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Biogenic calcium carbonate derived from waste shells for advanced material applications: A review

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Biogenic calcium carbonate derived from waste shells has received significant attention in the last 2 decades as a replacement for limestone due to its contribution to reducing environmental impact by turning wastes into value-added biomaterial and moving global society toward net-zero waste. Recently, several review papers have been published regarding applying biogenic derived calcium carbonate in engineering, biomedical, electrochemical, and environmental technologies. This review stands apart from other reviews on this topic in terms of focusing and reviewing the published papers used and reported indirect methods only to obtain calcium carbonate from biogenic waste shells and not by direct methods. The direct or untreated methods include simple grinding, ball milling, or mortar and pestle techniques. In contrast, the indirect methods covered in this review paper consist of precipitation and different chemical treatment techniques. Therefore, this review paper aims to comprehensively summarize the usage of calcium carbonate derived from eggshells and seashells by indirect methods and glance at its recent development for advanced material applications including water treatment, bio-filler, and reinforcement in polymer composites, energy application, pharmaceutical, biomedical, and drug delivery applications.

KEYWORDS

biogenic calcium carbonate, waste seashells, waste eggshells, bio-functional materials, advanced materials

1 Introduction

Calcium carbonate, which is usually mined from limestone sedimentary rock, is one of the most abundant biominerals on earth and is widely used in various applications due to its biocompatibility and low cost. However, an alternative and more sustainable method to obtain calcium carbonate is from biogenic waste shells such as poultry eggshells and seashells. Annually, millions of tons of biogenic waste shells are disposed of in landfills which tend to pose massive environmental pollution (Yoo et al., 2009; Awogbemi et al., 2020). According to the Environmental Protection Agency (EPA), biogenic waste shells

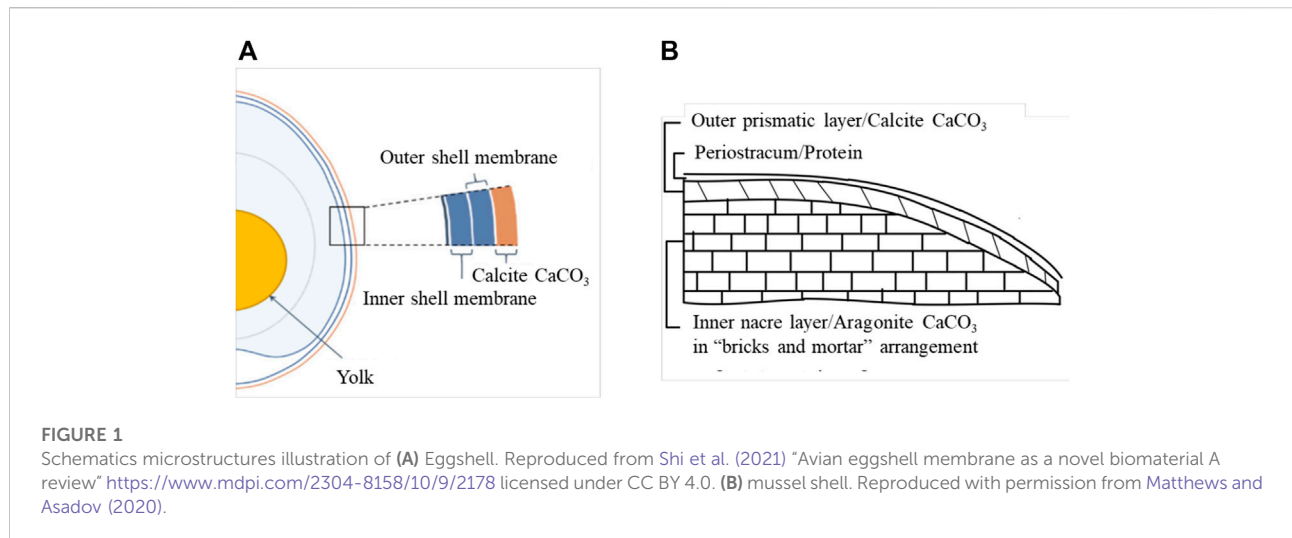


TABLE 1 Chemical composition of eggshell, cockle shell, and mussel shell (Hunton, 2005; Awang et al., 2007; Hamester et al., 2012; Chakraborty et al., 2020; Baláz et al., 2021).

Composition/elements	Eggshell (wt%)	Cockle shell (wt%)	Mussel shell (wt%)
Calcium carbonate	94–97 (calcite)	98–99 (aragonite)	95–96 (calcite/aragonite)
Organics	4	≤1	≤2
Magnesium oxide	0.83	0.05	0.6
Potassium oxide	0.08	0.04	0.5
Alumina	0.15	n/a	0.4
Sulphur oxide	0.66	n/a	0.7
Silica	n/a	0.03	0.9
Ferric oxide	n/a	0.15	0.7
Phosphorus oxide	0.43	0.02	n/a
Sodium oxide	n/a	0.9	n/a
Strontium oxide	n/a	n/a	0.4

have been ranked as the 15th major food industry pollution problem (Waheed et al., 2020). Therefore, turning those biogenic waste shells into usable value-added biomaterials would be distinctly eco-friendly and economical. The structure and chemical composition of eggshell, cockle shell, and mussel shells are presented in Figure 1 and Table 1.

Different methods recently came to light to process the calcium carbonate derived from eggshells and seashells. Thousands of research papers and more than 500 patents have emerged since the turn of the 21st century for sustainable development growth (SDG) (Ahmed et al., 2021). As a result, several review papers have been published about eggshell, and seashells derived calcium carbonate and its applications as filler in polymer composite preparations and pharmaceuticals applications (Rodríguez-navarro et al., 2015; Waheed et al., 2019; Hart, 2020; Baláz et al., 2021). However, there is no

review covering different approaches such as precipitation to obtain the specific polymorphic structure of calcium carbonate from biogenic wastes. The precipitation of calcium carbonate from biogenic waste shells enables the opportunity for the formation of four designs, including the amorphous phase and three polymorphs of vaterite, aragonite, and calcite (Trushina et al., 2016). This review presents a comprehensive overview of obtaining indirect (precipitated or treated) calcium carbonate from biogenic waste shells and covering its application in water treatment, bio-filler, and reinforcement in polymer composites, energy application, pharmaceutical, medical application, and drug delivery. Over and above that, the present review should serve as a solid platform for emerging novel methodologies to obtain pure treated or precipitated calcium carbonate with engineered polymorph structures and desired morphology and particle sizes from biogenic waste shells

for the development of advanced materials application. Therefore, it will be a contribution from science and technology to urge and support the bio-circular green (BCG) economy and global SDG.

2 Production of reduced size biogenic calcium carbonate

In order to obtain fine powders of calcium carbonate with nano/micron sizes, different approaches have been reported in the literature so far, including mechanochemical and precipitation methods. The mechanochemical method was employed using the ball milling or grinding process. However, this technique can also be combined with other methods to obtain more speciality properties. For instance, Hassan *et al.* (2013) have developed a combination of mechanochemical and sonochemical techniques to produce high surface area calcium carbonate nanoparticles from eggshells with the size of ~10 nm. However, a very recent review paper (Baláž *et al.*, 2021) covered only a mechanochemical approach to producing calcium carbonate particles from eggshell wastes. The disadvantage of the mechanochemical process would be the inability to control the polymorph structures of calcium carbonate, the chance of having impurity from biogenic wastes as it is used without any purification, and a high chance of contamination during the ball milling process.

However, the eggshells or seashells waste can be digested in acid and reformed in highly controlled conditions in the precipitation technique. Azarian *et al.* (Azarian and Sutapun, 2022) have recently precipitated the calcium carbonate particles from eggshells and showed that morphologies and polymorph structures of precipitated calcium carbonate (PCC) particles could be effectively tuned by changing the experimental parameters such as initial calcium ions molar concentration, using different polyelectrolytes (non-ionic or ionic) with different molecular weight, and concentration of polyelectrolyte solution. The advantages of this technique are the possibility of controlling the size and obtaining calcium carbonate with desired morphologies, i.e., star-shaped, yarn or spherical shapes with various polymorph crystal structures such as vaterite or calcite.

3 Calcium carbonate structures

There are six structures of calcium carbonate, one hydrous in the form of amorphous calcium carbonate and five crystalline polymorphs. The five crystalline polymorphs are three anhydrous crystallines, i.e., vaterite, aragonite, and calcite, and the other two hydrated crystalline forms of ikaite hexahydrate and monohydrate calcite with limited occurrence in nature (Beck and Andreassen, 2010; Bushuev

et al., 2015). It is interesting to note that all of those structures naturally exist. They can also be synthesized or precipitated with different morphologies or sizes and convert to other polymorph structures by several techniques such as microwave-assisted (Qi and Zhu, 2006; Qi *et al.*, 2014; Skubiszewska-Zięba *et al.*, 2017), carbonation (Hou and Feng, 2005; Beuvier *et al.*, 2011; Udrea *et al.*, 2012; Lai *et al.*, 2015; Yuan *et al.*, 2015), sonochemical (Zhou *et al.*, 2004; He *et al.*, 2005; Luo *et al.*, 2021), hydrothermal (Zhao *et al.*, 2011; Sulimai *et al.*, 2017) and wet precipitation technique (Brečević *et al.*, 1996). The neat calcium carbonate from eggshells exists in the calcite structure. However, the seashells are in the form of an aragonite and calcite mixture (Table 1).

3.1 Amorphous

Amorphous calcium carbonate (ACC) is the unstable phase before vaterite and calcite and is produced naturally by various invertebrates, which later grows into complex shapes crystals (Hincke *et al.*, 2012). The observable circular voids with a mean diameter of 313 ± 78 nm in Figure 2A are evidence regarding the presence of ACC in eggshell mineralization. Figure 2B relatively shows the ACC calcium carbonate spherical particles with sub-micron size synthesized in the laboratory from calcium chloride and sodium carbonate in a controlled condition. The dimensions of circular voids in eggshells are comparable to the synthetic ACC with the size of 850 ± 150 nm. Navarro *et al.* (Rodríguez-navarro *et al.*, 2015) have evaluated the mineralogy and crystallinity of eggshells during its formation process by XRD spectroscopy and SEM microscopy right after ovulation when nucleation sites appear at early mineralization and during the crystalline growth phase and rapid calcification about 14 h after ovulation. From SEM, eggshell mineral originates from the early accumulation of flat disk-shaped ACC particles on the eggshell membrane. As shown in Figure 3 1D-XRD patterns of non-mineralized eggshell membranes collected at the 5th hour show two broad bands attributed to the membrane's organic components and there is no peak related to Ca formation. However, in a sample collected after 5 h, with primitive calcium carbonate mineralization covering the surface no further diffraction peaks appear, which indicates that the calcium carbonate possesses an amorphous phase. At the 6th hour, while the membrane becomes further mineralized, weak calcite diffraction peaks appeared at two Theta 30° . With additional mineralization over 7 h and 14 h, the intensities of calcite peaks increased and became sharper, indicating highly crystalline calcite formations.

Another study reported by Lakshminarayanan *et al.* (2006) evaluated the biogenic calcium carbonate from quail eggshell

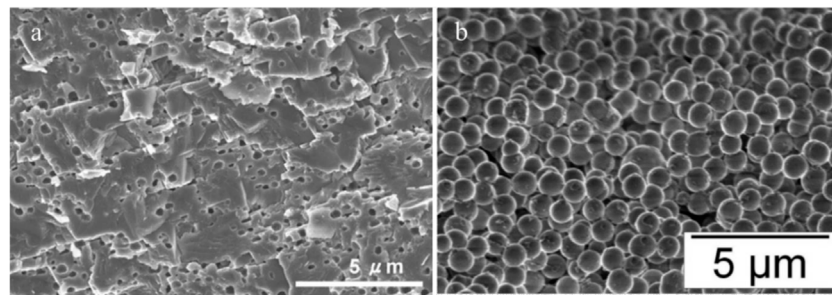


FIGURE 2

(A) Eggshell calcite and small spherical voids regarding the presence of ACC prior to calcite formation reproduced with permission from [Hincke et al. \(2008\)](#), (B) ACC calcium carbonate synthesis in the lab from calcium chloride and sodium carbonate. Adapted with permission from [Faatz et al. \(2005\)](#), American Chemical Society.

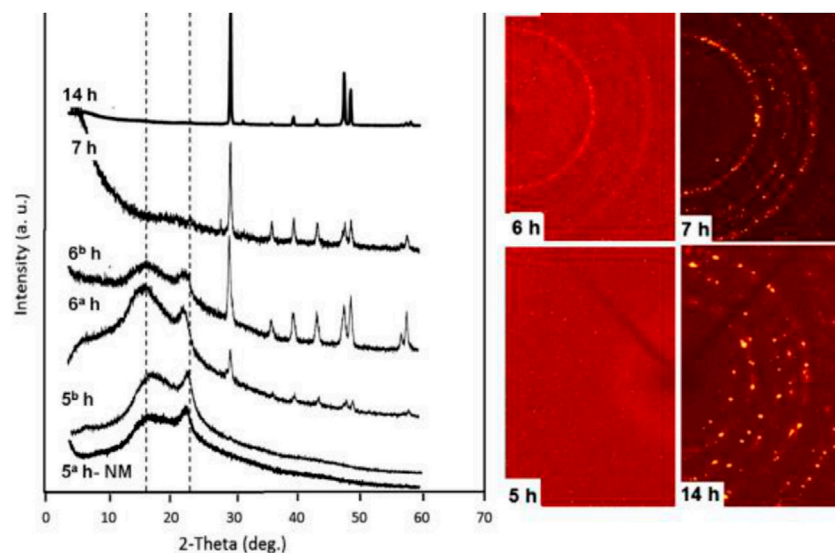


FIGURE 3

1D and 2D-XRD patterns of eggshell collected at different time intervals. Reproduced with permission from [Rodríguez-navarro et al. \(2015\)](#).

biomineralization by the calcium carbonate precipitation technique. The precipitation was performed by passing purified CO_2 gas through dispersed eggshell powder in water. After they dissolved, the solution was filtered, and CO_2 gas was bubbled through for another 30 min. Finally, the solution was placed on a petri dish undisturbedly, and calcium carbonate precipitated at various time intervals. The authors found that ACC was precipitated in the early stages, transforming into the most stable crystalline calcite phase ([Figure 4](#)). These results showed that precipitation of calcium carbonate follows the same mechanism, mineralogy, and crystallinity as the eggshell formation process.

3.2 Vaterite

Vaterite calcium carbonate with hexagonal crystal structure and spherical-like morphology has been formed and exists naturally in birds and many marine livings such as gastropods, mollusc pearls, fish otoliths, and ascidians ([Jessop et al., 2008](#); [Soldati et al., 2008](#); [Portugal et al., 2018](#)). As a metastable phase, it is likely to occur as a transient intermediate between the ACC phase and more stable calcite or aragonite ([Christy, 2017](#)). Vaterite is as unstable as ACC, with a spherical shape but bigger size than ACC. [Lin et al. \(2020\)](#) have prepared vaterite calcium

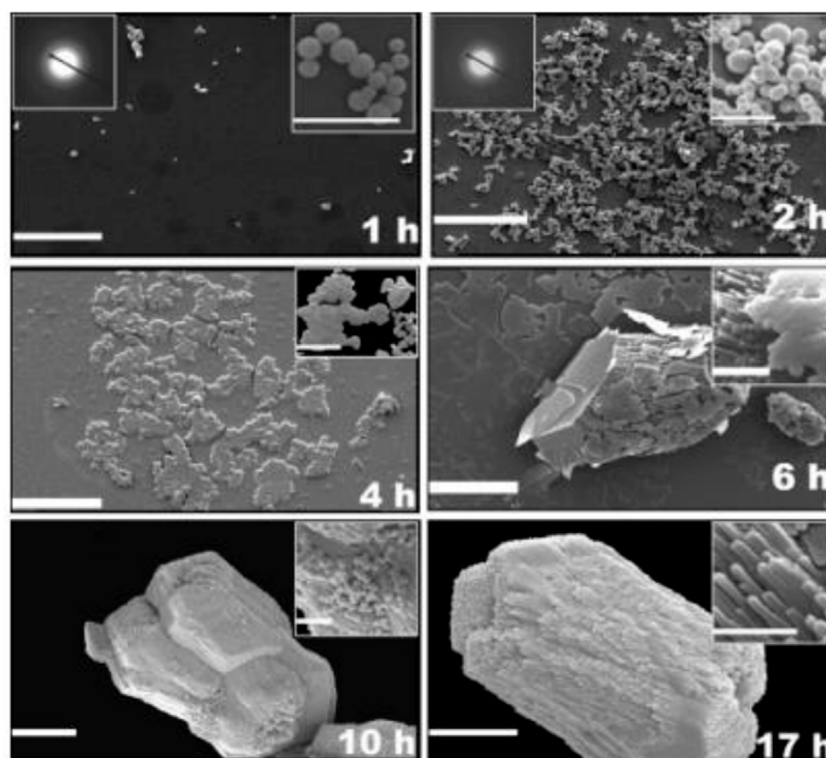


FIGURE 4

SEM micrographs of the calcium carbonate grown by the precipitation experiment at various time intervals. Scale bar and inset scale bar are 10 μm and 2 μm , respectively. Reproduced with permission from Lakshminarayanan et al. (2006), American Chemical Society.

carbonate microparticles from discarded oyster shells by digestion and precipitation of calcium carbonate in hydrochloric acid (Figure 5). The grinded oyster shells have irregular morphology prior to precipitation. After the precipitation, the morphology has been changed to spherical shape with the size of $4 \pm 2 \mu\text{m}$. The XRD analysis was performed on obtained microsphere and diffraction peaks located at 2θ of 20.9° (004), 24.8° (110), 27° (112), 32.8° (114), 43.7° (300), 50.1° (118), and 55.9° (224) indicated the existence of crystalline phase in vaterite structure. In the related research conducted by Sutapun et al. (2012), chicken eggshells were precipitated after digestion in hydrochloric acid with the addition of sodium carbonate in which vaterite and calcite mixture was obtained, and the surface area from untreated chicken eggshell particles increased from $2.55 \text{ [m}^2/\text{g]}$ to $4.38 \text{ [m}^2/\text{g]}$ after precipitation (Figure 6).

3.3 Aragonite

Aragonite calcium carbonate with orthorhombic crystal structure and needle-like morphology found naturally in

almost all mollusc shells, widely used as inorganic filler in polymers (Ramakrishna et al., 2017) and for biomedical applications (Mailafiya et al., 2019). For instance, Nurul et al. (Islam et al., 2013) have used a mechanical grinding in the presence of a biomineralization catalyst, i.e., dodecyl dimethyl betaine, to produce pure aragonite nanoparticles with an average diameter of 20 nm from cockle shell wastes. In another example, Habte et al. (2020) synthesized aragonite crystals from waste chicken eggshells and seashells (abalone, mussel, manila clam, scallop, and oyster shells) through wet carbonation method in aqueous suspensions with constraint carbon dioxide injection at 80°C . The authors reported that the obtained green aragonite calcium carbonate could be used for numerous applications and have the potential for commercial-scale synthesis from eggshells and bivalve seashells biogenic wastes as cheap and abundant precursors. Figures 7A,B show the TEM images of cockle shell powders before and after treatment, respectively. The cockle shell powders have irregular morphology which mainly transformed to needle shapes after treatment. Furthermore, Figures 7C,D show the SEM images of needle shape aragonite polymorph obtained from chicken eggshells and needle shape aragonite polymorph obtained from mixed bivalve seashells, respectively.

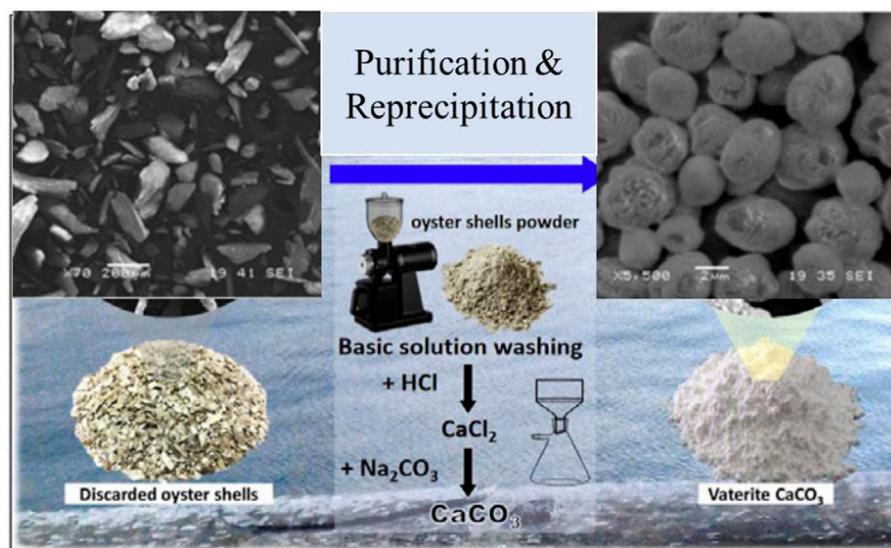


FIGURE 5

Schematic preparation process of vaterite calcium carbonate microspheres from oyster shells and SEM images of oyster shells and vaterite calcium carbonate microspheres. Reproduced with permission from Lin et al. (2020).

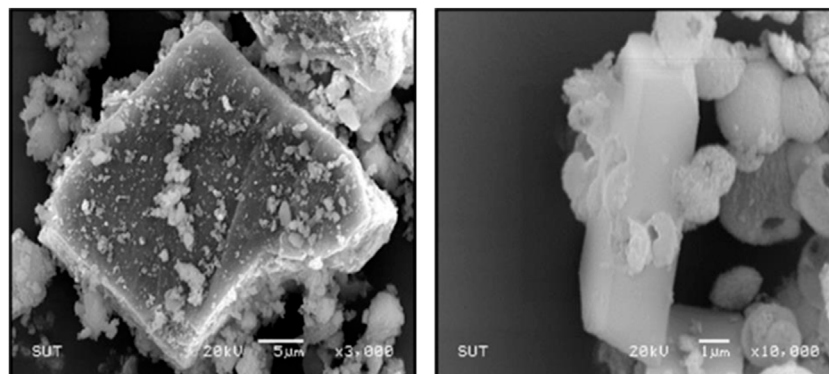


FIGURE 6

SEM microimages of chicken eggshell and precipitated chicken eggshells with a magnification of 3,000 X and 10,000 X, respectively. Reproduced with permission from Trans Tech Publications, Ltd., (Sutapun et al., 2012).

3.4 Calcite

Calcite with a rhombohedral crystal structure is the most abundant calcium carbonate and the major incorporator of poultry eggshells, limestone, and chalk (Athanasidou et al., 2018; Portugal et al., 2018). The rhombohedral phased calcite usually exists as cubic particles (Luo et al., 2020). Calcite calcium carbonate is widely used in cement and metallurgy industries due to its high corrosion resistance and good thermo-chemical

stabilities (Yang and Xu, 2011). In the study published by Hariharan et al. (2014), calcite calcium carbonate nanoparticles were prepared from cockle shells by precipitation technique using chitosan as a precursor. The ground cockle shells calcium carbonate was digested in concentrated hydrochloric acid and mixed with dissolved chitosan in acetic acid. This solution was then mixed with sodium carbonate solution and slightly heated overnight to obtain precipitated pure calcite calcium carbonate particles. In

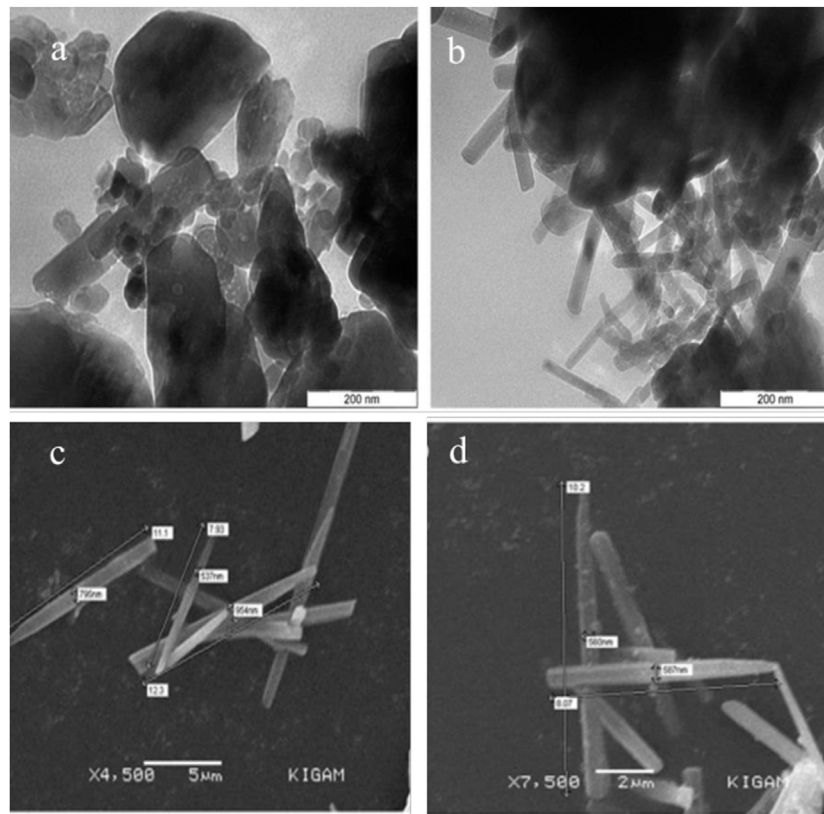


FIGURE 7

TEM microimages of aragonite crystals from cockle shell powders before (A) and after (B) the powder treatment. Reproduced with permission from Islam et al. (2013). SEM microimages of (C) aragonite crystals obtained from chicken eggshells and (D) aragonite crystals obtained from mixed bivalve seashells. Reproduced from Habte et al. (2020) "Synthesis, characterization and mechanism study of green aragonite crystals from waste biomaterials as calcium supplement" <https://www.mdpi.com/2071-1050/12/12/5062> licensed under CC BY 4.0.

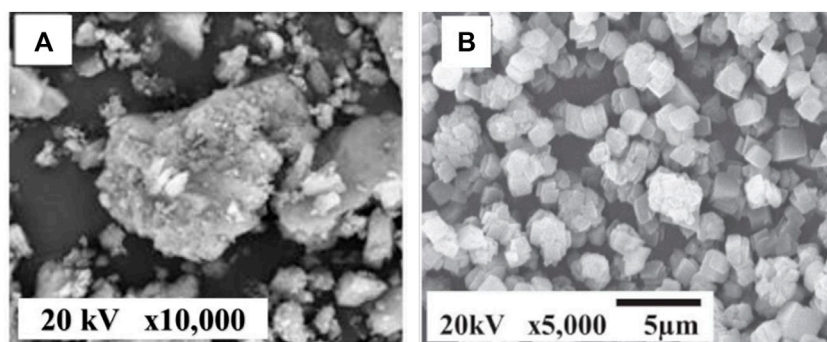
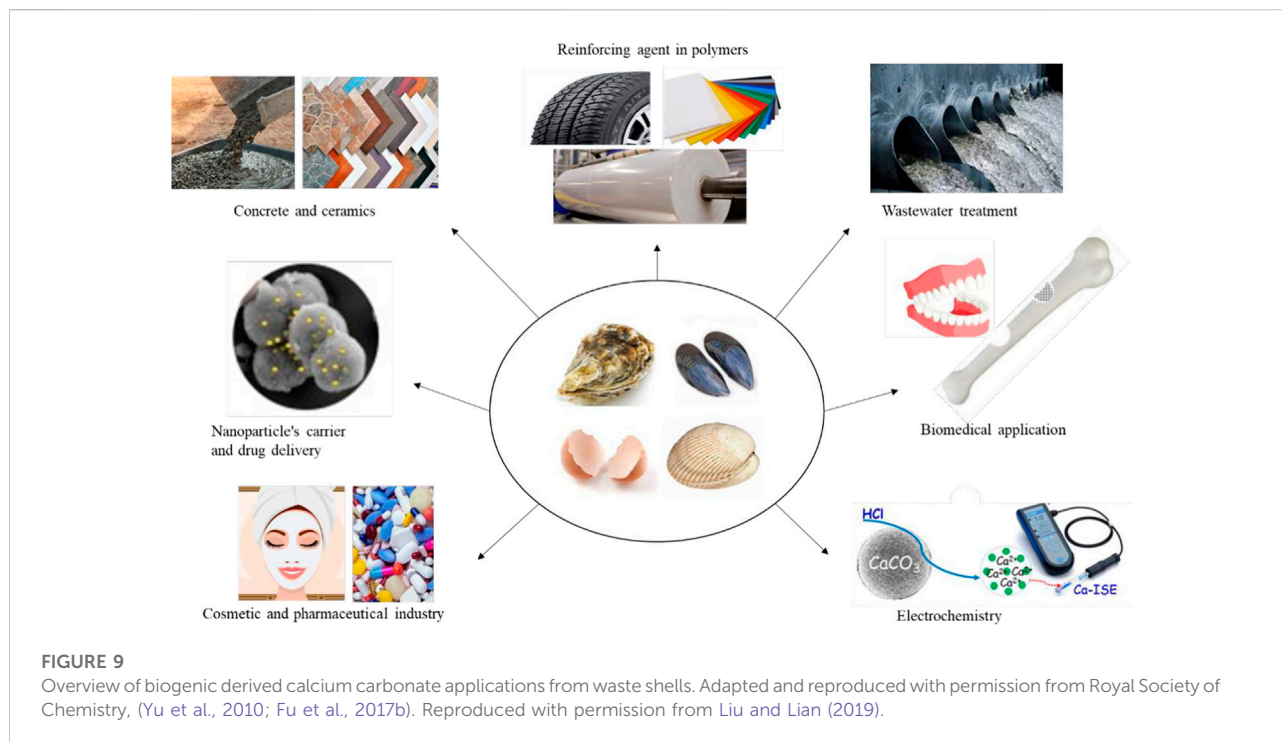


FIGURE 8

SEM microimages of (A) untreated calcite eggshell powders. Reproduce from Madiabu et al. (2021) "Equilibrium and Kinetic Study of Removal Copper(II) from Aqueous Solution Using Chicken Eggshells: Low Cost Sorbent" <https://ojs.jmolekul.com/ojs/index.php/jm/article/view/658> licensed under CC BY 4.0. (B) Precipitated calcite eggshell powders. Reproduced with permission from Putkham et al. (2018).



a related study, Putkham et al. (2018) have synthesized pure calcite calcium carbonate from eggshell waste *via* a simple liquid-liquid precipitation method. The eggshells were digested in hydrochloric acid with different concentrations to obtain calcium chloride solution first, which later reacted with sodium carbonate in various temperatures and agitation time to obtain different polymorphs of calcium carbonate. This liquid-liquid precipitation method allowed the production of micron particle sizes ranging from 4 to 11 μm with narrow particle size distribution. Notably, the pure cubic shape of calcium carbonate was formed at high reaction temperatures and low initial concentrations of calcium chloride solution. Figures 8A,B shows the SEM images of untreated eggshells powders and precipitated eggshells calcite calcium carbonate powders, respectively. These results indicated the importance of the precipitation technique to produce pure calcite calcium carbonate with controlled particle size and morphology.

4 Applications

Since the interest in using biogenic calcium carbonate has increased significantly, this brings a severe need to seek novel applications in advanced materials. To broaden its application, researchers have been trying in vast fields of materials science and developed new technologies accordingly. Figure 9 shows the schematic illustration of biogenic calcium carbonate used in different applications. Recently several commercial companies

have emerged worldwide using calcium carbonate derived from biogenic waste to produce various products on a large industrial scale. For instance, EUROATOMIZADO, S.A. company (Tiles Made With Eggshell. 2022), actively uses biogenic calcium carbonate to design, produce, and commercialize novel ceramic formulations at a pilot and industrial scale.

Similarly, EGGNOVO Co., Ltd. (Eggnovo, 2019) produces functional ingredients based on calcium carbonate derived from eggshell waste for the cosmetic, nutraceutical and pharmaceutical industries. Also, Justegg Co., Ltd. (JustEgg Chilled Foods Ltd., 2019) produces eggshell powders as a source of bio-calcium carbonate for possible application as bio-filters for reinforcing the plastics mainly used in Silvergate Plastics Co., Ltd. (Silvergate Plastics. 2003) masterbatch plastic products. The following sections will cover all the published research papers so far dealing with treated or modified bio-calcium carbonate in different applications.

4.1 Electrochemistry

Neat calcium carbonate derived from eggshells and seashells has the potential to be employed as electrodes in electrochemical cells. The pure calcite calcium carbonate can be used as a cathode, while calcinated calcium carbonate at relatively high temperatures may operate as an anode. At a temperature $>700^{\circ}\text{C}$, calcium carbonate is mainly oxidized to calcium oxide form, which is suitable to employ as an anode in an

electrochemical energy device. [Setiawan et al. \(2017\)](#) synthesized Ca-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode in the form of $\text{Li}_{4-x}\text{Ca}_x\text{Ti}_5\text{O}_{12}$ ($x = 0, 0.05, 0.075, \text{ and } 0.1$) using calcined calcium carbonate derived from waste eggshells as a source of calcium for lithium-ion battery application. The preliminary results indicated that calcium carbonate-derived eggshells could be used as a good dopant source for LTO, with the highest charge-discharge capacity of 177.14 mAh/g and 181.92 mAh/g obtained for $\text{Li}_{3.95}\text{Ca}_{0.05}\text{Ti}_5\text{O}_{12}$ anode system. In a similar study ([Minakshi et al., 2018](#)), the authors reported that calcium carbonate derived from waste eggshells could be used as an active electrode in Li-ion capacitors to store and release charges with a wide range electrochemical stability window. Initially, a slurry of chicken eggshell powders was prepared by mixing with carbon black (20 wt%) and polyvinylidene fluoride (10 wt%) as a binder and used as cathode against Li anode. The eggshell-Li electrochemical cell's initial discharge capacitance and reversible capacitance were 232 F g^{-1} and 120 F g^{-1} , respectively. Moreover, the eggshell-Li electrochemical cell maintained outstanding capacitance retention of 92% over 1,000 cycles, nearly equivalent to those electrochemical properties of commercialized activated carbon cathode.

In a relevant study, [Minakshi et al. \(2019\)](#) have demonstrated the use of wasted chicken eggshells in energy storage application and found that calcium carbonate derived from eggshell wastes are pretty suitable for both cathode and anode as they show a quasi-box-shaped potentiostatic curve indicating their capacitor-type behaviour. The pure calcium carbonate was used as a cathode and showed a modest discharge capacitance of 10 F g^{-1} . However, the calcined calcium carbonate (calcium oxide) or quicklime was used as the anode, which exhibited an excellent capacitance value of 47.5 F g^{-1} . The electrodes in both positive and negative regions showed a discharge capacitance of 55 F g^{-1} with close retention to about 100% after 1,000 cycles, indicating good electrochemical stability of calcium carbonate derived waste shells.

4.2 Polymer bio-filler composite

Inexpensive bio-fillers can be introduced to polymer matrix in order to improve properties and reduce the cost of final products. Calcite calcium carbonate obtained from limestone is the most widely used filler in polymer formulations. As a filler, calcium carbonate allows cost reduction and improved mechanical properties. Numerous papers have reported in the literature so far that the addition of calcium carbonate from seashells and eggshells is an effective way to improve the mechanical properties of the polymer matrix ([Toro et al., 2007](#); [Kang et al., 2010](#); [Feng et al., 2014](#); [Hassen et al., 2015](#); [Shafiur et al., 2016](#); [Essabir et al., 2017](#); [Murugan et al., 2017](#); [Hayemasae et al., 2019](#); [Munusamy et al., 2019](#); [Santu et al., 2020](#)). Recently, two review papers were published by [Vandeginste \(Vandeginste, 2021\)](#), and

[Owuamanam et al. \(Owuamanam and Cree, 2020\)](#) regarding the usage of eggshells and seashells derived calcium carbonate in composites with respect to different matrixes such as a polymer (thermoset, thermoplastics and rubber), ceramics and metal matrix. However, this section reviews only the precipitated or treated calcium carbonate from biogenic waste shells with modified structures as bio-filler. For instance, [Shuhadah et al. \(Shuhadah and Ghani 2009\)](#) have modified the eggshell powders with an isophthalic acid coupling agent, incorporated them in low-density polyethylene (LDPE), and compared the mechanical properties with LDPE filled with unmodified eggshell powders. The authors found that the tensile strength decreases with increasing filler loading, and LDPE/modified eggshell powder composites have higher strength and better interaction than LDPE/unmodified eggshell powder composites. However, improvement of elastic modulus was observed with increasing filler loading. The authors suggested that an increase in elastic modulus with more filler is due to higher stiffness than the neat polymer, making it less deformable against a greater load. Furthermore, elastic modulus for LDPE/modified eggshell powders composites was lower than LDPE/unmodified eggshell powders composites due to the presence of a coupling agent, which toughens the composites and thus decreases elastic modulus. In a similar study, [Yang et al. \(2011\)](#) modified the chicken eggshell wastes with pimelic acid (PA) through the solution and then incorporated them into polypropylene (PP) through the melt blending technique. The modification by PA improved the dispersion and interfacial bonding of eggshell calcium carbonate in PP and the impact strength of PP was enhanced by 228% compared to neat PP. However, the tensile properties and flexural properties of PP slightly decreased. This might be due to, the thermal decomposition of eggshells membrane, which have not been completely removed during the cleaning process of eggshells.

[Yan Li et al. \(Li et al., 2012\)](#) have used the waste shellfish shells as a precursor of calcium carbonate and prepared granules of shellfish shells by removing the cuticle, crushing, grinding and treating them with shearing emulsification. The treated shells were further introduced as a bio-filler to reinforce PP polymer. The authors claimed that the mechanical behaviour of PP composite shows a higher yield strain, yield strength, tensile strength, and elongation at break in comparison to conventional calcium carbonate filled PP and yield strength of PP composite improved by 11.1% with only 2 wt% loading of treated shellfish shells. The study by [Hassan et al. \(2014\)](#) showed that high surface area calcium carbonate nanoparticles could be obtained from waste shells by using an ultrasonic irradiation treatment. As low as 2 phr of obtained calcium carbonate nanoparticles were incorporated within Bioplast GS 2189 thermoplastic polymer, and mechanical results revealed flexural strength and elastic modulus of polymer enhanced by 35.3% and 30.5%, respectively.

Similarly, [Fombuena et al. \(2014\)](#) have treated the calcium carbonate from seashells with a silane coupling agent, used it as a

bio-filler in an epoxy matrix, and found that silane treatment can effectively prevent particle aggregation, thus leading to optimum calcium carbonate dispersion. Loading of 30 wt% of treated seashell increased the mechanical properties as well as flexural modulus (over 50%), hardness (around 6%) and thermal properties. Li et al. (2016) modified and functionalized the eggshell particles with phenyl phosphonic acid and incorporated them into polylactic acid (PLA) by melt blending to improve the crystallization behaviour and enhance the mechanical properties enzymatic hydrolysis of PLA polymer. With 20 phr loading of treated eggshell particles, the crystallization half-time of a PLA composite decreased significantly from 27.09 to 0.69 min at 130°C accordingly. Furthermore, the storage and tensile moduli enhanced with increasing modified eggshells loading in which tensile strength, tensile modulus and elongation at break were 53.4 MPa, 2,460 MPa, and 2.5%, respectively.

In another investigation, Tiimob et al. (2016) have used ultrasonication treatment with 50 amplitude after the ball milling process and successfully reduced the size of calcium carbonate particles derived from eggshell to less than 100 nm. 1, 2, 3, 4, 5, and 10 wt% of the obtained nano-eggshell particles were loaded to epoxy resin, and DMA/TMA analysis revealed significant improvements of 7–22% in the storage moduli and 3–17% in coefficient of thermal expansion, respectively. Furthermore, the flexure strength, modulus, and toughness significantly improved by 6–31%, 11–37%, and 10–36%, respectively. In another study, chicken eggshell particles were chemically modified with a silane coupling agent and introduced to high-density polyethylene (HDPE) to study its effects on tensile strength and elastic modulus (Sharweeni et al., 2016). The authors have also incorporated the unmodified eggshell particles for comparison purposes. Both systems exhibit higher tensile strength than neat HDPE at 10 phr and 20 phr filler loading. As the filler loading increases above 20 phr, the tensile strength drops for both systems due to the aggregation of eggshell particles and weakening the interfacial adhesion between eggshell particles and HDPE polymer matrix. However, modified eggshell particles/HDPE composites exhibit higher tensile strength at all filler loading up to 40 phr since the coupling agent promotes a better adhesion between polymer matrix and eggshell particles. The authors claimed that coupling agent treatment could improve the shear bond strength of eggshell particles towards the HDPE polymer matrix.

Similarly, Tiimob et al. (2017) have synthesized eggshell/Ag nanoparticles by ball milling of eggshell and AgNO₃ in polypropylene glycol (PPG) solution as a deflocculating agent. The polymer films obtained by dispersing obtained eggshell/Ag nanoparticles into poly (butylene adipate-co-terephthalate) (PBAT)/agro-based polylactic acid (PLA) blend by 3D printing and hot melt extrusion techniques for food packaging application. The tensile strength was reduced by incorporating the eggshell/Ag nanoparticles with 0.5–2.0 wt% due to poor

interaction between the polymer matrix and eggshell/Ag nanoparticles. However, the thermal analysis revealed the onset of thermal decomposition improved. In addition, the results from the antimicrobial study showed that the films have bacteriostatic effects on *Salmonella* Enteritidis and *Listeria Monocytogenes* bacteria. In another similar study, the silver nanoparticles were embedded in calcium carbonate particles (Ag/CaCO₃) by a precipitation method and further loaded in poly (L-lactic acid) nanofibers by electrospinning technique with potential usage for antimicrobial food adsorbent pads application (Zin and Sutapun, 2022).

This is worthy of mentioning that all of the research works available in the literature reported the chemical or physical treatment methods to reduce the size or modify eggshell particles to decrease the surface tension between eggshell particles and polymer matrix. Despite achieving nearly optimal eggshell particles dispersion through polymer matrix by those treatments, manipulation of eggshells particles to obtain different calcium carbonate crystal structures by precipitation technique and incorporate them into the polymer matrix is unexplored and remains as a large gap.

4.3 Biomedical materials

Among the polymorphs of calcium carbonate, aragonite calcium carbonate is the most reported crystal structure of calcium carbonate in bone tissue engineering and biomedical sciences application (Awang et al., 2007; Fu W. et al., 2017; Jaji et al., 2017; Ananthu et al., 2018). This is mainly due to its superior density over the other polymorphs structure (calcite and vaterite), making it more biocompatible to be integrated, resolved, and replaced by bones (Islam et al., 2011; Shafiu Kamba et al., 2013). This high-density feature of aragonite is very interested due to its similarities to the human bone density (Bharatham et al., 2014). Nurul et al. (Islam et al., 2012) have synthesized aragonite calcium carbonate nanoparticles from cockle shells suitable for repairing fractured bone and tissue scaffolds. The rod-shaped aragonite nanoparticles with a mean average diameter of 30 ± 5 nm were produced by mechanically mixing fine cockle shells powders with dodecyl dimethyl betaine (BS-12) for 90 min at ambient temperature.

Similarly, Mony et al. (2015) evaluated the remineralization potential of chicken eggshell powder solution and found that the digested chicken eggshells in 4% acetic acid solution can effectively remineralise the enamel surface lesion in the tooth. In a related study, Huang et al. (2020) coated the eggshell particles with MgO nanoparticles and fabricated a biomimetic active scaffold through the chemical crosslinking of the modified eggshell nanocomposite carboxymethyl chitosan (CMC) and bone morphogenetic protein 2. The results showed that the modulus and compressive strength of the new composite scaffold based on modified eggshells were higher than those of

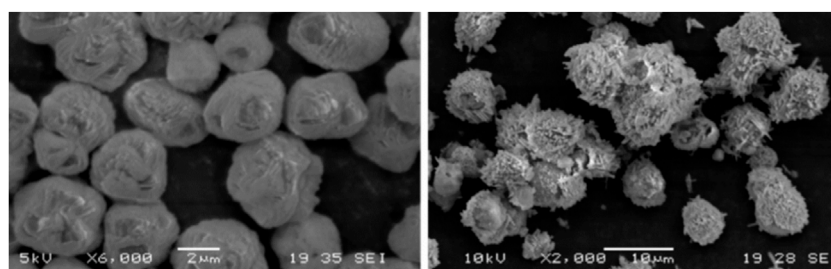


FIGURE 10

SEM microimages of vaterite calcium carbonate microspheres before and after Pb^{2+} removal. Reproduced with permission from Lin et al. (2020).

the CMC scaffold. Moreover, the composite scaffold exhibited significant mineralization ability and strong osteogenic (bone-forming) differentiation potential.

4.4 Wastewater treatment

Nowadays, contamination of water resources is a major environmental challenge worldwide. Especially, the relatively high content of heavy metals in water may bioaccumulate in food resources and impose a serious risk on the health. Calcium carbonate derived from biogenic waste shells can effectively adsorb and remove heavy metals from aqueous solutions such as Cd^{2+} , Pb^{2+} , and Cu^{2+} (Ahmad et al., 2012; Tizo et al., 2018). Up to now, there is scarcely any research in the literature regarding the use of treatment or precipitated biogenic calcium carbonate with tailored morphology for water treatment. For instance, Lin et al. (2020) have used the precipitated technique to obtain vaterite calcium carbonate granules from discarded oyster shells as an adsorbent for heavy metal ions removal. The vaterite calcium carbonate showed an excellent removal efficiency of 99.9%, 99.5%, 99.3%, and 57.1% for Pb^{2+} , Cr^{3+} , Fe^{3+} , and Cu^{2+} metal ions, respectively. The conventional calcium carbonate was also studied for the heavy metals removal efficiency compared with precipitated oyster shells, and results showed better removal efficiencies of vaterite calcium carbonate particles. Figure 10 shows the SEM image of vaterite calcium carbonate before and after Pb^{2+} removal. The removal efficiency of heavy metal ions consists of ion exchange reactions between vaterite calcium carbonate and heavy metal ions, which resulted in the recrystallization of calcium carbonate. The vaterite calcium carbonate particles from oyster shells obtained by precipitation technique have the advantage of low price, easy synthesis which can be potentially incorporated into household drinking water filtration systems. Other than heavy metals, calcium carbonate derived biogenic waste

have been also reported as effective adsorbent for removing organic dyes from waste water such as direct blue (Murcia-Salvador et al., 2020), methyl violet (Foroutan et al., 2019), red congo (Seyahmazegi et al., 2016), rhodamine B (Borhade and Kale, 2017) and acid orange (Tsai et al., 2008; Yari et al., 2015).

4.5 Nanoparticle's carrier and drug delivery

The calcium carbonate particles can be employed as vehicles for carrying nanoparticles or various drugs due to their biocompatibility (Trushina et al., 2023). In a study conducted by Than et al. (2012), modified eggshell powder as a pharmaceutical excipient in tablet and acetaminophen as a model drug were investigated. The eggshell powders were treated by surface modification using 1.0% w/v stearic acid in deionized water, ethanol and chloroform and untreated eggshell powder was used as control. The tablets, including acetaminophen, microcrystalline cellulose and treated eggshell powder, were prepared by direct compression method, and demonstrated that immediate release of acetaminophen was obtained from tablets containing untreated eggshell powder. In contrast, sustained release of the drug was obtained from the tablet formulations containing modified eggshell particles. Recently, silver nanoparticles loaded with calcium carbonate ($Ag/CaCO_3$) particles were prepared by precipitation technique and reported by Azarian et al (Azarian and Sutapun, 2022). As illustrated in Figure 11, spherical precipitated calcium carbonate (PCC) particles were deposited by silver nanoparticles and energy-dispersive X-ray spectroscopy mapping (EDS) images depicted a clear spherical pattern, indicating their loading at the outer layer of PCC particles with silver atomic weight percentage of 4.27 wt%.

Similarly, Apalangya et al. (2014) have prepared calcium carbonate silver hybrid nanoparticles with wet mechanochemical milling technique using chicken eggshell and silver nitrate as starting materials. The eggshell particles with crystalline calcite structure were embedded with silver

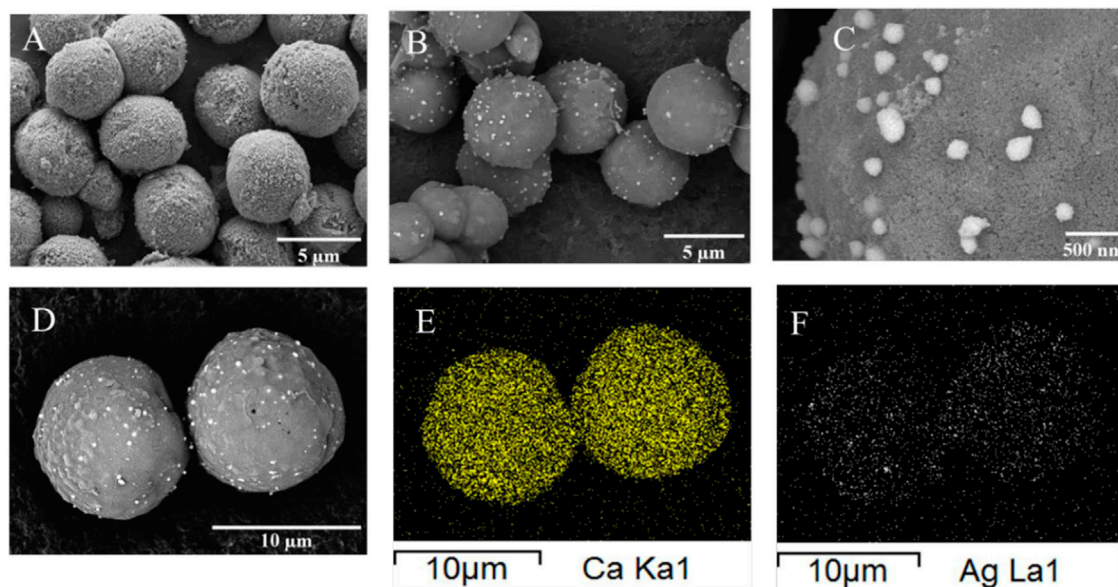


FIGURE 11

(A) SEM microimage of PCC particles without silver loading, (B) SEM microimage of PCC particles loaded with silver nanoparticles, (C) Higher magnification of SEM microimage (B), (D) SEM microimage of PCC loaded with silver nanoparticles. Reproduced from (Azarian and Sutapun, 2022) "Tuning polymorphs of precipitated calcium carbonate from discarded eggshells: effects of polyelectrolyte and salt concentration" <https://pubs.rsc.org/en/content/articlehtml/2022/ra/d2ra01673g> licensed under CC BY-NC 3.0.

nanoparticles ranging in size from 5 to 20 nm. The hybrid eggshell/silver nanocomposite exhibited superior inhibition of *E. coli* growth using the Kirby–Bauer discs diffusion assay. In a related study, the aragonite calcium carbonate from cockle shell have been synthesized *via* oil-in-water microemulsions in high-pressure homogenizer using Tween-80 and glycerol as surfactant and co-surfactant, respectively. The ciprofloxacin drug was loaded into obtained cockle shells aragonite calcium carbonate nanoparticles (encapsulation efficiency of 95%) in suspension by mechanically stirring, and antibacterial properties were studied by disc diffusion protocol on *Salmonella Typhimurium*. The results indicated that ciprofloxacin/calcium carbonate nanoparticles improved the antibacterial efficacy of the antibiotic by increasing the mean diameter of the inhibition zone from 11.7 ± 0.9 mm in ciprofloxacin alone to 18.6 ± 0.5 mm in calcium carbonate delivery system (Ja, 2016).

Dayanidhi *et al.* (2020) have synthesized the silver nanoparticles with an average particle size of 35 nm, using microwave and *Sapindus mukorossi* extract as a stabilizing agent. The obtained silver nanoparticles were immobilized on the surface of grounded eggshell powder with micron size in solution by overnight mechanical stirring. A recent review paper published by Ferreira *et al.* (2020) also reviewed the vaterite calcium carbonate crystals obtained from

precipitation technique as carriers for controlled delivery of antimicrobials.

4.6 Cement and bio-ceramics

Cement is one of the most used structural materials in constructions and buildings (Wan Mohammad *et al.*, 2017). Cement is an expensive mixture of raw materials, including iron, calcium, silicon, and aluminium which yields carbon dioxide emissions during production, making the cement industry one of the most significant contributors of greenhouse gas (7% of global CO₂ emission) (Benhelal *et al.*, 2013). Green cement can be produced by using biogenic calcium carbonate waste instead of limestone and clay raw materials in clinker production, consequently reducing carbon dioxide emissions (Tan *et al.*, 2018). In another study, Pliya *et al.* (Pliya and Cree, 2015) have studied the use of ground untreated white and brown chicken eggshell powders as potential replacements of calcium carbonate derived from limestone in cement mortars. The results indicated that the addition of untreated eggshell powders in cement reduced the compression and flexural strengths of the cement. The lower properties of calcium carbonate eggshell powders would be due to irregular calcite calcium carbonate particles with larger sizes

and residual of inner organic membrane of shells as they were obtained by only grinding without any treatment or precipitation method. This indicates the importance of precipitation technique or additional organic extraction treatment to obtain purer calcium carbonate with desirable size and controllable crystal structures. In another study, Cree *et al.* (Cree and Rutter, 2015) have applied heat and bleaching treatments to eggshell powders in order to obtain the purified form of calcite calcium carbonate as a potential replacement of limestone in the cement industry. Although pure calcite calcium carbonate was obtained by heat and bleaching treatments, irregular calcite morphology was observed under electron microscopy. Moreover, as stated by the same authors, bleaching treatment is unsustainable, and is not eco-friendly.

Choi *et al.* (2016) have introduced a method to generate bio-cementation in sand using microbially induced carbonate precipitation process from waste eggshells instead of using calcium chloride. The eggshells were digested in acetic acid and used for calcium carbonate precipitation in concrete, and a comparative study was performed between sand samples treated using precipitated calcium carbonate from eggshell and sands using precipitated calcium carbonate using calcium chloride. It was found that calcium carbonate produced from eggshells is just as good as using calcium chloride solution. The recent review paper published by Chong *et al.* (2020), have focused on the properties of concrete with untreated eggshell powders (eggshell concrete) based on previous studies, stated clearly in detail that at about 10 wt% eggshell powders, the cement possesses various advantages in comparison to conventional cement including improved hardened properties, lower setting time, and enhanced resistance to water penetration. However, there is a lack of research regarding eggshell cement's durability properties in different environments. Moreover, there is a lack of research regarding the usage of precipitated calcium carbonate from eggshell particles with desired size, structure and morphology in advanced cement and ceramics industries.

4.7 Cosmetic, pharmaceutical and food industry

Annually one-third of the food suitable for human consumption is wasted globally, which is also blameworthy for one-third of all greenhouse gases produced (Waheed *et al.*, 2019). Calcium carbonate is a vital mineral ingredient which tonnes of it discarded daily plays a significant role in supporting bone and teeth health. In research by Murakami *et al.* (2007) physicochemical properties of calcium carbonate from eggshells have been studied and found that calcium carbonates derived from eggshell wastes are more thermally stable than the conventional calcium carbonate with similar

crystallinity, indicating that eggshell calcium carbonate should be served as an alternative in pharmaceutical, food and cosmetic products. Recently, Hickman *et al.* (2019) have studied the composition of various calcium carbonate obtained from geological, synthetic and biological origins and found that biological calcium carbonate is not different from traditional calcium carbonate sources, plus the advantages of renewability and sustainability. However, the organic membrane of eggshells would bring out the need for some additional processing such as precipitation or treatment technique.

Furthermore, calcium carbonate can react with gastric HCl in the human body and act as an antacid. Several studies indicated that porous calcium carbonate derived from eggshell powder could be absorbed better in the human intestine than limestone calcium carbonate (Aditya *et al.*, 2021). Up to now, there is no study available in literature dealing with the usage of calcium carbonate with different polymorphic structures obtained from treated or precipitation techniques. However, plenty of research is available in the literature that used and reported the calcium carbonate derived biogenic waste in foods, cosmetics, and pharmaceutical industry by a simple direct method, which is out of the interest of the current review paper. There is also plenty of research in the literature that used the calcium carbonate derived biogenic waste as starting materials to obtain other calcium derivatives such as calcium citrate (Palacios *et al.*, 2021), hydroxyapatite (Alhussary *et al.*, 2020), and calcium lactate (Daengprok *et al.*, 2002) for pharmaceutical and food industry applications.

5 Conclusion and outlook

In this comprehensive, up-to-date review, we have summarized all the reported studies so far that applied treated or precipitated calcium carbonate derived from biogenic wastes for advanced materials application. The development of advanced material applications based on derived calcium carbonate from biogenic wastes showed significant progress due to its multiple impacts towards Sustainable Development Goals (SDGs) such as reducing environmental pollution, sustainability, and cost-effectiveness. The recently published research papers regarding the utilization of biogenic waste-derived calcium carbonate have significantly increased in different fields such as water treatment, filler, and reinforcement in polymer composites, energy storage devices, pharmaceutical, biomedical application, and drug delivery. However, most of the reported research in literature have used a direct method and employed simple mechanochemical or grinding techniques to reduce the size of calcium carbonate with only calcite crystal structures. The disadvantages of untreated or non-precipitated methods are obtaining impure irregular calcium carbonate particles with minimal control on

crystal structure, size, and morphology. As calcium carbonate derived from biogenic waste gains more attention, it is essential to seek new process routes to improve and boost its further progress in the future. Therefore, it is necessary to put additional efforts into investigating, formulating, and examining new methodologies such as indirect, i.e., treated or precipitation technique to obtain an engineered reduced-sized calcium carbonate with stable polymorphic structures and desired morphologies. Calcium carbonate is an excellent inorganic material for advanced materials with improved properties. The technique development for precipitation and usage of calcium carbonate from biogenic wastes is vital due to decreasing environmental pollution and the opportunity to engineer and obtain desired calcium carbonate polymorphic structures with intended particle sizes and shapes suitable for various applications.

Author contributions

MA reviewed the literature and drafted the review while corresponding author supervised, organized and reviewed the paper.

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