



## Review

## Eggshell waste as catalyst: A review



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## ABSTRACT

Agricultural wastes are some of the most emerging problems in food industries because of their disposal cost. However, it is also an opportunity for the bioeconomy society if new uses for these residual materials can be found. Eggshells, considered a hazardous waste by UE regulations, are discarded, amounting hundreds of thousands of tonnes worldwide. This egg processing waste is a valuable source material, which can be used in different fields such as fodder or fertilizer production. Additionally, this residue offers interesting characteristics to be used in other applications, like its employment as an environment-friendly catalyst. In the present review we provide a global view of eggshell waste uses as catalyst in different processes. According to reviewed researching works, a huge variety of added value products can be obtained by using this catalyst which emphasised the interest of further investigations in order to widen the possible uses of this cheap green catalyst.

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## 1. Introduction

Eggshell represents approximately 10% of hen egg, which is a basic foodstuff extensively consumed worldwide for home and industrial uses. Then, eggshell is produced at large amounts by egg processing industries, and high quantities of this solid residue are still disposed as waste in landfills without any pretreatment being a source of organic pollution (Gao and Xu, 2012; Oliveira et al., 2013).

The chicken eggshell is a natural porous bioceramic resulting from the sequential deposition of different layers around the

albumen in final sections of the hen oviduct. It is a perfectly ordered structure with a polycrystalline organization throughout the calcified shell (Nys and Gautron, 2007). It is composed of a foamy layer of cuticle, a calcite or calcium carbonate layer and two shell membranes, with 7000–17,000 funnel-shaped pore canals distributed unevenly on the shell surface for water and gases exchange (Li-Chang and Kim, 2008). Eggshell is composed of about 96% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, organic materials (mainly proteins) and water (Oliveira et al., 2013). In Fig. 1 it is shown the schematic illustration of eggshell structure, whereas in Fig. 2 it can be seen a micrograph of native hen eggshell.

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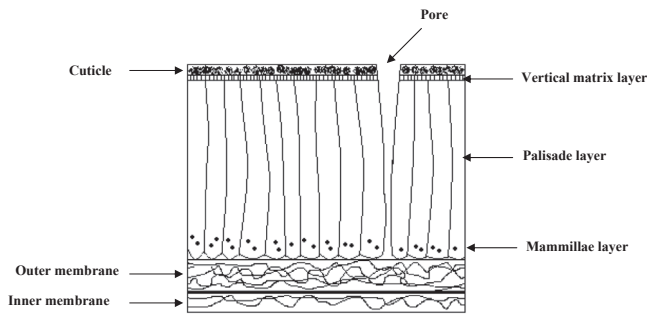


Fig. 1. Schematic illustration of eggshell structure.

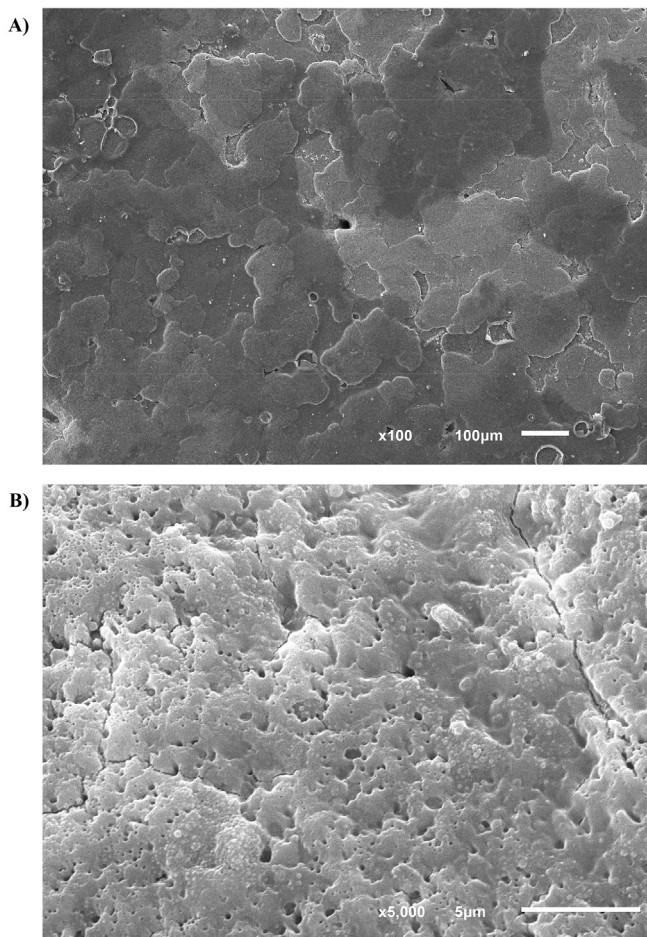


Fig. 2. SEM microstructures of native hen eggshell. Magnification and bars: 100 $\times$ , 100  $\mu\text{m}$  (A) and 5000 $\times$ , 5  $\mu\text{m}$  (B).

Nowadays, the functional characteristics of eggs are the object of intensive study, as it is the utilization of some of the components, previously considered as waste (Laca et al., 2014, 2015). Specifically, in recent years, great efforts have been conducted for the application of eggshells as value added products (Gao and Xu, 2012). These applications included different uses, such as the development of advanced materials for bone tissue repair (hydroxyapatite) (Ramesh et al., 2016) or its uses as adsorbent for many metal ions (Eletta et al., 2016). Additionally, there have recently been a drift towards the use of eggshell wastes in different process as an environment-friendly catalyst.

Some recent review papers dealing with uses of eggshell wastes as a whole or even of specific applications of eggshell membranes have recently been published (Baláz, 2014; Park et al., 2016; Quina et al., 2016). Last year, Tan et al. (2015) published a review on the potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from calcined eggshells. In addition, lately Shan et al. (2016) included in their review, which was related to the development of Ca-based catalysts for biodiesel production, eggshell as one of the waste material that can be employed. However, eggshell waste can be used as catalyst in many other processes. Hence, the present review compiles the studies recently developed, which show the potential of eggshell wastes to be used as low cost catalyst in the production of different compounds.

## 2. Uses of eggshell catalysts

In Fig. 3, it is shown an overview of eggshell waste applications as catalyst, whereas Table 1 summarized the different products synthesized employing eggshell as catalyst found in literature. This table also shows in short the procedures developed by different authors to prepare the eggshell catalysts.

### 2.1. Synthesis of biodiesel

Intensification of global warming and energy crises due to fossil fuel employment has stimulated the search of biofuels, such as biodiesel, derived from vegetable oils or animal fats. Biodiesel is generally synthesized through transesterification of triglycerides with methanol using homogeneous catalysts. However, the use of heterogeneous catalysts has been extensively studied in the last years and possesses several advantages compared to homogeneous catalyst, i.e. less environmental pollution, simpler separation, no toxicity and no corrosion (Viriyempikul et al., 2010; Chen et al., 2014; Tan et al., 2015; Ramkumar and Kirubakaran, 2016). One of the basic catalysts commonly employed is CaO, which can be obtained from waste materials such as ashes, bones shells and eggshells (Chen et al., 2014; Tan et al., 2015; Shan et al., 2016).

First works regarding the use of waste eggshell as solid catalyst to be used in biodiesel synthesis appeared few years ago. Wei et al. (2009) reported that high active, reusable solid catalyst was obtained just by calcining eggshell. Results showed that the most active catalyst (98% yield) was eggshell calcined above 800 °C, on the contrary a low activity (<30% yield) was observed when the calcination temperature was below 600 °C. The conditions employed were methanol/oil ratio 9:1, 3 wt% catalyst and 65 °C. In other study (Sharma et al., 2010) found a yield of 95% also using calcinated hen eggshells for biodiesel production from the pongam tree oil (alcohol/oil ratio 8:1, 2.5 wt% catalyst and 65 °C). In a recent work, Chavan et al. (2015) synthesized biodiesel from *Jatropha curcas* oil employing calcium oxide prepared from eggshell as catalyst. The optimum methanol/oil molar ratio resulted again to be 8:1 at a temperature of 60 °C and using 1.7% (v/v) H<sub>2</sub>SO<sub>4</sub>. The yield of the synthesized biodiesel obtained was 90%. The catalyst reusability was evaluated and it was found that the catalyst worked efficiently, without significant loss of activity, up to six times.

Cho and Seo (2010) investigated the transesterification of palm oil using calcium oxide catalysts obtained by calcining eggshells of quail and chicken. The quail eggshell presented better catalytic activity than the hen eggshell, this behaviour can be attributed to the higher number of strong basic sites produced on the pores in the eggshell palisade layer. In addition, the quail eggshell catalyst (oil:catalyst 2:0.03 wt) maintained high conversions (over 98%) during fivefold cycles (65 °C and methanol/oil 12:1). Viriyempikul et al. (2010) also used palm oil as substrate and the transesterification was developed at 60 °C (oil:catalyst 10 wt% and

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