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A literature review on adding value to solid residues: egg shells

D.A. Oliveira [a], P. Benelli [a], E.R. Amante [b,*]

[a] Department of Chemical and Food Engineering, Federal University of Santa Catarina, EQA/CTC/UFSC, 88040-900 Florianópolis, SC, Brazil
[b] Department of Food Science and Technology, Center of Agricultural Science, Federal University of Santa Catarina, Rod. Admar Gonzaga, 1346, Itacorubi, 88034-000 Florianópolis, SC, Brazil

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ABSTRACT

The production of chicken eggs on an industrial level leads to a considerable quantity of shell residue, which is considered as a waste or is used as a complement in agriculture. In general, egg shells are considered to have no economic value, even though they are rich in minerals and amino acids that could form the basis of several industries. In this study, information was reviewed on the technological potential for usage of the minerals and protein membranes of the egg shells. Possible applications range from low investment processes such as fertilizer and animal feed to high investment for transforming as the material for human consumption, absorption of heavy metals, paper treatment, catalysts for biodiesel production, production of hydrolyzed or concentrated protein, bone and dental implants. The last applications need large investments but can provide more valuable products. Based on this literature review, process alternatives and their estimated environmental impacts are considered as a preliminary study with a view to the development of industrial plants, which can use egg shell residues, in order to add value by using these materials in environmentally safe ways. In general, all processes suggested in this paper present high environmental and economic benefits.

1. Introduction

Since food industries produce a substantial amount of pollution, it is becoming more and more imperative to solve this problem. As the constraints related to environmental issues are becoming quite stringent, it is necessary to develop optimized systems for food waste treatment (Arvanitoyannis, 2008).

As a food, eggs are considered to be as important as milk, being highly nutritious and easy to prepare. They represent a source of high quality protein and have a low cost, containing many nutrients such as folic acid, choline, iron, selenium and vitamins A, B, D, E and K. They are also a good source of antioxidant carotenoids, lutein and zeaxanthin (Boron, 2004).

According to FAO (2009), in 2008 the world egg production was almost 62 million tons, China being the leader with 37.6% of the production. The industrialized production of egg products (e.g. powder, liquid and frozen forms) offers economic benefits, extending the product shelf-life and favoring its transportation and storage. However, a significant number of egg shells are still considered as waste. According to Boron (2004), the shell represents about 11% of the total egg weight, thus the waste generated can be estimated as being around 6.82 million t per year globally.

Basically, egg shells resulting from industrial processes are used for agriculture, in order to correct the pH of acid soils. Although they are of economic value when used in this way, this waste product is currently undervalued. Also, environmental issues should be considered in attempts to add value to egg shell materials instead of discarding them into the environment. Moreover, the use of these shells as an alternative source of $CaCO_3$ (calcium carbonate) may reduce the impact on the natural reserves of limestone, a non-renewable natural source (Neves, 1998; Boron, 2004).

Egg shells are a rich source of minerals, serving as a pharmaceutical excipient, a base material for developing medicinal and dental preparations, a food additive and calcium supplement, a diluent of solid dosage forms, use as an agricultural fertilizer component, and as a component for bone implants (Murakami et al., 2007).

The membrane of the shell is composed of glycoproteins, consisting of type I, V and X collagen, useful it can be used in the production of cosmetics. It is composed of keratin and dermatan sulfate, and glycosaminoglycans that are useful in the production of collagen and for the synthesis of other products such as chitin. It contains sialic acid, a sial-oligosaccharide that has therapeutic properties for problems such as anti-influenza (Fátima et al., 2005). It also contains bacteriolytic enzymes such as lysozyme and beta-N-acetyl glucosaminidase, which alter the thermal resistance of bacteria. Among other membrane components are amino acids such as lysine, proline, alanine, cysteine and phenylalanine (Boron, 2004).

* Corresponding author. Tel.: +55 48 3721 5371; fax: +55 48 3721 9943.
E-mail address: eamante@cca.ufsc.br (E.R. Amante).

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Despite containing these useful chemical components, egg shells have still not gained sufficient attention with regard to converting them from waste to new materials. In this context, this study was designed to offer recommendations for investors or egg processors, by reviewing information regarding the technological potentials of the mineral and membrane protein fractions of chicken egg shells. Also, the levels of economic investment required and the benefits available to industries able to process these materials to increase their value are discussed, along with the environmental issues. The results are presented in the form of a review, based upon waste characterization and alternative uses for these materials, which can be used as a basis for calculating the volumes generated in an egg processing company.

2. Residue characterization: egg shell

According to Neves (1998) and Boron (2004) the shell of an egg is a protective barrier, even against the penetration of microorganisms. The shell is a bioceramic composite material with an extracellularly assembled structure, whose function is to protect the contents of the egg and to ensure the calcium necessary for the formation of the chick's skeleton. The egg shell is composed of several porous layers, which are permeable to water and gases, allowing the embryo to breathe (Neves, 1998). During the industrial processing of egg shells the different components are separated.

Egg shells are comprised of a network of protein fibers, associated with crystals of calcium carbonate (96% of shell weight), magnesium carbonate (1%) and calcium phosphate (1%), and also of organic substances and water. Calcium carbonate ($CaCO_3$), the major constituent of the shell, is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal), with low water solubility (13 mg/L, at 18 °C) (Neves, 1998; Boron, 2004).

The egg shell has two internal membranes, consisting of a mixture of proteins and glycoproteins, which are closely associated with the shell, except at one end where they separate to form an air-chamber (Neves, 1998). Around 70–75% of the membrane structure is composed of proteins, such as desmosine and isodesmosine derived from lysine, collagen (10%) and glycoproteins (Boron, 2004).

3. Proposals for the use of egg shell waste

Chicken egg shells, a bioceramic composite rich in calcium, offers a unique combination of particle strength, reactivity and cost, is capable of absorbing acid gases such as carbon dioxide (Iyer et al., 2006).

Calcium Carbonate ($CaCO_3$) powder obtained from egg shells can act as an agent in the removal of heavy metals from water and soil. Liao et al. (2010) and De Paula et al. (2008) have shown that derivatives from egg shell waste can be used to effectively remove several divalent metal ions, such as lead, cadmium and copper, from aqueous solution. Ok et al. (2011) concluded that egg shell wastes could be used as an alternative to $CaCO_3$ for the immobilization of heavy metals in soils.

Calcium oxide (CaO) is a raw material used by the chemical industry in the production of lime. Egg shells are an excellent source of this substance and could provide an alternative raw material to that industrial sector, but with an economic disadvantage in competing with the mineral product (Neves, 1998). Egg shells can be used in a similar way to work done by Lee et al. (2009) who developed activated oyster shell (AOS) by pyrolysis at 750 °C under a nitrogen atmosphere. The AOS is a suitable and sustainable substance for phosphorus removal (eutrophication control) in wastewater treatment facilities. AOS would present significant advantage over lime as a source of hydroxyl ions because of its granular nature, which allows easy handling and leads to slow dissolution in water. However, according to Arvanitoyannis (2008), the pyrolysis is a high cost process.

According to Yoo et al. (2009), $CaCO_3$ from egg shells could provide a substitute for the minerals used in the treatment of paper, in order to improve brightness, opacity and strength. Calcium carbonate can also be used to improve the appearance and texture of paper, as well as the performance in relation to multi-color prints.

Another use of egg shells is as a solid catalyst in the transesterification of vegetable oils with methanol to produce biodiesel. Wei et al. (2009) obtained a highly active and reusable solid catalyst simply through the calcination of egg shells. This proposal of reusing egg shell waste to prepare such a catalyst can simultaneously minimize waste of valuable egg shell residues and develop a less expensive catalyst. This highly efficient and low-cost egg shell catalyst could make the process of biodiesel production more economically and environmentally friendly, by reducing the biodiesel cost and making it competitive with petroleum diesel.

The organic matter of the egg shell membranes contains valuable biomaterials such as collagen, polypeptides and amino acids, which are very useful for cosmetic and medical applications (Yoo et al., 2009). The membrane can also be used as an additive in animal feed, but the total separation of the carbonate and the membrane through an economically viable and environmentally safe procedure is one of the difficulties associated with the processing of egg shells.

The use of egg shells in food products increases its value, because of its valuable minerals. The $CaCO_3$ of the shell has a low bioavailability if directly consumed, but when transformed into calcium citrate it presents higher absorption levels and can be used as a dietary supplement. In oyster shells, the carbonate has traces of lead and traces of potentially toxic elements such as aluminum, cadmium and mercury, and therefore it is not recommended for food or animal feed purposes (Murakami et al., 2007).

Some studies on the reuse of egg shells can be found in the literature, but their application in industrial processes is not common. In this paper, some systems for adding value to egg shells as a raw material for new products are proposed based on the literature review.

4. Case study

The proposals to increase the value of egg shells are presented as flowcharts, mass balances and yields for each system, based on calculations and production data from a company which produces pasteurized liquid egg products with a monthly production capacity of 1000 t of final product. This production is considered to estimate both the amount of solid egg shell waste processed and the quantities of derivatives that could be produced. The efficiency of the chemical reactions is considered to be 80%, i.e., 20% is considered as losses or incomplete reactions, since some of the proposals do not have experimental data available in the literature.

5. New products from egg shells: proposals and potential yields

This paper proposes five products, which can be obtained from the mineral fraction and two from the shell membrane fraction. The company under study produces 1000 t/month of pasteurized liquid egg, using 1100 t/month of eggs, with the generation of 110 t/month of egg shells (considering 10% of egg weight).

5.1. Calcium for human nutritional supplement – System 1

Egg shells in their crude calcium carbonate form, without previous acid treatment, have low solubility, but they can be used