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Sustainable Bio-Inspired Limestone Eggshell Powder for Potential Industrialized Applications

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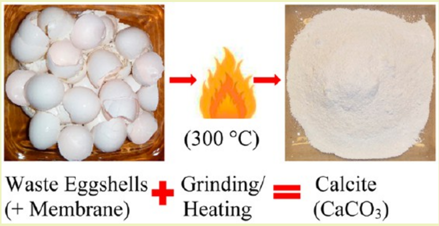

ABSTRACT: Biowaste chicken eggshells contain high amounts of calcium carbonate or calcite. Waste eggshells generated by processing industries have the potential to be used as limestone or lime in a variety of applications. Studies have shown removal of membrane from eggshells can be separated at the laboratory level, but mass production has not been industrialized. The aim of this study was to optimize two membrane removable techniques; heat treatment and bleach treatment. The as-received eggshell samples were first water ball milled into a 63 μm powder. In the first method, fine eggshell powders were submitted to elevated temperatures from 105 to 800 °C in air. The second method involved submitting the powder to a chemical treatment of 10% to 100% bleach concentrations and holding in the solutions for different soak times. The powdered samples were characterized for chemical composition and microstructural analysis. The results indicated pure calcite can be produced by heating to a temperature of 300 °C for a period of 2 h or a 10% bleach treatment for 48 h or a 50% bleach for 10 min. In addition, calcite from eggshells could be transformed into lime by heating to 750 °C for 1 h. The heat treatment method can easily be scaled up to mass production. This study signified eggshells can be used as a total or partial alternative replacement to mined limestone.

KEYWORDS: *Chicken eggshells, Elevated temperature, Bleach, Organic membrane, Biowaste*

INTRODUCTION

Attention has been growing globally on the need for new materials that are sustainable. Interest is forcing industry to change their approach to recyclability, reusability, and new materials production from renewable resources. The egg processing industry yields considerable waste of eggshells, specifically from egg farmers, chick hatcheries, and egg breaking plants. Eggshells are currently being disposed of in landfills at a cost to each egg processing plant of approximately \$100,000 annually for companies in the United States.[1] As an alternative, eggshells are agricultural byproducts that could be recuperated for use as limestone and/or lime powder as a partial or total substitute for natural mined limestone. This would have the benefit of potentially creating revenue from an otherwise biowaste material.

Eggs in Canada are graded into three categories for consumption. Grade A eggs are typically perfect eggs, while grade B eggs have a rougher surface, a flattened yoke, or watery whites, while grade C eggs can have a loose yolk and a cracked, deformed, or stained shell. In all cases, the eggs are good for human consumption. However, grade A eggs are sold in cartons for household use, whereas grade B and C eggs are shipped to a breaking plant where the eggs are mechanically separated from their shells. They are used for food production such as mayonnaise, ice cream, baked goods, and noodles, as well as nonfood items such as shampoo, pet food, pharmaceuticals, and adhesives. In 2011, Canada's annual egg production averaged 644 million dozens (7.7 billion eggs),[2] which includes eggs for consumption, hatching, and rejects. About 30% of eggs produced are sold for processing at breaking plants, which account for 2.3 billion eggs, a significant source of limestone waste. For example, an average egg weighs approximately 60 g, and the empty eggshell represents 11 wt %.[3] Therefore, about 15,000 tonnes of a pure form of limestone powder could be produced from eggshells annually. Consequently, for every 1 billion eggs that are discarded, 6600 tonnes of high grade limestone could be produced. This would provide a profit to an egg breaking plant of approximately \$660,000 based on an approximate commercial limestone powder value of \$100 per tonne.

Eggshells are rich in calcium carbonate ($CaCO_3$) or limestone. Studies concluded that 96−97% of the eggshell is a mineral of calcium carbonate with 3−4% organic matter.[4,5] The eggshell produces a purified form of mineral calcite, a more stable form of $CaCO_3$, as opposed to quarried limestone, which contains impurities such as clays, sands, and other minerals. The amount of limestone in sedimentary rocks varies depending on its source but should have at least 50% $CaCO_3$ for it to be used as limestone material. As a powder form, limestone finds many uses for fillers in cements, concretes, plastics, paints, and rubbers and in the metal purification process. In addition, heating $CaCO_3$ above 800 °C[6] transforms it to calcium oxide (CaO), also known as lime or quicklime. CaO is added to agricultural soils, gardens, and lawns to reduce

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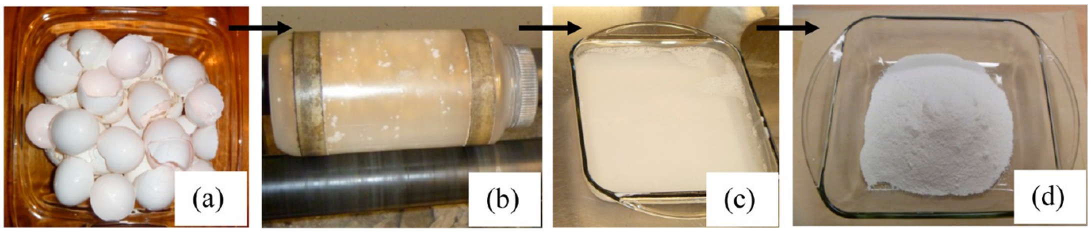

Figure 1. Digital image of fine eggshell powder laboratory manufacturing: (a) raw eggshells, (b) ball mill grinding process, (c) eggshell powder slurry, and (d) dried eggshell/membrane powder.

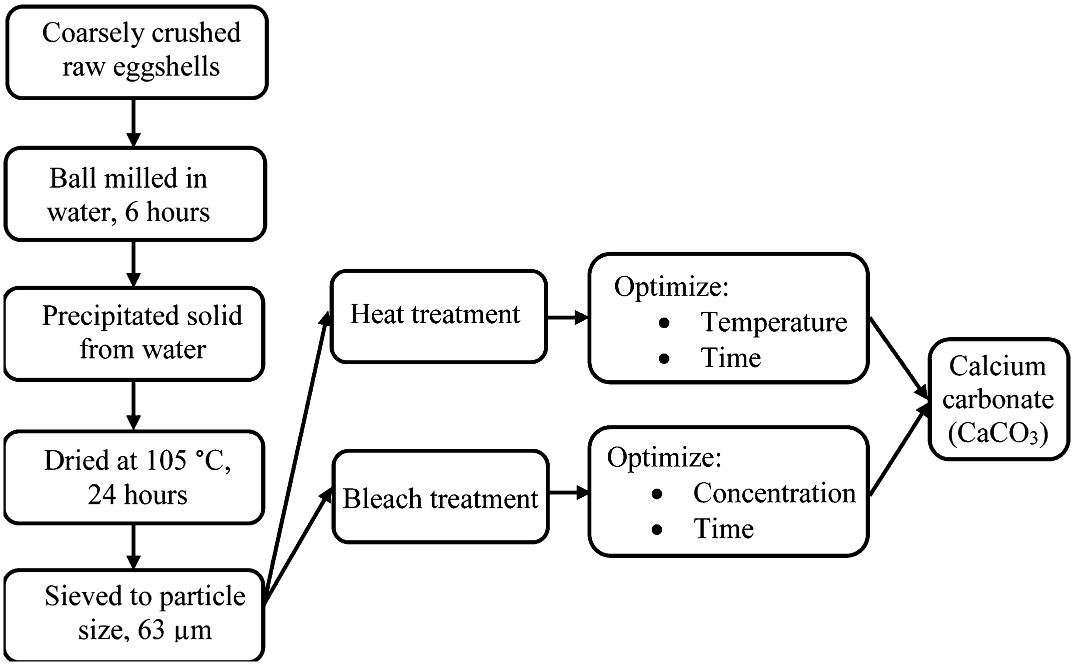

Figure 2. Experimental procedure for the production of $CaCO_3$ powder.

acidity and as an ingredient in Portland cement. Limestone and lime powders have numerous applications within and outside the egg farming community. In Canada, eggshell meal is an acceptable source of limestone for crop production as well as a mineral ingredient for use as feed for chickens, pigs, dairy cattle, and pets as it is a source of calcium. For example, one study showed eggshell diets significantly improved egg production over ground limestone.[7] Other nonfood related uses for eggshells are addition to cohesionless soils for stabilization analyses,[8] ceramic wall tiles,[9] fillers for polypropylene composite[10] and inepoxidized natural rubbers,[4] and in cement mortar[5] and cement paste.[11] Eggshells also contain an internal organic membrane that holds a percentage of collagen, a biomaterial used in cosmetic/medical applications for skin grafts, plastic surgery, and pharmaceuticals. Purified collagen sells up to US$1000 per gram. Studies in the literature have shown removal of membranes from eggshells at the laboratory level, but mass production has not been industrialized.

Feasible eggshell–membrane extraction methods require them to be cost effective, encompass minimal processing steps, and modest use of energy and chemicals. Recently, a literature review has been conducted on possible alternative separation techniques and general reuse of eggshells. A variety of eggshell extraction systems were evaluated and divided into low and high investment processes. The authors suggest that pilot projects are required to evaluate their implementation to a commercial scale.[12] A previous study determined sodium hypochlorite (bleach) was effective for membrane removal by immersing single chicken eggshells for 20 min.[13] Another investigation used alligator eggshells by first manually peeling the membrane from the shell and further soaking in sodium hypochlorite for 2 min to dissolve the remaining membrane.[14] Another technique for membrane removal involves oxidizing in air at elevated temperatures. In one study, a sample of chicken eggshells were coarsely crushed, mechanically stirred for 48 h in water to remove the membranes, and further heat treated to 600 °C for 2 h.[4] The final composition contained 96.56% $CaCO_3$. In another study, crushed eggshells were heated for 2 h at different temperatures in the range of 200 to 1000 °C. They determined that the formation of CaO below 600 °C did not occur. However, at 700 °C, the samples contained a major phase of $CaCO_3$ with a minor phase of CaO, while at 800 °C the entire sample was CaO.[6]

The objective of this work was to evaluate two eggshell extraction processes for possible application into a commercial processing plant, heat treatment and chlorinated bleach, both of which were evaluated as low investment processes. The goal was to optimize the processing techniques in the heat treatment or chemical bleach methods. A small-scale ball mill apparatus was used to grind eggshells into fine powder. X-ray diffraction, Fourier transform infrared spectroscopy, weight loss, thermal gravimetric analysis/differential thermal analysis, inductively coupled plasma-optical emission spectroscopy, and secondary electron microscope imaging were used to analyze the chemical composition and particle morphology of the chicken eggshell powders.

MATERIALS AND METHODS

Preparation of Materials. White chicken eggshells were obtained from eggs purchased from a local supermarket (Selection) as shown in Figure 1a. The eggshells containing membranes were first manually crushed in a mortar and pestle to a manageable volume. Coarse eggshell powder in the amount of 50 g, which passed through an ASTM No. 35 (500 μm), were ball milled in water at one time for 6 h as shown in Figure 1b. Several milling cycles were required to obtain a substantial amount for testing. Water was removed from the solid ground eggshells and inner membrane by a manual precipitation process, which left a slurry mixture as shown in Figure 1c and was further dried at 105 °C for 24 h. A fine powder containing eggshells and membrane was obtained, which passed through an ASTM No. 230 (63 μm) sieve as presented in Figure 1d.

Experimental Procedure. In order to use the purified form of calcite from the eggshell, the membrane must be removed without altering the composition of the calcium carbonate. Two treatments were studied to remove the inner eggshell membrane from the 63 μm or smaller eggshell powder. The experimental procedure is outlined in Figure 2. The factors considered for heat treatments were temperature, time, $CaCO_3$ concentration, and weight loss. The bleach treatment parameters evaluated were bleach concentration, time, and $CaCO_3$ concentration.

Weight losses were determined by oxidation in air at elevated temperature in a muffle furnace. Different temperatures and times were conducted to determine an optimum value to remove the membrane without converting calcite into lime. The eggshell powders were initially dried at 105 °C for 12 h prior to conducting weight loss measurements. The removal of the membrane by incineration used elevated temperature ranging from 150 to 800 °C at a heating rate of 10 °C/min. The holding temperatures were 0.5, 1, and 2 h. The powdered sample weights ranged from 2 to 3 g and were heated in triplicates.

The bleach treatment was used to remove the membrane while leaving behind the calcite eggshell particles. The ground eggshell powders were soaked in household chlorinated Clorox bleach (sodium hypochlorite). An amount of 5 g of powder was held in a bleach concentration of 10%, 50%, and 100% for 10 min as well as longer durations of 3, 24, 48, and 72 h. All tests were conducted in triplicate at room temperature. The samples were rinsed with water 4−5 times to remove any bleach residue.

X-ray diffractograms (XRD) of eggshell samples were recorded using a Philips X'Pert Pro diffractometer with Cu Kα radiation at an operating voltage of 45 kV and a current of 40 mA with a scanning speed of 0.02°/min. The measurements were made at diffraction angles of 2θ ranging between 20 to 70°. XRD was used to identify the crystalline structure (phases) and the qualitative composition after selected heat treatments and bleach treatments. Fourier transform infrared (FTIR) spectroscopy was performed on heat-treated eggshell powders at 105, 250, 300, 400, 650, 700, 750, and 800 °C. After the heat treatments, the samples were stored in glass vials. The FTIR spectra were conducted on a PerkinElmer (Wellesley, MA, U.S.A.) FTIR spectrum GX equipped with a DTGS detector and a KBr beam splitter. The spectra for each analysis were averaged over 16 scans using a nominal resolution of 4 cm^{-1}. FTIR specimens were compressed into a pellet containing 15 mg of eggshell powder with 235 mg of KBr, which were determined to be optimum amounts to have a good peak resolution and size. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed simultaneously on powdered chicken eggshells samples to evaluate the weight change and monitor thermal decomposition behavior. The apparatus was a Netzsch STA 449 F1 thermal analyzer, Germany. The heating temperature ranged from ambient temperature to 1000 °C and used a heating rate of 10 °C/min under a nitrogen atmosphere. Approximately 100 g of powder was loaded into an alumina crucible. Untreated and treated eggshell powders were analyzed for calcium concentration by inductively coupled plasma-optical emission spectroscopy (ICP-OES), model Varian AX-Vista Pro CCD Simultaneous. All eggshell samples (0.1 g) were digested in triplicate in nitric and hydrochloric (1:3) acid. Samples were made up in deionized distilled water and filtered prior to analysis. The morphology of the eggshell powder was evaluated using a scanning electron microscope (SEM), model Quanta 650 FEG with 10 kV.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis. The XRD patterns of the as-received ball-milled eggshell powder dried at 105 °C and heat-treated results from 150 to 800 °C for samples held for 2 h in the furnace are presented in Figure 3. The initial dried eggshell powder without either heat or bleach treatment should contain some amorphous membrane material, but there is no indication of this in the XRD pattern as observed in Figure 3a and Figure 4a, respectively. Although the organic membrane may be present, XRD cannot detect noncrystalline organic materials. The results suggest a fine powder of 63 μm and a thorough

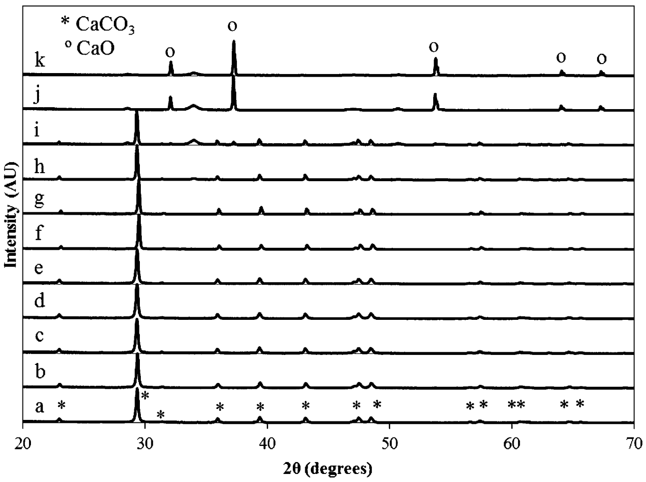

Figure 3. X-ray diffraction patterns of heat-treated eggshells each for a duration of 2 h: (a) crushed and dried, (b) 150 °C, (c) 250 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, (g) 600 °C, (h) 650 °C, (i) 700 °C, (j) 750 °C, and (k) 800 °C.

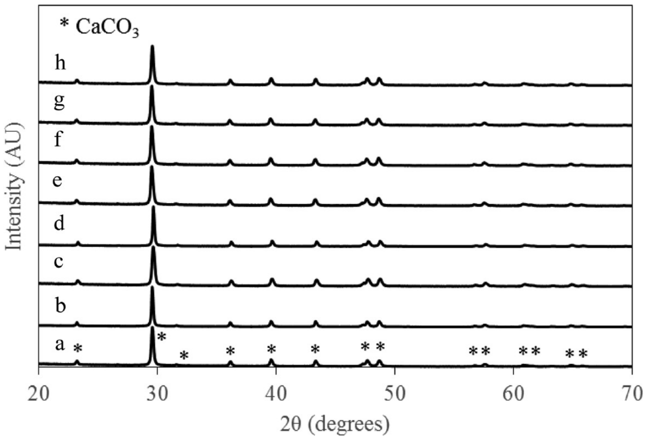

Figure 4. X-ray diffraction patterns of eggshells: (a) crushed and dried, (b) 300 °C for 2 h, (c) 300 °C for 3 h, (d) 300 °C for 4 h and 10% bleach for (e) 3 h, (f) 24 h, (g) 48 h, and (h) 72 h.

washing without a heat treatment may produce a product with a high content of $CaCO_3$. But a heat or bleach treatment can guarantee the removal any remaining combustible organic materials.

The XRD patterns from the heat-treated eggshells showed a similar pattern from 150 to 650 °C, irrespective of the temperature. Within this temperature range, the distinctive peaks showed a characteristic crystalline mineral phase of calcium carbonate in the form of calcite. Calcite is the most thermodynamically stable polymorph of $CaCO_3$ under ambient conditions.[15] The characteristic peaks for calcite appeared at approximately 2θ angles of 23.2°, 31.4°, 36.1°, 39.5°, 43.3°, 47.6°, 48.7°, 56.7°, 57.7°, 60.8°, 63.1°, 64.9°, and 65.8° with a major peak at 29.5°. Between the elevated temperature range and times tested, the results indicated the eggshell powders contained mainly $CaCO_3$ consistent with an earlier work.[6] The XRD patterns were not altered by submitting the eggshell powder to different temperatures up to 650 °C for a hold time of 2 h. Solid calcite ($CaCO_3$) transforms to solid calcium oxide or lime (CaO) and carbon dioxide (CO_2) by heating to an elevated temperature above 700 °C according to eq 1[9]

$$CaCO_3(s) + \text{heat} \rightarrow CaO(s) + CO_2(g) \tag{1}$$

The XRD pattern peaks for lime occurred at 2θ angles 32.3°, 37.4°, 53.9°, 64.2°, and 67.5° as determined from a previous study.[6] After heating at 700 °C for 2 h, the calcite began to transform to lime as observed from Figure 3i, while at 750 and 800 °C, the formations of CaO were more prominent as shown from the increased intensity of the XRD peaks in Figure 3j and k, respectively. Crystalline lime may have formed at 650 °C (Figure 3h), but its quantities may be lower than the detection limits of XRD, as discussed in detail below. At a greater temperature than 750 °C, the $CaCO_3$ peaks were not visible indicating the calcite was totally transformed to lime.

During the XRD investigation, a separate trial heat treatment was conducted on the eggshell powder at 300 °C and held in the furnace for 2, 3, and 4 h. The results are given in Figure 4b, c, and d, respectively, and compared against the as-received crushed and dried eggshells represented by the XRD pattern in Figure 4a. The XRD patterns did not show changes in crystalline material provided the eggshell powder is held in the furnace for longer than 2 h. XRD showed the eggshell mineral was crystalline calcite and remained as a calcite structure. No other crystalline material was detected. This indicated hold times greater than 2 h was not a significant factor in removing/incinerating the eggshell membrane.

Similarly, the XRD results of eggshell powders bleached for 3, 24, 48, and 72 h in a 10% bleach solution are shown in Figure 4e, f, g, and h, respectively. The XRD patterns showed peaks of calcite to be the main mineral. The intensity, thinning, or broadening of the calcite peaks remained relatively identical at all bleach soaking times. This suggested the rinsing procedure was adequate, and the bleach did not react to produce new crystalline compound materials.

FTIR Analysis. The FTIR spectrum was used to analyze the functional groups in the powdered eggshells submitted to elevated temperatures from 105 to 800 °C as presented in Figure 5. The spectra of eggshell powder from 105 to 300 °C were very similar. The broad absorption band at 3328 cm^{-1} was due to water molecules. This was attributed to the OH^- stretching vibration from the presence of absorbed moisture in the sample. The results are consistent with other studies where water in the calcium carbonate samples had transmission bands ranging from 3243 to 3440 cm^{-1}.[16,17]

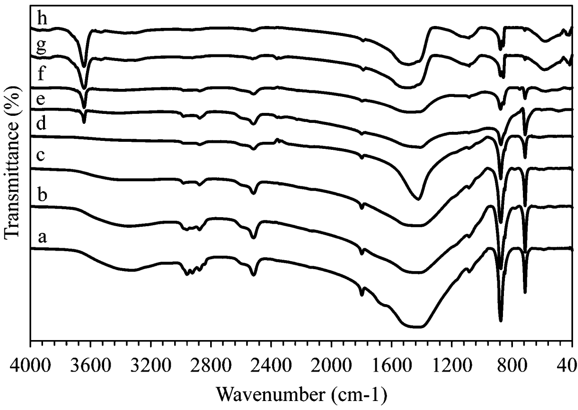

Figure 5. FTIR spectra of heat-treated eggshell powders each for a duration of 2 h: (a) 105 °C, (b) 250 °C, (c) 300 °C, (d) 400 °C, (e) 650 °C, (f) 700 °C, (g) 750 °C, and (h) 800 °C.

The calcite phase of eggshell powder exhibited significant characteristic absorption peaks at a very broad frequency band of 1420 cm^{-1}, one medium intensity band at 1084 cm^{-1}, and two sharp peaks at 875 and 713 cm^{-1}. These peaks corresponded to the vibration bands of the carbonate CO_3^{2-} molecular ion for C−O symmetric stretching-$\nu 1$, asymmetric stretching-$\nu 3$, out-of-plane bending-$\nu 2$, and in-plane bending-$\nu 4$, respectively. The results were comparable to published data: 1413 to 1453 cm^{-1},[18,19] 1067 to 1085 cm^{-1},[20,21] 872−879 cm^{-1},[22,23] and 700−712 cm^{-1},[23,24] respectively. Smaller vibration bands for the CO_3^{2-} molecular ion also occurred for different combined frequency modes at 1798, 2516, and 2877 cm^{-1} as compared to published data: 1793 to 1799 cm^{-1},[20,17] 2512−2517 cm^{-1},[4,21] 2873−2876 cm^{-1},[17,24] respectively. The frequency peak at 2516 cm^{-1} also showed the existence of HCO_3. As expected, the four prominent peaks and three smaller peaks in the FTIR spectra for the eggshell powders were identified as calcium carbonate.

At 400 °C, the characteristic calcium carbonate peaks had reduced considerably. The peak size is related to the concentration of the compound. For example, a peak with a small percent area has a reduced compound, while a larger peak area provides an increase concentration of a compound. As temperature rose to 650 °C, the 1420 cm^{-1} band shifted to 1409 cm^{-1}, and the peak intensities at 875 and 713 cm^{-1} were significantly decreased. In addition, at this temperature, a peak at 3644 cm^{-1} was due to the OH^- group, which corresponded to calcium hydroxide ($Ca(OH)_2$) from absorption of moisture in the sample by CaO. The literature data for this peak ranged from 3600 to 3643 cm^{-1}.[22,24] Additionally, at this temperature, the FTIR spectra showed the beginning of $CaCO_3$ conversion to CaO, while the XRD results indicated the CaO formation above 700 °C. At 750 °C, a frequency band at 586 cm^{-1} appeared, which represented the Ca−O bonding. Similarly, published data for this peak occurred between 500 to 670 cm^{-1}.[18,22] At this temperature, FTIR results showed complete conversion of $CaCO_3$ into CaO due to the Ca−O bond present, which is also indicated in the XRD results of Figure 3j.

Eggshell membranes are organic material that contain collagen, alkynes, alkanes, amines, and amides of proteins and carboxylic acids.[25] At 105 °C, the eggshell membrane functional groups were found at a band of 1651 and 2961 cm^{-1} and were

Table 1. Eggshell Weight Losses by Oxidation at Elevated Temperatures

temperature (°C)	time (h)	weight loss[a] (%)	powder color[b]	temperature (°C)	time (h)	weight loss[a] (%)	powder color[b]
150	0.5	0.07 ± 0.06	W	600	0.5	0.89 ± 0.01	B
	1	0.12 ± 0.09	W		1	1.15 ± 0.30	B
	2	0.13 ± 0.08	W		2	1.20 ± 0.07	B
250	0.5	0.11 ± 0.07	LB	650	0.5	0.92 ± 0.04	DG
	1	0.16 ± 0.13	LB		1	1.29 ± 0.07	DG
	2	0.22 ± 0.12	LB		2	1.61 ± 0.03	DG
300	0.5	0.25 ± 0.06	LB	700	0.5	1.12 ± 0.03	LG
	1	0.35 ± 0.11	LB		1	1.72 ± 0.35	LG
	2	0.42 ± 0.02	LB		2	2.09 ± 0.22	LG
350	0.5	0.42 ± 0.07	DG	750	0.5	2.58 ± 0.17	W
	1	0.50 ± 0.03	DG		1	3.94 ± 0.36	W
	2	0.53 ± 0.02	DG		2	4.34 ± 0.68	W
400	0.5	0.46 ± 0.03	DG	800	0.5	3.76 ± 0.30	W
	1	0.56 ± 0.03	DG		1	3.95 ± 0.57	W
	2	0.60 ± 0.01	DG		2	4.59 ± 0.43	W
500	0.5	0.67 ± 0.1	B				
	1	0.74 ± 0.1	B				
	2	0.97 ± 0.07	B				

[a] All weight losses are after drying at 105 °C. [b] (W, white; LB, light brown; DG, dark gray; B, black; LG, light gray).

attributed to the carbonyl group (−C═O) stretching for amides[26] and the −C−H stretching of alkanes for lipid and proteins,[25] respectively. In addition to the presence of water, the wide bands in the range between 3200 to 3500 cm^{-1} contain amides and amides.[26] From the FTIR results, below 300 °C, the eggshell powders were hygroscopic and easily absorbed moisture from the atmosphere. As temperatures were increased above 300 °C, the broad band characteristic of water and organic membrane vanished, indicating 300 °C was an optimum temperature for membrane removal.

Weight Loss Analysis. The weight losses for different temperatures and hold times are given in Table 1. On average, a weight loss of 6.37 ± 2.22% was observed after the initial drying procedure for 12 h. The (±) indicates one standard deviation. The final powder color was estimated by visual inspection. As was predicted, the results show an increase in weight loss as temperature increased.

After furnace drying the eggshell powder at 105 °C, a weight loss was due to some evaporation of the free or surface moisture in the membrane material. Chicken eggshells have three layers: an inner shell membrane, the calcified shell, and an outer shell membrane commonly referred to as the cuticle. The membranes are attached to the shell and are composed of organic materials. The major constituents are organic proteins such as collagens (types I, V, and X), osteopontin and sialoprotein[27] with smaller amounts of moisture, amino acids, and fats.[28] At 150 °C, bound (or absorbed) water within the membrane began to be removed. Organic eggshell membranes or biological templates started to decompose at 240 °C.[29] At 250 °C, all free and bound water are removed. Increasing the temperature to 300−500 °C, all organic materials were removed. From 300 to 500 °C, the weight loss increased by 168%, 111%, and 131% for furnace hold times of 0.5, 1, and 2 h, respectively. The soak times did not show a significant difference in weight losses.

At 500 °C, a slightly greater weight loss was observed, more than at 400 °C, and increases substantially to 700 °C. Assuming all organic materials are removed at 300 or 400 °C for hold times of 2 h, the samples would lose 0.42% and 0.60% of their initial dry weights, respectively. For samples held at 500 °C for 2 h, the weight loss would be 0.97% of their weight. The expected weight loss due to the transformation of limestone into lime at 500 °C would be 0.55% and 0.37%, respectively. It was determined from a former investigation that the very start of calcite decomposition into lime begins as low as 500 °C.[30] However, the XRD results in this study only began to show intensity peaks of CaO formation above 700 °C as shown in Figure 3i. This can be explained by the detection limits of the XRD apparatus. XRD cannot detect concentrations of crystalline solids in a material when they are lower than approximately 1 wt %. This implies there was less than 1 wt % CaO at 500 °C as XRD peaks of CaO were not visible in Figure 3f. Similarly, although there was a weight loss of the sample up to 700 °C, the CaO concentration was below 1 wt %. At 750 and 800 °C, the CaO concentrations in the sample increased and were well exposed in the XRD results as shown in Figure 3j. Therefore, between 500 to 700 °C, CaO gradually formed but was not detected by XRD until the temperature reached 750 and 800 °C where the CaO concentration (and weight losses) were amplified.

The chicken eggshell powder was observed to pass through a variation of colors after it was exposed to elevated temperature oxidation tests as noted in Table 1. The as-received and crushed powders after drying at 105 °C and heating to 150 °C were white (W). As temperature was increased to 250 and 300 °C, the powder transformed to light brown (LB), which is an indication of burning of some organic materials. At 350−400 °C, the color changed to dark gray (DG). Increasing the temperature from 500 to 600 °C, the powder changed to black (B). At 650 to 700 °C, the sample was altered to a dark gray and light gray (LG), respectively. After heating to 750−800 °C, the eggshell powders returned to a white color identical to $CaCO_3$ but a different purified phase of CaO. Depending on the origin and impurities contained in quarried limestone, the limestone rock can have a variety of colors such as white, yellow, red, brown, or a combination.[31] White colored limestone could be used as a commercial filler in materials such as polymers, ceramic tiles, and paints where pigment colors are vital. Colored limestone powder could be used in other industries where color is not as important. For example,

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limestone powder is used in the concrete industry as partial Portland cement replacements by as much as 15 wt % of limestone.[32] Limestone is also used in the iron and metal refinement industries.[31] Therefore, due to the different colors evolved during the heat treatments of waste eggshells, selected niches for colored limestone could be established for a variety of applications where limestone color will not affect the final product.

Thermogravimetric and Differential Thermal Analysis. Simultaneous thermogravimetric and differential thermal results as a function of temperature of the as-received chicken eggshell powder are shown in Figure 6. The weight loss can be divided into four events. The first region was a short decreasing plateau between 26 and 300 °C, which was attributed to moisture evaporation and some organic eggshell membrane decomposition. At 300 °C, the weight loss was approximately 1%. The second region had a slightly steeper slope where a weight loss of 2% was observed from 300 to 450 °C. Within this temperature range, all organics were removed, and the weight loss became reasonably constant after 450 °C. At 300 °C, the FTIR organic membrane characteristic bands at 1651 and 2961 cm^{-1} disappeared, which indicated a purified form of calcium carbonate eggshell. In the third region, the slope had a slight continuous drop in weight loss of about 2% between 450 and 700 °C. This was the beginning of the phase transition from calcite decomposing into lime, which started at 650 °C in the FTIR results shown in Figure 5e. Lastly, in the fourth region, a sharp drop in weight loss of 44% occurred between 700 and 900 °C. This was due to a greater amount of calcite converting into lime and the release of CO_2. After 900 °C, a constant weight loss of 54% was obtained, and the entire sample had converted to lime indicating complete thermal decomposition. However, XRD and FTIR results showed complete conversion of $CaCO_3$ into CaO at 750 °C. When samples were heated between 750 and 800 °C, the furnace hold time required was observed to be at least 1 h for the majority of the weight loss to occur as given in Table 1.The DTA results showed the main endothermic DTA peak for the eggshell was 884 °C, which suggested an important weight loss temperature generally associated with thermal decomposition of calcium carbonate.

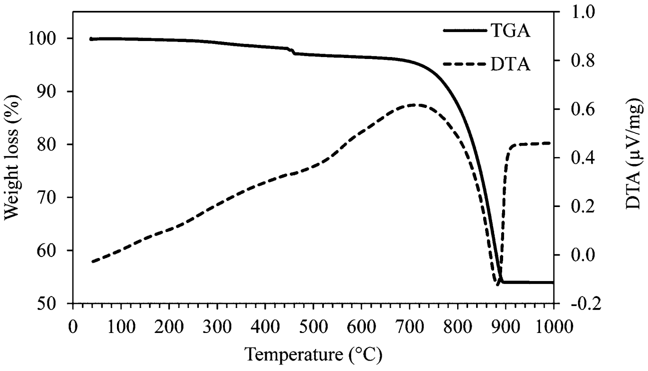

Figure 6. TGA-DTA results for the powdered chicken eggshell sample.

ICP-OES Analysis. The calcium carbonate theoretical compositions contained in the chicken eggshells were determined by ICP-OES after heating in air to different elevated temperatures and hold times as given in Table 2. The (±) indicates one standard deviation for the average of three samples. The amount of $CaCO_3$ was determined from Ca concentrations based on the theoretical percent calcium. The chemical analysis revealed theoretical calcite percentage in eggshell powders to be in the order of 77.8(±2.7)% after heating to 105 °C for 2 h. This value derived from the crushing process in water, while no extra treatments were performed on the powder. After heating to 250 °C for 2 h, the calcite percentage was increased to 90.6(±0.7)%. These lower values indicate possible organic material still remained within the shell particles. As the temperatures were increased, a gradual purified form of $CaCO_3$ evolved, which could have a maximum of 96–97%[4,5] for chicken eggshells. ICP-OES showed the eggshell powders could be heated to 300 °C with hold times of 2 h to be optimum parameters for organic membrane removal. At temperatures of 350 and 400 °C, hold times were increased to 3 and 4 h. The results indicated that prolong heating times did not increase $CaCO_3$ purity. At these temperatures, 2 h was sufficient to produce relatively pure calcite.

At low bleach concentrations of 10%, the $CaCO_3$ percentage increased as hold times increased as given in Table 2. In addition, high bleach concentrations of 50% and 100% required less soaking times to remove the organic membranes. Higher standard deviations were noted for bleach treatments, which may be due to variability in sample preparation.

The 10% bleach treatment with a soak time of 24 h had a theoretical calcite composition of 86% as illustrated by ICP-OES. It appears these two parameters were not able to remove the entire membrane. However, a 10% bleach concentration and soak time of 48 h were required to obtain an approximate $CaCO_3$ composition of 98 wt %. Extending the hold time to 72 h for the same bleach concentration did not have an added advantage. Furthermore, increasing the bleach concentration to 50% with a soak time of 10 min produced a high purity calcite of approximately 98%. The results suggest bleach concentration

Table 2. ICP-OES Results for $CaCO_3$ Composition (wt %) of Eggshell Calcium Carbonate

treatment								
elevated temperature	temperature (°C)							
duration (h)	105	250	300	350	400	500	700	900
2	77.8 (±2.7)	90.6 (±0.7)	95.6 (±2.2)	94.8 (±1.3)	97.4 (±2.3)	96.8 (±1.9)	96.9 (±1.4)	–
3	–	–	–	93.4 (±0.8)	95.8 (±2.1)	–	–	–
4	–	–	–	92.9 (±2.1)	94.0 (±1.1)	–	–	–
	soak time							
bleach concentration (%)	10 min	3 h	24 h	48 h	72 h	–	–	–
10	85.5 (±2.3)	86.9 (±1.7)	85.9 (±5.3)	98.1 (±6.6)	99.4 (±4.2)	–	–	–
50	97.9 (±3.5)	–	–	–	–	–	–	–
100	93.9 (±3.4)	–	–	–	–	–	–	–

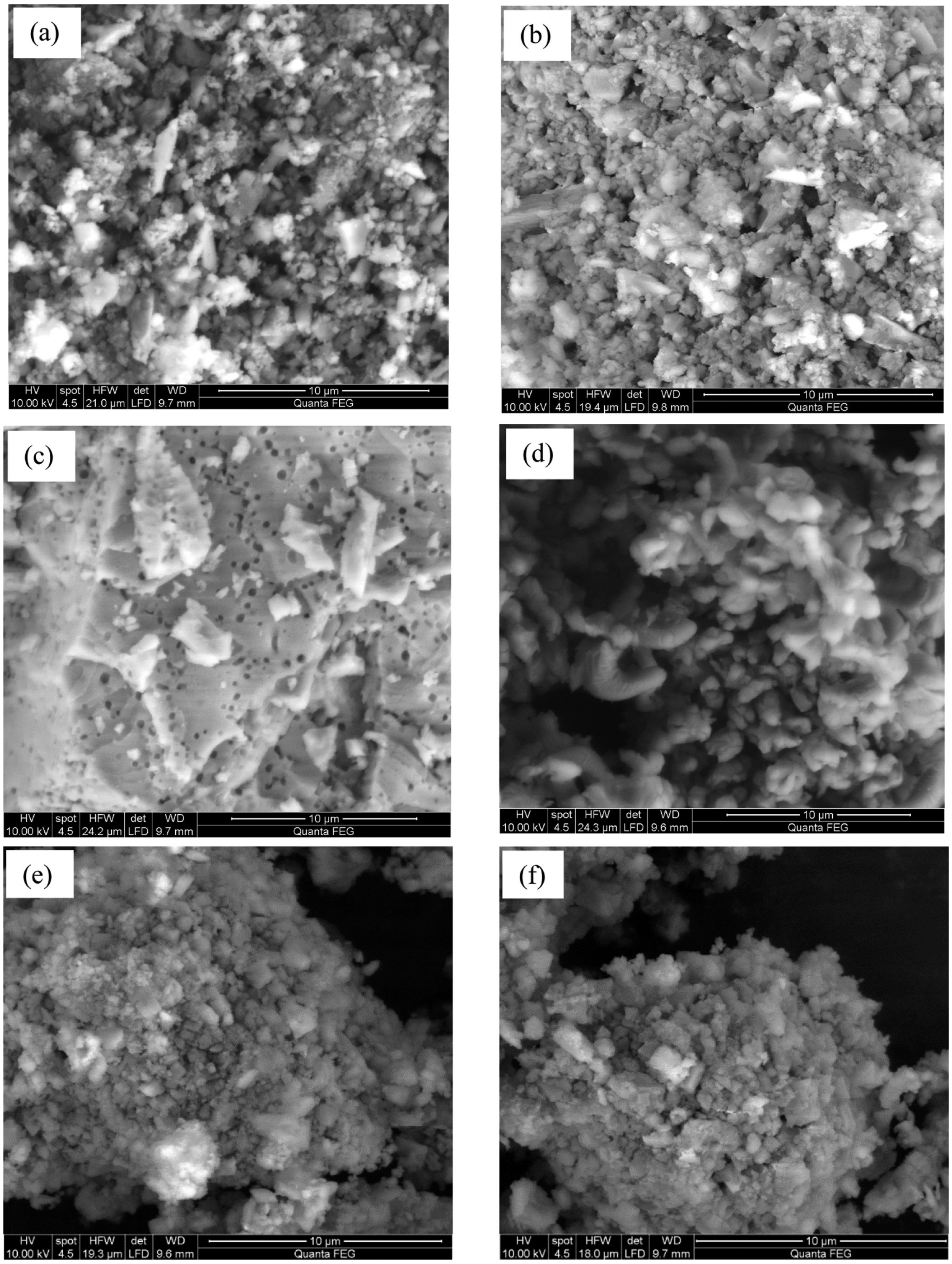

Figure 7. SEM image of eggshell powder morphology heated to (a) 105 °C, 12 h, (b) 250 °C, 2 h, (c) 500 °C, 2 h, (d) 800 °C, 2 h, (e) without bleach treatment, and (f) after a 10% bleach treatment for 48 h.

and soaking time require further work to optimize these parameters for an industrial application.

Eggshell Particle Morphology. Scanning electron microscopy images of the ball-milled chicken eggshells submitted to various stages of heat treatments are presented in Figure 7. The eggshell particles dried at 105 °C had an irregular and jagged morphology as shown in Figure 7a. At 250 and 400 °C, the $CaCO_3$ particles were similar in morphology when heated to 150 °C as observed in Figure 7b. However, when the particles were heated to 500 and 600 °C as shown in Figure 7c, a series of randomly distributed open pores were visible over the surface of the crystalline calcium carbonate. This phenomenon was not observed at temperatures up to 400 °C. Below 400 °C, the organic membrane was not distinctly visible in the images and may be covering the particles. This occurrence was also observed by another study and was believed to be due to decomposition of organic matter during the elevated temperature process.[4] Eggshells are porous in nature; these hollow pores exist between the crystalline calcite crystals to allow gaseous transfer from the inner to the outer side of the eggshell.[33] It appears these pores were only visible once the organic materials was thoroughly removed.

The eggshell particles heated to 800 °C are shown in Figure 7d. The morphology of the particles were depicted to be rounder in shape and smoother on their surface as compared to particles heated at lower temperatures. This change may have been due to the particles transforming from $CaCO_3$ to CaO and releasing CO_2.

The eggshell powder morphologies with and without bleach treatments are shown in Figure 7. After water ball-mill grinding, the eggshell powder particle shapes can be described as having rough angular particles with sharp jagged edges as shown in Figure 7e. After a 10% bleach treatment for 48 h, the eggshell particles are shown in Figure 7f. The particles were still agglomerated together and remained angularity in shape. From both SEM images, the thin eggshell membrane was not visible within the powdered sample.

The heat treatment method was determined to be quicker and more efficient then the bleach treatment. The results indicated it is possible to industrialize the heat treatment process for mass production of a purified form of $CaCO_3$ from chicken eggshell waste. A laboratory size sample of eggshell was produced using a small-scale ball mill apparatus. To increase the scale of production, a larger crushing device should be implemented.

Bleach treatment was found to be time intensive as it required bleaching, adequate rinsing with large amounts of water, and drying. In a commercial processing plant, this would relate to additional labor and processing costs. In addition, chemical disposal or treating of waste bleach is not environmentally friendly and may add to additional costs. In terms of sustainability, the drawback for using bleach is that the wastewater effluent left behind after the eggshell treatment has environmental concerns. Although bleach is used as a common household disinfectant, an industrial bleach treatment process may not be the best environmentally friendly method to remove the membrane, even at low concentrations. Other viable alternative routes to study the removal of eggshell membranes at a large scale would be to use a low powdered microwave heating,[34] which uses less electricity than conventional furnaces. In addition, another alternative would be to potentially digest the eggshell membranes by protease enzymes.[35] Both are relatively new techniques and should be investigated further. A third option would be to pulverize the waste eggshell into a very fine nanosized powder followed by rinsing with water to remove the membrane material. Membranes held onto smaller particles may be easier to remove under an agitation process. Nanosized limestone powder in polymers have shown improved properties to micron-sized particles.[36]

The purpose for recycling raw waste eggshells was to make a useful product from a sustainable material; however, as any raw product, it requires some form of processing. A low concentration bleach method was trial tested but appeared to require too much time at low concentrations to be effective at removing membranes. Therefore, an improved and cleaner production process was approached. The goal was to fine-tune and improve the heat treatment temperatures in order to make the process more sustainable. From the present study, heating to 300 °C was a relatively low temperature to remove the organic membrane as compared to previous work, which suggested 600 °C.[17]

In the following section, the cost of conducting a heat treatment on eggshell powder to remove the organic membrane was estimated using a rotary electric kiln furnace. It is assumed the eggshell powder would remain in a kiln for 10 h, which would include an 8 h drying period and a 2 h membrane calcination period. At a relatively low heating temperature of 300 °C, the power consumption was estimated to be 124 kJ/kg (0.034 kWh/kg).[37] Therefore, for one metric ton, the power consumption would be 34 kWh/ton, in addition to 24 kWh/ton for grinding[37] eggshells to a fine powder after heating. On the basis of these values, the total electricity consumed would be 58 kWh per ton of material. Supposing the average cost of electricity in North America is 10 cents per kWh and requires 10 h of operation, the cost of electricity would be \$58/ton. The estimated cost of ground calcium carbonate powder was estimated to be between \$75−350/ton.[38] The cost is dependent on purity, quality, and particle size. It is recommended as future work to study the quality and performance of eggshell based calcium carbonate in specific applications. Although the calculations were very conservative, there is a considerable savings for recycling eggshells.

From small-scale experimental results, the mass loss after heating 3 g of dry eggshells at 300 °C for 2 h was 0.42%, which resulted in 2.987 g of useful $CaCO_3$ and 0.013 g of charred organic membrane. Maintaining the same ratios for 1000 kg (one metric ton) of eggshells, approximately 995 kg of $CaCO_3$ would be produced, while 5 kg would be charred membrane. Overall, this research demonstration a greener process resulting from a renewable product.

■ CONCLUSION

In this study, recycling chicken eggshell biowaste was investigated in order to determine the most feasible and sustainable method to recuperate eggshells for their valuable limestone composition. XRD showed the eggshell mineral was crystalline calcite. FTIR showed the optimum temperature for membrane removal was about 300 °C, while above 250 °C, TGA showed the organic material began to decompose until a temperature of 460 °C. The weight loss and ICP-OES results indicated an optimum heating temperature of 300 °C for 2 h and a 10% bleach for 48 h or 50% bleach soaked for 10 min could remove the organic membrane to produce pure calcite. However, this method was deemed to be unsustainable and not environmentally friendly. SEM showed the morphology of eggshell particles to be irregular due to the grinding process. On the basis of preliminary calculations, the results indicated the process could be industrialized using a low temperature process. The advantage of utilizing waste eggshells can create profits to eggshell producers rather than expenses.

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Notes

The authors declare no competing financial interest.

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