



Original Research Paper

Preparation of amorphous calcium carbonate nanoparticles from impure dolomitic marble with the aid of poly(acrylic acid) as a stabilizer

M.M.M.G.P.G. Mantilaka^{a,b}, R.M.G. Rajapakse^a, D.G.G.P. Karunaratne^c, H.M.T.G.A. Pitawala^{d,*}^a Department of Chemistry, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka^b Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka^c Department of Chemical and Process Engineering, Faculty of Engineering, University of Peradeniya, Peradeniya, Sri Lanka^d Department of Geology, Faculty of Science, University of Peradeniya, Peradeniya 20400, Sri Lanka

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ABSTRACT

Nanomaterials of Precipitated Calcium Carbonate (PCC) such as Amorphous Calcium Carbonate (ACC) nanoparticles are highly demanded industrial products. These products are prepared in industrial scale, using pure CaCO₃ natural resources such as pure carbonate rocks, cockle shells, corals, and pearls. Such natural resources could be consumed rapidly due to their excessive use in PCC industries. Therefore, the development of novel procedures to prepare nanoparticles of PCC using impure minerals is desirable. Herein, we report a simple, novel and economical method to synthesize poly(acrylic acid) (PAA) stabilized ACC nanoparticles using extensively distributed impure dolomitic marbles in place of natural pure CaCO₃ raw materials. The yields of final ACC products are enhanced using a bubbling column which can produce small bubbles to improve bubbling efficiency. The average particle sizes of final calcium carbonate products are in the range 21–53 nm. The best conditions to produce ACC, among the conditions used in the proposed method, are temperature of 40 °C, pH of 4.5 and PAA concentration of 10⁻² M. One or more crystalline phase(s) of PCC is associated with ACC in each product and its nature depends on the conditions used in the synthesis of these products. The unstable vaterite form of PCC is formed when the PAA concentration is less than 0.5 M and at lower temperatures such as room temperature. The stability of the vaterite phase decreases when the temperature and the PAA concentration are increased. The synthesized ACC nanoparticles are in required purity and quality to be suitable for industrial applications.

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1. Introduction

Biomimetic synthesis of Precipitated Calcium Carbonate (PCC) with various phases, sizes and morphologies by using organic substrates has become an interesting topic in recent years [1–5]. PCC is a value-added product and is highly demanded in industries such as paper, textile, rubber, plastic, paint, cosmetic, sealant, tooth paste and food stuff [6–8]. Conventionally, powders of micrometer sized coarse particles of PCC are used in these industries. As far as the filling ability and the dramatic increase in the surface area-to-volume ratio are concerned, nanoparticles are much superior to conventional powders and many industries now opt for PCC nanoparticles [9,10]. PCC occurs in three crystalline forms (calcite, aragonite and vaterite) as well as in the metastable amorphous form [2]. Out of these structural forms, Amorphous Calcium Carbonate (ACC) nanoparticles have become an attractive product due to its

ability to function as a precursor phase to synthesize a particular crystalline form [11–14], its use as an inexpensive absorbent of toxic metals [15] and its role as a monodispersed filler for many polymers [16]. The thermodynamic stability of ACC is, however, low and is readily converted to the crystalline forms. Therefore, additives such as poly(acrylic acid) (PAA) and Mg²⁺ ions have to be used to stabilize ACC nanoparticles [13,15,17–19].

Production of PCC using natural resources is only done by pure carbonate resources such as carbonate rocks with high percentage of CaCO₃, cockle shells, corals, and pearls [20–23]. However, these valuable resources can be exhausted due to the widespread production of PCCs to meet with its high demand. Marble is the largest ore body for carbonate minerals in the world which contains dolomite and calcite as major rock forming minerals [24]. However, the use of marbles to synthesize PCC has been limited as a result of high variability of Ca and Mg percentages and due to the presence of impurities [25–27]. Therefore, the development of methods to synthesize PCC products from marbles is a timely needed requirement for fulfillment of current demand and to save the naturally

* Corresponding author. Tel.: +94 81 2394211.

E-mail address: apitawala@pdn.ac.lk (H.M.T.G.A. Pitawala).

occurring pure carbonate resources. To the best of our knowledge, marble has not yet been used to synthesize nanoparticles of ACC or nanocomposites of ACC and polymers.

There are two basic synthetic routes to synthesize PCC: (1) Solution route in which, carbonate salt and calcium salt in aqueous form are mixed together in equal molar ratio and (2) Carbonation route wherein, CO_2 is bubbled through a slurry of $\text{Ca}(\text{OH})_2$ or solutions of Ca^{2+} salts [25,28–31]. Most of researchers have synthesized ACC nanoparticles through solution routes [15,32,33]. However, the economical, conventional and industrial method that is often applied to synthesize PCC products from minerals is carbonation route [20,34]. ACC can be synthesized by bubbling CO_2 through a slurry of hydrated calcined dolomite which contains dissolved $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})_2(\text{s})$, $\text{MgO}(\text{s})$ and $\text{Mg}(\text{OH})_2(\text{s})$ and a very little amount of dissolved $\text{Mg}(\text{OH})_2$. The Mg^{2+} ions present in this mixture can penetrate to calcium carbonate structure and prevent the crystal growth thus facilitating the formation of ACC phase in the resulting PCC product [19]. However, the associated Mg^{2+} components will reduce the quality and purity of final ACC product which are crucial factors on value estimation. Therefore, it is required to remove Mg^{2+} component of dolomite before synthesis. Moreover, carbonation route is associated with a drawback of low reactivity of CO_2 with Ca^{2+} solution due to poor intermolecular interactions of the reactants as a result of low interfacial area [35,36]. This drawback can be overcome through the size reduction of CO_2 bubbles which strongly influences to enhance the reaction rate [35,37] and the yield of final PCC product.

Herein, we focus, for the first time, on synthesis of PAA stabilized ACC nanoparticles using dolomite *via* carbonation route by mimicking the biomineralization process. The CO_2 bubbling efficiency of the carbonation route has been improved by designing a bubbling column which produces small bubbles of CO_2 . Influences of pH of PAA solution and temperature of the reaction mixture on complexation of PAA and calcium sucrate as well as on the final PCC products are studied. Effect of PAA concentration on final PCC products is also reported. The proposed method is potentially important in the production of ACC in industrial scale by utilizing dolomite as calcium source in place of high quality calcium carbonate resources.

2. Experimental

2.1. Materials

Acrylic acid ($\geq 99\%$) and sodium persulfate ($\geq 99\%$) were purchased from Sigma–Aldrich. Dolomite samples were collected from a working marble quarry at Digana area located in the central part of Sri Lanka [25].

2.2. Preparation of soluble calcium sucrate from dolomite

This procedure has been documented elsewhere [25]. In brief, the dolomite samples were crushed, ground and filtered through 300 mesh sieve. The powder thus obtained was heated to $1000\text{ }^\circ\text{C}$ for 3 h in a Muffle furnace to produce calcined dolomite ($\text{CaO}\cdot\text{MgO}$). An aliquot of 5.00 g of calcined dolomite was dispersed in 100.0 mL of 0.50 M sucrose solution and stirred for 1 h. The suspension thus obtained was filtered under suction to obtain soluble calcium sucrate and thereby to remove insoluble Mg^{2+} components and silicate impurities.

2.3. Preparation of PAA/PCC composite

A stock solution of PAA was prepared (0.5 M of repeat unit) by the radical polymerization of acrylic acid (AA) using 1.00 g of

$\text{Na}_2\text{S}_2\text{O}_8$ initiator and dissolving the polymer formed in 1 M $\text{NaOH}(\text{aq})$. In the preparation of PAA stabilized PCC, 100.0 mL of previously prepared calcium sucrate solution was added dropwise to 100.0 mL of the above PAA solution while stirring. CO_2 was bubbled through the resulted reaction mixture at a flow rate of 1 L/min. The column designed for bubbling CO_2 through calcium sucrate is schematically illustrated in Fig. 1. It is a cylindrical design with 10 sieve plates fixed inside the cylinder together with down comers for the liquid to flow to the plate below the down comer (see Fig. 1). Carbon dioxide gas is bubbled counter currently and the pressure of CO_2 gas is maintained in such a way to prevent the leakage of the solution through the holes of sieve plates but to allow CO_2 gas to flow upwards through the holes in the plates. The operating principle of the column is equivalent to that of a bubble cap tray columns used in industry. The products obtained after bubbling CO_2 were collected into a flask and washed with 50.0 mL aliquots of hot water for three times to remove impurities and dried in a vacuum oven for 12 h at $45\text{ }^\circ\text{C}$ and 600 mm Hg pressure.

2.4. Characterization techniques used

The phases of PCC products were analyzed from the Fourier Transform Infrared (FT-IR) spectroscopy. The FTIR spectra of the products were recorded on a Shimadzu IRPrestige 21 instrument with the KBr pellet method. Each sample was well ground and thoroughly mixed to homogenize them. The homogenized samples were mixed with dry KBr in 1:40 mass ratio and pellets were pressed at 5 Tons. The spectra of the sample pellets were recorded by using pure KBr pellet as the blank. The X-ray diffraction (XRD) studies were performed to study the crystalline phases of synthesized PCC products. The XRD spectra were recorded with a Siemens D5000 X-ray Powder Diffractometer with $\text{Cu K}\alpha$ radiation of wavelength $\lambda = 0.1540562\text{ nm}$. The samples were carefully ground to a fine powder and thoroughly mixed to homogenize them and their powder XRD spectra were recorded. The resulted XRD patterns were analyzed using X Powder 12 software with the aid of ICDD PDF 2 database. Morphologies of the products were observed with the help of Hitachi SU6600 Scanning Electron Microscope (SEM).

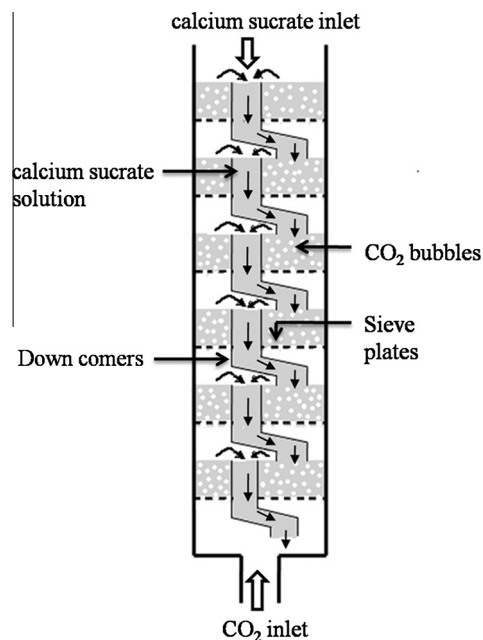


Fig. 1. Schematic illustration of carbonation column.

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