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Original Research Article

Characterization of Periwinkle Shell from Nembe, Rivers State, Nigeria

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ABSTRACT

Periwinkle shell is discarded in the environment after eating its meat. It constitutes environmental challenges such as undesirable sight, odour, breeding points for disease-causing agents especially in the Niger Delta area of Nigeria. Waste recycling has been recognised as an efficient way of tackling this kind of environmental menace. However, insufficient knowledge about the features of the shell may pose an obstacle against significant progress. Therefore, periwinkle shell powder was characterised to ascertain its suitability for the production of quicklime. This was done using the proximate analysis, X-Ray Fluorescence (XRF), X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM) techniques. The results show that raw periwinkle shell is high in calcium - 59% calcium oxide (CaO) and its mineral phase is aragonite. Deproteinization of shell sample has no beneficiation effect on its calcium carbonate ($CaCO_3$) content of the shell. Also, comparing the results to a commercial limestone shows that the shell will be suitable for use in soda ash production, sugar refining, flue gas desulphurization etc.

1. INTRODUCTION

Increasing human population normally has a direct effect on the volume of wastes generated, with consequential impact on the environment (Hiremath, 2016). Recycling is a major scheme to effectively manage solid wastes and is an area of active research among these wastes are mollusc shells (Jassim, 2017; Abdel-Shafy and Mansour, 2018).

Molluscs are organisms which inhabit the coastal areas. Common members are oyster, mussel, cockle and periwinkle. Like limestone, their shells are chiefly composed of $CaCO_3$. Periwinkle is found along the coast of West Africa: from Senegal to Cameroun (Ajang *et al.,* 2015; Appleton *et al.*, 2015). In Nigeria, they inhabit the brackish waters of the Niger Delta area and Lagos lagoon (Abdullahi and Sara, 2015). The periwinkle specie (*Tympanotonus fuscatus*) inhabits the Niger Delta area of Nigeria (Bob-Manuel, 2012 and

Iboh *et al.*, 2015) while another specie, *Pachymelania aurita*, is found in Badagry, Nigeria (Falade, 1995). Periwinkle shell is discarded in the environment after taking its meat as food. Otoko and Cynthia (2014) estimated the quantity of periwinkle shell generation in Port Harcourt, Nigeria as 6 ton per day.

The resemblance in the composition of mollusc shells to limestone presents the essence for both similar reaction and use (Yao *et al.,* 2014). Effective use of periwinkle shell which was hitherto a solid waste, especially in the coastal areas, can best be achieved after its features are known. Unfortunately, information on the characterization of periwinkle shell is limited in the literature. Therefore, the aim of this study was to present the characterization of periwinkle shell powder towards the production of CaO.

2. MATERIALS AND METHODS

2.1. Sample Preparation

The samples used in the study are raw periwinkle shell, deproteinised periwinkle shell and Okpella limestone. Periwinkle was supplied from Nembe, Rivers State. The ground Okpella limestone was obtained from Centre for Solid Minerals Research and Development, Kaduna Polytechnic, Kaduna, Nigeria. It was sieved into particle size 0.09 mm - 0.1 mm. Shambhavi IMPEX ball mill was used to crush the periwinkle shell to open its interior for better washing. Then pipe-borne water was used to wash away mud, decaying meat and maggots from the shell. The cleaned shell was then sun-dried for five days. Grinding followed using the same ball mill. The ground shell was sieved to 0.1 mm, 0.5 mm and 2 mm particle sizes; thereafter, it was stored at ambient conditions.

2.2. Deproteinization

The procedure for deproteinization was very much in the same way reported by Gbenebor *et al.* (2017). First, 50 g of the sample was placed in 1000 ml of 1.2 M NaOH solution. The mixture was stirred while undergoing heating at 100 ^oC for 1 hr. It was allowed to cool to room temperature. Thereafter, the clear solvent layer was decanted away and the remaining solution was filtered. To maximise the removal of protein, the filtration cake (sample) was, again, soaked in fresh 1.2 M NaOH solution for 18 hr at room temperature (32 ^oC). Thereafter, the sample went through decantation and filtration before washing with tap water until its pH was 7.1. Washing the sample was finally done with de-ionised water. Then the sample was filtered and dried in the oven for 3 hr at 70 ^oC.

2.3. Proximate Analysis

Based on the standard methods reported by Davies and Jamabo (2016), the parameters determined include moisture content, ash content and volatile matter. The usual Kjeldahl method was used to determine protein content (Sáez-Plaza *et al.,* 2013; Davies and Jamabo, 2016). The result for each of the sample characterizations can be found in Tables 1.

2.4. X-Ray Fluorescence (XRF)

A handheld Thermo Scientific NITON XL3t XRF machine was used to analyse the chemical composition of all the three samples. This technique is the ASTM C1271 standard for evaluating chemical compositions. To ensure better measurement from the machine, dry, fine and homogeneous samples were used.

2.5. X-Ray Diffractometry (XRD)

XRD technique was done using Phenom ProX machine to identify the crystal structure of $CaCO_3$ present in the samples. The XRD machine was operated at a voltage of 40 kV, a current of 20 mA within the position of 2θ values varying from 15 to 90^{o} at a scan rate of 1.0 s/step. Scanning was ended after obtaining optimum values by ensuring that the scan axis and angle between incident x-rays and sample surface no longer changed significantly. To identify phase(s) present in the sample, the diffraction pattern of periwinkle shell powder obtained were compared to reference patterns.

2.6. Scanning Electron Microscopy (SEM)

To observe the morphology of the samples, a desktop Phenom ProX was used. The sample was sprinkled on a sample stub. It was then taken to a sputter coater (quorum-Q150R Plus E) with 5 nm of gold. It was then placed on a charge reduction sample holder and introduced into the column of the SEM machine. The sample holder was viewed from a NavCam before it was sent to SEM mode. After adjustment of image brightness and contrast, images with different magnification were stored in a USB stick.

3. RESULTS AND DISCUSSION

3.1. Proximate Analysis

The proximate analysis outcome is presented in Table 1. It shows that the ash content of the periwinkle shell is 9.1% it indicates the presence of inorganic mineral such as $CaCO_3$ (Ismail, 2017). The shell moisture content is low, estimated at 2.5%. The low moisture content of the shell prevents longer residence time a sample spends in the kiln. Conversely, the high moisture content in the material will require more thermal energy for drying then for heating to the decomposition temperature. Therefore, more residence time is spent in the reactor which supports sintering (Takkinen *et al.,* 2011). The protein content is 0.34%, and a negligible fat content of 0.15% were evaluated. These results agree with the report of Kehinde *et al.* (2015).

Table 1: Proximate composition of periwinkle shell

Moisture content (%)	Ash content (%)	Fat (%)	Crude protein (%)	Crude fibre (%)	Carbohydrate (%)
2.5	9.1	0.15	0.34	0.43	87.48

3.2. XRF Analysis

It was thought that by eliminating the shell's organic component through deproteinization, a beneficiated sample could be achieved. Table 2 juxtaposes the XRF results of the raw and deproteinized periwinkle shell with limestone.

Table 2: Composition of $CaCO_3$ feedstock before and after calcination at 800 ^{o}C, 45 min

Compo – nent (%)	Okpella lime - stone	Calcined Okpella lime - stone	Deproteini-sed periwinkle shell	Calcined, deprotei - nised periwinkle shell	Periwin - kle shell	Calcined periwin - kle shell
CuO	0	0.003	0	0.003	0.003	0.004
NiO	0	0	0	0.006	0	0.008
Fe_2O_3	0.157	0.172	0.35	0.45	0.754	0.508
MnO	0	0	0.019	0.03	0.02	0.036
CaO	46.702	60.63	59.58	84.508	59.082	82.434
Al_2O_3	0.503	0.598	0.426	0.901	0.753	0.781
ZnO	0	0.002	0.006	0.011	0.018	0.014
SiO_2	1.445	2.193	1.307	1.197	1.296	1.549

Importantly, CaO is the main component of the samples. Its composition range for the uncalcined materials is 46.70% - 59.58% and it compares well to high-grade limestone reported by Harrison (1993). Another major component of limestone is MgO; though, it is not present in any of the samples under test. Impurities like SiO_2 and Al_2O_3 of the periwinkle shell sample are in quantities comparable to that of the limestone. Generally, the oxide content of the calcined samples appears to be more than the uncalcined ones. The observation could be based on the inference that some components were lost during the calcination which results in a product with enhanced components. However, the SiO_2 content of deproteinised periwinkle shell decreased from 1.307% to 1.1907%. Fe_2O_3 and ZnO content of periwinkle shell decreased from 0.754% to 0.504% and from 0.018% to 0.014 respectively. % Al_2O_3 quantity of raw periwinkle shell reduces from 0.753% to 0.426% due to deproteinization. This reduction in quantity brings it closer to that of limestone which is 0.503%. For the most part, the quantity of CaO is not influenced by deproteinization. In this work, periwinkle shell tested is of a higher grade than the Okpella limestone. It compares well with those reported by some workers (Ar and Doğŭ, 2001; Cheng and Specht, 2006; Tripathi *et al.,* 2016).

3.3. XRD Analysis

Result of the XRD analysis of the periwinkle shell is presented in Figure 1. The major peak stands at 26.2^o and identifies aragonite as the main phase of $CaCO_3$ present in the periwinkle shell. This result agrees with many reports on mollusc shells - cockle shell (Mohamad *et al.,* 2016) and mussel shell (Roy and Marie, 2012). According to Roy and Marie (2012), molluscs produce minerals that are different from their inorganic counterpart (limestone) in structure.

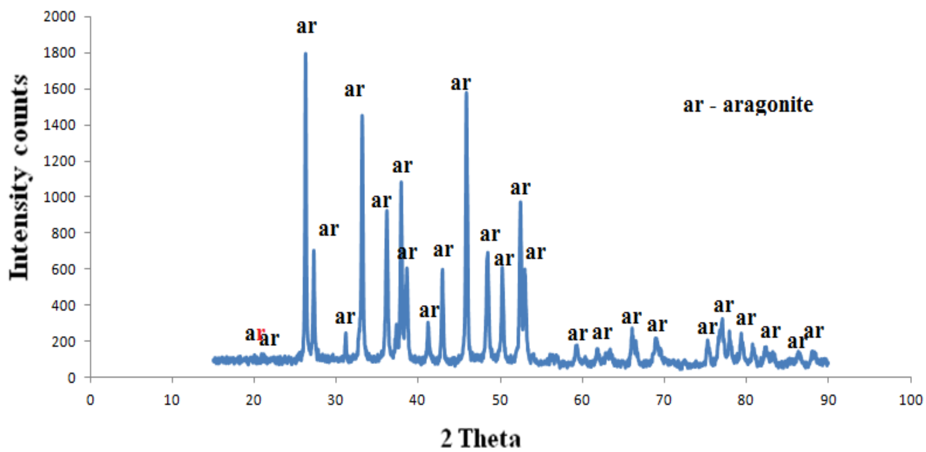

Figure 1: XRD pattern for periwinkle shell used for this study

3.4. SEM Analysis

The morphology of the samples before and after calcination is presented in Figures (2-5). As anticipated, the results reveal the rod-like structure of aragonite for all the periwinkle samples in Figures 2, 3 and 7. The results corroborate the XRD result of Figure 1. The SEM analyses also show the cubical shape of calcite in Okpella limestone (Figure 4 and 5). These results agree with the established literature (Mohamed *et al.,* 2012). For the conditions of calcination considered, the shell samples (Figure 7) show more formation of pores than the limestone sample (Figure 5). This could be explained from the point that calcite is more stable than aragonite (Hoque *et al.,* 2013).

Figure 2: SEM image of deproteinised periwinkle shell

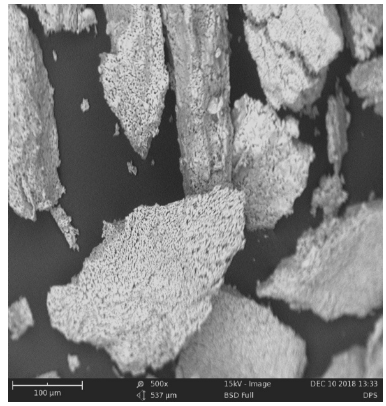

Figure 3: SEM image of deproteinised periwinkle shell calcined at 800 °C, 45 min

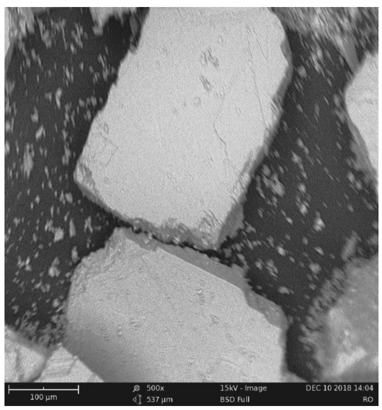

Figure 4: SEM micrograph of raw Okpella limestone

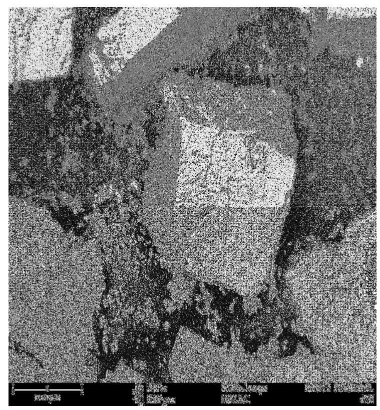

Figure 5: SEM micrograph of Okpella limestone calcined at 800 °C, 45 min

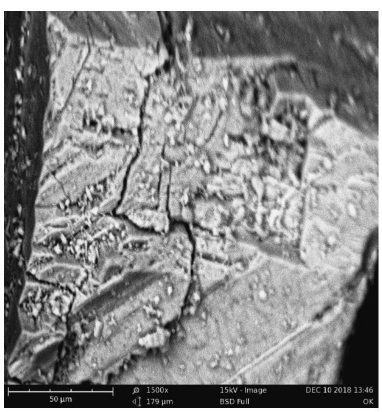

Figure 6: Magnified SEM image of Okpella limestone calcined at 800 °C, 45 min showing the formation of pores

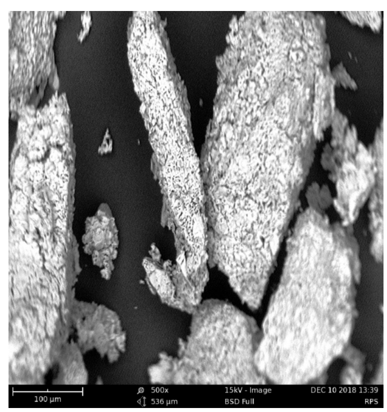

Figure 7: SEM micrograph of periwinkle shell calcined at 800 °C, 45 min

4. CONCLUSION

The characterization results of SEM and XRF show that deproteinization practically has no influence on the general composition of the periwinkle shell and will not affect its calcination. The XRF analysis shows that periwinkle shell composition compares to that of the commercial limestone. Therefore, it is suitable for use in the manufacture of soda ash, sugar refining, flue gas desulphurization etc.

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

Abdullahi, I. and Sara, S. G. (2015). Assessment of periwinkle shells ash as composite materials for particle board production. *International Conference on African Development Issues (CU-ICADI).* Materials Teclmology Track, pp. 158-163.

Abdel-Shafy, H. I. and Mansour, M. S. M. (2018). Solid waste issue: Sources, composition, disposal, recycling, and valorization. *Egyptian Journal of Petroleum,* 27(4), pp. 1275-1290.

Ajang, C. I., Odey, R. and Christian, S. (2015). Population estimation of periwinkles *Tympanotonus fuscatus* and *Parchymelania aurita* at Esuk Mba mangrove swamp along Cross River estuary. *Journal of Natural Sciences Research*, *5*(1), pp. 58–62.

Appleton, C., Jørgensen, A., Kristensen, T.K. and Stensgaard, A.-S. (2015). *Tympanotonus fuscatus*, mud-flat periwinkle. *The International Union for Conservation of Nature and Natural Resources Reproduction Red List of Threatened Species*, 8235, pp. 1-5.

Ar, I. and Dogŭ, G. (2001). Calcination kinetics of high purity limestones. *Chemical Engineering Journal*, *83*(2), pp. 131–137.

Bob-Manuel, F. G. (2012). A preliminary study on the population estimation of the periwinkles *Tympanotonus fuscatus* (Linnaeus, 1758) and *Pachymelania aurita* (Muller) at the Rumuolumeni mangrove swamp creek, Niger Delta, Nigeria. *Agriculture and Biology Journal of North America*, 1977, pp. 265–270.

Cheng, C. and Specht, E. (2006). Reaction rate coefficients in decomposition of lumpy limestone of different origin. *Thermochimica Acta*, *449*, pp. 8–15.

Davies, I. C. and Jamabo, N. A. (2016). Proximate composition of edible parts of shellfishes from Okpoka creeks in Rivers. *International Journal of Life Sciences Research*, *4*(2), pp. 247–252.

Falade, F. (1995). An investigation of periwinkle shells as coarse aggregate in concrete. *Building and Environment*, *30*(4), pp. 573–577.

Gbenebor, O. P., Akpan, E. I. and Adeosun, S. O. (2017). Thermal, structural and acetylation behaviour of snail and periwinkle shells chitin. *Progress in Biomaterials*, 6(3), pp. 97–111.

Hamester, M. R. R., Balzer, P. S. and Becker, D. (2012). Characterization of calcium carbonate obtained from oyster and mussel shells and incorporation in polypropylene. *Materials Research,* 15(2), pp. 204–208.

Harrison, D. J. (1993). Industrial minerals laboratory manual: Limestone. BGS Technical Report WG/92/29. Available electronically at *https://www.bgs.ac.uk/research/international/dfid-kar/WG92029_col.pdf*. Accessed on April, 2018.

Hiremath, S. S. (2016). Population growth and solid waste disposal: a burning problem in the Indian cities. *Indian Streams Research Journal, 6(1),* pp. 1-8.

Hoque, E., Shehryar, M. and Islam, K. N. (2013). Processing and characterization of cockle shell calcium carbonate ($CaCO_3$) bioceramic for potential application in bone tissue engineering. *Journal of Material Sciences and Engineering*, *2*(4), pp. 2–6.

Iboh, C. I., Ajang, R.O. and Ekoro, S.C. (2015). Population estimation of periwinkles tympanotonus fuscatus and parchymelania aurita at Esuk Mba mangrove swamp along Cross River estuary. *Journal of Natural Sciences Research.* 5 (1), pp. 58-62.

Ismail, B. P. (2017). *Ash Content Determination.* Food Science Text Series. Available electronically at https://sci-hub.tw/http://dx.doi.org/10.1007/978-3-319-44127-6_11. Accessed on September, 2019.

Jassim, A. K. (2017). *Sustainable solid waste recycling. Skills development for sustainable manufacturing*. In Tech. Available electronically at https://www.intechopen.com/books/skills-development-for-sustainable-manufacturing/sustainable-solid-waste-recycling. Accessed on September, 2019.

Kehinde, O., Mariam, Y., Adebimpe, O. and Blessing, A. (2015). Traditional utilization and biochemical composition of six mollusc shells in Nigeria, *Revista de Biologia Tropical,* 63(2), pp. 459-464.

Marin, F., Roy, N. L. and Marie, B. (2012). The formation and mineralization of mollusc shell. *Frontiers in Bioscience*, 4(3), pp. 1099-1125.

Mohamed, M., Yousuf, S. and Maitra, S. (2012). Decomposition study of calcium carbonate in cockle shell. *Journal of Engineering Science and Technology*, *7*(1), pp. 1–10.

Mohamad, S.F., Mohamad, S. and Jemaat, Z. (2016). Study of calcination condition on decomposition of calcium carbonate in waste cockle shell to calcium oxide using thermal gravimetric analysis. *ARPN Journal of Engineering and Applied Sciences*, *11*(16), pp. 9917–9921.

Takkinen, S., Saastamoinen, J. and Hyppänen, T. (2011). Heat and mass transfer in calcination of limestone particles. *American Institute of Chemical Engineers Journal,* 58(8), pp. 2563–2572.

Tripathi, H. S., Ghosh, A. and Mukherjee, B. (2016). Kinetics of non-isothermal and isothermal decomposition of limestone. *Transactions of the Indian Ceramic Society*, 63(3), pp. 155–158.

Sáez-Plaza, P., Navas, M. J., Wybraniec, S., Michałowski, T. and Asuero, A. G. (2013). An overview of the Kjeldahl method of nitrogen determination. Part II. Sample preparation, working scale, instrumental finish, and quality control. *Critical Reviews in Analytical Chemistry,* 43(4), pp. 224–272.

Yao, Z., Xia, M., Li, H., Chen, T., Ye, Y. and Zheng, H. (2014). Bivalve shell: Not an abundant useless waste but a functional and versatile biomaterial. *Critical Reviews in Environmental Science and Technology,* 44(22), pp. 2502–2530.