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Pharma Research

An International Peer Reviewed, Indexed Journal

10.62655/s-epub.2022.v14.i02.pp1-13

MESOPOROUS AEROGEL OF ARENGA PINNATA ENDOSPERM AND THEIR APPLICATION TO ADSORB VITAMIN E FROM PALM FATTY ACID DISTILLATE

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Article info

Published on:26-10-2022

ISSN: 0975-8216

Keywords:

Mesoporous aerogel, *Arenga pinnata* endosperm, Palm fatty acid distillate, Vitamin E

ABSTRACT

Objective: The mesoporous aerogel (MA) has been produced from *Arenga pinnata* endosperm (APE) and was used to adsorb vitamin E from palm fatty acid distillate (PFAD).

Methods: The adsorption process was carried out through the alcogel stage, followed by drying under dry air and reduced pressure. In the present work response surface methodology based on Box-Benhken design experiment was used to investigate the effect of dry APE types (1–3), the concentration of APE (1–1.5%, wt./v) and solvent exchange time (12–36 h).

hydrophobic phase, therefore, hydrophobic vitamin E are easy adsorbed on aerogels.

INTRODUCTION

Utilization of adsorption material based on the dispersion of active material in biocompatible and biodegradable material has been developed recently. For instance, adsorption of vitamin E using starch aerogel [1]. Natural polysaccharide, which has been

modified in form of aerogel is used widely in the pharmaceutical industry due to non- toxic, stable and biodegradable [2]. Matrix aerogel has open pore on its structure with largest surface area [3]. Some researcher have developed cellulose aerogel using freeze-drying method [4], starch aerogel using supercritical method [1] and dry air [5]. Silica aerogel also has been

studied, which have more pores and biocompatible, however, the utilization is limited due to non-biodegradable [3]. Based on this developing of sustainable, biocompatible and biodegradable aerogel using simple and cost-effective method from APE is necessary. To the best of knowledge, there is no literature regarding aerogel from APE. Our previous studied has demonstrated the absorption of vitamin E using galactomannan cross-linked phosphate with efficiency more than 90% [6].

Vitamin E is a fat-dissolved natural antioxidant which could inhibit oxidation [7, 8]. One of main vitamin E source is crude palm oil which contains 600–1,000 ppm. PFAD is a palm oil production by- product which also contains vitamin E (70% of tocotrienol and 30% of tocopherol) [9]. Vitamin E has been identified played important role in cell protection from free radical scavenging; degenerative diseases such as hearth coroner and cancer could be avoided using vitamin E [10, 11]. Commonly natural antioxidant is unstable and very sensitive to environmental and treatment such as light, oxygen and temperature [12]. Addition of porous material is usually used to protect vitamin E from degradation [13]. Polysaccharide like starch and its derivate, gums, pectin, alginate and other polysaccharides from animal and microbe such as chitosan and xanthan have been used as a matrix to protect vitamin E [14]. In this study, APE, which is naturally abundant, has been used in aerogel form.

APE is sell as “kolang-kaling” in the traditional market in Indonesia and its only used as cocktail and food [15]. Every year *Arenga pinnata*

tree could produce 100 Kg endosperm. APE contain high fibre and composed of water dissolved and undissolved fraction. Water dissolved fraction contains 62.49% polysaccharide and crude fibre of 1.11% [16]. Water dissolved and undissolved fibre has antioxidant activity [17]. Major polysaccharide in APE is galactomannan which is water dissolved polysaccharide [18] with ratio galactose: mannose of 1: 1.33 and has IC₅₀ value of 22.109 mg/ml [16]. Galactomannan contains branched-chain of galactose, which is polar and mannose, which is non-polar. Therefore, polysaccharide from APE could be used as absorbent and protector of vitamin E.

Based on that, this study aims to utilize APE as an adsorbent which has antioxidant activity, biocompatible and biodegradable to adsorb vitamin E from PFAD. The method developed in this study including hydrogel formation from APE, alcogel and aerogel through solvent exchange and drying method. The MA formed before and after vitamin E adsorption was analysed using spectrophotometer FT-IR, X-ray diffraction (X-RD), scanning electron microscope (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Barret-Joyner-Hallenda (BJH) and Brunauer-Emmet-Teller (BET). Absorption efficiency of vitamin E was determined using high-performance liquid chromatography (HPLC).

MATERIALS AND METHODS

The APE was bought from the local traditional market in Medan, Sumatera Utara–Indonesia. Vitamin E of PFAD was collected from local palm oil company in Medan. Ethanol and silica gel was bought from local chemical dealer.

The formation of APE hydrogel

The formation of APE hydrogel was investigated using the response surface method Box-Behnken design with 3 parameters. The effect of APE type, concentration of APE and solvent exchange time at 3 variable levels is showed in table 1. The dry APE with the appropriate type and concentration was dissolved in water and heated at 50 °C and stirred until completely dissolved. The solution formed was homogenized using shaker for 5 h at 50 °C and poured in 14 x 7 x 4 cm glass plate and stored in the fridge at 4-5 °C for 3 d.

Table 1: Independent variables and levels used of the operating parameters

Parameters	Symbol	Level		
		-1	0	1
APE type	A	1	2	3
Concentration of APE (wt./v)	B	1	1.25	1.5
Solvent exchange time (min)	C	12	36	48

APE: *Arenga pinnata*
endosperm

The formation of APE alcogel

The APE hydrogel was soaked in ethanol with a concentration of 30, 70, 90 and 100%, respectively, for 24 h. Similar procedure was conducted for solvent exchange time of 36 and 48 h. This procedure was developed from previous researchers with slightly modification [5, 19].

The Formation of APE aerogel

Alcogel formed from the previous procedure was stored in a desiccator containing silica gel and vacuum until the constant weight of aerogel obtained. The aerogel was characterized using FT-IR, X- RD, SEM and BET.

Adsorption of vitamin E from PFAD using aerogel

The Box-Behnken response surface method applied for alcogel formation showed that the lowest density occurred using a solvent exchange time of 36 h. Based on that, APE type 1–3 and 36 h solvent exchange time were used to determine the efficiency of vitamin E

adsorption. Alcogel was added by vitamin E and dried using a similar procedure in aerogel formation. The adsorption efficiency was determined using HPLC, while the mixture of aerogel+vitamin E was characterized using FT-IR, X-RD and SEM.

RESULTS AND DISCUSSION

The process steps to produce APE aerogels are solution-hydrogel- alkogel-aerogel[1]. The solution to hydrogel stage involves dissolving APE flour in a water medium, rendering structural changes (gelatinization stage) and structural rearrangement during the cooling stage (retrogradation stage). At the retrogradation process, no solid (slab) as in starch occurred; therefore, the solvent exchange process is carried out in a container (glass plate) [1]. In the solvent exchange process, slab formation occurs and the shape is not the same for each APE. The next process is the formation of aerogels through drying carried out in a vacuum and dry air. Aerogels obtained in foam form, as well as volume reduction from hydrogels to alkogels and from alkogels to aerogels, are shown in table 2.

Table 2: The volume changes of hydrogel, alcogel and aerogel

Sample number	Volume			% Volume changes	
	Hydrogel	Alcogel	Aerogel	1a	2b
1	100.62	43.436	2.637	56.83	93.93
2	101.40	56.925	6.527	43.86	88.53
3	101.40	41.215	4.116	59.75	90.01
4	101.40	55.825	8.388	44.95	84.97
5	95.16	43.261	6.187	54.54	85.70
6	97.50	63.913	5.160	34.45	91.93
7	101.40	51.920	6.239	48.80	87.98
8	92.16	44.058	3.469	52.19	92.13
9	102.18	59.378	6.903	41.89	88.37
10	107.52	51.597	7.497	52.01	85.47
11	101.40	79.704	4.985	21.40	93.75
12	97.50	52.839	12.863	45.81	75.66
13	99.84	55.963	10.749	43.95	80.79
14	101.40	63.189	5.879	37.68	90.70
15	101.40	46.994	6.250	53.65	86.70

^aDeficits volume from hydrogel to alcogel, ^bDeficits volume from alcogel to aerogel

Aerogel density of APE

The optimum condition of the density of APE aerogels is determined by the Box-Behnken surface experiment method that this method is better than conventional because it reduces the number of experiments and provides an appropriate model for the optimization process. Table 1 shows the Box-Behnken design matrix for 3 parameters such as the APE type, concentration of APE and solvent exchange time. The quadratic regression model was built using Sigma software embedded in microsoft excel was illustrated in equation 1. The model was predicted the determination coefficient (R square) and the adjusted coefficient (R square adjusted) were 89.16% and 69.65%, respectively. The high value of the coefficients denoted the significance of the model. The density predicted value from the model was reasonably close to the parameter value.

$$\begin{aligned} \text{Density} = & (0.1723) + (0.0350125) * A + \\ & (0.0249125 * B) + (-0.0557 * C) + \\ & (0.017625 * AB) + (-0.02285 * AC) + \\ & (-0.0124 * BC) + (0.0253375 * AA) \\ & + (3.75E - 05 * BB) + \\ & (-0.0114375 * CC) \dots\dots \text{Equation (1)} \end{aligned}$$

The effect of type and concentration of APE and solvent exchange time on aerogel density are shown in fig. 1, 2 and 3. As shown in fig. 1 that the type and concentration of APE has a significant effect on the density of aerogels. The low-density value was obtained in APE type 1 and 2, meaning that aerogels are more inflated. In the increasing of APE concentration, the density was increased as the solution became viscous. Furthermore, low density of APE aerogels as shown in fig. 2 was obtained in APE of 1 and 2 at 48 h of immersion while the highest density was occurred using APE type 3 and 24 h soaking time. This is due to the fact that the APE type 3 initially expands rapidly and which is collapse during the aerogel drying process. Probably this is due to the greater number of insoluble fractions (mannose) in APE type 3, giving the interaction between polymer chains is stronger. Low-density value also occurred in the concentration of APE of 1-1.15% w/v with a 48 hour immersion time, as showed in fig. 3. The density was increased in the longer immersion time. Based on fig. 1-3, aerogels with low density could be occurred if use APE type 1, the concentration of 1. 5% (wt/v) and 48 h soaking time.

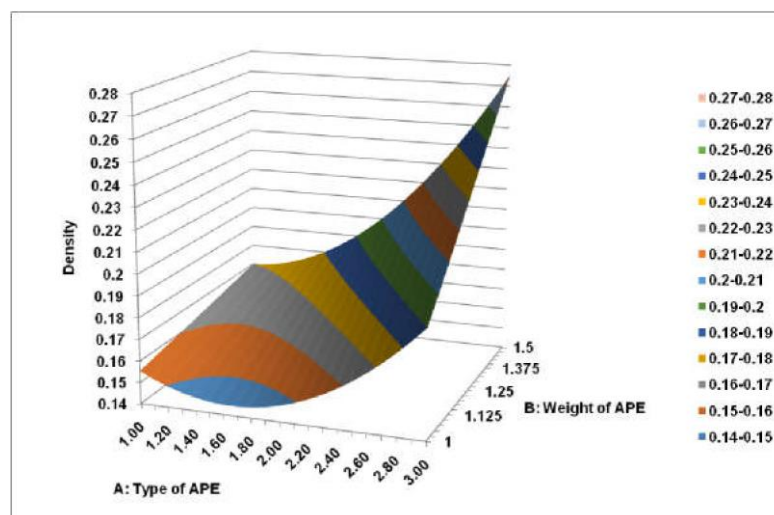


Fig. 1: Interaction APE type and weight of APE on the density of aerogel, APE: *Arenga pinnata* endosperm

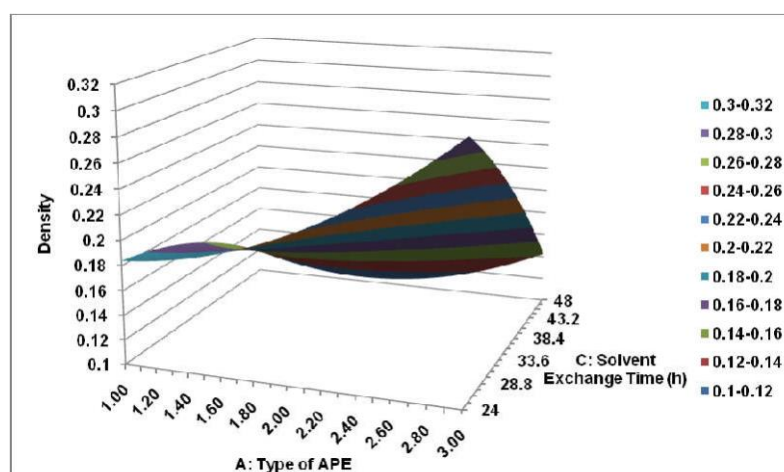


Fig. 2: Interaction of APE type and solvent exchange time on the density of aerogel, APE: *Arenga pinnata* endosperm

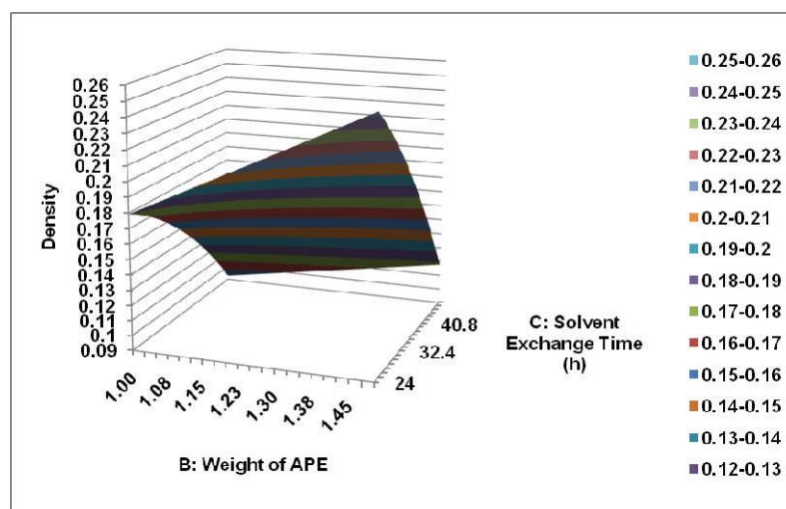


Fig. 3: Interaction of weight of APE and solvent exchange time on the density of aerogel, APE: *Arenga pinnata* endosperm

FT-IR analysis

Fig. 4 shows the FT-IR aerogel spectrum, vitamin E, and APE type 1-3 aerogel+vitamin E with the absorbance was recorded in the area of 4000-400 cm^{-1} . The FT-IR spectrum of APE type 2 (A) shows characteristic peaks at 3339 cm^{-1} indicating the vibration stretching of OH groups from polysaccharides supported by a peak at 1637 cm^{-1} due to interaction with water. The peak at 2900 cm^{-1} is the C-H stretching vibration supported by the bending vibration of the-CH₂-group at 1373 cm^{-1} . A strong absorption band at an area of 800-1200 cm^{-1} is a combination of vibrations from C-C-O, C-OH and C-O-C main devices. The peak at 1148 cm^{-1} is the C-O bending vibration of the pyranose ring. Absorption bands at 868 cm^{-1} are β -D-mannopyranose units and 810 cm^{-1} are α -D-galactopyranose units [20-22]. The vitamin E (B) FT- IR spectrum is similar to that shown in the literature [6, 23] with the absorption band at 3429 cm^{-1} is a stretching vibration of an-OH group

and a band at 1720 cm^{-1} is a stretching vibration of C=O while a peak at an area of 800-1200 cm^{-1} is a stretching-C-O-C-vibration. The strong peak at 2800-2950 cm^{-1} is the-C-H stretching vibration. The aerogel spectrum from APE 1-3+vitamin E shows similarities in all three spectra (C-E). The peak at 3364 cm^{-1} is the vibration peak of the OH group which is stronger than vitamin E. The absorption band at 1714 cm^{-1} is a stretching vibration of C = O from vitamin E [23], peak at 1644 cm^{-1} shows the OH group of polysaccharides and vitamin E which is bound to water. Absorption bands in the 800-1200 cm^{-1} region show a combined stretching vibration of CCO, C-OH, COC from polysaccharides and COC from vitamin E. Physical mixtures between aerogel BA1-3 and vitamin E show the same characteristic bands related to vibration stretching C = O, OH, CH, CO in palm sugar and vitamin E. This shows that vitamin E is present in polysaccharides and there is no modification in the two compounds in the formation of aerogels+vitamin E [6, 23, 24].

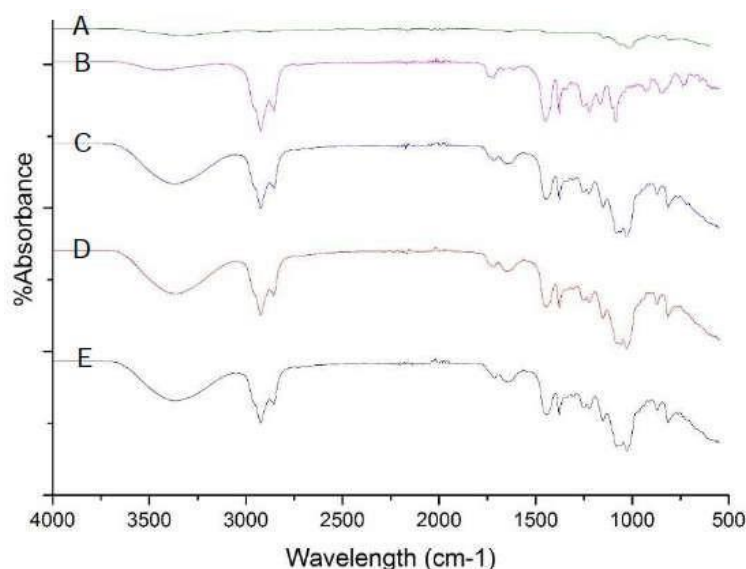


Fig. 4: Spectra FT-IR of (A) aerogel; (B) vitamin E; (C) aerogel from APE type 1+vitamin E; (D) aerogel from APE type 2+vitamin E; and (E) aerogel from APE type 3+vitamin E, APE: *Arenga pinnata* endosperm

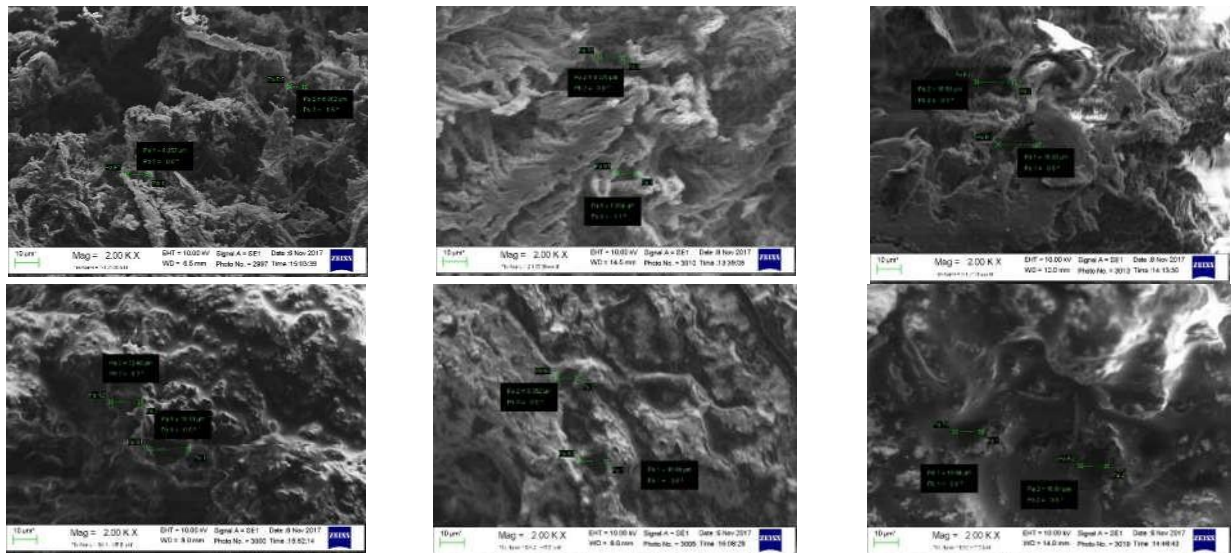


Fig. 5: SEM images of (A-C) aerogel from APE type 1–3 concentration of 1.25% and (D-F) aerogel from APE type 1–3 concentration of 1.5%+vitamin E in solvent exchange time of 36 h, APE: *Arenga pinnata* endosperm

SEM

The SEM analysis was used to study the surface morphology of the APE and the aerogel products containing vitamin E. Fig. 5 shows the morphology of APE aerogel surface and APE+vitamin E aerogel. The aerogel made from APE type 1-3 (A-C) with a concentration of 1.25% (w/v) and solvent exchange time of 36 h showed a fibrous, rough and hollow surface[1]. The surface after being added with vitamin E provides a smoother surface where the cavity has been covered by vitamin E. Therefore, it can be concluded that the aerogel could entrap vitamin E given the possibility to protect active compounds from the unnecessary environment.

BET

The surface area analysis using BET method was conducted to determine the surface area and pore volume of the aerogel. The surface area of APE type 1–3 aerogel produced from the concentration of 1.5 % and solvent exchange time of 36 h are 42–84 m²/g which similar with the previous result reported by Mehling, *et al.* (2009) on aerogel of corn starch fabricated using supercritical drying method [25]. Furthermore, the type of aerogel obtained was mesopore based on its diameter of 3.142-3.212 nm. The aerogel density of the APE was 0.1472–0.2834 g/cm³, which is less than the aerogel from starch with value of 0.32 g/cm³ [5].

Table 3: The properties of aerogel

Aerogel ^a	Bulk density (g/cm ³)	SBEI (m ² /g)	SBEH (m ² /g)	Pore volume (cm ³ /g)	Pore radius (nm)
APE-1	0.1472	52.630	518.848 (Ads) 501.09/ (Des)	0.807	1.590
APE-2	0.2143	83.620	645.583 (Ads) 642.626 (Des)	1.023	1.606
APE-3	0.2834	42.969	362.624 (Ads) 339.506 (Des)	0.555	1.571
APE-3+Vit E		24.869	199.749 (Ads) 213.015 (Des)	0.311	1.609

^aweight of APE used was same and solvent exchange time was 36 h, APE: *Arenga pinnata* endosperm

X-RD

X-ray diffraction (X-RD) was carried out to study the crystallization properties of aerogels, which adsorb vitamin PFAD. The diffraction of APE type 2 without adsorption process (A) and aerogel, which adsorbs vitamin PFAD (B-C) is shown in fig. 6. It is apparent from the graph that APE type 2 aerogels show a widening peak at 2θ =20°, which states that

the polysaccharides is amorphous. The aerogels from APE 1–3 which have absorbed vitamin E PFAD provide almost the same diffractogram, where the intensity of the amorphous peak decreases and appears several sharp peaks at 2θ =9°, 44° and 64°, respectively, which state the presence of crystalline compounds. The appearance of these crystals is likely due to the components of compounds contained in vitamin E PFAD [6], meaning aerogels from APE 1-3 have adsorbed vitamin E PFAD [1].

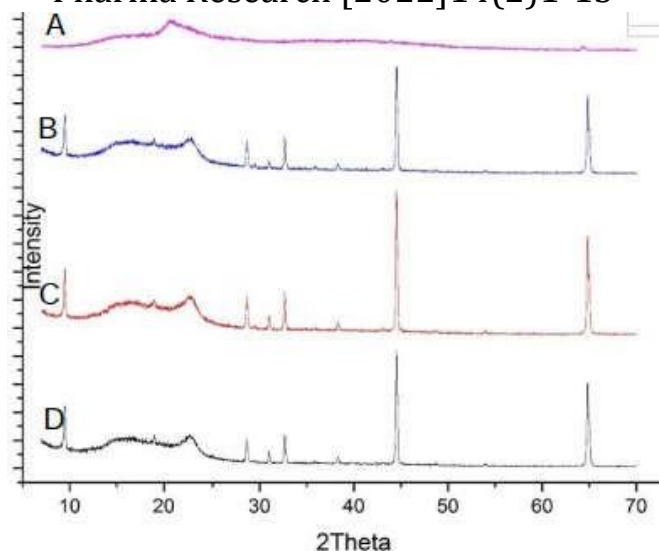


Fig. 6: X-RD spectra of (A) aerogel from APE type 2; (B) aerogel from APE type 1+vitamin E; (C) aerogel from APE type 2+vitamin E; and (D) aerogel from APE type 3+vitamin E, APE: *Arenga pinnata* endosperm

Tensile strength

The tensile strength was determined using a rectangular sample of 1 cm x 1 cm and the results were obtained from 3 separate study. The tensile strength of APE aerogels is only obtained in APE type 1 and 2 with the concentration of 1.5%. This concentration was chosen due to the thickness aerogel could obtain. The aerogel thickness after being pressed will affect the strength of the material until it breaks when the tensile strength test. As shown in fig. 7, the aerogel from

APE type 2 with solvent exchange change of 24 h have the better tensile strength.

Vitamin E PFAD absorption by aerogel APE

Based on the previous study, the concentration of vitamin E in PFAD was 70% [6]. The unabsorbed vitamin E was determined using HPLC and the absorbed vitamin E on aerogel of APE type 1–3 was calculated based on the equation established by previous researchers [6, 24]. Fig. 8 depict the

concentration of vitamin E which is adsorbed by aerogels APE type 1–3 were 64.01%; 63.36% and 64.29%, respectively. The APE aerogels absorbed vitamin is showed in fig. 9. The APE aerogels can adsorb vitamin E because the aerogels have pores as shown in SEM and X-RD

analysis, besides that the main components contained therein are galactomannan whose main chain structure of mannose is hydrophobic while its branches are galactose which are hydrophilic [23] therefore hydrophobic vitamin E will be adsorbed on aerogels.

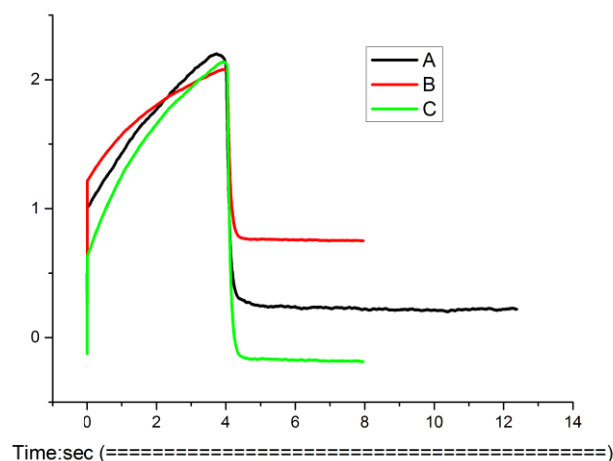


Fig. 7: Tensile strength of (A) aerogel No. 14 (APE type 2, weight of 1.5 and 24 h solvent exchange time); (B) aerogel No. 9 (APE type 1, the weight of 1.5 and 36 h solvent exchange time); and (C) (A) aerogel No. 12 (APE type 2, weight of 1.5 and 48 h solvent exchange time), APE: *Arenga pinnata* endosperm

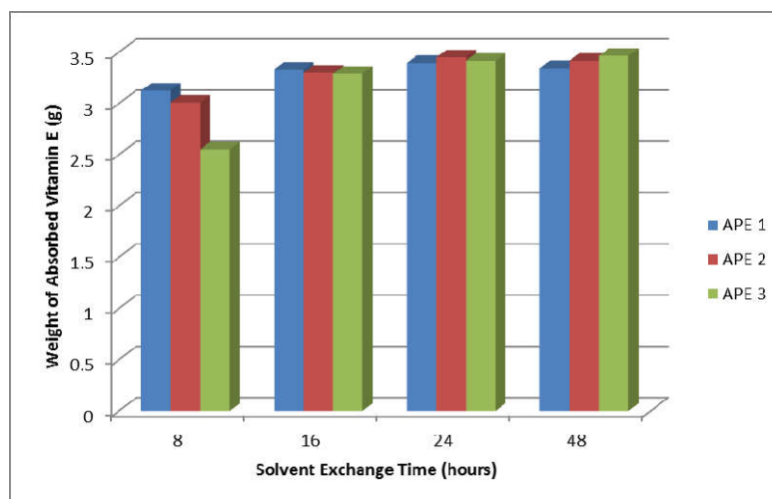


Fig. 8: Adsorption vitamin E on aerogel, APE: *Arenga pinnata* endosperm

CONCLUSION

The MA has been produced from APE and used to adsorb vitamin E from PFAD. The adsorption process is carried out through the alcogel stage, followed by drying under dry air and reduced pressure. In the present work response surface methodology based on Box-Benhken design experiment was used to investigate the effect of APE types 1–3, the concentration of APE 1–1.5% (wt./v) and solvent exchange time (12–36 h). Based on the result, the optimum parameter to produce aerogel with low-density value are as follows: APE types 1 with a concentration of 1.5% (wt./v) and 48 h solvent exchange time. The MA occurred from this parameters has diameter of 3.142–3.212 nm. The surface morphology of MA had changed from roughly hollowed to smooth and the amorf intensity decreased after vitamin E adsorption process.

ACKNOWLEDGMENT

Authors acknowledge the Directorate General of Higher Education– Ministry of Research, Technology and Higher Education, Indonesia and the Rector of University of Sumatera Utara for providing laboratory facilities.

FUNDING

The authors acknowledge the financial support from University of Sumatera Utara by TALENTA USU No. 5338/UN5.1. R/PPM/2017, date of 22 Mei 2017.

AUTHORS CONTRIBUTIONS

All the authors have contributed equally.

CONFLICT OF INTERESTS

The authors declare that no conflict of interest associated with this work.

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