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Proximate Analysis of Chicken Eggshell Using Fourier-Transform Infrared Spectroscopy Technique

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Abstract

The paper presents comprehensive proximate analysis of chicken eggshells using Fourier transform infrared (FTIR) spectroscopy. Chicken eggshells, are readily available bio-waste product, which constituent environmental nuisances if not properly managed. This study explores the potential of FTIR as a rapid and non-destructive technique for the proximate analysis of chicken eggshells. The study aimed to determine the chemical composition and structural characteristics of eggshells through the application of FTIR spectroscopy being a powerful analytical technique for investigation using molecular vibrations. Eggshells were collected from farms and restaurants around, cleaned, pulverized and used for the study. FTIR spectra were allowed to scan at a wavelength of 600-4000nm to obtain its spectra wavelength and analyzed for characteristic peaks corresponding to major functional groups and mineral components. The obtained FTIR spectrum revealed nineteen (19) distinct peaks at well-defined wavenumbers, which is indicative of various functional groups and molecular vibrations. The bands at 1444.636 cm^{-1}, 1347.831 cm^{-1}, 1007.913 cm^{-1}, 873.0817 cm^{-1}, and 709.1337 cm^{-1} Indicated presence of Calcium Carbonate in the tested sample. FTIR demonstrated remarkable efficacy for the rapid and accurate proximate analysis of chicken eggshells. The outcome provided valuable insights into the eggshell's mineral composition, opening avenues for further exploration of its potential applications in various fields, including bio-materials, agriculture, filler material in composite materials and bio-waste valorization taking eggshells as a bio-resource which offers environmental benefits by reducing waste. Poultry farmers will also benefit from findings of this research through the several novel potential areas of application suggested by this paper.

1.Introduction

Owing to increased egg consumption globally, a corresponding surge of about 18% in egg production has been recorded during the last decade [1]. Global egg production has hit 80-million metric-ton mark with China, USA and India, being the leading egg-producing countries contributing their share of 458, 109 and 95 billion eggs per annum, respectively [2]. In total, around 78 million tonnes of eggs were produced in 2018 and accounted for about 8.58 million tonnes of eggshell which was mostly thrown away as waste. The dumping of this calcium rich commodity into landfills leads to different environmental issues and should therefore be properly addressed [2]. Millions of tonnes, shell eggs are produced from processing plants, egg stations, poultry hatcheries, industry and households which could be used in a variety of applications. A brief description of the various uses of eggshells in our society, for example its use as a medicine supplement, bone graft substitute and base for dentures is given below, such as their use in medicinal supplements, bone graft substitute and denture base. Eggshells can also be employed in constructing floor tiles and in cement to enhance compressive strength. An eggshell can be used for a wide range of uses, including animal feed, fertilisers, batteries, inkjet printers, biodiesel production and removal of heavy metals [2].

Beyond basic needs of food and shelter for survival, an ever-growing global population requires a variety of resources. As a result, there has been an increase in urbanization, with greater level of demand for food and hence heightened food waste generation. Slower progress in the area of waste management has made this problem worse. Food waste may act as the raw material for manufacturing various value-added products, by storing a variety of nutrients. eggshells constitute a large waste of foodstuffs, and this dilemma is particularly embarrassing given that they are available in significant quantity [1]. In the past few years, with the increase in income and greater dietary acceptance, higher egg consumption has been observed This is more evident for developing countries, where the general population accepted eggs to be a source of high quality protein and influenced consumers' purchasing decisions in turn.. According to the report of World Agriculture Supply and Demand Estimates; in the United States of America alone, egg consumption is expected to augment from around 7951.8 million dozen in 2019 to over 8000 million dozen in 2020 [1]. Per capita annual egg consumption in the United States is reported to be around 280 eggs in 2019; thus, marking it to be the highest egg consumption level over the past 10 years. Egg consumption statistics has been projected US Department of Agriculture {USDA) to reach up to 8917 million dozen by 2028 [3]. Some of the countries with the highest annual egg consumption statistics are Japan, Paraguay and China where individuals consume 320, 309 and 300 eggs respectively [4]. This rise in egg consumption has triggered the corresponding surge in egg production globally e.g. continuing the example of United States, egg production was recorded to be around 9334 million dozen in 2019 and is expected to reach around 9410 million dozen in 2020 [3].

Global egg production is forecast to remain stable or slightly improved in major markets around the world, according to this scenario [1]. Egg production has increased by over 150% in the past 30 years and more progress was made in Asia, where there is a fourfold increase in egg production [1[. In 2016, there were reports of a 30-year high production of around 83 billion eggs in India [3]. For the production and processing of food, these large volumes of eggs are used at domestic and industrial level as a source of nutrition. Increased egg production will lead to more eggshell waste, which is usually discarded and disposed of in landfills. China, the world's largest producer of eggs with 24.8 billion kg in 2019, is projected to increase its production by more than 35 million tons in 2020 [1].

Nigeria's poultry sector is composed of about 180 million birds, up to 80 million in the extensive systems, down to 60 million in the Semi-Intensive System and 40 million in the

Intensive System [5]. Up to 300 million tonnes of poultry meat and 650 million tonnes of eggs are produced in Nigeria each year [5]. The Environmental Protection Agency (EPA) ranked eggshell waste as the fifteenth most important food industry pollution problem [1]. Eggshells are considered to be a major source of environmental pollution and due to fungal growth in these eggshells, they can cause health risks if not handled properly at specified locations [6]. Furthermore, non-disposal of waste in an effective way becomes critical for the survival of not only humans but also other contributors to the eco-system like animals and vegetation. In landfills, this great volume of waste eggshells is primarily discarded; these fills are already filled to capacity. Besides, many landfill operators are avoiding eggshells because they attract rats and other pests through the protein content of membranous. Although Eggshell is regarded as a waste product of the food industry, it should equally be considered as highly sophisticated composite [1]. The time has come for waste to be transformed into useful commodities for sustainable development in this era of ever increasing efforts to convert waste into wealth. The aim should be to recycle, reuse and channel waste products and to focus our efforts on the production of high value products.

An idea worthy of examination is the effectiveness of converting eggshell waste to usable products [7]. Although fertilized, unfertilized and embryo eggs have been used since ancient times to provide nutrition and to treat a variety of diseases, the fact that eggshells are rather a source of new life and are not primarily intended for human consumption should be borne in mind [7]. Provision of physical barrier to prevent microorganisms from invading the cell is one of the important functions of eggshell. Gas exchange is another vital function of eggshell as there are a lot of pores on its surface [7].

The shells make up about 9–12% of the total egg mass and, in view of the eggshell's chemistry, 98 % are composed of dried matter containing 2 % water. Mainly ash 93% and crude protein 5% constitute the dried matter. Microscopically, Eggshell is composed of a network of protein fibres, which in turn are associated with crystals of calcium, magnesium carbonate and calcium phosphate along with certain other organic substances like water [8, 1]. The utilization of eggshells in various products, ranging from food commodities to products of industrial applications, is mainly dependent upon its main component i.e. calcium carbonate [6]. Based on the above discussion, the current research aims to provide an insight into applications of eggshell aluminium composite. Poultry eggshells are agricultural waste materials generated from chick hatcheries, bakeries; fast food canteen and restaurants among others which can litter the environment and consequently constitutes environmental problems/pollution if not properly handed or managed.

Scanning electron microscopy (SEM, FEI ESEM Quanta 200) and energy-dispersive X-ray spectrometry (EDX, FEI ESEM Quanta 200) were used to study chicken eggshell by Kaewmanee, et al in [9]. The chicken eggshell were prepared and put in a Scanning Electron Microscope stud using a double-backed cellophane tape. The stub and sample were coated with gold and examined using the scanning electron microscope [9].

Al-awwal and Ali, 2015 in [10] conducted a study on eggshell using Atomic Absorption Spectrophotometer (AAS) and Flame Photometer (FP). The model of AAS used for the analysis of the chicken eggshell sample was AAS Buck scientific Accusys 211 equipped with air-acetylene for the flame. The automatic hollow cathode lamp switch attached to the AAS was used to measure the absorbance and concentration of the metals by direct aspiration into the burner through the sample introduction system at wavenumber corresponding to each element as given by the manufacturer. Calcium (Ca), magnesium (Mg), iron (Fe), zinc (Zn) and copper (Cu) were confirmed by [10] using AAS. While flame photometer was used to determine the concentration of sodium (Na) and potassium (K) in eggshell by [10]

Presently, scientists around the world are looking for better ways to turn industrial and agricultural wastes into raw materials for the manufacturing industry. However, not much has been reported on the elemental composition characterization of chicken eggshell using FTIR spectroscopy/technique and the possible commercial (economical) uses of chicken eggshell thereby creating knowledge gap that necessitated this study. The quest to meet the identified needs above necessitated this study.

The objective of this study is to determine the chemical composition/ elemental composition, functional group, surface morphology and structural characteristics of chicken eggshells through the application of FTIR spectroscopy/technique. These are with the primary intension of ascertaining the true quality and characteristics of the chicken eggshell in order to find a more economic application for it instead allowing them to continue to be waste which constitute environmental hazards and nuisance.

2.0: Material and Methods

2.1: Materials

The materials used for the research include: chicken eggshell; electronic weighing scale; electric blender; pen; field note; polyethylene plastic bag;

2.2: Methods

The method used for the study involved two phases: Preparation of Eggshell Powder; and Fourier-Transform Infrared Spectroscopy (FTIR) Analysis of Eggshell Powder.

2.2.1: Preparation of Eggshell Powder

2 kg of chicken eggshells were sourced locally from a farm and restaurant around Ozoro town which is located in Delta State, Nigeria. The collected eggshells were washed thoroughly with hot water, sterilized and sun dried to remove the unwanted membranes, dirts and other extraneous materials. It was then washed again properly. The sterilized eggshell was dried in an oven at 50° C for 2 days, then crushed and blended into smooth powder using an electric blender. After which the eggshell powder was sieved into fine powder with the aid of a laboratory stainless steel sieve with 0.5 mm (500 μm). The well sifted (sieved) eggshell powder prepared was stirred properly using **powder mixing** machines so as to improve the quality of **blends and ensure uniformity of eggshell powder.** The prepared eggshell powder was finally packed into a polyethylene plastic bag and sent to laboratory for Fourier-transform infrared spectroscopy (FTIR) Analysis**,** after which the eggshell powder was ready for use in blending with aluminium material.

The following safety precautions were applied: (1) the team ensured clean tools were used, such as a knife and eggshell cracker, to open the eggs were used; and (2) Eggshells were sterilized by baking them in an oven at a temperature sufficient to kill bacteria, such as 160-180°C (320-356°F), for at least 15-20 minutes.

2.2.2: Fourier-Transform Infrared Spectroscopy (FTIR) Analysis of Eggshell Powder

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique for analyzing the chemical composition of materials by identifying the functional groups that are present in such material sample based on the absorption of infrared radiation by the bonds within those groups. Sample of the eggshell powder prepared in 2.2.1 above was taken to laboratory for "FTIR" examination using M500Model of Buck Scientific FTIR equipment: At the laboratory; 0.5g of the sample was mixed with 0.5g of Potassium Bromide (KBr) after which 1ml of Nujol mineral oil (a solvent prepared by Buck M530 IR-spectrophotometer) was introduced into the eggshell sample with aid of a syringe to form a paste before introducing it into the instrument sample mould (M500Model of Buck Scientific FTIR equipment). 50

milligrams of the eggshell powder were placed onto a sample holder that is compatible with the FTIR instrument. The sample holder was placed in the sample compartment of the FTIR equipment. The equipment was turned on and allow to warm up according to the manufacturer's instructions. The equipment was set to scan at a wavelength of 600-4000nm with a resolution of 4 cm to obtain its spectra wavelength. 30 scans (multiple scans) were taken to improve signal-to-noise ratio and overall results of the FTIR study.
The obtained spectrum peaks characteristics were compared with reference spectra from databases to identify the functional groups that are present in the eggshells. The peaks in the spectrum obtained based on known vibrational frequencies of chemical bonds were interpreted. The entire research process is is summarized and represented in flow presented in Figure 1.

Figure 1: Flow chart of Research Process

3.0: Results and Discussion

The Fourier Transform Infrared Spectroscopy (FTIR) analysis of eggshell powder result is presented using the graph in Figure 2 and Table 1. The FTIR analysis was conducted to identify the functional group that is present in the powder eggshell.

Table 1: FTIR Analysis Eggshell Powder

S/N.	Wavelength (cm^{-1})	Assignment	Functional Group	Compound present
1.	709.1337	Bending vibrations (C-H, N-H, or C-O)	C-H, N-H, or C-O bonds.	Organic compounds with C-H, N-H, or C-O bonds
2.	873.0817	C-H bending vibrations	Alkanes or aliphatic compounds	Organic hydrocarbons, aliphatic structures
3.	1007.913	C-O stretching vibrations	Oxygen-bearing functional groups	Alcohols, ethers, esters, organic compounds with oxygen
4.	1347.831	C-H bending vibrations	Alkanes or aliphatic compounds	Organic hydrocarbons, aliphatic structures
5.	1444.636	Bending vibrations involving C-H and C-O bonds	(C-H, C-O)	Organic compounds with mixed C-H and C-O bonds
6.	1604.235	C=C stretching vibrations	Aromatic compounds	Aromatic hydrocarbons, organic matrix proteins
7.	1851.793	C=O stretching vibrations	Carbonyl groups	Aldehydes, ketones, carboxylic acids
8.	2038.969	Bending vibrations of C-H bonds	Aromatic compounds	Organic compounds with aromatic structures
9.	2211.572	Overtone or combination vibrations	Varied functional groups	Complex combinations of organic and inorganic functional groups
10.	2458.325	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures
11.	2555.958	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures
12.	2757.204	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures
13.	2831.326	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures

14.	3005.373	C-O stretching vibrations	Oxygen-bearing functional groups	Alcohols, ethers, esters, organic compounds with oxygen
15.	3134.619	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures
16.	3235.806	C-H stretching vibrations	Aliphatic or aromatic compounds	Organic hydrocarbons, aliphatic or aromatic structures
17.	3332.422	O-H stretching vibrations	Hydroxyl groups	Alcohols, phenols, organic compounds with hydroxyl groups
18.	3458.349	O-H stretching vibrations	Hydroxyl groups	Alcohols, phenols, organic compounds with hydroxyl groups
19	3797.291	O-H stretching vibrations	Hydroxyl groups	Alcohols, phenols, organic compounds with hydroxyl groups

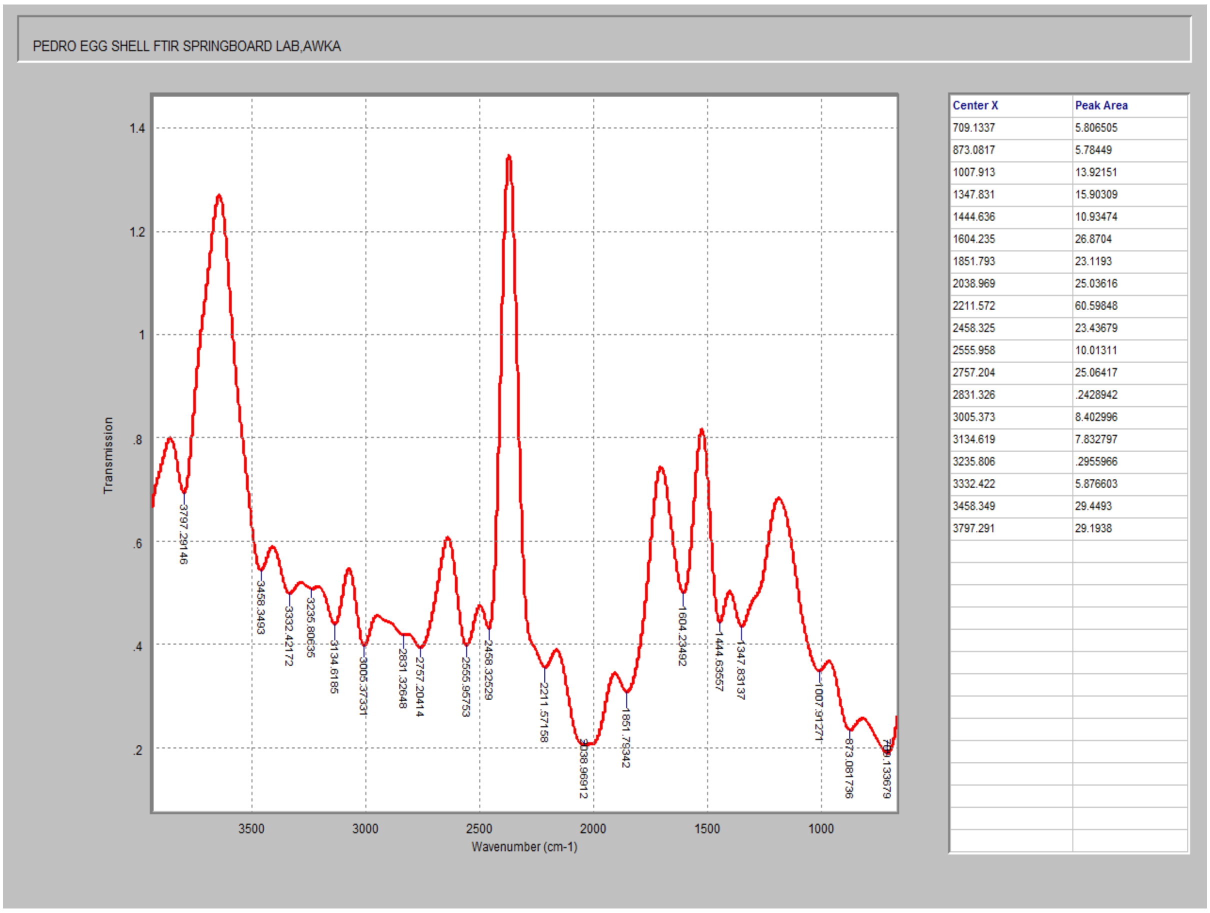

Figure 2: FTIR spectrum of eggshell powder

The obtained FTIR spectrum reveals nineteen (19) distinct peaks at well-defined wavenumbers, which is indicative of various functional groups and molecular vibrations. The summary of the FTIR analysis is presented in Figure 2.and Table 1. The peak at 709.1337 cm^{-1} signifies bending vibrations, possibly arising from C-H, N-H, or C-O functional groups. This suggests the presence of complex organic compounds within the eggshell matrix.
873.0817 cm^{-1} peak corresponds to C-H bending vibrations, indicative of aliphatic compounds or hydrocarbon chains. The peak observed at 1007.913 cm^{-1} corresponds to C-O stretching vibrations, indicating the presence of oxygen-bearing functional groups in organic compounds. The peak at 1347.831 cm^{-1} indicates possible C-H bending vibrations, likely originating from hydrocarbon moieties in the eggshell. The peak registered at 1444.636 cm^{-1} reveals combined bending vibrations involving both C-H and C-O bonds, suggesting intricate molecular arrangements. The prominent peak at 1604.235 cm^{-1} is representative of C=C stretching vibrations, characteristic of aromatic compounds found in the organic matrix proteins of eggshells. It is potentially adsorbent due to the presence of different functional groups in chicken eggshells [11].
The bands at 1444.636 cm^{-1}, 1347.831 cm^{-1}, 1007.913 cm^{-1}, 873.0817 cm^{-1}, and 709.1337 cm^{-1} indicated the presence of calcium carbonate in the tested sample. These findings correspond with the observations of Tlili et al (2021) [12]; Carvalho (2011) [13]; Pelin (2019) [14] that the observable peaks between 713 and 875 cm^{-1} should be associated with the presence of calcium carbonate. Since calcium and magnesium compete for absorption in the gut, too much of one can cause a deficiency in the other [15]. The eggshell can be used as an alternative to sand in making hollow blocks because it contains calcium carbonate that can provide the required hardness and strength in block making. Calcium is synonymous with bone, it gives bone its hardness, but it does not provide any flexibility [1]. Hard bone without any flexibility would be synonymous with chalk that is hard, but brittle, and very easy to break[1]. Also, Iram et al. (2019) [15] has reported that the bands concerned with calcium carbonate are 1430 cm^{-1}, 875 cm^{-1}, and 715 cm^{-1}, where the lowest band is considered as a weak band to indicate the presence of calcium carbonate.

A peak at 1851.793cm^{-1} corresponds to C=O stretching vibrations, pointing towards the presence of carbonyl groups such as aldehydes, ketones, or carboxylic acids. The peak at 2038.969 cm^{-1} signifies bending vibrations of C-H bonds in aromatic compounds, providing further evidence of complex organic constituents. The 2211.572 cm^{-1} peak is likely due to overtone or combination vibrations, possibly indicating intricate molecular interactions within the eggshell powder.

The peak at 2458.325 cm^{-1} corresponds to C-H stretching vibrations, implying the presence of aliphatic or aromatic compounds. At 2555.958 cm^{-1}, a peak signifies C-H stretching vibrations, providing additional evidence of the organic nature of the eggshell constituents. The peak at 2757.204 cm^{-1} indicates C-H stretching vibrations in organic compounds, reaffirming the rich molecular diversity present. A peak at 2831.326 cm^{-1} corresponds to C-H stretching vibrations, providing further confirmation of organic compounds containing hydrocarbon chains. The peak at 3005.373 cm^{-1} is characteristic of C-O stretching vibrations, corroborating the presence of oxygen-bearing functional groups. Observed at 3134.619 cm^{-1}, a peak corresponds to C-H stretching vibrations, further substantiating the organic composition of the eggshell powder. The peak at 3235.806 cm^{-1} signifies C-H stretching vibrations, offering insights into the nature of the carbon-hydrogen bonds present. A peak at 3332.422 cm^{-1} corresponds to O-H stretching vibrations, indicative of the presence of hydroxyl groups, potentially alcohols or phenols. The peak at 3458.349 cm^{-1} signifies stretching vibrations of O-H groups, potentially associated with organic functional groups. The peak observed at 3797.291 cm^{-1} indicates O-H stretching vibrations, providing further evidence of the presence of hydroxyl groups. These functional groups, along with the inorganic calcium carbonate component, make eggshell powder a potential candidate for reinforcing polymer composites. The combination of organic and inorganic constituents could enhance mechanical properties, such as tensile strength and impact resistance, contributing to its suitability as a filler material in materials engineering applications. The result obtained from FTIR is similar to the opinions of Polat & Sayan (2020) [12] and Waheed et al. (2020) [1] in which they stated that "microscopically, eggshell is composed of a network of protein fibres, which in turn are associated with crystals of calcium, magnesium carbonate and calcium phosphate along with certain other organic substances like water".

4.0. Conclusion

This study demonstrates the remarkable efficacy of Fourier-Transform Infrared Spectroscopy (FTIR) as a rapid and non-destructive technique for the proximate analysis of chicken eggshells. The obtained FTIR spectrum revealed nineteen (19) distinct peaks at well-defined wavenumbers, which is indicative of various functional groups and molecular vibrations. The bands at 1444.636 cm^{-1}, 1347.831 cm^{-1}, 1007.913 cm^{-1}, 873.0817 cm^{-1}, and 709.1337 cm^{-1} indicated the high presence of calcium carbonate in the tested sample. This detailed knowledge of eggshell constituents opens a treasure trove of opportunities for unlocking their inherent value. Understanding the eggshell's precise composition and functional groups paves the way for tailoring its properties for specific applications. The rapid and accurate nature of FTIR makes it ideal for real-time monitoring of eggshell quality during egg production, storage, and processing. This ensures consistent quality and reduces potential food waste.

The novelty of utilizing FTIR for eggshell analysis offers a faster and more accessible alternative to traditional wet chemical methods, potentially paving the way for wider adoption in research and industrial settings. The study provides a detailed picture of the eggshell's major components, including calcium carbonate, phosphates, and organic residues, highlighting its complex composition. The paper effectively points towards the potential of eggshells as a bio-resource in various fields, encouraging further exploration of their utilization in sustainable production of other goods and products for mankind. Eggshells, that was once considered waste, is emerging as a readily available bio-resource with immense potential in diverse application in fields of human endeavours. The high calcium content established in chicken eggshell offers promising avenues for its applications in industrial; biomedical; bio-materials, agricultural amendments, and construction materials applications thereby promoting a circular economy.

The carbohydrates were confirmed to be present in the chicken eggshell can be a source of energy in diets for human and animals. Meanwhile, carbohydrate is the primary source of energy in the body and this high amount found in the eggshell shows it can play a great role in human health. Aside from the supply of energy, carbohydrates have numerous importance in biochemical reactions that are not directly concerned with energy metabolism; it can be an alternative source of glucose. Chicken eggshell as a source of glucose can be used as carbon source in bioethanol production, organic acid synthesis, and other biochemical.

The chicken eggshell, can be utilized as food supplement and creature feed for man and animals separately. It could also be utilized in paper enterprises and in farming as a substitute for lime and for manure production. In building block making, chicken eggshell can be utilized because of the great centralization of calcium present in it. The pores in the chicken eggshell morphology makes it reasonable for heterogeneous impetus in biodiesel production. The presence of different utilitarian gatherings and the high carbon content in the eggshell makes it an important material for adsorbent to eliminate weighty metals and colors in wastewater. The study concluded that Chicken eggshells which primarily compose of calcium carbonate, which plays crucial roles in various industrial and biomedical applications.

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