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RESEARCH ARTICLE

Surfactant-assisted synthesis of pure calcium carbonate nanoparticles from Sri Lankan dolomite

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Abstract: Sri Lanka is rich in extensive deposits of dolomitic marbles with large quantities, which have not yet been exploited on an industrial-scale to produce value-added products such as precipitated calcium carbonate (PCC) nanoparticles. PCC is used extensively and is imported by Sri Lankan industries for application as a filler and extender. Hence, this work attempts to examine Sri Lankan impure dolomitic marbles as a source for the synthesis of pure PCC nanoparticles, so as to fulfill the current industrial demand and to add value to the cheap and mundane marbles. As reported in this paper, the calcium (Ca) components of the marbles can be extracted from impurities by preparing solutions of saturated calcium hydroxide, calcium citrate, Ca^{2+}-ethylenediaminetetraacetic acid complexes and calcium sucrate, separately from dolomite. PCC nanoparticles are then synthesized by adding sodium carbonate to each calcium extract. The results shows that the best extract to synthesize PCC nanoparticles with high yield and purity is calcium sucrate. Here, calcium sucrate has been used for surfactant assisted hydrothermal synthesis of PCC nanoparticles with particle sizes ranging from 38.9 − 51.6 nm, which is a novel effort. This method could be applied to manufacture PCC nanoparticles on an industrial-scale.

Keywords: Calcite, calcium carbonate, dolomitic marble nanoparticles, precipitated calcium carbonate, value addition.

INTRODUCTION

Extensive deposits of crystalline limestones, which are also known as marbles cover over 20 percent of the land area of Sri Lanka (Cooray, 1984). These rocks with large quantities are only distributed in places of the Highland Complex such as Kandy, Matale, Nalanda, Habarana, Badulla, Welimada and Balangoda (Cooray, 1984; Madugalla *et al.*, 2013). Most of the Sri Lankan marbles contain dolomite as the major mineral (Cooray, 1984). The accessory minerals found in these rocks are calcite, apatite, spinel, phlogopite, olivine, pyrite and iron oxides (Madugalla *et al.*, 2013). Throughout the world, marbles are of economical importance owing to their broad range of applications including preparation of dimensional or decorative stones, as a refractory material, as a catalyst, in the production of lime, as a fertilizer and as an additive in glass, paper, plastics and rubber industries (Varela *et al.*, 2006; Rabaha & Ewais, 2009; Sun *et al.*, 2012; Karatas *et al.*, 2013). These applications mainly depend on the grain size and purity of marbles (Varela *et al.*, 2006). The high variability of chemical and mineralogical composition (Pitawala *et al.*, 2003), high intensified fractures in the rock, coarse grained nature and higher quantities of impurities (Cooray, 1984; Madugalla *et al.*, 2013) in Sri Lankan marbles makes it unsuitable for most of the above applications. Hence, the current use of Sri Lankan marbles is limited to the lime industry, construction activities and the production of fertilizers (Mantilaka *et al.*, 2013a). However, based on the chemical composition, these rocks have a high potential to synthesize chemical products such as precipitated calcium carbonate (PCC), magnesium hydroxide, magnesium oxide and their nanomaterials (Mantilaka *et al.*, 2013 a; b; 2014 a;b). Of these products, PCC has a high economic potential as it is in great demand in industries such as paper, textile, rubber, plastic, paint, cosmetic, sealant, tooth paste and food stuff (Kim *et al.*, 2009; Price *et al.*,

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2011; Yamanaka *et al.*, 2012). Most of these industries are well established in Sri Lanka with large production capacities. Currently the demand for PCC in Sri Lankan industries is fulfilled by importing it from countries such as India, Malaysia and China at a high cost. However, the synthesis of PCC nanoparticles on an industrial scale has not yet been considered by the Sri Lankan industrialists despite the fact that several simple procedures have been documented by Mantilaka *et al.* (2013 b; 2014 a) and other researchers throughout the globe (El-Sheikh *et al.*, 2013). Therefore, the synthesis of PCC from Sri Lankan marbles is timely and needed and it also serves as a move towards value-addition to a Sri Lankan resource. Furthermore, nanoparticles of PCC are much more attractive to industries than the conventional coarse PCC particles because of the dramatic increase in the surface area-to-volume ratio in the nanometer scale. This contributes to astonishing catalytic powers and extraordinary interactions between these filling materials and their host materials when the nanoparticles are used as fillers in various products such as paper, textiles, rubber, plastics, paints, cosmetics and sealants (Periago *et al.*, 2010; El-Sheikh *et al.*, 2013; Senarathna *et al.*, 2014). PCC nanoparticles are very expensive when compared to conventional PCC products. Therefore, maximum value-addition to Sri Lankan marbles can be accomplished through the manufacture of PCC nanoparticles and its use in industries. However, due to the dolomitic nature of Sri Lankan marbles, it is necessary to first extract and separate the calcium components from impurities prior to the synthesis of PCC nanoparticles (Mantilaka *et al.*, 2013 b; 2014 a). Therefore, novel, simple and economical techniques to synthesize PCC nanoparticles from the Sri Lankan marbles are required.

The present study focused on three theoretically possible methods to extract the calcium components of dolomite in order to synthesize pure PCC nanoparticles. These methods were: (1) extraction of calcium components from dolomite into an aqueous solution through preparation of a saturated calcium hydroxide solution, (2) preparation of calcium citrate and calcium-ethylenediaminetetraacetic acid (Ca^{2+}-EDTA) complexes and (3) preparation of calcium sucrate by extracting calcium components to a sucrose solution. We have already documented the calcium sucrate method elsewhere (Mantilaka *et al.*, 2013 b; 2014 a). Out of these possible methods, the best method that meets the requirements for industrializing the production process of PCC nanoparticles was selected.

The best and most suitable method to synthesize PCC is through calcium sucrate route since the productivity of this method is higher compared to the other methods. Furthermore, the present study reports for the first time the synthesis of PCC nanoparticles through a surfactant-assisted hydrothermal method, starting from calcium sucrate prepared using dolomite. This method can be applied to manufacture PCC nanoparticles on an industrial scale in an effort to fulfill the current demand for PCC nanoparticles in local industries as well as for value-addition to dolomitic marbles.

METHODS AND MATERIALS

Materials

Sodium carbonate, sucrose, ethylenediaminetetraacetic acid (EDTA), trisodium citrate dihydrate and Triton X-100 of analytical grade were purchased from Sigma-Aldrich. Dolomitic marble samples were collected from a working marble quarry located in the Naula area in Sri Lanka. These rock samples were crushed, ground and the sieved fraction less than 150 μm was used for the synthesis. The powdered marble sample was heated at 900 °C for 3 h to produce calcined dolomite (CaO. MgO).

Preparation of PCC from saturated $Ca(OH)_2$ solution obtained from calcined dolomite

A saturated solution of $Ca(OH)_2$ was prepared by dissolving 0.265 g of calcined dolomite in 100.0 mL of distilled water and the mixture was stirred for 1 h. The solution was separated from the precipitate by filtering. A sodium carbonate solution (0.10 M, 10.0 mL) was added to the filtrate of saturated $Ca(OH)_2$ solution to precipitate calcium carbonate. The PCC product was collected by filtering and the product thus obtained was dried in a vacuum oven at 45 °C and 600 mm Hg conditions for 12 h.

PCC nanoparticles from Ca^{2+}- ligand complexes

Calcined dolomite (0.50 g) was added separately to trisodium citrate and EDTA (100.0 mL of 0.50 M each) solutions to produce calcium citrate and calcium EDTA complexes. The resulting solutions were collected by filtering. Sodium carbonate (0.50 M, 100 mL) was added drop-wise to the calcium-ligand complexes in order to synthesize PCC. The PCC product was collected by filtering and dried in vacuum oven at 45 °C and 600 mm Hg conditions for 12 h.

PCC nanoparticles using calcium sucrate solution

Calcined dolomite (5.00 g) was added to 0.50 M sucrose

(100.0 mL) and stirred for 1 h to prepare a calcium sucrate solution. The resulting calcium sucrate solution was collected by filtering under suction. Triton X-100 (0.50 mL) was added to the calcium sucrate solution and stirred for 1 h. A sodium carbonate solution (0.50 M, 100.0 mL) was added drop-wise to the reaction mixture while stirring in order to allow calcium carbonate to be precipitated. The precipitate was collected by centrifuging and dispersed in 30.0 mL of water. The dispersion was added to 50.0 mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 160 °C for 15 h. The synthesized PCC product was washed with 10.0 mL of ethanol and then with 50.0 mL of distilled water 3 times to remove the impurities including Triton X-100 and it was dried afterwards in a vacuum oven at 45 °C and 600 mm Hg conditions for 12 h.

Characterization

The Ca^{2+} and Mg^{2+} contents of calcium citrate, saturated calcium hydroxide and calcium sucrate were measured using Buck Scientific 200-A atomic absorption spectrophotometer (AAS). X-ray diffraction (XRD) analysis was performed to identify the crystalline phases of the final PCC products from Siemens D5000 X-ray powder diffractometer with Cu Kα radiation of wavelength $\lambda = 0.154$ nm and scanning rate 2° min^{-1}. The XRD patterns were analyzed with the aid of ICDD PDF 2 database. The average particle size of PCC products was estimated by means of the Debye–Scherrer formula using the full width of the half-maximum of the XRD major peaks. Morphology of the PCC was examined with the help of Hitachi SU6600 scanning electron microscope (SEM) at the acceleration voltage of 10 kV. The dynamic light scattering (DLS) particle size distribution curves of PCC nanoparticles prepared from calcium sucrate were obtained with the aid of CILAS Nano DS dual scattering particle size analyzer. The fourier transform infrared (FTIR) spectra of PCC products were recorded on Shimadzu IRPrestige 21 instrument with the KBr pellet method. Herein, KBr pellets were prepared by mixing the sample and KBr in the mass ratio of 1:40 and pressing the mixture by applying a pressure of 5 tons. Thermo gravimetric analysis (TGA) was performed using Scinco STA N-650 simultaneous thermal analyzer at a heating rate of 10 °C/min in the presence of air flow.

RESULTS AND DISCUSSION

Characterization of dolomitic marbles

The XRD pattern of dolomitic marble sample is given in Figure 1a. The XRD peaks of marble sample centered at 2θ values of 30.9°, 41.1°, 51.0° and 64.5° confirmed that the major mineral in the collected marble sample is dolomite (JCPDS card no. 84-1208). The TGA plot of the marble sample (Figure 1b) reveals a single-step decomposition with a mass loss of 40 % in the temperature ranging from 673 − 788 °C, which is attributed to the decomposition of $CaMg(CO_3)_2$ to CaO.MgO (Mantilaka *et al.*, 2013b). This single step decomposition of dolomite takes place under atmospheric pressure conditions (Samtani *et al.*, 2001). Based on the analyses, mass percentages of $CaCO_3$, $MgCO_3$ and impurities of the marble sample are 51.3, 45.6 and 3.1 %, respectively.

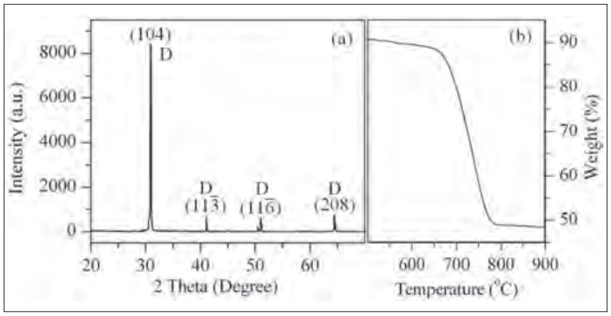

Figure 1: (a) XRD pattern; (b) TGA plot of the marble sample collected from Naula, Sri Lanka where, 'D' represents dolomite.

Separation techniques of Ca^{2+} and Mg^{2+} from dolomite

The first effort to extract Ca^{2+} in dolomite to synthesize PCC is through the preparation of a saturated $Ca(OH)_2$ solution by dissolving calcined dolomite in water. The required calcined dolomite (CaO.MgO) content to prepare 100.0 mL of saturated $Ca(OH)_2$ solution can be calculated by means of solubility product constant (K_{sp}) of $Ca(OH)_2$ ($K_{sp} = 6.5 \times 10^{-6}$ mol^3 dm^{-9} at 25 °C). In the hydration step of calcined dolomite, MgO component is converted to $Mg(OH)_2$, which has a very low solubility ($K_{sp} = 7.1 \times 10^{-12}$ mol^3 dm^{-9} at 25 °C) than that of $Ca(OH)_2$. Therefore, as calculated, more than 99.9 % of Mg^{2+} ions of dolomite are precipitated under saturation conditions of $Ca(OH)_2$.

In the second method, the Ca^{2+} content of dolomite is extracted to ligands of trisodium citrate and EDTA. These ligands form strong chelating complexes with Ca^{2+} ions (Jeffery *et al.*, 1989; Xiang *et al.*, 2002; Westin & Rasmuson, 2005 a;b) and the complexes are generated by dissolving calcined dolomite in the aqueous solutions of these ligands. Mg^{2+} ions also form similar type of complexes with these ligands (Jeffery *et al.*, 1989). However, the stability constants of each Ca^{2+}-

ligand complexes are greater than that of their Mg^{2+}-ligand complexes (Jeffery *et al.*, 1989). Therefore, the formation of Ca^{2+}-ligand complex is more favoured over that of the Mg^{2+}-ligand complex. This concept is useful for the extraction of Ca^{2+} component of the dolomite to synthesize PCC through the extraction of Ca^{2+} as complexes.

In the third method, a sucrose solution is employed to extract Ca^{2+} component from the calcined dolomite. Herein, CaO of the calcined dolomite is allowed to react with sucrose to form water soluble calcium sucrate (Wu *et al.*, 2007). MgO and other impurities in calcined dolomite do not react with sucrose and they will be present in the precipitated form (Seil, 1943; Mantilaka *et al.*, 2013b). The AAS analysis performed to determine the amounts of Ca^{2+} and Mg^{2+} that may be present in the extractions reveal the following information. The Ca^{2+} and Mg^{2+} mol percentages, can be calculated using the following equation,

$$\text{mol percentage} = \frac{\text{moles of } Ca^{2+} \text{ in the solution}}{\text{moles of } Ca^{2+} \text{ in the dolomitic marble}} \times 100\%$$

The Ca^{2+} and Mg^{2+} percentages of saturated $Ca(OH)_2$, calcium citrate, Ca^{2+}-EDTA complex and of calcium sucrate are tabulated in Table 1. The remaining Ca^{2+} ions are present in the precipitated components of calcined dolomite. Therefore, in all these methods, the separation of Mg^{2+} from Ca^{2+} has been almost completely accomplished. However, the Ca^{2+} content extracted in the citrate solution has been very low compared to the other solutions because calcium citrate has a low water-solublity. Hence, the use of citrates to extract Ca^{2+} is not suitable to prepare PCC in industrial scale. The best method to separate Ca^{2+} and Mg^{2+} from dolomite is the method that involves the use of EDTA. However, the Ca^{2+}-EDTA complex is highly stable due to the formation of hexadentate chelating complex (Jeffery *et al.*, 1989; Xiang *et al.*, 2002; Westin & Rasmuson, 2005a;b). Therefore, even after adding Na_2CO_3 at different pH conditions it did not result in PCC. Based on AAS results, the use of saturated $Ca(OH)_2$ solution and calcium sucrate was found to be the best Ca^{2+} sources to prepare PCC.

Table 1: Ca^{2+} and Mg^{2+} mol percentages of each calcium extraction based on AAS analysis

Calcium extraction	Ca^{2+} mol percentage	Mg^{2+} mol percentage
Saturated $Ca(OH)_2$	77.0	0.64
Calcium citrate	26.0	0.04
Ca^{2+}-EDTA complex	95.4	0.01
Calcium sucrate	87.0	0.18

XRD studies on PCC products

The XRD patterns of PCC products synthesized from different methods are depicted in Figure 2. The XRD peaks of all patterns located at 2θ values of 23.0°, 29.4°, 36.0°, 39.4°, 43.1°, 47.4°, 48.5°, 56.5° and 57.3° reveal the presence of calcite as the only polymorphic form of $CaCO_3$. $CaCO_3$ occurs in 3 polymorphic crystalline forms of calcite, vaterite and aragonite (Wang *et al.*, 2013), out of which, calcite is the thermodynamically most stable form of $CaCO_3$ (Park *et al.*, 2008). The remaining less stable forms are not found in any of these synthesized products. Aragonite is usually found in PCCs synthesized at temperatures over 80 °C (Wang *et al.*, 2006; Konopacka-Łyskawa & Lackowski, 2011). However, it was not formed in the PCC synthesized using calcium sucrate at the high temperature used in this work. Hence, it can be concluded that the sucrose molecules have inhibited the formation of aragonite and have stabilized the calcite phase. The average crystallite sizes of PCC synthesized using calcium sucrate and calcium citrate solutions as estimated by Debye-Scherrer formula are 41 and 30 nm, respectively. The particle sizes have been maintained in the nanoscale by sucrate and citrate together with Triton X-100. Out of these additives, citrate is the best additive to keep the particles in nanoscale compared to Triton X-100 surfactant. The dispersivity of the resulting PCC particles has been improved by the negative charges of citrates (Leeuwenburgh *et al.*, 2010). Therefore, the aggregation of PCC nanoparticles is prevented by citrate anions through electrostatic repulsions. Triton X-100 also functions to prevent the aggregation of PCC nanoparticles during formation by covering the particles by the micelles of these amphiphilic molecules, which

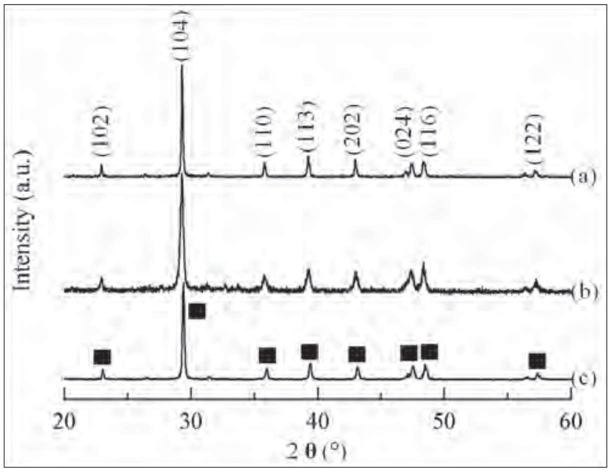

Figure 2: XRD patterns of PCC products prepared from (a) saturated solution of $Ca(OH)_2$; (b) calcium cirate complex and (c) calcium sucrate where, '■' represents calcite.

is commonly known as steric stabilization (Zhang *et al.*, 2006; Li *et al.*, 2010). However, the electrostatic forces are more effective than steric forces in the colloidal stabilization (Li *et al.*, 2010). Hence, citrate has more ability to keep PCC particles in nanoscale than that of Triton X-100. Further particle aggregation can be prevented by hydrothermal treatment.

FTIR studies of the PCC products

FTIR results of the PCC products agree well with the XRD results. The FTIR bands of PCC products (Figure 3a, 3b, and 3c) centered at 874 and 712 cm^{-1} reveal the presence of calcite (Sarkar & Mahapatra, 2010; Yao *et al.*, 2011; Zhao & Wang, 2012). The IR absorption bands of citrate are not found in the PCC product prepared by calcium citrate complex (Figure 3b and 3d). Therefore, the citrate ions in the calcium citrate complex have not been included or absorbed to the PCC product. The citrate ions in the complex may be recovered during the preparation of PCC product by exchanging Ca^{2+} ions with Na^+ ions of Na_2CO_3 at the carbonation stage. Furthermore, the FTIR bands of sucrose are not found in the PCC prepared from calcium sucrate and hence the sucrose used is recoverable at the end of $CaCO_3$ precipitation.

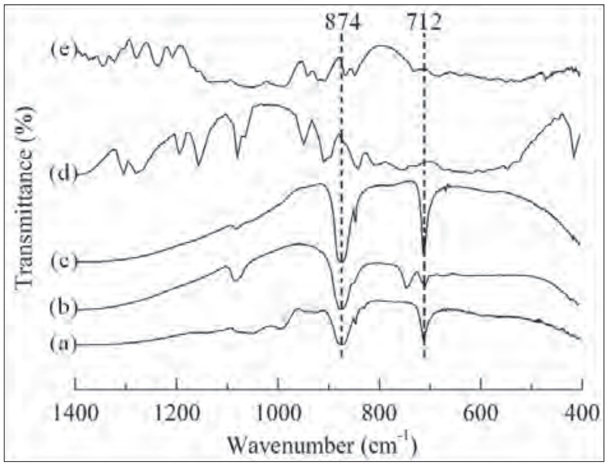

Figure 3: FTIR spectrum of PCC prepared from (a) a saturated solution of $Ca(OH)_2$; (b) calcium citrate complex; (c) calcium sucrate; (d) trisodium citrate and (e) sucrose

Industrials aspects of the devised methods

The yields of PCC products prepared using saturated $Ca(OH)_2$, calcium sucrate and calcium citrate are 71, 78 and 24 %, respectively. The remaining part of calcium is present in the precipitate obtained during the preparation of these extracts. Although the yield of PCC prepared from saturated $Ca(OH)_2$ is high, the productivity is very low, which is about 1.34 g of PCC that can be prepared using 1 L of aqueous saturated $Ca(OH)_2$ solution. Therefore, this method is not suitable for industrial scale production of PCC. However, about 33.20 g of PCC can be prepared from 1 L of 0.50 M calcium sucrate solution, which is a better productivity for industrial purposes. Moreover, in the calcium sucrate method, sucrose is recoverable after precipitating PCC. Therefore, the recovered sucrose is reusable to synthesize PCC to devise a continuous production process. As a result, the use of calcium sucrate is the best option to synthesize PCC and their nanoparticles from dolomitic marbles. As such, we have further characterized the PCC nanoparticles prepared from calcium sucrate using SEM and TGA and the corresponding results are given in Figure 4.

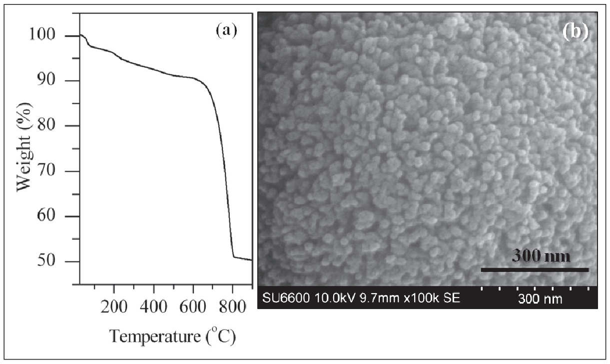

Figure 4: (a) TGA plot and (b) SEM image of PCC nanoparticles prepared from calcium sucrate

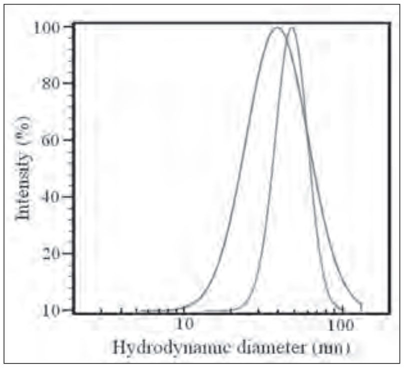

Figure 5: Particle size distribution curves of PCC nanoparticles prepared from calcium sucrate

The TGA plot of PCC synthesized by calcium sucrate depicted in Figure 4 (a), shows a single-step decomposition in the temperature range 724 − 806 °C, which gives a mass loss of 41 % that can be attributed to the decomposition of $CaCO_3$ to CaO and CO_2 (Wang *et al.*, 1999). Other than the $CaCO_3$ decomposition curve in the TGA, there are two mass losses at the temperature ranges of 41 − 84 °C and 174 − 226 °C, which can be attributed to the removal of physically and chemically bound water of the PCC product, respectively (Mantilaka *et al.*, 2013b). However, the total mass loss due to the removal of water is approximately 3 %. Since the surface area of a nanoparticle is high, water molecules can easily be adsorbed on to the surface of PCC nanoparticles during preparation (Mantilaka *et al.*, 2014a). Therefore, the presence of physically bound water is possible in PCC nanoparticles. The SEM image of the PCC product shown in Figure 4 (b) confirms that the particles are in spherical morphology with low particle aggregation. Also, the SEM image confirms the presence of particles in nanometer scale with the average particle size around 40 nm. The particle sizes of PCC synthesized from calcium sucrate are further analyzed with the help of DLS particle size analysis. There are two particle size distribution curves for PCC nanoparticles prepared from calcium sucrate as shown in Figure 5. The mean particle sizes of PCC nanoparticles based on these two size distribution curves are 38.9 and 51.6 nm. Therefore, it is further confirmed that the particles are in nanometer scale.

CONCLUSION

Sri Lankan dolomitic marbles can be used to synthesize PCC nanoparticles with high purity. The extraction of calcium components of calcined dolomite to sucrose is the best way for the preparation of PCC nanoparticles. Surfactants can be used to prevent the particle aggregation during the preparation of PCC nanoparticles using calcium sucrate. The sucrate ions stabilize calcite in the conditions favourable for aragonite. The synthesis of PCC nanoparticles for use in local industries and for the export market is a good method to add a very high value to the Sri Lankan dolomitic marbles.

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