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Application of eggshell wastes as valuable and utilizable products: A review

Hamideh Faridi, Akbar Arabhosseini*

Department of Agrotechnology, College of Abouraihan, University of Tehran, Iran

**Corresponding author: ahosseini@ut.ac.ir*

Abstract

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Eggshell is a solid waste, with production of several tons per day. Eggshell is mostly sent to the landfill with a high management cost. It is economical to transform the eggshell waste to create new values from these waste materials. The present article is an attempt to summarize the possible applications of eggshell. The eggshell waste can be used (a) at biodiesel production as a solid base catalyst used for biodiesel pollutants minimization, reducing the production costs of biodiesel and making the process of biodiesel production fully ecological and environment-friendly; (b) as an absorbent of heavy metals from wastewater as it is a serious environmental problem in the ecosystem; (c) as biomaterial in order to replace bone tissues due to the rise in the number of patients; (d) as a fertilizer and calcium supplement in nutrition for human, animals, plants, etc. Number of research articles have been included in this review to describe a methodical growth in this subject matter.

Keywords: biomaterial; fertilizer; waste; application; biodiesel

Farming processes generate different kinds of wastes. Reducing environmental problems caused by irresponsible disposal of waste relies on the sufficient utilization of agricultural waste. In the global scale, the management of agricultural wastes is essential and a crucial strategy as it becomes a critical factor for humans, animals and vegetation (Al Seadi, Holm-Nielsen 2004). The nature, quantity and type of the waste vary in different countries. Helping to protect the quality of the environment and health requires searching for an effective way to properly manage agricultural wastes. For these purposes, wastes should be recycled, reused and channelled towards the valuable and utilizable product. Nowadays, utilization of the waste is a priority for sustainable development achievement (Martin-Luengo et al. 2011a).

The agricultural waste could be categorized in biological, solid, hazardous and used oil, and then regulated according to how it can be disposed of. The solid waste includes any kind of garbage made by agricultural establishment, sludge from water treatment plants and any waste materials created during agricultural activity. Hazardous wastes which are also composed of chemicals may be explosive, corrosive or highly flammable and of course dangerous to humans, animals or the environment. Agricultural machinery often produces oils that are used repeatedly and gather other materials such as water, chemicals or dirt. The oils need to be replaced because of the performance reduction. To provide an agricultural establishment produces large amounts of used oil, and it is required to store them in tanks to prevent leaking of the oil into the surrounding environment.

Expecting the oils to be usable in medical sciences is a novel practice. Most agricultural waste researches basically concentrate on its energy potential or as a renewable raw material due to its abundance, cheapness and renewability (Peng et

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al. 2000; Ling, Zakari et al. 2010; Teo 2011; Surip et al. 2012). Microorganisms or their components carried out the transformation into precious products or energy sources (Di Gioia et al. 2011). Beneficial products were made from many agricultural wastes, to be used as an effective feedstock (Boonpoke et al. 2011; Xu et al. 2011; Rashidi et al. 2012) and as a good option as biomaterials in therapies that replace bone for the growth of the osteoblasts (Martin-Luengo et al. 2011a,b). The development of biomaterials is carried out due to the rise in the number of patients that need bone replacements. It is crucial that the biomaterials are biocompatible with sufficient mechanical strength to support the weight of human body before being used as bone implants (Li, Tjong 2011).

Eggshells are one of the widely used food processing and manufacturing plants by-products. Eggs represent a major ingredient in a large variety of products such as cakes, salad dressings and fast foods, whose production results in several daily tons of eggshell waste and incur considerable disposal costs in the world. About 250,000 tons of eggshell waste is produced annually worldwide (Verma et al. 2012).

Most of the eggshell wastes are currently cumulated on-site without any pre-treatment (Stadelman 2000; Tsai et al. 2008a). Also in view of the environmental odour from biodegradation, the waste management is not a pleasant function (Tsai et al. 2008b).

In recent years, great deals of efforts have been performed for transforming the eggshell wastes to a valuable product. These major applications included a possible bone substitute (Dupoirieux et al. 1995), the starting material to prepare calcium phosphate bioceramics such as hydroxyapatite (HAp) (Balázsi et al. 2007) and bone mineralization and growth, a low-cost adsorbent for removal of ionic pollutants from the aqueous solution (Tsai et al. 2008a), or a biodiesel catalyst.

Chicken eggshell is one of the agricultural wastes, which received attention today and has the potential of being used in medical and dental therapy. Eggshell has as an important constituent pure $CaCO_3$ and a little developed porosity. Its composition has been reported chemically (by weight) as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) (Stadelman 2000).

Another application of eggshell wastes was mentioned before as a biodiesel catalyst. Biodiesel, composed of the Greek word of "bio" and "diesel" from Rudolf Diesel, refers to a renewable alternative to petroleum diesel made of monoalkyl esters of fatty acids, similarly to petroleum diesel in terms of physical properties, unless capable of the incomparable benefits as renewable, biodegradable, non-toxic and low emissions (Ma, Hanna 1999; Demirbas 2009). It generally can be made from processed organic oils and fats such as soya bean, rapeseed, sunflower, coconut, corn, cotton seed, mustard, palm oil, peanut, animal fats, waste vegetable oil and algae by transesterification of them in the presence of catalysts (Ma, Hanna 1999; Huber et al. 2006; Demirbas 2009), such as NaOH, KOH or $NaOCH_3$, which are added in the transesterification because of the reaction rate they induce (Fadhil et al. 2016). The price of biodiesel could be reduced using the waste oils and non-edible oils (Maddikeri et al. 2012, 2014; Hosseini et al. 2015). Other important matter in the biodiesel yield is the catalyst selection (Chen et al. 2015). Both types of catalysts, homogeneous and heterogeneous, could catalyse transesterification. Homogeneous base catalysts such as NaOH and KOH have high catalytic activity but their separation and reusing after the reaction is difficult (Lee et al. 2015). Other homogeneous types such as alkali metal hydroxides and alkoxides and homogeneous acids such as H_2SO_4 are basically corrosive and also react with free fatty acid to create undesirable soap by-products that require expensive separation. Recycling of homogeneous acid catalysts is difficult because the process needs high temperature and sometimes cause serious environmental and corrosion problems.

Heterogeneous catalysts have received noticeable attention for solving the homogeneous catalyst problems, as they are non-corrosive, recyclable and effective and could simplify the separation and purification steps. Many heterogeneous catalysts for the transesterification of oils were studied such as eggshell due to its intrinsic pore structure in the calcified eggshell, high content of $CaCO_3$ and the amount in abundance. It is possible to prepare active heterogeneous catalyst from eggshell.

Another global crisis is water pollution and wastewater treatment especially of industrial wastewater contaminated with heavy metals commonly produced from many kinds of industrial processes. Hence, the wastewater without any treatment with a suitable process can cause a serious environmen-

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tal problem in the natural ecosystem and accumulation of metal ions will take place either through direct intake or food chains (Yoo et al. 2002). Accordingly, heavy metals should be prevented to reach the ecosystem because of their toxicity. Several approaches were suggested and investigated for this purpose including chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, evaporation and membrane methods. Some of these approaches are very expensive and less effective with some limitations such as requirement of several pre-treatments as well as additional treatments (Volesky 1990; Kim 2002; Kam et al. 2011). Because of these limitations, many researchers have selected natural wastes regeneration to treat heavy metals from aqueous solutions (Murakami et al. 1986; Roy et al. 1993; Cho 1994; Lee 1994; Chiron et al. 2003). The adsorption capacity of heavy metals with rice hulls and green algae was studied and evaluated by (Roy et al. 1993). Other researchers reported about the adsorption results of heavy metals on the shell of crab (Lee 1994) and shell of shrimp (Cho 1994). Potential possibility of regenerated wastes as adsorbents was proposed for the removal of lead by shell of crab (Lee 1994). In addition, other wastes were studied in terms of applicability such as scoria, fly ash, zeolite, chitosan, sawdust and coal (Nugteren et al. 2002; Cao et al. 2004; Inglezakis, Grigoropoulou 2004; Kwon et al. 2005). According to the crucial matters in the industrial process such as minimization of wastes, maximum regeneration of wastes and energy and recovery of precious material, development of various green and economical materials from wastewater treatment was carried out by several researches (Kumar, Bandyopadhyay 2006).

Utilization of activated carbon from sawdust as a wastewater dye eliminator was reported by (Malik 2004)B. Another recommendation for textile wastewater dye were orange peels stated by (Haddadian et al. 2013), which was quite remarkable for a treatment (Kyzas, Kostoglou 2014). The oyster shell was pretty impressive to adsorb the hydrogen sulfide from pore water (Asaoka et al. 2009).

There is no sufficient attention regarding the conversion of waste to useful materials, despite the beneficial properties. In this context, different applications of eggshell wastes were applied to offer suggestion for any egg processor, applicant and consumer, by reviewing information of the technological potentials of eggshell properties. In this regard, the applicants are priority that are economically feasible and the benefits available to industries to process them, along with the environmental issues.

This review presents the results 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. In addition, this study could demonstrate an economical treatment process to recycle useful products from eggshell waste and their utilization in different aspects that make the process cost-effective and environmentally friendly and give a novel avenue for solid waste management.

Medical application of eggshell

Agricultural wastes contain active compounds that are valuable in medical applications. Regarding this feature, biocompatible material or biomaterial production from them has added a different dimension to the utilization of agricultural waste.

An insight into utilization of avian eggshell as an agricultural waste, is to produce HAp. A calcium phosphate ceramics material was found to be crucial as a biomaterial because of its osteophilic nature and its incorporation into bone tissues (Ducheyne et al. 1986; Gergely et al. 2010). Discarded eggshells remain largely unutilized and untransformed. The eggshells consist of calcium carbonate as a useful material to produce HAp, which is the major inorganic part in bones used in bone and dental therapy (Fig. 1). Moreover, the use of eggshell to produce HAp will help reduce the pollution effect of the waste and the subsequent conversion of the waste into a highly valuable product as a good chance of reducing the cost of treatment in bone repair or replacement with little impact to the environment. The process of transforming eggshell into HAp and nano-HAp is an environmentally-friendly process.

(Wu et al. 2013) proposed a research of the chicken eggshells recycling as a way of improving the ecosphere; by reduction of waste management requirements and utilization of eggshells as useful raw materials for nanomaterials. The main component and the major inorganic substance in eggshells are calcium carbonate (calcite) and it makes up about 94% of chemical composition of eggshell. This makes it an essential material for HAp produc-

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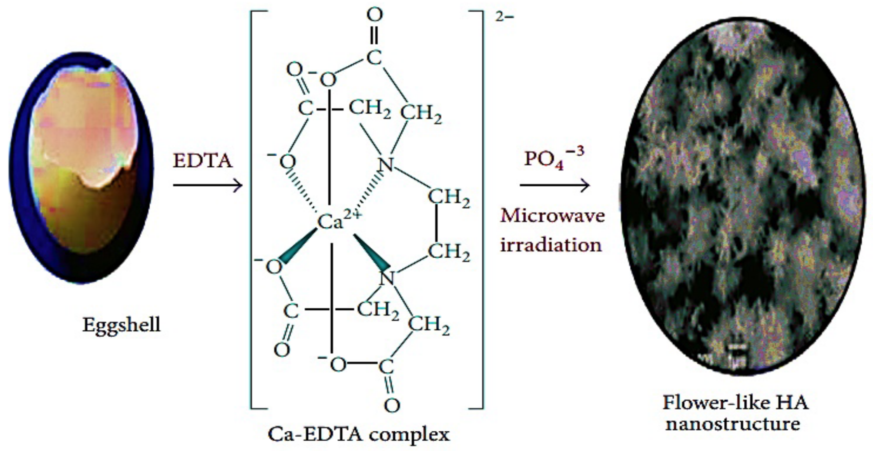

Fig. 1. A flower-like hydroxyapatite nanostructure of eggshells (Kumar et al. 2012)

tion (Li-Chan, Kim 2008). Others are organic matter which makes up 4%, magnesium carbonate (1%) and calcium phosphate (1%) as well as insoluble proteins (Rivera et al. 1999; Li-Chan, Kim 2008).

The calcite, the most stable form of calcium carbonate, forms elongated structures called columns, palisades or crystallite. One of the most rapid known processes of biomineralization is calcification of eggshells, which is contributed to better mechanical properties and strength of eggshell-based Hap. (Li-Chan, Kim 2008) demonstrated its superior sinterability when compared with HAp synthesized from other sources in terms of hardness, density and cell culture. Cytotoxicity test for evaluation of the biocompatibility of eggshell-based HAp (Krishna et al. 2007) shows that the eggshell-based HAp favours adhesion of the osteoblast cells and is noncytotoxic. This might be because of the biological nature of $CaCO_3$ that is able to improve the properties of the HAp (Krishna et al. 2007). The HAp from eggshells has a great quality due to its resemblance with human hard tissues (Akram et al. 2014). Smaller in size and cellular are the usual features of the HAp, which are contributed to the excellent quality of eggshell-based HAp that is much closer to the composition and structure of biological apatite. This is considered with a synthetic apatite as a major requirement used to repair damage and hard tissues (Han et al. 2002). A good perspective of using eggshell is its non-expensiveness. It is also an environmentally friendly source for HAp preparation (Balázsi et al. 2013).

The membrane of the shell composed of glycoproteins, consisting of collagen types can be used in the production of cosmetics (Boron 2004; Fátima et al. 2005).

Eggshell is 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, an agricultural fertilizer component, and as a component for bone implants (Murakami et al. 2007).

Application of eggshell in producing biodiesel

Calcium oxide (CaO) is one of the most promising alkaline earth metal oxides with high basicity, which is suitable for biodiesel production (Bal et al. 2001; Tsai et al. 2006; Syazwani et al. 2015). Mollusk shells, eggshells, and mussel shells could be calcined to take CaO used as a heterogeneous catalyst in biodiesel production (Nakatani et al. 2009; Gole, Gogate 2012; Rezaei et al. 2013).

Biodiesel has already been commercially produced from renewable resources such as soybean oil by transesterification reaction using homogeneous strong bases or acids as catalysts (Vicente et al. 2004; Di Serio et al. 2005; Morin et al. 2007; Chouhan, Sarma 2011). The chemical composition of waste eggshell is mainly calcium carbonate as reported by other researchers (Witoon, 2011). Due to intrinsic pore structure in eggshell surface and its abundance, eggshell is a good raw material for preparation of fine powder, which might pave the way for its utilization such as porous solid catalyst. In fact, the solid base catalysts derived from eggshell were prepared by calcinations (Wei et al. 2009; Viriya-Empikul et al. 2010; Witoon 2011; Khemthong et al. 2012).

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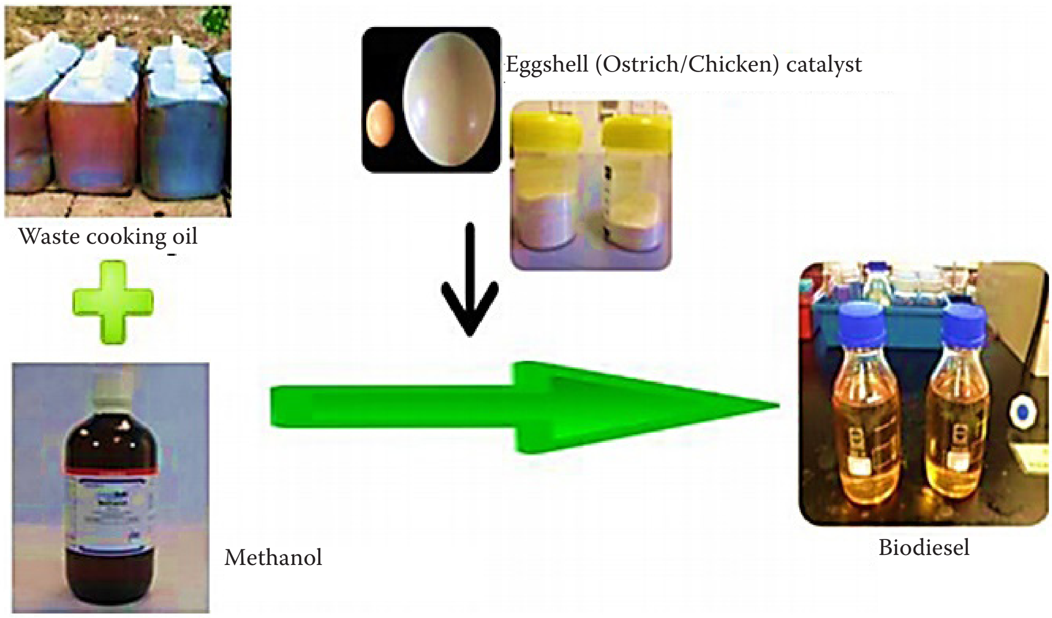

Fig. 2. Calcinations of waste eggshells in the transesterification process (Tan et al. 2015)

The possibility of application of eggshell as a catalyst in catalytic process of biodiesel production was investigated by (Wei et al. 2009). Reuse of eggshell as a low-cost catalyst for biodiesel production was assessed in the viewpoint of the eggshell waste recycling , minimization of contaminants, reducing the production costs of biodiesel (Rabu et al. 2013; Dawodu et al. 2014) and making the process of biodiesel production fully ecologically-friendly.

Eggshells wastes were used for the transesterification of used cooking oils and obtained a biodiesel yield of 100% using a 4 wt% catalyst for a reaction time of 5h (Navajas et al. 2013), while (Niju et al. 2014) used eggshells to undergo calcination–hydration–dehydration treatment to obtain a CaO catalyst. The transesterification of waste frying oil (WFO) results showed that the methyl ester conversion was 67.57% for commercial CaO and it was 94.52% for CaO obtained from the calcination–hydration–dehydration treatment of eggshell at a 5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65°C and are action time of 1h. Recently (Chen et al. 2014) derived CaO catalyst from ostrich eggshell and reported that maximum biodiesel yield (92.7%) was obtained from palm oil under the following conditions: catalyst 8 wt%, methanol-to-oil ratio 9:1, reaction time 60 min and ultrasonic power 60% amplitude. Besides, this CaO catalyst could be reused for more than 8 times without a significant loss of activity. All these studies on waste materials revealed that a higher catalyst wt% and longer reaction time are needed to achieve high biodiesel yields.

(Tan et al. 2015) showed that applications of heterogeneous base catalyst, CaO, which was obtained from calcinations of waste eggshells in the transesterification process, have a promising potential to be adopted in biodiesel production purpose (Fig. 2).

Another research was conducted by (Yin et al. 2016) on biodiesel production from soybean oil deodorizer distillate (SODD) using calcined duck eggshell (DES) as a catalyst, which is an inexpensive and environment-friendly source of calcium carbonate. The reusability of the DES-derived catalyst was tested and the results showed that the biodiesel yield was above 80% after 5-times usage and was lower than 60% after 8-times usage.

(Joshi et al. 2015) studied the transesterification of jatropha and karanja oils by using waste eggshells-derived calcium--based mixed metal oxides as a catalyst. High surface areas of the catalysts were observed when they were calcined at 900°C and therefore they showed a high catalytic activity. (Niju et al. 2014) revealed that the calcinations-hydration-dehydration treatment was a sufficient method to increase the catalytic activity of waste shells.

Active biodiesel production catalysts were derived from waste eggshells using simple calcination in air (Khemthong et al. 2012). The physicochem-

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ical properties of the activated catalysts were characterized by XRD, N_2 sorption, CO_2-TPD, TGA–DTG, XRF and SEM, while the catalytic activity was tested in producing biodiesel via transesterification on palm oil with methanol under microwave conditions. The effect of microwave power, reaction time, methanol-to-oil ratio and catalyst loading was investigated. The experimental results revealed that the catalysts exhibited a high content of CaO (99.2 wt%) with high density of strong base sites. The catalytic testing demonstrated a remarkable enhancement for biodiesel production using microwaves compared to conventional heating. The max. yield of fatty acid methyl esters reached 96.7% under the optimal condition of reaction time of 4 min with 900 W microwave power, methanol-to-oil ratio of 18:1, and catalyst loading of 15%. The results indicated that the CaO catalysts derived from eggshells showed good reusability and had a high potential to be used as biodiesel production catalysts under microwave-assisted transesterification of palm oil.

(Alba-Rubio et al. 2010) reported that the transesterification reaction of oil and methanol can be effectively catalysed by CaO with a biodiesel yield higher than 90%. This research also suggested that the basic strength of CaO is sufficient for this reaction which could be found from waste eggshells (Boro et al. 2011) not only to exhibit a high potential use as biodiesel synthesis catalysts but also to add value to the green biodiesel process due to their eco-friendly characteristics and low cost. In a research that investigated the transesterification of palm olein oil with methanol catalysed by CaO derived from the wastes of mollusk shell, bone, and eggshell, (Witoon 2011; Viriya-Empikul et al. 2012) found that these catalysts are active to biodiesel production resulting in fatty acid methyl ester (FAME) above 90%. Among the derived catalysts, an eggshell-derived catalyst displayed the highest catalytic performance when compared to others. However, those reactions require a longer time (> 60 min) to achieve a satisfactory conversion of oil to biodiesel because of heat and mass transfer limitations.

Eggshell as an absorbent

Many researches seek to evaluate the use of chicken eggshell as green and economical adsorbents for removing hydrogen sulphide from wastewaters. For this purpose, physical and chemical properties of the treated eggshell were investigated and potential applicability of the treated eggshell in the removal of heavy metals was studied with both synthetic and real wastewater. In this way, the removal capacity of toxic heavy metals by the reused eggshell was studied by (Park et al. 2007). As a pre-treatment process for the preparation of the reused material from the waste eggshell, calcination was performed in the furnace at 800°C for 2 h after crushing the dried waste eggshell. Although the natural eggshell had some removal capacity of Cd and Cr, a complete removal was not accomplished even after 60 min due to quite slower removal rate. However, in contrast to Cd and Cr, an efficient removal of Pb was observed with the natural eggshell rather than the calcined eggshell. From the application of the calcined eggshell in the treatment of real electroplating wastewater, the calcined eggshell showed a promising removal capacity of heavy metal ions as well as it had a good neutralization capacity in the treatment of strong acidic wastewater.

Habeeb et al. 2014 evaluated the characterization and application of chicken eggshell as green and economical adsorbents for the treatment of hydrogen sulfide from wastewaters, which is fatal to benthic aquatic lives as it depletes the dissolved oxygen in their ecosystem. The results showed that the calcinate waste eggshell had the highest adsorption capacity. It is concluded that the chickens' eggshells are very useful green and economic adsorbents due to their availability and absence of any toxic and hazardous constituent's elements from all adsorbents. The calcinate modified was the most suitable followed by the activated carbon modified adsorbent.

The ground chicken eggshell without treatments was the least suitable for the removal of H_2S from waste waters. Another research in this area was done about the influence of milling on the adsorption ability of eggshell waste (Baláž et al. 2016). The effect of ball milling on the structure and adsorption ability of eggshell (ES) and its membrane (ESM) was investigated, with the conclusion that milling is beneficial only for the ES. The adsorption experiments showed that the ESM is a selective adsorbent, as the adsorption ability toward different ions decreased in the following order: Ag (I) > Cd (II) > Zn (II). The potential industrial application of ES was also demonstrated by successful removal of Ag (I) from the technological waste.

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Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution was carried out by (Tsai et al. 2008a). From the results of their research, it is feasible to utilize the ground eggshell waste as an effective adsorbent for removal of anionic dye from aqueous solutions.

Application of eggshell as a fertilizer

A great quantity of eggshells is generated as biowaste all over the world each day. Not only does the odour of eggshell provide site for flies and abrasiveness, but also many useful materials are lost. Among the applications of eggshell waste mentioned before, it might be used as a fertilizer for plants, as they might help reduce the plant blossom-end rot (BER) disease and the cost of plantation. It also increases the nutritional intake of plants (Hamester et al. 2012). Also, it will be used as a calcium supplement tablet for females as a substitute for CIPCAL-500.

Basically, eggshells resulting from industrial processes are used in 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

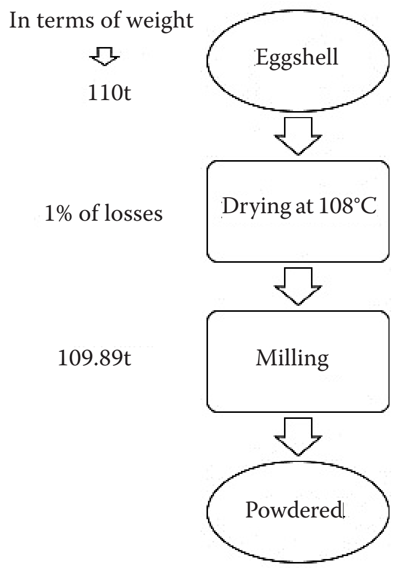

Fig. 3. Process flowchart of the powdered eggshell used for animal feed, fertilizer and removal of heavy metals (Oliveira et al. 2013).

eggshell 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).

The advantage of eggshells in comparison with other natural sources of calcium is the low level of toxic substances present (Boron 2004). Occasionally, parts of this waste are used as fertilizer, due to its high content of calcium and nitrogen. However, eggshells are a potentially polluting industrial waste when not properly managed because they support microbiological action. Studies focused on the conversion of eggshells to animal feed (particularly for poultry) recommend pre-treatment at approximately 80°C to reduce microbiologic contamination of the powdered shell (Rivera et al. 1999). The powder obtained through this process, presented in Fig. 3, besides being a calcium source, contains proteins remaining from the albumen (egg white), the membranes and the shell matrix. (Ok et al. 2011) described a similar process, but with drying the eggshells at 105°C for 72 h, to remove Cd and Pb from the contaminated oil.

(Chakraborty 2007) reported that eggshell has a huge amount of calcium which can be used very effectively in various applications. As a fertilizer, it enriched the pH and calcium content of the soil. This enrichment is very beneficial for plants suffering from blossom-end rot disease, for example tomato plants, berry plants, etc. In another application, the chicken eggshell powder was used up to make tablets (Fig. 4) that were tested for equivalency to CIPCAL-500 calcium supplement tablets. The analysis results were comparable, while the source availability and extraction of chicken eggshell are much easier as compared to the oyster shell which is the main source for CIPCAL-500 tablets production (Lozano et al. 1994).

The effect of eggshell powder on the stabilizing potential of lime on expansive clay soil was studied by (Amu et al. 2005). From the results obtained, it could be concluded that lime has exhibited its superior potency over eggshell as a stabilizing agent in all ramifications.

Effects of using eggshell waste as a calcium source were evaluated in the diet of the Rhode Island Red roosters on semen quality, gonadal development, plasma calcium and bone status (Gongruttananun 2011). It was apparent that eggshell can be

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Fig. 4. Chicken eggshell tablets (Chakraborty 2007)

fully used as a calcium source in diets without any detrimental effects on the live performance, semen quality, reproductive development and calcium homeostasis of breeder male chickens.

Conclusion

This review presents the results based upon waste characterization and alternative uses for these materials. They can be used as a basis for calculating the volumes generated in an egg processing company. Eggshells are one of the widely used food processing and manufacturing plants by-products. Most of the waste eggshells are currently cumulated on-site without any pre-treatment. However, if the wastes are treated and processed according to any aims mentioned in this review, they are highlighted when recycled, reused as a source of raw materials for other industries, and channelled towards valuable and utilizable products; for instance as a possible bone substitute, the starting material to prepare calcium phosphate bioceramics (e.g. HAp), a low-cost adsorbent for removal of ionic pollutants from the aqueous solution and a biodiesel catalyst. Thus, it can be concluded that chicken eggshell cannot be just considered as a waste and can be effectively used for many applications as a valuable product.

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