Nanodots from Palm Kernel Cake

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Abstract. Palm kernel cake (PKC) is the remaining of a palm (*Elaeis guineensis*) kernel after its oil is separated. Oversupply of this biomass could become an environmental problem. Meanwhile, its moist property makes it suitable for a hydrothermal carbonization to afford added values for the biomass and overcome its potential environmental problem. From the hydrothermal processes of PKC with aquadest and nanobubbled water at 200 ºC for 6 hours, nanodots with the size around 50 nm were obtained. The nanodots may be decorated with amides on their surface. Upon illumination by an ultra-violet A wave (350 nm), the nanodots emitted lights with a maximum around blue region (450 nm). No significant differences were found between the nanodots from the hydrothermal carbonizations of PKC with aquadest and the ones from the hydrothermal carbonizations of the biomass with nanobubbled water. The fluorescence property of nanodots from PKC opens up the possibility for these carbon materials to be applied in agriculture. To the best of our knowledge, this kind of research has never been reported before.

1 Introduction

Our country, Indonesia, is home to the largest palm oil industries in the world [1]. In our palm oil industries, the oil is still obtained by mechanically pressing two parts of oil palm fruits (*Elaeis guineensis*): their flesh and their kernel. After the oil is separated from the kernel, what remains is called palm kernel cake (PKC) [2]. Its crude protein content is between 14 – 20%, while its crude fiber content is between 12 – 25%, that it has been utilized as a component of feed for ruminants [3]. However, oversupply of this biomass could become an environmental problem.

During the mechanical pressing of palm kernel, the oil is not completely separated from the kernel. Therefore, PKC is still moist afterwards. This property makes PKC suitable for a hydrothermal carbonization. This process usually involves submersion of a carbon-rich biomass in water in a closed reactor, which is followed by heating the reactor in an oven at 180 – 250 ºC for 0.5 – 10 hours [4]. In this process, heat and water vapor will jointly break the overall molecular structures of the biomass, and turn the biomass into carbon materials.

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According to Ang and colleagues (2020) [5], hydrothermal treatment of palm kernel shell (PKS) could turn some of the biomass into carbon dots. Carbon dots are carbon materials, with sphere sizes of ≤ 10 nm, which can emit visible light waves upon illumination by an ultraviolet or a shorter visible light wave [6]. The emitted visible light waves are related to functional groups which decorate the surface of the carbon dots. The size and fluorescence of carbon dots make them attractive as absorbents and photon-transfer materials. Taking the discovery by Ang and colleagues into account, we hypothesized that hydrothermal carbonization of PKC would turn the biomass into fluorescent spherical carbon materials as well, although their sizes may not be ≤ 10 nm.

In this research, PKC was subjected into a laboratory-scale hydrothermal carbonization to afford added values for the biomass and overcome its potential environmental problem. Two factors were varied in this process: solvent and temperature. Firstly, for the submersion of the biomass, nanobubbled water was utilized as a comparison to aquadest. The nanobubbles were expected to add pressures to the biomass and help breaking its molecular structures. Secondly, the process temperature was varied from 160 to 200 ºC to give understanding of the effect of temperature to this process. To the best of our knowledge, this kind of research has never been reported before.

2 Materials and Methods

PKC was purchased as powder from Tokopedia (https://www.tokopedia.com/). Nanobubbled water was generated by dissolving ambient air into aquadest according to the method which had been described by Alam and colleagues (2022) [7], until their density was ≥ 100 per mL. At that time, the average size of the bubbles was less than 100 nm, while their average zeta potential was around -20 mV. The nanobubbled water was used for this research within 5 months after its generation.

To afford a hydrothermal carbonization, 5 g of the PKC powder was submerged into 50 mL of aquadest in a 100 mL teflon reactor. A mixture of 5 g of the powder in 50 mL of the nanobubbled water in another 100 mL Teflon reactor was provided as a comparison. Both mixtures were heated at 200 ºC for 6 hours using the same oven. The same couple of mixtures was provided twice more. The first couple of mixture was heated at 180 ºC, while the other one was heated at 160 ºC, for the same amount of time using the same oven. Afterwards, each mixture was filtered, and the filtrates were provided for characterizations.

Ultra-violet and visible light (200 – 600 nm) absorption of all filtrates was measured. Filtrates from the hydrothermal processes at 200 ºC were selected to be characterized by infra-red spectrophotometer and transmission electron microscope. Afterwards, all filtrates were illuminated by ultra-violet A wave (350 nm), upon which their light emissions were measured and photographed.

3 Results and Discussion

Filtrates from all the above hydrothermal processes appeared as dark colloids. Ultra violet and visible light absorption spectra of the colloids (**Fig. 1**) show that the expected carbonization of PKC may have taken place. With the increase of the hydrothermal process temperature, more molecular structures of PKC may have been broken, and therefore less amount of ultra-violet and visible waves was absorbed by the product. In this research, the hydrothermal carbonization seems to work the best at 200 ºC.

The ultra violet and visible light absorption spectra of the colloids (**Fig. 1**) consistently show absorption of 200 – 500 nm waves with maxima around 225 and 275 nm. A maximum absorption at these wavelengths is usually caused by an electronic transition from $\pi \rightarrow \pi^*$, which is typical for a conjugated carbonyl group. Therefore, the molecules of the colloids may possess conjugated carbonyl groups.

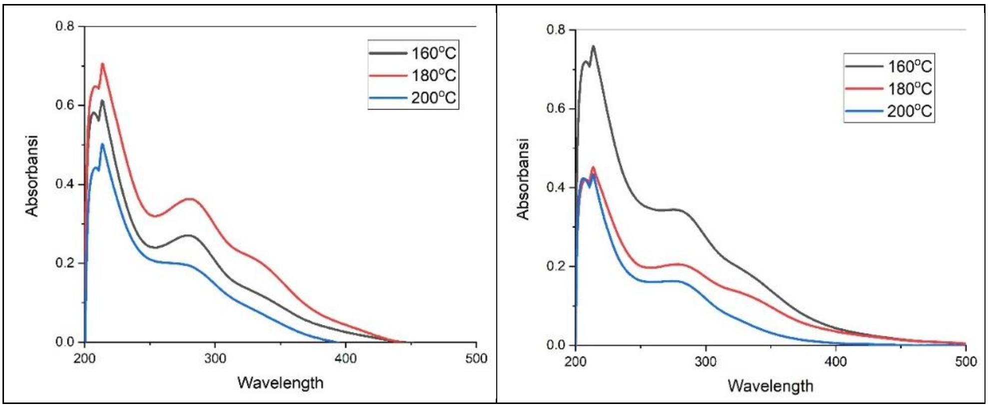

Fig. 1. Ultra violet and visible light absorption spectra of the colloids from the hydrothermal processes at 160, 180, and 200 ºC with aquadest (left) and nanobubbled water (right).

The idea that the molecule of the colloids may possess conjugated carbonyl groups is supported by mid-infra-red spectra of the colloids from the hydrothermal processes at 200 ºC (**Fig. 2**). The spectra show a strong absorption of mid-infra-red waves around 1,640 cm^{-1} which indicates a carbonyl group (–C=O). Considering another strong absorption of mid-infra-red waves around 3,330 cm^{-1} (**Fig. 2**) which indicates an amine (–NH) group, we postulated that the molecular surface of the colloids may be decorated with amides. The amides may have come from oxidation of primary hydroxyl groups, and further reaction with amine groups, in the fiber components of PKC.

Under transmission electron microscopy, the colloids from the hydrothermal processes at 200 ºC were found to contain spheres with sizes around 50 nm (**Fig. 3**). These spheres do not fit the strict definition of carbon dots. Therefore, for further discussions, we simply refer them as nanodots.

Since we are interested to apply the nanodots for the absorption of ultra-violet A waves (320 – 400 nm) from the sun, we illuminated the nanodots with ultra-violet A lamp (350 nm). Upon excitation by the ultra-violet A wave, the nanodots consistently emitted lights with a maximum around blue region (450 nm) (**Fig. 4 and 5**). The aforementioned surface-decorating amides of the nanodots may have been responsible for this fluorescent color. Again, with the increase of the hydrothermal process temperature, more molecular structures of PKC may have been broken, and therefore less amount of visible wave was emitted by the product.

The fluorescence property of nanodots from PKC opens up the possibility for these carbon materials to be applied in agriculture. As demonstrated by Al-Mayahi (2016) [8], blue light is beneficial for the growth of palm date (*Phoenix dactylifera*), a plant species which is classified in the same family with oil palm (*Elaeis guineensis*). The application of nanodots from PKC for the growth of oil palm would create a circular economy for the oil palm sector in our country and elsewhere.

It is worth to mention here that no significant differences were found between the nanodots from the hydrothermal carbonizations of PKC with aquadest and the ones from the hydrothermal carbonizations of the biomass with nanobubbled water.

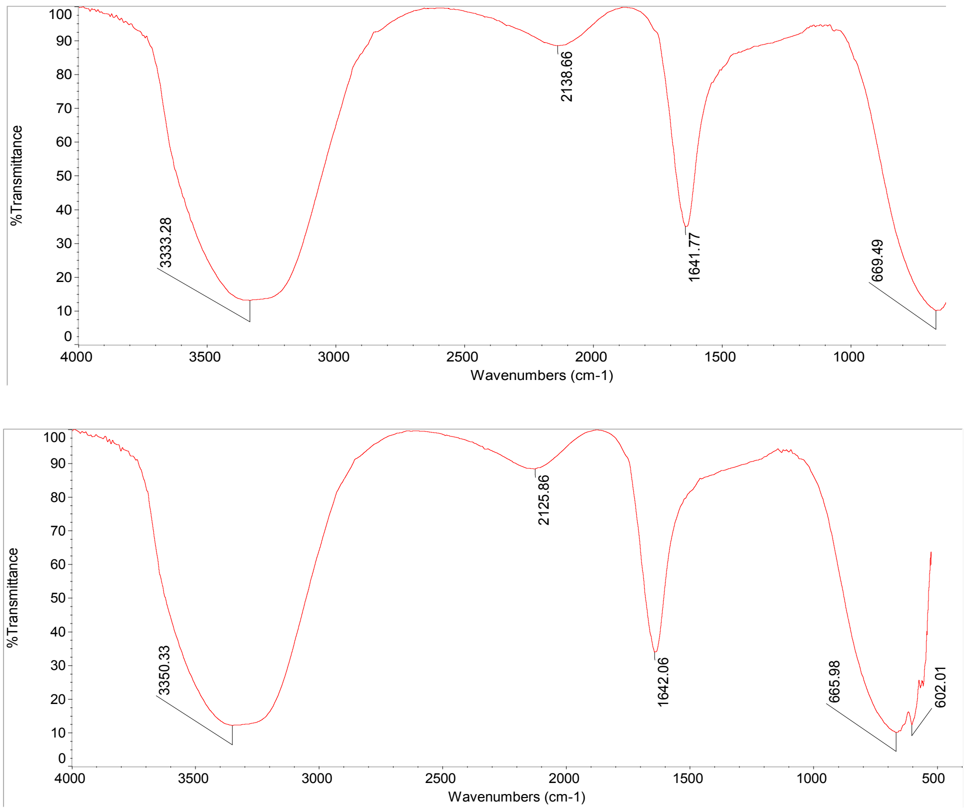

Fig. 2. Mid-infra-red spectra of the colloids from the hydrothermal processes at 200 ºC with aquadest (top) and nanobubbled water (bottom).

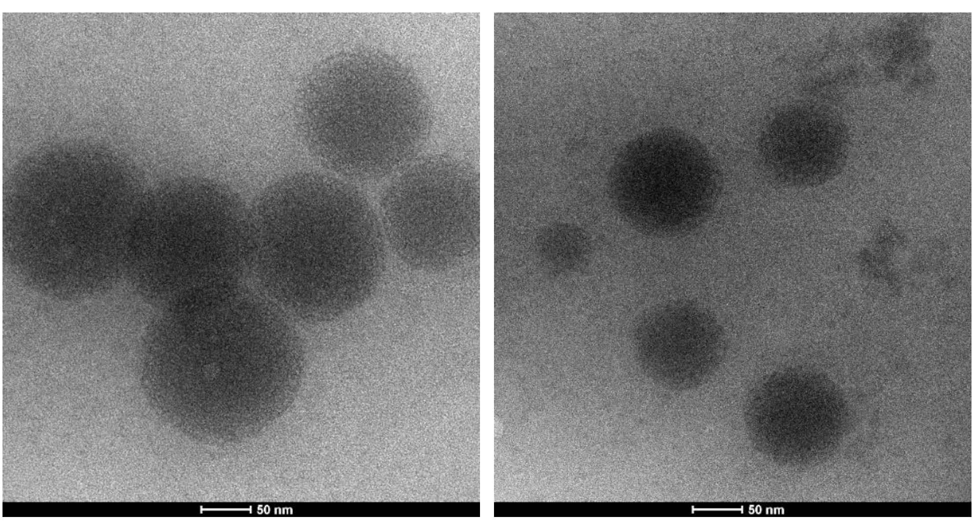

Fig. 3. Transmission electron microscopy image of filtrates from the hydrothermal processes at 200 ºC with aquadest (left) and nanobubbled water (right).

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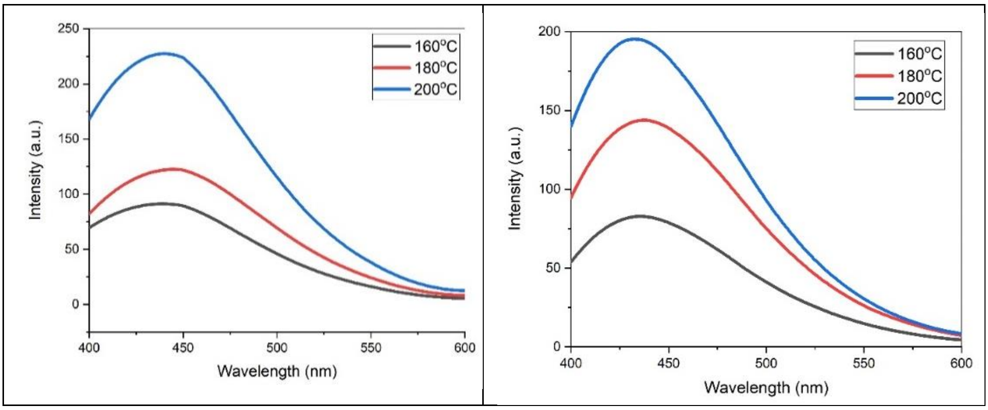

Fig. 4. Visible light emission spectra of filtrates from the hydrothermal processes at 160, 180, and 200 ºC with aquadest (left) and nanobubbled water (right) upon excitation by 350 nm light wave.

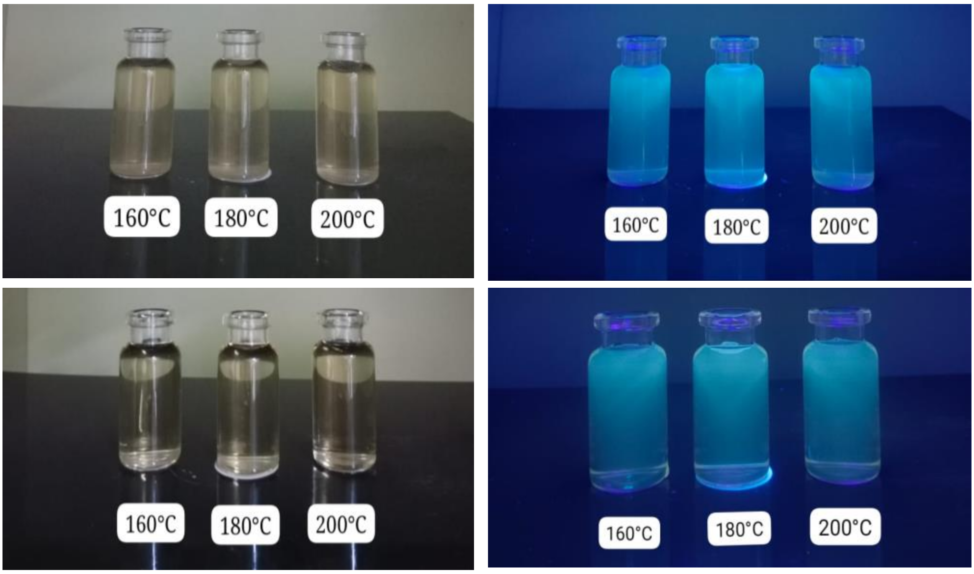

Fig. 5. Photographs of the filtrates from the hydrothermal processes at 160, 180, and 200 ºC with aquadest (top) and nanobubbled water (bottom) before (left) and upon (right) illumination with 350 nm light wave.

4 Conclusions

From the hydrothermal processes of PKC at 160, 180, and 200 ºC with aquadest and nanobubbled water, nanodots with the size around 50 nm were obtained. The process seems to work the best at 200 ºC. However, no significant differences were found between the nanodots from the hydrothermal carbonizations of PKC with aquadest and the ones from the hydrothermal carbonizations of the biomass with nanobubbled water. The nanodots may be decorated with amides on their surface. Upon excitation by the ultra-violet A wave (350 nm), the nanodots emitted lights with a maximum around blue region (450 nm).

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