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## INFLUENCE OF HCL 0.02 M ON PHASE AND SIZE OF CaCO<sub>3</sub> VIA FINE BUBBLE DIFFUSER METHOD AS DENTAL BIOMATERIAL

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### KEYWORDS

CaCO<sub>3</sub>  
HCl  
Fine bubble diffuser  
Dental biomaterial

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### ABSTRACT

**Background.** Particles of calcium carbonate (CaCO<sub>3</sub>) have been applied in a number of fields, including as dental biomaterial. Because CaCO<sub>3</sub> particles have three distinct polymorphs and complex crystallization behavior, it is difficult to systematically adjust their physical properties for desired applications. **Objective.** This investigation aims to examine the influence of the addition of the 0.02 M HCl additive on the phase and size of the CaCO<sub>3</sub> particles synthesized with the fine bubble diffuser method. **Methods.** The type of research is descriptive explorative. There were two sample groups in this study, and each group had three replications (n = 3). Group 1 added 0.02 M of HCl as an addition to the as-prepared material, while Group 2 added no HCl at all. The phase of CaCO<sub>3</sub> was evaluated by using the FTIR (Thermo Scientific Nicolet iS5), while the particle size was measured via DLS (Horiba Scientifica SZ-100 Nanopartica) **Result.** The results showed the sample of CaCO<sub>3</sub> without any additive possesses Amorphous Calcium Carbonate (ACC) and calcite. Meanwhile, sample of CaCO<sub>3</sub> with addition of HCL 0.02 M showed ACC, calcites and vaterite phase. Particle size of CaCO<sub>3</sub> without additive is larger than another one. **Conclusion.** In this study, the addition of the additive HCl 0.02 resulted in a decrease in the pH of the solution resulting in a phase change from calcite to vaterite as well as decreasing the particle size of CaCO<sub>3</sub>.

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### INTRODUCTION

These days, a vast range of processes and applications are made possible by the features of nano and micro materials. They have high volumes and surface areas, which favor the interaction with other compounds to control and assist chemical processes by improving mass and heat transfer and providing contact area. Depending on the synthesis technique, the qualities of the materials can be modified. Supersaturation, temperature, pH, ionic

strength, stirring, and other factors all have a significant impact on final properties of the materials. Calcium carbonate (CaCO<sub>3</sub>) is one of the most researched materials due to vast utilization of CaCO<sub>3</sub> as biomaterials in medical and dental fields.<sup>1</sup>

The sedimentation of small fossilized snail, mussel, and coral shells produces CaCO<sub>3</sub>, which is found in nature as chalk, limestone, and marble. There are three distinct crystalline forms of CaCO<sub>3</sub>: calcite, aragonite, and

vaterite, in order of stability.<sup>2</sup> The crystal morphologies and topologies of these CaCO<sub>3</sub> crystalline phases vary. The structure of aragonite crystals is orthorhombic, that of calcite crystals is rhombohedral, and that of vaterite crystals is hexagonal.<sup>3</sup>

Three primary phases mechanism of CaCO<sub>3</sub> precipitation: i) Amorphous calcium carbonate (ACC) is nucleated at the start of the process; ii) unstable ACC dissolves and recrystallizes into vaterite and calcite. iii) the metastable vaterite dissolving and recrystallizing into calcite, the most stable crystalline form. Nevertheless, by changing the synthesis parameters, such as temperature, pH, saturation levels, and additive concentration, the other polymorphic forms, vaterite and aragonite, can be produced.<sup>4-6</sup>

CaCO<sub>3</sub> is regarded as being easily manufactured, and various biomimetic techniques are used in an effort to replicate the natural process for the synthesis of intricate and exquisite forms. These days, reducing CO<sub>2</sub> emissions is a significant challenge that is receiving a lot of study attention. Due to its long-term storage of carbon dioxide (CO<sub>2</sub>) derived from industrial gaseous streams, carbonation method for instance fine bubble diffuser method appears to be an effective technique. In order to create CaCO<sub>3</sub> particles with a certain polymorphism, additives are highly helpful. Although calcite can be made without any additional ingredients, vaterite and aragonite are generally made using them. Nevertheless, several chemicals are used to

regulate the size or shape of particles, even calcite ones.<sup>7-10</sup>

Numerous additives are added to biomimetic processes (in small amounts, ppm or g/L), which do not change the chemical composition of CaCO<sub>3</sub>. The primary functions of additives are to interact with Ca<sup>2+</sup>, offer nucleation sites, and then form a bond with a preferred surface by inhibiting or promoting the formation of CaCO<sub>3</sub> particles in particular crystallographic planes. This allows for size control and stabilizes many morphologies, including pyramidal, flower-like, laminated, hollow, and spherical particles. Additionally, the additives may interact with the surface to stabilize vaterite or metastable aragonite particles above stable calcite particles.<sup>1,11,12</sup>

Additive compounds can modify the CaCO<sub>3</sub> crystals through concentration parameters, active agent, pH changes, etc.<sup>13</sup> Generally, Additive used are organic compound such as amino acids glycine, leucine, histidin, serine and sistine.<sup>14</sup> However, studies of vaterite synthesis using simple additive such as HCl, have not been found. HCl is known to be a strong acid that can produce H<sup>+</sup> ions and modify the pH of the solution.<sup>15</sup>

This study aims to look at the effect of HCl 0.02 M on the phase and size of the particle CaCO<sub>3</sub> via fine bubble diffuser as dental biomaterials. The phase of CaCO<sub>3</sub> was evaluated by using the Fourier-transform infrared spectroscopy (FTIR), while the particle size was measured via Dynamic light scattering (DLS).

## METHODS

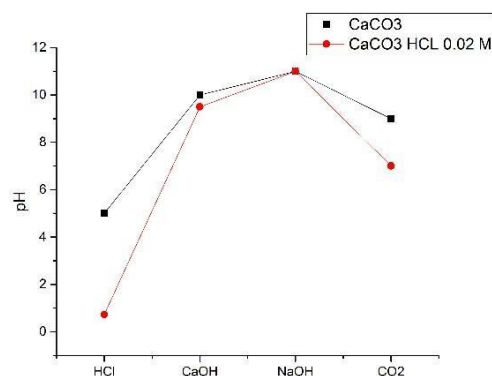
The type of research is descriptive explorative.  $\text{Ca}(\text{OH})_2$ , which is obtained from natural limestone, was used in the study as the precursor (PT. Batu Wangi Putra Sejahtera, Padalarang, Indonesia) The solvents that are used are aquadest and ethanol. As carbonate ions and additives, respectively, carbon dioxide ( $\text{CO}_2$ ) from Samator Indo Gas, Ciroyom, Indonesia, and HCl from PT. Smart Lab Indonesia are utilized. The research was conducted from December 2022 to May 2023 at the Nano Technology Laboratory, FINDER-U CoE, Universitas Padjadjaran.

There were two sample groups in this study, and each group had three replications ( $n = 3$ ). Group 1,  $\text{CaCO}_3$  is synthesized without the use of HCL additives. Group 2 added 0.02 M of HCl as an addition to the as-prepared material. The procedures begin as the following, prepare two liters of aquadest as the solvent, next, incorporate 3.3 ml of HCl 0.02 M into the solvent and mix the mixture until it becomes homogeneous. At this point, the pH of the solution is measured and recorded. Next,  $\text{Ca}(\text{OH})_2$  powder is dissolved at a concentration of 0.02 M (2,96 g) in the solvent. pH was subsequently recorded. NaOH is then added to increase the pH of the solution to reach a value of 11 and then adjust the temperature to  $20 \pm 3$  °C. Next, the carbonation process was carried out for 120 minutes (300 rpm; 1 L/min) using a fine bubble diffuser and the pH was also recorded. After that, the suspension was left to rest for a

full day (aging process). After obtaining  $\text{CaCO}_3$ , it is dried in an oven at 40 °C after filtering. The phase of  $\text{CaCO}_3$  was evaluated by using the FTIR (Thermo Scientific Nicolet iS5), while the particle size was measured via DLS (Horiba Scientifica SZ-100 Nanopartica)

## RESULTS

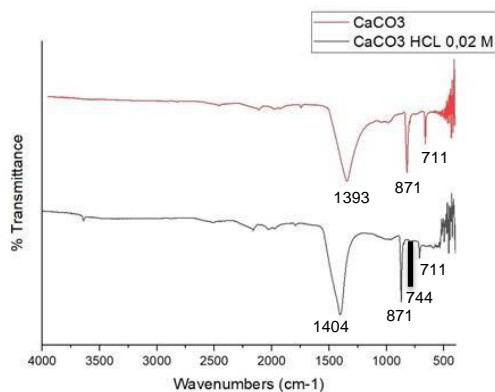
Figure 1 shows a change in the pH value of the  $\text{CaCO}_3$  group showing the pH of the solution without addition of HCl is 5, then after addition of CaOH increases to 10. pH then rises to 11 following addition of NaOH and decreases to 9 after administration of  $\text{CO}_2$ . Then, the  $\text{CaCO}_3$  group with the addition of HCL showed a pH value of 0.73 then increased to 9.5 after the added CaOH. pH rises to 11 after NaOH addition and then drops to 7.01 after  $\text{CO}_2$  addition.



**Figure 1.** Changes in pH values at each stage of the synthesis process

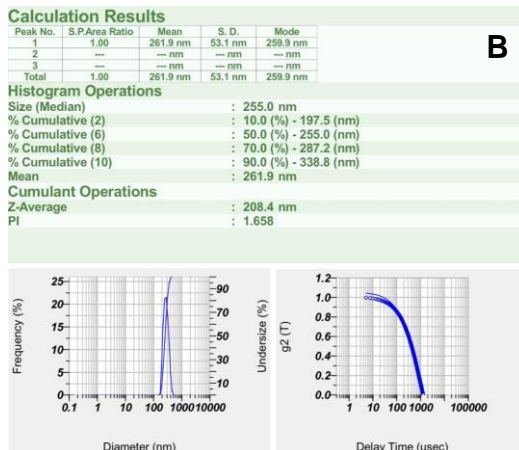
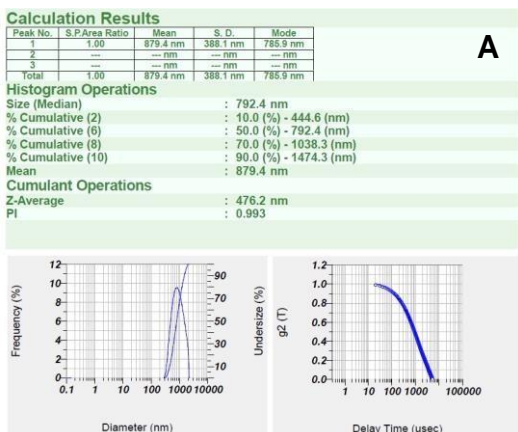
Figure 2 shows the FTIR spectrum of  $\text{CaCO}_3$  without any additive and  $\text{CaCO}_3$  with additive HCl 0.02 M.  $\text{CaCO}_3$  sample shows a number of  $1393 \text{ cm}^{-1}$  indicating Amorphous Calcium Carbonate (ACC),  $871$  and  $711 \text{ cm}^{-1}$  which indicates calcite phase. Meanwhile, a sample

of CaCO<sub>3</sub> HCL 0.02 M showed ACC groups at a wave number of 1404 cm<sup>-1</sup>, a calcite groups at 871 and 711 cm<sup>-1</sup>. However, the sample showed a decrease in the peak intensity of calcites at the wave number of 711cm<sup>-1</sup> and the appearance of the vaterite phase at the wave number of 744cm<sup>-1</sup>.



**Figure 2.** The CaCO<sub>3</sub> sample shows the ACC and calcite phases, whereas the CaCO<sub>3</sub> with HCL 0.02M shows ACC, calcites and vaterites.

Figure 3 shows that the particle size of CaCO<sub>3</sub> without additives has a particulate size of about 879.4 nm, whereas the particle size of CaCO<sub>3</sub> with the addition of the additive HCL 0.02 M has a smaller particle Size of 261.9 nm.



**Figure 3.** The size of the CaCO<sub>3</sub> particle without additive (a) has a larger size than the particle of CaCO<sub>3</sub>, with the addition of the additive HCL 0.02 M (b).

## DISCUSSION

The usage of additives is quite beneficial in obtaining CaCO<sub>3</sub> particles with a particular polymorphism. Although calcite particles can be made without additives, vaterite and aragonite particles are primarily made with additives. Nevertheless, certain additives are used to regulate the size or morphology of CaCO<sub>3</sub> particles. The additive in this initiation uses HCL 0.02 M which can lower the pH (in Fig 1) of the solution allowing for phase-forming modification of the CaCO<sub>3</sub> particle.<sup>16,17</sup>

The addition of HCl to the synthesis of CaCO<sub>3</sub> produces a vaterite phase that is visible at a wavelength of 744 cm<sup>-1</sup> (Fig 2). Vaterite to calcite polymorphic transformation was seen with a rise in pH, regardless of the [Ca<sup>2+</sup>]:[CO<sub>3</sub><sup>2-</sup>] ratios. This phenomena may have something to do with how supersaturation varies in response to pH variations. Supersaturation of the solution rise with increasing [Ca<sup>2+</sup>]:[CO<sub>3</sub><sup>2-</sup>] ratio,

according to estimates on supersaturation ( $S = (IAP/K_{sp})^{1/2}$ , where IAP is Ionic Activity Product ( $IAP = [Ca^{2+}][CO_3^{2-}]$ ) and  $K_{sp}$  is Solubility Product.

Short induction durations at high pH solutions enable Oral et al. to discover a significant decrease in supersaturation during the synthesis of  $CaCO_3$  particles.<sup>18</sup> They hypothesize that at this molarity ratio, vaterite particles were formed in the early stages regardless of pH. In contrast, vaterite particles remained stable during low pH synthesis circumstances. Later on, however, supersaturation drastically diminished due to high nucleation rates reported at high pH solutions and vaterite particles changed to calcite by dissolution and recrystallization.<sup>18</sup> The relationship between  $CaCO_3$  particle size and precursor solution pH, whereby larger  $CaCO_3$  particle size was correlated with more basic precursor solutions and vice versa (Fig 3). The polymorphic shift from vaterite to calcite was the most pronounced in terms of size change. By choosing the right pH, it was also possible to create  $CaCO_3$  particles with fine dimensions. The results of this study are in line with oral studies et al. They indicated that the smaller particle size of  $CaCO_3$  is 660 nm at a lower pH of 8. whereas  $CaCO_3$ , at a pH of 13 is known to have a particulate size of 4 microns.<sup>16,19,20</sup>

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## CONCLUSION

In this study, the addition of the additive HCl 0.02 resulted in a decrease in the pH of the

solution resulting in a phase change from calcite to vaterite as well as decreasing the particle size of  $CaCO_3$ .

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