JURNAL INTEGRASI PROSES

Website: http://jurnal.untirta.ac.id/index.php/jip

***Submitted : 10 Juni 2022*** ***Revised : 27 Oktober 2022*** ***Accepted : 30 November 2022***

# NANO CARBON SYNTHESIS FROM MICROALGAE *CHLORELLA VULGARIS* AS PRECURSOR OF SOLID PHASE CARBON

**Alexander William Prijadi, Arenst Andreas Arie*, Budi Husodo Bisowarno**
Department of Chemical Engineering, Faculty of Industrial Technology,
Parahyangan Catholic University, Ciumbuleuit 94, West Java, Indonesia 40141
*Email: arenst@unpar.ac.id

**Abstract**

Nanocarbon is a nanometer-scale substance made entirely of carbon atoms. Generally, the synthesis of nanocarbon is usually conducted using a gas-phase carbon raw material which is toxic. Therefore, the use of solid-phase carbon raw material to synthesize nanocarbon started to develop. In this research, nanocarbon will be synthesized using variations of solid-phase carbon raw material derived from a novel carbon precursor, microalgae *Chlorella vulgaris*. Nanocarbons produced were analyzed using SEM, XRD, and TEM. SEM analysis did not show the nanocarbon formed. However, this may be due to the nanocarbon being very small. To ensure whether nanocarbon is formed or not, XRD analysis is conducted. XRD analysis shows the possibility of forming carbon nanotubes from the sample with activated carbon as a raw material. There were peaks at diffraction angles of 24–26° and 42–43,5°, which indicated carbon nanotubes. In addition, the dc value of this sample has a value like carbon nanotubes, which is 0.344 nm. In contrast, the other two samples, which used hydrochar and microalgae as raw materials, only indicated activated carbon after the synthesis. The TEM analysis supported by XRD analysis for a sample with activated carbon as a raw material showed the presence of carbon nanotubes. This is indicated by their rope-like morphology, which is not visible in SEM analysis due to their tiny size. At the same time, the other two samples did not show any morphology indicating the presence of nanocarbon. So, it can be concluded that the synthesis of nano carbon has been successfully carried out using activated carbon as raw material and produces nano carbon with the type of carbon nanotubes.

**Keywords***:* Nanocarbon, Carbon Nanotubes, Activated Carbon, Hydrochar, *Chlorella vulgaris*

## 1. INTRODUCTION

Carbon is one of the most abundant materials in this world. Carbon has many allotropes including diamond, graphite, and nanocarbon (Krueger, 2010; Peterson et al., 2008; Pierson, 1994; Saifuddin & Juniazah, 2013). Nanocarbon is an allotrope of carbon that is generally divided into two types, namely carbon nanosphere and carbon nanotubes.

Carbon nanotubes are one of the artificial allotropes of carbon with $sp^2$ hybridization bonds in the form of long cylinders with nano size. This long cylinder is formed from a graphene layer that is made circular. This allotrope was first discovered by Sumio Iijima in 1991 and is currently being researched because it has excellent thermal (thermal conductivity = 6000 W/m.K) and mechanical characteristics (modulus of elasticity = 1054 – 1200 GPa; tensile strength = 75 – 150 GPa). In addition, nanocarbon also has good electrical properties even though carbon itself is not a good electrical conductor (carbon nanotubes electrical conductivity = $10^6$ – $10^7$ S/m) and can be compared to copper (copper electrical conductivity = 5,96 × $10^7$) (Meguid and Weng 2017; Meyyappan 2005; Pitroda 2016; Xiao, Huang, and Li 2017). These excellent properties will certainly cause nanocarbon to be used in various fields, such as drug carriers, antioxidants, sensors, electrodes, fuel cells, and composite materials (Han & Fina, 2011; Liu et al., 2015; Xiao et al., 2017).

Carbon nanotubes themselves are generally synthesized by a chemical vapor deposition process from gas-phase carbon precursors with the help of a ferrocene catalyst and substrate (Lim et al., 2017). The catalyst used will be heated until it melts and sticks to the substrate. The gas phase carbon will then dissolve into the catalyst which will reach its saturation point. When the carbon reaches its saturation point, adding more carbon will grow carbon nanotubes with 2 possibilities shown in Figure 1 below. It should be emphasized that until now the mechanism for the formation of carbon nanotubes is still a hypothetical process (Kumar 2011).

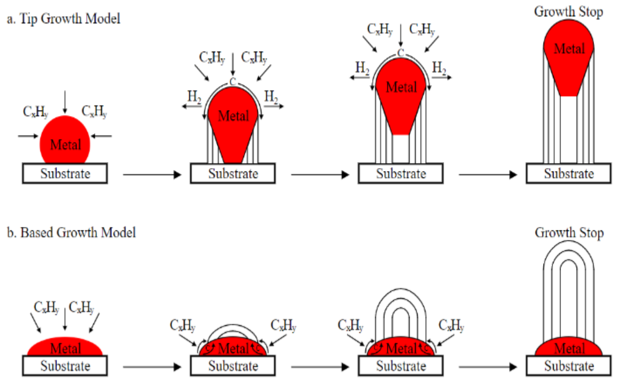


**Figure 1.** Carbon nanotubes growth mechanism

However, the use of raw materials in the gas phase has several drawbacks, such as storage which is toxic raw material. The synthesis of nanocarbon can be done with solid-phase precursors. This process is called solid-phase pyrolysis. Not much information is known about this process. However, the synthesis of carbon nanotubes was successfully carried out using activated carbon or hydrochar as a carbon precursor derived from biomass with the help of ferrocene and nickel nitrate catalyst (Fathy, 2017; Lotfy et al., 2018; Osman et al., 2019).

The manufacture of activated carbon itself initially used coal as its raw material. However, coal is a non-renewable energy source. Therefore, activated carbon synthesis has begun to be developed from raw materials other than coal, namely biomass such as wood, rice husks, coconut shells, and others (Lempang, 2014). However, biomass utilization on an industrial scale will not necessarily be stable because its production depends on the weather. Another alternative that can be used and does not depend on the weather for its production is microalgae (Alam et al., 2015; Lee et al., 2017; Sukoyo et al., 2019). The most common way to synthesize activated carbon from microalgae is hydrothermal carbonization with chemical activation (Heilmann et al., 2010).

Previous research successfully synthesized carbon nanotubes with 2nd generation biomass as carbon precursors, such as potato peel waste and rice straw residue. In this research, carbon nanotubes will be synthesized with 3rd generation biomass as carbon precursor, which is microalgae *Chlorella vulgaris* with the help of ferrocene and nickel nitrate as the catalyst. Microalgae as carbon precursors will be processed with hydrothermal carbonization to form hydrochar and the activation step to form activated carbon to variates the form of raw material used in carbon nanotubes synthesis. In this paper, the term raw material will mean the solid phase form which was mixed with a catalyst and processed for the synthesis of carbon nanotubes (microalgae, hydrochar, activated carbon), while the term carbon precursor will mean the carbon source used (microalgae *Chlorella Vulgaris*). This research was focus on studying the effect of variations in the raw materials used for the synthesis of carbon nanotubes on the nanocarbon products that will be produced. The novelty of this research was focus on the use of the microalgae *Chlorella vulgaris* as a carbon precursor in the synthesis of solid-phase carbon nanotubes that have never been used before. In addition, variations of microalgae that was directly synthesized into carbon nanotubes have also never been tried before.

## 2. MATERIALS AND METHOD

### 2.1 Raw Material

The microalgae *Chlorella vulgaris* was obtained from Syah.home, Tangerang, Banten, Indonesia. Initially the microalgae were dried in an oven at a temperature of 110ºC for 1 hour. Pottasium hydroxide (KOH) (p.a., solid 85%) were obtained from CV Mekar Pancaraya (Indonesia). Nickel nitrate ($NiNO_3$) (99%) used were obtained from PT Smart Lab Indonesia (Indonesia). Ferrocene ($Fe(C_5H_5)_2$) (98%) used was obtained from Sigma Aldrich (USA).

### 2.2 Hydrothermal Carbonization

Hydrothermal carbonization was carried out in a 100 ml of teflon autoclave. Microalgae that had been dried were put into an autoclave and then 80 mL of distilled water was added. The autoclave was then heated to 200°C for 24 hours. Afterwards the autoclave was cooled to room temperature and the solid product was filtered by Buchner funnel. The solids obtained then washed by ethanol and distilled water to remove the impurities. Then the solid product was dried in an oven at a temperature of 110°C for 24 hours so that hydrochar was obtained (Prijadi, 2020).

### 2.3 Chemical Activation

Hydrochar was then impregnated with KOH solution in a ratio of 1:4 (hydrochar:KOH) for 24 hours while stirring. The solution was then dried in the oven for 24 hours at a temperature of 110°C. The mixture was then heated in a tubular furnace at a temperature of 800°C for 1 hour with nitrogen gas flowing. Afterwards the furnace was cooled to room temperature and the remaining solids was washed with HCl and distilled water (Prijadi 2020). The washed solids were then filtered and dried in an oven at a temperature of 110°C for 24 hours to obtain activated carbon.

### 2.4 Nanocarbon Synthesis

The synthesis of nanocarbon were carried out with 3 variations of raw materials, namely microalgae, hydrochar, and activated carbon. The raw materials were mixed with a mixture of ferrocene and nickel nitrate catalysts with variations of 10:1, 10:2, and 10:4. Then the mixture was put into the furnace with nitrogen flowing and the temperature was raised to 300°C for 10 minutes. Then the temperature of the furnace was raised to 830°C without nitrogen flowing for 1 hour. Afterwards the furnace was cooled to room temperature and the residual solids of the furnace were took and washed using a solution of $HNO_3$, $H_2SO_4$, and hot distilled water (Lotfy, Fathy, and Basta 2018). The washed solid was then dried in an oven at a temperature of 110°C for 24 hours so that nanocarbon was obtained.

### 2.5 Characterization

There were 3 samples that were analyzed, namely nanocarbon which was synthesized from activated carbon, hydrochar, and microalgae. The three samples were analyzed using SEM, XRD, and TEM. SEM and TEM analysis were used to see the morphology of the sample. While XRD analysis will be used to determine and ascertain what compounds are formed in the resulting nanocarbon sample, as well as determine the interlayer spacing of the resulting sample.

## 3. RESULT AND DISCUSSION

Microalgae *Chlorella Vulgaris* processed with hydrothermal carbonization will produce hydrochar by hydrolyzing compounds that exist in microalgae, namely hemicellulose, protein, and lignin (Leng et al. 2021). This process will produce carbon compounds that have graphene groups such as activated carbon, but the hydrochar formed generally still has impurities such as tar (Marsh and Rodríguez-Reinoso 2006; Pierson 1994). These impurities will be removed using an activation process using KOH which will produce activated carbon. Microalgae, hydrochar, and activated carbon that formed then will be mixed with catalyst and synthesized to form nanocarbon (Marsh and Rodríguez-Reinoso 2006). As previously explained, the mechanism for synthesizing nanocarbon using solid-phase raw materials is still unknown. However, looking at the approach to the synthesis of nanocarbon using gas-phase raw materials, the carbon used needs to be dissolved into the catalyst used past its saturation limit (Kumar 2011). In addition, it is not known whether there is an impact if there are other compounds other than carbon dissolved into the catalyst used.

### 3.1 SEM Analysis

Figure 2 shows the results of the SEM analysis of carbon nanocomposites formed from activated carbon, hydrochar, and microalgae. The results of the SEM analysis of nanocarbon should describe a morphology that resembles a long thread/string (Lotfy, Fathy, and Basta 2018; Osman et al. 2019). However, from the results, all three samples do not represent nanocarbon. The results of the SEM analysis showed the morphology of the porous carbon material. The only visible difference is that the composite material produced from activated carbon has more pores. However, before drawing the conclusion that nanocarbon are not formed, another analysis will be carried out first.

### 3.2 XRD Analysis

The results of the XRD analysis are shown in Figure 3 with the help of the Origin application. In the three XRD results below, the three samples both have peaks at diffraction angles of 24 – 26° which indicate the presence of graphene compounds (Deck and Vecchio 2006). This peak with a peak at a diffraction angle of 44 – 44.5° is generally found in activated carbon materials, namely activated carbon (Kristianto et al. 2015). From this analysis, it can be concluded that the synthesis of nanocarbon from hydrochar and microalgae resulting activated carbon. However, the nanocarbon produced from activated carbon raw material has a peak at a diffraction angle of 42 – 43.5° which indicates the presence of carbon nanotubes (Osman et al. 2019; Selen et al. 2016). This indicates the possibility of carbon nanotubes formed on nanocarbon derived from activated carbon.

In addition, when compared to nanocarbon derived from hydrochar and microalgae raw material, there are other peaks appear, such as at the diffraction angles of 30°, 35°, 57°, and 63°. The three peaks generally appear in $FeO_3$ compounds (Kristianto et al. 2015). So that it can be seen that in the nanocarbon sample made from activated carbon, Fe compounds derived from ferrocene are remaining in the sample which usually found in carbon nanotubes sample that using ferrocene as catalyst (Osman et al. 2019).

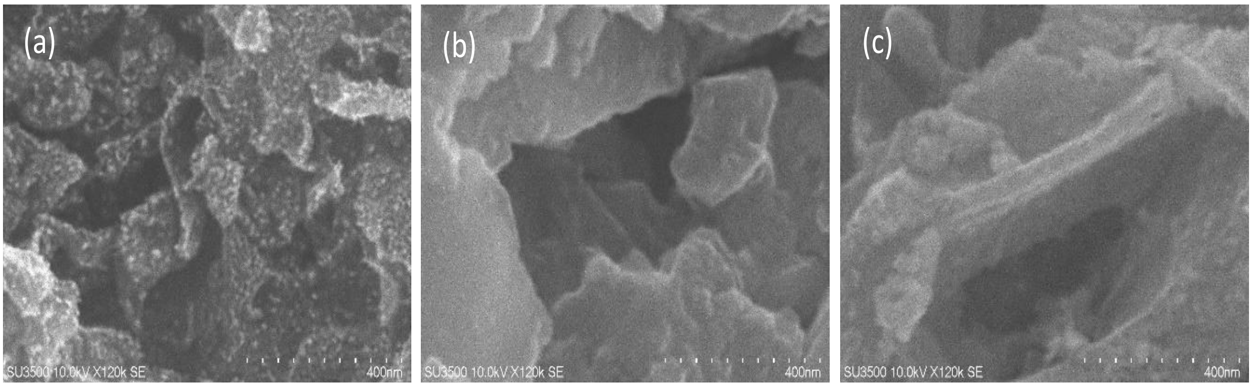


**Figure 2.** SEM analysis of nanocarbon with (a) Activated carbon, (b) Hydrochar, and (c) Microalgae as a raw material

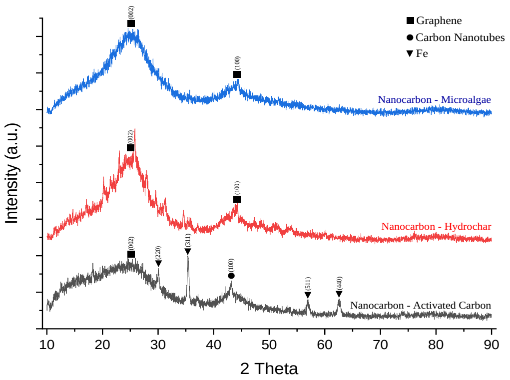


**Figure 3.** XRD analysis of nanocarbon with (a) Activated carbon, (b) Hydrochar, and (c) Microalgae as a raw material

In addition, the results of the XRD analysis can be seen from the results of the XRD analysis of the interlayer spacing for carbon compounds. The interlayer spacing will be calculated using Bragg's law below (Khosravi, Bashirpour, and Nematpour 2014):

$$d_{hkl} = \frac{\lambda}{2\sin\theta_{hkl}}, hkl = (002)\ or\ (100) \qquad (1)$$

with:
$\lambda$ = X-ray wavelength (0.15406 nm)
$\theta$ = Bragg angle at the diffraction peak
$d_{(002)} = d_c$ = intercrystallite and micro crystallite distance (nm)
$d_{(100)} = d_a$ = starling interlayer (nm)

The results of these calculations can be seen in Table 1. From the dc results that have been obtained, there are different values for nanocarbon derived from microalgae and hydrochar, with nanocarbon derived from activated carbon. The $d_a$ value of the three resulting samples, all three have relatively the same value. The $d_a$ values of activated carbon and carbon nanotubes do have relatively the same values, namely 0.215 nm and 0.213 nm, so it will be difficult to determine the difference both of them using $d_a$ (Saito et al. 1993; Xie et al. 2014). In contrast to the $d_a$ value, the $d_c$ value of the nanocarbon from activated carbon was slightly lower than the other. Activated carbon material and carbon nanotubes have different $d_c$ values, namely 0.3646 nm and 0.344 nm (Jiang et al. 2008; Saito et al. 1993), thus strengthening the possibility of the presence of carbon nanotubes in nanocarbon derived from activated carbon.

**Table 1.** Bragg calculation on XRD analysis

| Parameter | Nanocarbon Raw Material | | |
|---|---|---|---|
| | Microalgae | Hydrochar | Activated Carbon |
| $\theta_{002}$ | 24.60° | 24.27° | 25.91° |
| $d_c$ | 0.364 nm | 0.366 nm | 0.344 nm |
| $\theta_{100}$ | 44.45° | 44.24° | 43.16° |
| $d_a$ | 0.204 nm | 0.205 nm | 0.209 nm |

### 3.3 TEM Analysis

To ensure the presence or absence of carbon nanotubes and to better analyze the morphology of the formed samples, an analysis using TEM was carried out. The results of the TEM analysis for samples of carbon nanotubes should have a morphology in the form of long threads/strings (Lotfy, Fathy, and Basta 2018). The results of the analysis of the formed nanocarbon can be seen in Figure 4 below. From the results obtained, the samples produced from hydrochar and microalgae raw materials did not show the presence of carbon nanotubes, which is confirmed by SEM and XRD analysis before. However, the nanocarbon sample formed from activated carbon raw material has a morphological shape like thread/rope which indicates the presence of carbon nanotubes compounds. This shows that the synthesis of nanocarbon with activated carbon as raw material formed from the precursor of the microalgae *Chlorella vulgaris* has been successfully carried out and resulting in nanocarbon in the form of carbon nanotubes.

One of the things that support the formation of carbon nanotubes from activated carbon raw material is that activated carbon has a graphene layer that has been cleaned of impurities (Prasek et al. 2011). As previously explained, the synthesis of carbon nanotubes requires carbon to dissolve into the catalyst until it is saturated. Then the addition of carbon into the catalyst will grow carbon nanotubes (Kumar 2011). In the case of the synthesis of solid-phase carbon nanotubes, the presence of a graphene layer can help the formation of carbon nanotubes. Although there is no definite explanation, this may be because the carbon nanotubes themselves are formed from a circular layer of graphene.

When compared to activated carbon and hydrochar, both compounds have a graphene layer, so these two raw materials have the potential to produce carbon nanotubes. However, hydrochar has a lot of

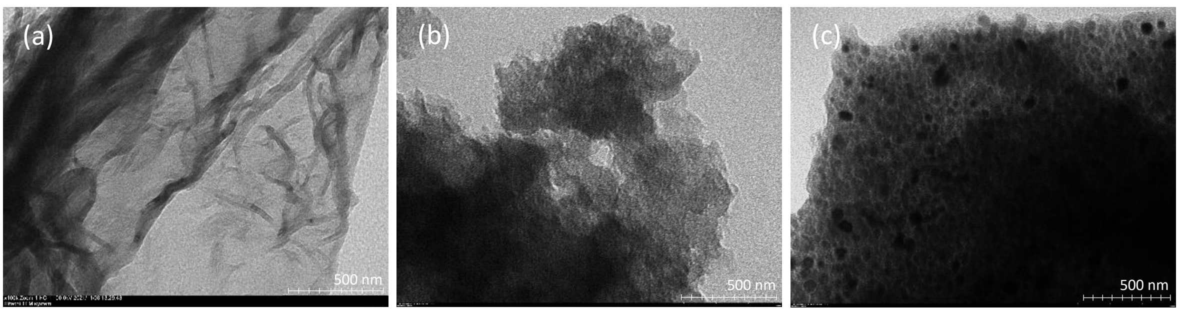


**Figure 3.** TEM analysis of carbon nanotubes with (a) Activated carbon, (b) Hydrochar, and (c) Microalgae as a raw material

impurities resulting from the hydrothermal process, namely tar (Pierson 1994). These impurities may interfere with the synthesis process of carbon nanotubes, especially in the part of dissolving carbon into the catalyst. In addition to the impurity factor, there is also a factor in the amount of carbon present, which can dissolve into the catalyst. As previously explained, the synthesis of carbon nanotubes requires the carbon raw materials used to completely dissolve in the catalyst first and then grow. When compared to activated carbon that has been cleaned, of course, the carbon contained in the hydrochar is less, making it difficult to saturate the catalyst (Pitroda 2016).

For microalgae raw materials, the failure to form carbon nanotubes is thought to be caused by microalgae having complex constituent compounds such as hemicellulose, protein, and lignin (Leng et al. 2021). The presence of these compounds that have not been broken down can make it difficult to dissolve the element carbon into the catalyst. In addition, microalgae also do not have a graphene layer that supports the formation of carbon nanotubes.

## 4. CONCLUSION

This research shows that the synthesis of nanocarbon with activated carbon has been successfully carried out. The activated carbon used was made from the microalgae *Chlorella vulgaris* which was hydrothermally and chemically activated using KOH. The nanocarbon produced has been confirmed as carbon nanotubes from peaks in XRD, with dc and da values of 0.344 and 0.209 nm, as well as morphology such as long strings/threads on TEM analysis, while nanocarbon synthesized from hydrochar and microalgae resulting activated carbon. It concludes that the most successful raw material for nanocarbon synthesis is activated carbon. This success is due to the graphene layer on activated carbon which is quite pure due to the activation step. The raw materials for the synthesis of hydrochar and microalgae in this study did not produce nanocarbon due to the presence of less graphene layer and impurities. For future research, the nanocarbon can be directly synthesized from hydrochar which is given an activator to inhibit the formation of tar in the hydrothermal process instead of activated carbon for shorter syntehsis step.

## 5. REFERENCES

Deck, C. P., & Vecchio, K. (2006). Prediction of Carbon Nanotube Growth Success by the Analysis of Carbon-Catalyst Binary Phase Diagrams. Carbon, 44(2), 267–275. https://doi.org/10.1016/j.carbon.2005.07.023

Jiang, B., Zhang, Y., Zhou, J., Zhang, K., & Chen, S. (2008). Effects of Chemical Modification of Petroleum Cokes on The Properties of The Resulting Activated Carbon. Fuel, 87(10–11), 1844–1848. https://doi.org/10.1016/j.fuel.2007.11.010

Khosravi, M., Bashirpour, N., & Nematpour, F. (2014). Synthesis of Hard Carbon as Anode Material for Lithium Ion Battery. Advanced Materials Research, 829(November 2013), 922–926. https://doi.org/10.4028/www.scientific.net/AMR.829.922

Kristianto, H., Putra, C. D., Arie, A. A., Halim, M., & Lee, J. K. (2015). Synthesis and Characterization of Carbon Nanospheres Using Cooking Palm Oil as Natural Precursors onto Activated Carbon Support. Procedia Chemistry, 16, 328–333. https://doi.org/10.1016/j.proche.2015.12.060

Kumar, M. (2011). Carbon Nanotube Synthesis and Growth Mechanism. Carbon Nanotubes - Synthesis, Characterization, Applications, Cvd. https://doi.org/10.5772/19331

Leng, L., Yang, L., Leng, S., Zhang, W., Zhou, Y., Peng, H., Li, H., Hu, Y., Jiang, S., & Li, H. (2021). A Review on Nitrogen Transformation in Hydrochar During Hydrothermal Carbonization of Biomass Containing Nitrogen. Science of the Total Environment, 756, 143679. https://doi.org/10.1016/j.scitotenv.2020.143679

Lotfy, V. F., Fathy, N. A., & Basta, A. H. (2018). Novel Approach for Synthesizing Different Shapes of Carbon Nanotubes from Rice Straw Residue. Journal of Environmental Chemical Engineering, 6(5), 6263–6274. https://doi.org/10.1016/j.jece.2018.09.055

Marsh, H., & Rodríguez-Reinoso, F. (2006). Characterization of Activated Carbon. In Activated Carbon. https://doi.org/10.1016/b978-008044463-5/50018-2

Meguid, S. A., & Weng, G. J. (2017). Micromechanics and Nanomechanics of Composite Solids. In Micromechanics and Nanomechanics of Composite Solids. https://doi.org/10.1007/978-3-319-52794-9

Meyyappan, M. (2005). Carbon Nanotubes Science and Applications. In New York.

Osman, A. I., Blewitt, J., Abu-Dahrieh, J. K., Farrell, C., Al-Muhtaseb, A. H., Harrison, J., & Rooney, D. W. (2019). Production and Characterisation of Activated Carbon and Carbon Nanotubes from Potato Peel Waste and Their Application in Heavy Metal Removal. Environmental Science and Pollution Research, 26(36), 37228–37241. https://doi.org/10.1007/s11356-019-06594-w

Pierson, H. (1994). Handbook of Carbon, Graphite, Diamond and Fullerenes. Noyes Publications, 262–264. https://books.google.com/books?hl=en&lr=&id=Ub-GAAAAQBAJ&oi=fnd&pg=PP1&dq=1.%09Pierson,+H.+O.+(2012).+Handbook+of+carbon,+graphite,+diamonds+and+fullerenes:++++processing,+properties+and+applications.+William+Andrew.&ots=FE_uLUho9d&sig=t1uEbBfOu-2Dqwj4u9n

Pitroda, J. (2016). A Critical Review on Carbon Nanotubes. International Journal of Constructive Research in Civil Engineering, 2(5), 36–42. https://doi.org/10.20431/2454-8693.0205007

Prasek, J., Drbohlavova, J., Chomoucka, J., Hubalek, J., Jasek, O., Adam, V., & Kizek, R. (2011). Methods for

Carbon Nanotubes Synthesis - Review. Journal of Materials Chemistry, 21(40), 15872–15884. https://doi.org/10.1039/c1jm12254a

Prijadi, A. W. (2020). Sintesis Komposit Karbon Sulfur dari Limbah Kulit Bawang Bombay. http://repository.unpar.ac.id/handle/123456789/10981

Saito, Y., Yoshikawa, T., Bandow, S., Tomita, M., & Hayashi, T. (1993). Interlayer Spacings in Carbon Nanotubes. Physical Review B, 48(3), 1907–1909. https://doi.org/10.1103/PhysRevB.48.1907

Selen, V., Güler, Ö., Özer, D., & Evin, E. (2016). Synthesized Multi-Walled Carbon Nanotubes as a Potential Adsorbent for the Removal of Methylene Blue Dye: Kinetics, Isotherms, and Thermodynamics. Desalination and Water Treatment, 57(19), 8826–8838. https://doi.org/10.1080/19443994.2015.1025851

Xiao, S. X., Huang, C. S., & Li, Y. L. (2017). Carbon Materials. In Modern Inorganic Synthetic Chemistry: Second Edition. https://doi.org/10.1016/B978-0-444-63591-4.00016-1

Xie, Z., Guan, W., Ji, F., Song, Z., & Zhao, Y. (2014). Production of Biologically Activated Carbon from Orange Peel and Landfill Leachate Subsequent Treatment Technology. Journal of Chemistry, 2014(6). https://doi.org/10.1155/2014/491912