Utilization of Snail (*Achatina fulica*) Shell Waste for Synthesis of Calcium Tartrate Tetrahydrate ($CaC_4H_4O_6.4H_2O$) Single Crystals in Silica Gel

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ABSTRACT

Snail (*Achatina fulica*) shell waste is massively produced by many home industries in Indonesia, especially in East Java. The snail shell is known for high calcium; therefore it is potential to be used as calcium source of supernatant in the synthesis of piezoeletric material, such as single crystal of calcium tartrate tetrahydrate (CaTT). The aim of this research is to study the synthesis and characterization of CaTT or $CaC_4H_4O_6.4H_2O$ from snail shell waste in silica gel. Supernatant solution of $CaCl_2$ was prepared from CaO, which previously made by calcinating the shell at 1000°C, and then reacted with HCl 1.5M. Synthesis of CaTT was conducted in a single-tube reaction at room temperature in which silica gel was used as growth medium with gelling time of 10 days and growth time of 2 weeks. The pH of gel and $CaCl_2$ concentration were varied, 3.00; 3.50; 4.00; 4.50; 5.00; and 0.27; 0.36; 0.45; 0.54 M respectively, in order to obtain optimum condition of the synthesis, which is indicated from crystal yields. The synthesized crystals were characterized by atomic adsorption spectrophotometry (AAS), infrared spectroscopy (IR) and powder X-ray diffraction (XRD). Experimental data shows that optimum condition was obtained at pH of 3.50 and $[CaCl_2]$ of 0.45M with yield of 69.37%. The obtained single crystal has clear color and octahedral-like shape with size ranged between 4 – 9 mm. Analysis data by FTIR and powder XRD confirmed that the obtained crystal was CaTT single crystals with crystal system of orthorhombic.

Keywords: *CaTT*, snail shell waste, silica gel, supernatant

INTRODUCTION

In some part of Indonesia, snail (*Achatina fulica*) has been intentionally populated as the main ingredients of food supplement or local culinary such as satays or snacks. As a result, high amount of snail shell waste is generated and most of the wastes are abandoned. Only few farmers used it as an additional ingredient of their livestock's foods. Some research also reported that the shell can be used as adsorbents of textile dyes after converted into chitin or chitosan [1, 2] or coagulant for liquid waste water treatment [3]. Hence, research on the utilization of snail shell into valuable materials is needed not only to treat the waste but also to increase its value, which may open new industry for local community.

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In this research, we try to utilize the shell as the main ingredient of calcium supernatant. Single crystal of calcium tartrate tetrahydrate (CaTT) is known for its interesting properties. Due to its ferroelectricity [4] and non-linear optical properties [5], transducers and many linear and nonlinear mechanical devices are using this crystals [6, 7, 8]. Piezoelectricity is also exhibited by some of this metal tartrate crystals [9, 10, 11].

Similar research had been conducted previously by our group. Synthesis of CaTT, in which the supernatant was prepared from sugar cane industrial waste, was also performed and gives 5% of yield [12]. In addition, single crystals of brushite ($CaHPO_4.2H_2O$), fluorite (CaF_2), and bruggenite ($Ca(IO_3)_2.H_2O$) are also succesfully made. In this case, the supernatants were prepared from gypsum waste as the by-product of phosporic acid production [13, 14, 15]. All of those crystals were successfully grown in silica gel.

In the present study, we optimized the synthesis of CaTT from snail shell waste by varying the pH of silica gel and concentration of $CaCl_2$. Mean while, characterization of obtained

crystals were conducted by FTIR, AAS, and XRD.

MATERIALS AND METHODS

Materials and Instrumentations

Laboratory chemical reagents were obtained from standard commercial suppliers and used without further purification. The chemicals are tartaric acid ($C_4H_6O_6$), sodium metasilicate ($Na_2SiO_4.9H_2O$), HCl, $CaCl_2.2H_2O$, and aquadest.

Laboratory instrumentations used in this research were a high temperature Barnstead Thermolyne and a HERAEUS KR170E Oven, an Orion 420A pH-meter, a Shimadzu FTIR-8601PC, an AA-6200 and Perkin Elmer Analyst 100 AAS, and a Panalytical PHILIPS-XPERT XRD.

Preparation of Supernatant

Supernatant solution of calcium were made by calcinating the powdery shell at 1000°C, and then reacted with HCl 1.5M until all dissolved. The solution was then concentrated by evaporation in a hotplate. White precipitation was yielded after placing the concentrated solution in a cold water bath. The solid was then isolated, dried in an oven (±110°C) for three hours and directly save it in a desiccator. The white solid was then analyzed by AAS to confirm the purity of $CaCl_2$. Finally, the supernantant solution of $CaCl_2$ was prepared by dissolving 0.6; 0.8; 1.0; and 1.2 g of $CaCl_2$ with 20 mL of aquadest. The supernatant solutions were coded as supernatant A, B, C, D, respectively.

Determination of Optimum pH

The gel was made by adding sodium metasilicate 1M in five different beaker glass which already contain 80 mL of tartaric acid 1M. The mixed solution was set at pH of 3.0; 3.5; 4.0; 4.5 and 5.0 using pH-meter. Three experiments were conducted for each pH. Then, 40 mL of each solution was transferred in a single tube glass (*h = 20cm; d = 25mm*) and keep it at room temperature for 10 days. After the gel was formed, supernatant C was added slowly into the gel through the inner wall of the tube to avoid any damage of the gel surface which might disturb the diffusion. The tube was then closed with alumunium foil and placed in a tube rack. The reaction was stand at room temperature for 2 weeks.

Determination of Optimum $CaCl_2$ Concentration

Optimum pH obtained from previous step was used in this section, while the procedures are similar to previous step. The different is only in supernatant solutions in which all supernatant solutions (A, B, C, D) were added slowly into four different gels at optimum pH. The reaction was also stand at room temperature for 2 weeks.

Characterization of Obtained Crystals

Only good quality of single crystals were analyzed by infrared spectrophotometry (FTIR) in order to determine the presence of tartaric ions in the crystal, and powder X-ray diffraction (XRD) in order to confirm the crystal system of obtained CaTT. The sample was taken from crystal that produced by optimum $CaCl_2$ concentration. Physical characterization was conducted by checking the crystal's color and shape, as well as the crystal's hardness based on Moh's scale.

RESULTS AND DISSCUSION

Preparation of Supernatant

A 35.85g of CaO was yielded from 70g of dry powdery snail shell waste and 36.23g of $CaCl_2$ hydrate was produced from 23g of CaO, therefore the conversion of dry powdery shell to $CaCl_2$ has efficiency of 79.6%. Based on AAS data, the purity of synthesized $CaCl_2$ hydrate was found only 82.6%. To decrease the impurity, re-crystallization of $CaCl_2$ from concentrated solution can be done once again. However, based on our previous research, although the impurity of the obtained $CaCl_2$ was high, the $CaCl_2$ is still suitable to be used without further purification in the synthesis of CaTT in silica gel.

Effect of pH and $CaCl_2$ Concentration toward Crystal Yields

Determination of optimum pH of gel and $CaCl_2$ concentration of supernatant were conducted in order to study both parameters effects toward crystal yields (%). Although many journals reported that CaTT crystals were easily grown in pH around 3-5, due to some impurity contain in supernatant, i.e. Mg, the optimum pH

of gel should be determined first. Mean while, theoretically, the supernatant concentration will affect the diffusion rate and finally influence the size and yield of obtained crystals. The effect of gel and $CaCl_2$ concentration toward crystals yields were given in Figure 1 and 2.

At equal $CaCl_2$ concentration used of 0.45 M (supernatant C), the optimum pH of gel was obtained at 3.5 with yield of 69.37%. At pH 3, due to many H^+ ions in the solution, the gel formation takes longer time, hence when the supernatant solution was added, the gel was not appropriately ready for crystal growing. Mean while, at pH above 3.5, the yields were gradually decreased. As predicted, the less H^+ ions in the solution, the gel formation also take less time. Hence, when the supernatant solution was added, the gel surface is much harder which make many crystals nuclei forms just few millimeters under the gel surface, which is only grew into small polycrystalline CaTT. Consequently, less Ca^{2+} diffuse deeper into the gel and form bigger CaTT crystals.
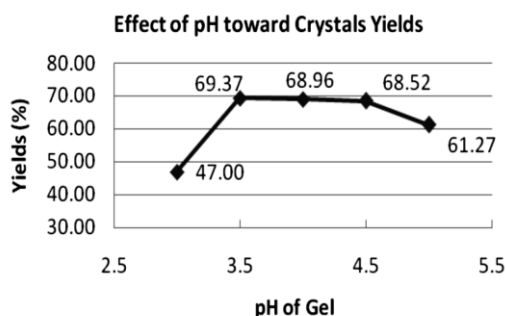

Figure 1. Effect of pH toward crystal yields

Surprisingly, the optimum $CaCl_2$ concentration at optimum pH of 3.5 was also gained at 0.45M (supernatant C) with yield of 69.37%. However, the profile in Figure 2 is different with those in Figure 1. In Figure 2, the crystal yields is increased significantly from 0.27 to 0.45M and then steadily declined. This result shows that until it reaches the optimum point, the higher Ca^{2+} ions in the solution, the higher yield of crystals produced. In contrast, when higher $CaCl_2$ concentration (0.54M) was applied, concentration gradients between tartrate ions in the gel and Ca^{2+} of supernatant were too high. Hence, similar to previous result (optimum pH determination), more crystals nuclei forms just few millimeters under the gel surface, which is only grew into small polycrystalline CaTT and blocked Ca^{2+} diffusion between Si-O-Si crosslink channels. As a result, it is hard for

other Ca^{2+} ions to diffuse deeper into the gel and only few bigger crystals can be harvested.
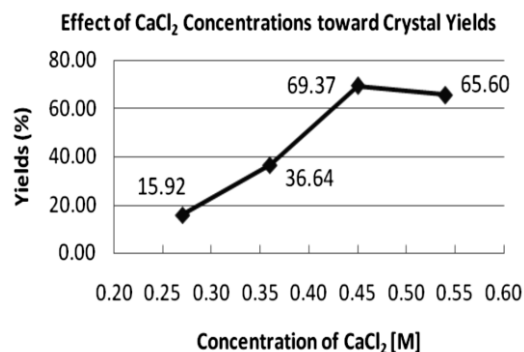

Figure 2. Effect of $CaCl_2$ concentration toward crystal yields

Characterization of Obtained Crystals

Single crystal that produced from optimum pH and $CaCl_2$ concentration has clear color with size around 4-9 mm (Figure 3). The obtained crystals mostly have octahedral shape, in which in some bigger crystals each equatorial corner has square shape, as shown in Figure 3. As many journal reported, bigger crystal were grown in the middle of the gel, while below the surface many small, in some case single crystals, were yielded. Mean while, the hardness test shows that the crystal gives value of 2-3 on Moh's scale, which is nearly equal to calcite's hardness (natural minerals of $CaCO_3$).

Figure 3. Single crystal of obtained CaTT

Analysis using infrared spectrophotometry (FTIR) reveals that the obtained crystal contains tartrate ions (Figure 4). The tartrate ions presences can be identified from specific peaks observed in IR spectrum, such as C=O, C-OH, C-C, and C-H as presented in Figure 5 and Table 1. In addition, the hydrate in the crystal lattice was confirmed by broad peaks in wavelength around 3000 cm^{-1}. As reference, the other IR spectrum of CaTT from different journal is also given in Table 1.
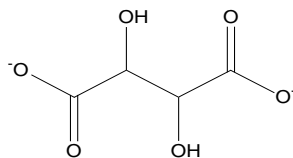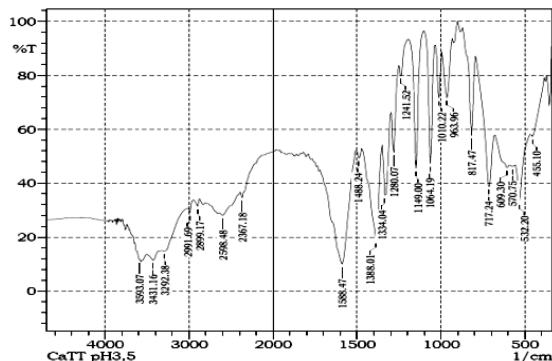
Figure 4. Tartaric ions structure

Figure 5. FTIR spectrum of obtained CaTT

Tabel 1. Infrared spectrum of obtained CaTT and other journal as reference

1	2	Notes
3261	3292.38	water, O-H, C-H *stretch*
2881	2899.17	
2573	2598.48	
1588	1588.47	C=O *stretch*
1382	1388.01	C=O *symmetric*
1326	1334.04	C-O *stretch*
1278	1280.07	C-H *bend*
957	963.96	C-C *stretch*
813	817.47	C-OH *bend*

Note: (1) CaTT crystal reported by Shajan and Mahadevan (2004);
(2) obtained CaTT

Furthermore, analysis using powder-XRD confirms that the obtained crystal is CaTT single crystals. The XRD analysis of obtained crystal is given in Figure 6, whereas the h k l data and *d-spacing* value of both obtained CaTT and JCPDS is presented in Table 2. To determine the crystal system, the *d spacing*-value of obtained CaTT, which is calculated from Bragg's law (d = λ/2sinθ with λ = 1.54056 Å) was compared with *d spacing*–value, which is calculated from *h k l* data of *JCPDS*, with parameter cells of, *a* = 9.627; *b* = 10.560; and *c* = 9.215, as stated in equation below:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Based on the calculation, the average difference of *d-spacing* value between JCPDS and obtained CaTT was insignificant (±0.0030). Hence, it is concluded that the obtained CaTT

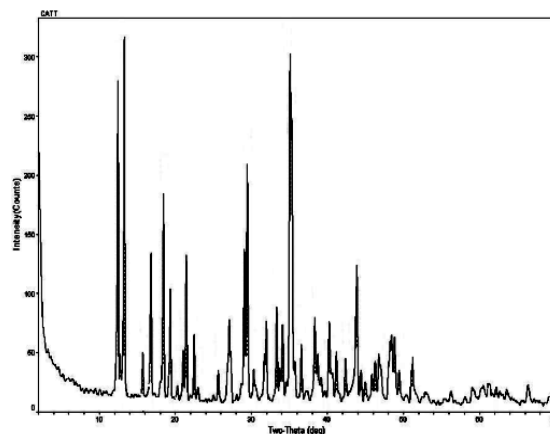has identical crystal system with CaTT from JCPDS, which is orthorhombic.

Figure 6. powder XRD diffractogram of obtained CaTT

Table 2. The h k l and d-spacing value of obtained CaTT and JCPDS*

JCPDS			Obtained CaTT			h k l
2θ(°)	d(Å)	I/Io	2θ(°)	d (Å)	I/Io	
12.4318	7.1200	60	12.461	7.0974	88.3	1 1 0
13.2942	6.6600	100	13.318	6.6425	100	1 0 1
16.7913	5.2800	35	16.799	5.2732	42.3	0 2 0
18.4456	4.8100	35	18.459	4.8026	58	2 0 0
29.4795	3.0300	40	29.481	3.0273	65.9	3 0 1
35.0522	2.6300	40	35.12	2.5531	95.6	1 2 3
35.3660	2.5380	55	35.32	2.5391	78.2	0 4 1
43.8846	2.0630	35	43.880	2.0616	38.8	1 2 4

*: only several peaks with high I/Io (more than 30) were presented

CONCLUSIONS

Single crystal of CaTT was successfully made in silica gel by utilizing the calcium of snail shell waste as the supernatant ingredient. Optimum condition of the synthesis was obtained at pH of 3.50 and [CaCl₂] of 0.45 M with yield of 69.37%. The obtained single crystal has clear color and octahedral-like shape with size ranged between 4 –9 mm. Analysis data by FTIR and powder XRD confirmed that the obtained crystal was CaTT single crystals with crystal system of orthorhombic.

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