PRINT ISSN 1119-8362
Electronic ISSN 2659-1499

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 28 (8) 2449-2454 August 2024

Evaluation of Physicochemical Properties and Heavy Metal Content of Domestic Wastewaters Treated With Clay-To-Stone Formulation from Urovie and Agbor in Delta State and Aba in Abia State, Nigeria

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ABSTRACT: Wastewater treatment processes eliminate contaminants before being discharged into the immediate environment. Therefore, the objective of this paper is to evaluate the physicochemical properties and heavy metal content of the kitchen, toilet, bathroom and laundry wastewaters treated with clay-to-stone formulations from Urovie (UR) and Agbor (OT) in Delta State and Aba (AB) in Abia State, Nigeria using various standard methods. Mineralogical and geochemical composition revealed the clays as predominantly kaolin, smectite, illite, mixed layer quartz and saponite. The presence of Al_2O_3 and SiO_2 confirmed the hydrated aluminosilicate nature of the clays. An improvement of clay with small stones in the ratio 1:4 (clay to stone) employed in the treatment of the wastewater effluents reveals that pollution biomarkers were significantly altered after treatment using all three enhanced clay formulations (UR, AB and OT). Treatment of wastewater using enhanced clay formulation can therefore be thought of as an effective wastewater purification system. It is a simple, low-energy consuming and cost-effective decentralized wastewater treatment system.

DOI: https://dx.doi.org/10.4314/jasem.v28i8.22

Cite this Article as: UMUDI, E. Q; UMUDI, O. P; IGERE, O. F. (2024). Evaluation of Physicochemical Properties and Heavy Metal Content of Domestic Wastewaters Treated With Clay-To-Stone Formulation from Urovie and Agbor in Delta State and Aba in Abia State, Nigeria. *J. Appl. Sci. Environ. Manage.* 28 (8) 2449-2454

Dates: Received: 04 June 2024; Revised: 27 June 2024; Accepted: 11 July 2024 Published: 05 August 2024

Keywords: Wastewater treatment; Clay; Mineralogical; Geochemical; Physicochemical properties; Heavy metals

Water is important to life, a catalyst in most chemical reactions and a solvent medium. It is required for well-being, social economic and survival of humanity. It is an argument for peace, twining and cooperation (Shanmugam *et al.*, 2017). This indispensable position of water left it with the only option of recycling for use. Wastewater over the years have increased with growing population, economic growth and improved standard of living. Wastewater is seen only as a pollution source and need to be treated and disposed. There is a paradigm shift with developing countries in improved wastewater management, from just treatment to recovering of water resources facilities (Villarin and Merel, 2020). These will produce potable water, nutrients recovery and low-energy consuming techniques. These avenues are only put in place, with little portion of wastewater-produced treatment not as a recovery of resources. It is estimated that about 70% of wastewater generated is discharged into the environment without adequate treatment. Over the decades, different treatment methods as reverse osmosis, membrane filtration, nanomembrane separation etc, have been used. All these treatment methods are expensive, energy-consuming, and

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difficult to operate for users in private sectors. It should be a simple, reliable low-cost technology that is affordable to be operated with little skill (Khan *et al*., 2023; Umudi and Awatefe, 2018). Percolation of wastewater through one or more types of percolator materials, is a common treatment technology that fulfils these criteria (Khan *et al.*, 2023; Umudi and Awatefe, 2018). In this process, the wastewater is purified by physiochemical/microbial degradation process (Chahouri *et al*., 2019). Different types of materials have been used, such as clay and grindstone, soil and sand, organic materials like bamboo and straw, soil and peat, sand and gravel, zeolites, etc. (Dawood and Sen, 2014). It is reported that peat is effective in the removal of textile dyes, pesticides, heavy metals and radioactive materials (Lee *et al*., 2015).

Naturally occurring materials like zeolite with silicates has strong affinity for heavy metals and other pollutants. The absorbing properties from their ion exchange capacities and the metal ion adsorption capacity of clays are due to their large surface areas (Fareed *et al*., 2019). The two distinctive properties of clay which renders them technologically useful are plasticity when wet and extremely fine crystal, often colloidal in size, planty in shape and its cation exchange capacity (Nkosi and Thembane, 2024; Kumari and Mohan, 2021).

There is therefore need to provide a simple, low-energy consuming and unassuming technological wastewater purifying process using clay materials fortified with small stones to ease flow of solvent (wastewater). Hence the objective of this paper is to evaluate the physicochemical properties and heavy metal content of kitchen, toilet, bathroom and laundry wastewaters treated with clay-to-stone formulation by clays from Urovie (UR) and Agbor (OT) in Delta State and Aba (AB) in Abia State, Nigeria.

MATERIALS AND METHODS

Sample Area: Samples of domestic sewage were collected from inlet pipes of a conventional treatment system at Delta Steel Company Senior Staff Quarters, Aladja, in Udu Local Government Area of Delta State, Nigeria.

Fig 1: Map showing Delta Steel Company (DSC)
Source*: Google maps, 2024*

Sample Collection: Wastewater samples were sourced from kitchen, toilet, bathrooms and laundry services, and collected in 20 litres plastic containers at a 2-hourly interval, commencing at 8:00 am and ending by 8:00 pm. The samples were observed to be tendering toward putrefaction and brownish in colour.

Clay Collection and Enhancement: Small stones were collected from sharp sand dug from Udu Bridge River from Udu Local Government Area of Delta state, thoroughly washed, air dried and stored in polybags. Clays were collected from Uruovie (UR) and Agbor (OT) in Delta State and Abia (AB) in Abia State. They were air-dried, pulverized with laboratory mortar and sieved with 0.05 sized filter. Mineralogical analysis was carried out with PW Phillips 1800 X-ray diffractometer, while Atomic Absorption Spectrophotometer Aigen Model 18250 was used for geochemical analysis. Cation exchange capacity was determined using the method described by Cheng and Heidari (2018) while pH, turbidity, TS, DS, SS, DO, COD, BOD, NH_4^+-N, Pb, Hg, and Ni were analyzed using APHA standard methods (APHA, 2012). The bacterial count was done by the method described by Uwidia (2020). A plastic vat of 200 cm length and 20 cm diameter was used as a packing column with small stones in 1:4 ratio. Simulated cotton wool was placed at the base of the vat to 25 cm. It was made to percolate through the batch, and the parameters of wastewater before and after running through the column were analyzed according to Umudi and Awatefe (2018).

Data Analysis: Data for the physicochemical parameters were generated in triplicates and the mean values reported, while mineralogical and geochemical data were presented as percentages.

RESULTS AND DISCUSSION

The results of geochemical analysis of the different clay types are presented in Table 1. From the result of the geochemical analysis shown above, the clays show SiO_2 and Al_2O_3 as the dominant clay minerals oxides. They are aluminosilicate clays with some amount of water molecules (Maj and Matus, 2023) with haemitite as impurity. Clay AB has more silicate than the other two types (UR and OT). Fe_2O_3 was highest in OT (8.80) as a result of haematite found in OT mineral composition.

Table 1: Geochemical analysis of clay samples (%).

Metal oxide	UR	AB	OT
SiO_2	40.109	54.08	42.79
Al_2O_3	20	23.577	25
Fe_2O_3	1.40	2.02	8.80
MgO	7.8	0.98	0.86
CaO	8.01	1.40	5.67
Na_2O	1.61	1.07	2.01
K_2O	2.84	3.31	1.67
TiO_2	0.21	0.41	0.98
P_2O_5	0.01	0.01	0.02
MnO	0.001	0.003	0.03
H_2O^*	18.01	13.14	12.17

H_2O^*: structural water

Table 2: Mineralogical composition of the clay samples (%).

Mineral clays	UR	AB	OT
Kaolinites	26.4	29.2	33
Smectite	8.7	20	2.1
Illite	6	10.88	2
Mixed Layer	14.04	20	11
Quartz	37.86	19.92	39.9
Saponite	6	0	2
Haematite	1	0	10

Table 2 shows the mineralogical analysis of the clay types used for this study. Kaolinite mineral was present in all the clays in different percentages – 26.4% (UR), 29.2% (AB) and 33.0% (OT). Other minerals present included smectite – 8.7% (UR), 20.0% (AB), 2.1% (OT); and illite – 6.0% (UR), 10.88% (AB) and 2.00% (OT). Quartz was found in all clay types (UR, AB and OT) in appreciable quantities of 37.86, 19.92 and 39.90 respectively. Mixed layer in UR was 14.04%, while in AB, it was 20.00% and in OT, 11.00%. Saponite was present only in UR (6.0%) and OT (2.0%) respectively.

Table 3: Cation Exchange Capacity (CEC) of clay samples.

Samples (Clays)	Cmol/kg
UR	64.00
AB	73.00
OT	16.00

The cation exchange capacity (CEC) revealed that clay AB had the highest CEC of 73.00 Cmol/kg, followed by UR (64 Cmol/kg) and OT (16.00 Cmol/kg) as observed in Table 3. This is traceable to their mineralogical compositions. For smectic clay type, their CEC is usually between 80-120 Cmol/kg higher than the kaolin (3-10 Cmol/kg) and low swelling capacity. That of smectite is owing to their swelling rate and isomorphic substitution given rise to high potential for pollutant removal. These values may have different variations because of the mixture of minerals present in them (Ismadji *et al.,* 2015).

Figure 2 shows the values obtained from the analysis of pollution parameters in pre-treated wastewater and post-treated wastewater using different clay type formulations. The analysis shows an increase in pH after treatment, with neutral pH in AB clay type but slightly alkaline in the others. Increase in pH values were caused by loosely held cations on clay surfaces which were exchanged for pollutants in wastewater (Umudi, 2012). Dissolved oxygen increased showing a marked improvement in water quality, which was due to the elimination of dissolved and suspended solids, making it easier for oxygen to penetrate the water. The effectiveness of the clay in the removal of pollutants follows this order AB>UR>OT.

Table 4 shows the percentage reduction in pollution parameters after subjecting the polluted wastewater effluent to treatment using the enhanced UR, AB and OT clay formulations. It was observed that there was a 99.3%, 99.5% and 98.9% reduction in turbidity using UR, AB and OT clay formations respectively, while that of total solids (TS) were 97.1% (UR), 97.4% (AB) and 93.6 (OT). The percentage reduction of biological oxygen demand (BOD) levels for UR, AB and OT were 92.0%, 96.2% and 91.0% respectively. For NH_4^+-N, UR (93.1), AB (98.2), OT (83.0), while percentage reduction of NO_3-N in UR, AB and OT clays were 83.0%, 94.0% and 71.6% respectively. Pb (8.51) UR and OT (48.4). Total bacteria reduction in percentage was 46.20%, 71.80% and 41.0% for UR, AB and OT respectively. These enters the effluents to form hydroxides of metals as seen in clays UR and AB. Its effect was less in OT clay with more kaolin and low CEC with few exchangeable cations. Small stones were added to improve the permeability of clay to wastewater and surface for microorganism biodegradation (Uwidia, 2020). Turbidity which is an indication of how polluted a water body is, reduced by approximately 99%, due to the properties of clays, which is a function of the reduction in total solids. The COD and BOD reduction was compared with previous works (Ewis *et al*., 2022). These reductions depend on the state in which the pollutants are present either as organic or inorganic ions.

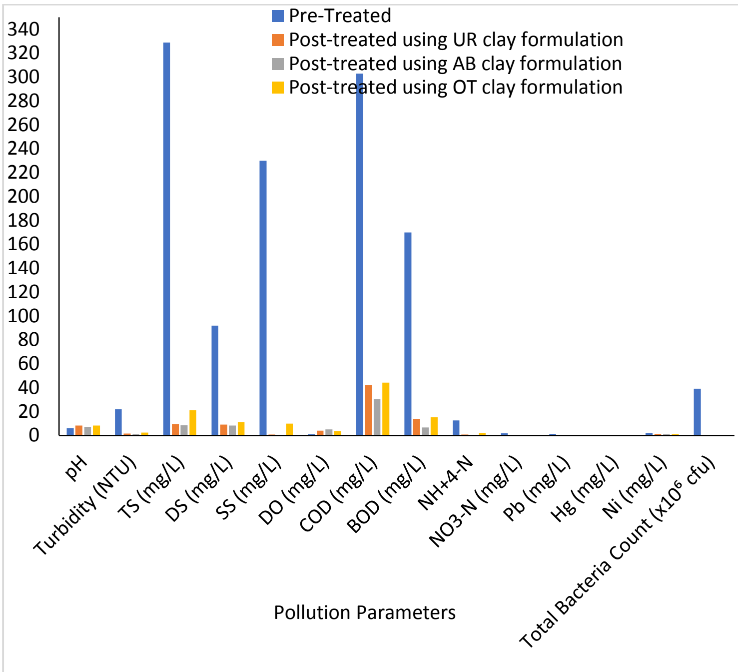

Fig 2: Values of pollution parameters in pre-treated and post-treated wastewater effluents.

Table 4: Percentage reduction of pollution parameters in pre-treated and post-treated wastewater.

Parameter	Pre-treated wastewater	Post-treated wastewater		
		% reduction using UR clay formulation	**% reduction using AB clay formulation**	**% reduction using OT clay formulation**
pH	6.1			
Turbidity (NTU)	22.00	99.3	99.5	98.9
Total solids (mg/L)	329	97.1	97.4	93.6
Dissolved solids (mg/L)	92	90.2	91.1	87.7
Suspended solids (mg/L)	230	99.7	99.9	95.7
Dissolved oxygen (mg/L)	1.00			
Chemical oxygen demand (mg/L)	303.00	86.0	90.1	85.4
Biological oxygen demand (mg/L)	170.00	92.0	96.2	91.00
NH_4^+-N (mg/L)	12.50	93.1	98.2	83.0
NO_3-N (mg/L)	1.80	83.0	94.0	71.6
Lead (mg/L)	1.21	85.1	99.9	88.4
Mercury (mg/L)	ND	ND	ND	ND
Nickel (mg/L)	2.13	47.0	53.1	48.4
Total bacteria count (cfu)	3.9×10^7	46.20	71.80	41.0

CEC is due to isomorphic substitution in the crystal lattice and ionization of hydroxyl groups on the edge of the clay mineral (Unuabomah *et al*., 2018). The hydroxyl group held by the organic colloids and silicates clays become ionized and are replaceable. COD and BOD values are related to dissolved oxygen contents. For samples with low BOD and COD values, the DO values are expected to be high and vice versa. The nitrogen compounds NH_4^+-N and NO_3-N in both organic and inorganic forms were removed at 70% and above. The form in which it is present dictates its means of removal, it is least with NO_3-N and higher for NH_4^+-N. When nitrogen compounds are positively charged, they will replace the exchangeable cation or be absorbed by clay – neutralizing the electrical charges that are negative for ease of cation exchange capacity of clays.

Total bacteria removal was 41% and above in all effluents. Since bacteria act as charged particles similar to colloid (Ademoroti, 1996), likened to amphoteric amino acids, forming cations in acidic solution and anion in basic solution and neutral in some intermediate pH. Thus, bacteria can be removed from wastewater either as charged or neutral molecules. Water can be disinfected to kill the remaining bacteria.

Metal ion removal is favourable with clay because of their high surface area. The ability of metal ion for a ligand binding site on any biomass is affected by the coordination of that metal ion (Yaqoob *et al*., 2020). This could be traced also to their mineral composition, with AB performing better because of the smectite group. Nickel was not appreciably removed 0.1 mg/L for EPA, this could be attributed to the preferences of clays for one metal over another and their coordination characteristics (Uddin, 2017; Noman, 2022). Nickel causes allergy, cardiovascular and kidney diseases, lung fibrosis, lung and nasal cancers. It reduces seed germination, root and shoot growth, biomass accumulation, chlorosis inhibits photosynthesis and oxidative damage in plants.

Conclusion: The study revealed that clay can purify wastewater with variations in its capacities based on the mineral composition of each clay type. There was a significant reduction in pollution characteristics with clay types containing smectite, illite and mixed layer UR and AB than OT. This study also revealed that a percolating column is a good medium for treating wastewater.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the first author or corresponding author.

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