



## Research Article

# Porous clays as low cost adsorbent to reduce chloride in seawater

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## ABSTRACT

The Ocean water from the Atlantic Ocean (Forcados/Ogulagha) axis which is in Southwest of Delta State, Nigeria, provides for various uses. High level of chloride can cause pollution level in the environment. In man, disturbance in blood chloride level is related to the kidney. It is an important electrolyte, along with sodium are responsible for osmotic pressure and acid base balance it help keep the fluid inside and outside of our body in balance, so it needs to be checked and balanced. Ocean water from Ogulagha axis was analysed using standard methods and three Nigeria clay types coded Otorho (OT), Abbi (BB) and Umutu (UM) were used as adsorbents using XRD X ray diffraction. Clays fortified with stone pebbles in ration 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.

**Keywords:** Chloride, Clay, Column, Ocean, Percolation.

## INTRODUCTION

Chlorides are salts resulting from the combination of the gas chlorine with a metal. Some common chlorides are Sodium Chloride (NaCl) and Magnesium Chloride (MgCl<sub>2</sub>). Chlorine gas alone (Cl<sub>2</sub>) 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 250 mg/L (Naswir 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 250 mg/L, Less than 600 mg/L for Chronic (long term) exposure and 1200 mg/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 97-107 mEq/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., 2016). 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 come from what we eat, drink, absorb by your intestine and leaves through urine or sweat. Chloride along with sodium is responsible for osmotic pressure and acid-base balance for production of gastric hydrochloric acid secreted from the stomach. It is needed for vitamin B12 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 retention of sodium at the expense of hydrogen. Chloride concentration level is greater than 108 Eq/L is hyperchloremia (Bendal et al., 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 et al., 2012; Yuliyanti et al., 2011). In this study, Kaolin clay was used as alternative material because it is cost effective and low energy consuming. It can reduce environmental management cost.

## MATERIALS AND METHODS

The physico-chemical properties of clay minerals are used for the process. Ions found on clay particles surfaces replace one another in the process of cation exchange.

### Materials

Three earth clay minerals were used, smooth small pebbles and seawater.

Reagents used were as given by standard methods (APHA, 1995) 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 (Figures 1-3). 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 Ethiopie River, carefully washed with distilled water and stored in polyethene bags, clay and stone pebbles were carefully mixed together w/w in ratio 1:3.

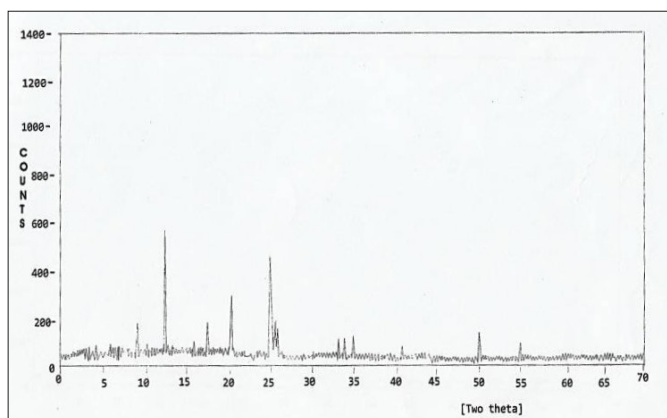


Figure 1: Clay soil Type OT, X-ray diffractogram of clay OT.

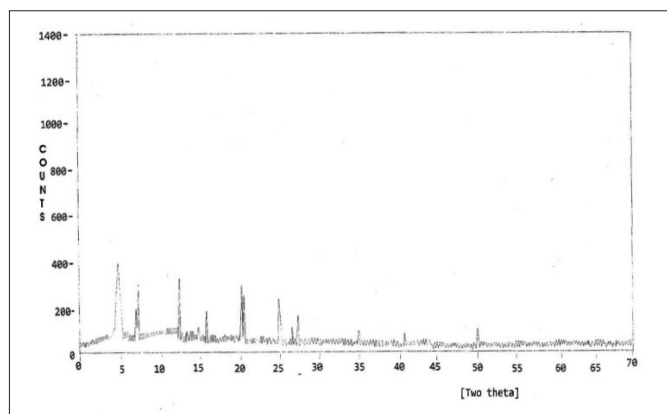


Figure 2: Clay soil Type BB, X-ray diffractogram of clay BB.

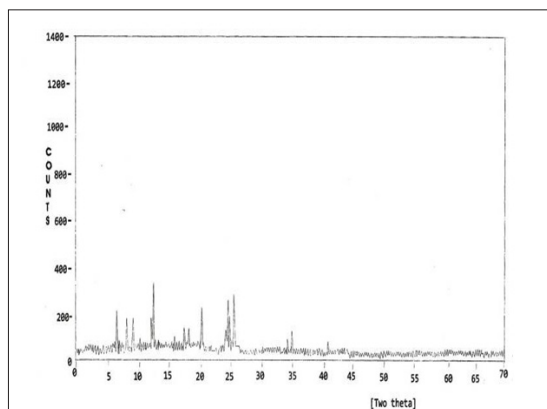


Figure 3: Clay soil Type UM, X-ray diffractogram of clay UM.

Suitable amount of sea water were collected at different times in 20 litres clean, plastic containers with sinkers tied 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) 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.

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  $\text{HClO}_4$  in ratios (3:2:1) and elemental analysis with Atomic Absorption Spectrometer (Varian 10) and structural water determined as loss on ignition. 5 g of air dried clay was weighed into 250 ml Erlenmeyer flask and 30 ml 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 20 ml of 1 ml ammonium acetate at pH7 used for their determination of Cation Exchange Capacity (CEC)=(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, 100 ml distilled water, 1 ml of  $\text{K}_2\text{CrO}_4$  and 0.2 ml of 0.0282 M  $\text{AgNO}_3$  solution was added and shaken, allowed to stand which was used for colour comparison.

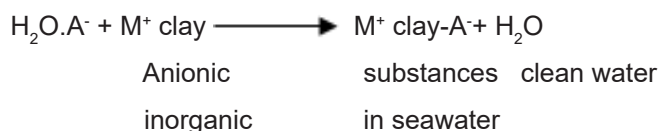
## RESULTS AND DISCUSSION

X-Ray Diffractometer mineralogical composition of each sample as shown in Table 1 below.

From the different clays Table 1 studied kaolin group was present in all the clay types in various percentage. OT clay type having the highest 58.20%, BB clay type 39.40% and UM clay type 31.20%.

**Table 1.** Percentage of composition of clay.

Clay mineral	Abbi clay (BB)	Otorho clay (OT)	Umutu clay (UM)
Saponite	Nil	Nil	5.8
Smectite group	7.3	Nil	6.1
Chloride	Nil	Nil	10.3
Illite	13.4	10.1	7.2
Illite and montmorillonite	15.4	Nil	29.4
Kaolinite	39.4	58.2	31.2
Hermatite	Nil	4.2	Nil



Where, A=OH<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> etc.

The results obtained combined with the equation above explains the ability of clay in removal of chloride from seawater (Umudi et al., 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 analysis Table 2 showed that all the clay types contain mainly silica (SiO<sub>2</sub>) and alumina. Others are magnesium and potassium. Since they are mixture of kaolinite, quartz, montmorillonite, it may expand and have high adsorption of cations. It was duely observed that clay minerals containing illite and montmorillonite, do expand and swell to absorb either anionic, cationic or neutral pollutants in the presence of water (Holmboe et al., 2012; Pawar et al., 2016) smectite and mix layer has large surface area, the larger the surface area, the larger the absorption occurs.

**Table 2.** Percentage of composition of oxides from geochemical analysis.

% oxide	BB	OT	UM
SiO <sub>2</sub>	44.4	43.3	43.1
Al <sub>2</sub> O <sub>3</sub>	38.80	38.63	39.97
Fe <sub>2</sub> O <sub>3</sub>	7.67	6.65	6.89
Na <sub>2</sub> O	0.67	1.97	0.88
MgO	1.82	1.93	1.9
K <sub>2</sub> O	1.68	2.69	1.6
TiO <sub>2</sub>	0.98	0.99	0.93
CaO	0.21	0.31	3.21
H <sub>2</sub> O*	3.51	3.53	1.52

**Note:** H<sub>2</sub>O\*: Structural water

The contact time is one of the decisive factors in the adsorption 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 aluminosilicate clays of Kaoline in different percentages, which are 1:1 clay with low cation exchangeability. Illite was presented all through which are 2:1 clays. They showed intermediate cation exchange capacity. So that a small amount of such expensive mineral interlayer with a little expandable component would greatly enhance the ease of splitting of the unit and its dispersion.

The Cation Exchange Capacity (CEC) Table 3 is of great fundamental and practical importance in clay mineral investigation (Holmboe 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.

**Table 3.** Cation Exchange Capacity (CEC) and percolation studies.

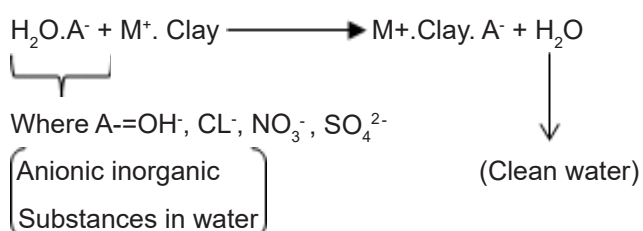
Clay sample	C.E.C	Time for first drop	Time to obtain 100 ml
BB	70	3 hours 48 minutes	4 hours 34 minutes
OT	1	2 hours 55 minutes	4 hours 45 minutes
UM	8	4 hours 13 minutes	8 hours 12 minutes

From the result of Table 4 the chloride concentrations were reduced. The pH was slightly reduced due to biodegradable matters in the seawater producing CO<sub>2</sub> which dissolves in water forming weak acid solution (Yuliyanti et al., 2011).

Table 4. One flow through and three flow throughs (means values).

<b>One flow-through</b>							
Characteristics	Raw values	BB mean	% reduction	OT	% reduction	UM	% reduction
Chloride	19705.5	8524.3	56	6808.4	65.4	4557.9	75.3
pH	7	5.65		5.4		5.3	
<b>Three flow-troughs</b>							
Chloride	19705.5	3875	98	166.1	99.2	0.16	99.9
pH	7	5.77		5.8		5.3	

The CO<sub>2</sub> thus produced affect the absorption because the mineral acid can dissolve the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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. 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<sub>2</sub>O<sub>3</sub>), alumina oxide (Al<sub>2</sub>O<sub>3</sub>) and SiO<sub>2</sub> 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<sup>+</sup> ions or releasing OH<sup>-</sup> ions, on the surface of the clay then becomes positively charged by the presence of H<sup>+</sup> and Al<sup>3+</sup> (Naswir et al., 2019). The formation of a positive charge on the clay minerals is caused by the inclusion of H<sup>+</sup> ions in the octahedral layer into Al(OH)<sub>3</sub> and the tetrahedral layer into SiOH forming a hydrogen bond so as to bind the negatively charged chloride.



Other natural materials apart from kaolin clays such as chitosan, bentonite and activated carbon can reduce other parameters like COD, BOD, TSS etc. (Lam et al., 2019). Thus these clay minerals can reduce other parameters and reduce environmental damage by industrial activities (Umudi et al., 2012).

### CONCLUSION

Kaolin clays are raw materials for reducing chloride in sea (ocean) water. They are low cost adsorbent for the reduction of chloride. The optimum residence time for chloride removal of 99.9% was UM 8 hours 12 minutes. 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.

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