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Facile Synthesis of Aqueous Calcium Acetate from Discarded Egg Shells of Locally Bred Hybrid Chicken.

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Abstract: *There are a lot of wasted eggshells because of the high egg consumption rate which consequently has been an agent of pollution to the environment. However, they can easily be transformed into low- or high-purity grade of calcium carbonate by washing, pulverizing, drying, and sieving. This grade was then used as feedstock for generating a value added calcium acetate via a direct reaction with acetic acid. A maximum yield of 97.5% for 216 mg of acetate salt of calcium was obtained as FT-IR was initially engaged in the chemical identification of $CaCO_3$ prior to the reaction with 2M acetic acid and with the final product under the same working conditions. This result lends credence to the idea of zero waste production in order to create products with added value in order to achieve sustainable development, which may be chosen as an alternative method of material recycling and waste management in the future.*

Keywords— Broiler chicken, Eggshells, Calcium acetate solution, Acetic acid and Physicochemical parameters.

1. INTRODUCTION

The ever-growing global population has an increased demand for resources beyond what is necessary for basic human life, increased urbanization, food demand, and ultimately increased food waste generation. This issue was made worse by the delayed progress in waste management, value-added applications, and poor applications or as a raw material to make a variety of novel products. Due to an upsurge in nutritional awareness, broader dietary acceptance, and increased egg consumption over the past few years now make up the majority of the trash in term of eggshell wastes [1]. The acceptance of eggs as a decent source of high-quality protein, which influenced consumers' purchasing decisions, makes this tendency more obvious in emerging nations. Egg consumption was anticipated to increase from over 7951.8 million dozen to above 8000 million dozen in the year 2019 and 2020, respectively, based on the remarks of global agriculture demand and supply estimates in US [2]. Similarly, WATT Global Media's Administrative protocol to global Poultry Trends, revealed that the growing egg consumption around the world has led to an increase of around 18% in egg production over the past ten years.

United States, China and India were the top three egg-producing nations in 2017, providing 458.9 million metric tons, 109.0,000,000 metric tons, and 95.9 billion eggs annually, respectively [3]. In 2018, there were 78,000,000 metric tons generated worldwide, which produced 8.58,000,000 metric tons of eggshells that were primarily discarded as trash [3]. Despite this, this naturally occurring, calcium-rich product is disposed of improperly, creating a number of environmental problems.

Similarly millions of metric tons of eggshells are obtained from egg processing facilities, egg stations, chicken hatcheries, enterprises, and houses [4]. These large volumes of eggs are exploited at domestic and industrial levels to manufacture and process foods as a source of nutrition. The production level of eggs will generate eggshell waste in greater quantity, which is typically discarded in an open spaces and landfills. China produced waste eggshell of about 24.8 billion kilograms in 2019 and was projected to increase output by over 35,000,000 metric tons in 2020 [5]. In reference to the Environmental Protection Agency, eggshell waste is the 15th biggest food industry pollution issue as they are considered as a major source of environmental pollution when not properly dumped off in specified locations, thus causing health hazards due to fungal growth around them [6, 7]. This huge amount of waste eggshell produced is mostly relinquished in the landfills while many landfill operators steer clear of eggshells because the membranous portion, which is protein rich, attracts pests [6]. Eggshell is often thought of as a food industry waste product, but it may also be a highly advanced raw material for other goods. When studying the chemical makeup of an eggshell, 98% of the eggshell are factors of dry matter and 2% water. Eggshells account for 9-12% of the overall egg weight. Ash (93%) and crude protein (5% of dry matter) make up the majority of the composition [8, 9].

When examined under a microscope, eggshell is a units of protein fibers that are linked to crystals of magnesium, calcium carbonate, and calcium phosphate as well as certain other organic materials such as water [10, 11]. Eggshells are used in a variety of products, from food items to products for industrial purposes, and their primary component, calcium carbonate, is responsible for this [12].

Table 1. Proximate compositions of eggshell.

Components	Concentration (%)
Protein	3.92
Moisture	0.46
Fat	0.35
Ash	94.61
Calcium	34.12
Magnesium	0.29
Phosphorus	0.04
Potassium	0.03
Copper	1ppm
Sodium	0.05
Iron	22ppm
Manganese	1ppm
Zinc	1ppm

Physically eggshells from hens typically weigh 5.5 g and range in thickness from 280 to 400 m. Minerals make up 95.1% of the eggshell's contents with majority as calcium, which accounts for 37.3% of the total weight. Calcium carbonate ($CaCO_3$), which makes up 93.6% of all calcium in crystalline form, is followed by calcium triphosphate (0.8%) and magnesium carbonate [13]. According to the different structures of the egg, the protein content in the eggshell could vary. A protein-polysaccharide combination with at least 70% proteins and 11% polysaccharides makes up the majority of the eggshell's organic matrix [13].
Eggshells can be used as a direct source of calcium carbonate in the synthesis of calcium acetate (Ca ($CH_3OO)_2{\cdot}2H_2O$), also known as lime acetate and vinegar salts. The dihydrate or monohydrate forms of calcium acetate are more prevalent because the anhydrous version is much more hygroscopic with its hemihydrate, whose structural structure has been investigated [14].
Calcium carbonate, a common carbonate rock found in eggshells, common carbonate rocks like limestone or marble, or hydrated lime, has been used to synthesize calcium acetate by soaking them in vinegar [14].

$$CaCO_3(s) + 2CH_3COOH\ (aq) \longrightarrow Ca\ (CH_3COO)_2 .\ nH_2O\ (s) + CO_2\ (g) \quad (1)$$

$$Ca\ (OH)_2\ (s) + 2CH_3COOH\ (aq) \longrightarrow Ca(CH_3OO)_2 .\ 2H_2O\ (s) \quad (2)$$

It has been widely reported that the acetate salt of calcium is an organic chemical with great potential for industrial and environmental applications as a potent SO_2, NO_X, and harmful particle emission control agent in coal combustion processes to lessen acid rain [14], as an effective catalyst for the facilitation of coal combustion [15], as the best alternative material for replacing the corrosive and environmentally unacceptable deicers (sodium chloride and calcium chloride) [16], and as an adsorbent of carbon dioxide [17]. In the food industries, it has been applied as a stabilizer and preservative in many food substances under the number E263, as a stabilizer in most hard candies, as a stabilizer in baby food and syrups, and as a coagulant for soy milk in the commercial manufacture of tofu [18]. It has recently been employed to separate fat globule membrane fragments from a dairy byproduct [18]. In the medical field, it is used for treating or preventing calcium deficiency and hypophosphatemia in individuals with renal disease [19, 20].
It has been utilized in agriculture as a foliar fertilizer, soil pH adjuster, soil amendment, and plant micronutrient [21]. Calcium Acetate has recently been employed to reduce rice yield loss and assess the potential acidity of tropical soils [21]. Other applications include the manufacture of calcium phosphates, acetone, composite ceramic compounds, anhydrite calcium sulfate nano whiskers, and cement mortar using Calcium Acetate as a starting reagent to return to common compounds such as nano-CaO and $CaCO_3$ [21]. Hence, this research aims to synthesize pure Calcium Acetate from the local eggshells of broiler chicken as the source of calcium carbonate and to evaluate the quality of the product by standard specified characterization.

2. METHODOLOGY

2.1 Materials

Discarded egg shells, Analar-grade concentrated acetic acid (99%w/w CH_3COOH, Merck), 3M hydrochloric acid, 0.05M edetate disodium solution, 1M sodium hydroxide, hydroxyl naphthol blue, sodium carbonate and distilled water.

2.2 Equipment and Instrumentations

Glassware, porcelain cup, Teflon container, magnetic stirrer rod, Whatman 42 filter paper, hot plate, analytical balance, drying oven, muffle furnace, desiccator, X-Ray Diffractometer (X-RD), Digital pH meter, Fourier Transform Infrared Spectroscopy (FTIR).

2.3 Methods

2.3.1 Preparation of the Broiler Egg shells powder

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The eggshells were air-dried and washed with deionized water to remove dust and possible impurities. They were then dried in an oven at 105°C for 1 h and pulverized with sieving to obtain a uniform powder of about 50 meshes. The eggshell powder was stored in an airtight container.

2.3.2 Preparation of Calcium Acetate

50g of the eggshell powder ($CaCO_3$) was mixed with 50 ml of distilled water and 50 ml of 2M acetic acid of the density 1.049g/ml with % a purity of 99.7%. The mixed suspension reaction was an exothermic process and was stirred until carbon dioxide completely evolved, and then it was left at room temperature until the pale cream solution was obtained [22].

2.3.3 Assaying of Prepared Calcium Acetate solution

20 ml of the test solution was used for pH determination [23].

2.3.4 Water Insoluble fraction of the Calcium Acetate solution

A previously dried and pre-weighed crucible was used to weigh accurately about 50ml of Calcium Acetate solution with agitation for a few minutes. It was filtered through the glass filter, and the residue was washed on the filter with 30 ml of water. The filter with the residue was dried at 105 ºC for 2 hours, cool in desiccators, and weighed accurately [24].

2.3.5 Quantitative determination of the Calcium Acetate solution

About 100 ml of Calcium Acetate to 150 mL was added to water containing 2 mL of 3 N hydrochloric acids. While stirring with a magnetic stirrer, add about 30 mL of 0.05 M edetate disodium from a 50 mL burette. Add 15 mL of 1 N sodium hydroxide and 300 mg of hydroxyl naphthol blue, and titration was conducted to a blue endpoint [25].

2.3.6 Determination of oxidizable fraction of the Calcium Acetate solution

Precisely 5ml of Calcium Acetate solution was added to 0.5 g anhydrous sodium carbonate. Adopting a standard method of [26].

2.3.7 Loss on Ignition

This was conducted according to the standard method of Nelson and Sommers, 1996 where 5ml of the sample solution was ignited in a muffle furnace for 2 hours at 360ºC. [27]

2.3.8 FT-IR Characterizations of the egg shell powder and Calcium Acetate solution

IR Fourier-transform infrared measurements were performed on FTIR spectrometer, operating in normal transmission mode. The sample was analyzed over the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1}. The peak positions were mainly observed to identify the functional groups in the calcium acetate.

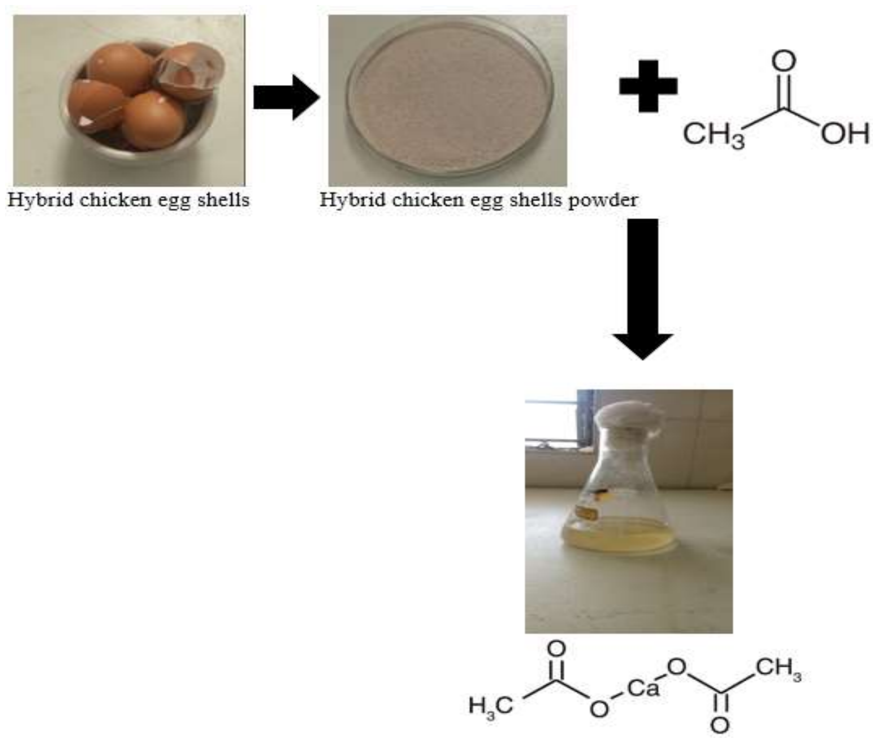

Figure 1. Synthesis of Calcium acetate from eggshells

3.0 RESULTS AND DISCUSSIONS

The preparation of Calcium Acetate compound was successful with the reaction of the eggshell powder with 2M

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concentrations of acetic acid. Important factors to assess with the production of Calcium Acetate from the eggshell powder with an acetic acid were the reaction time and temperature of the reaction. The production of Calcium Acetate from waste material is only advantageous if a high yield is attained with a short reaction time and at a low reaction temperature.

The specification of the obtained Calcium Acetate products based on the pH [28], water-insoluble substance [29], oxidizable content, and loss on ignition analysis were explicitly declared.

Table 1. pH of synthesized Calcium Acetate solution

1st run	2nd run	3rd run	4th run	5th run
8.3	7.6	7.5	8.2	7.5
Actual value	7.7 ± 0.3367			

Basically, at this estimated value of pH, calcium carbonate; the starting framework retains poor solubility in a nonacid or alkaline environment, which is evidence for poor solvation in an aqueous system even at elevated temperature. Calcium acetate is more soluble and stable at the same pH, which is in the range of 6.0–9.0 supporting studies that establish calcium acetate to be more reactive than calcium carbonate at binding intestinal phosphate at a mmol of supplied elemental calcium [30].

Table 2. Water insoluble substance of Calcium Acetate solution

	1st run	2nd run	3rd run	4th run	5th run
Empty crucible (g)	12.44	12.44	12.44	12.44	12.44
Crucible + 50ml sample(g)	69.44	69.44	69.44	69.44	69.44
Empty filter paper (g)	0.86	0.86	0.86	0.86	0.86
Filter paper + residue (g)	1.08	1.09	1.10	1.08	1.09
% of insoluble substance	0.39	0.40	0.42	0.39	0.40
Average % insoluble substance	0.40 ± 0.01				

Ionic compounds that cannot dissolve in water and instead produce a suspension in which the salt remains a solid instead of dissolving are known as insoluble substances in the form of salts, as polar and nonpolar compounds cannot be combined [31]. Therefore, 0.38% was evaluated for the synthesized calcium acetate solution. This simply implies a 0.08% difference with the standard Analar grade calcium acetate.

Table 3. Quantitative determination of calcium acetate with 0.05M edetate disodium

	1st Run	2nd Run	3rd Run	4th Run	5th Run
Final volume (ml)	26.50	27.31	27.30	27.30	27.31
Initial volume (ml)	0.00	0.00	0.00	0.00	0.00
Actual value(ml)	26.50	27.31	27.30	27.30	27.31
Average titre value (ml)	27.31 ± 0.006				
Quantity (mg)	216				

One of the methods to be adopted in quantifying calcium acetate is volumetric titration, which is a quantitative chemical technique that establishes the precise concentration of the sample to react with another substance of known volume and concentration. 0.05 M edetate disodium was titrated against the synthesized calcium acetate to achieve 27.31 ml of titrant to 100 mL of the sample solution. Meanwhile, 1mL of 0.05M edetate disodium is equivalent to 7.909 mg of $C_4H_6CaO_4$ (Calcium Acetate) [32].

Table 4. Titration with 0.1 M sodium thiosulphate for oxidizable substance of calcium acetate solution

	Blank	1st Run	2nd Run	3rd Run	4th Run	5th Run
Final volume (ml)	14.36	26.39	38.52	12.13	24.27	36.41
Initial volume (ml)	0.00	14.25	26.39	0.00	12.13	24.27
Actual value	14.36	12.14	12.13	12.13	12.14	12.14

(ml)						
Average Titre value (ml)		12.13 ± 0.005				

Calculate the content of readily oxidizable substances (HCOOH) by the formula:
Content (μg/g) of readily oxidizable substances as HCOOH.

$$\frac{(a - b) \times 2301}{\text{Weight of the sample}}$$

a= volume (ml) of 0.1 mol/L sodium thiosulfate consumed in the blank test (14.45ml).
b= volume (ml) of 0.1 mol/L sodium thiosulfate consumed in the test (12.13ml).
Sample weight= 5g

Calculate the content of readily oxidizable substances = $\frac{[14.36-12.13] \times 2301}{5}$ = 1,026.25 μg/g of HCOOH

Oxidizable Substances tests for the activity of organic species such as biological chemicals, metal-containing compounds, and microbiological organisms that easily mix with oxygen were measured in terms of HCOOH. This is, however, quite higher than the standard value required [33].

Table 5. Loss on ignition

	1st run	2nd run	3rd run	4th run	5th run
Empty crucible (g)	12.44	12.44	12.44	12.44	12.44
Crucible + sample(Initial)(g)	22.14	22.14	22.14	22.14	22.14
Crucible + sample (Final)(g)	21.04	21.03	21.04	21.04	21.04
% loss	11.34	11.44	11.34	11.34	11.34
% Average loss	11.37 ± 0.05				

A material's ignition loss is described as an oxide or elemental investigation of a mineral, which is estimated by interacting with the quantity before and after being exposed to high-temperature effects. This test represents the aggregate of organic material that was in the sample. Therefore, 11.37% declare the level of an organic fraction of the product.

Table.6 The percentage yield of calcium acetate from local hybrid chicken egg shells

Weigh of the egg shell powder (g)	50
Estimated weight of the calcium acetate (g)	0.216
Percentage yield (%)	97.5

$$\text{Calcium acetate yield (\%)} = \frac{M}{m} \times 100$$

Where M is the actual yield of calcium acetate;
m is the theoretical yield,
The ratio of the precise output to that of the theoretical estimate is referred to as the "percent yield." In chemistry, the term "yield" refers to a measurement of the amount of product molarity relative to the amount of reactant used in a reaction. The percentage yield is the variance between the amount of the actual product and the maximum calculated yield. The yield of 97.5% was obtained.

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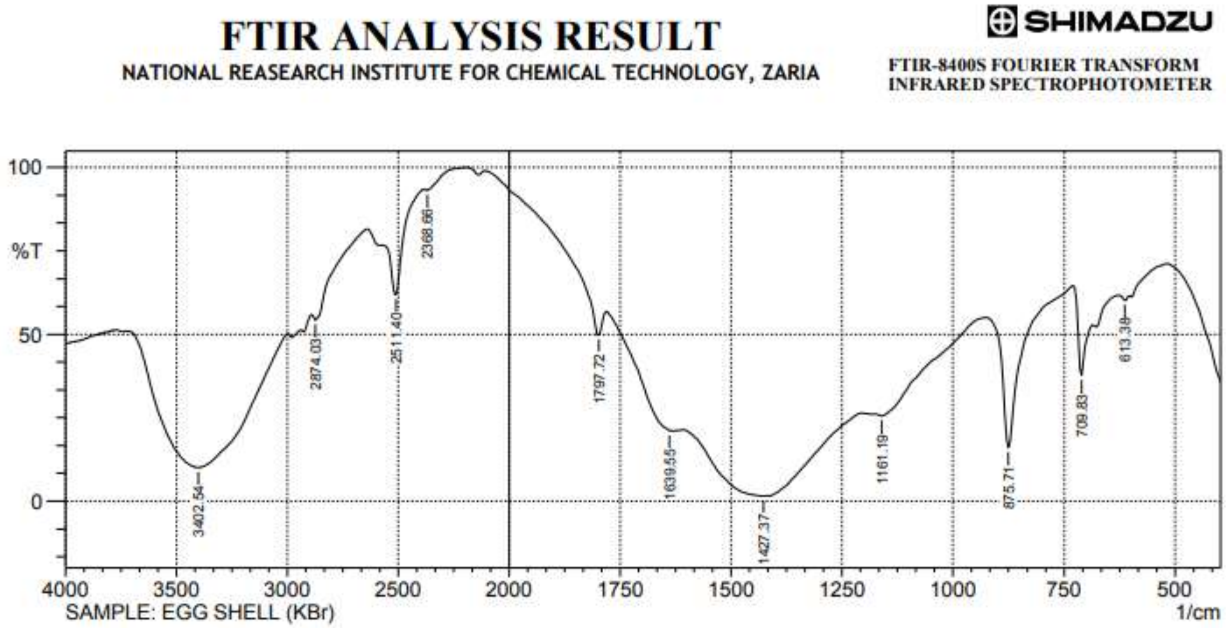

Figure 2. The FT-IR spectrum of Locally Breed Hybrid Chicken egg shell powder

Table 1. The FT-IR dimensions of Locally Breed Hybrid Chicken egg shell powder

No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	613.38	60.126	1.503	624.96	601.81	4.979	0.113
2	709.83	37.744	21.486	729.12	686.68	13.034	3.117
3	875.71	15.961	41.474	925.86	729.12	63.007	18.806
4	1161.19	25.559	2.322	1176.62	925.86	101.627	-4.088
5	1427.37	1.462	1.341	1608.69	1415.8	236.336	-1.035
6	1639.55	21.021	1.066	1782.29	1635.69	64.692	-2.745
7	1797.72	88.393	9.108	2110.19	1782.29	29.121	-11.805
8	2368.66	93.215	0.744	2384.1	2195.07	2.18	-0.613
9	2511.4	61.808	20.598	2576.98	2384.1	19.552	5.608
10	2874.03	54.318	3.098	2889.46	2638.71	39.359	-3.491
11	3402.54	10.07	40.578	3718.88	2997.48	459.491	246.059

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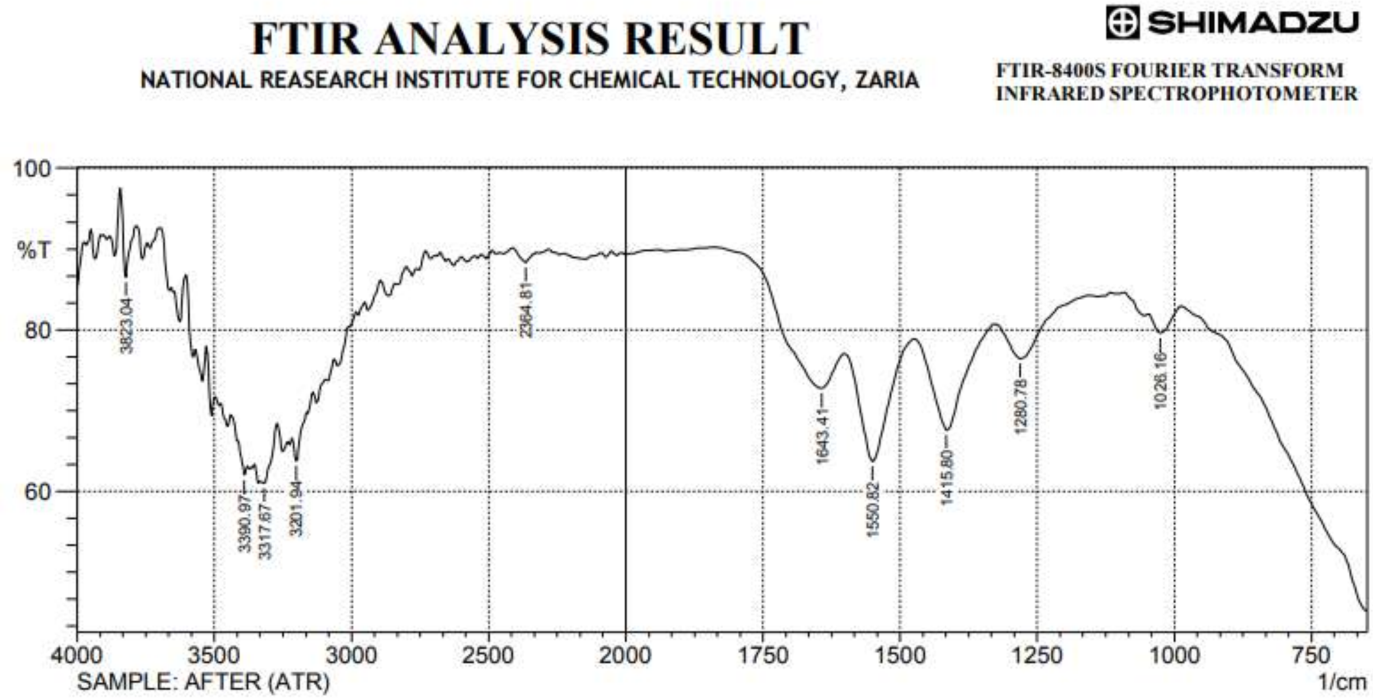

Figure 3. FTIR spectrum of calcium acetate solution generated from the egg shells of locally bred hybrid chicken

Table 2. The FT-IR dimensions of Calcium Acetate solution

	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	1026.16	79.603	2.701	1049.31	987.59	5.638	0.459
2	1280.78	76.435	5.223	1327.07	1153.47	16.239	1.704
3	1415.8	67.624	11.97	1473.66	1327.07	18.732	4.353
4	1550.82	63.748	14.005	1600.97	1473.66	18.379	4.6
5	1643.41	72.751	6.619	1840.15	1600.97	21.162	2.264
6	2364.81	88.375	1.438	2411.1	2326.23	4.25	0.301
7	3201.94	63.796	3.744	3217.37	3163.36	9.525	0.543
8	3317.67	61.04	2.009	3333.1	3271.38	12.208	0.554
9	3390.97	62.033	2.259	3441.12	3379.4	11.326	0.27
10	3823.04	86.5	9.333	3842.33	3788.32	2.283	1.114

The FT-IR spectra of the locally bred hybrid chicken eggshell powder and the Calcium Acetate solution prepared by 2M acetic acid concentrations are shown in Figures 2 and 3, respectively. The fundamental vibration of CO_3^{2-} anion as a block unit in $CaCO_3$ structure was visible in the FTIR spectra of the eggshell powder [34, 35]. The prominent absorption peak of CO_3^{2-} at 1427.37 cm^{-1} was related to the asymmetric stretching method of the C-O bond. A band at 1797.72 cm^{-1} was due to the carbonyl (C=O) stretching vibration. The symmetric stretching mode of the C-O bond and the out of plane and in plane bending of CO_3 anion were assigned to the vibrational peaks at 875.71 and 709.83 cm^{-1}, respectively. A weak band at 2511.4 cm^{-1} and broad adsorption around 2874.03 cm^{-1} could be assigned to the combination and overtone of the asymmetric and symmetric stretching modes of the C-O bond. These vibrational modes are confirmed as the CO_3^{2-} of the aragonite phase of calcium carbonate [36, 37, 38]. The broad bands in Figure 2 were caused by methyl stretching vibrational bands [the antisymmetric (CH_3) and symmetric (CH_3)] and a water molecule [the antisymmetric (OH) and symmetric (OH)]. Two strong bands observed at 1550.82 cm-1 were due to antisymmetric C-O [vas(C-O)] stretching vibrations, while two intense bands at 1415.8 cm^{-1} may be attributed to the symmetric stretching frequency of the C-O bond [(C-O)].

The out-of-plane stretching vibration of the methyl group (CH_3)) was split into two peaks at 1026.16 cm^{-1} [39, 40].

Hence, with the abundance of bioactive chemicals in eggshell waste, research funding for the creation of commercially viable, value-added ES-derived products is growing [41]. Numerous applications to produce value-added goods from ES trash have been patented; in the past two decades, their number has grown tremendously.

4. CONCLUSION

The egg industry has developed rapidly in recent decades owing to increased nutritional awareness. Society has now adopted it as a good source of high-quality protein. But at the same time, a heck of a pile of eggshells is discarded in the environment, causing environmental pollution. These eggshells are a valuable resource that can be used to create a wide range of goods with potential uses in medicine, pharmaceuticals, and industry. Additionally, this raw material is inexpensive and conveniently accessible. With eggshells being regarded as the 15th leading cause of environmental pollution, it is time to reuse and recycle this industrial food waste for the sustainable development of our globe. Though this could not play a drastic role in eliminating pollution, at least it could be a step forward toward a better environment.

5. ACKNOWLEDGMENT

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