Effect of eggshell/N,N-dimethylformamide (DMF) mixing ratios on the sonochemical production of CaCO₃ nanoparticles

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Abstract

Bio-CaCO₃ nanoparticles have several applications and have attracted significant attention in current research. N,N-dimethylformamide (DMF) has been proven to be an effective non-volatile solvent for synthesizing bio-CaCO₃ nanomaterials from eggshell. However, the optimum ratio of eggshell and DMF need to be specified to achieve maximum nano-CaCO₃ production for large-scale purposes. Thus, this work investigated the effect of eggshell/DMF mixing ratios on the production of CaCO₃ nanoparticles from the chicken eggshell. The nano-CaCO₃ were synthesized via dry milling and then sonication at a frequency of 40 kHz for 6 h in the presence of DMF. The eggshell mass was varied from 0.5 to 20 g per 100 mL of DMF. The synthesized CaCO₃ materials were characterized using SEM, TEM, EDX, XRD, and BET surface analysis. The eggshell/DMF ratio was optimized to maximize the production of CaCO₃ nanoparticles, and its effect on the size, crystallinity, surface area, and porosity of the CaCO₃ particles were discussed. Increasing eggshell/DMF ratio decreased the sonication efficiency with increasing crystallite and particle size. The specific surface area of the synthesized CaCO₃ particles decreased with increasing eggshell/DMF ratio. 1 g/100 mL was the optimum or highest ratio to obtain 100% nano-CaCO₃. At 1 g/100 mL ratio, the bio-CaCO₃ contained a crystallite size of 23.08 nm, particle size between 5 and 30 nm and surface area of 47.44 m² g⁻¹.

Keywords: Nanoparticles, Bio-CaCO₃, Recycling, Eggshell, Ultrasonic irradiation

Introduction

Current waste management strategies involve minimizing waste, as well as collection and storage/treatment [1, 2]. However, waste such as biomass generated from agricultural and domestic activities is inevitable [3]. These biomasses like eggshells are generated daily in enormous quantities since their main products are life-dependent: source of food [4, 5]. Although agro-biomass is biodegradable in the natural environment, the biomass contains vital compounds or elements that have many uses [6]. For instance, carbon found in biomass can serve as a precursor for producing fuels, gas, adsorbents, and several others [5, 7–10]. Hence, waste biomasses are valuable materials, and the...
valorization of such waste is sustainable, economical, and generally eco-friendly [11, 12]. Moreover, recycling waste offers a more cost-effective approach to managing waste and preventing environmental pollution [13].

Eggshells are industrial and household byproducts; thus, they are abundant and available at a low cost. The global egg production is around 77 million tonnes, resulting in over a million tonnes of eggshell biomass created as waste each year [14, 15]. However, the majority of eggshells are disposed in landfills [5]. Meanwhile, eggshell is a biodegradable material with extraordinary properties such as a unique natural porous structure and a high calcium carbonate (bio-CaCO₃) concentration (95 wt%) in the form of calcite [16, 17]. Thus, eggshells can be used in various applications, including as a biosorbent for environmental treatment, where it has a strong affinity for heavy metal ions and dyes [18, 19]. The calcite in eggshell can also be used: in the production of biocompatible ceramic materials, as an abrasive ingredient in toothpaste, coating pigments for ink-jet printing paper, as bio-filler to improve the properties of polymer nanocomposites, to improve the mechanical behavior and tensile properties of polypropylene composites, controlled epoxy resin composite, and improve the thermal stability and glass transition temperature of normal corn starch foams [12, 17, 20, 21].

On the other hand, nanotechnology involves the conversion of bulk materials to nanometric size (< 100 nm) [22, 23]. Nanotechnology introduces unique characteristics into materials and makes them widely applicable as catalysts, structural components, information storage, electronics, and sensors [24–28]. Hence, nanomaterials have been the focus of current research [28, 29]. Studies have shown that the conversion of eggshells into nanometric size presents significant advantages over bulk or micrometer-sized eggshells [17, 30]. Nanometric eggshell has a relatively high surface area and uniform pore distribution. Therefore, nano-eggshell is used as a more efficient adsorbent for dyes and metals in solution and additive for plastics and ceramic composites to improve their properties [17]. Other studies have shown that nanometric eggshells can be more effectively deposited on the biochar matrix to improve the adsorption capabilities [18].

Meanwhile, several top-bottom methods can be used to synthesize nanomaterials [31]. High-energy ball milling is the most widely used method in producing nanomaterials because ball milling is simple, applicable for numerous materials, and can be advanced quickly for commercial production [32]. However, the comminution of particles from micrometer to nanometer scale by milling requires much energy and is costly [32]. Further drawbacks of milling include particle agglomeration and nanomaterial contamination [32]. Consequently, other methods such as ultrasonic irradiation have been employed as an effective alternative for synthesizing nanomaterials with remarkable properties [17].

Sonochemistry is an acoustic cavitation process that involves the creation, growth, and implosive collapse of bubbles in a liquid medium [33]. This result in extreme conditions such as high temperatures (> 5000 K), high pressure (> 20 MPa), and high cooling rate (> 107 K s⁻¹) [34]. These extreme conditions introduce many unique properties in the irradiated solution, affecting the size reduction [34]. Sonication is a suitable method for reducing the particle size of many inorganic materials while preserving the crystalline structure [35]. A study by Hassan et al. (2013) investigated the preparation of bio-CaCO₃ nanoparticles from eggshell using wet ball milling with polypropylene glycol. The ball-milled eggshell particles were then irradiated a sonochemical process in
the presence of N,N-dimethylformamide (DMF), decahydronaphthalene (Decalin), and tetrahydrofuran (THF). DMF was reported as the most effective solvent [17]. Low volatile solvents like DMF have relatively low vapor pressures and are effective solvents for synthesizing biobased nanomaterials via the sonochemical process [17, 35].

Nevertheless, a crucial aspect of the nano-CaCO₃ preparation via the sonochemical process which includes optimizing the mixing ratios between the eggshell powder and solvent has not been discussed [36–39]. Such study is vital to the large-scale production of the bio-CaCO₃ nanoparticles from this process. This can specify the maximum eggshell/DMF ratio required to produce high yield eggshell nanoparticles via the sonochemical process. Moreover, studies have shown that the efficiency of sonochemical processes is critically dependent on the solid/solvent ratio [40].

This present study investigates the effect of eggshell/DMF mixing ratios on the sonochemical production of CaCO₃ nanoparticles for large-scale applications. This is the first study that examines the eggshell/DMF mixing ratios and optimizes the ratios to maximize CaCO₃ nanoparticle production. This work further discusses the effect of the mixing ratios on the size, crystallinity, and porosity of the CaCO₃ nanoparticles.

Materials and experimental method

Materials and reagents

Chicken eggshells were collected from a local restaurant in Borg El Arab, Egypt. Acetone (99.8%) was purchased from Fisher Scientific in the UK. N,N-dimethylformamide (99.8% DMF) was purchased from Sigma-Aldrich in Germany. Ethanol (70%) was procured from Brand Chemicals in Egypt.

Synthesis of CaCO₃ nanoparticles

A modified method of synthesizing CaCO₃ nanoparticles from the chicken eggshell powder was used, as illustrated in Fig. 1a–f [17, 18]. The eggshells were thoroughly washed with demineralized water and dried overnight in a 110 °C oven (Fig. 1a). The dry eggshells were pulverized for 5 min using a blender to obtain an eggshell powder. The fine eggshell powder was then soaked in acetone and stirred for 2 h. The shells were then dried in an oven at 60 °C for 2 h. The dried eggshell powder was ground to
below 106 μm sizes using a Retsch PM 400 planetary mill with 1 mm diameter ceramic balls at a ratio of 1:1 for 5 h (Fig. 1b). An amount of the eggshell powder (Fig. 1c) was irradiated in the presence of a fixed 100 mL DMF in a glass beaker at a frequency of 40 kHz using Cole-Parmer digital ultrasonicator for 6 h (Fig. 1c). The suspensions were manually stirred regularly to reduce particle settling. After the sonochemical reaction, the particles were collected and washed repeatedly with ethanol (Fig. 1e). The final product was centrifuged at 6000 rpm for 30 min using Hettich EBA 20 centrifuge to separate the eggshell particles from the solvents. Eggshell particles were then dried under vacuum for 24 h (Fig. 1f) and stored in a vacuum desiccator. The samples were labelled ES-1, ES-2, ES-3, ES-4, ES-5, and ES-6, corresponding to an eggshell powder mass of 0.5, 1, 2, 5, 10, and 20 g, respectively.

**Characterization techniques for the CaCO₃ nanoparticles**

Surface morphological analysis and size measurement of the prepared CaCO₃ samples was conducted using a scanning electron microscope (SEM) (JEOL, JSM-6010LV, Japan). Higher-resolution micrographs of the morphology, nano-size particle measurement, and elemental composition of the samples were determined using a transmission electron microscope (TEM) equipped with energy dispersion X-ray spectroscopy (EDX) (JEOL, JEM-2100F, Japan). Bruker D2 Phaser was used to generate X-ray diffraction (XRD) crystallographic information of the CaCO₃ samples. Nitrogen gas (N₂) adsorption-desorption test and the Barrett, Joyner, and Halenda (BJH) analysis were conducted to examine the surface texture and pore size distributions. The Brunauer-Emmett-Teller (BET) surface area, mean pore size and total pore volume of the char products were analyzed with Microtrac MRB Belsorp Mini X, Japan.

**Results and discussion**

The XRD patterns of the prepared bio-CaCO₃ (Fig. 2) show peaks at 2θ° of approximately 23°, 29°, 36°, 39°, 43°, 47°, 48°, 57°, 61°, and 65° corresponding to the (012), (104), (113), (202), (016), (018), (122), (224), and (036) diffraction planes of calcite phase of CaCO₃ (JCPDS card No. 47-1743) [17, 21]. The presence of sharp peaks indicates highly crystalline CaCO₃ in all samples. The characteristic calcite diffraction peaks present in all samples are positioned at approximately the same angles indicating that the sonochemical irradiation caused no structural changes to the chemical composition of the sonicated samples. Moreover, calcite is the most stable polymorph of calcium carbonate and will not easily undergo any structural changes [21, 41, 42]. The EDX spectra (Fig. 3) confirm peaks of calcium (Ca), carbon (C), and oxygen (O), confirming the presence of CaCO₃ with no impurities in all prepared bio-CaCO₃.

OriginPro 9.8 software was used to estimate the full width at half maximum (FWHM) for all the bio-CaCO₃ samples by fitting the Gaussian model on the most intense (104) peak at 2θ° of ~ 29°. The obtained FWHM values were used to calculate the crystallite size of the prepared bio-CaCO₃ using the conventional Scherrer Equation at an X-ray wavelength of 0.154 nm and shape factor of 0.94. The FWHM value of the (104) peak of the bio-CaCO₃ particles decreased with the increasing ratio of eggshell/DMF with a corresponding increase in crystallite size (Table 1). This indicates that the smaller sizes of bio-CaCO₃ particles are achievable at lower eggshell/DMF ratios. Studies have
shown that solid particles tend to aggregate quickly in their suspensions when the solids mass increases [10]. Consequently, increasing CaCO₃ particles aggregation with increasing eggshell mass caused the eggshell particles to settle quickly, impeding sonochemical process efficiency at higher eggshell concentrations [40, 43]. Moreover, the transfer principle states that the increasing concentration gradient between the substance and the solvent is the driving factor for mass transfer [40]. Hence, increasing the eggshell mass causes rapid saturation of the DMF solvent, which reduces the efficiency of solids dispersion and accordingly decreases the sonochemical process efficiency [40, 43]. Contrarily, larger volume of solvent enhances the solvent extraction capability, preventing early saturation and enabling a higher production of nano-CaCO₃ [40]. The crystallite sizes of ES-1 and ES-2 (18.07 and 23.08 respectively) are close to the crystalline size of nano-CaCO₃ particles that were synthesized through the precipitation of dissolved Ca(NO₃)₂·4H₂O [44]. This indicates a possible production of nano-CaCO₃ particles from ES-1 and ES-2.

SEM micrographs of the bio-CaCO₃ show clusters and agglomerations of calcite particles with irregular sizes and shapes (Fig. 4). Several fragmented bio-CaCO₃ particles were observed in ES-1 (Fig. 4a) and ES-2 (Fig. 4b), illustrating the impact of sono-irradiation in breaking down the eggshell particles. However, the particle size of the prepared bio-CaCO₃ increased with increasing eggshell/DMF ratio. From Fig. 4c (ES-3), Fig. 4d (ES-4), Fig. 4e (ES-5), and Fig. 4f (ES-6), a blend of fragmented and larger lumps of bio-CaCO₃ are observed with an increasing amount of larger lumps with higher eggshell/DMF ratio. This confirms the results from the XRD analysis illustrating the effect of eggshell/DMF mixing ratio on the sonochemical production of bio-CaCO₃.

TEM analysis provided further detailed imagery of the morphology (Fig. 5) and measurements of the particle sizes of the synthesized bio-CaCO₃ (Table 2). The TEM
Fig. 3 EDX spectra of a ES-1, b ES-2, c ES-3, d ES-4, e ES-5, and f ES-6

Table 1  Crystallite size of bio-CaCO$_3$

| Sample | FWHM at 29° 2θ | Crystallite size at 29° 2θ (nm) |
|--------|-----------------|---------------------------------|
| ES-1   | 0.474           | 18.07                           |
| ES-2   | 0.371           | 23.08                           |
| ES-3   | 0.349           | 24.54                           |
| ES-4   | 0.277           | 30.92                           |
| ES-5   | 0.275           | 31.14                           |
| ES-6   | 0.246           | 34.81                           |
micrographs show the presence of CaCO₃ platelets in all samples with shadows depicting agglomerations (Fig. 5). ES-1 (Fig. 5a) and ES-2 (Fig. 5b) contain irregular shapes of CaCO₃ nano-platelets (< 100 nm). However, ES-3 (Fig. 5c) contains similar irregular shapes of both nano and micro sizes. Meanwhile, ES-4 (Fig. 5d), ES-5 (Fig. 5e), and ES-6 (Fig. 5f) contain a blend of nanometric and micro-size CaCO₃ platelets with an increasing amount of micro-size CaCO₃ particles as the eggshell concentration increases. Thus, 1 g/100 mL (ES-2) is the maximum eggshell/DMF ratio to produce 100% CaCO₃ nanoparticles (less than 100 nm sizes).

The N₂ adsorption and desorption isotherm curves of the bio-CaCO₃ samples show increasing N₂ sorption at high relative pressures as shown in Fig. 6a, which is characteristic of type-III isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification [45]. This describes a mesoporous texture of all prepared bio-CaCO₃ [46]. Meanwhile, for an equal volume of a specific material, the samples with smaller sizes have relatively high specific surface
area [43, 47, 48]. Accordingly, the N₂ adsorption capacity increased with decreasing eggshell concentration depicting a relatively high surface of CaCO₃ prepared from lower eggshell/DMF ratios (ES-1 >> ES-6). This result confirms the production of smaller bio-CaCO₃ particles with decreasing eggshell concentrations due to the subsequent improvement in the sonochemical process (slow saturation, lower

Table 2

| Sample | Particle size range (nm) | Morphology                        |
|--------|--------------------------|----------------------------------|
| ES-1   | 5–20                     | Irregular-shaped platelets        |
| ES-2   | 5–30                     | Irregular-shaped platelets        |
| ES-3   | 10⁴ × 10⁴                | Irregular-shaped platelets        |
| ES-4   | 10⁻¹⁷ × 10⁴              | Blend of irregular and few rectangular platelets |
| ES-5   | 15–10⁵                   | Blend of irregular and rectangular platelets |
| ES-6   | 20–10⁵                   | Predominantly rectangular platelets |
tendency of particle agglomeration, and slower rate settling at lower eggshell concentration) at lower eggshell/DMF ratio. On the other hand, all the prepared bio-CaCO₃ samples have broadly distributed pores ranging from 10 to > 100 nm (Fig. 6b). This shows that the sonochemical process had less impact on the porosity of the prepared bio-CaCO₃. The BET surface area, average pore diameter and total pore volume of the prepared bio-CaCO₃ are summarized in Table 3.

**Conclusion**

This work studied the effect of eggshell/DMF mixing ratio (0.5 to 20 g eggshell powder per 100 mL of DMF) on the sonochemical production of bio-CaCO₃ nanoparticles. The size of the prepared bio-CaCO₃ platelets increased with increasing eggshell/DMF ratio due to particle agglomeration, solvent saturation and rapid settling. The eggshell/DMF ratio was optimized to achieve maximum production of

**Table 3** Textural properties of bio-CaCO₃

| Sample | BET surface area (m² g⁻¹) | Total pore volume (cm³ g⁻¹) | Mean pore diameter (nm) |
|--------|--------------------------|-----------------------------|-------------------------|
| ES-1   | 52.62                    | 0.181                       | 39.30                   |
| ES-2   | 47.44                    | 0.179                       | 41.22                   |
| ES-3   | 42.38                    | 0.164                       | 35.27                   |
| ES-4   | 27.39                    | 0.159                       | 36.01                   |
| ES-5   | 14.43                    | 0.154                       | 48.08                   |
| ES-6   | 13.25                    | 0.142                       | 39.35                   |
100% nano-CaCO₃ at ES-2 (1 g/100 mL eggshell/DMF ratio) and a sonication frequency of 40 kHz for 6 h. The prepared nano-CaCO₃ from ES-2 has a crystallite size of 23.08 nm and particle sizes between 5 and 30 nm. The surface area of the prepared bio-CaCO₃ decreased with increasing eggshell/DMF ratio due to the presence of large and lumpy CaCO₃ fragments that remained at higher eggshell/DMF ratios (≥ 2 g/100 mL). At ES-2 (1 g/100 mL eggshell/DMF ratio), the BET surface area, pore volume and average pore diameter of the prepared nano-CaCO₃ were 47.44 m² g⁻¹, 0.179 cm³ g⁻¹, and 41.22 nm, respectively. The prepared bio-CaCO₃ nanoparticles can be used in large-scale applications such as adsorption, polymer composites, and catalyst.

Abbreviations
ES: Eggshell; DMF: N,N-dimethylformamide; CaCO₃: Calcium carbonate; SEM: Scanning electron microscope; TEM: Transmission electron microscope; EDX: Energy dispersion X-ray spectroscopy; XRD: X-ray diffraction; BET: Brunauer-Emmett-Teller; BJH: Barrett, Joyner, and Halenda; N₂: Nitrogen gas; Ca: Calcium; C: Carbon; O: Oxygen; FWHM: Full width at half maximum; IUPAC: International Union of Pure and Applied Chemistry

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Authors’ contributions
KM conceptualization, visualization, methodology—experimental work, formal analysis, writing—original draft; writing—review and editing; AMA: conceptualization, methodology—experimental work, writing—review and editing; HS: supervision, writing—review and editing. All authors read and approved the final manuscript.

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Declarations
Competing interests
The authors declare that they have no competing interests.

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