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COMPARATIVE STUDY ON THE CHARACTERISTICS OF EGGSHELL WASTES FOR PREPARATION OF CALCIUM ACETATE

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Abstract

Eggshells are a rich source of mineral salts mainly calcium carbonate. This work was aimed to study the elemental contents and to characterize the egg shell wastes such as chicken, duck and quail eggshells for the preparation of calcium acetate. Relative abundances of elements in eggshells were determined by using X-ray fluorescence technique. Results of X-ray diffraction showed that the crystalline phase present in the waste sample is calcium carbonate in the form of calcite ($CaCO_3$).The comparative analysis of calcium carbonate contents was carried out for the selected eggshells by using back titration method. Furthermore, preparations of calcium acetate were done from three eggshell samples by soaking calcium carbonate in vinegar. The yield percent of the prepared calcium acetate were 46.76 % for chicken eggshell, 33.00 % for duck eggshell and 32.27 % for quail eggshell. Melting point determinations of calcium acetate were also done for three eggshell samples. The functional groups present in calcium acetate prepared from three eggshell samples were confirmed by FTIR analysis. The prepared calcium acetate were also be examined by EDXRF and SEM analysis. Chicken eggshell waste is appropriate and cheap source for preparation of calcium acetate.

Keywords: Eggshells, calciumcarbonate, calcium acetate, melting point, back titration

Introduction

Nowadays, there is a great interest in finding new pure calcium carbonate sources (Daengprok *et al*., 2000). Calcium carbonate ($CaCO_3$) can be found in large quantities in nature, with applications mostly as raw material for the ceramic calcium carbonate development in rapidly growing technology and research, such as hydroxyl apatite material synthesis as an alternative to the teeth and bones of human. Calcium carbonate obtained from bones flour, does not contain the same bioavailability of calcium obtained from synthetic sources. Calcium carbonate from oyster shells contain lead vestige among the

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others potential toxical elements such as aluminium, cadmium and mercury (Schaafsma,1997). On the other hand, eggshells have an advantage for not containing toxical elements (Macneil,1997). The word eggshell is a general name given to the hard exterial cover of the egg which consists of several constituent with calcium carbonate is the major one. Egg products industries produce great amount of shells and their final destiny is an environmental impact challenge.

Calcium acetate is one of a number of calcium salts used to treat hyperphosphatemia (too much phosphates in the blood) in patients with end stage kidney disease who are on dialysis (Chan *et al*., 2017). Calcium acetate works by binding with the phosphate in the food in the body, so that it is eliminated from the body without being absorbed. Preparations of calcium acetate from littleneck clam shell (Park *et al*., 2015) and butter clam shell (Lee *et al*., 2015) have been reported. Calcium acetate has been used in the manufacture of metallic soaps and synthetic resins; in lubricants as a corrosion inhibitor and as a mordant in dyeing. On the basis of these facts the synthesis and characterization of calcium acetate from waste eggshells as calcium source were conducted in this study due to the high content of calcium carbonate in the eggshells.

Materials and Methods

Sample Preparation and Characterization

Three different types of eggshells *viz*.,chicken, duck and quail eggshell samples were collected from Myoma market, Taunggyi Township, Southern Shan State. After removing the dirt particles, the samples were dried, ground and finally sieved to prepare fine powder.

The relative abundances of elements in eggshells powder samples were determined by EDXRF (Shimadzu-8000). The surface morphology of eggshells were examined by SEM (JSM 5610 LV,JEOL Ltd), the crystal structures by XRD (Rigaku Co., Japan) with Cu Kα (λ =1.54056 $\dot{A}$) radiation over a range of 2θ angles from 10° to 70°) and thermal properties by TG-DTA by using DTG-60 H Detector, at temperature 30 to 600 °C with a scanning rate of 50 mL/min, under nitrogen.

Determination of Calcium Carbonate Content in Eggshells

Each of the sample(0.2 g) was put into a conical flask by adding several drops of ethanol as a wetting agent. After that, 25 mL of 0.1 M hydrochloric acid solution was added into each flask and swirled the flask to wet the solid. The solutions in the flask were heated until they began to boil for complete digestion and were allowed to cool. Next, 3 drops of phenolphthalein were added to each flask and titrated against sodium hydroxide solution to the first persistent pink colour. Then the titration for the other samples were repeated and the percentage of calcium carbonate in each shell was calculated.

Preparation of Calcium Acetate from Eggshell Samples

Eggshells samples (20 g each) were boiled with 100 mL of vinegar for 1 h. Then the solutions were filtered and the filtrate solutions were placed in a small beaker on a hot plate at 50 °C to yield calcium acetate via forced evaporation. The remaining solution was allowed to stand at room temperature and seeded with a cotton thread to initiate crystal growth.

Melting Point Determination for Calcium Acetate Prepared from Three Eggshell Samples

The melting points of the three eggshell samples were determined by MPA 100 Automated Melting Point Apparatus.

Functional Groups of Calcium Acetate from Three Eggshell Samples

The functional groups present in prepararared calcium acetate samples were investigated by FT IR spectrometer measured at the Universities' Research Centre, Yangon University.

Energy Dispersive X Ray Fluorescence Analysis of Prepared Calcium Acetate from Three Eggshell Samples

The relative abundances of the prepared calcium acetate were determined by EDXRF spectrometer at the Universities' Research Centre, Yangon University.

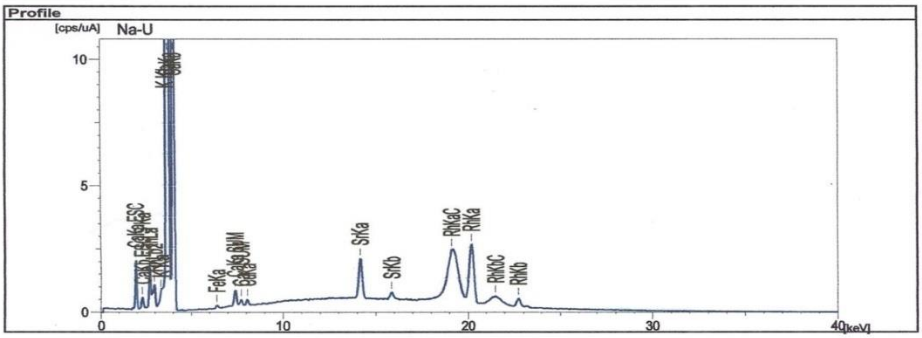
SEM Analysis of Prepared Calcium Acetate from Three Eggshell Samples

SEM analysis of the prepared calcium acetate from three eggshell samples were conducted at the Universities' Research Centre, Yangon University.

Results and Discussion

Energy Dispersive X-Ray Fluorescence from Three Eggshell Samples

Relative abundances of elements present in eggshell samples were determined by EDXRF spectrometer. The EDXRF spectra obtained are shown in Figure1.



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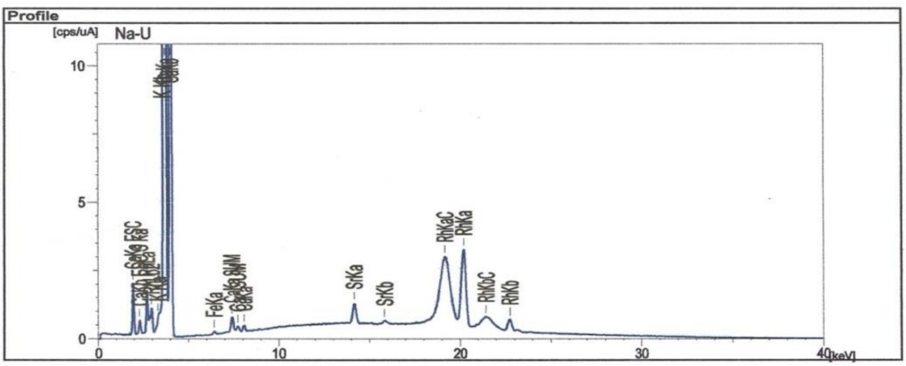

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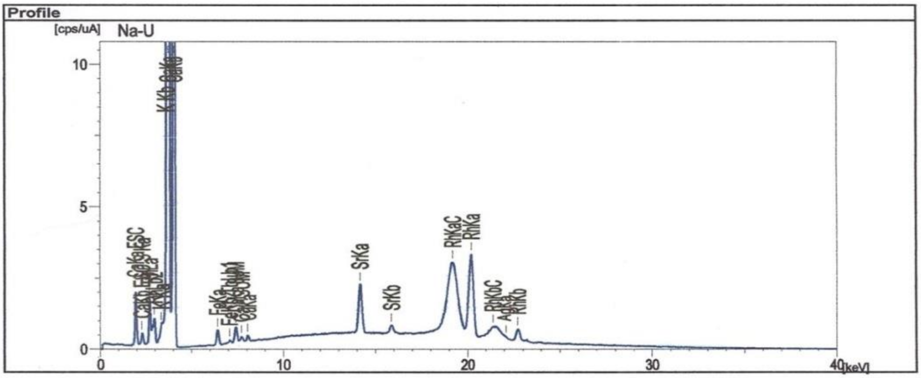

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Figure 1: EDXRF spectra of eggshell samples (a) chicken (b) duck and (c) quail

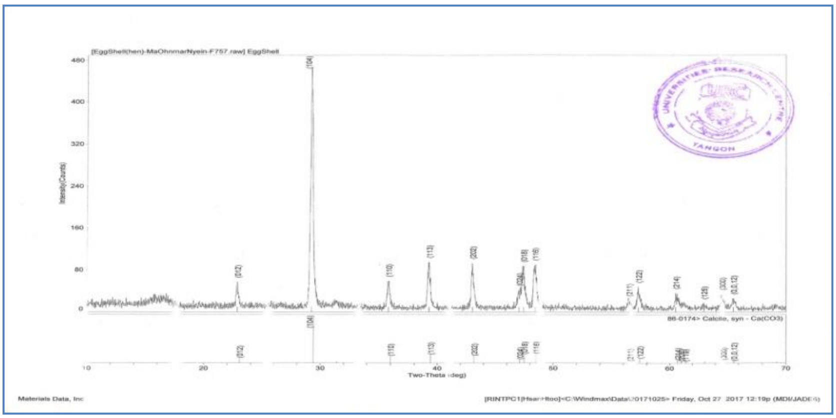
Ca was found to be highest among the elements found in eggshell powder samples ranging from 26.189 % to 29.263 % (Table 1).Ca content in chicken eggshell was 29.263 %and found to be the highest. The high amount of calcium is associated with the presence of calcium carbonate which is the main component of eggshell (Leach, 1982). K and S were found as second and third abundant elements in the samples with minor amounts. Moreover, trace amounts of Sr (0.011 % to 0.027 %), Fe (0.007 % to 0.025 %) and Cu (0.006 % to 0.007 %) were also found in eggshell powder samples.

Table 1: Relative Abundance of Elements in Three Different Eggshell Samples

No	**Elements**	**Relative abundance (%)**		
		Chicken eggshell	**Duck eggshell**	**Quail eggshell**
1	Ca	29.263	28.559	26.189
2	K	0.239	0.230	0.263
3	S	0.102	0.171	0.102
4	Sr	0.025	0.011	0.027
5	Fe	0.007	0.007	0.025
6	Cu	0.007	0.007	0.006
7	Ag	-	-	0.006
8	COH	70.358	71.016	73.383

X-ray Diffraction Analysis of Eggshell Samples

The XRD patterns for different eggshell powder samples are shown in Figure 2. The XRD pattern of chicken eggshell powder exhibited the characteristic peaks at the Miller indices of (012), (104), (110), (113), (202) and (024) corresponding to the 2θ values of 22.840˚ , 29.227˚ , 35.803˚ , 39.271˚ , 43.014˚ and 46.997˚ respectively (Table 2). Similarly, duck eggshell sample showed peaks at Miller indices of (012), (104), (110), (113) and (202) corresponding to the 2θ values of 22.936˚ , 29.304˚ , 39.898˚ , 39.342˚ and 43.078˚ and quail eggshell powder showed diffraction peaks at the Miller indices of (012), (104), (110), (113), (202) and (204) corresponding to the 2θ values of 23.102˚ , 29.218˚ , 35.804˚ , 39.277˚ , 43.000˚ and 46.174˚ respectively. The peaks appeared in the diffractograms were found to be well-matched with both the peak location and the relative peak intensities of the diffraction data of the calcite phase. Similar reults were also found by Choudhary *et al*. (2015) and Freire and Holanda (2006). All the eggshell powder samples studied were indexed as hexagonal structure with lattice constants of equal ′a′ and ′b′ and longer ′c′ (Table 3).



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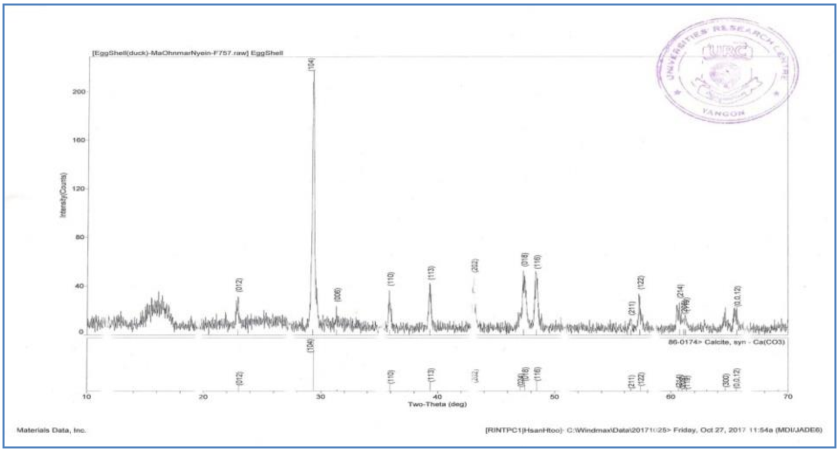

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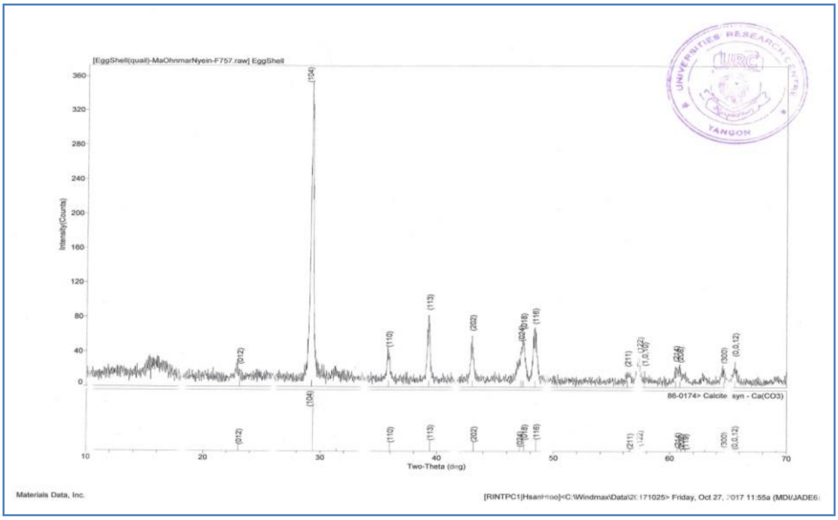

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Figure2: XRD patterns of eggshell Samples (a) chicken (b) duck and (c) quail

Table 2: Miller Indices, Peak Position and Interplanar Spacing for Eggshell Samples

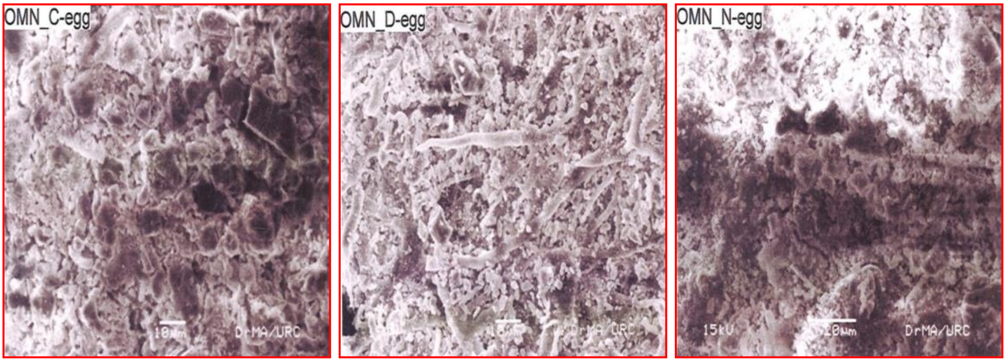
No	Miller indices h	k	l	Eggshell Sample	Peak position 2θ (degree)	Interplanar spacing d (Å)
1.	0	1	2	Chicken	22.840	3.8903
				Duck	22.936	3.8743
				Quail	23.102	3.8467
2.	1	0	4	Chicken	29.227	3.0531
				Duck	29.304	3.0452
				Quail	29.218	3.0540
3.	1	1	0	Chicken	35.803	2.5059
				Duck	39.898	2.4995
				Quail	35.804	2.5059
4.	1	1	3	Chicken	39.271	2.2923
				Duck	39.342	2.2883
				Quail	39.277	2.2919
5.	2	0	2	Chicken	43.014	2.1011
				Duck	43.078	2.0981
				Quail	43.000	2.1017
6.	0	2	4	Chicken	46.997	1.9318
				Duck	-	-
				Quail	46.174	1.9250

Table 3: Lattice Constant and Structure of Eggshell Powder Samples

No	Eggshell powder	Lattice constant (Å)			Structure
		a-axis	b-axis	c-axis	
1	Chicken	4.9982	4.9982	17.7387	Hexagonal
2	Duck	4.9934	4.9934	17.4162	Hexagonal
3	Quail	5.0005	5.0005	16.8550	Hexagonal

SEM Analysis for Three Eggshell Samples

The morphology of the eggshell sample were investigated by SEM as shown in Figure 3. According to the SEM images, the eggshell samples comprise irregular shape of particles with various sizes and shapes. Small holes called pore canals were seen on the surface of the shell for gas-exchange.

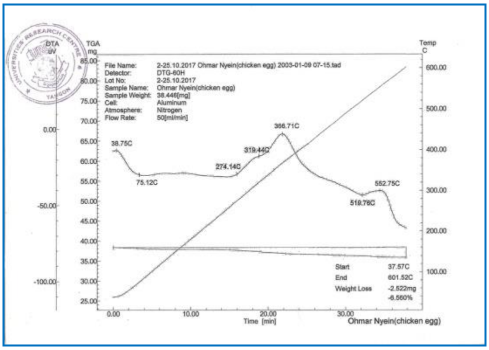


(a) (b) (c)

Figure 3: SEM images of eggshell samples (a) chicken (b) duck and (c) quail at 1000X magnification

Thermogravimetric Differential Thermal Analysis for Eggshell Samples

The thermal behaviour of the each eggshell waste sample was investigated by TG-DTA. The TG-DTA thermograms of eggshell waste samples are shown in Figure 4 and the results are summarized in Table 4. The results showed the presence of two thermal events. The first event below 140 ºC (75 ºC in chicken eggshell sample, 82 ºC in duck eggshell sample and 117 ºC in quail eggshell sample) is endothermic and is attributed to the removal of physically adsorbed water (moisture) on the particles of the waste sample. The second event between 140 and 600 ºC (327 ºC in chicken eggshell sample, 387 ºC in duck eggshell sample and 368 ºC in quail eggshell sample) is exothermic, and related to combustion of organic matter..



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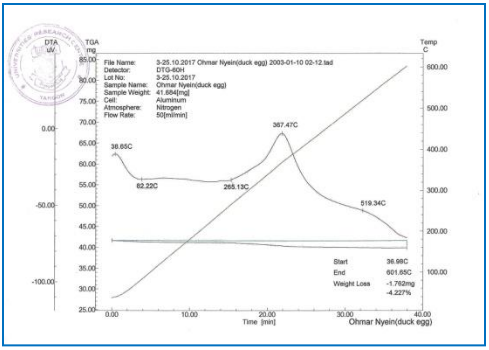

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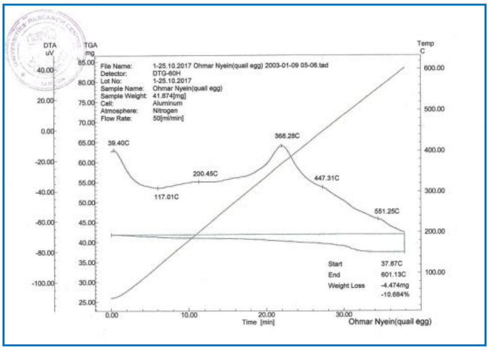

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Figure 4:TG-DTA thermograms of eggshell samples (a) chicken (b) duck and (c) quail

Table 4: Thermal Analysis Data of Eggshell Samples

No	Sample	Peak's Temperature (°C)	Weight loss (%)	Nature of Peak	Remark
1	Chicken eggshell	75	1.73	Endothermic	Due to the removal of moisture
	Duck eggshell	82	1.71	Endothermic	
	Quail eggshell	117	1.49	Endothermic	
2	Chicken eggshell	327	4.83	Exothermic	Due to the combustion of organic matter
	Duck eggshell	387	2.52	Exothermic	
	Quail eggshell	368	9.19	Exothermic	

Calcium Carbonate in Eggshell Samples

In this experiment, the calcium carbonate content in eggshell was determined by back titration method. The percentages of calcium carbonate in three eggshell samples are tabulated in Table 5. According to the results obtained from experimental analysis, chicken eggshell contains the highest calcium carbonate content of 61.75 % followed by duck eggshell (60.30%) and quail eggshell (59.80 %).

Table 5: Calcium Carbonate Contents in Eggshell Samples

Samples	$CaCO_3$ content (%)
Chicken Eggshell	61.75
Duck Eggshell	60.30
Quail Eggshell	59.80

Prepared Calcium Acetate from Three Eggshell Samples

Eggshells are made up of calcium carbonate and vinegar is a mixture made up of very dilute acetic acid. The calcium carbonate in the eggshell and the acetic acid in vinegar interact setting off a chemical reaction. First, the acetic acid and calcium carbonate form carbonic acid and calcium acetate.

$$CH_3\,COOH + Ca\,CO_3 \rightarrow H_2\,CO_3 + Ca\,(CH_3\,COO)_2$$

Next, the carbonic acid breaks down to form carbon dioxide and water.

$$H_2\,CO_3 \rightarrow H_2O + CO_2$$

The overall reaction is

$$2CH_3\,COOH + Ca\,CO_3 \rightarrow H_2O + CO_2 + Ca\,(CH_3\,COO)_2$$

Needle shape crystals of prepared calcium acetate from three eggshell samples are clearly observed in Figure 5.

Figure 5: Crystallization of calcium acetate from (a) chicken eggshell(b) duck eggshell and (c)quail eggshell

The yield percentages of calcium acetate are tabulated in Table 6. Highest amount of calcium acetate (46.76 %) from chicken eggshell was obtained followed by 33.00 % from duck eggshell and 32.27 % from quail eggshell.

Table 6: The Amounts of the Calcium Acetate Prepared from Three Different Eggshell Samples

Samples	**$(CH_3COO)_2Ca$ (%)**
Chicken Eggshell	46.76
Duck Eggshell	33.00
Quail Eggshell	32.27

Melting Point of Calcium Acetate

The melting points of calcium acetate obtained from the three eggshell samples were determined by the melting point apparatus. The results are mentioned in Table 7. Melting points of calcium acetate samples were 160-161 ^{o}C, the literature value being 160 ^{o}C (NIOSH, 2015).

Table 7: Melting Points of Calcium Acetate from Different Eggshell Samples

Raw materials	Melting Point (°C)of Calcium Acetate
Chicken Eggshell	160-161
Duck Eggshell	160-161
Quail Eggshell	160-161

FT IR Analysis of the Prepared Calcium Acetate from Eggshell Samples

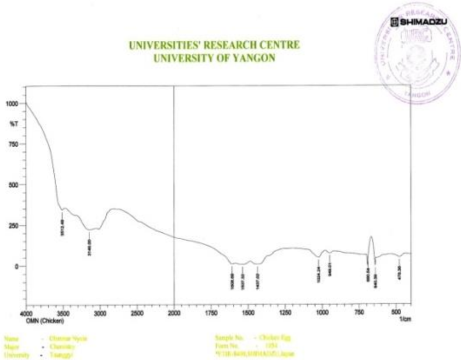
FT IR spectra of calcium acetate obtained from eggshell samples are shown in Figure 6 and band assignments are indicated in Table 8.

Each spectrum has been divided into three regions. The first region between 2700-3700 cm^{-1} which is dominated by stretching vibrations of O-H and C-H groups from calcium acetate monohydrate (Frost *et al*., 2004). The two weak bands at 3512 cm^{-1} and 3146 cm^{-1} in the spectrum of chicken eggshell sample, 3497 cm^{-1} and 3201 cm^{-1} in the spectrum of duck eggshell sample and 3348 cm^{-1} in the spectrum of quail eggshell sample are due to (O-H) stretching vibration. C-H stretching vibration of methyl group were observed at 2980 cm^{-1}, 2990 cm^{-1} and 2996 cm^{-1}, respectively, for chicken, duck and quail eggshell samples .

The second region of each spectrum from 1100-1600 cm^{-1} concerned with CH_3 bending and C-O stretching vibrations.The calcium acetate formed through forced evaporation showed some very weak bands at 1640, 1645 and 1645 cm^{-1} in FT IR spectra of chicken, duck and quail eggshell powder samples respectively, due to stretching of the carbonyl C=O bond present. The band appeared at 1537, 1539 and 1546 cm^{-1} and 1437, 1440 and 1454 cm^{-1} in the spectra of chicken, duck and quail eggshell samples respectively, due to the asymmetric and symmetric stretching vibrations of C-O.The in plane bending vibration of the methyl group appeared at 1024 cm^{-1} and the υ(C – C) stretching vibration of the acetate anion was observed at about 950 cm^{-1}.

The low wavenumber region of the FT IR spectrum from 600-500 cm^{-1} concerned with the vibrations of O − C − O. The calcium acetate prepared from chicken, duck and quail eggshell samples exhibited two poorly defined peaks at 690 cm^{-1} and 640 cm^{-1}, 690 cm^{-1} and 617 cm^{-1} and 673 cm^{-1} and

621 cm^{-1}, respectively, due to out of planestretching and bending vibrations of O − C − O fragment of the acetate anion (Frost *et al*., 2004).



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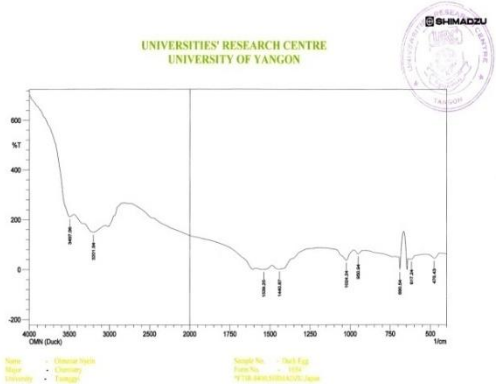

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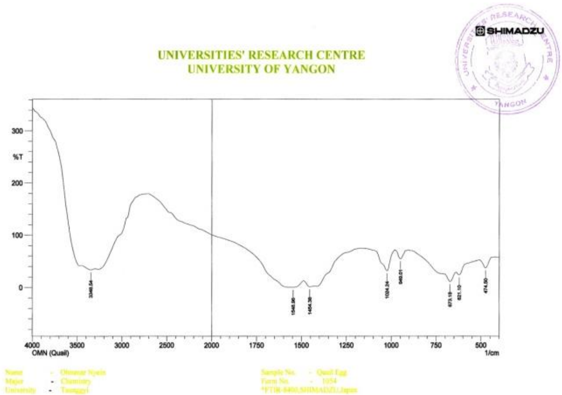

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Figure 6: FT IR spectra of calcium acetate from eggshell samples (a) chicken (b) duck and (c) quail

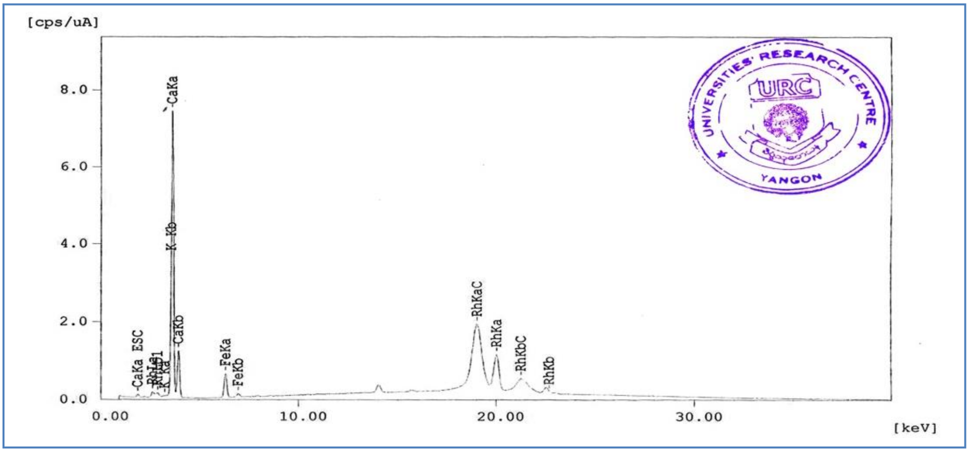
Table 7: FT IR Spectral Data for Prepared Calcium Acetate from Eggshell Powders

No	Observed wavenumber (cm^{-1})			*Reported wavenumber (cm^{-1})	Remark
	Chicken	Duck	Quail		
1	3512-3146	3497-3201	3348	3571-3147	O-H stretching vibration
2	2980	2990	2996	2927	C-H stretching of CH_3
3	1640	1645	1645	1648-1689	C=O stretching of carbonyl group in acetate anion
4	1537	1539	1546	1540 -1604	Asymmetric stretching vibration of C-O
5	1437	1440	1454	1442-1459	Symmetric stretching vibration of C-O
6	1024	1024	1024	1030	In plane bending vibration of the methyl group
7	949	950	949	925-951	Symmetric C-C stretching vibration
8	690	690	673	659-672	Out of plane stretching vibration of O-C-O group
9	640	617	621	616-623	Out of plane bending vibration of O-C-O group

*****Frost *et al*., 2007

Energy Dispersive X Ray Fluorescence of Calcium Acetate from Three Eggshell Samples

The relative abundances of elements in prepared calcium acetate were determined by EDXRF spectrometer. The results obtained are shown in Figure 7.



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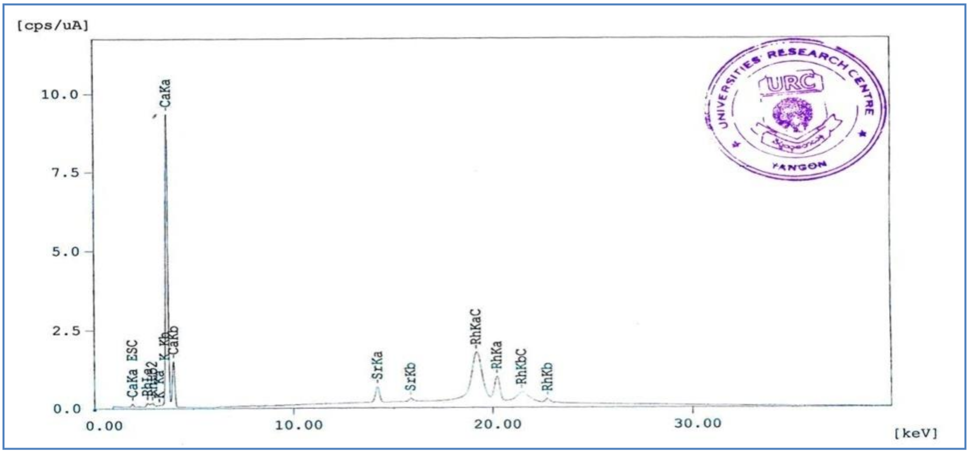

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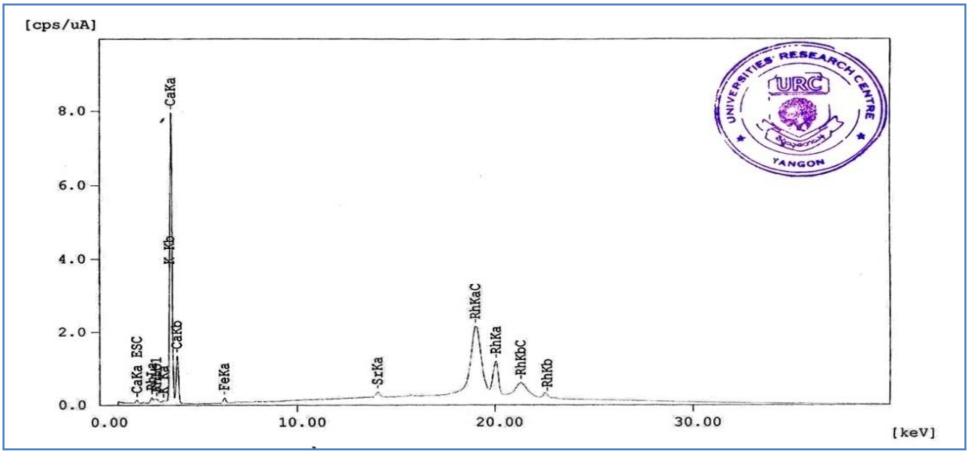

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Figure 7: EDXRF spectra of calcium acetate from three eggshell samples (a) chicken (b) duck and (c) quail

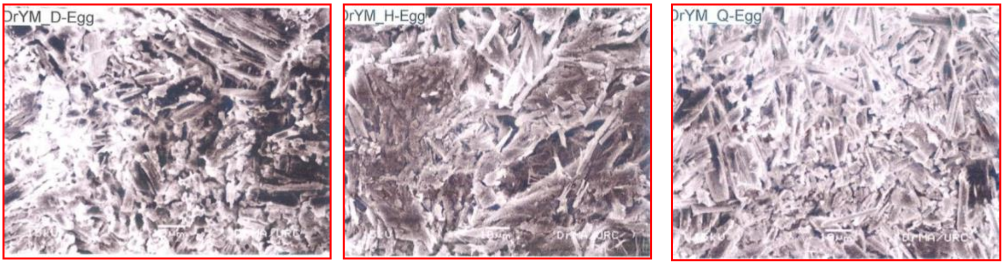
Ca was found to be highest among the elements in calcium acetate ranging from 94.455 % to 98.615 %. Trace amount of Fe, K and Sr were also found. The highest percentage of calcium acetate was obtained from chicken eggshell.

Table 8: EDXRF Data for Prepared Calcium Acetate from Eggshell Samples

No.	Elements	Relative abundance (%)		
		Chicken eggshell	Duck eggshell	Quail eggshell
1.	Ca	98.615	97.797	94.455
2.	Fe	-	0.995	4.589
3.	K	0.713	0.973	0.956
4.	Sr	0.672	0.236	-

SEM Analysis of Prepared Calcium Acetate from Three Eggshell Samples

The surface morphology of resulting calcium acetate was analysed using Scanning Electron Microscopy. It was seen that the three crystal structures were seen to be needle like crystals (Figure 7).



(a) (b) (c)

Figure 7: SEM images of calcium acetate from three eggshell samples (a) chicken (b) duck (c) quail at 1000 X magnification

Conclusion

In this study, the chemical, physical and morphological characteristics of the eggshell samples were investigated by using EDXRF, XRD and SEM. The results obtained from EDXRF spectrum showed that the most inorganic compounds in eggshell samples were calcium (29.26 % in chicken, 28.56 % in duck and 26.19 % in quail). XRD patterns of the three eggshell samples are identical with the calcite phase with hexagonal crystal system with lattice constant values of equal a and b axes and longer c axis. According to SEM micrographs, the eggshells were composed of calcium carbonate layer with small holes called pore canals on the surface of the shell for gas-exchange. Thermal behaviour of eggshell samples showed the presence of two thermal events, loss of moisture and combustion of organic matter accompanied by endothermic peaks and exothermic peaks respectively.The calcium carbonate content from three eggshell samples were found to be 61.75 % in chicken, 60.3 % in duck and 59.8 % in quail and thus these eggshell were good source of calcium. The shapes of the calcium acetate samples prepared form eggshell waste samples were needle like structure. The calcium acetate contents from eggshell samples were 46.76 % from chicken, 33.00 % from duck and 32.27 % from quail. The characteristic peaks of calcium acetate prepared from eggshell samples were found in corresponding FT IR spectra. Calcium acetate obtained from chicken eggshell gave the highest amount of calcium. From the results chicken eggshell waste contained the highest amount of calcium carbonate yielding the highest amount of calcium acetate.Thus, chicken eggshell waste is appropriate for preparation of calcium acetate, a pharmaceutical excipient.

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