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The technology of green synthesis of calcium acetate from quail egg shells

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Abstract. The concept of sustainable development is centred around recycling waste materials generated by the agro-industrial complex. One of the ways to achieve this is by using biowaste derived from food products, such as quail eggshells, as a sustainable and eco-friendly raw material to replace limestone or carbonate stone in the production of calcium acetate ($Ca(CH_3COO)_2 \cdot H_2O$). This research shows the possibility of producing calcium acetate in laboratory conditions by chemical transformation with acetic acid using quail eggshells as the raw material. 50 g of quail eggshells were subjected to chemical treatment with 10% acetic acid, producing 60.09 g of calcium acetate monohydrate, with a maximum yield of 76%. The X-ray diffraction data of the resulting product strongly suggested the presence of calcium acetate, and the crystallinity of the salt was found to be 72.57%. Based on these observations, it can be concluded that quail eggshells can be used as an alternative raw material for producing calcium acetate in a sustainable manner.

1 Introduction

In developing countries, industrialization can be achieved through a focus on agricultural, livestock, and poultry development. However, to accomplish this objective, innovative solutions that enhance technological processes are vital. As livestock farming grows, the amount of waste generated also increases, leading to environmental and health concerns. For instance, in Uzbekistan, the production of chicken eggs has increased tremendously in recent years, with a total of 8129.3 million eggs produced in January-December. The production of quail eggs is also on the rise. Therefore, there is a need to implement sustainable practices that minimize waste and ensure the responsible use of resources to support the growth of the agricultural and livestock sectors [1]. Livestock production causes significant environmental damage, including deforestation, soil erosion, water pollution, and the spread of pathogens [2]. The search for methods to recycle animal waste that offer economic benefits to businesses while also addressing environmental issues has become increasingly important. The recycling of chicken egg shells has garnered attention in recent times, but other waste materials, such as sea shells, citrus peels, and coffee grounds, can also be repurposed. Moreover, recent research has revealed that quail egg shells can function as a catalyst in the

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transesterification process of palm oil with methanol. These findings highlight the potential for utilizing diverse forms of waste to address environmental concerns while simultaneously providing economic benefits to businesses [3,4]. We decided to use quail egg shells in our research and subsequently use them in the pharmaceutical industry as a drug for the treatment of hyperphosphatemia [5] since quail eggs are consumed daily by the population of Uzbekistan. For example, national pilaf is a symbol of Uzbek cuisine, which is prepared in large quantities in restaurants and teahouses. It is often served with quail eggs, and 3-4 eggs are added per serving, as a result of which a large amount of quail egg shells is thrown away [6].

As for the structure and composition of quail eggs, they differ from chicken eggs both in size and composition (Fig. 1). They are smaller, weighing around 10 grams on average. Quail eggs contain 56.5% protein, 32.6% yolk, and have a shell thickness of 0.19 millimeters which makes them thinner than chicken eggs.

Fig. 1. Chicken egg and quail egg

Quail eggs are packed with essential macro- and microelements, as well as vitamins, compared to chicken eggs. For example, they contain 64 mg of calcium, 3.65 mg of iron, 13 mg of magnesium, 226 mg of phosphorus, 1.47 mg of zinc, 0.13 mg of thiamine, 0.790 mg of riboflavin, 0.150 mg of niacin, 1.761 mg of pantothenic acid and others. The shell of a quail egg is 90% calcium carbonate [7,8]. Because of this, it can be used as an alternative substitute for CaO and $CaCO_3$ [9]. The aim of our research was to obtain calcium acetate, a compound widely used in the pharmaceutical and food industries. Ivica Strelec and co previously studied the production of calcium acetate monohydrate from chicken eggshells, which is of interest to the food industry [10]. Our study focused on obtaining calcium acetate from quail egg shells and modified the production process. Specifically, we sterilised the shells by boiling them, carefully separated them from the eggs, and treated them with acetic acid without removing the inner shell membrane. The resulting product is a crystalline powder with a vinegar aroma. The synthesis of calcium acetate involves the reaction of calcium carbonate rocks with vinegar, as shown in equation (1). The process we developed has potential applications in the food and pharmaceutical industries, as it provides an alternative method for obtaining calcium acetate from a readily available source.

$$CaCO_3(s) + CH_3COOH\ (aq) \rightarrow Ca\ (CH_3COO)_2 + H_2O + CO_2(g) \quad (1)$$

Calcium acetate is a commonly used stabilizer in food products such as hard candies and bakery items [11]. Our research is unique because we were able to extract calcium acetate from quail eggs without separating the membrane part of the shell. This is because the membrane contains a considerable number of proteins, collagen, ovocleidin-116, ovalbumin, ovocalyxin-36, and other essential substances [12].

2 Materials and methods

We collected quail egg shells from local restaurants and purchased quail eggs from the local bazaar. First, we washed the eggs with egg shells carefully in a soapy solution to remove any contaminants, then rinsed them in running water. After that, we boiled the eggs and egg shells for 30 minutes at a temperature of 100-125 °C and then carefully separated the shells from the boiled eggs. The shells were dried at room temperature for 6 hours and stored in plastic bags at room temperature. We purchased glacial acetic acid (99.9%) and ethyl alcohol 96% from Chemical Invest (Tashkent, Uzbekistan). We obtained distilled water from the Institute of Bioorganic Chemistry named after Academician A.S. Sadykov. Finally, we determined the physicochemical properties of the resulting calcium acetate using powder X-ray diffraction analysis.

Powder X-ray diffraction is a powerful method for studying the structural characteristics of a material. It involves the use of X-ray diffraction on a powder or polycrystalline sample of the material being studied. The result of the study is a graph that shows the intensity of scattered radiation at different scattering angles. The advantage of this method is that the Debyegram of each substance is unique, which means it allows substances to be identified even if their structure is unknown. In this study, the structure and composition of calcium acetate obtained from the shell of quail eggs were thoroughly studied using X-ray phase analysis. This enabled a detailed examination of the mineralogical and phase compositions of the sample. To test a material, a monochromatic X-ray beam is directed at a sample that has been ground into a powder. The scattered radiation produces a Debyegram - an image in the form of rings on photographic film wrapped around the sample. By measuring the distance between the lines of the same ring on the Debye diagram, the Bragg reflection angles can be determined. The Bragg-Wolf formula ($2d\ \sin\Theta = n\lambda$) helps to obtain the ratio d/n of the distance between reflecting planes to the order of reflection, revealing valuable insights into the material being studied [8,10,13].

2.1 Synthesis of calcium acetate

To synthesize calcium acetate, first prepare 10% acetic acid from glacial acetic acid. To prepare 1000 ml of 10% acid, 99.7% glacial acetic acid, a volume of 105.3 ml was diluted with 894.7 ml of distilled water.

To 50 g of shell, 500 ml of 10% acetic acid was added in portions, since when acetic acid is added, foaming occurs and carbon dioxide (CO_2) is released. Then, at 80°C, it was stirred for 6 hours using a magnetic stirrer (MS-H280-Pro, China) at 250 rpm. The resulting mixture was filtered using a plastic mesh with a pore size of 0.8 mm. During filtration, the membrane separated from the calcified part of the shell. Then, the solution was steamed at 80-90 °C to 1/2 volume. Precipitation of crystals from saturated salt solutions cooled to room temperature was carried out by adding 2 volumes of 96% ethyl alcohol. The resulting residue was dried at 30-40 °C for 12 hours. After this, the dried salts were crushed using a ceramic mortar and pestle and stored in sealed plastic containers at room temperature until analysis (Fig. 2.).

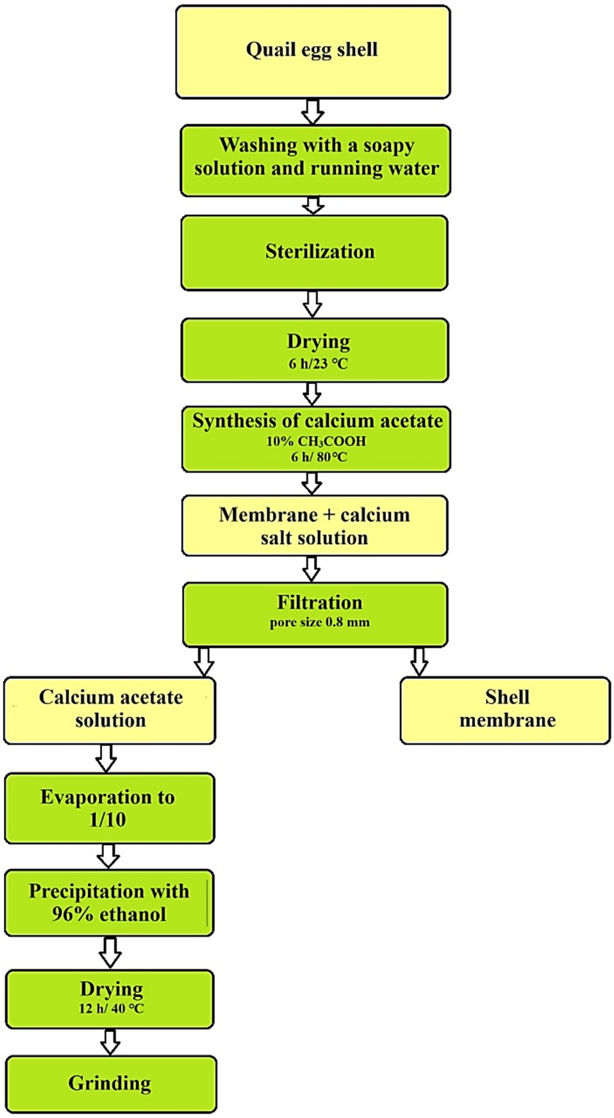

Fig.2. Schematic representation of the proposed quail shell waste recycling process

The chemical yield of salts was calculated using reaction equation (1) and formula (2):

$$\omega_{yield} = m_{practical} / m_{theoretical} \times 100\% \quad (1)$$

Based on reaction equation (1), the expected yield of calcium acetate is 79 grams. However, only 60.09 grams were obtained, resulting in a product yield of 76%.

2.2 Powder X-ray diffraction analysis

The crystal structure of the resulting salts was characterized using an XRD-6100 X-ray diffractometer (Shimadzu, Japan) with Cu Kα radiation (β-filter, Cu-anticathode, λ=1.54178 Å, current and voltage in the X-ray tube 20 mA, 40 kV). At In this case, the constant rotation speed of the detector was 4 degrees/min, with a step of 0.0500 (ω/2θ), and the scanning angle was taken from 100 to 700. Samples were analyzed in a rotating chamber with a rotation speed of 30 rpm.

3 Results and Discussion

The purpose of this study was to obtain calcium acetate from quail eggs. Calcium acetate salts have been successfully prepared by reacting $CaCO_3$ from quail egg shells with 10% CH_3COOH. The resulting salts were light brown in colour due to the presence of pigments in the eggshell.

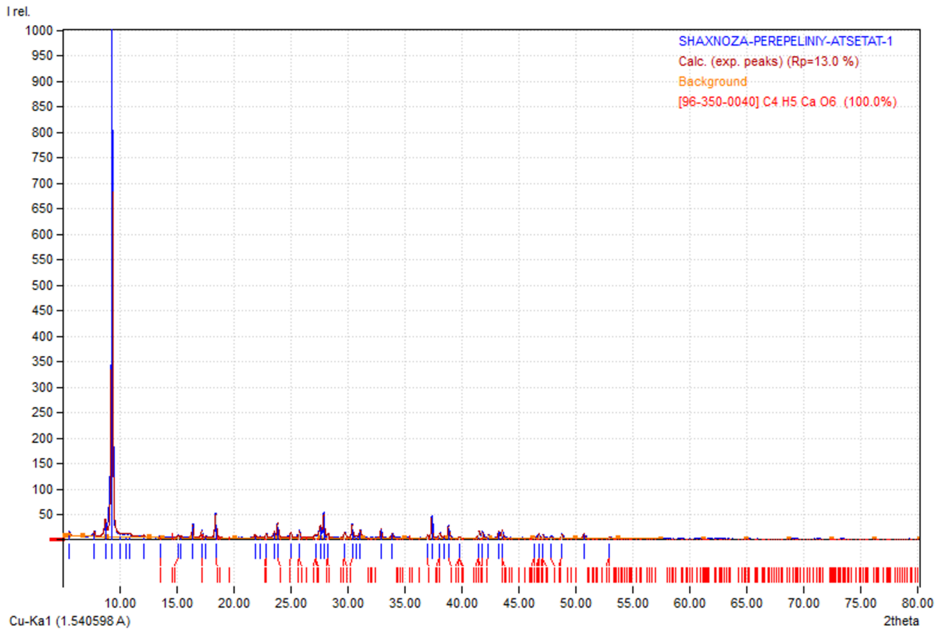

Fig. 3. X-ray diffractogram of a calcium acetate sample obtained from quail shells

During the reaction process, the membrane can be easily separated from the shell. The cost of production was low due to the availability of raw materials derived from waste generated by restaurants. The final product had a yield of 76% using the aforementioned conditions.

The purity and crystallinity of $Ca(CH_3COO)_2 \cdot H_2O$ were characterized using XRD. Figure 3 illustrates the X-ray diffraction pattern of a calcium acetate sample extracted from a quail shell. The chemical and elemental composition were determined by utilizing the Rietveld method and the "Search-Match!3" program. The X-ray diffraction analysis results were also compared with the outcomes of previously conducted studies on calcium acetate [10,11,14].

Table 1. Physical properties of the obtained calcium acetate salts

Name	Crystallite size D, nm	Crystallinity	Amorphous
$Ca(CH_3COO)_2$	D1=57 nm D2=74,87 nm D3=74,62 nm	72.57%	27.43%

As can be seen from Table 1, the crystallite sizes determined by the Debye-Scherrer formula D=Kλ/(β cosθ) for calcium acetate have dimensions in the region of 57÷75 nm. The crystal system is orthorhombic. The lattice parameters are a = 6.863 Å, b = 7.766 Å and c = 12.069 Å. The grating angles are $\alpha = 116.50°$, $\beta = 92.41°$ and $\gamma = 97.32°$. This indicates that the powder we synthesized is a nanomaterial. Another point of the study shows that the crystallinity of this material is 72.57%, which exceeds its amorphousness - 27.43%. All these data obtained by X-ray powder diffraction analysis prove the nano-size of the resulting salt.

4 Conclusion

Quail egg shells and acetic acid were used to successfully synthesize calcium acetate. The membrane easily separated during the reaction, resulting in milky colored salts with a slightly vinegary odor. The shells easily reacted with the acetic acid. XRD results confirmed that the dimensions of the crystallite sizes of calcium acetate, as determined by the Debye-Scherrer formula $D=K\lambda/(\beta \cos\theta)$, range from 57 to 75 nm. Moreover, the crystallinity of this salt is higher than its amorphousness. This study presents an alternative method for obtaining calcium acetate, which was derived from quail eggs. Obtaining calcium acetate from quail eggs is a unique aspect of this study, and waste recycling can help in reducing greenhouse gas emissions and minimizing the use of calcium carbonate from ore sources. Overall, this study provides valuable information and presents an alternative route for the production of calcium acetate.

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