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Manufacture and Use of Mesoporous Magnesium Silicate for Increasing Vitamin E Concentrate from Candlenut Oil

Benri Simanjuntak, and Nimpan Bangun[*]

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jalan Bioteknologi No.1 Kampus USU Medan 20155, Indonesia

Abstract. Magnesium silicate 75, magnesium silicate 90, and magnesium silicate MgO have been synthesized to increase the concentration of vitamin E from candlenut oil. The reaction of MgO and SiO_2 synthesizes the adsorbent magnesium silicate—X H_2O by hydrothermal method. The magnesium silicate obtained was characterized by BET, showing the pore size of the three different types of adsorbents, namely magnesium silicate 75 (6.118 nm), magnesium silicate 90 (6.248 nm), and magnesium silicate MgO (3.2238 nm). The adsorbent is used to increase the concentration of vitamin E in candlenut oil. Pecan oil is dissolved with n-hexane in a ratio of 1: 1 in a column containing the adsorbent. After the n-hexane descends from the column tool, vacuum to remove the solvent. Then the results are collected into vials. Then vitamin E levels wer measured by HPLC using standard Tocopherol and tocotrienol. The results of the HPLC test obtained a comparison of the three types of adsorbents' ability to increase levels of vitamin E from candlenut oil, where the adsorbent of magnesium silicate MgO can only increase vitamin E levels which were 429 ppm to 248.72 ppm (0.57 times enriched). In contrast, the magnesium silicate adsorbents 75 and 90 can increase vitamin E levels from 429 ppm to 733.73 ppm (1. 71 times improved) and 855.97 ppm (1.99 times enriched)..

Keywords: Adsorbent, Adsorption, Magnesium Silicate, Vitamin E, Candlenut Oil.

1 Introduction

Vitamin E is an ingredient that has an essential role in health because it can act as an antioxidant and also prevent cells that cause cancer, premature ageing, and cataracts (Rauf, 2015, Sayuti, 2016). Vitamin E is contained in vegetable oils from seed plants. The state of vitamin E is always mixed with fat or oil in the form of triglycerides, diglycerides, and monoglycerides. The presence of a non-polar fatty acid chain makes the non-polar affinity of vitamin E very stable and difficult to separate except by changing its properties affinity

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*Corresponding author at: Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Sumatera Utara, Medan, Indonesia.

E-mail address: nimpanbangun@usu.ac.id

Methods of obtaining vitamin E concentrate from vegetable oils have been reported utilizing adsorption. Some adsorbents used to adsorb vitamin E from palm oil generally use polar adsorbents such as silica gel and alumina oxide. There are also non-polar adsorbents such as polyaromatic, brominates SP 207, polyaromatic dowex optipore L-285, and amber lite XAD-1180. Of the five adsorbents, silica gel adsorbed vitamin E from palm oil as high as 78.98%, and desorption reached 83.31% (Chu, 2004).

Other adsorbents such as Calcium Polystyrene Sulfonate (Ca-PSS), Aluminum Polystyrene Sulfonate (Al-PSS), Calcium Methyl Ester Sulfonate Palmitate (Ca-MESP), and Calcium Silicate (Ca-S) have also been used to adsorb vitamin E from candlenut oil. Among all the adsorbents used, Ca-PSS has a higher adsorption power than the others. It is Tocopherol (TP) 26 times and Tocotrienol (TT) 22 times, and for calcium silicate adsorbents only obtain Tocopherol (TP) levels 23 times and Tocotrienol (TT) 19 times (Sebayang et al. 2016).

Even though calcium silicate has low adsorption properties and significant desorption results, resulting in low yields of vitamin E, calcium silicate is easier to regenerate (wash, heat, and reuse). The smaller size of the cation makes the adsorption power greater. Therefore, it is necessary to use magnesium silicate with minor Mg^{2+} ions so it is more robust for the adsorption of vitamin E. However, it is not yet known how far magnesium silicate's ability to desorption vitamin E from candlenut oil is. The method will be used to obtain mesoporous magnesium silicate, namely by the hydrothermal method. This method was carried out by reacting $Mg(NO_3)_2 .6H_2O$ and $Na_2 SiO_3 .9H_2O$ with the addition of ethanol solvent in different amounts, namely 75% and 90%. The best results obtained were magnesium silicate with the addition of 90% ethanol which produced a surface area of 650.50 m^2/g and an average pore diameter of 6.89 nm (Huang, 2017).

2   Materials and Methods

2.1   Materials

The study materials included $MgCl_2.6H_2O$, $Na_2 SiO_3.9H_2O$, absolute ethanol, distilled water, and candlenut.

2.2   Sample Manufacturing of Magnesium Silicate 75

As much as 1.666 g of $MgCl_2.6H_2O$ was put into a beaker glass. Then, 27.5 mL of distilled water and 82.5 ml of absolute ethanol were added while stirring rapidly to produce solution A. Solution B was prepared by dissolving 2,3 g of $Na_2SiO_3 .9H_2O$ with 10 mL of distilled water. Next, solutions A and B were mixed while stirring using a magnetic stirrer to produce a white suspension and kept stirring for 5 minutes. The suspension was put into the autoclave, heated at 170°C, and vigorously stirred for 24 hours. The mixture was cooled at room temperature, filtered, and washed with distilled water until pH = 7; a white precipitate was obtained and then dried at

60°C for 24 hours. After drying, 2.0804 g of magnesium silicate was obtained. Then the results were characterized by XRD, BET, and SEM-EDX.

2.3 Manufacturing of Magnesium Silicate 90

A total of 1.666 g $MgCl_2$.$6H_2O$ was put into a beaker glass. Then, 27.5 mL of distilled water and 82.5 mL of absolute ethanol were added while stirring rapidly to produce solution A. Solution B was prepared by dissolving 2,3 g Na_2SiO_3.$9H_2O$ with 10 mL of distilled water. The solutions A and B were mixed while stirring using a magnetic stirrer to produce a white suspension and kept stirring for 5 minutes. The suspension was put into the autoclave and Then heated at 170°C with vigorous stirring for 24 hours. The mixture was cooled at room temperature, filtered, and washed with distilled water until pH = 7; a white precipitate was obtained and then dried at 60°C for 24 hours. After drying, 2.1829 g of magnesium silicate was obtained. Then the results were characterized by XRD, BET, and SEM-EDX.

2.4 Manufacturing of Magnesium Silicate MgO

As much as 0.9574 g $Mg(OH)_2$ was put into a beaker glass. Then 27.5 mL of distilled water and 82.5 mL of absolute ethanol were added while stirring rapidly to produce solution A. Solution B was prepared by dissolving 4 .9475 g SiO_2 .xH_2O with 10 mL of aquabidest. The solutions A and B were mixed while stirring using a magnetic stirrer to produce a white suspension and kept stirring for 5 minutes. The suspension was put into the autoclave, heated at 170°C, and vigorously stirred for 24 hours. The mixture was cooled at room temperature, filtered, and washed with aquabidest until pH = 7; a white precipitate was obtained and then dried at 60°C for 24 hours. After drying, 3.4772 g of magnesium silicate was obtained. Then the results were characterized by XRD, BET, and SEM-EDX.

2.5 Fruit Seed Maceration Process of Candlenut

The candlenut seeds were ground and weighed as much as 250 g, then put into a plastic bottle. Next, add 1 litre of n-hexane solvent, place it in a shaker incubator for 48 hours, filter it, take the filtrate, separate the solvent and oil with a rotary evaporator, and then the resulting hazelnut oil in characterization by HPLC.

2.6 Adsorption and Desorption of Vitamin E from Candlenut Oil with Magnesium Silicate 75

As much as 3 g of hazelnut oil was put into the glass column. Into the column passed. Set aside until the oil mixes with the adsorbent. Then into the queue is passed 6 ml of n-hexane. Wait until no liquid drips from the column. The liquid obtained was vacuumed until a light yellow viscous liquid, free of solvents, was produced. The mass of the liquid was weighed and characterized using HPLC.

2.7 Adsorption and Desorption of Vitamin E from Candlenut Oil with Magnesium Silicate 90

As much as 3 g of magnesium silicate adsorbent was added to the glass column and passed 3 g of candlenut oil. Set aside until the oil mixes with the adsorbent. Then into the column is passed 6 ml of n-hexane. Wait until no liquid drips from the queue. The liquid obtained was vacuumed until a light yellow viscous liquid, free of solvents, was produced. Weigh the mass of the liquid and characterize it as HPLC.

2.8 Adsorption and Desorption of Vitamin E from Candlenut Oil with Magnesium Silicate MgO

As much as 3 g of magnesium silicate adsorbent was added to the glass column, and 3 g of hazelnut oil was passed into the queue. Set aside until the oil mixes with the adsorbent. Then into the column is passed 6 ml of n-hexane. Wait until no liquid drips from the column. The liquid obtained was vacuumed until a light yellow viscous liquid, free of solvents, was produced. Weigh the mass of the liquid and characterize it as HPLC.

3 RESULT AND DISCUSSION

3.1 X-Ray Diffraction (XRD) Analysis

3.1.1 Magnesium Silicate 75

Magnesium silicate 75 means the adsorbent is made using a mixture of aquabidest and absolute ethanol. The synthesized magnesium silicate obtained was characterized by XRD analysis to identify the components present in the sample. The results of the XRD analysis are shown in Figure 1
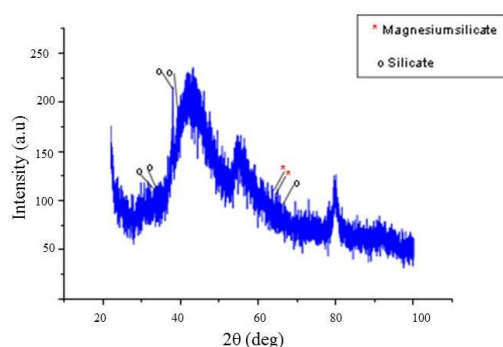

Figure 1. XRD diffractogram of Magnesium Silicate 75

The diffractogram shows the angle of 2Θ shows several different peaks; namely, 12 peaks were read and three heights with sharp intensity. The sharp peaks indicate the presence of silica (SiO_2) in the 17.90°, 17.99°, 20.90°, and 47.52 0 areas and magnesium silicate ($MgSiO_3$) in the 46.53° and 47.22°.

3.1.2 Magnesium Silicate 90

Magnesium silicate 90 means the adsorbent is made using a mixture of aquabidest and absolute ethanol. The results of the XRD analysis are shown in Figure 2.
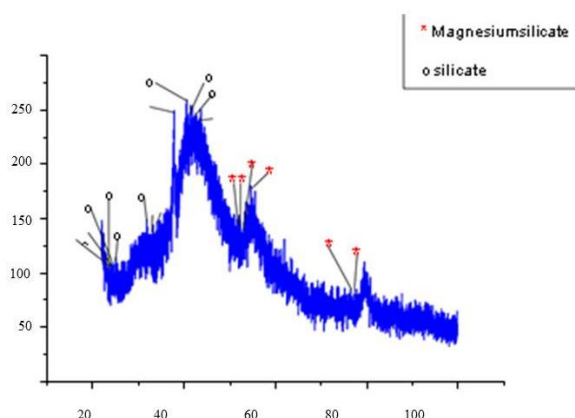

Figure 2. XRD diffractogram of Magnesium Silicate 90

The diffractogram shown in the table at an angle of 2Ө shows several different peaks. That is, 20 peaks were read, and three peaks whose intensity was quite sharp. The list of pretty sharp peaks indicates the presence of silica (SiO_2) in the area 5.59°, 6.06°, 6.47°, 6.66°, 7.04°, 17.51°, 17.89°, 19.98°, 21.31°, 21.55°, 22.00°, 22.14°, and 23.72°, and magnesium silicate ($MgSiO_3$) on area 32.34°, 33.62°, 34.76°, 36.36°, 58.15°, and 59.61°.

3.1.3 Magnesium Silicate MgO

Magnesium silicate MgO means that this adsorbent is prepared using a mixture of aquabidest, absolute ethanol, and the MgO oxidation reaction. The results of the XRD analysis are shown in Figure 3:
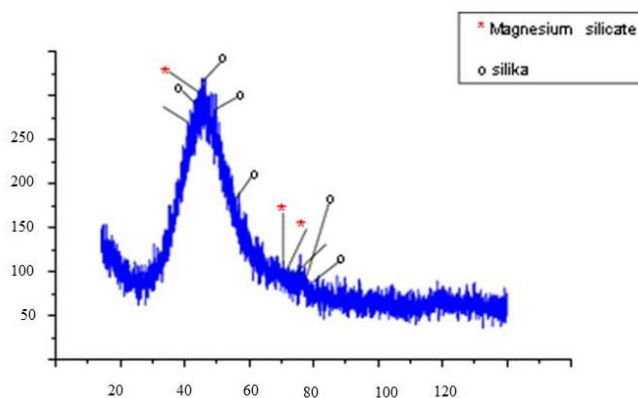
Figure 3. XRD diffractogram of Magnesium Silicate MgO

The list of sharp peaks indicates the presence of silica (SiO_2) in the area 23.07°, 20.79°, 21.98°, 24.45°, 27.63°, 36.15, 37.61°, 38.56°, 21.31 and magnesium silicate ($MgSiO_3$) in the area 35.37°, 35.67°. There is also magnesium silicate (Mg_2O_4Si) in the area of 22.53°.

From the three images, the XRD results from the adsorbent can be matched with JCPDS standard data to determine the types of three types of magnesium silicate.

3.2   Brunauer-Emmet-Teller (BET) Analysis

The BET analysis results of the three types of magnesium silicate adsorbents are shown in Figure 4. The differences in adsorption isotherms for adsorbents A, B, and C can be seen. The graph above can be determined as the type of graph according to IUPAC and Hysteresis Loops. Based on the grouping according to IUPAC, the adsorption-desorption isotherm graph of magnesium silicate adsorbents MgO, magnesium silicate 75, and magnesium silicate 90 classified by type VWhere in type V explains that material is material mesoporous (2 nm < d > 50nm) with weak interaction between adsorbate and adsorbent (Kanellopoulos. 2011).

Based on the classification according to Hysteresis Loops, the graphs of the three types of adsorbents above are classified into the H3 type. Type H3 explains that the material is due to particles such as plates/plates that form nonrigid aggregates with slit-shaped pores (Rouqe-Malherbe, 2007).

Nitrogen adsorption-desorption isotherms also produce the pore size distribution of the magnesium silicate adsorbent. The pore size distribution was calculated using the Barret-Joyner-Halenda (BJH) method, and the results are shown in Figure 4.7 below.
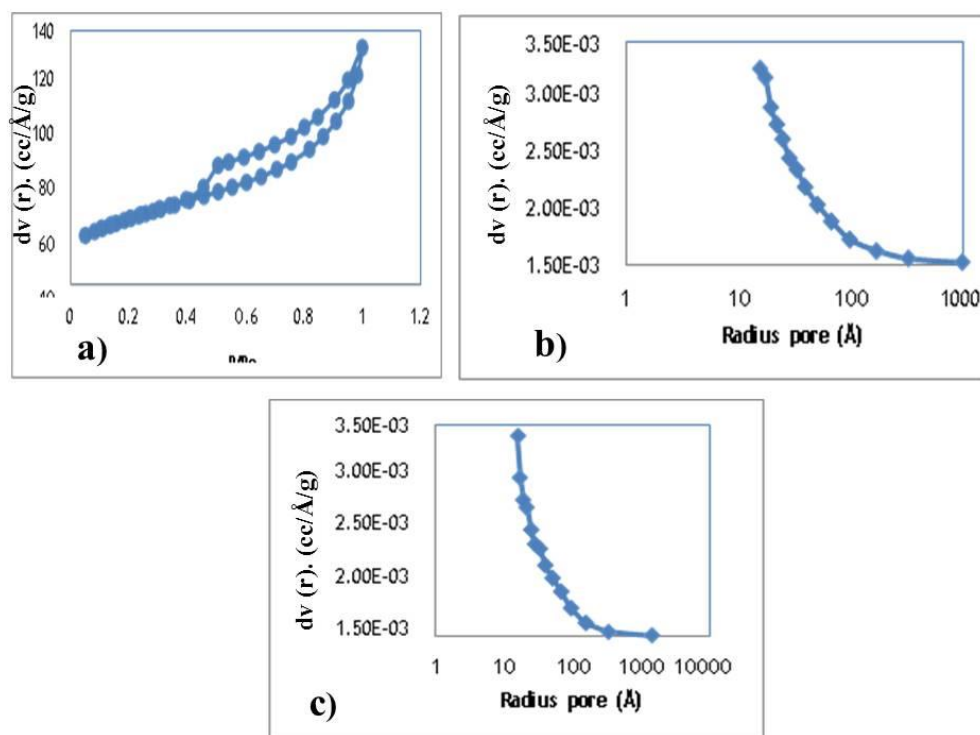

Figure 4. Magnesium Silicate MgO

From Figure 4, the difference in the pore size distribution of the three types of adsorbents can be seen. In magnesium silicate, MgO has a diameter of 32.2382 Å (3.22382 nm). Magnesium silicate 75 has a diameter of 61.18 Å (6.118 nm), and magnesium silicate 90 has a dominant pore size distribution of 62.48 Å (6.248 nm). These three adsorbents are categorized as adsorbents with tiny pores (mesopores) with pore sizes ranging from 2 nm to 50 nm shown in Table 1.

Table 1. Mechanical Properties of Edible Film

Results Analysis	Magnesium Silicate 75	Magnesium Silicate 90	Magnesium Silicate MgO
Surface area (m^2/g)	54.324	61.194	59.272
Pore volume (cc/g)	0.086	0.175	0.162
Pore size (nm)	3.2238	6.118	6.248

3.3 Selectivity Test of Vitamin E Absorption of Candlenut Oil from Types of Magnesium Silicate Adsorbents

Candlenut oil solution has been tested for initial vitamin E levels of 429 ppm. Then the adsorption and desorption processes of vitamin E were carried out with the three magnesium silicate adsorbents. After the adsorption process is carried out, the desorption process results in oil mixed with an amount of vitamin E, as seen in Table 2.

Table 2. HPLC Analysis of Vitamin E from Candlenut Oil

Oil mass (g)	Adsorbant	Adsorbent mass	Vitamin E (ppm)	Enrichment level
Oil beginning	-	-	429	-
3	Mg-S MgO	3	248.72	0.57
3	Mg-S 75%	3	733.73	1.71
5	Mg-S 90%	3	855.97	1.99

From the data above, it can be concluded that the highest concentration of vitamin E from candlenut oil was found in the oil fraction resulting from the adsorption and desorption of the adsorbent magnesium silicate 90, followed by the oil fraction resulting from the adsorption and desorption of the adsorbent magnesium silicate 75, and finally, the oil fraction from adsorption and desorption results using magnesium silicate MgO adsorbent. It can be concluded that of the three adsorbents above, magnesium silicate 90 has the best adsorption and desorption abilities because it produces concentrates with higher levels of vitamin E. Due to the pore size of magnesium silicate, 90 is more significant than magnesium silicate 75 and magnesium silicate MgO. The larger the adsorbent's pore size, the better the power adsorption.

4 Conclusion

The synthesized magnesium silicate has different pore sizes of 62.48 Å (magnesium silicate 90), 61.18 Å (magnesium silicate 75), and 16.119 Å (magnesium silicate MgO). Meanwhile, the adsorbent with the highest ability to increase the concentration of candlenut oil is magnesium silicate 90, which can increase vitamin E levels from 429 ppm to 855.97 ppm (1.71 times enriched). The larger the pore size of the adsorbent, the better the power adsorption.

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