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WASTE EGGSHELLS AS CATALYSTS: AN ENVIRONMENTALLY-FRIENDLY APPROACH

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ABSTRACT

The survival of mankind, the ecosystem and the development of society is inextricably linked to sustainability. The land has become heavily polluted following the uncontrolled dumping of huge quantities of waste. To address this issue, an environmentally-friendly protocol capable of yielding heterogeneous catalysts of immense value from waste eggshells whilst minimizing pollution has been designed. These synthesized heterogeneous catalysts developed from waste eggshells will replace the existing homogeneous process. This article highlights the key aspects of preparing heterogeneous catalysts from waste eggshells for use in the synthesis of CaO, to be applied in Biodiesel synthesis, environmental remediation, and organic transformation. It moreover addresses key issues relating to future recommendations for the development of more efficient CaO catalysts from waste eggshells. These CaO eggshell catalysts are characterized by X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), Thermogravimetric-Differential Thermal Analyzer (TG-DTA), Scanning electron microscope (SEM), and Brunauer-Emmett-Teller (BET) surface area, showing the structure, morphology, porosity, thermal stability, reusability, of catalysts. Indeed, eco-friendly heterogeneous catalysts developed from eggshell wastes via biochemical methods represent a cleaner and reusable method and, over the next two decades, are destined to become increasingly popular and to promote the global economic growth of Namibia.

1. INTRODUCTION

The modern era has been facing severe challenges of climate change and energy depletion (Malins et al., 2014). Due to industrialization and rapid population growth, energy consumption has increased rapidly over the last two decades and will continue to grow at an alarming rate in the future (Uslu et al., 2008). Every year, millions of tons of potentially valuable eggshell waste is trapped in landfills. However, in the European Union, by the year 2030 an estimated 44 million tons of MSW will have been deposited, whilst oil reserves will be exhausted over the next 63 years (Tabatabaei et al., 2015). Although 8.7 million tons of energy have been recovered from household waste, the presence of incineration plants in the EU increased by a negligible 0.7% in 2013 (Tabatabaei et al., 2015). Jayathilakan et al. (2012) reported the higher viability of readily available animal bones and seafood wastes as feedstocks for the production of calcium-based catalysts. Global production of mollusks and meat is estimated to exceed 160 and 300 million tons per annum, respectively, with up to 28 wt% of the livestock ending up as non-edible solid waste, including bone. Waste generated from the shrimp, crab and lobster market currently averages between 6 and 8 million tons per annum. However, a recent increase in the cost of waste export and storage has been observed, leading to the notion whereby waste incineration plants might start to monopolize the waste management market. Regulations established for the energy sector advocate the use of more efficient sources of primary energy and a substantial reduction in the use of energy from alternative fuels (Jayathilakan et al., 2012). The storage of waste is strongly discouraged due to possible pollution of the air (greenhouse gas (GHG) emissions), soil, and vegetation, ultimately placing wildlife at harm as they consume waste or rotten food.

Furthermore, at times components from unprocessed waste are discharged into water reservoirs resulting in the pollution of water bodies and posing a significant threat to the aquatic environment. For example, garbage patches (clusters of garbage floating freely on the surface) that form in streams, ponds, lakes, rivers, seas, and oceans are one of the greatest threats to the aquatic environment (Fava et al., 2015). Data present in literature illustrate how a new area of catalysis is starting to attract more attention.

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The use of homogeneous catalysts in the field of biodiesel production is well known, although difficulties are encountered in separating these catalysts; this type of problem however may be mitigated by replacing homogeneous catalysis with solid heterogeneous catalysts.

However, in transesterification reactions, calcium compounds, solid base catalysts, have been exploited in diverse forms (oxide, hydroxide, carbonate, and diglyceroxides). CaO is an environmentally friendly material classified as a heterogeneous base catalyst generally derived from $CaCO_3$, $Ca(NO_3)_2$ or $Ca(OH)_2$ as raw materials. Limestone is frequently used to obtain CaO, although the less expensive but lengthy process required for the synthesis route is not easy to achieve. Accordingly, this option is not a preferred option due in large part to its non-renewable nature (Correia et al., 2014). Based on this limitation, eggshell waste catalysts have been reported to be excellent heterogeneous catalysts for use in the transformation of a series of organic compounds, including the production of biodiesel from waste cooking oil, the synthesis of bioactive compounds and environmental applications (Fava et al., 2015).

2. ECONOMIC FACTORS

In 2023 Lanzon et al. reported a continued growth in the production of hen eggs in recent decades, reaching a total of 82.4 million tons in 2019, i.e. approximately 1480 billion eggs per year (Lanzon et al., 2023). The European Commission predicts a projected increase in the per capita consumption of eggs to 15.0 kg (14.2 kg in 2021), with production expected to increase up to 6.77 million tons (with an average annual growth rate of 0.7%) by 2030 (Arizzi et al., 2015). Moreover, from a green chemistry and global point of view, the reaction illustrated in below in equations 1 and 2 results in a higher atom economy (62.7%) compared to both conventional routes using NaOH and $CaCl_2$ (38.74%) or those involving polymeric exchange resins (51.03%) (Anastas & Warner, 1998). Finally, the CO_2 emission factor is comparable to or even lower than that associated with manufactured chemical reagents. Although the first step (eq. 1) entails CO_2 release, $Ca(OH)_2$ is later transformed into $CaCO_3$, making the CO_2 balance stoichiometrically neutral for the chemical reaction. In addition, the CO_2 emission factor associated with CaO fabrication from $CaCO_3$ is estimated to be about 0.79 kg of CO_2/kg (Anastas & Warner, 1998).

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \quad (1)$$
$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

Due the huge quantities involved, eggshell waste constitutes a considerable burden, leading to economic loss and environmental pollution, although, as reported by Fava et al. (2015) this waste is readily convertible into a series of valuable commodities for domestic and industrial applications. Transition metal oxides (TMOs) such as zirconia and titanium oxide were initially studied to evaluate the feasibility of their use as solid acid catalysts in the field of biodiesel production (Xie & Li, 2006). The main limitations of using acid catalysts are associated with long reaction times and high reaction temperatures (Xie & Li, 2006). Solid base catalysts such as calcium oxide (Kim et al., 2010), magnesium oxide (Noiroj et al., 2009), alkali alumina (Freedman et al., 1986), hydrotalcite (Ilgen et al., 2009), zeolite (Zabeti et al., 2015) are promising for use as heterogeneous catalysts to substitute acidic and basic catalysts. However, the majority of processes use very expensive synthetic chemicals, although literature data report how eggshell wastes are well known for their use in a range of applications as heterogeneous catalysts. One notable example is biodiesel production by means of a conventional transesterification process using a homogeneous alkaline catalyst (Ghosh et al., 2016). This process is fast and efficient, achieving a conversion rate of more than 95% at 60°C over a 1 h reaction time. However, the process also has a number of limitations, including formation of side products and soaps (Ravindran et al., 2012) and being a complicated process to achieve separation of the product using homogeneous catalysts (Loehr, 2012). Indeed, a series of different methods have been developed or are undergoing development for the production of catalysts from eggshell wastes.

3. METHODS

The synthesis of calcium oxide and calcium oxide NPs differ, invariably favoring the process which yields the best performance over a high surface area (Habte et al., 2019). Synthetic methods are generally classified into physical, chemical, and biological. Physical methods include thermal decomposition Sadeghi et al., 2022), the sono-chemical method (Alavi & Morsali, 2010), microwave processing (Roy et al., 2013), co-precipitation (Ghiasi & Malekzadeh, 2012), and the sol-gel method (Darcanova et al., 2015). Ball milled grinding methods are used for the preparation of CaO nanoparticles (Darcanova et al., 2015). Synthesis of Nano CaO from waste eggshell is achieved using plant extracts such as Mentha piperita (Ijaz et al., 2017), benign papaya leaf extract and green tea extract (Anantharaman et al., 2016), and rhododendron arboretum extracts (Ramola et al., 2019). These plant extracts contain bioactive compounds including antioxidants, phenols, enzymes, amino acids, and sterols acting as reducing agents (Aljabali et al., 2018). CaO from waste eggshell was prepared by boiling in water, followed by calcination of the waste eggshell at 900°C for 3 hours (Awogbemi et al., 2020; Lanzon et al., 2023). Initially, the eggshells were washed with deionized water and dried at 130°C for three hours. The dry material was heated at 550°C for five hours to eliminate the remaining organic matter. In the final step, the dry shell was calcined at 1100°C for two hours to form CaO (Awogbemi et al., 2020). Osman et al. (2022) reported grinding dried eggshells using an electrical milling machine for 5 min, after which the fine powder was calcined at 900°C for one hour, resulting in CaO.

This novelty of this article focuses on the benefits represented by synthesizing CaO catalysts from eggshell waste with the aim of minimizing environmental pollution and reducing the amount of wastes forwarded to land fill, thus complying better with environmental regulations; this eco-friendly process therefore plays a major role in converting eggshell waste into a valuable heterogeneous catalyst for use in a range of applications. CaO from waste eggshells is produced in large quantities by simply calcining eggshells in air at high temperatures - the method used is simple, the reaction time is relatively short, and the product yield is high, with a large surface area. Eggshell waste catalysts can be used in a wide range of applications in biodiesel production, civil engineering, medicine, water treatment, and synthesizing bioactive compounds.

3.1 Relevance

A wide range of physical, chemical and biological techniques are adopted in the synthesis of CaO from waste eggshells, yielding a compound featuring a relatively high catalytic activity, good thermal-electrical properties and chemical stability. The synthesis of CaO focuses on environmentally friendly and economical processes. The synthesis of waste eggshells is moreover a highly economical and socially-acceptable process. Going forwards, additional efforts will focus on waste prevention and the recycling of waste eggshell into high-quality CaO catalysts as secondary raw materials.

3.2 The Rationale

A series of different methods are available for use in the synthesis of CaO, all of which may be further modified changing reaction parameters. CaO is used in synthesizing composites, cosmetics, cement production, and $CaCO_3$ particles as fillers in polymer composites, construction materials, metal and antimicrobial activity. Eggshell waste yields a range of potential benefits including use as an additive in calcium phosphate bio-ceramics as a calcium supplement (Sakai et al., 2017); Siemiradzka et al., 2018), adsorbent material (Witoon, 2011), as a solid catalyst for biodiesel production (Gupta et al., 2018; Huang et al., 2020), bone graft substitute (Salama et al., 2019), and for environmental remediation (Mignardi et al., 2020). Ok et al. (2011) investigated the use of CaO in heavy metal removal, whilst Choi & Lee (2015) looked at the use of CaO to produce green hydrogen in renewable energy streams. In the medical field, CaO NPs have been successfully applied in drug delivery. Ali et al. (2015) conducted a study in rats using manual hematoxylin and eosin staining protocols, reporting a finding of toxicity of CaO nanoparticles featuring acute tubular and hepatic degenerations in the rat kidneys and liver, respectively. Tangboriboon et al., 2012, reported how CaO prepared from waste eggshells is characterized by the use of physical methods such as XRD, SEM, TGA and FTIR. From this study, the organic (C/H/N) composition of raw duck eggshells were investigated using an elemental analyzer. The average percentages detected of carbon, hydrogen, and nitrogen amounted to 13.64%, 0.49%, and 0.63%, respectively.

4. FOOD WASTE MATERIALS FOR THE PRODUCTION OF NANOPARTICLES

The development of efficient and cost-effective approaches aimed at decreasing organic waste and developing better food waste operational practices, capable of improving overall management of the food supply chain is paramount. Several techniques for the processing of waste fruits, vegetables and grains have been explored (Ghosh et al., 2016); Ravindran & Jaiswal, 2016). These approaches aim to exploit the value and practical advantages of food waste, eventually reducing the amount of waste deposited at landfills (Loehr, 2012). Food waste and nanoparticle synthesis may, at first sight, appear an unlikely partnership. However, recent studies reported in the literature have revealed the active role that biomolecules play in reducing precursor metal ions in aqueous solutions to produce nanoparticles (particles less than 100 nm) featuring exceptional medicinal and pharmaceutical properties. The biomolecules also act as reducing agents/capping agents that promote particle growth in different angles and prevent nanoparticle agglomeration (Shah et al., 2015). The synthesis of nanoparticles from food waste has the potential to deliver consistently sustainable and green chemistry-based technologies that are eco-friendly, hence reducing the human health and environmental risks generally associated with the use of toxic solvents and chemicals with conventional processes (Anastas & Warner, 2000). In recent decades, considerable interest has been generated amongst the scientific community in nanotechnology research due to their exceptional physiochemical properties and application in several fields such as pharmaceuticals, biomedicine, electrical, environmental, food, and agriculture industry. The small size and large surface area to volume ratio are two substantial features of nanoparticles, which display improved properties compared to conventional processes (Willems, & van den Wildenberg, 2005). For example, gold (Au) nanoparticles are now widely used in medicine for diagnostics (Torres-Chavolla et al., 2010), targeted delivery of pharmaceuticals (Bhumkar et al., 2007), Paciotti et al., 2004) and tumor destruction via hyperthermia (Huang et al., 2006). Silver (Ag) nanoparticles display a broad range of antimicrobial activity against numerous human and animal pathogens (AshaRani et al., 2009); as a result, they are used as antimicrobial agents in a wide variety of medical and consumer products (Tran et al., 2013). Moreover, platinum (Pt) and palladium (Pd) nanoparticles have been used as catalysts in the production of value-added products (Cheong et al., 2010; Lin et al., 2011).

Furthermore, metal oxide nanoparticles such as copper oxide (Cu_2O, CuO) and zinc oxide (ZnO) have displayed antimicrobial activity (Abboud et al., 2014); accordingly, ZnO nanoparticles have been used in a variety of food packaging applications (Espitia et al., 2012). Dubey et al. (2010) reported the formation of 16-nm Ag spheres and 11-nm Au nano-triangles when Tanacetum vulgare (tansy fruit) extract was reacted with aqueous solutions of $AuCl_4^-$ ions and Ag^+ ions, respectively. In addition, numerous other food waste extracts, including Pyrus sp. (pear fruit) and Mangifera indica (mango peel), have displayed the potential to reduce Au (III) ions to form Au nanoparticles (Yang et al., 2014; Edison & Sethuraman, 2012). Citrus sinensis (orange peel) and Ananas comosus (pineapple) extracts have revealed potential in reducing Ag^+ ions in aqueous solutions to form Ag nanoparticles (Kaviya et al, 2011). Similarly, Pt and Pd nanoparticles have been synthesized via Musa paradisiac (banana peel), tea, coffee extracts, and lignin (Namvar et al., 2015; Nadagouda & Varma, 2008). Kaviya et al. (2011) studied the formation of Ag nanoparticles using Citrus sinensis (orange) peel extract as the reducing agent; the reduction of Ag nanoparticles was formed swiftly in 20 min, with the observation that NPs formation changed swiftly from colorless to yellowish-brown. Consequently, the characterization of Ag nanoparticles from SEM analysis revealed a spherical nanoparticle morphology, with a profoundly changed size depending on reaction temperature. At 25°C, mean particle size was 35 ± 2 nm; at 60°C, size was 10 ±1 nm (Kaviya et al., 2011). Furthermore, Ateeq et al. (2021) reported the synthesis of Ag NPs from *Pennisetum Glacuum* rice husks for the removal of algae from wastewater. In this study, AgNPs were doped on charcoal for the oxidation of benzyl alcohol to benzaldehyde. A significant role is played by food waste due to the presence of a wide range of phytochemicals, such as polyphenols, which act as capping agents, influencing the orientation and assembly of smaller particles during subsequent growth. The modelling action designed by surfactants during biological synthesis indicates that the change in NPs occurs following the pathway (Chiu & Ruan, 2013; Gao et al., 2020).

Nanoparticle growth ultimately leads to the formation of morphological structures such as spheres, cubes, triangles, hexagons, pentagons, and wires (Akhtar, Panwar, & Yun, 2013). The following experimental parameters play a significant role in the formation of nanoparticles: (1) the nature of food waste extract, (2) the concentration of food waste extract in the reaction mixture, (3) metal ion concentration in the source solution; (4) reaction mixture pH; (5) reaction mixture temperature; (6) contact time and (7) choice of solvent. All these parameters are vital for nanoparticle formation and exhibit their physiochemical properties (Dwivedi & Gopal, 2011; Obadiah et al., 2013).

Nasrollahzadeh et al. (2016) reported the synthesis of nanocomposites with eggshell catalysts by reduction method, i.e. mixing dried eggshell powered with $CuCl_2$ and $FeCl_3$ and aqueous extract of Orchis mascula L.in alkaline medium. The removal of dyes from wastewater was observed by heating at (70°C), stirring and filtering (Nasrollahzadeh et al., 2016). Vandeginste (2021) reported the synthesis of nanocomposites from corn starch, bioplastics, bacterial cellulose, polypropylene carbonate, polylactic acid, poly (diethylene glycol succinate) (PDEGS), polypropylene (PP), and polyvinyl alcohol (PVA) using eggshell, $NaClO_2$ solution, NaCl solution, NaOH solution, methanol, acetone or dimethylformamide. After washing, the eggshells were dried at room temperature or in an oven (either in air or under vacuum) at an elevated temperature, 50-110°C. Different parameters are used for the synthesis of nanocomposites derived from eggshells (Huang et al., 2020). In recent years, there has been an extensive search for natural antimicrobial agents capable of overcoming the limitations of currently available synthetic antimicrobial pharmaceuticals. For example, copper (Cu) and Cu oxide nanoparticles are natural antimicrobial agents that have been biosynthesized using a variety of plant-derived extracts. Lee et al. (2011), reported the synthesis of Cu nanoparticles from leaf extract of Magnolia Kobus. Spherical particles of Cu nanoparticles formed in the 40 to 100 nm range and displayed excellent antimicrobial properties towards Escherichia coli (Lee et al., 2011). From a marine phytoplankton perspective, Abboud et al. (2014) reported the biosynthesis of copper oxide nanoparticles using brown algal extract from Bifurcaria bifurcata. The resulting Cu nanoparticles were spherical, ranged in size from 5 to 45 nm and displayed good antibacterial properties towards both Enterobacter aerogenes and Staphylococcus aureus (Abboud et al., 2014). Nagarajan & Kuppusamy (2013) reported the synthesis of zinc oxide (ZnO) nanoparticles from a brown seaweed extract (Sargassum myriocystum) that displayed excellent antimicrobial properties against several bacteria and fungi. In an attempt to provide a solution to the above shortcomings, the following should be achieved: (1) development of a mechanism for nanoparticle formation, (2) investigation of experimental parameters on nanoparticle size, shape and solvent dispersion, (3) refining of the biosynthesis process to improve reproducibility and activity of NPs for antimicrobial activity, any biochemical reactions and environmental remediation (Jha et al., 2009). Moreover, to promote commercialization the following are required: (1) development of new technologies to overcome the limitations of scaling up the biosynthesis process; (2) development of a continuous supply route for suitable aquacultural and horticultural food waste; and (3) optimization of the waste management chain to utilize biomolecules and bioactive chemicals present in aquacultural and horticultural food waste to produce nanoparticles (Parfitt et al., 2010).

4.1 Eggshell waste as catalysts

Eggshell represents approx. 10% of a hen egg, an elementary foodstuff widely consumed worldwide for domestic and industrial uses. Eggshells are generally produced in large amounts by egg processing industries. Vast quantities of this solid residue are still disposed of as waste in landfills without any pretreatment, which leads to organic pollution of the environment (Gao & Xu, 2012). Eggshell is made up of 96% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, organic materials (mainly proteins) and water (Oulego et al., 2020). The structure of an eggshell can be divided into three layers: a thin mammillary inner layer without pores, a thick palisade middle layer comprising many large pores, and a thin cuticle outer layer with no pores (Tan et al., 2015). However, the eggshell contains approximately 7,000-17,000 funnel-shaped canals distributed unevenly on the eggshell surface, which makes it a highly feasible option for energy and mass transfer (Guo et al., 2019). However, eggshell waste is an excellent bio-template that can be recycled as an economical and eco-friendly carrier of metal nanomaterials. Eggshell waste has been used in numerous studies performed to date as a low-cost catalyst for biodiesel production and an adsorbent for the removal of metal ions from wastewater (Goli & Sahu, 2018), as displayed in Table 1. In addition, the use of eggshell membranes as a catalyst has been studied in wastewater treatment processes (Oulego et al., 2020). Al-Ghouti & Salih (2018) reported how the use of waste eggshells as a catalyst eliminates waste whilst

TABLE 1: Comparation of eggshell catalysts and applications.

Product	Process	Egg catalysts preparation	Reference
Hydrogen/Syngas	Methane oxidation/Wood gasification	Methane oxidation Wash with deionized water and calcined (100°C, 4 h). Remove the membranes, wash and dry. Crush, sieved (250 mm), dry and calcine (900°C, 2 h).	Karoshi et al., 2015
Wood	Coal gasification	Wash and dry (70°C, overnight). Ground and sieved to 210 mm. Calcine (800°C, 2 h).	Taufiq-Yap et al., 2013
Biodiesel	Oil transesterification		Shinha & Murugavelh, 2016
Hydrogen	Syngas	Methane oxidation Wash with deionized water and calcined (1000°C, 4 h).	Shinha & Murugavelh, 2016
	Coal gasification	Wash and dry (70°C, overnight). Ground and sieved to 210 mm. Calcined (800°C, 2 h).	Shinha & Murugavelh, 2016
Dimethyl carbonate	Propylene carbonate and methanol transesterification	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. Wash and dry at room temperature. Crush and mill by mortar.	Gao & Xu, 2012
Bioactive Compounds	Chromenones Pyrans	Heterogeneous base catalyzed organic synthesis. Wash, clean, dry and treat by ball-mill. Wash and remove the membranes. Wash and dry (120°C, 1 h). Mill and calcined (900°C, 1 h).	Mosaddegh & Mosaddegh, 2013
	Pyrans Heterogeneous based catalyzed organic synthesis	Dry (100°C), crush and calcined (900°C, 3 h)	Hassankhani et al., 2016
Benzylidenepropanedinitrile	Knoevenagel condensation Derivatives	Wash and dry (80-90°C, 24 h). Ground by mortar and calcined (900°C).	Patil et al., 2013
Polyhydroquinoline	Hantzsch condensation	Wash and dry (80-90°C, 24 h). Ground by mortar and calcined (900°C) 3-4 hours.	Patil et al., 2013
Benzothiazoles	Heterogeneous base catalyzed organic synthesis	The raw eggshell powder was calcined up to 900°C, and this temperature was maintained for 3 h. Wash, dry (105°C, 4-24 h), ground (~5 mm)	Borhade et al., 2016
Lactulose Lactose	Isomerization	The egg shells were washed with water; subsequently the eggshells were dried at 105°C for 12 h, grounded and sieved by 80 mesh screen (mesh size, 177 lm).	Nooshkam & Madadlou, 2016
Nanocomposites Nano composites (PP, Corn starch, Bioplast, bacterial cellulose, Polypropylene carbonate, Polylactic acid, poly(diethylene glycol succinate) (PDEGS), polyvinyl alcohol (PVA).	Reduction	Eggshells with a $NaClO_2$ solution, NaCl solution, NaOH solution, methanol, acetone or dimethylformamide. After washing, the eggshells are dried at room temperature or in an oven (either in air or under vacuum) at elevated temperature, generally between 50 and 110°C, and there are a few studies that report drying at 200 or 250°C. The drying time varies from half an hour to several days.	Vandeginste et al., 2021
Egg shell supported CuO catalysts	Blue 19 degradation	Egg shell washed with deionized water and dried in oven at 80°C, powdered sieved through 100 mesh. Then known amount egg shell and $CuSO_4$ solution is is added and stirred for 16hr at room temperature. Then the blue solids were washed with ethanol and deionized water several times and dried in oven at 80°C. And then CuO was obtained by calcining the prepared CuO egg shell at 600°C for 2 hours.	Xu et al., 2022
Valorization of eggshell waste	Construction materials: Concrete, clay bricks, ceramic tiles, Compressed stabilized blocks (CSBs)	The Egg shell washed with deionized water and dried in oven at 100°C for 24 hours. And calcined between 600-1000°C in oven for 2-4 hours.	Ngayakamo & Onwualu, 2022
Waste mud crab shell	Transesterification reaction.	Waste shell is washed with water and dried in oven at 105°C for overnight. Then calcined in furnace at 900°C for 2 hours.	Boey et al., 2009
Egg shell waste	For removal of phenol from aqueous solution	Eggshells were prepared and sieved with a sieve of 425 µm. And the egg shells were at different temperatures at 200˚C, 400˚C, 600˚C, 800˚C and 1000˚C for 2 h.	Chiraibi et al., 2016

Valorization of eggshell waste	Removal of Co^{2+} ions from aqueus solutions	Eggshells were washed several times with tap and they were dried at 105˚C for 24 h in an oven, then the catalysts were calined in furnace at 600˚C for 2 hours.	Mignardi et al., 2020
Waste egg shell catalysts	Biodiesel production	Egg shell poweder was calcined at 900˚C for 2 hours to produce CaO catalysts.	Ari et al., 2017
Egg shell catalysts	Synthesis of 2-arylbenzothi-azole derivatives	Egg shell powder is shwahse with water and ried in oven at 100˚C for 2 hours. Then calciend in furnace at 900˚C for 3 horus.	Borhade et al., 2016
Calcined waste egg shell	Material science in catalysis, pharmaceutical and mechano-chemistry	Waste egg shell is converted to CaO cata-lysts by many methods ie calcined at 900˚C in furnace for 2 hours.	Balaz et al., 2021
Monetite micro particles from eggshell waste	Environmental applications, fuel additive	Calcined egg shell and disodium phosphate were added into it and pH 2 was adjusted with concentrated hydrochloric acid and stirred for 30 min at room temperature and refluxed at 80˚C for 2 h. Then it was dried in an oven at 80˚C for 24 h and ground to fine powder.	Khan et al., 2020

concomitantly producing low-cost catalysts. This contributes towards maintaining a clean environment and, at the same time, reducing prices of the end-products. Shan et al. (2016) reported how the development of CaO-based catalysts for biodiesel production from waste eggshells represents a promising technology. However, the present review focuses on recently developed studies, showing the potential of eggshell waste to be used as a low-cost catalyst in the manufacture of various compounds. CaO from waste eggshell catalysts is characterized by XRD, FTIR, TG-DTA, SEM spectroscopy and BET surface area (Shan et al., 2016). Table 1 presents the details of egg catalysts developed for use in a wide range of applications.

4.2 Synthesis of biodiesel with eggshell catalysts

A rise in global warming and fossil fuel energy crises have prompted scientists/researchers to seek alternative fuels, with proving to be the most prominent alternative fuel. Biodiesel is renewable, nontoxic, and environmentally-friendly, being synthesized from oils and animal fats (Goli & Sahu, 2018). However, the use of expensive catalysts has made this process unsustainable in the long-term. The first use of eggshell as a catalyst in the production biodiesel with a 98% yield was reported by Shan et al in 2016 and Al-Ghouti & Salih in 2018. Several modifications have since been developed for the synthesis of CaO catalysts from waste eggshells to improve the yield of biodiesel (Oulego et al., 2020). Calcination temperature has emerged as a pivotal factor in the production of efficient solid base catalysts from mollusk/eggshells comprised of $CaCO_3$. The Thermal Gravimetric Analysis (TGA) and X-Ray diffraction (XRD) characterization analysis shows the decomposition of $CaCO_3$ to CaO at temperatures of 700°C, resulting in active transesterification catalysts, typically offering >90% conversion of palm, soybean and Karanja oils in 2-6 hours at 60-70°C reaction temperatures with alcohol:oil molar ratios around 10, and catalyst loadings of 2-5 wt%. Regeneration of deactivated eggshell-based catalysts is usually achieved through re-calcination at 900°C. Another major drawback with these catalysts is the leaching of Ca^{2+} into the alcohol phase of the reaction media, leading to a gradual loss of activity (Boey et al., 2009). However, deactivation of CaO catalysts is caused by exposure to air (Birl et al., 2012). As reported by Corrie et al. (2014) when compared with the calcined crab waste, the high Ca content present on calcined surface of eggshells is attributed to a better catalytic performance in the transesterification of waste cotton cooking oil with calcined eggshells. However, using pistachios, shell yield was 84% (catalyst 3 wt%, methanol/oil molar ratio 9-12:1 at 60°C). Roschat et al., 2017, reported the potential of use of rubber seed oil in the production of biodiesel using coral 10 wt% CaO-based catalysts in methanol in 180 minutes, resulting in a 97% yield. With 100% coral catalysts, the transesterification reaction took longer (210 min) under optimum conditions (catalyst 9 wt%, 12/1 methanol/oil molar ratio and 65°C). Asri et al. (2017) reported how using eggshell catalysts, biodiesel yields gradually increased from 72.05 to 75.92% over a period of 6-7 hours at 65°C. Crushed eggshell chips were powdered and passed through 100 and 200 micron sieves and egg catalysts were then calcined at 900°C for one hour (Asri et al., 2017). Farooq et al. (2018) reported the preparation of an effective catalyst from waste chicken eggshells at three different temperatures (800°C, 900°C and 1000°C). Date seed oil, 5 wt.% catalyst, 12:1 methanol: oil ratio and conversion efficiency of biodiesel was 93.5% at the end of 1.5 hours (Farooq et al., 2018). However, a similar study conducted by Obadiah et al. (2012) reported order of magnitude increases in surface area from 680 m^2g^{-1} to 885 m^2g^{-1} of calcined sheep bone with calcination temperature, 600-800°C (Obadiah et al., 2012). Chakraborty et al. (2010) studied the preparation of calcium-based catalysts from ash scales using a similar route, with calcination at 900°C for 2 hours yielding a porous material comprised of mainly b-tricalcium phosphate with a surface area of 39 m^2g^{-1}, resulting in 98% fatty acid methyl esters (FAME) and transesterification of soybean oil for 5 hours at 70°C using merely 1 wt% of eggshell catalyst and low methanol: oil ratio of 6. In another study, Zn/CaO was synthesized from waste hen eggshells and investigated for use in the synthesis of biodiesel using waste frying oil (WFO) as a feedstock (Rahman et al., 2021; Rahman et al., 2022). The waste eggshells were calcined at 900°C to obtain CaO, with Zn impregnated on CaO via the wet incipient impregnation method, resulting in a yield ranging from 64 to 91% of biodiesel oil. Khan et al. (2022) reported on the preparation and application of mussel shell CaO catalysts impregnated with praseodymium to obtain CaO-praseodymium catalysts 3, 5, 7, 9 & 11 wt% for use in the production of biodiesel by transesterification reaction from castor oil. However, Khan et al. (2022) reported that the optimization of reaction time, temperature, and transesterification was carried out at different temperatures: 50°C, 55°C, 60°C, 65°C with different intervals of time from two to 5 hours, 2.5% catalyst loading rate and 8:1 methanol to oil ratio. The maximum yield obtained was 87.42% over a 4-hour period (Khan et al., 2022). Anantharaman et al. (2016) studied biodiesel production using eggshell catalysts prepared by washing with deionized water and oven drying at 100°C for 24 hours. The catalysts were calcined in the range of 700-1000°C in a furnace for 2-4 hours, resulting in an 80% yield of biodiesel.

5. APPLICATIONS OF EGGSHELL CATALYSTS

5.1 Synthesis of bioactive compounds

Eggshell-derived catalysts have been used for the synthesis of bioactive compounds such as benzothiazoles, bioactive molecules scaffolds with antitumor, antiallergic, antidiabetic, and antimicrobial agents (Balaz et al., 2021). Eggshell CaO catalysts have been applied to produce critical industrial chemicals, such as dimethyl-carbonate, oximes, and glycerol oligomers. CaO eggshell catalysts were simply prepared by milling using low-cost tools such as mortar and pestle. Other methods used in the preparation of eggshell catalysts include mechanochemical methods, ultrasound treatment, and impregnation approaches (Balaz et al., 2021). Oulego et al. (2020) reported the conversion of eggshell wastes to CaO catalysts and subsequent use in the synthesis of different bioactive compounds such as chromenones, pyran derivatives, polyhydroquinolines, aromatic aldehydes, and carbohydrates. Nitrogen-containing phthalazine compounds and other N-heterocycles are potentially indicated for a range of antimicrobial, antioxidant, and anti-convulsant applications. These compounds are synthesized through a multicomponent reaction using heterogeneous catalysts (Balaz et al., 2021). In a study by Balaz et al. (2021), eggshell-derived catalysts were employed to synthesize pyrozolo-phthalazine derivatives through four-component condensation, such as Knoevenagel-Michael reaction. This reaction was conducted in water as a green solvent under moderate conditions (temperature, shorter reaction time). The study revealed a good catalytic performance for eggshell catalysts, achieving up to 98% yield of the end product (Balaz et al., 2021). Chromenes and Pyrans were produced using heterogeneous base catalysts prepared from eggshells. The eggshell catalysts were synthesized by washing and removing the membranes and were then dried at 120°C for one hour. The milled eggshell powder was mixed with CH_2Cl_2 and placed in an ultrasonic bath at 60 Hz, 50°C for one hour. The catalysts were filtered and dried at room temperature before being calcined at 900°C for one hour to yield CaO catalysts (Mosaddegh, 2013; Mosaddegh & Hassankhani, 2014). In another study, the benzylidene propanedinitrile derivative was synthesized via Knoevenagel condensation (Patil et al., 2013). In this study, eggshells were dried at 100°C, crushed and calcined at 900°C for three hours, yielding 97% CaO catalysts. Polyhydroquinone was synthesized by means of the Hanzsch reaction over a 45-minute period, providing a yield of 84-96%. Eggshell catalysts were crushed and dried at 100°C for 2 hours and then calcined at (900°C, 3 h) (Borhade et al., 2016; Nooshkam & Madadlou 2016). Borhade et al. (2016) reported the synthesis of unsymmetrical benzothiazoles with eggshell catalysts synthesized in solvent-free conditions using a grinding method at room temperature. The reaction proceeded smoothly and resulted in excellent yields (86-97%), with a shorter reaction time (15-48 min). Catalysts were dried at 100°C for two hours and crushed and calcined at 900°C for three hours (Borhade et al., 2016). Lactulose and lactose were obtained with 70% conversion with eggshell catalysts, washed, dried at 105°C for 4-24 h, and ground (~5 mm). The second set of eggshells was washed, dried (105°C, 12 h), ground and sieved (177 mm) (Nooshkam & Madadlou, 2016) as summarized in Table 1.

5.2 Other applications

The use of eggshell waste as a catalyst has also been investigated in the synthesis of hydrogen; d during hydrogen production, biomass gasification, on wood for example, was carried out in the presence of an eggshell catalyst. Hydrogen production is an alternative, environmentally-friendly source of energy. Oulego et al. (2020) reported the observation of an increase in hydrogen production of up to 23% when CaO from eggshell was utilized as a catalyst. Another green chemistry/environmentally friendly reaction that spiked interest involved the use of eggshell waste to produce dimethyl carbonate. Dimethyl carbonate can replace dimethyl sulfate and methyl halides in methylation reactions and harmful phosgene in polycarbonate and isocyanate synthesis. Eggshell catalysts is used to synthesize dimethyl carbonate through transesterification of propylene carbonate. The conversion of propylene carbonate and the yield of dimethyl carbonate was observed as 75%, and 80%, respectively as reported by Oulego et al. (2020). Additionally, dimethyl carbonate was prepared from propylene carbonate and methanol. The eggshell catalysts used were washed with deionized water, dried at (100°C, for 24 h), and calcined (1000°C, 2 h), resulting in a 12-66% yield (Gao & Xui et al., 2012; Ngayakamo & Onwualu, 2022). Ngayakamo & Onwualu (2022) reported the possibility of using eggshell catalysts as filler in construction materials such as concrete, clay bricks, ceramic tiles, and compressed stabilized blocks (CSBs) with valorization of eggshell catalysts. Solid base catalysts developed from heterogeneous waste solid bases characteristically offer considerably higher rates of transesterification reaction than solid acid catalysts (Boey, et al., 2009). A plethora of literature exists with regard to the application of CaO as transesterification catalysts due to the presence of calcium-rich eggshells, with the majority of these catalysts synthesized at high temperatures. Calcination at 800°C of shells from shellfish and snails has been reported (Boey et al., 2009; Birla et al., 2012; Viriya-empikul et al., 2012). This green method is an economical route for the disposal of maricultural/agricultural wastes and development of value-added products for the conversion of other wastes (Birla et al., 2012; Taufiq-Yap et al., 2013; Laca et al., 2017). Viriya-empikul et al. (2012) highlighted the crucial role played by calcination temperature in the production of efficient solid base catalysts from mollusks/ eggshells. These shells mostly possess $CaCO_3$; TGA and XRD characterization studies reveal that the decomposition to CaO at temperatures >700 results in active catalysts for transesterification reaction with the conversion of palm > 90%, soybean and karanja oils in 2-6 hours at 60-70°C, alcohol: oil molar ratios around 10, and catalyst loadings of 2-5 wt.%. (Viriya-empikul et al, 2012). Nurfitri et al. (2013) observed that deactivated waste shell-based catalysts can be regenerated by re-calcination at 900°C. However, regeneration of these catalysts by calcination implies higher energy costs and may not be feasible for industrial processes, as reported by Boro et al. (2012). The major concern with these catalysts is the leaching of Ca^{2+} in the reaction of the alcohol phase, which leads to the loss of activity of catalysts due to formation of a homogeneous solution in the reaction, as well as the saponification method, in which impure or untreated oils are routinely used. Deactivation of CaO catalysts may occur due to poisoning of catalysts upon exposure to air (Bennet et al., 2016). Many calcium-containing catalysts have been developed from waste such as coral, bones, scales, and calcite-containing rocks (Bennet et al., 2016). Bennet et al. (2016) confirmed that corals are marine polyps with calcareous exoskeletons formed from aragonite, a crystalline form of $CaCO_3$. Roschat et al. (2017) studied the conversion of coral fragments to CaO by calcination at 700°C. These catalysts were used in the transesterification of various oils, including palm, soybean, rice bran and waste cooking oils, with methanol (Bennet et al., 2016). Indeed, calcination conducted at temperatures > 650°C under ideal conditions has yielded bone-derived catalysts intended to deliver conversions achieving grades comparable to laboratory grade CaO using high catalyst loadings (8-20 wt.%) with reaction temperature 80°C and alcohol, oil and CaO catalysts synthesized from mollusks or eggshells. Bennet et al. (2016) obtained conversion to fatty acid methyl esters (FAME) of 95%, 97% and 98% from waste cooking oil, safflower oil and soybean oil, respectively, after 6 h at 60 °C with a methanol: oil ratio of 12 and 7.5 wt% catalyst. A similar study was performed by Obadiah et al. (2012), who observed an order of magnitude of increases in the surface area from 680 m^2g^{-1} to 885 m^2g^{-1} of calcined sheep bone with calcination temperature in the range of 800-1000°C and conversions to fatty acid methyl esters (FAME) of 93% (Obadiah et al., 2012). Chakraborty et al. (2010) reported the preparation of calcium-based catalysts from ash scales through calcination at 900°C for 2 hours, yielding a porous material comprised of mainly b-tricalcium phosphate with a surface area of 39 m^2g^{-1}, resulting in 98% FAME in the transesterification of soybean oil for 5 hours at 70°C with merely 1 wt% catalyst and low methanol: oil ratio of 6. However, a series of ecological and sustainability issues are associated with the utilization of calcium obtained from coral and turtle shells for the industrial production of solid base heterogeneous catalysts (Chakraborty et al., 2010). A study by Khan et al. (2020) reported on issues relating to fuel addition and coating with monetite particles using eggshell waste. Karoshi et al. (2015) studied the production of hydrogen through methane oxidation; catalysts were washed with deionized water and calcined at 1000°C for 4 hours, achieving a conversion rate of 26%. Furthermore, Osman et al. (2016) reported the washing of catalysts with deionized water and subsequent calcination at (200-500°C) for use in the oxidation of methane. Eggshell catalysts were washed and dried at 70°C overnight and then crushed, ground to fine powder, and sieved at 210 mm, whilst CaO catalysts were calcined at 800°C, for 2 hours and final catalysts applied to produce important industrial chemicals such as dimethyl-carbonate, oximes, and glycerol oligomers (Osman et al., 2016), thus avoiding the presence of toxic chemicals such as dimethyl sulfate methyl halides in methylation reactions and phosgene in polycarbonate and isocyanate synthesis, dimethyl carbonate. Indeed, CaO catalysts from waste eggshells have proved to act as effective catalysts for use in the development of important pharmaceutical drugs, particularly as they meet a series of requirements established for sustainable and green chemistry techniques (Roschat et al., 2017).

5.3 Wastewater treatment

Eggshell CaO catalysts and membranes have been investigated for use in the removal of iron, cadmium, chromium, Cu (II), reactive dyes, Pb (II), phenol and iodosulphate compound (Xu et al., 2022; Chraibi et al., 2016). Cyanide was removed from wastewater using calcined eggshell catalysts and reached an excellent adsorption efficiency of 84.53% (Eletta et al., 2016; Xu et al., 2022; Chraibi et al., 2016). Another study reported the use of eggshell membranes and modified eggshell membranes as bio-sorbents for the remediation of boron from desalinated water. The eggshell membrane adsorbed 97% of boron, while the modified eggshell membrane adsorbed 95% of boron (Al-Ghouti & Salih, 2018). Adsorption technology has advanced over the decades for wastewater treatment technology. As a result, researchers/scientists have investigated various materials as adsorbents to remove pollutants from wastewater. Activated carbon as an adsorbent is synthesized from coconut husks, date seeds, pistachio seed coat, and macadamia carbonaceous bark (Ateeq et al., 2021). Recently, eggshells have attracted increasing attention for application in the removal of heavy metals and other elements from wastewater (Al-Ghouti & Salih, 2018). Eggshells are potentially capable of removing these pollutants, possessing other advantages such as being environmentally-friendly, readily available and cost-effective. Khan et al. (2020) reported how monetite particles and eggshells facilitated the degradation of Congo red dye, a carcinogenic dye and water decontamination. Monetite is an active catalyst capable of eliciting an increase in kapp value i from 0.0077 to 0.00114 min^{-1} by increasing catalyst dosage from 1.0 to 2.5 mg/ mL. It is also a good additive that results in an increased calorific value from 2.55 to 8.902 MJ/kg at a higher additive dosage of 10 to 40 ppm, as reported by Khan et al. (2020). Xu et al. (2022) prepared eggshell-supported CuO catalysts by washing with deionized water, drying at 80°C, and sieving the powder through 100 mesh; a known amount of eggshell and $CuSO_4$ solution was then added and stirred for 16 h at room temperature and blue solids were washed with ethanol, deionized water several times, and dried in an oven at 80°C. CuO was obtained by calcining the prepared CuO eggshell at 600°C for 2 hours for the degradation of blue dye, with 99.05% yield obtained in 20 min. However, the end-product was unsuitable for use as a catalyst due to the ease of aggregation of CuO nanoparticles. However, this may have been due to excessive loading of Cu solution leading to the aggregation of catalyst particles and reduction of active sites, thus inhibiting catalyst activity (Xu et al., 2022). Oulego et al. (2020) observed degradation of humic acids, analyzing the evolution over time of COD, biodegradability index (BOD5/COD), color number and pH. They achieved excellent results using 15% Cu and 5% Fe catalysts with a COD reduction of 82.3% and 75.1%, respectively, whereas use of non-impregnated eggshell catalysts produced a COD reduction of 58%. This could be attributed to metal loading and excellent metal distribution on the surface of the support (Oulego et al., 2020). Mignardi et al. (2020) reported the removal of metals from water in the range of 70-80% using eggshell catalysts.

5.4 Characterization of eggshell catalysts

Eggshell catalysts were characterized by means of XRD, SEM, DTA-TGA, FT-IR, and BET surface area.

5.4.1 X-ray Diffraction

X-ray Diffraction (XRD) is commonly used to analyze nanoparticle structure, composition and size. The eggshell catalysts were characterized by XRD, which showed a 2θ range from 10° to 90° (Wong & Ang, 2018). Eggshells possess calcium carbonate, which is the major compound. After calcination at 800°C, the concentration of calcium carbonate changed compared to the uncalcined eggshells due to the transformation of calcium carbonate into calcium oxide, leading to the observation of a calcium oxide peak which appeared after calcination at 1000°C under nitrogen gas flow (C) and in open air (D). This was attributed to the high thermal shift that occurred in the eggshells, due to the complete decomposition of calcium carbonate into calcium oxide at 1000°C (Wong & Ang, 2018). On comparing eggshell-derived CaO with commercial CaO catalyst, the peaks of the XRD profile appeared in the vicinity of the 2θ value at 35, confirming the presence of CaO.

5.4.2 Scanning Electron Microscopy

Cheng et al. (2021) reported that the morphologies of CaO, CaDG (calcium diglyceroxide), CaG (calcium glycerolate), and CaG-E (Calcium oxide from eggshell) catalysts were analyzed by Scanning Electron microscopy (SEM). The CaO surface exhibited irregularly shaped particles with considerable gaps and relatively large pores, attributable to the hollow structure of the eggshells. Commercial CaO offers a broader particle size distribution compared to eggshell-derived CaO. The large image shows the presence of cracks on the particle surface, which is ascribed to the overflow of CO_2 gas during the calcination process. The SEM image of CaDG displays particle size in the range of 7 to 10 μm and sharp rock shapes, which is consistently reported by Cheng et al. (2021). The SEM image of the synthesized CaG surface displays the formation of a single layer of irregular sheet structures. Based on these assumptions, it is evident that the large specific surface area enables the dissolution of CaG in glycerol during reuse. Hence, CaG can be utilized as a homogeneous catalyst in the macrolactonisation process. EDX analysis was evaluated to determine the composition of CaGE, with the results revealing the presence of 13 wt% carbon, 32 wt% oxygen, and 55 wt% calcium, as displayed in Figure 1 (Cheng et al., 2021).

5.4.3 Differential Thermal Analysis-Thermogravimetric Analysis

Cheng et al. (2021) reported the findings of TG/DTG analysis of the eggshell powder. The calcination process of waste eggshell powder was characterized by Thermogravimetric/Differential Thermal analysis (TG/DTA). The eggshell powder was heated from 30 to 1000°C at 10°C min−1 in N_2 atmosphere. The reduction of eggshell powder ranged from 30-500°C due to the decomposition of organic matter and removal of moisture from the eggshells. The quality of the eggshell powder had changed dramatically due to the removal of carbon dioxide at 600-800°C, whilst at a temperature of At 850°C the quality of eggshell was found to change repeatedly, likely due to the complete decomposition of $CaCO_3$. These results highlighted the formation of CaO during TG/DTG analysis, further revealing how $CaCO_3$ began to decompose at 600°C, consistent with XRD data analysis reported by Cheng et al. (2021).

5.4.4 Fourier-Transform Infrared

Awogbemi et al., 2020 reported the use of Fourier-Transform Infrared (FTIR) spectroscopy to study the structure and functional group of eggshell CaO catalysts. FTIR analysis was compared for raw, boiled, and calcined chicken eggshell powders, representing similar spectra, with raw and boiled eggshell powders featuring remarkably different spectra versus the calcined eggshell sample. Principal absorption bands of uncalcined raw and boiled chicken eggshell samples appeared at 1394 cm^{-1}, 873 cm^{-1}, and 712 cm^{-1}. This was ascribed to asymmetric stretch, out-of-plane bend and in-plane bend vibration modes for CO_3^{2-} molecules (Awogbemi et al., 2020). The organic matter displayed absorption bands at 2513 cm^{-1} and 1795 cm^{-1} that disappeared after calcination of the raw eggshell samples. However, a slight difference was observed between the absorption band appearing at 1071 cm^{-1} and 1092 cm^{-1} for the raw and boiled eggshell samples. However, calcined chicken eggshell displayed a sharp stretching band at 3642 $cm^{-1,}$ due to presence of the OH^{-1} group (Awogbemi et al., 2020). The absorption peak for calcined eggshell appeared at 3642 cm^{-1}, corresponding to stretching vibration and bending of hydroxyl groups present in $Ca(OH)_2$. However, during the calcination process, carbonate in the chicken eggshells decomposes to CaO and the absorption bands of CO_3^{2-} molecules migrated to higher energy and bands, which were observed at 1403 cm^{-1}, 1065 cm^{-1}, 878

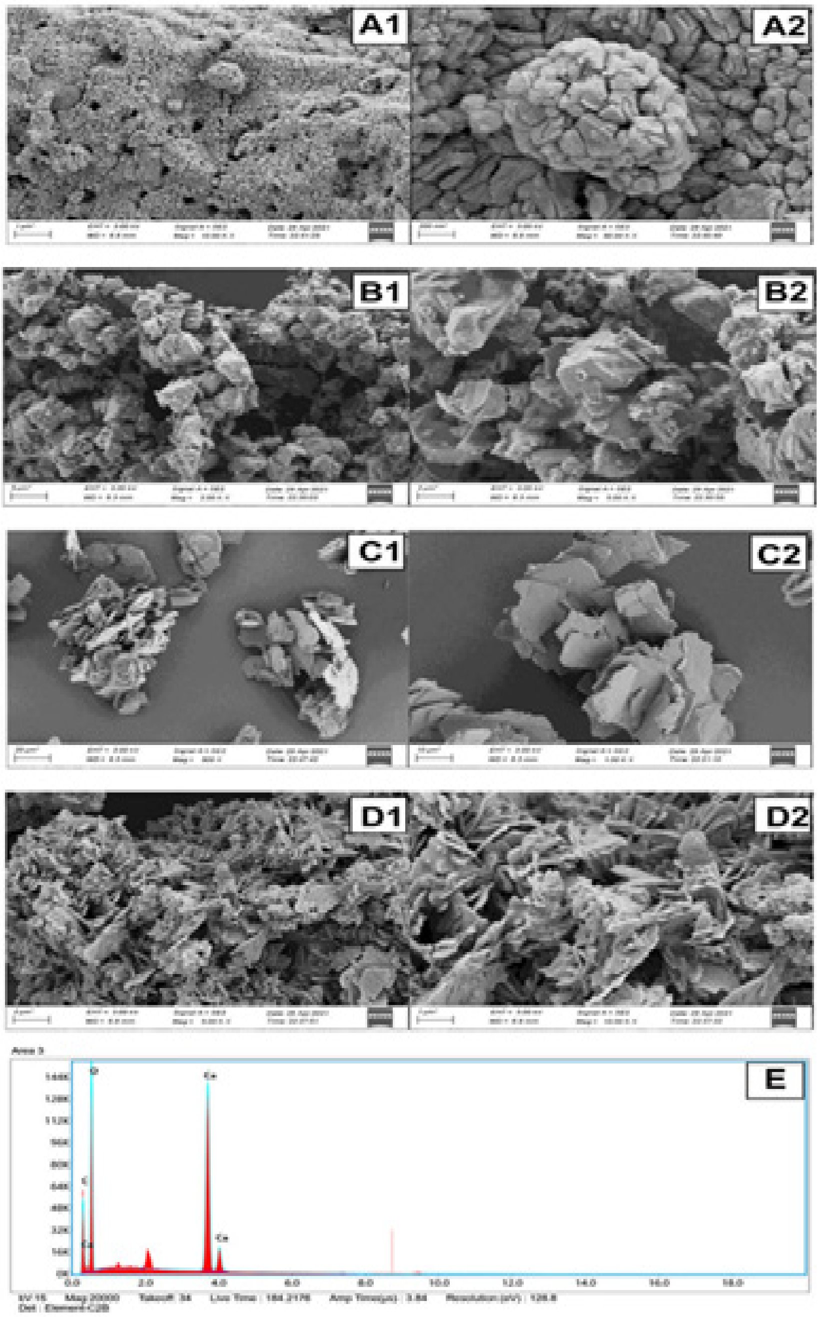

FIGURE 1: SEM images (A) Fresh CaO (B) CaDG (Calcium diglyceroxide) (C) CaG (Calcium glycerolate) and (D) CaO-E Calcium oxide from egg shell samples (E) EDX of CaO-E catalysts Birla et al., 2012.

cm^{-1}, and 529 cm^{-1}. However, a reduction in mass of the functional group attached to CO_3^{2-} ions contributed to the formation of CaO. Commercial CaO showed a good correspondence between spectral bands at 867 cm-1 and 1477 cm-1 and CaO synthesized from waste chicken eggshell due to the vibration modes of mono and bidentate carbonates. The calcined chicken eggshell band peak appeared at 3642 cm^{-1} versus the commercial CaO band at 3460 cm^{-1} (Awogbemi et al, 2020).

5.4.5 Brunauer-Emmett-Teller Analysis

Analysis of surface area and textural properties was performed using Brunauer-Emmett-Teller (BET). Calcined chicken eggshell displayed a higher BET surface area and external surface area compared to uncalcined samples. The external surface area of the eggshell was found to have a greater surface area than that of raw eggshell, likely due to the boiling and calcination of eggshell powders, leading to an increase in both BET and external surface area. The higher surface area promotes a higher catalytic activity of the eggshell powder for transesterification reaction catalyst and wastewater treatment (Tan et al., 2015). However, due to these attributes, CaO derived from eggshells displays better catalytic activity than commercial CaO. Anjana et al. (2016) reported that the high value of the pore radius and particle size of the eggshell powder is further pulverized from the current 75 μm and reduced to nano-size for improved catalytic activity (Anjana et al., 2016). This was credited to better surface exfoliation compared with CaO derived from waste eggshells (Badnore et al., 2018).

5.4.6 Other Characterization Analysis

Hammett method and temperature programmed desorption method (TPD) were used to analyze basicity, strength and site of the prepared catalysts. Hammett indicators (phenolphthalein, dinotroaniline, bromothymol blue, indigo carmine, nitroaniline) were used to measure basicity of eggshell catalysts. The basicity and basic strength of a catalyst play an essential role in the macrolactonisation reaction. Low basicity indicates strong stability of the catalyst; hence, it is assumed that the catalyst is resistant to air moisture. On the other hand, high basic strength and presence of a high number of basic sites indicate that the catalyst is able to moderately function at ambient temperature (Granados et al., 2007). The basic sites of standard CaO can absorb CO_2 and H_2O if exposed to the air (Furuta et al., 2006). Previous studies have proved that modifying different reaction parameters during the synthesis of eggshell catalysts improves the surface area; subsequently yielding larger basic sites (Granados et al., 2007; Liu et al., 2007; Xie & Li, 2006). A total basicity of eggshell catalyst after calcination was recorded as ranging from 2.8 to 3.5mmol/g. At the same time, basic strength ranged between $15.0 < H < 18.4$, similar to a commercial CaO catalyst (Xie & Li, 2006; Kim et al., 2010).

5.4.7 Current Opinion and Future Trends for Eggshell Catalysts

Current opinion and associated future trends relating to the use of eggshell waste in the development of reusable CaO catalysts point to the advantageous reproduction of these green catalysts using an economical process to yield value-added products. A series of different metals have been experimentally incorporated into the process to evaluate the potential use of eggshell waste catalysts as active CaO green catalysts for application in a wide range of scientific fields, including the environment, engineering, medicine, renewable energy, and catalysis. Additional studies should focus on tunable catalysts featuring active metal centers or sites for the development of an environmentally-friendly process based on the concept of green chemistry. Crucial general areas investigated in the literature can be categorized as important variables for the purpose of catalyst synthesis, characterization, and applications for different reactions. Eggshell catalysts have indeed proved effective in fields such as organic transformation, medicine, the environment, and manifold areas of science and engineering. Future studies should be undertaken to assess the feasibility of process commercialization, including physical characterization and optimization studies. The treatment of eggshell CaO catalysts with a series of different reagents and varied parameters should be investigated and pilot-scale studies set up.

6. CONCLUSIONS

This article illustrates the development of CaO catalysts from waste eggshells. The enormous quantities of eggs consumed by humans daily leads to the generation of tons of waste eggshells. CaO and nano CaO derived from eggshell waste are synthesized using a series of different methods and characterized by a range of distinct applications and socioeconomic properties of CaO. The fields indicated for potential applications include biodiesel production, drug synthesis, catalysts for organic transformations such as Knoevenegal reaction, environmental remediation, wastewater treatment, civil engineering (construction), cancer medicine and antimicrobial activity. The physical properties of CaO are studied and further characterized according to XRD, FT-IR, SEM, DSC-TGA and BET surface area. However, studies aimed at developing modified eggshell CaO catalysts should be undertaken to asseess potential novel applications suited to the tunable nature of eggshell CaO catalysts, and exceptional properties represented by their active sites, reusability, and stability for longer reaction times, irrespective of reaction parameters applied. The simple method of synthesis should indeed be further developed for use on an industrial scale as an economic and eco-friendly process. Based on this summary of the most critical and recent achievements obtained in studies of eggshell CaO catalysts, and with the aim of providing a comprehensive overview of the current state-of-the-art, the Authors maintain that this novel use of eggshell wastes may herald the widespread development of a promising heterogeneous catalyst.

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