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The Effect of Different Synthesis Solvents and Dialysis Processes on the Optical Properties of Carbon Dots from Spent Coffee Grounds using the Solvotermal Method

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Abstract: The distinctive optical properties of carbon dot (CD) make CD is one of the most widely developed carbon nanomaterials today. CD can be synthesized from materials that high in carbon content, such as spent coffee grounds. The optical properties of synthesized CD are influenced by several factors, including the solvent used to synthesize it and the purification method. The purification process that can be done is dialysis. However, this technique is not always used in several researches to purify CD. This study aims to synthesize CD from spent coffee grounds through solvothermal methods with three different solvents, which are water, 50% ethanol (v/v), and absolute ethanol that purified by dialysis and without dialysis and to characterize the differences in its optical properties. The results showed that CD was successfully synthesized with these three solvents, but the optical properties were different. All three solvents produce CD that emits blue light, but differ in intensity. The addition of ethanol can double the luminescence intensity of CD and CD synthesized with 50% ethanol produce the highest luminescence intensity. In addition, CD purified without dialysis produce twice as high luminescence intensity as CD purified by dialysis.

Keywords: spent coffee grounds, CD, dialysis, solvents, optical properties

Abstrak: *Sifat optik karbon dot (CD) yang khas membuat CD menjadi salah satu nanomaterial karbon yang banyak dikembangkan saat ini. CD dapat disintesis dari material yang tinggi akan kandungan karbon, seperti ampas kopi. Sifat optik CD hasil sintesis dipengaruhi oleh beberapa faktor, salah satunya adalah pelarut yang digunakan untuk menyintesisnya. Selain itu, sifat optik yang dihasilkan pun dipengaruhi oleh proses permunian yang dilakukan. Salah satu proses pemurnian yang dapat dilakukan adalah dialisis. Namun, teknik ini tidak selalu digunakan dalam beberapa penelitian untuk memurnikan CD. Penelitian ini bertujuan menyintesis CD dari ampas kopi melalui metode solvotermal dengan tiga pelarut berbeda, yaitu air, etanol 50% (v/v), dan etanol absolut yang dimurnikan dengan dialisis dan tanpa dialisis serta mencirikan perbedaan sifat optik yang dihasilkan. Hasil penelitian menunjukkan bahwa CD berhasil disintesis dengan tiga pelarut tersebut, namun sifat optik yang dihasilkan berbeda. Ketiga pelarut menghasilkan CD yang mengemisikan cahaya biru, namun intensitasnya berbeda. Penambahan etanol dapat meningkatkan intensitas pendaran CD hingga dua kali lipat dan CD yang disintesis dengan etanol 50% menghasilkan intensitas pendaran tertinggi. Selain itu, CD yang dimurnikan tanpa dialisis menghasilkan intensitas pendaran dua kali lebih tinggi dibandingkan CD yang dimurnikan dengan dialisis.*

Kata kunci: *ampas kopi, CD, dialisis, pelarut, sifat optik*

INTRODUCTION

Coffee is a commodity that is widely consumed today. Coffee consumption in 2015–2017 is estimated to reach 9.1–9.4 million tons. The ever-increasing consumption of coffee causes the production of large amounts of waste originating from the processing of coffee beans into coffee. One type of waste that is often produced is spent coffee grounds which are simply thrown into trash cans or sinks which eventually reach water bodies (Arya *et al.* 2022). In fact, spent coffee grounds contain compounds that are rich in carbon, such as cellulose, hemicellulose and lignin. Apart from that, coffee grounds are also reported to contain 17.4% protein and 2.3% lipids. The carbon contained in coffee grounds reaches 52.2% (Ballesteros *et al.* 2014; Kourmentza *et al.* 2018). This means that spent coffee grounds can be used as a precursor to synthesize carbon dots (CD).

CD is a type of zero-dimensional carbon nanomaterial that is currently being developed because it has unique optical properties (Kang *et al.* 2020). The optical properties of a CD depend on the state of its surface, namely the carbon backbone framework and the functional groups on its surface (Zhu *et al.* 2015). One of the factors that influences the surface state of CDs is the solvent used to synthesize them. This is due to differences in interactions between the precursor and the solvent during the synthesis process (Ding *et al.* 2018). Bettini *et al.* (2021) have succeeded in synthesizing CD from spent coffee grounds using a water solvent (hydrothermal). The resulting CD emits blue light with functional groups identified using a Fourier transform infrared spectrophotometer, namely hydroxyl, carbonyl, carboxyl, alkene and amine groups.

In this research, CDs were synthesized from coffee grounds using three different solvents, namely water, 50% ethanol (v/v), and absolute ethanol via the solvothermal method to identify the effect of different solvents used on the optical properties of the CDs produced. According to Ren *et al.* (2021), organic solvents can promote the carbonization of precursors better than water solvents, which leads to changes in the optical properties of CDs. In addition to the differences in solvents used to synthesize CDs, this study also identified the influence of the dialysis process on the optical properties of CDs from coffee grounds. Dialysis is one of the most widely used CD purification methods. Dialysis is a method that allows components smaller than the pore size of the dialysis membrane to be passively filtered into dialysis water (dialysate), while allowing larger particles to remain trapped in the dialysis membrane. This allows the CD to remain in the dialysis membrane and incomplete reaction side products to exit the dialysis membrane (Noun *et al*. 2020).

CDs synthesized from the same precursor do not necessarily produce the same optical properties if the CD purification process is different (Noun *et al.* 2020). Based on research conducted by Ullal *et al*. (2024), the presence of fluorescent small molecules or oligomeric impurities and by-products resulting from incomplete precursor reactions can contribute to CD emission and can greatly influence the optical properties. The optical properties of synthesized CDs may therefore differ when synthesized CDs are purified with dialysis and without dialysis. So far, there has been no research that uses solvents other than water to synthesize CDs from spent coffee grounds and no research has identified the effect of dialysis on the optical properties of CDs from spent coffee grounds synthesized using hydrothermal and solvothermal methods, so this research is important to do to develop purer CDs, especially CDs synthesized from biomass waste such as spent coffee grounds.

MATERIALS AND METHOD

Materials

The tools used in this research were glassware, mortar, 40 mesh sieve, Teflon lined autoclave, magnetic stirrer, syringe, 0.22 µm nylon syringe filter, 2 mL microtube, oven (Memmert), bath plate and stirrer (IKA C-MAG HS 7), UV lamp cabinet (CAMAG), analytical balance (Bell), microcentrifuge (Centurion Scientific Ltd), *Fourier transform infrared* (FTIR) spectrophotometer (PerkinElmer), UV-Vis spectrophotometer (Unic), and *laser induced fluorescence* spectrophotometer (Ocean optics USB 4000). The materials used in this research were spent coffee grounds, aquabides, urea (Merck), absolute ethanol (Merck), HNO_3 65% (Merck), NaOH (Merck), KBr, filter paper, dialysis membrane, and universal indicator.

Spent Coffee Grounds Sample Preparation

Spent coffee grounds were obtained from Kopicentrum, Dramaga, Bogor Regency. The spent coffee grounds were washed and then dried at 105 ºC for 2 hours. The spent coffee grounds were then filtered using a 40 mesh sieve to separate the spent coffee grounds from larger particles.

Synthesis of CD from Spent Coffee Grounds

A total of 1.5 g of spent coffee grounds and 0.3 g of urea were weighed. A mixture of urea and spent coffee grounds was then added to 65 mL of distilled water and 1.5 mL of HNO_3. The mixture was then put into a Teflon lined autoclave and heated at 200 ºC for 6 hours. The Teflon lined autoclave was then allowed to cool to room temperature. The dark black solution in Teflon was then filtered and neutralized with several drops of 1 M NaOH (Hong *et al.,* 2021). The same procedure was carried out by replacing the aquabides with 50% ethanol and ethanol, respectively.

CD Purification

The neutral black solution was then separated from the large particles with a microcentrifuge at a speed of 10,000 rpm for 20 minutes. The supernatant was then purified by dialysis for 24 hours. After 24 hours, the brown solution in the dialysis membrane was evaporated until a black powder was obtained. The same procedure was carried out to purify CDs without dialysis by replacing the dialysis process with filtration using a 0.22 µm nylon syringe filter (Lee *et al.* 2019; Costa *et al.* 2022).

Characterization of CDs

All CD samples were characterized by FTIR spectrophotometer (PerkinElmer) to identify functional groups, UV-vis spectrophotometer (Unic) to determine absorption peaks, laser induced fluorescence spectrophotometer (Ocean optics USB 4000) to determine emission wavelengths, and UV light cabinet (CAMAG) to identify the resulting emission colors. The characterization results of each CD sample were then compared to determine the effect of different solvents and dialysis processes on the optical properties of CDs from spent coffee grounds.

RESULT AND DISSCUSION

CD from spent coffee grounds

CD from spent coffee grounds synthesized by hydrothermal method generally goes through five stages, namely hydrolysis, dehydration, polymerization, carbonization, and passivation. Macromolecules such as cellulose, hemicellulose, and lignin contained in spent coffee grounds will undergo hydrolysis into their monomers. The monomers resulting from hydrolysis will experience dehydration into furfural compounds which then polymerize and undergo aromatization. Nucleation through the polymerization process occurs through the formation of cross-linking bonds between macromolecules (Chang *et al.* 2016). Urea as a passivation agent was added to synthesize CD from coffee grounds in this study. Passivation agents play a role in stabilizing the surface state of CD which can increase its fluorescence intensity (Ding *et al.* 2020).

CDs produced from synthesis with three different solvents and purified by dialysis are in the form of black powder. A different thing happens when CDs are purified without dialysis. CDs produced without dialysis are in the form of a black paste that is very hygroscopic (Figure 1). Both the powder and paste produced are highly soluble in water, unlike its precursor, coffee grounds, which are difficult to dissolve in water. This confirms that there has been a change from coffee grounds to CDs. CD has high solubility in water due to the many hydrophilic groups on its surface (Prasannan & Imae 2013; Bhartiya *et al*. 2016; Kang *et al*. 2020). The differences in the form of the CDs produced have been previously reported by Meiling *et al.* (2018) who stated that the synthesized CDs can have different hygroscopic properties, so that the CDs can be in the form of powder, paste, or very thick liquid. This depends on the functional groups present on the surface of each CD and its quantum yield. CDs that are richer in functional groups that absorb water on their surface and CDs that have a higher quantum yield will more easily absorb water from the environment, so that the CD can be in the form of a paste or a liquid. According to Meiling *et al*. (2018), dried CDs can be in the form of powder (quantum yield < 15%), paste (quantum yield < 50%), and thick liquid (quantum yield < 80%).

FTIR Spectrum of CD from Spent Coffee Grounds

FTIR spectrum was used to identify the differences in functional groups resulting from the synthesis using three different solvents and to confirm the success of the synthesis process. Characterization using FTIR was carried out on powdered CDs. Figure 2 shows the difference in spectra resulting from the synthesis with three

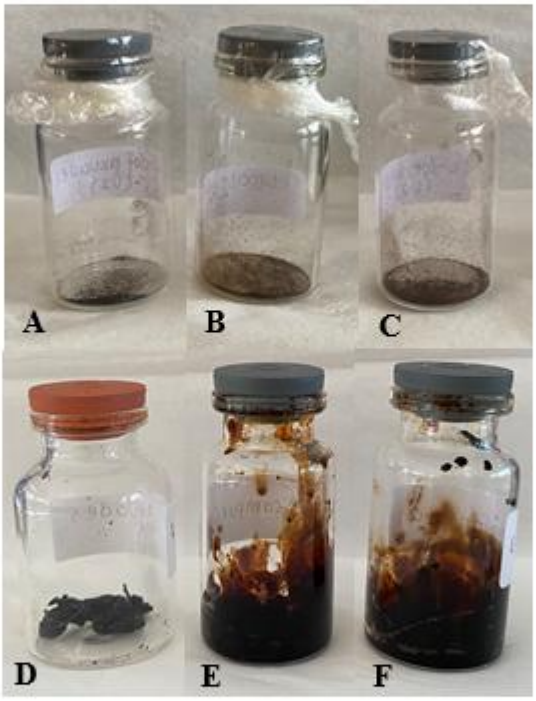

Figure 1. CD from spent coffee grounds. (Caption: A: CD water with dialysis; B: CD ethanol 50% with dialysis; C: CD ethanol dialysis; D: CD water without dialysis; E: CD ethanol 50% without dialysis; F: CD ethanol without dialysis)

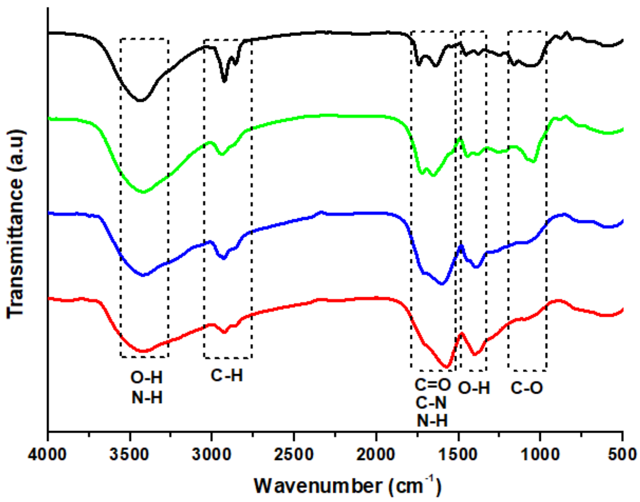

Figure 2. FTIR spectrum of CD and spent coffee grounds. (Description: black: spent coffee grounds; green: ethanol CD; blue: 50% ethanol CD; red: water CD)

different solvents and their comparison with the initial precursor, namely spent coffee grounds. The spent coffee grounds sample produced a band at a wavenumber of 3450 cm^{-1} which is the stretching vibration of the O-H and N-H bonds of cellulose, lignin, and protein contained in the spent coffee grounds (Li *et al.* 2014). The presence of the macromolecules was also identified from the appearance of a band between the wavenumbers 2850 cm^{-1} and 2930 cm^{-1} which is the symmetric and asymmetric stretching vibration of the C-H sp^3 bond. In addition, the band at the wavenumber 1747 cm^{-1} shows the stretching vibration of the C=O bond (Zarrinbakhsh *et al.* 2016).

The three CD samples showed the same absorption band at wavenumber 3452 cm^{-1} indicating that the CD samples contained O-H and N-H groups originating from spent coffee grounds and urea. In addition, the absorption band appearing at wavenumber 2851 cm^{-1} for the three CD samples also indicated that CD contained C-H sp^3 groups but its intensity was greatly reduced compared to its initial precursor, namely spent coffee grounds. This shows the change from C-H sp^3 originating from macromolecules contained in spent coffee grounds to C-H sp^3 of the CD core framework. According to Yan *et al.* (2019), the CD core framework can be either sp^2 carbon or sp^3 carbon.

The absorption band that appears at wavenumber 1745 cm^{-1} in the FTIR spectrum of spent coffee grounds comes from the ester group in lipids (Zarrinbakhsh *et al.* 2016). This band is missing in the FTIR spectra of the three CD samples. However, CDs synthesized using water and 50% ethanol show a band at 1703 cm^{-1} originating from the C=O carboxylate group (Nandiyanto *et al.* 2019). This is due to the presence of an absorption band that appears at the wavenumber 1603 cm^{-1} which originates from the COO^- stretching vibration (Xu *et al.* 2015, Xie *et al.* 2019). Based on this, the CD from coffee grounds that has been synthesized in this study contains functional groups O-H, COOH, and N-H. These groups make the CD easier to react with water causes the CD to be hydrophilic so that it is very soluble in water (Meiling *et al.* 2018; Kang *et al.* 2020).

Optical Properties of CDs from Spent Coffee Grounds

The optical properties of the synthesized CDs were characterized using UV light, UV-vis spectrophotometer, and laser induced fluorescence spectrometer. As a comparison, the optical properties of CDs purified by dialysis and CDs purified without dialysis were characterized. Figure 3 shows the fluorescence of CDs under 366 nm UV light. CDs purified without dialysis appear to have stronger fluorescence than CDs purified with dialysis. CDs synthesized using water alone and purified without dialysis produced similar luminescence as in the study conducted by Costa *et al.* (2022). The luminescence of CDs synthesized with the addition of ethanol was stronger than that of CDs synthesized with water alone, both for CDs purified with and without dialysis. CDs purified without dialysis produce brighter fluorescence, which may be due to the presence of other by-products which are fluorophores that are not removed if the CDs are not purified by dialysis (Noun *et al.* 2020).

The absorption peaks of CDs were determined using a UV-vis spectrophotometer. Figure 4 shows the absorption peaks of purified CDs without dialysis and with dialysis. The visible absorption peaks indicate the electronic transition of CD electrons when irradiated by light with a certain wavelength from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Pan *et al.* 2010). CD purified by dialysis showed the occurrence of two electronic transitions at wavelengths of 220–230 nm and 250–275 nm for the

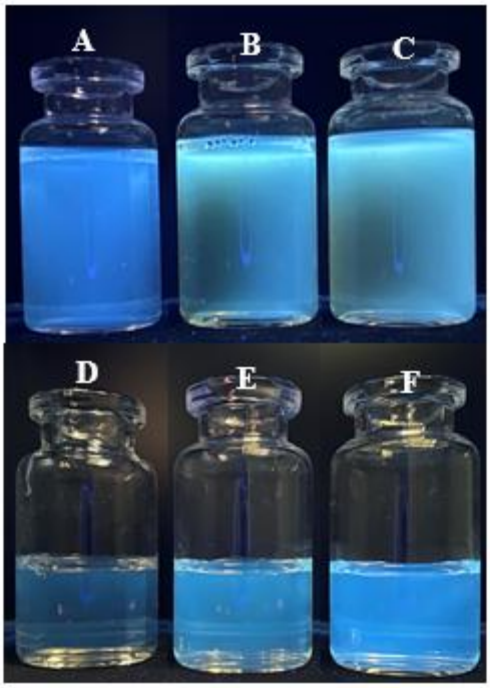

Figure 3. Fluorescence of CDs under 366 nm UV light. (Description: A: CDs water with dialysis; B: CDs 50% ethanol with dialysis; C: CDs ethanol with dialysis; D: CDs water without dialysis; E: CDs 50% ethanol without dialysis; F: CDs ethanol without dialysis).

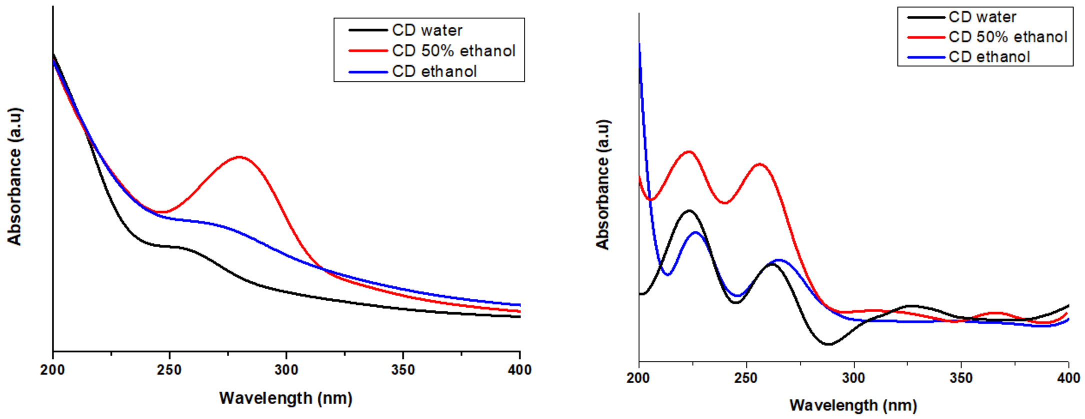

Figure 4. Absorption spectrum of CD. (left: without dialysis; right: with dialysis).

π→π* and n→π* transitions, respectively (Alarfaj *et al.* 2020).

In contrast to CDs purified by dialysis, CDs purified without dialysis only produce one electronic transition at 250–275 nm. This can occur because there are still many side products that are fluorophores in CDs purified without dialysis. According to Noun *et al.* (2020), The difference in absorption peaks can occur in CDs purified without dialysis because of the large number of by-products that aggregate, causing the peak that appears at a wavelength of 220 nm to shift towards 270 nm. The difference in absorption peaks in CDs purified without dialysis and with dialysis occurs because the peak that should appear at 220–230 nm shifts towards 270 nm and overlaps, so that the peak that appears on CDs purified without dialysis is only one and widens.

The optical properties of the synthesized CDs are also characterized by their emission spectra. Figure 5 shows the emission spectra for CDs synthesized with three different solvents and purified with and without dialysis. The results of this characterization are in line with the characterization using UV light, showing that CD purified without dialysis produces higher intensity than CD purified without dialysis. These results support the hypothesis that there are indeed other fluorophores in CD that are purified without dialysis so that the intensity becomes higher (Noun *et al*. 2020)

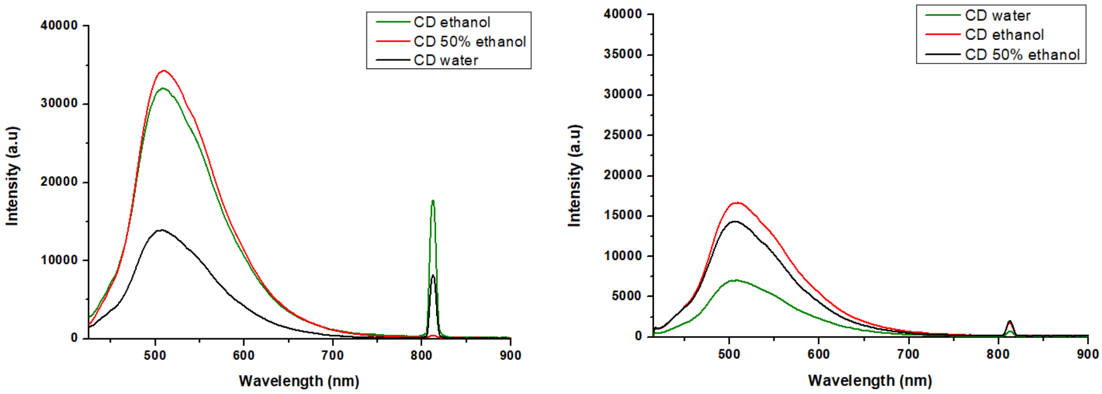

Figure 5. CD emission spectrum. (left: without dialysis; right: with dialysis)

The addition of ethanol solvent as a solvothermal reaction medium can increase the fluorescence intensity of CD up to two times. The best intensity was produced by CD synthesized with 50% ethanol solvent. Ethanol mixed with water in a ratio of 1:1 (v/v) can extract compounds in polar and less polar coffee grounds better than water solvent alone or ethanol solvent alone. A mixture of alcohol and water is better for breaking down lignocellulose components. Lignin and cellulose are contained in coffee grounds. Water has a better ability to break down cellulose, while lignin can be broken down better using ethanol (Yogalakshmi *et al.* 2023). Therefore, the hydroxyl and carboxyl functional groups on the CD synthesized using 50% ethanol increase, so that the fluorescence intensity of the CD produced increases.

CONCLUSION

CD was successfully synthesized from coffee grounds using three different solvents, namely water, 50% ethanol, and ethanol. The optical properties of CD from coffee grounds are influenced by the synthesis solvent and the purification process carried out. The addition of ethanol can increase the fluorescence intensity of CD up to two-fold. The best fluorescence intensity was produced by CDs synthesized with 50% ethanol solvent. Purification without dialysis makes the fluorescence intensity of CDs twice as high as that of CDs purified by dialysis.

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