Chemical composition of edible Oyster and Thales shells by X-ray fluorescence spectroscopy

Onojake M. C.[1,2]* and Osakwe J. O.[3]

[1]Department of Pure and Industrial Chemistry, University of Port Harcourt, P. M. B 5323, Choba, Port Harcourt, Nigeria.
[2]Centre for Marine Pollution Monitoring and Seafood Safety, University of Port Harcourt, P. M. B 5323, Choba, Port Harcourt, Nigeria.
[3]Qaulity Assurance/Quality Control Laboratory, Notore Chemical Industries PLC, Onne, Rivers State, Nigeria.
*Corresponding author. E-mail : ononed@yahoo.com, mudiaga.onojake@uniport.edu.ng. Tel: +234-8035404696.

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Oysters and Thales shells collected from the coastal areas of Nigeria were analyzed for their chemical compositions using X-ray fluorescence Spectrophotometer. The results of the elemental analyses of Oyster shell showed Ca: 47.34 ± 8.23%; Si: 23.17 ± 1.87%; Fe: 14. 83 ± 2.44% and Al: 14.65 ± 1.59%. The results of the oxides are CaO: 61.55; SiO_2: 49.57; Fe_2O_3: 21.20; Fe_3O_4: 20.50; FeO: 19.08; Al_2O_3: 27.68. Thales showed the following elemental composition Ca: 37.23 ± 8.13; Si: 23.46 ± 8.13; Fe:14.61 ± 2.09 and Al 24.70 ± 1.65. The results of Thales oxides are CaO: 48.41; SiO_2: 50.19; Fe_2O_3: 20.89; Fe_3O_4 : 20.19; FeO : 18.80; Al_2O_3: 46.67. The ranking of the elements are Ca>Si>Fe>Al, while the ranking order in Thales is Ca>Al >Si>Fe. The Oyster sell is composed of 95% Ca ($CaCO_3$) and some other minerals in different percentages. The percentage of Ca ($CaCO_3$) in Thales is about 90%. Because of the high content of CaO and $CaCO_3$ in Oyster and Thales shells, they can be used to synthesise Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$. They are potential raw materials with huge ecological, agricultural and engineering benefits.

Key words: Hydroxyapatite, oysters, orthopaedic, calcium carbonate, *Crassostrea*, X-ray fluorescence

INTRODUCTION

Oysters are categorized into the genus *Crassostrea*. There are various species of Oysters such as *Saccostrea*. There are four main species of oysters, under the sub-family *Crassostrinae, Crassostrea madrasensis* (Indian backwater Oyster), *Crassostrea gryphoides* (West coast Oyster), Chinese oyster *Crassostrea rivularis* and Indian rock oyster *Saccostrea cucullata*. Other species include the Bombay Oyster, *Saccostrea cucullata*, and giant Oyster *Hyotissa hyotis*. They are found in India, Asia, China, and much more in abundance in Africa in the coastal waters. It occurs as thick beds in estuaries, backwaters, ports and harbours and only sporadically on the open coasts. Oyster shell is composed of protein polysaccharides and minerals including calcium, magnesium, sodium, copper, iron, nickel, strontium and some microelements. Chemical and microstructure analysis showed that Oyster-shells are predominantly composed of calcium carbonate with rare impurities

Thales or Clams is a common name for different types of bivalve Mollusca that fall within the Animalia kingdom. Clams possess two shells that are of equal sizes which are connected by two adductor muscles and they have a strong burrowing foot. There are different classes of Clams ranging from hard shell Clams, soft shell Clams to manila Clams (Elliot, 2013) (Phases 1 and 2).

Countries like South Korea are well known to be most productive areas for Oyster

Phase 1. Oyster shells waste.
Source:popsci.com.

Phase 2. Thales or Clam shells waste.
Source:twenty20.com.

with estimated capacity of about 300,000 tons of Oyster shells which cover 4100 ha of coastal ocean (Korea Development Institute, 2002). Due to its chemical constituents it is used in South Korea as shell meal fertilizer and catching materials for Oyster seedlings pollution of coastal fisheries. Oyster and Thales shells are waste products from marine aquaculture that presents a major disposal problem in coastal regions especially in countries like Nigeria. Large amounts of Oyster shell are being constantly disposed illicitly into public waters and along coastal areas causing environmental nuisance and other problems such as the management problem of public water surface, damage of natural landscape, and health/sanitation problems (Yoon et al., 2003; Lee et al., 2005; Yang, et al., 2005)

Pile of mollusc shells contributes to over seven million tons of "nuisance waste" discarded on yearly basis by the seafood industries that throw the shell into landfills or dump it into the ocean (Morris et al., 2019). Some researchers call this practice "a colossal waste of potentially useful biomaterials’’. Huge ecological benefits could be reaped from the waste from the shell of the molluscs (Morris et al., 2019). A discovery of the chemical constituent of the Oyster and Thales shells will deal with situation of converting from environmental hazards to a more beneficial and viable products. X-ray fluorescence (XRF) spectroscopy is an entrenched analytical method for the assessment of the chemical composition of a sample. Over the years, the XRF instruments have been applied successfully in the laboratory to evaluate different samples for various applications such as geochemical, industrial, and archaeological applications (Jenkins et al., 1995; Jenkins, 1999; Beckhoff et al., 2006). The reduction in the size of the instrument to handheld XRF (hXRF) has made it possible to collect compositional information and carry out *in-situ* analysis in the field (Shackley, 2010; Liritzis and Zacharias, 2010; Zurfluh et al., 2011; Margui et al., 2012). The use of hXRF equipment provides rapid, *in-situ* data to the user to inform them about the composition of samples at their study area. By this time and money spent on laboratory analyses are reduced to barest minimum.

X-ray Fluorescence Spectroscopy (XRF) is the common technique employed for elemental identification and quantification. The method involves irradiating the sample with X-ray radiation (Primary X-ray) from the X-ray source, knocks out electron from the inner shell of the atoms while leaving them excited. On relaxation of these atoms, electrons are knocked off from the outer shell into the innermost shell; the excess energy is released and expended as X-ray radiation (Secondary X-ray). The energy of the emitted X-ray hinges on difference in the higher and lower state which is represented mathematically as:

$$E = hf = E_1 – E_2$$

Where: E = X-ray Energy; hf = Frequency or Planck's constant; E_2 = Energy level of the outer shell electron; E_1 = Energy level of the inner shell electron (Skoog et al., 2004). The detector detects x-rays and converts them to voltages, usually associated with noise. The voltage gives a smooth signal measured in counts as x-rays processed by the detector after shaping and noise reduction (James, 2012). The energy and intensity (count) of this radiation is dependent on material composition. The aim of this article is to determine the chemical composition of the shells of Oyster and Thales and their potential applications for ecological, agricultural and engineering benefits.

MATERIALS AND METHODS

The shells of Oyster and Thales were collected in Port Harcourt region close to the New Calabar River and transported to our laboratory. The shells were thoroughly washed with deionized water and air dried to remove all moisture. After drying, the shells were ground to generate a fine powder and sieved to different mesh sizes. The Oxford instruments hand held X- ray fluorescence (hXRF) does not require extensive sample preparation. The sample to be evaluated is aligned close to the detector window of a handheld XRF at the front of the spectrometer (X-ray source) and held down for 15.5 seconds to flush with the sample. The compartment lid is then closed and caution must be taken to allow the instrument to completely flush with the sample surface, to avoid possibility of errant X-rays that do not interact with the sample from escaping into the area surrounding in the front of the instrument. Care should be taken to ensure that the instrument is in its normal, recommended mode and not to put anybody's part directly next to where the instrument is touching the sample. The concentration of the various elements present in the sample is displayed on screen and printed out immediately.

RESULTS AND DISCUSSION

The results of the elemental composition of Oyster and Thales and their oxides are shown in Table 1 (Figure 1). The percentage of Ca in the Oyster shell is 47.34 ± 8.23, .Si: 23.17 ± 1.87, Fe: 14. 83 ± 2.44 and Al: 14.65 ± 1.59; the ranking of the elements is Ca>Si>Fe>Al. Thales has the following elemental compositions: Ca 37.23 ± 8.13; Si 23.46 ± 8.13, Fe 14.61 ± 2.09 and Al 24.70 ± 1.65 percent. The order of ranking of the elements is Ca>Al >Si>Fe. The percentage compositions of the oxides in Oyster are CaO 61.55; SiO_2 49.57; Fe_2O_3 21.20; Fe_3O_4 20.50; FeO 19.08; Al_2O_3 27.68; the compositions in Thales

Table 1. Results of the X-Ray Fluorescence (XRF) analysis of the elements and their oxide in percentage.

Element	RESULTS ± SD	
	Oyster	Thales
Ca	47.34 ± 8.23	37.23 ± 8.13
Si	23.17 ± 1.87	23.46 ± 1.73
Fe	14.83 ± 2.44	14.61 ± 2.09
Al	14.65 ± 1.59	24.70 ± 1.65
Oxides		
CaO	61.55	48.41
SiO_2	49.57	50.19
Fe_2O_3	21.20	20.89
Fe_3O_4	20.50	20.19
FeO	19.08	18.80
Al_2O_3	27.68	46.67

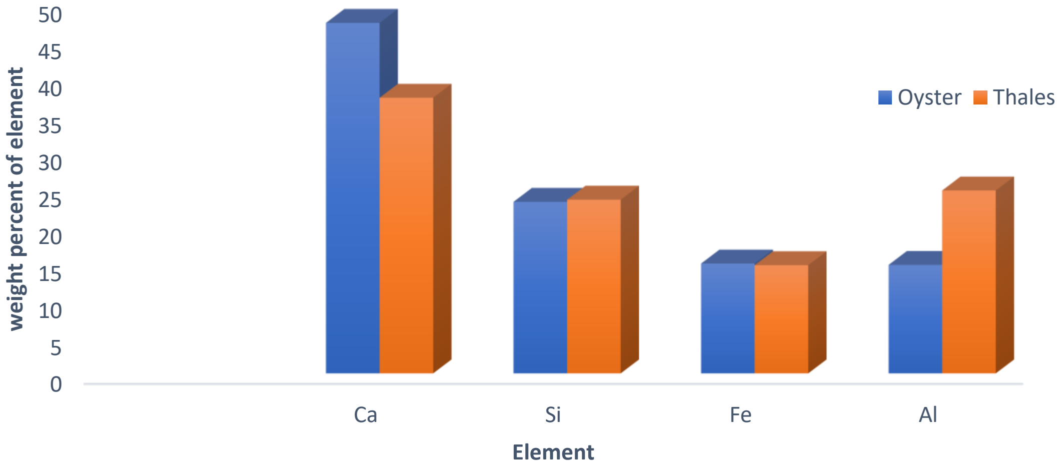

Figure 1. Comparison of the results of the elemental composition of Oyster and Thales shells.

are CaO 48.41; SiO_2 50.19; Fe_2O_3 20.89; Fe_3O_4 20.19; FeO 18.80; Al_2O_3 46.67 (Table 1).

The low percentages of the oxide are in agreement with other research on the shell of some seafoods such as mussels, clams. The Oyster sell is composed of 95% Ca ($CaCO_3$) and some other minerals in different percentages. The percentage of Ca ($CaCO_3$) in Thales is about 90%. The shells of Oyster and Thales can be calcined, converted to CaO and ($CaCO_3$) (Rujitanapanich et al.; 2014). Because of the high content of CaO and $CaCO_3$ in Oyster and Thales shell, it can be used to synthesise Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ through a process of precipitation, which is the main mineral constituent in human bones and teeth. Hydroxyapatite is widely used in orthopaedic applications and the manufacture of artificial teeth and bones. The advantages of Hydroxyapatite are its biocompatibility, non-toxic, non-immunogenic, non-inflammatory and bioactive (Fathi et al.; 2008; Zang, 2007). It has the ability to bond directly the host bones and teeth. The development of the processes in biominerilization has led to the production of new generation biomaterials using biogenic materials such as seashells, animal bone, eggshell and *Thunnus obesus* bone (Pallela et al.; 2011). Figure 2 shows a comparison of the oxides of the various elements in Oyster and Thales. CaO was higher in oyster (61.55%) compared to Thales with value of 48.41%.

So the Oyster shells will be more economical in the production of Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ and other orthopaedic applications than the Thales. The Thales shell is richer in the oxides of SiO_2 and Al_2O_3 with values

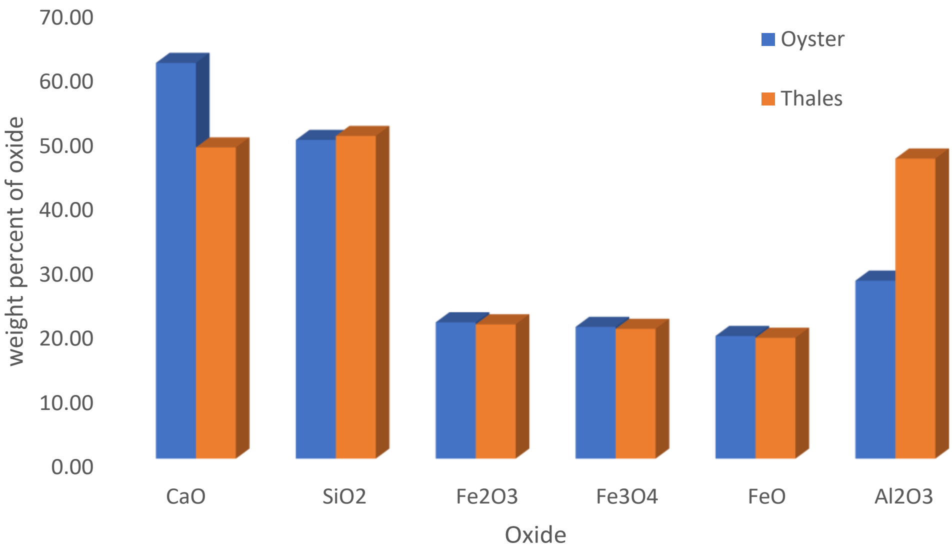

Figure 2. Comparison of the results of the oxides composition of Oyster and Thales shells.

of 50.19 and 46.67%. Investigations should be carried out on the application of the oxides or element with direct benefit for man. The oxides of iron are almost in equal values in both Oyster and Thales (Figure 2). Moreover, researchers such as Nciri et al. (2018) converted the Oyster shell powder ($CaCO_3$) and proposed that they have high content of natural hydrophilic material that has the tendency to form strong bonds with hydrophobic organic compounds like bitumen. Crushed Oyster and Thales shells have been used in clay materials and their applications. When they are finely crushed, the fine power serves as source of oxide, which can be used for coating, paints, varnishes, seals, cover etc. Due to the lower Fe and Al contents, they serve as the purest source of calcium carbonate. Some researchers showed that the concentration or percentages of the CaO, SiO_2, Fe_2O_3 and low percentages are in harmony with other types of sea shells (mussels, clams), MgO is higher, Al_2O_3 is lower. All are quite similar to limestone.

Researchers such as Du et al. (2011) suggested that the powder of mollusc and Thales shells which are rich in calcite and aragonite can be used for the treatment of heavy metal contaminated wastewater. Both shell powders have the capacity to adsorb Zn^{2+} in contaminated waste water. However, when the shells of Oyster and Thales powders were investigated, the Oyster powder showed a better adsorption capacity for Pb^{2+} sorbent, while the Thales powder had a better capacity for the adsorption of Cd^{2+} from contaminated wastewater.

Other applications of Oyster and Thales shells are potential source of raw materials for the productions of soda lime glasses. Other researchers had proposed that the huge ecological benefits from the waste from crushed shells of the Oyster and Thales are their applications for agricultural and engineering activities. Due to the harmful and unsustainability of limestone as source of calcium carbonate, it was postulated that shell of Oysters and Thales can comfortably replace limestone as source of calcium carbonate of the main ingredient in cement. They can also be used in waste water treatment. They can be crushed and fed to chickens and hens as source of calcium supplement or spread on soil surface to control soil acidity (Morris et al., 2019).

Conclusion

Our research on the chemical constituent of Oyster and Thales shells has shown that the major component of the Oyster shell is composed of 95% Ca ($CaCO_3$). The order of ranking of the elements in percent for Oyster is Ca>Si>Fe>Al. Thales shells also have Ca as the highest element with about 90% of $CaCO_3$. There is a little variation in the order of ranking of the elements shown as Ca>Al >Si>Fe. The low percentage of other oxides in Oyster and Thales is in agreement with published work of other researchers on the shell of some seafood such as mussels. Based on the major constituents of the shell of these seafood, they can serve as potential raw materials with huge ecological, agricultural and engineering benefits. Some of the applications include sources of raw material for the productions of soda lime glasses. They can be used as main ingredient in cement production, biofilters in waste water treatment, source of calcium supplements for chickens and hens, spread on soil surface to control soil acidity, pharmaceuticals, fertilizer, cement (limestone), coatings, paints, varnishes, seals, and used in orthopaedic applications and the manufacture of artificial teeth and bones.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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