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Carbon Dots Synthesized from Tofu Pulp for Liquid Tofu Waste Photo-degradation

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ABSTRACT

This study was aimed to prepare and characterize carbon dots (CDs) from tofu pulp for liquid tofu wastes photo-degradation. The tofu pulp was dried, heated in an oven for an hour at 250 ºC, mashed into powder, weighted as much as (g) 1; 2; 3; 4; and 5, dissolved into 100 ml distilled water, filtered, and characterized using UV-Vis, PL, and FTIR. The photo-degradation experiment was conducted for pure waste, waste + CDs, and waste + CDs + UV light, then the BODs were measured. The CDs reduced the wastes to 14.29% and 53.90% without and with UV light, respectively. The pure wastes, wastes + CDs, and wastes + CDs + UV light produced BOD values of (mg/l) 385; 200; and 135, respectively. The decrease in BOD showed that CDs with and without UV light successfully restore dissolved oxygen in the wastes.

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I. Introduction

Carbon dots (CDs) are new carbon-based materials that have attracted attention due to their optical properties. Unlike other carbon-based materials, CDs have strong fluorescence properties. Compared to other fluorescence materials like semiconductor quantum dots, CDs have advantages such as biocompatibility, low toxicity, easy functionalization, chemical inertness, and water solubility [1]. CDs have been used for various applications, such as bio-imaging [2], sensing [3], light-emitting diode [4], bio-medicine [5], and catalyst [6].

The synthesis of CDs is relatively simple and requires cheap raw materials. There are two main types of CDs synthesis, i.e., physical and chemical methods [1]. The physical method includes laser ablation and arc discharge. The chemical method includes electrochemical, hydrothermal, carbonization, and combustion. Materials that contain carbon elements can potentially be used as raw materials or precursors to produce CDs. Due to their high carbon content, bio-mass waste has been exploited for synthesizing CDs. CDs have been prepared from fast food waste [7,8], coconut shell [9], rice husk [10], banana peels [11], orange peels [12], coffee [13], and seeds [14].

One application of CDs that has been a current research topic is for waste treatment. CDs have been used for carbamazepine removal from water [15], dye-containing wastewater treatment [16], and removing heavy metals such as Cd^{2+} and Pb^{2+} in drink water [17]. Since CDs can be synthesized from carbon waste and can be used for waste treatment, a new concept called for waste by waste is emerging [18].

Tofu is a popular food in Asia. The tofu production process produces by-products, such as pulp and liquid wastes. Many traditional tofu industries in Indonesia directly release liquid waste to the environment and cause water pollutions [19]. The liquid waste from tofu production is high in organic substances, such that the biochemical oxygen demand (BOD) ranges from 6000 - 8000 mg/L and the chemical oxygen demand (COD) ranges from 7500 - 14000 mg/L. Due to the high content of organic substances, liquid waste of tofu production causes pollution in the surface and groundwater. The solid waste or pulp contains 20.93% protein, 21.43% fiber, 10.31% crude fat, 0.72% calcium, 0.55% phosphor, and 36.69% other compounds [19]. Pulp waste of tofu production is carbonous material, which can be used as a precursor for CDs. In this work, we are putting an effort to conduct the “for waste by waste” concept by utilizing the pulp as a raw material to synthesize CDs and then use the CDs for liquid tofu waste treatment.

II. Theory

CDs

CDs are new emerging zero-dimensional (0D) carbon-based nanomaterial. Typically, the CDs diameter is less than 10 nm [20]. CDs consist of two main parts, i.e., core and surface states. CD core has mainly consisted of C=C bonding. Meanwhile, the surface state can consist of various functional groups such as -COOH, -OH, and -NH_2 [21]. CDs are known for having strong optical properties. The strong optical properties are due to the quantum confinement effect and surface effect. Mostly, CDs pose strong optical absorption at the wavelength of 230 nm to 320 nm. The peak at around 230 nm is associated with the $\pi \rightarrow \pi^*$ electronic transition related to the C=C bonds in the core of CDs. A shouldering peak sometimes appears at a wavelength of around 300 nm. It is ascribed to the $n \rightarrow \pi^*$ electronic transition of C=O bonds or other functional groups of the surface state [20].

Biochemical Oxygen Demand (BOD)

BOD is an indicator of the organic pollution of water. Traditionally, BOD is estimated in a five-day period. The parameter is defined as the amount of oxygen divided by the system’s volume, taken up through the respiratory activity of microorganisms growing on the organic compounds present in the sample when incubated for a certain period at a certain temperature. In brief, BOD measures the organic pollution of water that can be degraded biologically. The unit of BOD is milligrams O_2 per liter. BOD is usually used to indicate wastewater discharge criteria and determine the waste treatment method [22].

Photo-degradation

Organic pollutants can be degraded using light and O_2 under ambient conditions. The process is called photo-degradation. The photo-degradation process can be applied to eliminate organic pollutants from water. In the photo-degradation process, catalysts can accelerate the reaction between organic pollutants and O2. The catalysis process lowers the energy barrier of the degradation reaction [23]. CDs can be used appropriately for this purpose.

III. Method

CDs Preparation

The main material for the CDs was pulp waste from the tofu production process. The pulp waste was obtained from a local traditional tofu industry in Yogyakarta, Indonesia. CDs were prepared using carbonization or a simple heating method. The pulp wastes from tofu production were placed in an oven at 250 ^oC for an hour. This process produced black carbon charcoal. The charcoal was then mashed with a porcelain mortar into powder. The powder was weighed for (g) 1, 2, 3, 4, and 5, and then each of them was mixed with 100 mL distillate water. Hence, we get 5 samples with concentrations (in g/mL), i.e.: 0.01; 0.02; 0.03; 0.04; and 0.05, which were then filtered using filtering papers, producing samples of CD A; B; C; D; and E, respectively.

CDs Characterization

The as-prepared CDs were characterized using photoluminescence (PL), UV-Vis spectrophotometer (UV-Vis), and Fourier-transform infrared (FT-IR) spectroscopy. The UV-Vis spectroscopy was conducted with a Shimadzu UV spectrophotometer. The PL spectroscopy was carried out using a custom-configured device with an Ocean Optics USB4000 spectrometer. The FT-IR analysis was conducted using FTIR Thermo Nicolet Avatar 360.

Liquid Tofu Waste Treatment

To investigate the possible application of CDs for liquid tofu waste treatment, three samples were prepared, i.e., pure liquid tofu waste (sample I), liquid tofu waste added with CDs (liquid tofu waste + CDs, sample II), and liquid tofu waste added with CDs and exposed by UV light (liquid tofu waste + CDs + UV light, sample III). All samples (I, II, and III) are left alone for seven days (one week). Especially for sample III, the mixed solution of CDs C with liquid tofu waste was illuminated with UV light for 2 hours per day (for a total of seven days). The BODs were then measured for all samples.

IV. Results and Discussion

The absorption spectra of CDs are investigated using a UV-Vis spectrophotometer. The UV-Vis spectra of synthesized CDs are presented in Figure 1. The CD A sample does not feature any clear absorbance peak. Meanwhile, CD B to CD E samples obtained from the precursor concentrations of (in g/mL) 0.02; 0.03; 0.04; and 0.05 produce an absorbance peak at wavelengths of 206 nm, 215 nm, 220 nm, and 226 nm, respectively. Hence, the absorbance peak shifts to longer wavelengths as the precursor concentration increases (red-shift), according to the study in [24]. It may also be observed that a higher absorbance value is obtained with higher precursor concentration as more CDs are produced. There is also a weak shouldering peak at around 250 nm for all CD solutions. This shouldering peak shows $\pi \rightarrow \pi^*$ electronic transitions associated with C=C bonding of the CDs’ core.

Moreover, another shouldering peak occurs at a wavelength of 320 nm for all CD samples, showing the CDs’ surface state. This indicates the $n \rightarrow \pi^*$ electronic transitions of oxygen functional groups. Therefore, the presence of both of these absorbance peaks indicates the formation of CDs, which is in agreement with Dai *et al.* [25].

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Figure 2 shows the PL spectra of prepared CDs samples. The maximum PL intensity occurs at different wavelengths for different CD samples. Under the excitation wavelength of 410 nm, the maximum PL emission wavelength appears at 499.173 nm; 499.173 nm; 507.988 nm; 511.686 nm; and 523.553 nm for CD A; B; C; D; and E, respectively. Hence, all CD samples have cyan emission because the range of cyan luminescence is around 485 nm to 500 nm. According to the qualitative test, these PL results show all CD samples emit cyan luminescence under UV laser (see Figure 3). As the precursor concentration increases, the emission peaks occur at a longer wavelength, and the intensity gets stronger. Hence, the PL intensity depends upon the concentration of the CDs [20]. A higher intensity peak in the sample with higher precursor concentration is because more CDs are in the samples. This is again following the PL results in [25]. A possible underlying argument behind the dependence of the PL peaks upon the concentration of the CDs is the different particle sizes that occur in the CDs [20].

Figure 4 shows the FT-IR spectra of CD samples with precursor concentrations of 0.01 g/mL (CD A); 0.03 g/mL (CD C); and 0.05 g/mL (CD E). For all samples, absorption bands appear at around 3400 cm^{-1}; 1600 cm^{-1}; and 600 cm^{-1}, corresponding to O-H; C=C; and C-C bonds. The existence of the C=C bonds indicates the core of the CDs, hence confirming the formation of CDs following the UV-Vis results. Moreover, there are no significant differences between the bands of the CDs samples, which means that the precursor concentration does not affect the functional groups in the CDs. The FT-IR result is comparable to the FT-IR results in [26]. It can also be observed that the FT-IR spectrum of CD C is lower than CD A. This may be caused by the smaller amount of the CD C sample being characterized than the amount of the CD A sample.

The prepared CDs from the tofu pulp production are used to treat the tofu production's liquid waste. BOD tests are carried out for three samples. The sample I is a pure liquid waste of tofu production. Sample II is a mixture of liquid waste from tofu production and CDs (wastes + CDs). Finally, sample III is the same solutions as Sample II but illuminated by UV light for two hours each day for seven consecutive days (wastes + CDs + UV light). The amount of the liquid waste is the same in samples I, II, and III. The BOD test result can be seen in Table 1.

Table 1. BOD test results.

Samples	BOD (mg/L)
I	385.00
II	200.00
III	135.00

Based on Table 1, sample I has the highest BOD, i.e., 385 mg/L. The BOD reduces to 200 mg/L in sample II. In sample III, the BOD is reduced up to 135 mg/L. The maximum BOD permitted by the Indonesian Ministry of Environment, especially for liquid tofu wastes, is 150 mg/L [27]. The BOD value of sample I is above the permitted value. However, treating the liquid tofu waste using the CDs with UV light successfully reduces the BOD value under the permitted value. Hence, this result indicates that the CDs synthesized from the solid waste of tofu can reduce BOD in the liquid waste of tofu production. The CDs act as catalysts for photo-degradation of the liquid tofu wastes. Moreover, we also find that the photo-degradation can be enhanced under UV-light radiation, which produces the lowest BOD in sample III.

Under visible light, it can be observed that sample I looks cloudy (murky) and produces sediments. On the other hand, sample III is seen clearer and contains fewer sediments than other samples (see Figure 5).

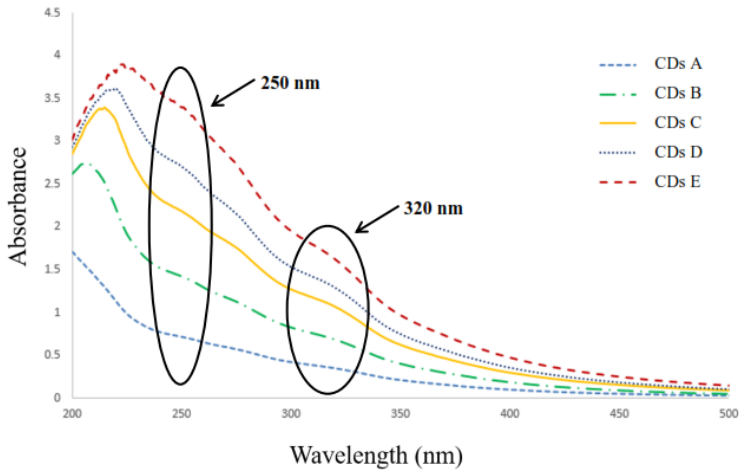

Figure 1. UV-Vis spectra of the synthesized CD samples.

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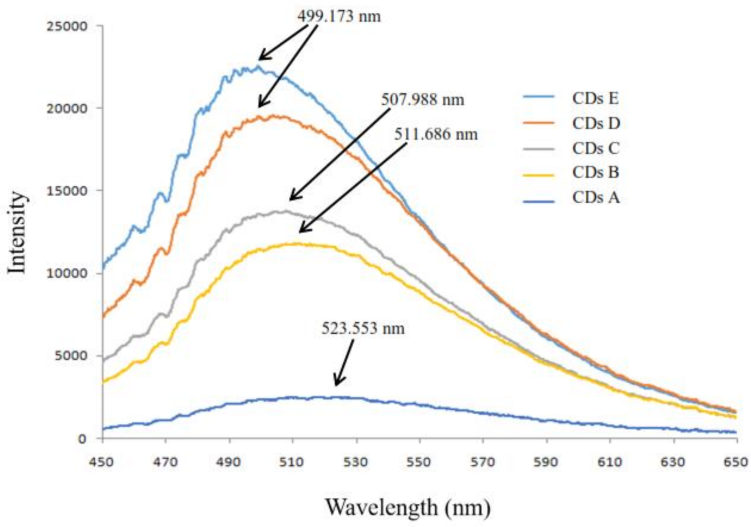

Figure 2. PL spectra of prepared CDs samples.

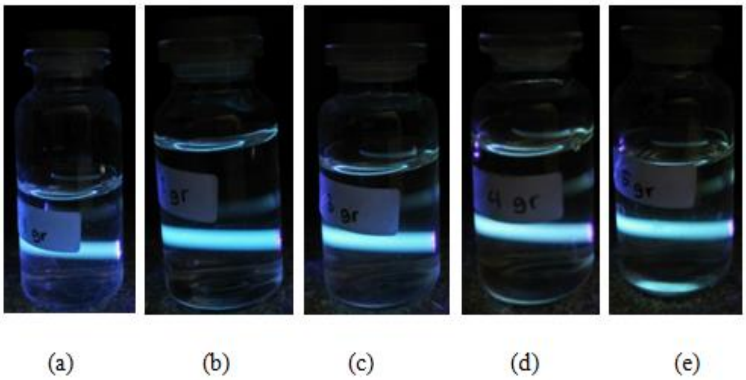

Figure 3. CDs with precursor concentrations of 0.01 g/mL (a); 0.02 g/mL (b); 0.03 g/mL (c); 0.04 g/mL (d); and 0.05 g/mL (e) exposed to UV/violet laser.

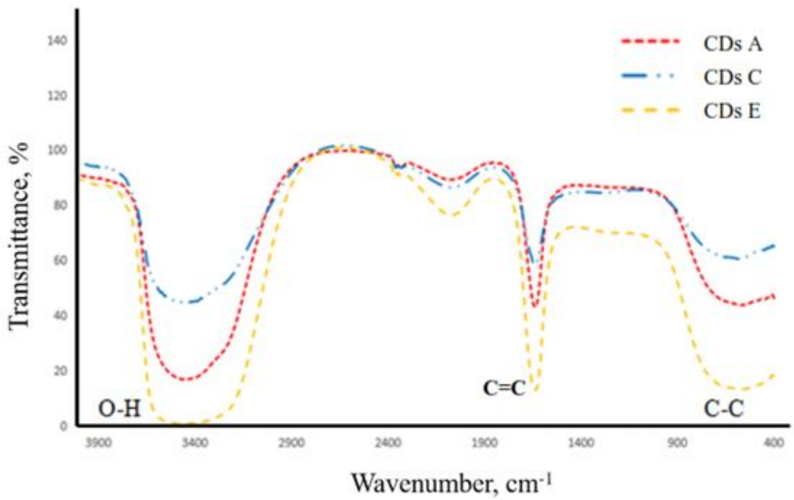

Figure 4. FT-IR spectra of CD samples.

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Figure 5. Solution comparison of sample I (a), sample II (b), and sample III (c).

V. Conclusion

In this study, we have synthesized CDs from the pulp of tofu productions. The CD samples produce two shouldering peaks at 250 nm and 320 nm from the UV-Vis characterization. Based on the PL characterization, the synthesized CDs show a peak at wavelengths of 499 nm to 523 nm, which means that the CDs emit cyan luminescence. The functional groups of the CDs obtained from the FT-IR test are C=C, OH, and C-C bonds. The CDs have been applied as catalysts for photo-degradation of liquid tofu wastes. The BOD in the liquid waste is reduced significantly by adding CDs with UV light.

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