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Evaluation of Kaolin as Adsorbent for Chlorine Reduction in Seawater from Forcados/Ogulagha Axis of Southwest Delta State, Nigeria

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ABSTRACT: This paper evaluates the use of three Nigerian clay types Otorho (OT, Abbi (BB) and Umutu (UM) as adsorbent for the reduction of chlorine in seawater from (Forcados/Ogulagha aix in Southwest Delta State using XRD X ray diffraction and Atomic Absorption Spectrophotometer. The alumino silicate nature of the clays was confirmed by the presence of SiO_2 and Al_2O_3 and the presence of other elements (Na, K, Ca, Mg, Fe and Ti) in trace quantities. Percolation rate studies showed that clay UN had the lowest while OT had the highest. Clays fortified with stone pebbles in ratios 1:3 in columns in one flow-through and three flow troughs were used in different arrangements. Fortified clay (UM) gave the highest percentage reduction of 99.9%, BB clay 98.0% and OT clay 99.2%. The results showed that clay UM removed >99% of chloride.

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Keywords; Chloride, Clay, Column, Ocean, Percolation.

Chlorides are salts resulting from the combination of the gas chlorine with a metal. Some common chlorides sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). Chlorine gas alone as Cl_2 is highly toxic and used as disinfectant. In combination with a metal as sodium, It becomes essential for life .The sodium part of table salt has been linked to heart and kidney diseases. Sodium Chloride may impart a salty taste at 250mg/L (Nasuir, *et al.*, 2014). Chloride may get into surface water from rock, agricultural runoff, waste water from industries, oil well effluent from treatment plants and road salting. Water used in industries or processed for any use has a recommended maximum Chloride level. Fish and aquatic communities cannot survive in high level of Chlorides. Public drinking water standard require Chloride levels not to exceed 250mg/L, Less than 600mg/L for Chronic (long term) exposure and 1,200mg/L for short term exposure. Hyperchloremia is an electrolyte imbalance indicated by a high level of Chloride in the blood, normal adult level of chloride is 97- 107mEq/L. It works to ensure that your body metabolism is working correctly. Kidney controls the level of chloride in your blood. Therefore, when there is disturbance in the blood chloride level, is related to kidney chloride since it helps to keep the acid and base balance in the body (Pawar *et al.*, 2010). It is an important electrolyte in the body to keep the amount of fluid inside and outside of the cells in balance. It helps maintain proper blood volume, blood pressure and pH of the body fluids. Chlorides comes from what we eat, drink, absorb by your intestine and leaves through urine or sweat. Chloride along with sodium are responsible for osmotic pressure and acid-base balance for production of gastric hydrochloric acid secreted from the stomach. It is needed for vitamin B_{12} absorption and mucosa digestion since HCL acts as a bacteria preventing overgrowth of the gastric intestinal tract. It functions in urine outpour and renal countercurrent mechanism its main function is to concentrate urine in the kidney. It accelerates the retension of sodium at the expense of hydrogen. Chloride concentration level greater than 108Eq/L is hyperchloremia (Bendon and Amman, 2014), as a result of dehydration or excess administration of sodium. Kaolin clay aided with stone pebbles in column is a raw material that could reduce chloride in ocean or sea water. It is a potential low-cost adsorbent to reduce chloride (Umudi, 2012)

(Yaleyanti, *et al.,* 2011). Therefore, the objective of this paper is to evaluate the use of kaoline as adsorbent form chlorine reduction in seawater obtained from Forcados/Ogulagha axis of Southwest of Delta State, Nigeria.

MATERIALS AND METHODS

Three earth clay minerals were used, smooth small pebbles and seawater. Reagents used were as given by standard methods (APHA, 1995).

*Sample collection:*Clays were collected from Abbi (BB) in Ndokwa West, Otorho-Edo in Ughelli South (OT) and Umutu (UM) in Ukwani all in Delta State and seawater from Ogulahai (Fig. 1). The Earth clays used were collected from Umutu, Abbi and Otorho in Delta State, Nigeria.

*Description of study area:*Umutu lies between longitude $6^0$13' and $6^0$15' East of Greenwich Meridian and Latitudes $05^0$50' and $05^0$52' North of the Equator.Abbi lies between longitudes $06^0$05' and $06^0$10' East of Greenwich meridian and latitudes $05^0$43' and $05^0$45' North of the Equator. Smooth small stone pebbels were collected from the bank of River Ethiope a fast moving river in Abraka in Ethiope East Local Government Area of Delta State, lying between longitudes $05^0$45' and $05^0$50' North. It is a semi-urban area especially with the establishment of the State University. River Ethiope took its source from Umuaja in Ukwani Local Government Area of Delta State. It flows westward for about 10 kilometres before it discharges into Benin River at Sapele. Seawater was collected from the Atlantic Ocean at a convenient point lying between longitudes $05^0$45' and $05^0$49' East of Greenwich Meridian and Latitudes $05^0$35' and $05^0$45' North of the equator (See Fig. 1). The location on the ocean is about 2km from Forcados/Ogulaha axis which is in Southwest of Delta State, Nigeria. Suitable amounts of seawater were collected at different times in 20 litres clean plastic containers. The ocean is underlain by crystalline rocks consisting of a series of granites, gneisses, migmatites and narrow belts of low grade schists. There are two predominant soil types: the ferrasols, the hydromorphic and alluvia soils. Ogulagha lies in the mangrove belt of Nigeria, with swampy forest occurring in flat-floored valley and adjoining low-lying areas that are seasonally or permanently water logged.

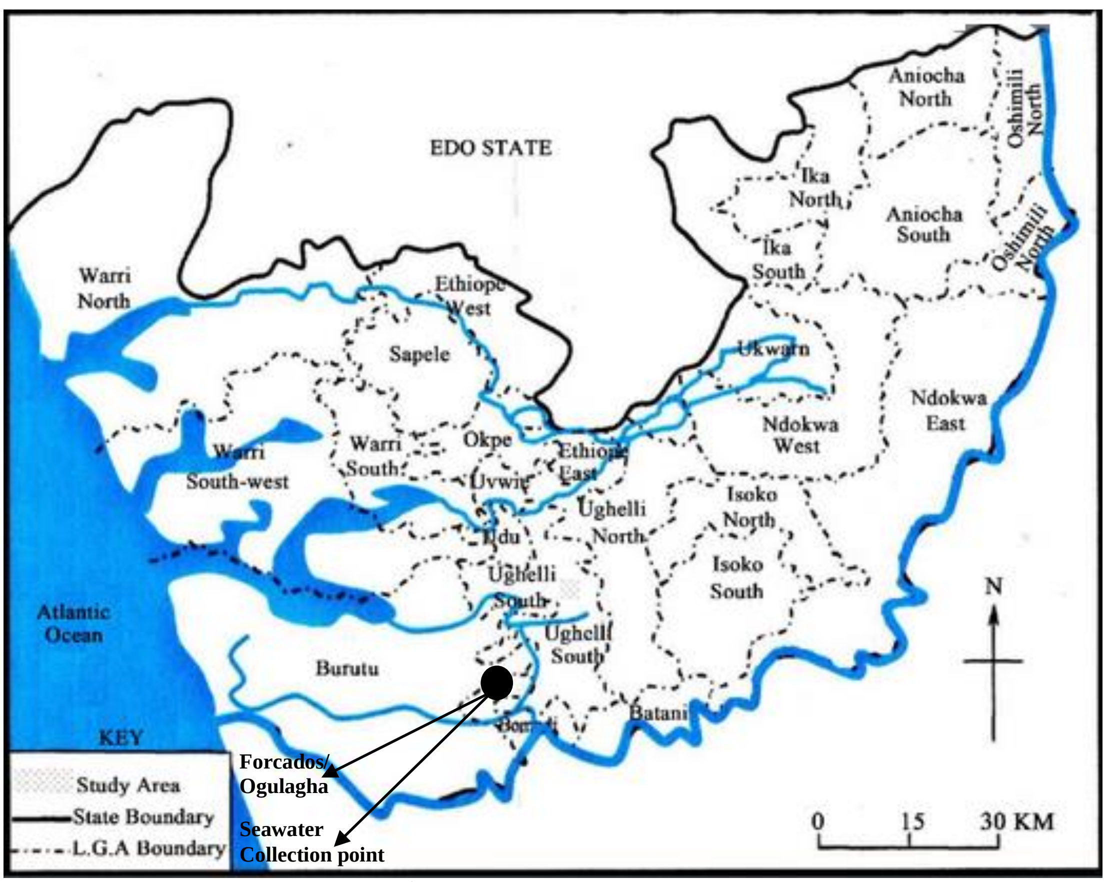

Fig 1: Map of Delta State showing seawater collection point.

The soils are deeply weathered and nutrient deficient, being derived from unconsolidated sediments of sand stone. The climate is humid subequatorial. It rains all throughout the year but there are generally four months of dry seasons from December to March and eight months of raining season from April to November. Annual rainfall might reach a height of 3,300mm with average temperature of about 27-30^{0}C with seasonal variation not exceeding 3^{0}C. Humidity is high. The topography and terrain are relatively flat with thick forest vegetation, related to its proximity to River Niger. It covers an area of about 5,950km^2. It is 200 – 500cm above sea level. It has multiplicity of creeks and rivers bordered by mangrove trees. The trees thrive best in saline environment. This saline water serves the inhabitants for both drinking and domestic purposes.

*Sample preparation:*Earth clays were collected using chisel, plastic, shovel and hammer. They were air dried on a flat dry plastic sheet and pulverized in a motor using pestle. 2 um sieve was used for sieving and were stored in a polyethene bags and labelled and coded for easy identification. Smooth small stone pebbles were obtained from Ethiope River, carefully washed with distilled water andstored in polyethene bags, clay and stone pebbles were carefully mixed together w/w in ratio 1:3. Suitable amount of sea water were collected at different times in 20 litres clean, plastic containers with sinkers tired to them. Time and days of sampling were varied to account for tidal variation at Forcados/Ogulahai axis against current. A large plastic aspirator (50 litres) was used for holding seawater to constitute constant pressure head and having a tap at the bottom to control sea water flow through the column. Column made of plastic with height 100 cm and 10 cm diameter were used, graduated 1 cm apart. Glass wool well packed to a depth of 2 cm into its base and finally loaded with mixed quantities of pebbles/clay to 80 cm mark of the columns.

*Sample analysis:*Mineralogical analysis was carried out using X-ray diffractometer (PW 1800 powder) diffractometer with inbuilt standard using XSPEX version 5.62. Geochemical analysis was done using 1 gram of air dried clay sample digested with analyte grade hydrofluoric acid (HF), hydrochloric acid (HCl) and perchloric acid $HClO_4$ in ratios (3:2:1) and elemental analysis with Atomic Absorption Spectrometer (Varian 10) and structural water determined as loss on ignition. 5g of air dried clay was weighed into 250ml Erlenmeryer flask and 30ml ammonium ethanoate (acetate) was added, shaken for 2 hours and filtered through a Buchnar funnel. It was washed with 95% alcohol exchangeable sodium was leached five times with 20ml of 1ml ammonium acetate at pH7used for their determination of cation exchange capacity C.E.C = (mol/kg soil). Percolation studies were carried out to determine the residence time of seawater in each of the percolating media. Organic debris in clay was washed off by flushing with distilled water until a clear effluent was obtained. Seawater was then loaded into the columns, the effluents collected and analysed for various characteristics as directed by (APHA, 1995), (AOAC, 2005).Chloride was determined using Mohr's method, 100m distilled water, 1ml K_2Cr0_4 and 0.2ml of 0.0282M $AgNO_3$ solution was added and shaken, allowed to stand which was used for colour comparism.
Statistical evaluation data was done using percentage data.

RESULTS AND DISCUSSION

The results obtained for the percent composition of clay in the study area is presented in Table 1, while the X-Ray Diffractometer mineralogical composition of each sample is shown figures 2 to 4. From the different clays studied kaolin group was present in all the clay types in various percentages. OT clay type having the highest 58.20%, BB clay type 39.40% and UM clay type 31.20%.

Table 1: Percentage composition of clay

Clay mineral	Abbi Clay (BB)	Otorho Clay (OT)	Umutu Clay (UM)
Saponite	Nil	Nil	5.80
Smectite group	7.30	Nil	6.10
Chloride	Nil	Nil	10.30
Illite	13.40	10.10	7.20
Illite and montmornollite	15.40	Nil	29.40
Kaolinite	39.40	58.20	31.20
Hermatite	Nil	4.20	Nil

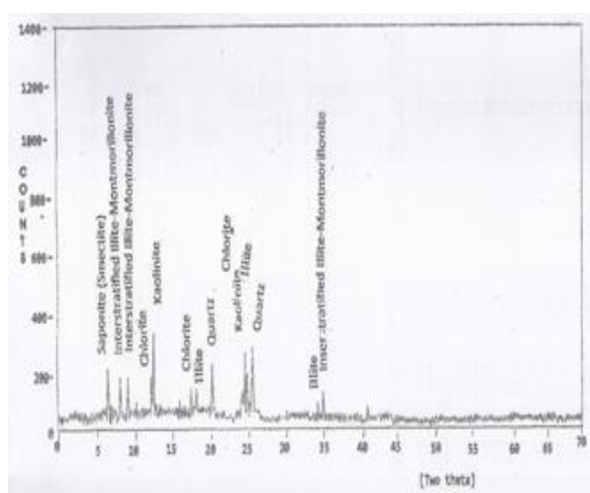

Fig 2: X-Ray Refractogram of Clay BB

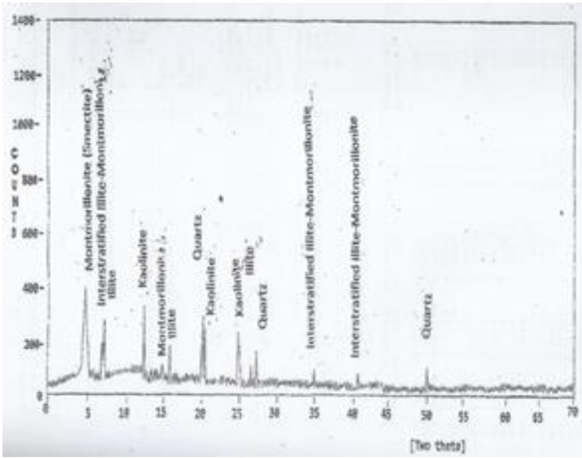

Fig. 3: X-Ray Refractogram of Clay OT

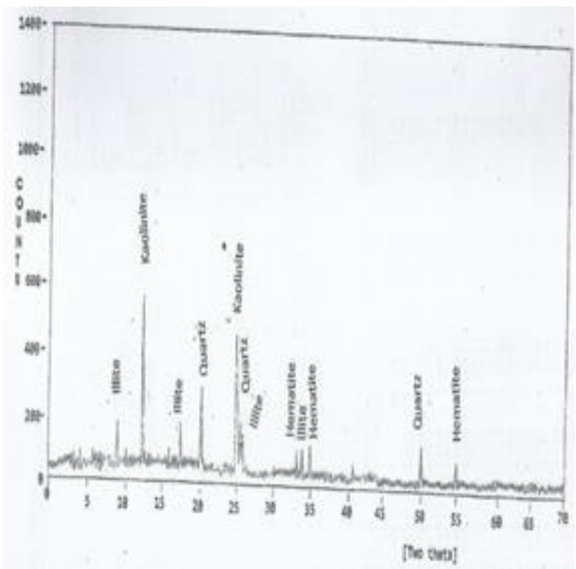

Fig. 4: X-Ray Refractogram of Clay UM

$$H_2O.A^- + M^+clay \rightarrow M^+clay - A^- + H_2O$$

Anionic inorganic — Substances in seawater — Clean water

Where A = $OH^-, CL^-, NO_3^-, SO_4^{2-}$ etc.

Table 2: Percentage composition of oxides from Geochemical Analysis.

% Oxide	BB	OT	UM
SiO_2	44.40	43.30	43.10
Al_2O_3	38. 80	38.63	39.97
Fe_2O_3	7. 67	6.65	6.89
Na_2O	0.67	1.97	0.88
M_gO	1.82	1.93	1.90
K_2O	1.68	2.69	1.60
TiO_2	0.98	0.99	0.93
CaO	0.21	0.31	3.21
H_2O*	3.51	3.53	1.52

The results obtained combined with the equation above explains the ability of clay in removal of chloride from seawater (Umudi, 2012). Clay minerals possess OH groups which are exposed to external reacting species, attached to silicon and aluminium liable to dissociate or accept a proton giving positively charged clays which can take part in anion exchange (Pawar, *et al*, 2016). The results from geochemical showed that all the clay types contain mainly silica (SiO_2) and alumina. Others are magnesium and potassium. Since they are mixture of kaolinite, quartz, montmorillonite, it may expand and have high adsorption of cations and anions. It was duely observed that clay minerals containing illite and montmonillonitre, do expand and swell to absorb either anionic, cationic or neutral species. Pollutants in the presence of water, smectite and mix layer has large surface area, the larger the surface area, the larger the absorption occurs.Presence of water (Holmoboe *et al.*, 2012; Pawar, *et al.*, 2016.

Table 3: Cation Exchange Capacity (C.E.C) and Percolation studies

Clay sample	C.E.C	Time for first drop	Time to obtain 100ml
BB	70	3hrs 48mins	4hrs 34mins
OT	17	2hrs 55mins	4hrs 45mins
UM	84	4hrs 13mins	8hrs 12mins

The contact time is one of the decisive factors in the adsopriton process. The contact time is also the time used by the adsorbent and the adsorbate to interact directly. The mineral composition showed that they are all alumino silicate clays of Kaoline in different percentages, which are 1:1 clay with low cation exchangeabability. Illite was present all through which are 2:1 clays. They showed intermediate cation exchange capacity. So that a small amount of such expansible mineral interlayer with a little expansible component would greatly enhance the ease of splitting of the unit and its dispersion. The Cation Exchange Capacity (C.E.C) is of great fundament and practical importance in clay mineral investigation (Homlmboe, *et al.*, 2012). This may be responsible for the time to collect the first and 100 ml known as the residence time because of their expansion and swelling abilities. The longer the residence time in the column, the lower the percolation rate. From the result of Table 4 the chloride concentrations were reduced after treatment. The pH were slightly reduced due to biodegradable matters in the seawater producing CO_2 which dissolves in water forming weak acid solution and ions of hydrogen or it could be due to volatile acids breaking down organic matters to ethanoic acid and finally CO_2, dissolving in water forming a weak acid which would decrease the value of pH. (Yuli-Yanti, *et al.,* 2011).

Table 4: One flow through and three flow through (means values) one flow-through

Characteristics	Raw values	BB mean	% Reduction	OT	% reduction	UM	% reduction
Chloride	19705.5	8524.3	56.0	6808.4	65.4	4557.9	75.3
pH	7.0	5.65		5.4		5.3	
DO	4.70	7.30		6.00		8.30	
Three flow-troughs							
Chloride	19705.5	3875	98.0	166.1	99.2	0.16	99.9
pH	7.0	5.77		5.8		5.3	
DO		7.40		8.00		8.40	

The CO_2 thus produced affect the absorption because the mineral acid can dissolve the SiO_2 and Al_2O_3 components that fill the pores of the adsorbent. This will bring about the opening of closed pores which increases the surface area of the adsorbent. (Kobayashi, *et al.,* 2017). At the decrease in chloride content, the percentage reductions were between 56.7 – 75.3% for one flow through to 99.2% - 99.9% for three flow-troughs. The surface of the negatively charged clays, with the presence of iron oxide (Fe_2O_3), alumina oxide (Al_2O_3) and SiO_2 which is an active site in the clay network or framework will help the chloride ion adsorption process. Fe and Al ions on the surface of the clay minerals will react with water molecules in the chloride solution. The hydrated charge forms a positive charge by capturing H+ ions or releasing OH^-ions, on the surface of the clay then becomes positively charged by the presence of H^+ and Al_3^+ (Muhammadi, *et al.,* 2019). The formation of a positive charge on the clay minerals is caused by the inclusion of H^+ ions in the octahedral layer into $Al(OH)_3$ and the tetrahedral layer into SiOH forming a hydrogen bond so as to bind the negatively charged chloride.

$$\underbrace{H_2O.A^- + M^+}_{\substack{anionic\ inorganic\\ substances\ in\ water}}\ .Clay \rightarrow M^+.Clay.A^- \ + \underbrace{H_2O}_{\substack{clean\\ water}}$$

Where $A^- = OH^-, CL^-, NO_3^-, SO_4^{2-}$ etc.

One of the most recent addition to the list of micronutrients for growth and health though rare too much or too little mimic more common problem is chloride. In plants it is essential to chemical reaction i.e. opening and closing of stomata, tiny pores that allows gas and water exchange between plants and air around. Without which photosynthesis cannot occur (Tomilin, 2019).It can altar community composition of plants, facilitates the inversion of salt water species into previously freshwater ecosystem, inhibits denitrification – microbial property critical for removing nitrate and maintaining water quality and respiration of organic matter, affect primary production, decomposition of nutrients, nutrients recycling in lakes and food chain (Kulpmann, 2005). Monovalent chloride Cl^- is more toxic to aquatic animals and is related to temperature. From the result of chloride decreases dissolved oxygen (DO) increases, the DO of any water is an index of pollution, the pH became acidic from both one flow through and three flow through, it could be a result of the long retention time – this could be that the CO_2 produced from the decomposition or digestion of biodegradable matters in the seawater by microorganisms dissolves in water forming a weak acid which would decrease the value of pH (Umudi, 2012, Tchounwou, *et* al., 2014).In human chloride raises blood pressure i.e. increase in mortality because of multiple small cerebral infarets. The combination of a tendency by the kidney to retain sodium chloride, together with a high NaCl intake can produce a blood pressure rise susceptible in human and animals. This, which augement renal sodium chloride excretion and retain previous NaCl balance of which renal abnormalities are present in people susceptible to hypertension. Once chlorides have reached the reinforcement in sufficient quality they will rejuvenate the embedded steel by breaking down the protective oxide layer normally maintained by the alkaline environment and hence cause. Corrosion, the rust formed has a large volume than that of the steel consumed, which will cause concrete to crack (Adaikpo, *et al.*, 2000). Other natural materials apart from kaolin clays such as chitosan, bentonite and activated carbon can reduce other parameters like COD, BOD, TSS etc (Liew, *et al.*, 2019). Thus these clay minerals can reduce other parameters and reduce environmental damage by industrial activities (Umudi, 2012).

Conclusion: Kaolin clays are raw materials for reducing chloride in sea (ocean) water. The ability of pollutants removal can be linked with the mineral composition of clays. They are low cost adsorbent for the reduction of chloride. Which was shown in the optimum residues time for UM clay. This research is helpful in solving (environmental friendly) and clay is abundance in their area of location and can be applied to other waste waters. It is low energy consuming, less expensive and easy to operate.

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