See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/319464095

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

Article *in* Research in Agricultural Engineering · August 2018 DOI: 10.17221/6/2017-RAE

CITATIONS 13	5	READS 10,690	
2 authors:			
<b>B</b>	H. Faridi University of Tehran 14 PUBLICATIONS 22 CITATIONS SEE PROFILE		Akbar Arabhosseini University of Tehran 105 PUBLICATIONS 720 CITATIONS SEE PROFILE
Some of the authors of this publication are also working on these related projects:			

Design and construction of a Die Roller equipped with kneader extruder system View project

Simulation of greenhouse cooling-heating system using earth-air exchanger View project

# 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

Arabhosseini A., Faridi H. (2018): Application of eggshell wastes as valuable and utilizable products: A review. Res. Agr. Eng., 64: 104–114.

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

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<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub> 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<sub>3</sub> 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-

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 (Muкаками 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 (Сно 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 (HADDAD-IAN 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 costeffective 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 environmentallyfriendly 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 egg-shells are calcium carbonate (calcite) and it makes up about 94% of chemical composition of eggshell. This makes it an essential material for HAp produc-



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 eggshellbased 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 eggshellbased 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<sub>2</sub> 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; FÁTI-MA 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 (MURAKA-MI 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).



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 calcinationshydration-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-

ical properties of the activated catalysts were characterized by XRD, N2 sorption, CO2-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, methanolto-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.

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 (NE-VES 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 (GONGRUTTAN-ANUN 2011). It was apparent that eggshell can be

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 lowcost 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.

#### References

Akram M., Ahmed R., Shakir I., Ibrahim W.A.W., Hussain R. (2014): Extracting hydroxyapatite and its precursors

from natural resources. Journal of Materials Science, 49: 1461–1475.

- Al Seadi T., Holm-Nielsen J.B. (2004): III. 2 Agricultural wastes. Waste Management Series, 4: 207–215.
- Alba-Rubio A.C., Santamaría-González J., Mérida-Robles J.M., Moreno-Tost R., Martín-Alonso D., Jiménez-López A., Maireles-Torres P. (2010): Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts. Catal Today, 149: 281–287.
- Amu O., Fajobi A., Oke B. (2005): Effect of eggshell powder on the stabilizing potential of lime on an expansive clay soil. Journal of Applied Science, 5: 1474–1478.
- Asaoka S., Yamamoto T., Kondo S., Hayakawa S. (2009): Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments. Bioresource Technology, 100: 4127–4132.
- Bal R., Tope B., Das T., Hegde S., Sivasanker S. (2001): Alkaliloaded silica, a solid base: investigation by FTIR spectroscopy of adsorbed  $\rm CO_2$  and its catalytic activity. Journal of Catalysis, 204: 358–363.
- Baláž M., Ficeriová J., Briančin J. (2016): Influence of milling on the adsorption ability of eggshell waste. chemosphere, 146: 458–471.
- Balázsi C., Wéber F., Kövér Z., Horváth E., Németh C. (2007): Preparation of calcium-phosphate bioceramics from natural resources. Journal of the European Ceramic Society, 27: 1601–1606.
- Balázsi K., Sim H.Y., Choi J.Y., Kim S.G., Chae C.H., Balázsi C. (2013): Biogenic nanosized hydroxyapatite for tissue engineering applications. In: International Symposium on Biomedical Engineering and Medical Physics, Riga, Latvia. Springer. October 10–12, 2012: 190–193.
- Boonpoke A., Chiarakorn S., Laosiripojana N., Towprayoon S., Chidthaisong A. (2011): Synthesis of activated carbon and MCM-41 from bagasse and rice husk and their carbon dioxide adsorption capacity. JREE, 2: 77–81
- Boro J., Thakur A.J., Deka D. (2011): Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. Fuel Process Technology, 92: 2061–2067.
- Boron, L. (2004). Citrato de cálcio obtido da casca de ovo: biodisponibilidade e uso como suplemento alimentar. [Ph.D. Thesis.].
- Cao L.Q., Xu S.M., Feng S., Peng G., Wang J.D. (2004): Adsorption of Zn (II) ion onto crosslinked amphoteric starch in aqueous solutions. Journal of Polymer Research, 11: 105–108.
- Chakraborty M.A. (2007): Chicken eggshell as calcium supplement tablet. international Journal of Innovative Research in Science, 5: 3520–3525.
- Chen G., Shan R., Shi J., Liu C., Yan B. (2015): Biodiesel production from palm oil using active and stable K doped

hydroxyapatite catalysts. Energy Conversion Managment, 98: 463–469.

- Chen G., Shan R., Shi J., Yan B.(2014): Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. Bioresource Technology, 171: 428–432.
- Chiron N., Guilet R., Deydier E. (2003): Adsorption of Cu (II) and Pb (II) onto a grafted silica: isotherms and kinetic models. Water Research, 37: 3079–3086.
- Cho B. (1994): A study on heavy metal adsorption using shrimp shell [D]. [Master's degree Thesis.]. Chosun University, Korea.
- Chouhan A.S., Sarma A. (2011): Modern heterogeneous catalysts for biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews, 15: 4378–4399.
- Dawodu F.A., Ayodele O., Xin J., Zhang S., Yan D. (2014): Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst. Applied Energy, 114: 819–826.
- Demirbas A. (2009): Progress and recent trends in biodiesel fuels. Energy Conversion Management, 50: 14–34.
- Di Gioia D., Fava F., Luziatelli F., Ruzzi M. (2011). 6.50-Vanillin Production from Agro-Industrial Wastes.[Ph.D. Thesis.].Universita di Bologna.
- Di Serio M., Tesser R., Dimiccoli M., Cammarota F., Nastasi M., Santacesaria E. (2005): Synthesis of biodiesel via homogeneous Lewis acid catalyst. Journal of Molecular Catalysis A: Chemical, 239: 111–115.
- Ducheyne P., Van Raemdonck W., Heughebaert J., Heughebaert M. (1986): Structural analysis of hydroxyapatite coatings on titanium. Biomaterials, 7: 97–103.
- Dupoirieux L., Pourquier D., Souyris F. (1995): Powdered eggshell: a pilot study on a new bone substitute for use in maxillofacial surgery. Journal of Cranio-Maxillofacial Surgery, 23: 187–194.
- Fadhil A.B., Aziz A.M., Al-Tamer M.H. (2016): Biodiesel production from Silybum marianum L. seed oil with high FFA content using sulfonated carbon catalyst for esterification and base catalyst for transesterification. Energy Conversion Managment, 108: 255–265.
- Fátima A., Baptistella L.H.B., Pilli R.A., Modolo L.V. (2005): Ácidos siálicos–da compreensão do seu envolvimento em processos biológicos ao desenvolvimento de fármacos contra o agente etiológico da gripe. Quim Nova, 28: 306–316.
- Gergely G., Wéber F., Lukács I., Tóth A.L., Horváth Z.E., Mihály J., Balázsi C. (2010): Preparation and characterization of hydroxyapatite from eggshell. Ceramics Intertional, 36: 803–806.
- Gole V.L., Gogate P.R. (2012): A review on intensification of synthesis of biodiesel from sustainable feed stock using sonochemical reactors. Chemical Engineering and Processing: Process Intensification, 53: 1–9.

- Gongruttananun N. (2011): Effects of using eggshell waste as a calcium source in the diet of rhode island red roosters on semen quality, gonadal development, plasma calcium and bone status. Kasetsart Journal – Natural Science, 45: 413–421.
- Habeeb O.A., Yasin F.M., Danhassan U.A. (2014): Characterization and application of chicken eggshell as green adsorbents for removal of  $H_2S$  from wastewaters. IOSR Journal of Environmental Science, Toxicology and Food Technology, 8: 7–12
- Haddadian Z., Shavandi M.A., Abidin Z.Z., Fakhru'l-Razi A., Ismail M.H.S. (2013): Removal methyl orange from aqueous solutions using dragon fruit (Hylocereusundatus) foliage. Chemical Science Transaction, 2: 900–910.
- Hamester M.R.R., Balzer P.S., Becker D. (2012): Characterization of calcium carbonate obtained from oyster and mussel shells and incorporation in polypropylene. Materials Research, 15: 204–208.
- Han Y., Xu K., Montay G., Fu T., Lu J. (2002): Evaluation of nanostructured carbonated hydroxyapatite coatings formed by a hybrid process of plasma spraying and hydrothermal synthesis. Journal of Biomedical Materials Research, 60: 511–516.
- Hosseini S., Janaun J., Choong T.S. (2015): Feasibility of honeycomb monolith supported sugar catalyst to produce biodiesel from palm fatty acid distillate (PFAD). Process Safety and Environmental Protection, 98: 285–295.
- Huber G.W., Iborra S., Corma A. (2006): Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chemical Reviews, 106: 4044–4098.
- Inglezakis V., Grigoropoulou H. (2004): Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors. Journal of Hazardous Materials, 112: 37–43.
- Joshi G., Rawat D.S., Lamba B.Y., Bisht K.K., Kumar P., Kumar N., Kumar S. (2015): Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides. Energy Conversion Managment, 96: 258–267.
- Kam S.K., Hyun S.S., Lee M.G. (2011): Removal of divalent heavy metal ions by Na-P1 synthesized from Jeju Scoria. Journal of Environmental Science International, 20: 1337–1345.
- Khemthong P., Luadthong C., Nualpaeng W., Changsuwan P., Tongprem P., Viriya-Empikul N., Faungnawakij K. (2012): Industrial eggshell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production. Catalysis Today, 190: 112–116.
- Kim D.S. (2002): A study on the removal of mixed heavy metal ions using crab shell. Journal of Environmental Science International, 11: 729–735.

- Krishna D.S.R., Siddharthan A., Seshadri S., Kumar T.S. (2007): A novel route for synthesis of nanocrystalline hydroxyapatite from eggshell waste. Journal of Materials Science: Materials in Medicine, 18: 1735–1743.
- Kumar U., Bandyopadhyay M. (2006): Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresource Technology, 97: 104–109.
- Kumer G.S., Thamizhavel A., Girija E.K. (2012): Microwave conversion of eggshells into flower-like hydroxyapatite nanostructure for biomedical applications. Materials Letters, 76: 198–200.
- Kwon J.S., Yun S.T., Kim S.O., Mayer B., Hutcheon I. (2005): Sorption of Zn (II) in aqueous solutions by scoria. Chemosphere, 60: 1416–1426.

Kyzas G.Z., Kostoglou M. (2014): Green adsorbents for wastewaters: A critical review. Materials, 7: 333–364.

Lee S. (1994): Study on the adsorption characteristics of heavy metals onto the crab, Portunus trituberculatus shell. [Doctor's degree thesis]. Hyosung Womans University.

Lee S.L., Wong Y.C., Tan Y.P., Yew S.Y. (2015): Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. Energy Conversion Managment, 93: 282–288.

Li-Chan E.C., Kim H.O. (2008): Structure and chemical composition of eggs. Egg Bioscience and Biotechnology. Willey: 1–6.

- Li K., Tjong S.C. (2011): Preparation and characterization of isotactic polypropylene reinforced with hydroxyapatite nanorods. Journal of Macromolecular Science, Part B, 50: 1983–1995.
- Ling I., Teo D.L. (2011): Lightweight concrete bricks produced from industrial and agricultural solid waste. In: Sustainable Technologies (WCST) 2011 World Congress on IEEE: 148–152.

Lozano R., Joseph J.M., Kline B.J. (1994): Temperature, pH and agitation rate as dissolution test discriminators of zofenopril calcium tablets. Journal of pharmaceutical and biomedical analysis, 12: 173–177.

Ma F., Hanna M.A. (1999): Biodiesel production: a review. Bioresource Technology, 70: 1–15.

Maddikeri G.L., Gogate P.R., Pandit A.B. (2014): Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil. fuel, 137: 285–292.

Maddikeri G.L., Pandit A.B., Gogate P.R. (2012): Intensification approaches for biodiesel synthesis from waste cooking oil: a review. Industrial and Engineering Chemical Research, 51: 14610–14628.

Malik P. (2004): Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. Journal of Hazardous Materials, 113: 81–88.

- Martin-Luengo M., Yates M., Ramos M., Saez Rojo E., Martinez Serrano A., Gonzalez Gil L., Hitzky E.R. (2011a): Biomaterials from beer manufacture waste for bone growth scaffolds. Green Chemical Letter Review, 4: 229–233.
- Martin-Luengo M., Yates M., Ramos M., Salgado J., Aranda R.M., Plou F., Sanz J.L., Pirrongelli R.L., Rojo E.S., Gil L.G. (2011b): Renewable raw materials for advanced applications. In: Sustainable Technologies (WCST) 2011 World Congress on IEEE: 19–22.
- Morin P., Hamad B., Sapaly G., Rocha M.C., de Oliveira P.P., Gonzalez W., Sales E.A., Essayem N. (2007): Transesterification of rapeseed oil with ethanol: I. Catalysis with homogeneous Keggin heteropolyacids. Applied Catalysis A: General, 330: 69–76.
- Murakami F.S., Rodrigues P.O., Campos C.M.T.d., Silva M.A.S. (2007): Physicochemical study of CaCO<sub>3</sub> from egg shells. Food Science and Technology (Campinas), 27: 658–662.
- Murakami Y., Iijima A., Ward J.W. (1986): New developments in zeolite science and technology. Elsevier, 28.
- Nakatani N., Takamori H., Takeda K., Sakugawa H. (2009): Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresource Technology, 100: 1510–1513.

Navajas A., Issariyakul T., Arzamendi G., Gandía L., Dalai A. (2013): Development of eggshell derived catalyst for transesterification of used cooking oil for biodiesel production. Asia–Pacific Journal of Chemical Engineering, 8: 742–748.

Neves M.A.d. (1998): Alternativas para a valorização da casca de ovo como complemento alimentar e em implantes ósseos.

Niju S., Meera K., Begum S., Anantharaman N. (2014): Modification of egg shell and its application in biodiesel production. Journal of Saudi Chemical Society, 18: 702–706.

- Nugteren H.W., Janssen-Jurkovícová M., Scarlett B. (2002): Removal of heavy metals from fly ash and the impact on its quality. Journal of Chemical Technology Biotechnology, 77: 389–395.
- Ok Y.S., Lee S.S., Jeon W.T., Oh S.E., Usman A.R., Moon D.H. (2011): Application of eggshell waste for the immobilization of cadmium and lead in a contaminated soil. Environmental geochemistry and health, 33: 31–39.
- Oliveira D., Benelli P., Amante E. (2013). A literature review on adding value to solid residues: egg shells. Journal of Cleaner Production, 46: 42–47.
- Park H.J., Jeong S.W., Yang J.K., Kim B.G., Lee S.M. (2007): Removal of heavy metals using waste eggshell. Journal of Environmental Sciences, 19: 1436–1441.
- Peng G.Y., Fang Y.S., Zhe Z.J., Chen W.Z., Yu Z.M. (2000): Preparation of active carbon with high specific surface area from rice husks. Chemical Journal of Chinese Universities, 21: 335–338.

- Rabu R.A., Janajreh I., Honnery D. (2013): Transesterification of waste cooking oil: process optimization and conversion rate evaluation. Energy Conversion Management, 65: 764–769.
- Rashidi N.A., Yusup S., Ahmad M.M., Mohamed N.M., Hameed B.H. (2012): Activated carbon from the renewable agricultural residues using single step physical activation: a preliminary analysis. APCBEE Procedia, 3: 84–92.
- Rezaei R., Mohadesi M., Moradi G. (2013): Optimization of biodiesel production using waste mussel shell catalyst. Fuel, 109: 534–541.
- Rivera E.M., Araiza M., Brostow W., Castano V.M., Diaz-Estrada J., Hernandez R., Rodriguez J.R. (1999): Synthesis of hydroxyapatite from eggshells. Materials Letters, 41: 128–134.
- Roy D., Greenlaw P.N., Shane B.S. (1993): Adsorption of heavy metals by green algae and ground rice hulls. Journal of Environmental Science & Health Part A: Environmental Science and Engineering and Toxicology, 28: 37–50.
- Stadelman W. (2000): Encyclopedia of Food Science and Technology. New York, John Wiley and Sons: 593–599.
- Surip S., Bonnia N., Anuar H., Hassan N., Yusof N. (2012): Nanofibers from oil palm trunk (OPT): preparation & chemical analysis. In: Business, Engineering and Industrial Applications (ISBEIA), 2012 IEEE Symposium on IEEE: 809–812.
- Syazwani O.N., Rashid U., Yap Y.H.T. (2015): Low-cost solid catalyst derived from waste *Cyrtopleura costata* (Angel Wing Shell) for biodiesel production using microalgae oil. Energy Conversion Management, 101: 749–756.
- Tan Y.H., Abdullah M.O., Nolasco-Hipolito C. (2015): The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance. Renewable and Sustainable Energy Reviews, 47: 589–603.
- Tsai W.T., Hsien K.J., Hsu H.C., Lin C.M., Lin K.Y., Chiu C.H. (2008a): Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresource Technology, 99: 1623–1629.
- Tsai W.T., Yang J.M., Hsu H.C., Lin C.M., Lin K.Y., Chiu C.H. (2008b): Development and characterization of mesoporosity in eggshell ground by planetary ball milling. Microporous and Mesoporous Materials, 111: 379–386.
- Tsai W., Yang J., Lai C., Cheng Y., Lin C., Yeh C. (2006): Characterization and adsorption properties of eggshells and eggshell membrane. Bioresource Technology, 97: 488–493.

- Verma, N., Kumar, V., & Bansal, M. C. (2012). Utilization of egg shell waste in cellulase production by *Neurospora crassa* under Wheat bran-based solid state fermentation. Polish Journal of Environmental Studies, 21: 491–497.
- Vicente G., Martinez M., Aracil J. (2004): Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresource Technology, 92: 297–305.
- Viriya-Empikul N., Krasae P., Nualpaeng W., Yoosuk B., Faungnawakij K. (2012): Biodiesel production over Cabased solid catalysts derived from industrial wastes. fuel, 92: 239–244.
- Viriya-Empikul N., Krasae P., Puttasawat B., Yoosuk B., Chollacoop N., Faungnawakij K. (2010): Waste shells of mollusk and egg as biodiesel production catalysts. Bioresource Technology, 101: 3765–3767.
- Volesky B. (1990): Biosorption of heavy metals. CRC press.
- Wei Z., Xu C., Li B. (2009): Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresource Technology, 100: 2883–2885.
- Witoon T. (2011): Characterization of calcium oxide derived from waste eggshell and its application as  $CO_2$  sorbent. Ceramic International, 37: 3291–3298.
- Wu S.C., Tsou H.K., Hsu H.C., Hsu S.K., Liou S.P., Ho W.F. (2013): A hydrothermal synthesis of eggshell and fruit waste extract to produce nanosized hydroxyapatite. Ceramic International, 39: 8183–8188.
- Xu Z., Zhu Y., Liang M., Zhang H., Liu H. (2011): Optimization of the preparation conditions for activated carbons from sugarcane bagasse: an agricultural waste. In: Computer distributed control and intelligent environmental monitoring (CDCIEM), 2011 International Conference on IEEE: 555–559.
- Yin X., Duan X., You Q., Dai C., Tan Z., Zhu X. (2016): Biodiesel production from soybean oil deodorizer distillate usingcalcined duck eggshell as catalyst. Energy Conversion Management, 112: 199–207.
- Yoo H., Lee H., Jeong W. (2002): Preparation of ion exchanger from waste paper cup and removal characteristics of heavy metal. Journal of Korean environment science, 11: 993–999.
- Zakari Z., Buniran S., Ishak M.I. (2010): Nanopores activated carbon rice husk. In: Enabling Science and Nanotechnology (ESciNano), 2010 International Conference on IEEE: 1–2.

Received for publication January 10, 2017 Accepted after corrections August 8, 2017