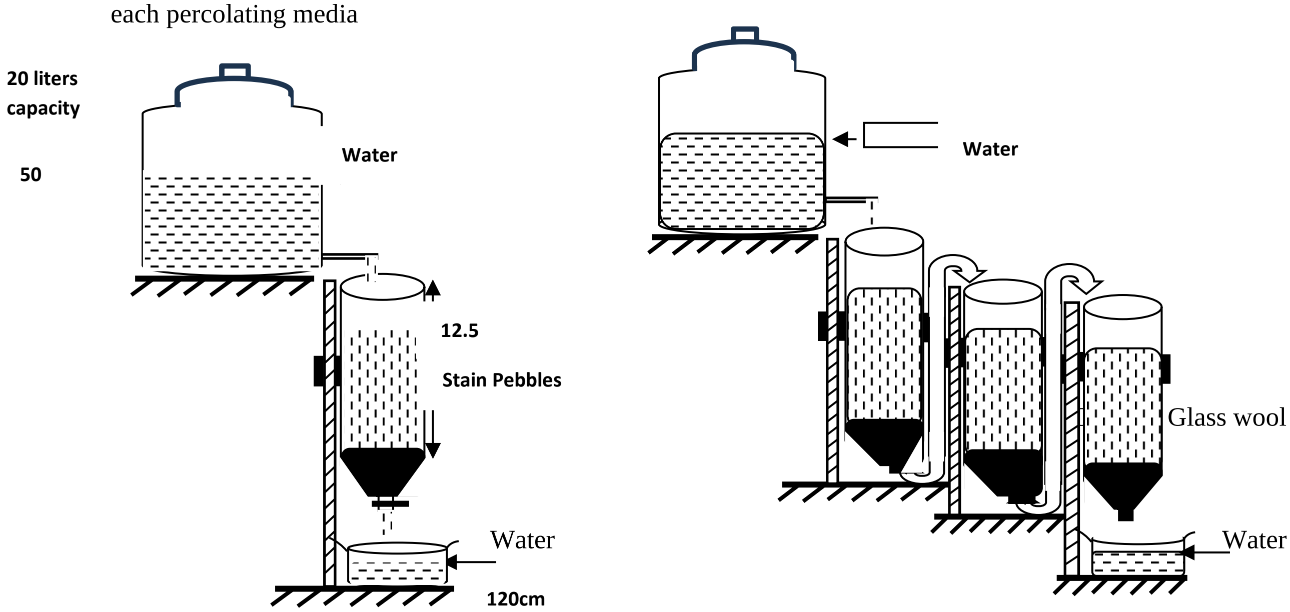
Ethiope East Local Government area of Delta State. They were washed under running tap, air dried and stored in polyethene bags.

Water samples were collected from convenient points on the streams, they were collected in 20 litres plastic sterile containers at hourly interval. The flow rate was measured with a flow meter. A composite sample was made by mixing together 12 separate hourly samples using proportion according to their flow rates. The pH determinations were carried out on the field and dissolved oxygen was fixed as directed by (Akinyele and Shonkubbi, 2017) in standard method using HACH pH metre HQ20 and HACH, DO metre, the pH values were maintained between 4.00 and 6.0 to prevent precipitations as hydroxides. Plastic vats were made with columns of plastics with height of 120cm with a diameter of 12.5cm. class wool was well packed to a depth of 4cm into the base; finally, carefully mixed quantities of pebbles and clay were carefully loaded to 70cm mark in ratio 1:3 for both batch and continuous treatment methods.

2.2 **Sample Analysis**

The samples (clays) were pulverized, 2.0g was measured and mixed with sodium-based coagulant and paste smeared on a thin layer into the X-ray. The dried past was later heated to burn off friable substances. The diffractometer cross-matched the peaks and came out with the mineral constituents using soft XSPEX version 5.62. Geometric Geochemical analysis was done using concentrated hydrofluoric acid (HF) and perchloric acide acid HCO4 for digestion using Atomic Absorption Speetrophotometer (Buck scientific Model 200A). Turbidity was done by Nepohelmetric method using HACH 2100P, HACK cension 5 Turbidimeter. Conductivity using Thermo oriental conductivity meter, while Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand was by standard methods, posphorous by ascorbic acid method and nitrate by colourimetric method using sodium salilate using DR4000V spectrophotometer. Cationic Exchange Capacity C.E.C by Zhoa, et al., (2016). Percolation rate was done to determine the residence time of wastewater in each percolating media

each percolating media



Batch Treatment Continuous Treatment

2.3 Statistical Analysis

The obtained results were analyzed using SPSS windows version 19 (SPSS Inc. Chicago, II) range, mean percentage reduction of the pollutant.

3.0. Results and Discussions

Table 1. Mineralogical composition of clays.

Clay mineral	OZ	UR	AU
Saponite	1.00	3.4	Nil
Montmonllonite (Smeetite group)	29.3	6.1	1.20
Chloride	2.0	21.3	3.10
Iuite	8.3	5.2	9.10
Mixed layer	17.4	23.4	3.00
Kaollinite	40.02	28.2	46.20
Quartz	10.9	12.4	31.20
Hematite	6.00	Nil	6.20

Table 2. Percentage composition of oxides from geochemical Analysis.

% oxide	OZ	UR	AU
$Si0_2$	49.44	43.00	43.30
Al_20_3	33.80	39.07	36.60
Fe_20_3	4.60	5.89	6.61
Na_20	2.96	1.88	3.97
Mg0	1.52	1.70	2.93
K_20	1.98	1.80	3.69
TiO_2	0.88	0.93	0.99
Ca0	0.31	3.21	1.31
H_20	3.15	1.52	0.60

Table 3. cation exchange capacity measurement/Percolation rate studies

Sample of clay	Percolation rate studies	Time 100ml to
OZ	82	6 hours
UR	64	4 hours 30second s
AU	10	2hours 52mins

Table 4: Percentage of Pollutants Reduction for Batch Treatment

			AU			UR			OZ		
Characteristics	**Unit**	**Raw water**	**Range of mean values**	**Mean**	**% reduction**	**Range of mean values**	**Mean**	**% reduction**	**Range of mean values**	**Mean**	**% reduction**
Ph		6.8	7.2-7.10	7.05		6.9-7.10	7.00		6.60-6.90	6.75	
Temperature	^{o}C	29.20	28.32-30.00	29.16		27.01.29.00	28.01		27.20-28.50	27.85	
Colour	Hazen	11.50	9.30-10.30	9.80	14.00	9.50-9.80	9.65	16.00	8.20-8.30	8.20	28.70
Turbidity	Hazen	55.00	51.21-53.10	52.16	5.16	50.10-51.31	50.71	7.80	45.10-45.20	45.15	17.90
Conductivity	us/cm^3	416.02	412.00-411.00	411.50	1.10	3.00-360.50	360.25	13.01	340.00-345.00	342.50	17.67
DO	mg/l	4.32	7.82-8.00	7.91		8.21-52	8.37		8.50-8.99	8.75	
BOD	mg/l	51.10	47.00-49.00	49.00	4.11	45.00-46.10	45.55	10.86	43.22-43.51	43.37	14.93
COD	mg/l	73.20	72.31-70.00	7.16	2.79	66.21-66.82	66.52	9.13	60.10-63.23	61.67	15.75
Phosphate	mg/l	13.31	12.20-13.00	12.60	5.33	11.20-11.60	11.40	14.00	11.00-11.42	11.21	15.78
Nitrates	mg/l	19.01	18.00-18.50	18.25	4.00	17.33-18.01	17.67	7.10	17.01-17.33	17.17	9.70
Fe	mg/l	2.00	1.72-1.91	1.57	21.00	1.49-1.50	1.47	26.50	1.47-1.49	1.48	26.00
Pb	mg/l	0.0	0.01-0.01	0		0001		0001	ND		
Cr	mg/l	1.21	0.54-0.61	0.85	30.00	0.41-0.42	0.42	65.29	0.40-0.41	0.41	66.12
Cu	mg/l	2.41	2.00-2.10	2.05	15.00	1.94-1.95	1.95	19.10	1.81-1.82	1.82	24.49
Zn	mg/l	3.21	3.00-3.01	3.01	6.20	2.95-2.94	2.93	8.72	2.77-2.82	2.78	13.40

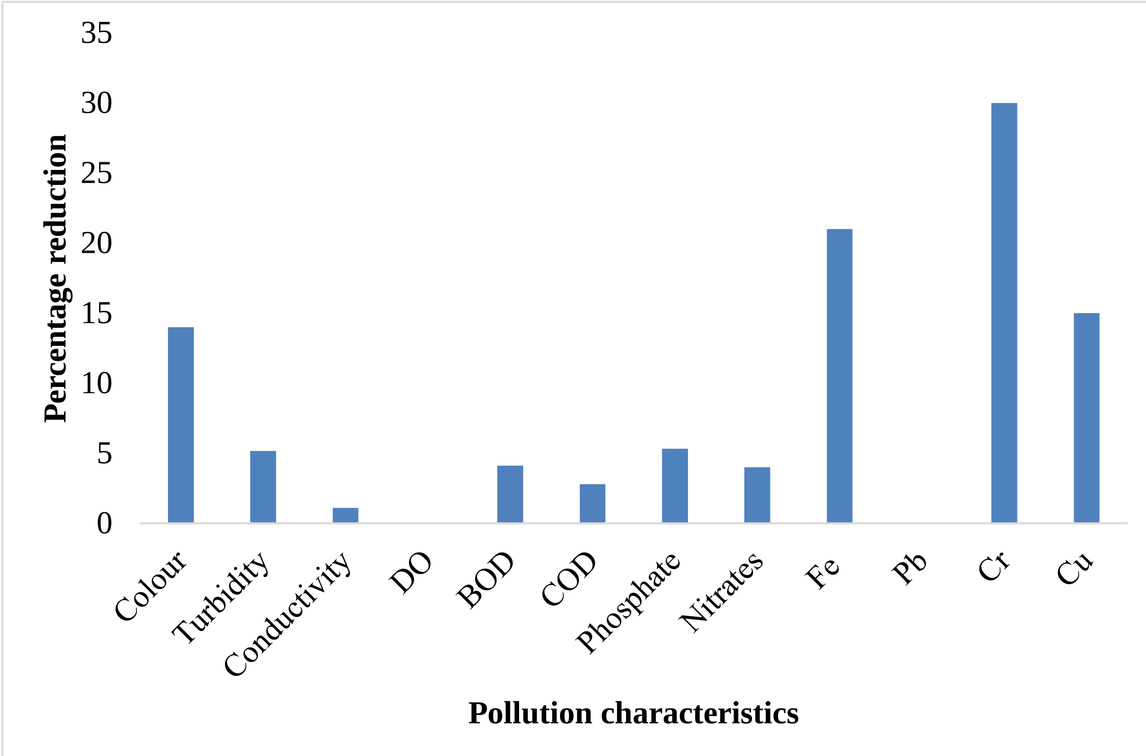


Fig. 1: Percentage of pollutant reduction for batch treatment (AU Clays)

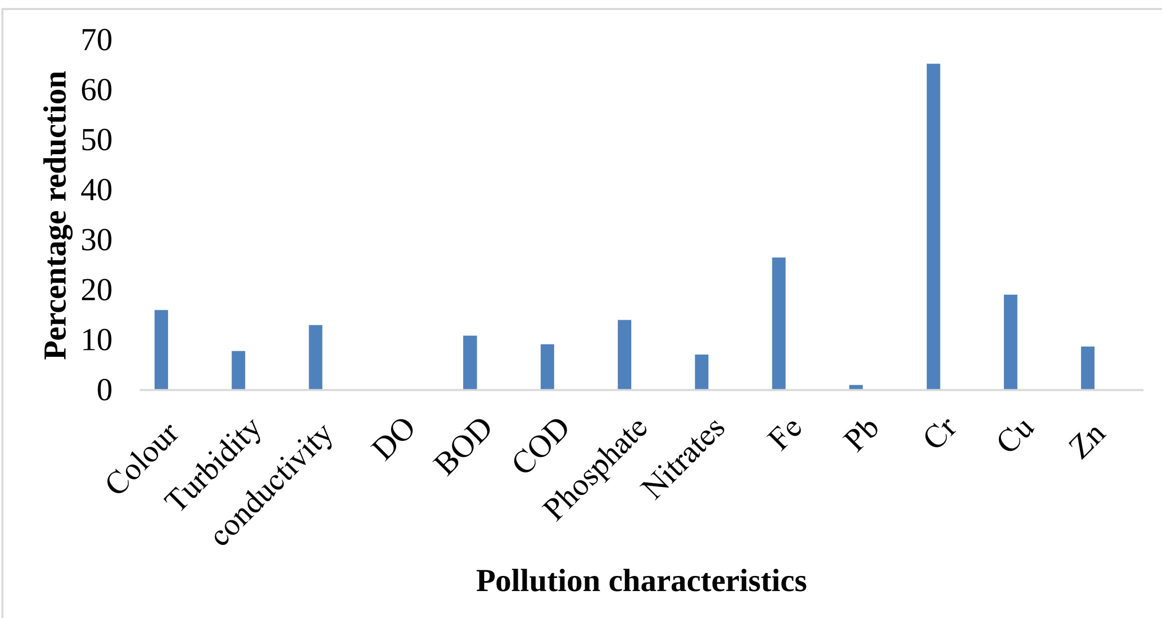


Fig. 2 Percentage of Pollutants Reduction for Batch Treatment (UR Clay)

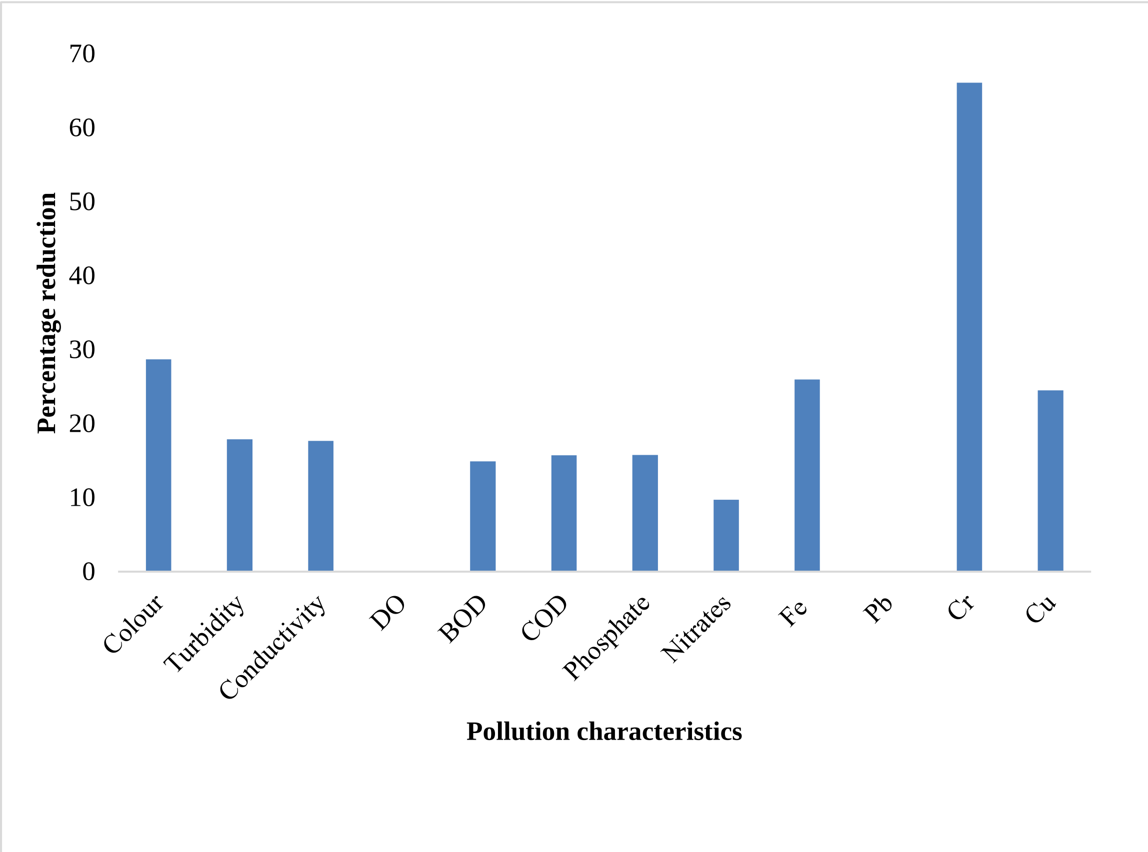


Fig.3 Percentage of Pollutants Reduction for Batch Treatment (OZ Clay)

Table 5: Percentage of Pollutants Reduction (Continuous Treatment)

			AU			UR			OZ		
Characteristics	**Unit**	**Raw water**	**Range of mean values**	**Mean**	**% reduction**	**Range of mean values**	**Mean**	**% reduction**	**Range of mean values**	**Mean**	**% reduction**
pH		6.8	7.00-7.10	7.05	-	6.40-7.00	6.52		6.4-6.9	6.65	
Temperature	^{o}C	29.20	27.00-27.00	27.00	-	26.81-27.00	26.91		27.00-27.10	27.01	
Colour	Hazen	11.50	3.39-4.10	3.75	67.39	2.13-2.18	2.16	81.22	0.25-0.30	0.25	97.74
Turbidity	Hazen	55.00	10.10-10.22	10.16	81.53	9.34-9.50	9.42	82.29	2.45-2.74	2.65	95.29
Conductivity	us/cm^3	416.02	28.21-28.52	28.37	93.18	23.01-23.21	23.11	94.45	17.41-18.20	17.81	95.72
DO	mg/l	4.32	6.31-6.37		-	7.42-7.89			9.31-5.62	9.67	-
BOD	mg/l	51.10	5.10-5.40	5.25	89.73	4.20-4.46	4.33	91.53	2.20-2.46	2.33	95.54
COD	mg/l	78.20	10.41-10.69	10.55	86.50	8.62-8.82	8.72	88.85	7.41-7.69	7.55	90.35
Phosphate	mg/l	13.31	3.00-3.10	2.99	77.10	2.94-3.10	3.02	77.31	1.94-2.10	2.02	84.82
Nitrates	mg/l	19.01	3.01-3.40	8.21	56.51	6.62-6.81	6.47	65.97	4.43-4.01	4.72	75.17
Fe	mg/l	2.00	0.26-0.28	0.27	86.50	0.24-0.26	0.25	87.50	0.17-0.19	0.18	91.00
Pb	mg/l	0.012	<0.01			<0.01			0.00-0.00	00.00	100
Cr	mg/l	1.21	0.04-0.06	0.1	82.65	0.04-0.06	82.65		0.00-0.01	0.01	99.98
Cu	mg/l	2.41	ND			Nd			0.09-1.00	0.55	96.20
Zn	mg/l	3.21	0.23-0.31	0.27	91.60	Nd					
Ca	mg/l	45.20	2.33-2.38	2.36	94.78	6.21-6.98	6.60	85.40	1.56-2.00		96.10

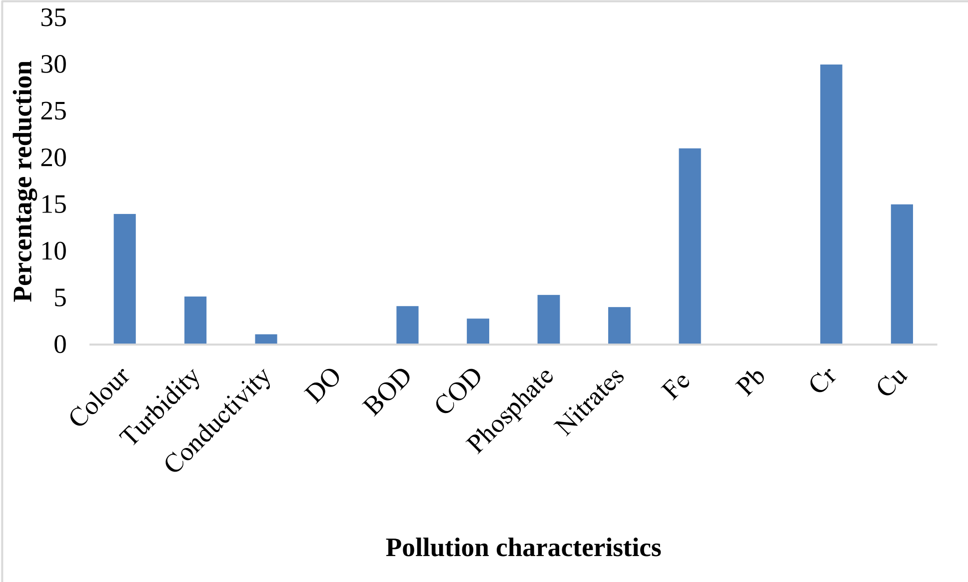


Fig.4: Percentage of Pollutants Reduction for Batch Treatment (AU Clay)

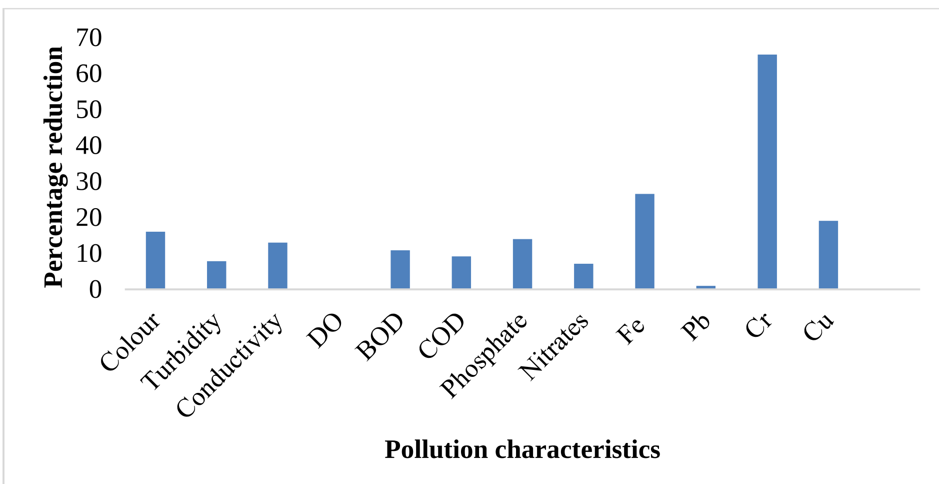


Fig.5: Percentage of Pollutants Reduction Continuous Treatment by (UR Clay)

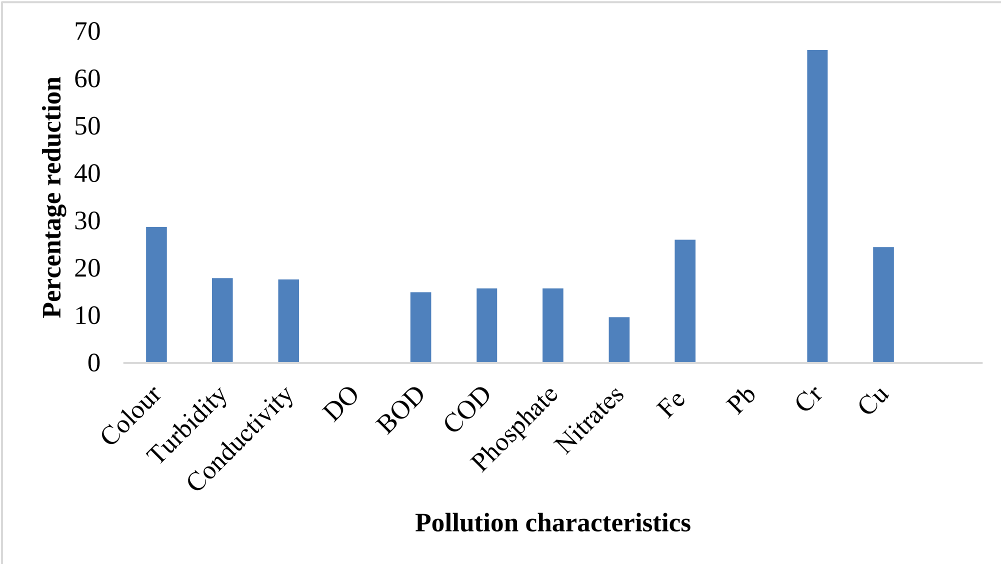


Fig.6 Percentage of Pollutants Reduction Continuous Treatment by (OZ Clay)

Table I showed the results of the mineralogical analysis of each of the clay sample and their different proportions. All clay types consist of kaolin with AU having the highest (46.20%) Montmorillonites (Smectite) group was also present with OZ having the highest composition of 20.30% Other clay minerals were mixed layer, quartz, illite and chlorides. Geochemcial analysis result is as presented in Table 2 with Fe203 present in all the clay samples. The results showed that they are alumino-silicate clays, SiO2 OZ is more siliceous (49.44%) and UR (43.00%) with Fe203 as a tracer element present as hematite. OZ and UR have the highest CEC of 82 and 64 cmol/kg as shown in Table 3. This could be traced to the smectite clay type found in OZ (Smectite group which is a 2: l clay having CEC= 80-120 cmd/kg higher than 1:1 clay (Koalinites) low cation exchange capacity. The Kaolin 1:1 clay allows for little expansion and less substitution with low swelling capacity, hence 10cmol/kg.

The property of ion exchange is of great fundament and practical importance in investigating characteristics of clay materials, which influenced by its physical properties, and their particle size decreases because of broken bonds around the edges of silica alumina units, substitution within the lattice and hydroxyl in smeetite clays group of exposed hydrogen may be replaced by a cation which would be exchangeable. In percolation rate study (Jingfa, et al., 2023), the order of first drop from each media is in accordance with the composition of the minerals present in each clay types as in (Table 1). The longer the residence time of the wastewater, the lower the percolation rates. OZ has the lowest percolation rate of 6(six) hours-smectite swells when soaked in water and other Polar solvents. The higher the swelling rate of any soil (clay type) (Avik, et al., 2023). when soaked, the longer the permeability and the higher the residence time of solvent in it. This is depicted in table 3.

In obtaining 100ml of wastewater from the clay medium, it could be arranged as follows OZ > UR >AU, AU has the highest rate and while OZ has the least percolation rate and the longest residence time. For the batch treatment, different clays showed remarkable improvement in effluents from each percolator (Shahab, et al., 2023) as presented in Table 4. The pH were becoming neutral, with increase in pH there might occur, metal ion binding-since it has attraction with the negative charge on the groups with organic functional groups in agreement with (Gina, et al, 2020). He observed that the percentage adsorption increased with increase in pH from 2-6 and remained so up to 10. Turbidity reduction was 5.10% for AU, 7.80% for UR and 17.90 for OZ clay type. BOD reduction % of 4.11 for AU, 10.86 for UR and 14.93 for OZ, for CoD reduction 2.79% for AU, 9.13 for UR and 15.75% for OZ, for phosphate % reduction 5.33% for AU, 14.00% for UR and 15.78% for OZ in agreement with (Muhammad, et al, 2019) for batch treatment. There was slight improvement in dissolved oxygen content. Some percentage reductions of pollutants are as shown in Table 4. one noticeable fact is that the variation in characteristics of the wastewater effluents is peculiar to each clay under study (Zhai, et al, 2017). Elevated levels of phosphates in surface water contributes to eutrophication and impairment of water quality, high level of nitrates causes was blue baby syndrome (WHO, 2017).

In continuous treatment method, for media in series connection of partly treated effluent form the first to the second and third percolator was ensured. A general overview showed improvement in quality of wastewater better than the batch treatment as presented in Table 5. Turbidity was highly reduced, in the following order OZ > UR >AU, with equivalent of 95.29% removal for OZ which is below the acceptable limit of 5. ONTU. This followed the trend that conductivity will be reduced. Same occurred with BOD removal below 5.0mg recommended values for OZ we have above 95% removal. For COD we have observed 86.5% for AU, 88.85% for UR and 90.35% for OZ (Darajeh, et al., 2016). Phosphate was greatly reduced lower than 3.5mgk of recommended value. (WHO, 2017; APHA, 2017). For heavy metals we have percentage reduction of not less than 82% and total removal 100%) in some metals which was not obtainable in some characteristics studied using batch treatment method. The reason for fortifying clays with stone pebbles was to improve its permeability which has been one of the drawbacks for on-site material for water and wastewater treatment (Azikiwe, 2020). The general performance of all the percolating media in the purification of wastewater depends on the state in which these organic pollutants or inorganic pollutants are present and which in turns determines the mechanism for their removal, as represented in the equations 1, 2, 3 and 4 under different conditions of pollutants.

That for cationic is shown in equation 1 and 2.

$$H_2O.M^{n+} + clay.\ A^{n+} \qquad M^{n+} - clay.\ A^{n+} + H_2O \qquad (1)$$

RNH■(+@3) + M-clay RNH■(4@3) – clay+M (2)

RNH■(+@3) is an organic cation and M+ another cation on clay mineral, Na^+, Mg^{2+} etc

An+ = SO_4^{2-}, CO_3^{2-}, OH^- etc.

Many neutral molecules may become cationic after absorption on clay by protonation. A compound with exchangeable H^+ to form cationic specie as in equation 3.

H20-RNH3+[H-Clay] [RNH■(+@3) – clay] + H20 (clean water) (3)

RNH_2 is a neutral impurity (amine).

While that for anionic pollutants followed that of equation 4.

H_2O. A^- + M^+ . Clay M^+-Clay. A^- + H_2O (4)

Anionic Inorganic substance A= OH^-, SO_4^{2-}, NO_3^-

The metal ion serve as adsorption site for polar non - ionic molecules by coordinating. The greater affinity of the exchangeable cation, for electrons, the greater the interaction with polar groups donating electrons.

The preferential adsorption of copper and other metal ions by the different clay minerals may be attributed to their chemical coordination characteristics.

4.0.**Conclusion**

A survey of performance efficiency of each of the fortified column clay OZ, UR and AU in all the treatment of wastewater revealed that clays have high potential in wastewater treatment (purification) depending on their mineralogical composition clays have ability for uptake of pollutants. And percolating media is a good option for wastewater treatment and is environmentally friendly. It is pertinent to note that this method is low energy consuming and easy to manipulate as well as alleviate the problem of freshwater shortage in our communities

Recommendation

Future research should be focused on characterizing the clays for other applications and mechanism for the uptake/removal using kinetic studies.

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