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EFFECT OF DISACCHARIDE SOLUTION ON PRODUCTION OF PRECIPITATED CALCIUM CARBONATE

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Abstract

The current global demand for industrial paint, paper, polymer and adhesive materials witnesses an ascending growth. This market demand cannot be commercially fulfilled without unique and high-quality precipitated calcium carbonate (PCC). Over the years, PCC plays a role as a key component of the modern paper and plastic industry. Interestingly, owing to its wide-range adaptable characteristics, PCC has also exhibited high potential to be applied in modern pharmaceutical and biomedical application. Therefore, various techniques have been developed in producing the profitably versatile PCC. In attaining required properties, particle size and morphology, processing parameters should be prudently controlled and optimized. PCC can be optimally synthesized using solid–liquid method or the gas–solid–liquid carbonation reaction via CO2 gas bubbling through a concentrated calcium based slurry i.e. calcium hydroxide ($Ca(OH)_2$) and/or calcium magnesium hydroxide ($Ca{\cdot}Mg(OH)_2$) slurry with suitable organic additives. In this present work, PCC was produced by continuously introducing CO2 gas into a clear calcium ion (Ca^{2+})-rich solution. Prior to the carbonation reaction, natural disaccharide solution was used to efficiently promote an extraction of Ca^{2+} ions from calcium-based mineral, thus producing Ca-rich ionic solution as a main precursor. This current finding showed the concentration of disaccharide solution significantly affected the PCC yield as 48.28 g of PCC was attained by utilizing 20 °Bx as compared to only 8.23 g of PCC produced using 5 °Bx of disaccharide solution. There was no significant change on the phase formation and morphology of the produced PCC with a dominant calcite phase and rhombohedral structure, respectively. Increasing the concentration of disaccharide solution resulted in a slight change on the particle size distribution and kinetic stability of the PCC. This current finding signified the use of disaccharide solution in promoting Ca^{2+} ions extraction offered a significant increase in a production yield of the PCC which might be profitably applied by the industrial manufacturer.

Keywords: Precipitated calcium carbonate; Disaccharide; Ionic solution; Carbon dioxide; Feasible carbonation

1.0 INTRODUCTION

A concern of rapid and depletion of mineral resources has driven to redirection of developing a renewable and more eco-friendly material. Precipitated calcium carbonate (PCC) is a versatile mineral filler that has been widely applied in numerous industrial applications. Owing to its wide-range properties, lowest price and best available commercial filler, the market demand has shown an ascending trend of this versatile filler. Synthesis of calcium carbonate ($CaCO_3$) based on the precipitation reaction is an important industrial process attributed to the substantial applications of $CaCO_3$ as a raw material in paints, paper, plastic, adhesive and rubber industries [1,2]. For better effectiveness in the end application, attaining narrow particle size distribution, uniform shape and crystallinity for the PCC powders is very crucial, which is usually dependent on the synthesis conditions.

Pure $CaCO_3$ has three distinct crystalline forms (polymorphs) i.e. calcite, aragonite and vaterite. These polymorphs are morphologically perceived as rhombohedral, needle-like and spheroidal, respectively. Vaterite and aragonite are thermodynamically less stable than the calcite form and these two metastable phases eventually transform into calcite via a recrystallization mechanism [3, 4]. Its high purity and closed controlled particle size and structure make the PCC as a white filler of choice. The produced PCC with various properties and morphologies can be achieved by controlling the processing parameters. Over the years, numerous techniques have been designed for producing high-grade PCC including carbonation method, microemulsion method, solvothermal method, double decomposition method and biomimetic synthesis method [5,6,7]. Decomposition of carbonate compound is one of the most commonly applied routes in mineralizing PCC. Via this technique, the carbonate compound has been utilized as a main source of CO_3^{2-} ions including calcium bicarbonate ($Ca(HCO_3)_2$), sodium carbonate (Na_2CO_3), and ammonium bicarbonate (NH_4HCO_3) to react with calcium chloride ($CaCl_2$) as a aqueous mixture [8,9,10]. However, with a concern to the rising of the main greenhouse gas i.e. carbon dioxide (CO_2) gas emission, the PCC can be produced by directly applied the CO_2 gas as one of the main precursors. This phenomenon has become a crucial environmental concern as CO_2 gas might trap heat in the atmosphere leading to global warming [11]. Therefore, this facile carbonation might drive a redirection of CO_2 gas into a more constructive usage rather than be increasingly release to the environment.

As another consideration, the morphology of PCC can be affected by the use of additives either via solution reaction approach or carbonation route [12, 13]. In this research work, a natural disaccharide ($C_{12}H_{22}O_{11}$) additive was utilised as a promoter agent in enhancing the production rate of PCC rather than to alter its morphology. The disaccharide is made from two monosaccharides i.e. glucose and fructose units. The glucose and fructose units are joined by an acetal oxygen bridge in the alpha orientation. This structure is easy to recognize as it contains the six-member ring of glucose and the five-member ring of fructose. The chair structure of a down projection was denoted by the hydroxyl (-OH) in a hemiacetal [14]. Thus, attributable to the high number of -OH group, this promoter agent was introduced in order to optimize the extraction of calcium ions from the source of calcium materials, thus increasing the production rate.

Via extracting Ca^{2+} ions using this natural disaccharide additive, the production of PCC can be achieved even from as low grade as waste particularly carbide lime waste. Carbide lime waste has been abundantly produced from acetylene gas manufacturing. Global market reported acetylene demand show a stable ascending growth owing to its high market demand. This circumstance discloses the generation of carbide lime waste will also proportionally increase thus might harm the environment. This by-product is classified as a scheduled waste under Malaysian Environmental Quality Act: EQA 1974 (SW 427) due to its high alkalinity (pH 12) and cause skin and throat irritation. The outcome of this work might be applied in revolutionising industrial waste into a marketable PCC.

In this current work, the production of PCC was performed by carbonation reaction via bubbling CO_2 gas into a rich-Ca^{2+} ionic solution. The carbonation process was allowed to occur under atmospheric at room temperature using ionic solution of natural-disaccharide base with initial pH of ~12. In order to investigate effects of the promoter agent on yield, particles size and morphology of the produced PCC, the concentration of the natural-disaccharide was controlled (i.e. 5, 10, 15 and 20 °Bx). This research work can be considered as a starting stride in mitigating the accumulative wastes for recycling the carbide lime waste and CO_2 gas waste into high-grade PCC.

2.0 RESEARCH METHODOLOGY

Materials

Quicklime (CaO) as a calcium (Ca)-based starting material was supplied from Simpang Pulai quarry in Malaysia. Sucrose that acted as a promoter agent was purchased from a local company and compact CO_2 gas of 99% purity was supplied by Linde Malaysia Sdn. Bhd.

PCC Production using Promoter Agent

In this present work, the precipitation of $CaCO_3$ was conducted via carbonation of Ca-rich ionic solution under continuous flow of CO_2 gas. Prior to a preparation of Ca-rich ionic solution, disaccharide solution as a promoter agent was prepared as a medium for optimally extracting calcium ions (Ca^{2+}) from the Ca-based starting material. About 4 wt.% of quicklime was added into 1 L of disaccharide solution. This Ca-containing solution was mixed homogenously and left overnight in order to allow the optimum extraction the of Ca^{2+} ions into the solution. Afterwards, the Ca-ionic solution was filter in attaining a clear Ca^{2+}-rich ionic solution and removing the residue. The effect of the promoter agent on the carbonation and production of PCC was investigated by varying the concentration of the disaccharide solution i.e. 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% corresponding to 5 °Bx, 10 °Bx, 15 °Bx and 20 °Bx.

Subsequently, CO_2 gas was continuously introduced into the Ca^{2+}-rich ionic solution in order to provide an effective carbonation process. The carbonation process was performed under atmospheric condition and mechanically stirred at a constant rotational speed of 1000 rpm. The additional mechanical disturbance might enhance the precipitation mechanism of PCC and avoid an excessive growth of PCC particles. The carbonation process was monitored by pH value and the process was stop at ±pH 8 where the precipitation of the $CaCO_3$ was considerably completed. The synthesized PCC was then filtered and washed using warm water to remove any excess promoter agent. The filtrate was dried in an oven at 60 °C for 24 hours. The time taken for the carbonation process and weight of the PCC yield was measured. **Fig. 1** illustrates a set-up of carbonation process in producing PCC via CO_2 gas bubbling.

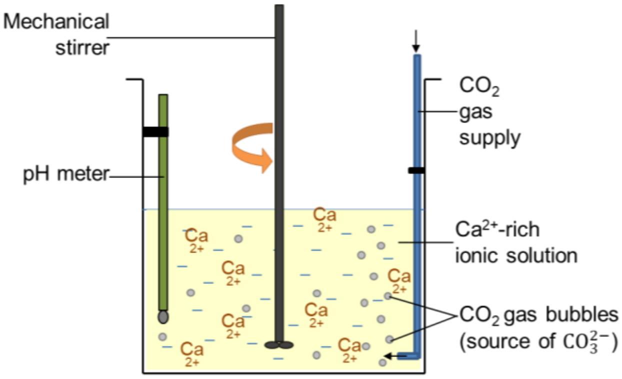

Fig. 1. A set-up of carbonation process in producing PCC via CO_2 gas bubbling

Characterization of Produced PCC

The morphology of the synthesized PCC was evaluated using Field Emission Scanning Electron Microscope (FESEM) *Supra 40V Zeiss, Germany*. The particle size distribution of the PCC was measured using Laser Particle Size Analyzer. Analysis of the oxide element in PCC was using X-Ray Fluorescence Spectrometer, *XRF-1700, Shimadzu, Japan*

3.0 RESULTS AND DISCUSSION

Carbonation Time and PCC Yield

Fig. 2 shows carbonation time and weight of produced PCC using various concentrations of disaccharide solution. The carbonation time gradually increased with the increasing disaccharide concentration. Higher concentration of disaccharide contained higher functional OH^- contents, thus providing higher tendency to extract more Ca^{2+} from the Ca-based material. This phenomenon resulted in prolonging carbonation time in order to achieve a complete precipitation mechanism of the PCC. In addition to the increasing carbonation time, the PCC yield was also tremendously increased from only 8.23 g up to 48.28 g of PCC using 5 °Bx and 20 °Bx of disaccharide solution, respectively. The remarkable increase of the PCC yield as a function of disaccharide incorporation offered positive impact to industry as this approach might be applied in order to enhance the efficiency and production rate of massive PCC. Interestingly, by extracting Ca^{2+} ions using the disaccharide as a promoter agent, any grade of calcium-based material can be considerably utilized as a calcium precursor including recycling calcium based industrial residue i.e. carbide lime waste.

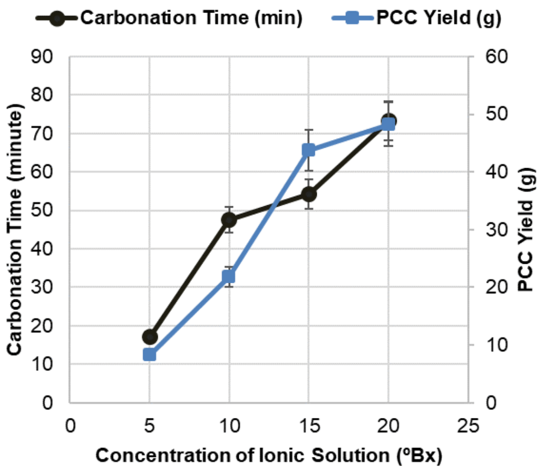

Fig. 2. Carbonation time and weight of PCC yield at various atomizing air pressure

Particle Size Distribution

Fig. 3 displays the size distribution of PCC particles increased as a function of concentration of the disaccharide solution. The PCC particle sizes were between 11 µm to 23 µm. As can be seen, the coarsest PCC particles (23.43 µm) were obtained at 20 °Bx which might be due to the particle intergrowth phenomenon that occurred during the carbonation reaction [10]. The particle growth of PCC with increasing concentration of disaccharide solution was attributed to the presence of higher content of Ca^{2+} ions and a longer time taken for the complete precipitation allowed to the PCC particle to gradually enlarge unreservedly.

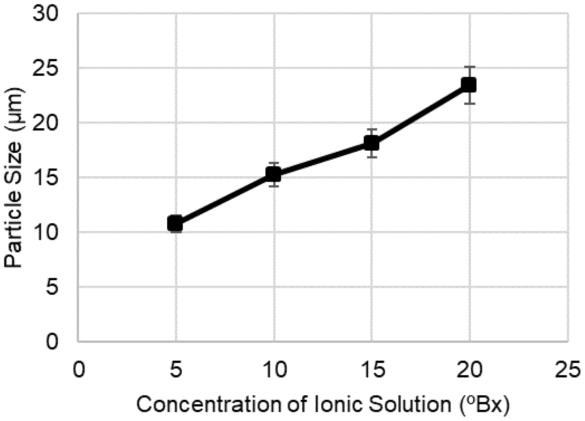

Fig. 3. Particle size distribution of produced PCC using various concentrations of ionic solution

The continuous introduction of CO_2 gas into Ca^{2+}-rich ionic solution increased the effectiveness of the carbonation rate. Due to high content of Ca^{2+} ions, the CO_2 gas can directly react with the ions thus enhancing a quick precipitation of PCC. The carbonation reaction occurred as followed:

$$Ca^{2+}_{\text{(ionic solution)}} + CO_{2\,\text{(gas)}} \longrightarrow CaCO_{3\text{(precipitate)}} \quad (1)$$

Phase Analysis

Fig. 4 shows XRD spectra of PCC samples those were produced from various concentrations of disaccharide solution. All samples display almost similar diffraction peaks position and intensity. Apparently, there was only a detection of calcite phase in the studied PCC samples. Calcite ($CaCO_3$) presents in a hexagonal crystal structure with lattice constants of a=b=4.990 Å, c=17.061 Å, α=β=90° and γ=120°, a space group of R-3c and a punctual group of symmetry of -32/m [2,9]. According to the diffraction peaks, there was a slight left-hand-side shift of the peak position with increasing the concentration up to 10 °Bx. This peak shifting suggested a possibility of crystallite size or internal strain change in the PCC [5]. The diffractogram shows the strongest diffraction intensity was a characteristic of calcite crystal lattice. The formation of a single-phase calcite in all studied samples via this carbonation method indicated that the crystallinity of the PCC was not affected by the concentration of disaccharide solution.

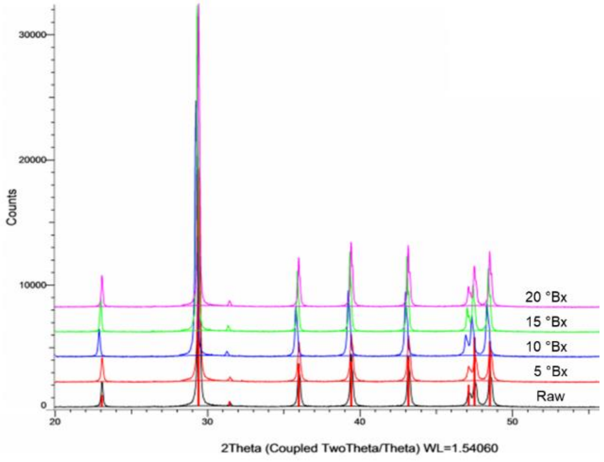

Fig. 4. XRD pattern of PCC produced using various concentrations of disaccharide solution

Morphological Analysis

Crystallization of calcium carbonate can result in a formation of several polymorphs hence a careful control of processing parameters was required in order to attain the desired final product. **Fig. 5** illustrates the morphologies of PCC particles at different concentrations of disaccharide solution. According to the required in order to attain micrographs, the PCC was significantly formed in rhombohedral structure with no remarkable change of PCC morphology. However, increasing the concentration of disaccharide resulted in increment of the particle size distribution. Apparently, PCC produced using 5 °Bx provided the finest particle with less uniformity of particle structure. This phenomenon was due to insufficient of Ca^{2+} ions supply that limited a reaction with CO_2 thus hindering the growth of particles. Increasing the disaccharide concentration up to 10 °Bx resulted in a slight enlargement of PCC particles. At this concentration, the PCC particles were homogenously distributed with uniform cubicle structure. This phenomenon suggested the Ca^{2+} ions and CO_3^{2-} ions reacted in a sufficient ion concentration within a necessary carbonation time.

The PCC particles started to attach together with increasing the disaccharide concentration up to 15 °Bx. This particle agglomeration described the carbonation reaction occurred in higher rate as compared to the samples produced using lower disaccharide solution, where at this concentration the PCC yield (43.72 g) was two times higher the PCC produced using 10 °Bx of disaccharide (21.84 g). Further increase in concentration up to 20 °Bx yielded an inhomogeneous particles distribution. According to the micrograph, there was a formation of intergrowth particles which resulted in enlargement of particles size. There was also a formation of fine particles that dispersed among the large particles. This scenario might be resulted by excessive Ca^{2+} ions supply and insufficient mechanical disturbance due to stirring action of the precipitation that occurred in a longer time. The prolonged carbonation time allowed the growth of PCC particles. Remarkably, the utilisation of disaccharide solution did not affect the morphological structure of the produced PCC, however a significant effect was attained on the particle growth. This current finding signified that sufficient reactant of both Ca^{2+} ions and CO_3^{2-} ions at ambient temperature by this carbonation mechanism might provide a favourable condition for the formation of homogeneous distribution of rhombohedral calcite.

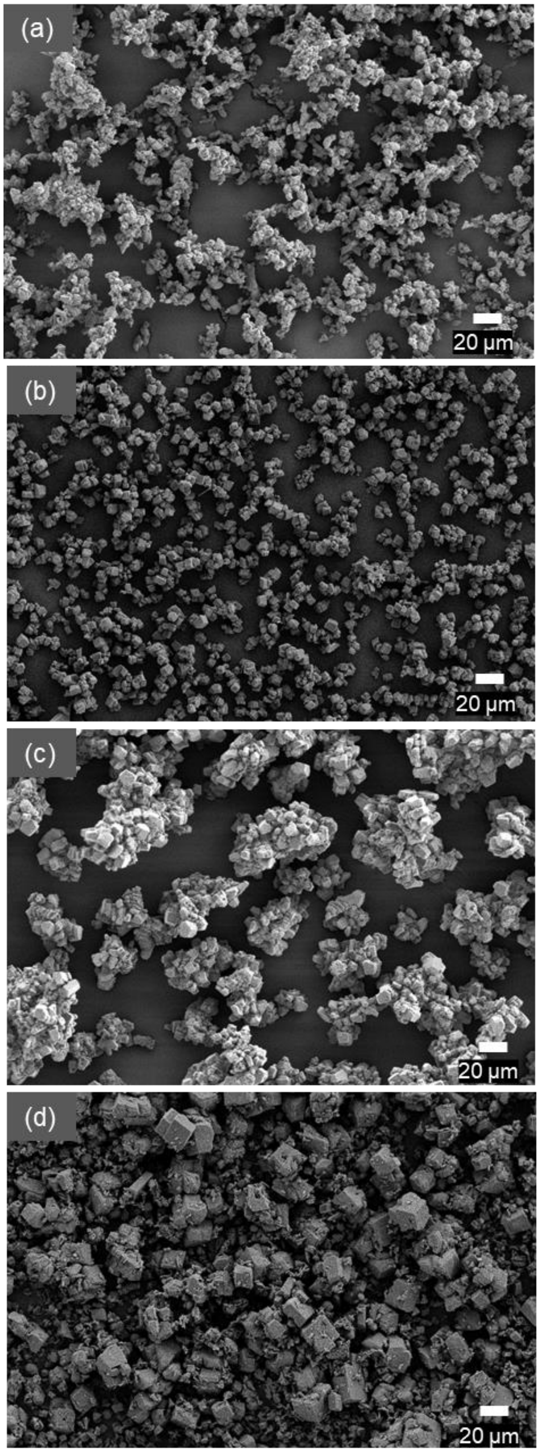

Fig. 5. Micrograph of PCC particles at (a) 5, (b) 10, (c) 15 and (d) 20 °Bx

Zeta (ζ) potential

Fig. 6 shows Zeta potentials of the PCC samples produced using various concentrations of disaccharide solution. In general, a precipitation of $CaCO_3$ (calcite) presents in negative charge with the principal potential determining ions in solution are Ca^{2+}, CO_3^{2-}, HCO_3^- and the secondary ones are H^+ and OH^-. The neutral sites on the $CaCO_3$ surface may also be denoted as -CaOH° and -CO_3H°. The produced PCC indicated the negative potential in a range of -9 to -14 mV. This finding suggested the precipitation of $CaCO_3$ was dominated by negative species of HCO_3^- and CO_3^{2-}, thus resulted in a net negative charge of calcite via hydrolysis reaction. The Zeta potential reduced with increasing the concentration of disaccharide up to 15 °Bx. A further concentration increase resulted in increasing Zeta potential. The higher Zeta potential specified that there was a slight positive net charge on the $CaCO_3$ surface immediately after the precipitation conceivably originating from the surface -Ca^{2+} sites [15]. The closer the potential to the zero line, the lower the mobility of the particles and the higher the Zeta potential (farther from the zero line) offered the more stable its ionic kinetic. However, most of PCC application requires the lower potential in order to sustain its properties during the service duration.

Apparently, the highest negative potential of -13.72 mV was demonstrated by PCC of 5 °Bx. This finding was attributed to the distribution of finest PCC particles (10.81 µm) thus offered the highest kinetic stability. The increasing the disaccharide concentration up to 15 °Bx resulted in a potential reduction to -9.76 mV. This phenomenon was attributed to the particle size distribution where the finer the particles the higher the motion and higher kinetic stability. This finding can be supported by the FESEM micrographs as there was numerous distributions of agglomerated particles at high concentration of disaccharide, thus reducing its mobility. Although the particle distribution of the PCC powder produced using 20 °Bx was the coarsest (23.43 µm) but presence of fine particles between the coarse particles (as shown in **Fig. 5**) assisted in increasing the kinetic stability of the particles thus generating slightly high potential of -11.45 mV.

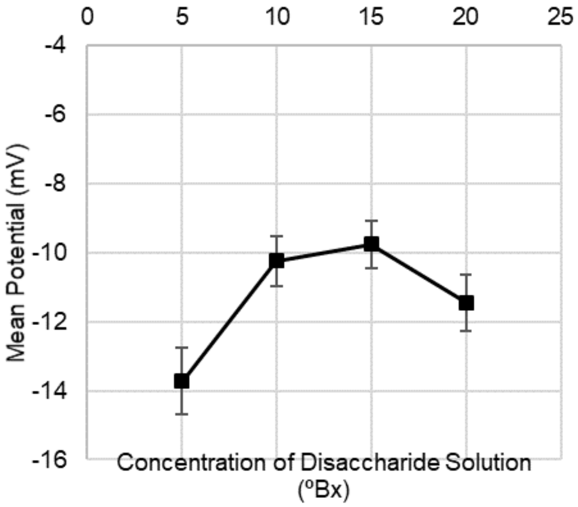

Fig. 6. Zeta potential of PCC as a function of concentration of disaccharide solution

4.0 CONCLUSION

The currently used technique showed high potential in extracting Ca^{2+} ions from calcium-based mineral using disaccharide solution for producing versatile PCC via carbonation technique. Effectively, the utilisation of disaccharide-promoted ionic solution as a feed stock exhibited a significant increase in PCC yield as a function of disaccharide concentration up to 48.28 g of PCC. The carbonation time and size distribution of PCC particles were also increased with increasing the concentration of disaccharide solution i.e. between 17.13 minutes to 73.30 minutes and 11 µm to 23 µm, respectively.

According to the phase and morphological study, only calcite-PCC phase with the dominant rhombohedral structure of PCC particles were formed at different disaccharide concentrations. Increasing the concentration of disaccharide solution resulted in a slight change on kinetic stability of the PCC. This phenomenon suggested the use of disaccharide solution in promoting Ca^{2+} ions extraction offered a significant increase in a production yield of the PCC which might be profitably applied by the industrial manufacturer. Effectively, CO_2 gas was used as a main source of CO_3^{2-} ions, thus can alleviate its excessive emission into the atmosphere. Consequently, this scenario might support to preserve the environmental sustainability.

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