

Adsorption of carbon dioxide with nanofibers based on alginate/polyethylene oxide/triton X-100

Faryda Veronica Lamma Koly^{a*}, Adhitasari Suratman^b, Suyanta^b

^aDepartment of Chemistry, Faculty of Mathematics and Science, Tribuana Kalabahi University, Alor 85812, Indonesia

^bDepartment of Chemistry, Faculty of Mathematics and Science, Universitas Gadjah Mada, Yogyakarta 55284, Indonesia

Abstract

Nanofiber is a material composed of nanometer-scale fibers with carbon or polymer base materials. The most economical method of nanofibers synthesis is electrospinning. Nanofiber has a high potential for CO₂ adsorption because it has high gas transport resistance and high kinetic [1]. Research on synthesis of Alginate/Polyethylene oxide/Triton X-100 nanofibers (Alg/PEO/TX NFs) by electrospinning for CO₂ adsorption was carried out. The purpose of this research were to study the effect of adding PEO and TX to the electrospinnability of the solution, and the effect of the gas flow rate and contact time on adsorption capacity of Alg/PEO/TX NFs. Polymer solutions were characterized by the conductivity meter and tensiometer, while the nanofibers were analyzed using optical microscopy, SEM, and FTIR. The study of CO₂ contact time includes the effect of flow rate and CO₂ contact time on nanofiber. The results showed that Alg/PEO/TX NFs were successfully synthesized with a volume ratio 1/2 of Alg/PEO blends solutions and a small addition of 0.5% (v/v) TX. The beads-free nanofibers produced was 201 ± 48 nm in diameter and with a surface area of $34,963 \text{ m}^2\cdot\text{g}^{-1}$. The optimum adsorption capacity was $12,398 \text{ mmol}\cdot\text{g}^{-1}$, which was obtained at the flow rate of $10 \text{ mL}\cdot\text{minute}^{-1}$ and a contact time of 25 minutes.

* Corresponding author:

faryda.veronica.l.k@gmail.com

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1. Introduction

Carbon dioxide (CO₂) is one of the greenhouse gas that produced naturally from human respiration, animals, microbiology and geothermal processes. In addition, anthropogenic CO₂ sources come from industrial emissions, motor vehicles and the results of other human activities. According to Callendar (2007) [2], the increase of temperature every year in the atmosphere is caused by an increase in the CO₂ concentration derived from emissions of the used of fossil energy. CO₂ gas is recognized as a major contributor to global warming, which is around 64% [3]. The efforts to reduce CO₂ concentrations in the atmosphere were tree planting, increasing energy efficiency, and reducing CO₂ gas emissions. Some ways of reducing CO₂ emissions were increasing the use of renewable energy or nuclear energy, and *Carbon dioxide Capture and Storage* (CCS). The adsorption method is one of the important stages in CCS. In general, the adsorption is a method that is more widely used because of the low energy consumption, the cost of equipment is cheap and easy in application. A number of materials have been developed to adsorb CO₂, including activated carbon [4], mesopore carbon [5], zeolite [6], mesopore silica [7], and nanomaterial. Nanomaterials relatively has a higher potential for CO₂ captured or adsorbed, because it has a high surface area. Materials with a high surface area provide more reaction sites so as to increase adsorption capacity. Several new materials has been developed for CO₂ adsorption, such as Ionic Liquids (ILs), Metal-Organic Frameworks (MOFs), membranes, and electrospinning nanofiber. Nanofiber is a material composed of nanometer-scale fibers with carbon or polymer base material. Electrospinning is the easiest and most economical method of nanofiber synthesis. The polymer solution was given a voltage will form the fiber between the two electrodes, and the fibers will be collected in the negative electrode. Nanofiber has a high potential for CO₂ adsorption because it has low gas transport resistance and high kinetic [1]. Nanofiber used for adsorption of CO₂ has been carried out, such as Alg/PVA NFs [8], Alg/PVA/zeolite NFs [9] and Alg/pectin/PVA [10]. Alginate is a natural polymer that has the potential for CO₂ adsorption due to the availability of carboxylic groups (COOH). Alginate and most other natural polymers cannot be electrospinning because they have high polyelectrolyte properties. Therefore, alginate solutions need to be combined with synthetic polymers such as PVA, PAN, or PEO to improve solution electrospinnability. The addition of PEO in the synthesis of alginate nanofiber is considered to be relatively more suitable because both can dissolve in water at room temperature, easily degraded and relatively non-toxic. To produce Alg/PEO nanofiber without beads with high alginate composition, Bonino *et al.*, (2011) [11] carried out the addition of non-ionic surfactant, Triton X-100 (TX). Although synthesis of Alg/PEO/TX NFs has been done, its application for CO₂ adsorption has never been done before. Based on this, the synthesis of Alg/PEO NFs and Alg/PEO/TX NFs were carried out using the *electrospinning* method then applied for CO₂ adsorption. Nanofiber synthesis was carried out by studying the effect of PEO concentration on the electrospinnability of Alg/PEO blends and the effect of TX concentration on the electrospinnability of the Alg/PEO/TX blends. Furthermore, CO₂ adsorption was carried out to determine the adsorption capacity of Alg/PEO/TX NFs nanofiber at optimum contact time and gas flow rate.

2. Experimental

2.1. Material and solution preparation and characterization

Sodium alginate (medium viscosity) and polyethylene oxide (Mv 600 kDa) were obtained from Sigma Aldrich and used without further purification. Triton X-100 was obtained from Merck and CO₂ gas from SAMATOR Yogyakarta. The solutions were prepared by making separate solutions of alginate (2 wt%) and PEO (6 wt%) in distilled water by stirred at room temperature for 2 and 6 hours, respectively. After that, solutions were mixed by several volume ratios of Alg/PEO (1/0, 2/1, 1/1, 1/2 and 0/1) with stirring at room temperature for 6 hours with a magnetic stir bar. These solutions were used for study the electrospinnability of Alg/PEO solutions. In addition, the solutions of Alg/PEO/TX

with several concentration of TX (0%, 0.5%, 1.0% and 1.5%) were prepared by stirring at room temperature for 6 hours. These solutions were used to study the influence of TX concentration to the electrospinnability of the solution, and to obtain the optimum concentration of TX to resulting the uniform fibers without beads (beaded-free fibers). Solution conductivity was measured with a conductivity meter (Ohaus ST10C-B) for the different ratio of Alg/PEO solution, and surface tension was measured using a tensiometer for Alg/PEO/TX solutions with all difference concentration of TX.

2.2. Electrospinning and characterization of nanofibers

The design of the electrospinning setup was described in Fig. 1. Each solution was placed into 10 mL syringe (a) capped with 0.5 mm blunt needle (d). Electrospinning of all solutions was carried out by giving voltage (c) of 5 kV and a tip to collector distance (TTCD) of 13 cm. The collector (b) was placed by object glass for morphology evaluation with microscope optic. The electrospinning process for this section run by several minutes only. In addition, the gauze was placed on the collector for CO₂ adsorption test. For this section, the electrospinning process was run for 2 hours to obtain the thicker nanofibers.

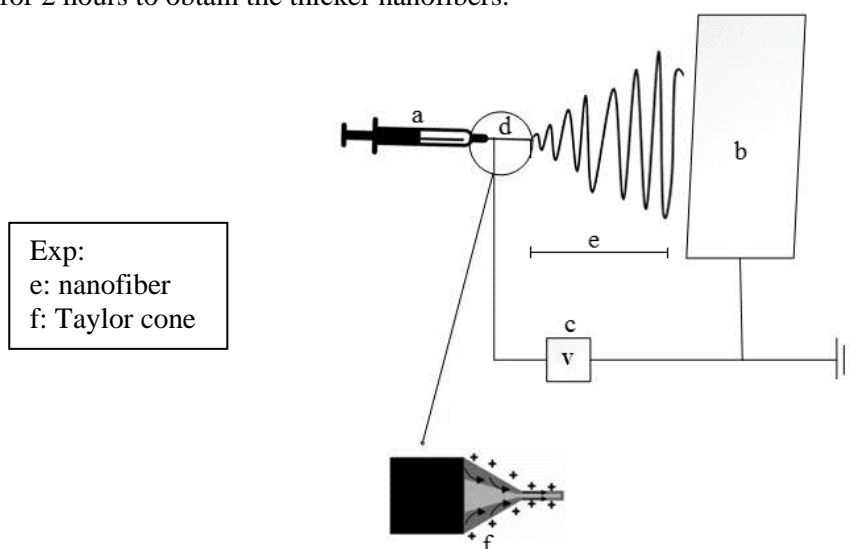


Figure 1: Electrospinning setup design

After electrospinning, uniform fiber resulting from electrospinning were analyzed with a scanning electron microscope (SEM), and fiber diameters were measured using Image-J software based on the SEM morphograph. In the other side, Na-Alginate powder, PEO NFs, Alg/PEO NFs and Alg/PEO/TX NFs were characterized using FTIR to observe the functional group of the nanofiber. The surface area of Alg/PEO/TX NFs was determined by the BET method.

2.3. Adsorption of CO₂ on nanofiber

The adsorption capacity of Alg/PEO/TX NFs was determined by column method at room temperature. Alg/PEO/TX NFs membrane was cutted of 4.8 cm diameter circle and placed into the adsorption devices (Figure 2). CO₂ concentration absorbed in the absorbent solution was carried out using the titrimetric method, Warder titration. Mol CO₂ adsorbed in Alg/PEO/TX NFs was obtained from the difference between the amount of CO₂ that was absorbed in the NaOH solution after passing through the column with and without the nanofiber (blank). Determination of the effect of CO₂ flow rate on the adsorption capacity of Alg/PEO/TX NFs was carried out at flow rates of 6, 8, 10, 20, 30,

and 40 mL.min⁻¹ for 20 minutes, while determination of effect of contact time on the adsorption capacity Alg/PEO/TX NFs to CO₂ performed for 5, 10, 15, 20, 25 and 30 minutes.

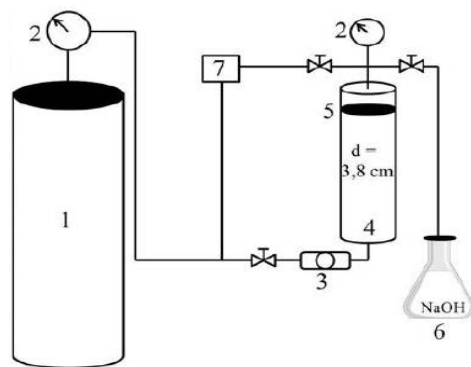


Figure 2: CO₂ adsorption setup design

3. Results and discussion

3.1. The effect of PEO on electrospinnability

Table 1 shows the conductivity of Alg/PEO blends with varying of PEO concentration. It shows that the increasing of PEO concentration in the blends causes the conductivity decrease dramatically. Alg/PEO blends with volume ratio of 1/0 dan 2/1 cannot be detected by the conductivity meter. This is assumed because the solution has a higher conductivity than 1999 $\mu\text{S.cm}^{-1}$ which is the detection limit of the instrument.

Table 1: Conductivity of Alg/PEO blends and observation of nanofiber morphology

Alg/PEO volume ratio	PEO Concentration (% (v/v))	Conductivity ($\mu\text{S.cm}^{-1}$)
1/0	0	---
2/1	33	---
1/1	50	1894
1/2	67	1029
0/1	100	107

Electrospinnability is the ability of a polymer solution to form uniform fibers using the electrospinning method. Initial attempt electrospinning pure alginate nanofibers focused on a solution containing 2 wt% of sodium alginate aqueous solutions. Attempt to electrospinning resulted in beads or droplets but no nanofibers (data not shown). Bonino et al. (2011) [11] also reported a similar result when attempting to electrospinning aqueous alginate solutions. They noted that the strain rate at the transition between the Taylor cone and the jet during the electrospinning process is high. According to Table 1, the conductivity of the alginate solution was too high. It creates the repulsion to reject the charge from solution to collector electric charge [12]. Alg/PEO blends with all ratio concentrations of PEO were observed using an optical microscope to see the formation of electrospun fibers. Figure 3 showed that the amount of electrospun fiber increases with increasing of PEO composition in the blends. It means, the electrospinnability of the blends increases as much as the increase in PEO concentration. With increasing PEO concentration in the blends, the conductivity decrease dramatically (Table 1), indicating that electrospinnability can be risen by decreasing the solution conductivity. This is consistent with the statement of Lu et al. [13] that the conductivity of Alg/PEO solutions

decreases with decreasing proportion of alginate. The presence of PEO help reduces alginate-alginate interactions so that alginate-PEO interaction can be formed. According to Saquing et al. [14], PEO has the ability to coordinate with metal cations such as the sodium cation (Na^+) in sodium alginate. PEO coordinates through the oxygen of the ether group (COC) forming a pseudo-crown ether with Na^+ in the solutions, as shown at Fig. 9 [15].

3.2. The effect of TX on electrospinnability

Table 2 shows the surface tension of Alg/PEO/TX blends with varying of TX concentration. It shows that the increasing of TX concentration in the blends cause the surface tension to decrease significantly.

Table 2: Surface tension of Alg/PEO/TX blends and observation of nanofiber morphology

Alg/PEO ratio	TX concentration (% (v/v))	Surface Tension (dyne.cm ⁻¹)
1/2	0	57.57
1/2	0.5	30.83
1/2	1.0	30.07
1/2	1.5	28.10

The effect of the nonionic surfactant Triton X-100 (TX) on the properties of Alg/PEO blends and the morphology of nanofibers were investigated. Alg/PEO blends with a volume ratio of 1/2 produce beaded fibers (Fig. 6a) after electrospinning. However, the addition of small amounts (0.5 % (v/v)) of TX to the sample generate bead-free fibers (Fig. 6b). This was caused by the surface tension of the solution. Surface tension is an intermolecular force formed by the attraction of molecules in solution. Each molecule is pulled in all directions with neighboring molecules and produces a zero knit force. High surface tension indicates the high tensile strength between molecules in solution. This causes the solution to be difficult to stretch and the tendency of the solution to form rounds (beads) becomes higher. The presence of TX weakens the bonds of polymers that form intramolecular forces so that surface tension decreases [14]. The tendency of molecules in a solution to gather and form a weaker circle, so the possibility of formation of fine fibers is getting higher. The addition of 1.0% and 1.5% of TX also produced a uniform or bead-free fiber, but it wasn't recommended to use by CO_2 adsorbent. The reason is the unfocused nanofiber was collected on the collector surface, therefore a little difficulty to collect the thicker fiber. The increasing of surfactants causes the fibers to formed smoother and thinner. Surface tension of the solution were too low is assumed to cause the use of a 5 kV DC voltage to be too high. Too high electric voltage causes Taylor's cone to be smaller and jet diameter formed smaller and unstable [16].

3.3. Characterization of nanofiber

The result of electrospun Alg/PEO blends in varying concentration of PEO were showed by Fig. 3. Alg/PEO blends with volume ratio of 2/1 and 1/1 produced beads electrospun with formed of a little fibers (Fig. 3b and c). Uniform fibers without beads were produced by PEO solution only (Fig. 3d). Although the Alg/PEO blends at a volume ratio of 1/2 produce beaded nanofibers (Fig. 4a) after electrospinning, the addition of small amounts (0.5% (v/v)) of TX to the blends generate bead-free fibers (Fig. 4b). The addition of 1.0% and 1.5% of TX also produced a uniform or bead-free fiber (Fig. 4c and d), but it wasn't applied as CO_2 adsorbents. The reason is the unfocused nanofiber was collected on the collector surface, therefore a little difficult to collect the thicker fiber.

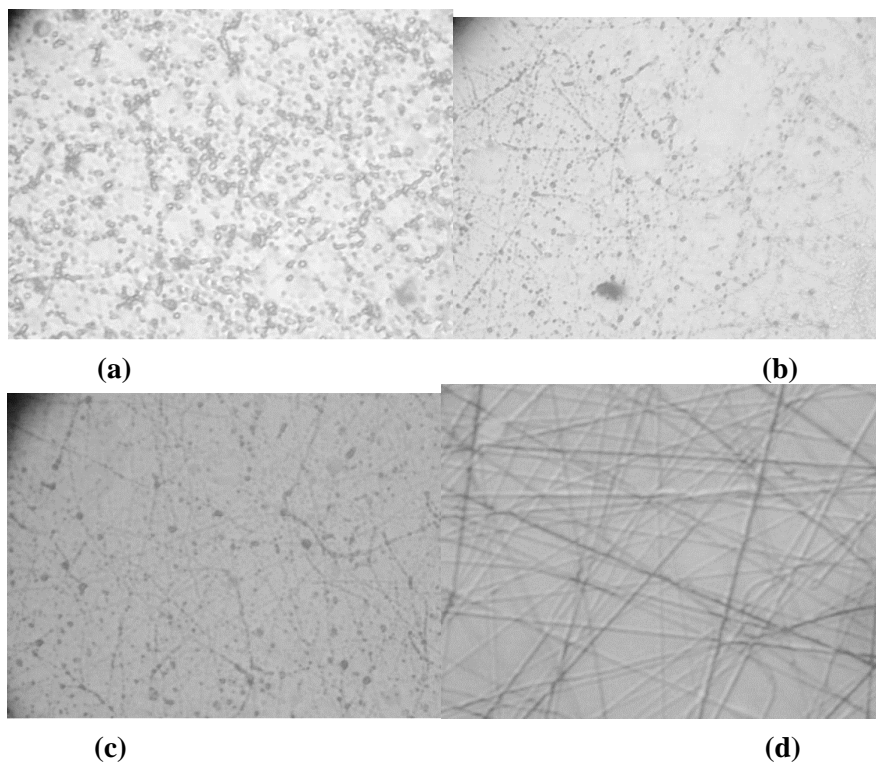


Figure 3: Optical microscopy images of electrospun mats of Alg/PEO blends with different PEO concentration: a) 33% b) 50% c) 67%, and d) 100%

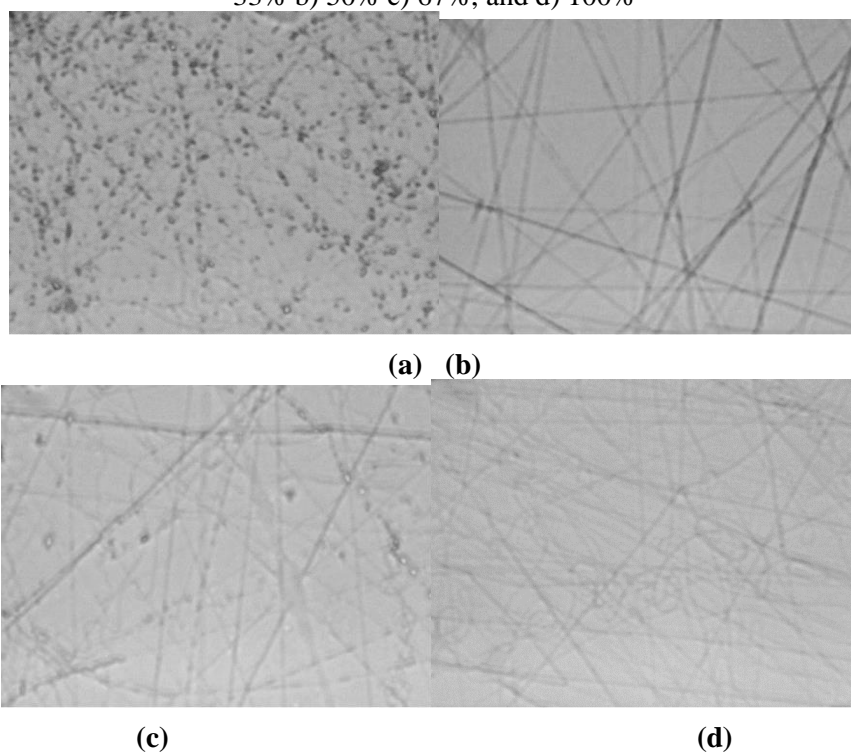


Figure 4: Optical microscopy images of electrospun mats of Alg/PEO (1/2) blends with different TX concentration: a) 0%, b) 0.5%, c) 1.0% and d) 1.5%

3.4. Fourier Transform Infrared

Figure 5 shows the FTIR spectra of Alg/PEO/TX NFs, Alg/PEO NFs, PEO NFs and sodium alginate powder. The characteristic bands for the OH stretching vibration, CO single band vibration, and asymmetric vibration of C=O groups from alginate were observed at 3448, 1033, and 1627 cm^{-1} , respectively. On the other hand, for the PEO, the

band appeared at 2885 cm^{-1} belong to CH band [17]. The bands appeared at 1103 and 840 cm^{-1} were belong to the COC stretching and bending vibration [11,18]. For the Alg/PEO/TX NFs, the presence of OH group at 3410 cm^{-1} and vibrations of C=O groups at 1604 cm^{-1} which were the characteristic of alginate. The vibration produced by the CH group at 2885 cm^{-1} . The vibration of COC band appears at 1103 cm^{-1} for stretching and 840 cm^{-1} for bending which was characteristic absorption of the PEO. FTIR spectra of the Alg/PEO/TX NFs have similar absorption peaks with alginate and PEO.

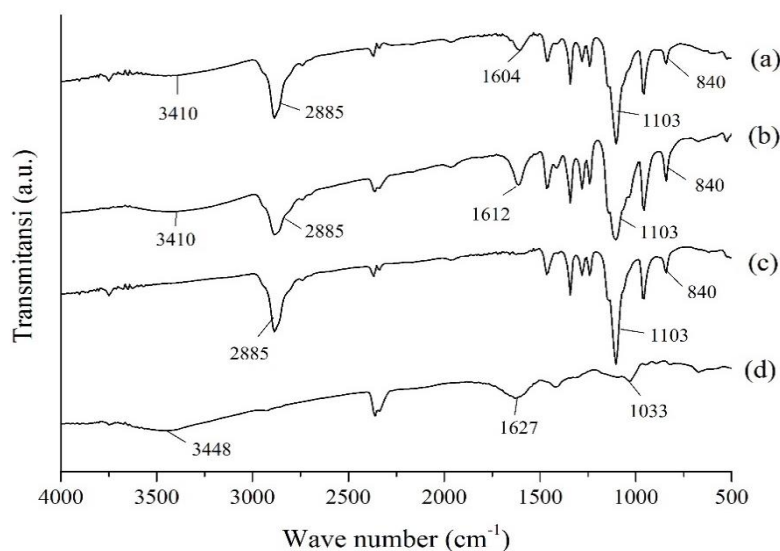
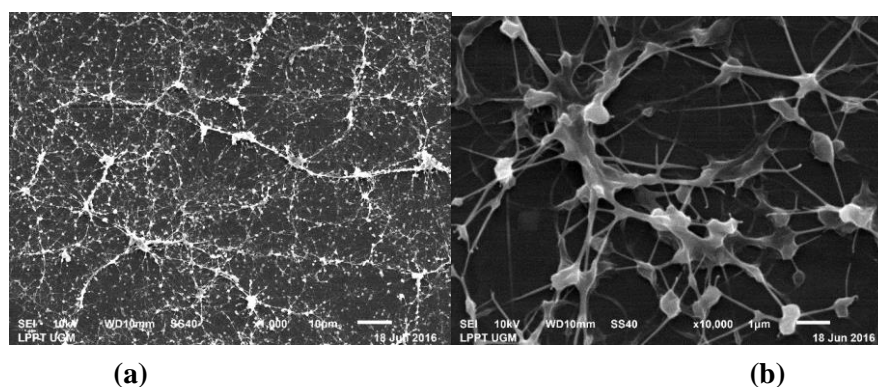


Figure 5: FTIR spectra of (a) Alg/PEO/TX NFs, (b) Alg/PEO NFs, (c) PEO NFs and (d) Na-alginate

3.5. Scanning Electron Microscopy (SEM)

Electrospun nanofibers of Alg/PEO and Alg/PEO/TX blends solution were characterized by SEM to observe the morphology of fiber at the magnification of 1000 and 10000 times. The SEM morphograph were used to determine the diameter of the uniform fibers. Figure 6 shows the beaded-fiber electrospun of Alg/PEO blends solution (a) and the beaded-free fibers of Alg/PEO/TX NFs. The result the mean diameter of Alg/PEO/TX NFs was $201 \pm 48\text{ nm}$. Nanofiber diameter measurements were carried out to prove that the fiber from the electrospinning of Alg/PEO/TX blends solution was a nanofiber.



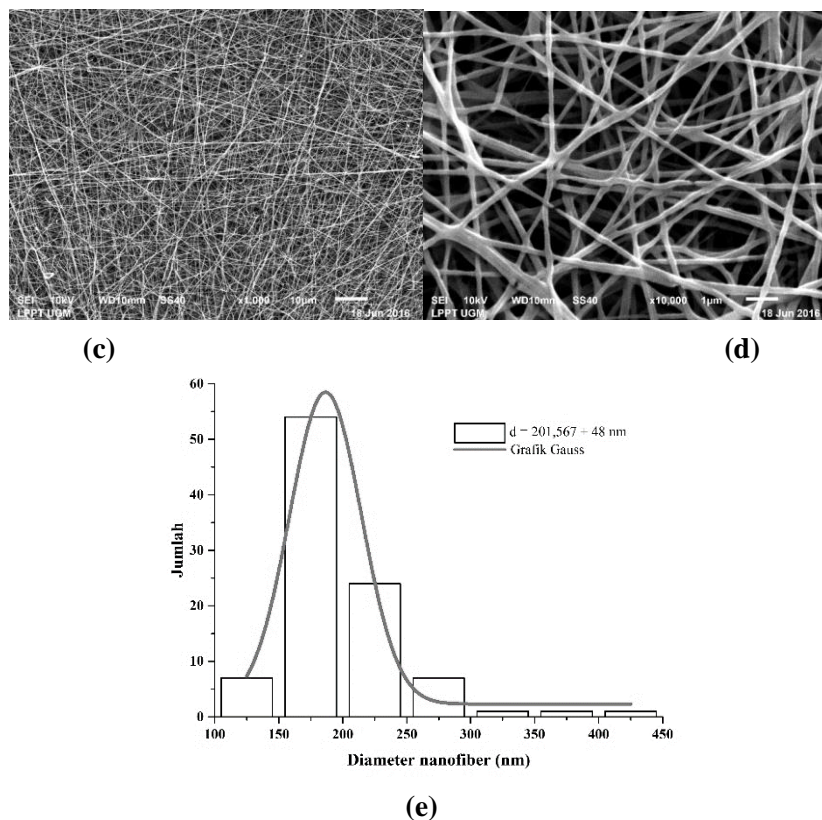


Figure 6: SEM image of electrospun nanofibers from (a) and (b) Alg/PEO blends solution, (c) and (d) Alg/PEO/TX blend solutions and (e) the diameter distribution of Alg/PEO/TX NFs

Characterization results using XRD showed that the compound produced from calcination of chicken eggshells at 900°C for 2.5 hours was CaO. In the diffractogram in Fig. 2, shows that the diffraction pattern of eggshell CaO has 20 peaks which correspond to the character of commercial CaO. The narrow and high intense peaks of the calcinated catalyst show the catalyst crystal structure which consists mainly of active CaO materials. The XRD results are in accordance with the results of research conducted by [15,16] which calcined eggshells at 900°C.

3.6. Surface Area Analysis of nanofiber

The surface area of Alg/PEO/TX NFs was determined by the BET method. The results showed that the Alg/PEO/TX NFs have a surface area of 34.963 m².g⁻¹. This is in accordance with the theory that nanofiber with diameters ranging from 5-500 nm has a surface area of about 10-1,000 m².g⁻¹ [19].

3.7. The effect of flow rate on adsorption capacity

Figure 7 shows a graph of the effect of flow rate on CO₂ adsorption capacity carried out for 20 minutes. Increased adsorption capacity occurs when the flow rate is increased from 6-10 mL.minutes⁻¹. A decrease in CO₂ adsorption capacity by Alg/PEO/TX NFs occurs significantly when the flow rate continues to be increased to 20-40 mL.minutes⁻¹. Thus it can be said that the optimum flow rate of CO₂ is 10 mL.minutes⁻¹ and gives an adsorption capacity value of 8.031 mmol.g⁻¹.

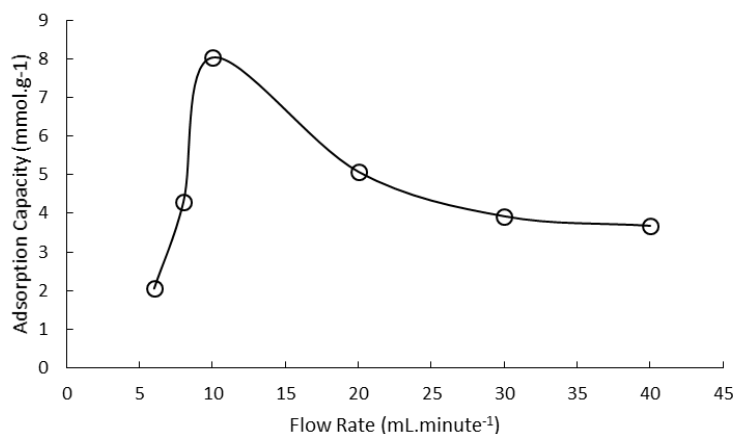


Figure 7: Graph of CO₂ adsorption capacity in Alg/PEO/TX NFs at various of flow rates

The adsorption capacity of CO₂ was increase at the higher of the flow rate is causes the higher the pressure or concentration of CO₂ in the reactor. The interaction is occurs between CO₂ molecules and C=O groups of nanofibers. The more gas feed into the adsorption reactor, the higher the number of gas molecules that interact with the adsorbent [19]. A decrease in CO₂ adsorption capacity by Alg/PEO/TX NFs occurs significantly when the flow rate continues to be increased to 20-40 mL minutes⁻¹. The gas flow rate that is too high causes the interaction of the gas with the adsorbent to decrease because the movement of gas molecules which is too fast reduces the effectiveness of the interaction. It is according to Ahmed at al. that by lowering gas flow rate, the adsorbent had enough time to adsorp the gas perfectly [20].

3.8. Effect of contact time on adsorption capacity

Figure 8 shows that in the first 25 minutes there was a significant increase in adsorption capacity. The optimum adsorption capacity occurs at 25 minutes contact time which is equal to 12.398 mmol.g⁻¹. Adsorption capacity has decreased at 30 minutes contact time.

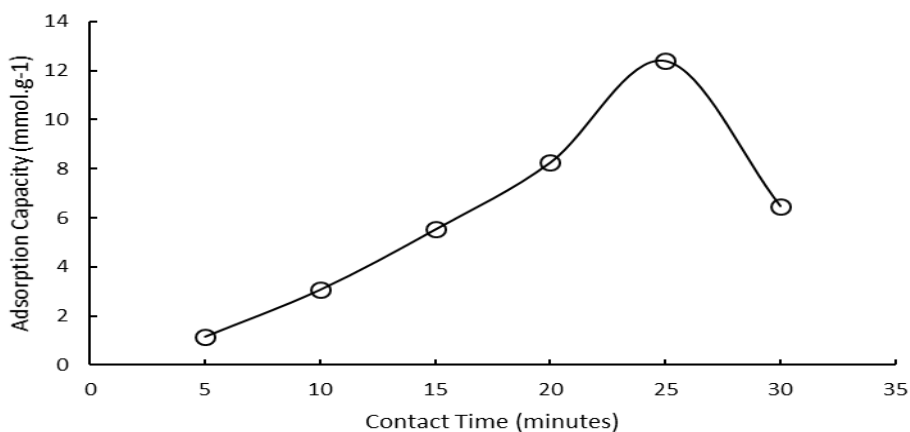


Figure 8: Graph of adsorption capacity of CO₂ in Alg/PEO/TX NFs at various contact time

Increased adsorption capacity occurs because active groups in Alg/PEO/TX NFs are still available. Increased contact time causes interactions between CO₂ and C=O groups on the surface of the Alg/PEO/TX NFs to be more effective. The optimum adsorption capacity means that all C=O groups in Alg/PEO/TX NFs have been bound to CO₂. The

decrease in adsorption capacity was caused by the tendency of CO₂ molecules which bind to the Alg/PEO/TX NFs to be released again after optimum contact time.

3.9. The comparison between Alg/PEO/TX NFs and other alginate nanofibers

Alg/PEO/TX-100 NFs has the advantage of having a CO₂ adsorption capacity that is relatively higher than another alginate-based nanofiber. Table 3 shows the comparison of the adsorption capacity of Alg/PEO/TX-100 NFs with others. However, these nanofibers have a limitation of low tensile strength, that was 0.524 MPa.

Table 3: The adsorption capacity of several kinds of alginate-based nanofiber

Nanofiber	Diameter (nm)	Surface area (m ² /g)	Adsorption Capacity (mmol/gram)	Reference
Alg/PVA	202 ± 43	(not tested)	3.286	[8]
Alg-P PVA	224 ± 53	18.585	6.83	[10]
Alg/PVA/Z	250 ± 60	25.998	10.718	[9]
Alg/PEO/TX	201 ± 57	34.963	12.398	This research

4. Conclusion

The results of this research showed that the addition of synthetic polymer such as PEO solutions and anionic surfactant as Triton X-100 (TX) can overcome the poor of the electrospinnability of Na-alginate. The conductivity and surface tension measurements of the blended solution showed that the Na-alginate solution conductivity and surface tension decreased by increasing the PEO and TX concentration. Alg/PEO/TX solution with a volume ratio of 2/1 (2 % alginate/6 % PEO), and with a small addition of TX (0,5 %) were successfully electrospun with a voltage of 5 kV and tip to collector distances of 13 cm to formed uniform beaded-free fibers. There was the influence of adding PEO and TX to the morphology and electrospinnability of the solution. The higher of PEO and TX concentration increases the electrospinnability of the solution. Alg/PEO/TX NFs with a mean diameter of 201 ± 48 nm have an adsorption capacity of 12,398 mmol.g⁻¹ at the flow rate and contact time optimum of 10 mL.minutes⁻¹ and 25 minutes, respectively. Alg/PEO/TX NFs has a CO₂ adsorption capacity that is relatively higher than another alginate-based nanofiber, but it has a limitation of low tensile strength. Therefore, further research is needed to synthesize Alg/PEO/TX-100 NFs with the addition of certain compounds to increase the tensile strength of nanofiber.

References

- [1] X. Wang, B. Li, *Electrospun Nanofibers Energy Environ. Appl.*, Springer, (2014) 249–263.
- [2] G.S. Callendar, Q. J. R. Meteorol. Soc. 64 (1938) 223–240.
- [3] J.G.J. Oliver, G.J. Maenhout, M. Muntean, J.A.H. Peters, *Trends in Global CO₂ Emissions: 2015 Report*, Netherlands, 2015.
- [4] B. Guo, L. Chang, K. Xie, *J. Nat. Gas Chem.* 15 (2006) 223–229.
- [5] B. Yuan, X. Wu, Y. Chen, J. Huang, H. Luo, S. Deng, *Adsorption of CO₂, CH₄, and N₂ on Ordered Mesoporous Carbon: Approach for Greenhouse Gases Capture and Biogas Upgrading Chemical Engineering Department*, New Mexico State University, Las Cruces, New, (2013).
- [6] R. V Siriwardane, M. Shen, E.P. Fisher, J. Losch, (2005) 1153–1159.
- [7] G. Zhao, B. Aziz, N. Hedin, *Appl. Energy.* 87 (2010) 2907–2913.

- [8] D.. Astuti, Nanofiber Alginat/Poli(vinil alkohol) (PVA) untuk Adsorpsi CO₂, Universitas Gadjah Mada, 2016.
- [9] R. Jonathan, Komposit Nanofiber PVA/Alginat/Zeolit sebagai Adsorben CO₂, Universitas Gadjah Mada, 2016.
- [10] N. Tsurayya, Nanofiber Alginat-Pektin-Polivinil Alkohol sebagai Adsorben CO₂, Universitas Gadjah Mada, 2016.
- [11] C.A. Bonino, M.D. Krebs, C.D. Saquing, S. In, K.L. Shearer, E. Alsberg, S.A. Khan, Carbohydr. Polym. 85 (2011) 111–119.
- [12] A.. Baunsele, Sintesis Nanofiber Polivinil Alkohol/Kitosan/Iota-Karaginan Sebagai Adsorben Pb(II) dan Cu(II), Universitas Gadjah Mada, 2015.
- [13] C.D. Saquing, C. Tang, B. Monian, C.A. Bonino, J.L. Manasco, E. Alsberg, S.A. Khan, Ind. Eng. Chem. Res. 52 (2013) 8692–8704.
- [14] T. Terashima, M. Kawabe, Y. Miyabara, H. Yoda, M. Sawamoto, Nat. Commun. 4 (2013) 1–9.
- [15] C.J. Angammana, A Study of the Effects of Solution and Process Parameters on the Electrospinning Process and Nanofibre Morphology, (2011).
- [16] A. Buasri, V. Loryuenyong, Mater. Today Proc. 4 (2017) 6051–6059. doi:10.1016/j.matpr.2017.06.093.
- [17] N.P. Asri, B. Podjojono, R. Fujiani, Nuraini, IOP Conf. Ser. Earth Environ. Sci. 67 (2017) 1–7.
- [18] F.K. Ko, Y. Wan, Introduction to nanofiber materials, Cambridge University Press, 2014.
- [19] E. Apriyanti, Adsorpsi CO₂ menggunakan Zeolit Sintetis 4A: Aplikasi pada Pemurnian Produk Biogas, (2011).
- [20] M.I. Alhamid, M.B. Perdana, Int. J. Technol. 6 (2015) 584–593.