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.

Keywords: eggshell waste, catalyst, synthesis, biodiesel, syngas, bioactive compounds.

Contents

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 7000-17000 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 Figure 1 it is shown the schematic illustration of eggshell structure, whereas in Figure 2 it can be seen a micrograph of native hen eggshell.

Nowadays, the functional characteristics of eggs are the object of intensive study, as it is the utilisation of some of the components, previously considered as waste (Laca et al., 2014, Laca et al., 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 be published (Baláž, 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 Figure 3, it is shown an overview of eggshell waste applications as catalyst, whereas Table 1 summarized the different products synthetized 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 (Viriya-empikul, 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 ºC, on the contrary a low activity (<30% yield) was observed when the calcination temperature was below 600 ºC. The conditions employed were methanol/oil ratio 9:1, 3wt.% catalyst and 65 ºC.

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 ºC). In a recent work, Chavan et al. (2015) synthetized 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 ºC and using 1.7% (v/v) H_2SO_4. 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 ºC and methanol/oil 12:1). Viriya-Empikul et al. (2010) also used palm oil as substrate and the transesterification was developed at 60ºC (oil:catalyst 10 wt.% and methanol/vegetable oil 18:1). These authors compared the performance of the CaO catalysts obtained from eggshell, meretrix venus shell and golden apple snail shell. All catalyst exhibited high yields (greater than 90%); however, the eggshell catalyst presented the highest value (95%).

Biodiesel was produced from Jatropha oil using as catalyst a mixture of seashell and eggshell in complexation with TiO_2. Reactions were carried out with a methanol/oil molar ratio 20:1 and 10 wt.% catalyst at 140-190 ºC and 60-80 bar, yields of 95% were achieved (Semwal et al., 2011). The same year, Olutoye et al. (2011) published a work that employed eggshell modified with magnesium and potassium nitrates as catalyst for the transesterification of palm oil at 65 °C. The conditions that achieved the highest

yield (86%) was 5.3 wt.% catalyst, methanol/oil molar ratio of 16:1 and reaction time 4.6 h. At these conditions, catalyst was reusable for three times.

Khemthong et al. (2012), demonstrated that, in comparison with conventional heating, a significant enhancement for biodiesel synthesis was achieved by using microwaves when a solid CaO catalyst derived from waste eggshells was employed. A yield above 96% was reached at the optimal conditions (reaction time 4 min, microwave power 900 W, methanol/oil ratio 18:1 and catalyst 15 wt.%).

Furthermore, Navajas et al. (2013) reached a yield of 100% for biodiesel production from used cooking oil using eggshell catalyst (60 ºC, 5 h, methanol/oil ratio 24:1 and 4 wt% catalyst). This work reported that the surface morphology of the catalyst, a key parameter for the catalyst activity, was determined by the type of eggshell used. More recently, El-Gendy and Deriase (2015) employed waste eggshells for biodiesel production from a variety of waste cooking oil. An empirical quadratic regression equation model was used to select the optimum values of the variables considered (methanol/oil molar ratio 9.15:1, catalyst concentration 7.7 wt.% and reaction time 75 min). For these conditions the conversion to biodiesel was predicted to be 90%, which was in agreement with the real yield value. In a just-published work, Majhi and Ray (2016) evaluated the performance of a catalyst derived from eggshell in the biodiesel production. The study reported a yield of around 90 % using methanol/oil molar ratio of 18:1 and 10 wt.% catalyst calcined at 950 ºC.

Correia et al. (2014) compared the catalytic activities of calcium oxide obtained from crab shell and eggshell. Employing natural shells, the conversion from triglycerides (sunflower oil) to methyl ester was not observed, on the contrary using the calcined catalysts the yields were 83% and 98% for crab shell and egg shell, respectively (methanol/oil molar ratio 1:6-9, catalyst 3 wt.%, 60 ºC). These results were

in accordance to those reported by Viriya-Empikul et al. (2010). Compared with the calcined crab waste, the higher content of Ca in the surface of the calcined eggshell justified the better catalytic performance. It is frequent to find in literature a better behaviour as catalyst of eggshell than other wastes. So, Sinha and Murugavelh (2016) reported for the transesterification of waste cotton cooking oil a yield of 92% with calcined eggshell catalyst, whereas the yield with pistachio shell was 84% (catalyst 3 wt.%, methanol/oil molar ratio 9-12:1 and 60ºC). In addition, in a work that has just been published (Roschat et al., 2017), rubber seed oil was successfully employed as substrate to obtain biodiesel using waste coral and eggshell catalysts. Eggshell catalyst gave a yield of 97% in 180 min, whereas coral catalyst needed a longer time (210 min) and more amount of catalyst (100 wt.%) to completed the transesterification under optimum conditions (catalyst 9 wt.%, 12/1 methanol/oil molar ratio and 65 °C).

Although most researches regarding the uses of eggshell as catalyst have been developed on hen eggshell, some authors have employed other bird eggs. As it has been commented above, Cho and Seo (2010) reported a greater catalytic activity of CaO catalysts obtained from quail eggshells compared to that obtained with hen eggshells. On the opposite, a recent study (Reyero et al 2015) found no differences between the properties and catalytic performance of the CaO catalysts prepared from hen or quail eggshells. A 98% oil conversion in 120 min of reaction (60 ºC, methanol/oil molar ratio 12:1 and catalyst 2 wt.%) was achieved with the catalyst calcined at 850 ºC for 3 h. These authors reported very similar catalytic activities despite of the type of eggs, the procedure of milling and the size fraction of the calcined eggshells.

Chen et al. (2014) obtained a CaO catalyst from ostrich eggshell and reported a biodiesel yield of 93% using an ultrasonic method (catalyst 8 wt.%, methanol/oil molar ratio 9:1 and ultrasonic power 60% amplitude). This catalyst was reused without loss of

activity for more than 8 times. Tan et al. (2015), also investigated the performance of ostrich- and chicken-eggshells as catalyst for biodiesel production from used cooking oil. In both cases yields above 90% were obtained (1.5 wt.% catalyst, methanol/oil molar ratio 12:1 and 65 ºC). Calcined duck eggshell has also been employed as catalyst in biodiesel production employing as substrate soybean oil (Yin et al., 2016). Different temperatures of calcination were assayed and the best results were achieved at 900 ºC, in accordance with Reyero et al. (2015). The biodiesel yield at optimal conditions (catalyst 10 wt.%, methanol/oil molar ratio 10:1 and 60 ºC) was 94.6%. The reusability of the catalyst was evaluated and after 5 cycles biodiesel yield was still above 80%. Additionally, Zeng et al. (2015) prepared an eggshell catalyst by KF modification and thermal treatment. This catalyst could be reusable at least 10 times with a yield higher than 80% (catalyst 2 wt.%, methanol/oil molar ratio 12:1 and 65 ºC).

According to all the studies reported above, it is evident that different factors are involved in the performance of eggshell as heterogeneous catalyst in biodiesel production: methanol/oil ratio, reaction time, raw material, catalyst load, etc. However, catalyst surface area and calcium oxide content have been identified as the key parameters which specifically affect the catalytic activity (Viriya-Empikul et al., 2010). Furthermore, these two parameters are determined by the calcination step. In fact, and as it is summarized in Table 1, the calcination, with slightly modifications, is a common procedure in eggshell catalyst preparation in all works related to biodiesel production. Several characterization techniques have been employed in order to obtain information that can be correlated with catalyst activity, i.e., X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, differential thermal analysis/thermogravimetric analysis (DTA/TGA), BET adsorption isotherm and scanning electron microscopy (SEM).

Regarding composition, XRD an FTIR analysis verified the presence of calcium carbonate in the uncalcined eggshell catalyst, whereas calcium oxide was identified in the calcined catalyst (Wei et al., 2009; Sharma et al., 2010; Khemthong et al. 2012; Navajas et al., 2013; Correia et al., 2014; Yin et al., 2016). Additionally, Tan et al. 2015 found that the eggshell based catalyst contained a mixture of CaO and $Ca(OH)_2$. The existence of hydroxyl species was attributed to the adsorption of atmospheric moisture onto the surface of calcined eggshells. As above commented, when the uncalcined eggshell was used as catalyst no conversion was observed (Navajas et al., 2013). However, during calcination, the $CaCO_3$ is decomposed to CaO, which did show catalytic activity. In this context, TGA analyses indicated that, although decomposition of calcium carbonate started at 700-800 ºC, complete decomposition occurred at 800-900 ºC. Calcination of chicken eggshells above 800 ºC could completely convert $CaCO_3$ to CaO and CO_2 (Wei et al., 2009; Viriya-Empikul et al, 2010; Navajas et al., 2013; Yin et al., 2016). Hence, the need for calcination of the eggshell at 800-900 ºC is justified in order to appropriately activate the catalysts by completely removing of the $CaCO_3$ from the surface (Reyero et al., 2015).

According with Tan et al. (2015), the change of eggshell structure is mainly originated from the change of composition. It can be found in literature that the morphology of natural eggshell exhibited a typical layered architecture with macropores and irregular particles of different sizes. On the contrary, when the eggshell is calcined the morphology of calcium oxide particle shapes become more regular (Correia et al., 2014; Tan et al., 2015; Zeng et al., 2015; Yin et al., 2016). Khemthong et al. (2012) described the shape of CaO particles as rod, dumbbell, and rod-dumbbell connected shapes constructing a termite nest-like macroporous structure. Reyero et al. (2015) and Tan et al. (2015) also indicated that calcination contribute to homogenize the catalyst

textural properties, particularly at temperatures above 850ºC. An example of the commented structures can be observed in Figures 2 and 4. The surface area of a solid catalyst has direct impact on its catalytic activity. Specifically, and, as it is well known, a higher surface area is expected to show higher catalytic activity. BET analysis demonstrated that the surface area of eggshells after calcinations was higher than before the thermal treatment (Viriya-Empikul et al, 2010; Tan et al.; 2015; Zeng et al., 2015). Concretely, Reyero et al. (2015) pointed out that BET surface of eggshell catalyst exhibited an optimum around 600 ºC and 12 h of calcination (17 m^2/g) since higher temperatures and/or longer times led to sintering of the CaO particles formed with the consequent loss in surface area.

If attention is paid to catalyst reuse, the deactivation of eggshell derived catalyst may be attributed to its structure change. In fact, XRD analyses indicated that after several cycles the major phase of catalyst has changed from CaO to $Ca(OH)_2$ since the reactants contained a little amount of water (Wei et al., 2009). Yin et al. (2016) noted that the XRD pattern of the recycled catalyst showed notable displacement of the peaks and the peaks of CaO and $CaCO_3$ disappeared. These authors justified this result as the used catalysts were covered by intermediates or products such as glycerol or biodiesel. In addition, it was observed that after 5 times usage, the cluster of CaO cubic crystal was disappeared, and the pores in the used catalyst were almost destroyed reducing the surface area of the catalyst. Tan et al. (2015) also reported the agglomeration of the catalyst particles by the glycerol coverage on the catalyst surface as responsible of the gradual drop in activity during repeated cycles. In this context, Reyero et al., (2015) identified by XRD the formation of calcium glyceroxide in the regenerated samples.

Zen et al. (2015) characterised by means XRD, FTIR and SEM a catalyst prepared from waste eggshell by KF modification and thermal treatment. In this case,

the characterization show that KOH generated in the modification process enhances the basicity and catalytic ability of the catalyst.

A new trend is to combine eggshell with other compounds to improve catalyst activity. Indeed, Chen et al. (2015a) synthetized CaO-SiO_2 catalysts from eggshell and Na_2SiO_3. When they were used for transesterification of palm oil, these catalysts showed a decrease in catalytic activity and an increase in reusability as the amount of Si compounds increased. Small differences were found by SEM between catalyst with and without Si, i.e. the Si catalyst showed larger and more regular pieces, which could be due to the coverage of CaO surface with Si compounds. FTIR spectra suggested that, with the lowest Na_2SiO_3 concentration, all the SiO_2 generated from the silicification process reacted with CaO to form a new $CaSiO_3$ or Ca_2SiO_4 compound. XRD patterns proved that the peaks of SiO_2, $CaSiO_3$ and Ca_2SiO_4 appeared when the Na_2SiO_3 concentration increased, while CaO and $Ca(OH)_2$ phases completely disappeared. In other work, these same authors (Chen et al., 2015b) employed rice husk ash and calcined eggshell to prepare catalysts. The catalysts developed with 30% and 70% of calcined eggshell and calcined rice husk, respectively, presented the highest activity. More specifically, the biodiesel yield was 91.5% when the reaction was carried out with methanol/oil molar ratio of 9:1, a reaction time of 4 h and catalyst loading of 7 wt.%. Besides, the yield achieved was above 80% after being reused 8 cycles.

2.2. Synthesis of hydrogen/syngas

CO_2 is considered the major greenhouse gas emitted through anthropogenic activities, for this reason, hydrogen has recently been receiving a lot of attention as a clean alternative fuel. In particular, hydrogen production from gasification has become an interesting research topic in the last decades. A variety of carbonaceous material,

such as wood and coals, can be gasified for the production of hydrogen through advanced gasification processes. These processes can be improved by the use of catalyst (Mostafavi et al., 2015).

Taufiq-Yap et al. (2013) evaluated the hydrogen production from wood gasification favoured by waste eggshell catalyst. Specifically, biomass gasification of *Azadirachta excelsa* wood was carried out with addition of CaO catalyst derived from eggshells. As indicated in Table 1, the eggshell was calcined at 900 ºC for 2 h and the catalyst so obtained showed a cubic structure, similar to pure CaO, observed by SEM. A temperature-programmed gasification technique was employed (50 to 1000 °C in 5% O_2/He with flow rate 10 ml/min). During gasification process, biomass is decomposed into various gases (H_2, CH_4, CO and CO_2) and some unwanted products such as tar and char. Compared to the reaction without catalyst, the addition of eggshell suppressed CO_2 production, which was absorbed by CaO, promoting H_2 generation by water gas shift reaction (Taufiq-Yap et al., 2013). These authors also reported that the addition of eggshell catalyst favoured tar and char gasification, increasing the amount of gaseous products. The effect of catalyst loading was investigated and hydrogen production was increased with the catalyst loading to a maximum of 73% compared to gasification without catalyst. Moreover, it was observed that CH_4 production temperature was lower when catalyst load was higher. This was explained by the fact that CH_4 is mainly produced from cracking reactions of liquid hydrocarbons that are catalysed by the presence of CaO. More recently, the effect of composite catalyst (K_2CO_3 and CaO derived from eggshell) on gasification of coal has been studied (Fan et al., 2016). After completion of the pyrolysis process, chars produced were gasified with a flow of H_2O and N_2. Higher amounts of H_2 and CO, compared with the non-catalytic gasification, were obtained in the presence of the composite catalyst. Specially, this composite

catalyst increased the yields of H_2 by 6% and 123%, in comparison with the utilization of pure K_2CO_3 and absence of catalyst, respectively. Additionally, the carbon conversion rate was increased by more than three times by the composite catalyst. Various kinetic models have been studied in order to explain the char gasification mechanism, the random pore model (RPM) is widely used and it is applied in terms of a pore size distribution in the reacting solid. In this work the RPM was successfully employed to describe the conversion rates.

Another possible source to produce syngas is methane, an abundant resource that can be found in natural gas reserves and can be produced by anaerobic digestion from organic wastes (Osman et al., 2016). Catalytic partial oxidation of methane into syngas suitable for synfuels generation is considered as an advantageous route from both economic and technical points of view (Shelepova et al., 2016). In this context, Karoshi et al. (2015) tested the use of calcined eggshell as catalyst for selective oxidation of methane using a packed bed reactor. The partial oxidation of methane on calcined eggshell yielded higher hydrocarbons (C2-C7). Nevertheless, the achieved average fractional methane conversion was quite low, approximately 30%. Several factors, like flow rate, temperature and oxygen concentration, influence methane conversion and product selectivity. In literature it is proposed that oxidation of methane over pure CaO catalyst proceeded via formation and homogeneous coupling of methyl radicals assisted by active O^{2-} and Ca^{2+} Karoshi et al. (2015). In this work, the authors suggested that methane was converted into ethylene and ethane via oxidative coupling of methane and was further transformed to C3-C7 hydrocarbons via coupling or aromatization. Additionally, it was suggested that the CaO active sites in the calcined eggshell could retain certain degree of orientation which facilitates surface bound coupling or aromatization reaction. However, the reaction mechanism that occurs on eggshell

catalyst is not clear and further studies on kinetics of methane oxidation should be carried out.

The syngas so synthetized could be used to produce synthetic petroleum via the Fischer-Tropsch process. Precisely, Han et al. (2016) have recently reported a multiscale analysis of an eggshell-Co-based catalyst prepared by wetness impregnation for this synthesis.

2.3. Synthesis of dimethyl carbonate (DMC)

DMC is an important methylating and carbonylating agent because of its biodegradability, low bioaccumulation and persistence, as well as its low toxicity. So the production and chemical application of this compound have attracted much attention in the so-called "green chemistry". DMC can be used for replacing dimethylsulfate and methylhalides in methylation reactions and harmful phosgene in polycarbonate and isocyanate synthesis (Gao and Xu, 2012; Wang et al., 2015). As it is reported in Table 1, the only research work focused on the use of eggshell-derived catalyst for DMC synthesis was developed by Gao and Xu (2012). In their work, they studied this chemical synthesis by the transesterification of propylene carbonate and methanol employing eggshell as catalyst. The conversion of propylene carbonate and the yield of DMC reached maximum values after 1 h (80 and 75%, respectively) under the optimum conditions (methanol/propylene carbonate molar ratio 10:1, 0.8 wt.% eggshell catalyst, room temperature and 1 atm pressure). In addition, the eggshell catalyst can be reused in four cycles with slightly deactivation. The eggshell showed a catalytic behaviour similar to pure CaO. The catalyst was characterized by XRD, TGA and nitrogen adsorption (BET) and similar results to those described in section 2.1 were reported. In short, calcium carbonate from eggshell is decomposed to calcium oxide during calcination and

this change regarding composition originates a homogenization of structure increasing the BET area. In this work it was concluded that the eggshell-derived material is a renewable effective solid base catalyst.

2.4. Synthesis of bioactive compounds

Catalysts based on eggshell wastes have been also used to synthetize different bioactive compounds summarised in Table 1.

Chromenones are bioactive compounds extensively employed as pigments, cosmetics and potential biodegradable agrochemicals. They also possess diuretic, anticarcinogenic, antioxidative, antidepressant, antihypertensive, anticoagulant, antibacterial, antifungal and antiviral activities (Kachkovski et al., 2004). The use of eggshell in the synthesis of chromenones was investigated by Mosaddegh (2013), specifically 2-aminochromenes, under thermal solvent-free conditions. This heterogeneous nanocatalyst was sonochemical prepared in a CH_2Cl_2 solution. Furthermore, a trial to develop nano eggshell powder using microwave irradiation was also carried out without success. This author found that sonicated eggshell catalyzed the reaction with more effectiveness than $CaCO_3$ and eggshell powder obtained by ball milling. Moreover, the nano eggshell catalyst could be repeatedly used six times without any loss of activity. In addition, this same author (Mosaddegh and Hassankhani; 2013) employed eggshells washed with distilled water, dried at room temperature and crushed by mortar, as catalyst to synthesis of 7,8-dihydro-4H-chromen-5(6H)-ones at ambient temperature. The eggshell catalyst could be reused in five cycles keeping its catalytic activity. Furthermore, these authors proved that without the addition of the catalyst, only alkene 5 and neither 2-amino-chromenes 4 nor 7,8-dihydro-4H-chromen-

5(6H)-one 4 were produced. So, it was concluded that the eggshell has an essential effect on the reaction selectivity.

Many pyran derivatives have been described as compounds with important bioactive properties (antimicrobial, antifungal, antiviral, anticancer and anti-inflammatory activities). Nano-bio calcite ($CaCO_3$) and nano-CaO prepared from hen eggshell were used as catalyst in the production of pyrano[4,3-*b*]pyrans. Both catalysts exhibited a high catalytic activity (yields ~ 90%) and also high reusability in the synthesis of these compounds (Mosaddegh et al., 2013; Mosaddegh and Hassankhani, 2014).

Calcined eggshell has been evaluated too for Knoevenagel condensation of aromatic aldehydes (Patil et al., 2013). This is a procedure employed for the synthesis of organic compounds with interesting properties from a pharmaceutical point of view. Knoevenagel condensation using calcined eggshell were compared with other reported catalysts for the synthesis of benzylidenepropanedinitrile. Results showed that this eggshell catalyst gave better yields and at the same time allowed to reduce the reaction time. The activity of calcined eggshell was compared with the activity of pure CaO and a similar catalytic performance was obtained with the advantage of being derived from a renewable resource.

More recently, Morbale et al. (2015) used modified eggshells as catalyst for the synthesis of 1,4-dihydropyridine and polyhydroquinolines. These compounds show different biological activities (antitumor, anti-inflammatory, antianginal, antitubercular and analgesic). These authors reported as advantages for the developed process the removal of corrosive catalysts, organic solvents and toxic reagents. Additionally, the in vitro assays have shown interesting antibacterial and antifungal effects of these synthesized molecules. The reaction was also evaluated employing pure CaO as

catalyst. A very low amount of the desirable molecules was obtained, in addition, a reaction time of five times higher was needed than using eggshell.

Benzothiazoles exhibit antitumor, antimicrobial, anticancer and antidiabetic activities (Stone et al., 2015; Bhoi et al., 2016; Borhade et al., 2016; Harrouche et al., 2016). In this context, Borhade et al. (2016) reported a one-pot synthesis of 2-arylbenzothiazoles by a reaction of o-aminothiophenol with differently substituted aromatic aldehydes. The reaction was carried out at room temperature and a mixture of a suitable aldehyde, o-aminothiophenol and, as catalyst, calcinized eggshell were grinded under solvent free conditions.

These authors compared their work with other procedures reported in the literature for the synthesis of 2-arylbenzothiazole derivatives and concluded that calcined eggshell was an effective catalyst with regards to yields and reaction times. In addition, the method was also developed with $Ca(OH)_2$, $CaCO_3$ and pure CaO, as catalysts. It was observed that the reaction did not take place by using pure $Ca(OH)_2$ and $CaCO_3$ even after a long time (5 h). On the contrary, pure CaO catalyzed the reaction, but with a very low yield (30%), and it takes a longer time (5 h) than using the eggshell catalyst, which obtained a 92% yield in 16 min.

Special attention should be pay to lactulose as bioactive compound. In recent year, this chemical has obtained increasing interest because of its commercial applicability in food and pharmaceutical fields. Lactulose is considered a prebiotic as it stimulates the growth of bifidobacteria and lactobacilli in the gastrointestinal tract and at the same time inhibits pathogenic bacteria such as *Salmonella* (Seo et al., 2016; Panesar et al., 2011). Other functionalities of lactulose include reduction of blood ammonia and serum lipids, anti-gallstone formation, anti-endotoxic effects, control of blood glucose and insulin, relieve constipation, mineral absorption stimulation and anti-carcinoma

effects (Panesar and Kumari, 2011; Seo et al., 2016; Nooshkam and Madadlou, 2016). Lactulose can be obtained from lactose by isomerization. Montilla et al. (2005) employed raw eggshell as catalyst for this process, and investigated the effect of catalyst loadings, lactose concentration and pH. The maximum production of lactulose achieved from milk permeate was around 25%, with respect to the initial lactose concentration, after 90 min at 98 ºC and using 4 mg/mL of catalyst. Recently, Nooshkam and Madadlou (2016) employed milk ultrafiltration permeate in a similar procedure to obtain lactulose. The isomerization was carried out by heating the permeate at 97 ºC in the presence of eggshell power for 60 min. Approximately 17% of lactose were converted into lactulose. The isomerized permeate was afterwards purified to a lactulose-rich product through crystallizing lactose out by methanol. Hence, eggshell was employed with success as catalyst for lactose isomerization to lactulose. Furthermore, isomerization yields were similar to those reported for other calcium carbonate-based catalysts (18-21%) (Panesar and Kumari, 2011); however, they were lower than those obtained using ammonium carbonate catalyst (28%) (Seo et al., 2016).

A characterization of the described eggshell catalysts was carried out in some of these works and they agree again that surface area and composition were the determinant factors on catalyst performance. Additionally, possible mechanisms for the formation of the described products were proposed in several cases. However, in general, further studies are necessary to contribute to clarify the role played by eggshell catalysts in the synthesis of these different bioactive compounds.

2.5. Wastewater treatment

Nasrollahzadeh et al. (2016) proposed a one-step green route for the synthesis from waste hen eggshell of Cu/eggshell, Fe_3O_4/eggshell and Cu/Fe_3O_4/eggshell

nanocomposites. Aqueous extract of the leaves of *Orchis mascula* L. was used as a stabilizing and reducing agent for the synthesis of the nanoparticles. The process of synthesis is recorded in Table 1, dried powered of eggshell was mixed with $CuCl_2$ and/or $FeCl_3$ and the aqueous plant extract in alkaline medium. The mixture was shaken, while heating at 70ºC, in order to form the nanocomposite, and finally filtered. These materials were characterized by field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS) and FTIR. Results showed that, as was already commented, the eggshell is a macroporous network composed of C, Ca and O, on whose surface the copper and iron nanoparticles were immobilized. The highly porous structure increased the contact area and allowed high loads of nanoparticles. In fact, eggshell porous were almost covered with Cu and Fe_3O_4 particles uniformly distributed on the superficies, which modified the roughness of the eggshell surface. These metallic nanocomposites showed high catalytic activity in the reduction of a variety of dyes in water at room temperature. Moreover, these catalysts could be easily removed from the media and reused in several cycles without any loss on the efficiency, which remained almost constant up to seven reuses.

Additionally, eggshells can be employed to develop different materials that can be potentially used in sorption processes for environmental protection and waste treatment (soil, water, and air). For example, CaO prepared from the pyrolysis of chicken eggshells was employed as starting material for the synthesis of calcium zeolite type A ($CaNaAlSi_2O_7$) (Tangboribooron et al.; 2011). The specific surface area was 55.15 m^2/g, a value quite moderate in comparison with commercial zeolites, and the average pore diameter was 37.19 nm. These authors suggested the possible employment of this material as adsorbent in wastewater treatment. Other properties that could make

this zeolite interesting for industrial uses would be its ability as catalyst, ion exchanger or molecular sieve. However, further work would be necessary in this area.

3. CONCLUSIONS

Green eggshell-derived catalysts were successfully used for biodiesel production with numerous works published about this topic. When eggshell is calcined different changes in composition and structure can be observed. During calcination, the $CaCO_3$ is decomposed to CaO. Simultaneously, this thermal treatment contributes to homogenize the catalyst textural properties, originating a homogeneous macroporous structure and increasing its surface area. The effect of these factors on catalyst activity for biodiesel production has been widely studied and it is clear that in the development of eggshell catalyst to obtain biodiesel the calcination conditions are determinant on catalyst performance. Temperatures given as optimal for calcinations vary between 600 and 1000ºC, depending on the authors. In addition, catalyst deactivation after several cycles of use was related to a reduction of the surface area due to structure modifications and/or deposits of intermediates on catalysts surface that leads to a decrease of catalytic activity.

Eggshell-derived catalysts have been also tested in the synthesis of H_2/syngas, DMC and different bioactive compounds such as chromenones, pyrans, benzothiazoles or lactulose. Moreover, it is noticeable that in most cases eggshell catalysts achieved yield values similar or even better than those obtained with catalysts developed from other sources. Although there is less information published about the relationship between catalyst characteristics and properties in these applications, the calcination step, which is determining for catalysts structure and composition, is in most cases again

reported as the main responsible of the catalyst behaviour. Additionally, eggshell has also been employed as support for the development of nanocomposites to treat wastewaters. Further investigations about catalysts properties and catalytic mechanisms focused on these processes should be developed.

To sum up, the successful application of eggshell waste-derived catalysts, with so many different purposes, highlights the interest of testing the use of these renewable catalysts in multiple other processes, which, as exposed in this review, can include from synthesis of value-added products to wastewater treatment.

AKNOWLEDGEMENTS

This study was developed thanks to funding from the Economy and Employment Office of Principality of Asturias (Spain) through project GRUPIN14-140.

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FIGURE CAPTIONS

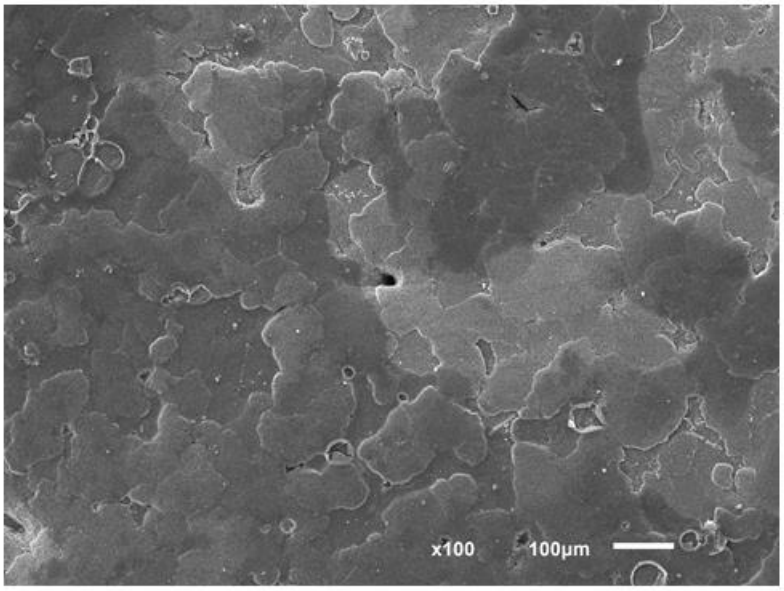
Figure 1. Schematic illustration of eggshell structure.

Figure 2. SEM microstructures of native hen eggshell. Magnification and bars: 100x, 100 µm (A) and 5000x, 5 µm (B).

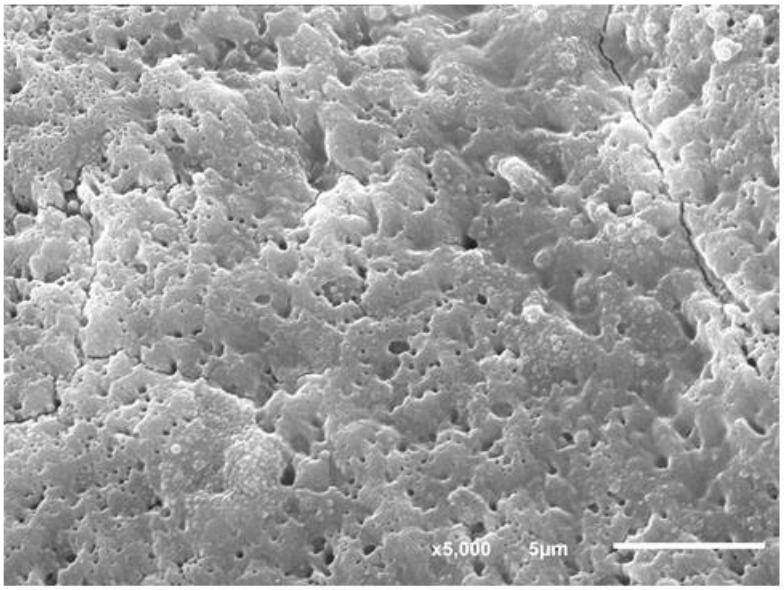
Figure 3. Overview of eggshell waste applications as catalyst.

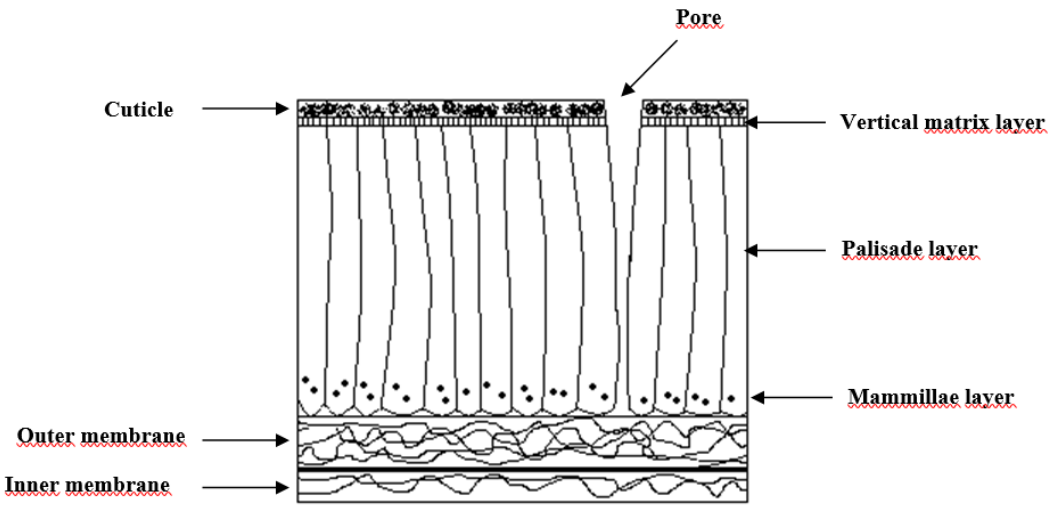
Figure 4. SEM microstructures of calcined hen eggshells. Eggshells were washed and membranes were manually removed, then they were dried (100 ºC, 2 h), crushed by mortar and calcined (900 ºC at a heating rate 2ºC/min for 3 h), finally calcined power was sieved by 250 µm opening). Magnification and bars: 500x, 50 µm (A) and 5000x, 5 µm (B).

A)

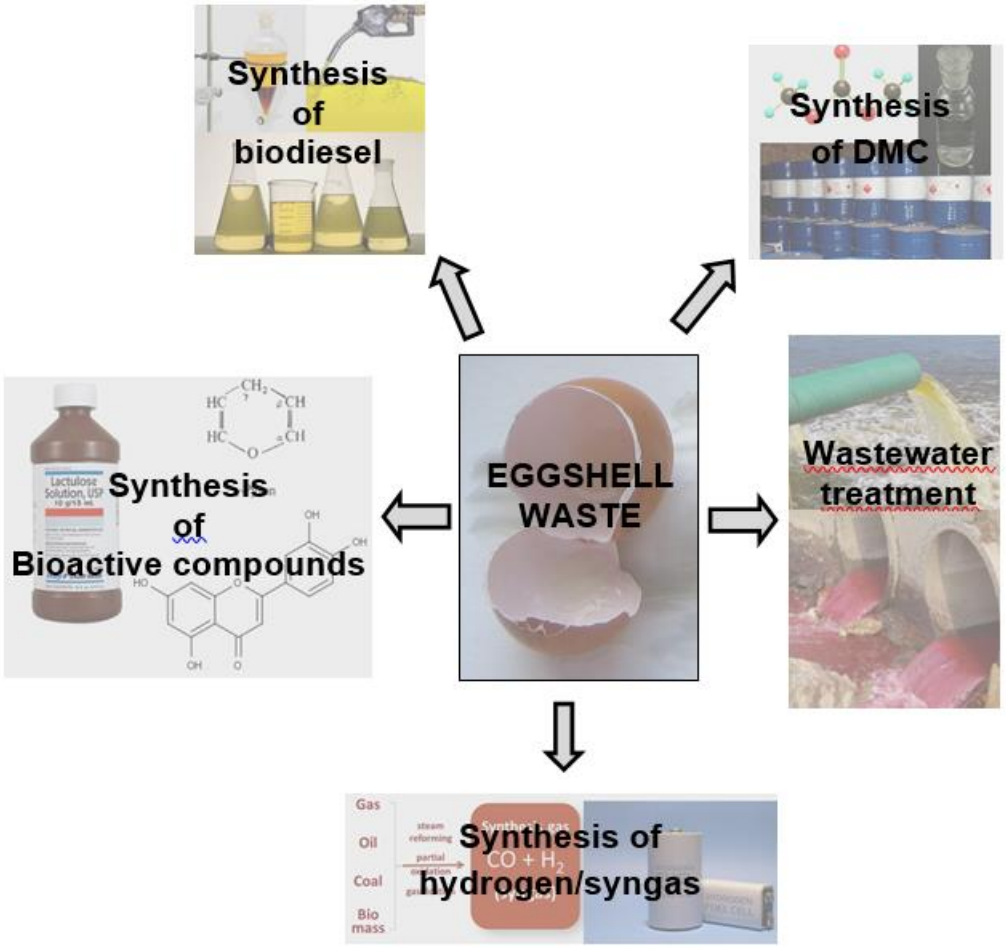


B)

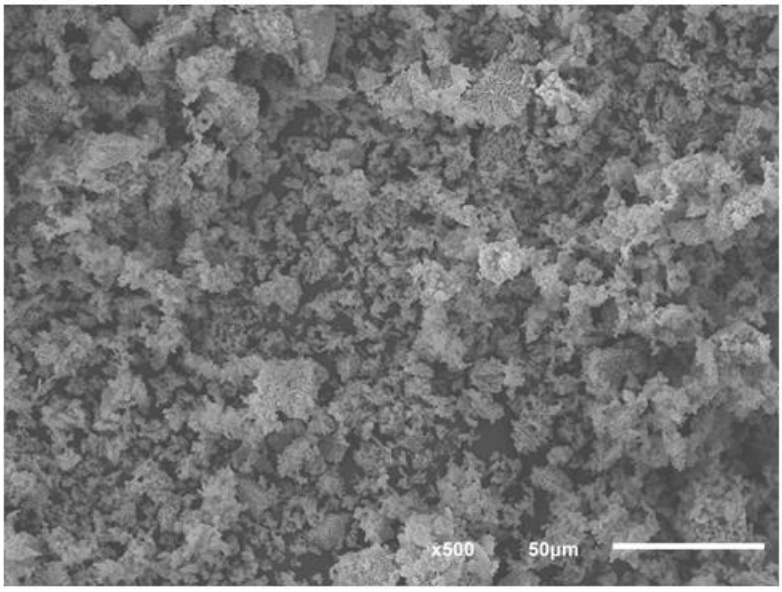



Pore
Cuticle
Vertical matrix layer
Palisade layer
Mammillae layer
Outer membrane
Inner membrane

/


Synthesis of biodiesel
Synthesis of DMC
Synthesis of Bioactive compounds
EGGSHELL WASTE
Wastewater treatment
Gas
Oil
Coal
Bio mass
Synthesis of hydrogen/syngas

A)



B)

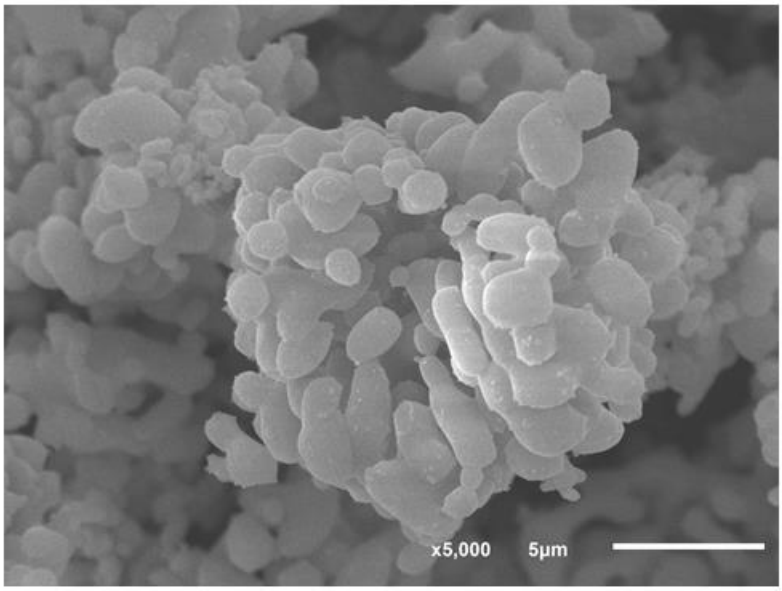


Table 1. Comparation of eggshell catalyst found in literature.

Product	Process	Eggshell catalyst preparation	Reference
Biodiesel	Oil transesterification	Wash, dry (100-110 °C, overnight-24 h), crush and calcine (200 °C-1000 °C, 2-4 h).	Wei et al. (2009) Sharma et al. (2010) Viriya-empikul et al. (2010) Khemthong et al. (2012) Correia et al (2014) Chen et al. (2014) Chavan et al. (2015) El-Gendy and Deriase (2015) Reyero et al (2015) Tan et al. (2015) Majhi and Ray (2016) Sinha and Murugavelh (2016) Yin et al. (2016) Roschat et al. (2017)
		Treat with 0.005M HCl (2 h) and calcine (800 °C)	Cho & Seo (2010)
		Wash, dry (110°C, 6 h), mix egg shells and sea shells (1:1 wt.) and calcine (550°C, 3 h). Mill with TiO_2 and calcine (550°C, 1 h and 1050°C, 3.5 h). Mix with binder, pseudoboehmite or γ-aluminium oxyhydroxide (3:1 wt.) using 2.5 % (v/v) nitric acid and extrude (2.5 mm diameter).	Semwal et al. (2011)
		Wash, remove membranes, dry (70°C, overnight), ground (<1 mm), calcine. Impregnation/co-precipitation with magnesium and potassium nitrates and calcine (830 °C, 4 h).	Olutoye et al. (2011)
		Wash, dry (120°C, 10 h), crush and sieve (100-150 mm), KF modification-thermal treatment and calcine (800 °C, 12 h)	Zeng et al. (2015)
		Wash, dry (overnight, 105 °C) and crush. Mix with Na_2SiO_3 solution at pH 8.0. Stir the mixture (500 rpm, 4 h), dry (100 °C, overnight) and calcine (800 °C, 4 h)	Chen et al. (2015a)
		Sieve dry raw rice husk, wash, filter, dry (105 °C) and calcine. Wash the eggshell, dry (105 °C, 24 h) and calcine (800 °C, 4 h). Load calcined eggshell onto the ash by wet impregnation method	Chen et al. (2015b)
Hydrogen/Syngas	Methane oxidation	Wash with deionized water and calcine (100 °C, 4 h)	Karoshi et al. (2015)
	Wood gasification	Remove the membranes, wash and dry. Crush, sieved (250 μm), dry and calcine (900 °C, 2 h)	Taufiq-Yap et al. (2013)
	Coal gasification	Wash and dry (70 °C, overnight). Ground and sieved to 210 μm. Calcine (800 °C, 2 h)	Fan et al. (2016)
Dimethyl carbonate	Propylene carbonate and methanol transesterification	Wash with deionized water, dry (100 °C, 24 h), calcine (1000 °C, 2 h) and crush.	Gao and Xu (2012)
Bioactive compounds	Chromenones	Heterogeneous base catalyzed organic synthesis	Wash and remove the membranes. Dry (120 °C, 1 h). Mill and mix the eggshell powder with CH_2Cl_2 and place in an ultrasonic bath (60 Hz, 50 °C, 1 h). Filter and dry at room temperature.	Mosaddegh (2013)
			Wash and remove the membranes. Wash and dry at room temperature. Crush and mill by mortar.	Mosaddegh & Hassankhani (2013)
	Pyrans	Heterogeneous base catalyzed organic synthesis	Wash, clean, dry and treat by ball-mill.	Mosaddegh et al. (2013)
			Wash and remove the membranes. Wash and dry (120 °C, 1 h).Mill and calcine (900 °C, 1 h).	Mosaddegh and Hassankhani (2014)
	Benzylideneprop anedinitrile	Knoevenagel condensation	Dry (100 °C), crush and calcine (900 °C, 3 h).	Patil et al. (2013)
	Polyhydroquinoline derivatives	Unsymmetrical Hantzsch condensation	Wash and dry (80-90 °C, 24 h). Ground by mortar and calcine (900 °C).	Morbale et al. (2015)
	Benzothiazoles	Heterogeneous base catalyzed organic synthesis	Dry (100 °C, 2 h), crush and calcine (900 °C, 3 h).	Borhade et al. (2016)
	Lactulose	Lactose isomerisation	Wash, dry (105° C, 4-24 h), ground (~5 μm)	Montilla et al. (2005)
			Wash, dry (105°C, 12 h), ground and sieved (177 μm)	Nooshkam & Madadlou (2016)
Nanocomposites	Reduction of dyes in wastewater	Mix dried powered of eggshell with $CuCl_2$ and/or $FeCl_3$ and aqueous extract of *Orchis mascula* L. in alkaline medium. Heat (70 °C), shake and filter	Nasrollahzadeh et al. (2016)