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IMPROVING CARBON DOTS OPTICAL PROPERTIES OF MOLASSES USING EDTA AS A PASSIVATION AGENT WITH THE MICROWAVE METHOD

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ABSTRACT

Synthesis of carbon dots from molasses using the microwave method with the addition of EDTA as a passivation agent has been carried out. Addition of EDTA to improve the optical properties of the carbon dots. The resulting carbon dots were characterized by UV, UV-Visible, PL, FTIR, and TEM lamps. A physical test of carbon dots under a UV lamp showed a change in light intensity, carbon dots with the addition of a passivation agent were brighter than those without a passivation agent. Analysis of the optical properties of carbon dots using UV-Vis spectrophotometer and photoluminescence showed a significant increase in absorbance intensity and emission intensity from 500 a.u to 3600 a.u. FTIR analysis shows the formation of carbon dots which are indicated by the presence of C=C, O-H, C-H, C-O-C, and C-N groups at certain wavenumbers. TEM analysis showed that the carbon dots produced had an average diameter of 1.8 nm. From the analysis, it is identified that the addition of EDTA can improve carbon dots' optical properties.

Keywords: Carbon Dots, Optical Properties, Fluorescence Intensity, Microwave, EDTA

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INTRODUCTION

Sugarcane drops or molasses are a by-product of the sugar-making process. has a high content of sugar compounds, 50-65%.[1] The sugar content in molasses consists of 35% sucrose, 7% glucose, 9% fructose, and 4% other carbohydrates. Molasses is cheap, it is very little utilized and often becomes a problem of environmental pollution because molasses contains calcium oxide which can reduce soil oxygen levels.[2] Due to the high carbohydrate content of molasses, molasses has the potential to be used as an ingredient in the manufacture of Carbon dots, new carbon materials that is below ~10 nm. C-dots are in great demand by researchers due to several advantages, namely unique optical properties, environmental friendliness, low cost, good biocompatibility, electron mobility, high stability, and abundant functional groups.[3] Carbon dots can improve their optical properties by adding passivation agents or heteroatom doping, which aims to form a passive film on the surface to protect the material,[4] to increase the selectivity of a material, to increase the photoluminescence properties of the C–dots surface, to increase the photoluminescence intensity on the carbon dots. Passivation agents that are often used in the synthesis of carbon dots are urea, histidine, PEG, thiourea ethylenediamine, and many other types.[5] In this study, EDTA (Ethylenediaminetetraacetate) was used as a passive agent on the surface of carbon dots. EDTA is cheaper than other chelating agents.[6] The presence of nitrogen contained in EDTA has the potential to improve optical properties and can change the physical properties of carbon dots through the surface of the Carbon dots using a coordinating chemical bond to selectively bind through its amine and carboxylate groups. Several researchers have succeeded in synthesizing carbon dots from various carbon sources, such as[7] synthesizing Carbon dots from cellulose nanocrystals isolated from oil palm empty fruit bunches by the microwave method,[8] synthesis of Carbon dots from granulated sugar as a metal detector for Iron (Fe^{2+})· synthesizing Carbon dots from Carica papaya pulp waste to detect chromium content in water using ethylenediaminetetraacetic acid (EDTA) as a passivation agent.[9] One of the easy and simple

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methods in the synthesis of carbon dots is the microwave method namely a bottom-up approach to synthesizing C-dots simply with several advantages, such as cheap and easy-to-obtain precursors, short reaction time, simple process,[10] has a simple working step. The principle of the microwave method is to vibrate the molecules so that the C-dots are superior. The vibration process causes the carbon chains to undergo rearrangement so that the result does not reduce the water content much in the solution and will not produce C-dots in the form of a gel.[11] Based on the explanation above, the researchers were interested in synthesizing carbon dots from molasses and adding EDTA as a passivation agent using the microwave method to produce carbon dots that have high fluorescence and leaching properties so they can dissolve completely in water.

EXPERIMENTAL

Molasses used in the study was taken from the Talitakum farm shop in the Tanjung Morawa area, Medan. EDTA (Ethylenediaminetetraacetate) was purchased at Merck, Indonesia. The aqua dest and aquabidest used were made in the laboratory during the research.

Synthesis of Carbon Dots from Molasses

A total of 10 g of molasses and 100 mL of water were stirred using a magnetic stirrer while heated at a temperature of 70ºC for 15 minutes. Then was heated using a microwave for 20 minutes to produce a liquid on the bottom of a glass beaker and aerated indoors and then dissolved with added 100 mL water. The solution obtained was centrifuged at a speed of 4500 rpm for 30 minutes to separate the Carbon dots solution from the precipitate. It was dialyzed using a dialysis membrane for 24 hours. The filtrate that has been dialyzed is then concentrated by evaporation to obtain Carbon dots in a blackish-brown liquid.

Synthesis of Carbon Dots from Molasses Addition of Passivation Agent

A total of 10 g of molasses, 10 g of EDTA, and 100 mL of water were stirred using a magnetic stirrer while heated at a temperature of 70˚C for 15 minutes. The solution was heated using a microwave for 20 minutes until a crust was formed on the bottom of the glass beaker. it was created indoors and dissolved with added 100 mL water. The solution obtained was centrifuged at 4500 rpm for 30 minutes. The resulting filtrate was dialyzed using a dialysis membrane for 24 hours. The filtrate that has been dialyzed is then concentrated by evaporation to obtain Carbon dots in a yellowish-brown liquid.

Characterization of Carbon Dots

The physical properties of the synthesized carbon dots were tested for irradiation characterization under a UV lamp, to see the color of the luminescence produced, UV-Vis analysis was used to see the peak absorbance wavelength of the carbon dots, photoluminescence analysis was used to see the long peaks. emission waves and changes in the optical properties of carbon dots, FTIR analysis which is used to determine the functional groups that make up the core and surface state of the carbon dots and Transmission Electron Microscopy (TEM) which is used to determine the average size of the resulting carbon dots.

RESULTS AND DISCUSSION

Synthesis of Carbon Dots from Molasses

Synthesis of carbon dots from molasses without and with the addition of EDTA as a passivation agent using the microwave method has been successfully carried out. The result of heating molasses without a passivation agent produces a reddish-brown crust, while molasses with the addition of a passivation agent produces a blackish-brown crust. The results of microwave heating can be seen in Fig.-1 below.

Fig.-1: Results of Microwave Heating (a) Molasses Without a Passivation Agent (b) Molasses with the Addition of a Passivation Agent

The crust obtained from the carbon dots synthesis process was then added with distilled water and followed by a centrifugation and dialysis process to produce a carbon dots solution as shown in Fig.-2 below.

Fig.-2: Carbon Dots without Passivation Agent (a) Carbon Dots with Passivation Agent (b)

The resulting carbon dots will then be characterized using a UV lamp, UV-Visible spectrophotometer, FTIR, and TEM.

Analysis with UV Lamp

Physical properties tests of carbon dots without and with passivating agents can be carried out using a simple analysis under a 366 nm UV lamp. The results of the analysis can be seen in Fig.-3 and Fig.-4 below

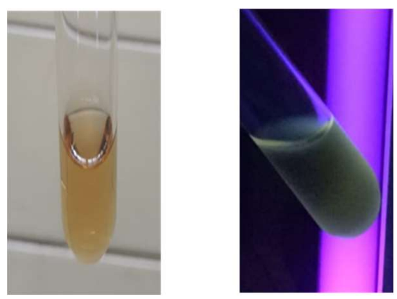

Fig.-3: Carbon Dots Solution Without Passivation Agent (a) in Visible Light (b) in UV Light

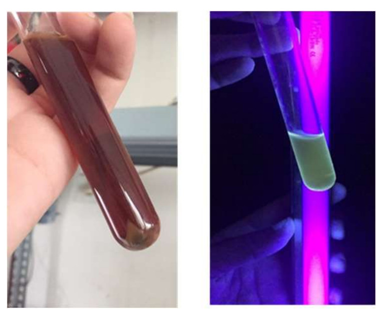

Fig.-4: Carbon Dots Solution with Passivation Agent (a) in Visible Light (b) in UV Light

The results of testing the physical properties of carbon dots under a UV lamp show that there are differences in the luminescence of carbon dots without a passivating agent and with a passivation agent. Based on the test results of the two samples of carbon dots showed a green color was emitted. For carbon dots with the addition of a passivation agent, it looks brighter than those without a passivation agent. This indicates that there has been a change in the physical properties of the carbon dots after the addition of EDTA as a passive agent of the carbon dots and the results obtained are by the results of research[9] which has succeeded in synthesizing carbon dots from papaya peel waste.

Absorbance Spectrum Analysis with UV-Vis Spectrophotometer

The optical properties of carbon dots were characterized by using a Shimadzu UV-Vis 1700 spectrophotometer which was used to determine the peak absorbance wavelength of carbon dots molasses without passivation agent and with passivation agent. The results of the carbon dots analysis are shown in Fig.-5 below.

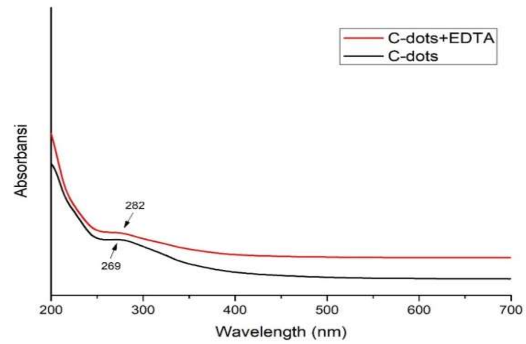

Fig.-5: Absorbance and Wavelength Curves of Carbon Dots Without Passivation Agent and with Passivation Agent

The results of the absorption measurement of carbon dots based on molasses showed a shift in the absorption peak after the addition of EDTA as a passivation agent from a wavelength of 269 nm to 282 nm. These two absorption peaks indicate the existence of an electron transition from $\pi \rightarrow \pi^*$, which indicates the presence of a C=C group which is the core constituent of the carbon dots. Along with the shift in wavelength, carbon dots with the addition of a passivation agent also experienced a change in the increase in the absorbance peak to be higher than carbon dots without a passivation agent. This indicates that there has been a change in the optical properties of the carbon dots after the addition of EDTA as a passive agent on the surface of the carbon dots. The analysis results obtained are by the research reported by[12] which has succeeded in synthesizing carbon dots from graphite as a precursor with UV-Vis results showing a shift in wavelength towards red after the addition of passivation agents/heteroatom doping. The size of the Carbon dots affects the fluorescence and the wavelength to be absorbed, where the smaller the size of the Carbon dots, the smaller the absorbed wavelength.[13] So the results obtained indicate that the carbon dots with the addition of a passivation agent have a larger size than the carbon dots without a passivation agent.

Analysis of Photoluminescence Carbon Dots Without and With Passivating Agent

Analysis of the optical properties of carbon dots was also carried out using a fluorescence spectrophotometer Ocean Optics SpectraSuite HR2000. This analysis was carried out to see the peak emission wavelength produced from carbon dots molasses without a passivation agent and with a passivation agent using an excitation wavelength of 405 nm. Figure-6 shows the fluorescent intensity relationship curve with a wavelength of the carbon dots without the addition of a passivation agent and with the addition of a passivation agent.

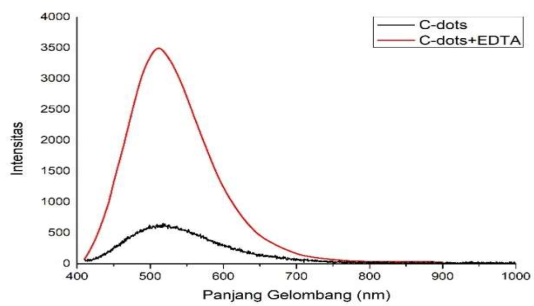

Fig.-6: Fluorescent Intensity Relationship Curve with Wavelength

Based on the characterization results in Fig.-6, the photoluminescence analysis of carbon dots molasses without a passivation agent shows the emission peak is at a wavelength of 510 nm while with the addition of a passivation agent, it is at a wavelength of 515 nm. The results obtained are from previous studies where the emission wavelengths produced from sugar-based carbon dots are in the range of 420-560 nm.[14] Carbon dots with the addition of EDTA as a surface passive agent were also shown to have an increase in optical properties, which was indicated by an increase in the photoluminescence intensity of the carbon dots after the addition of the passivation agent. This is to previous studies which stated that the addition of a passivation agent to carbon dots could increase the fluorescence intensity.[15]

Functional Group Analysis with FT-IR

The results of the FTIR analysis of molasses-based carbon dots without a passivation agent and carbon dots with a passivation agent can be seen in Fig.-7.

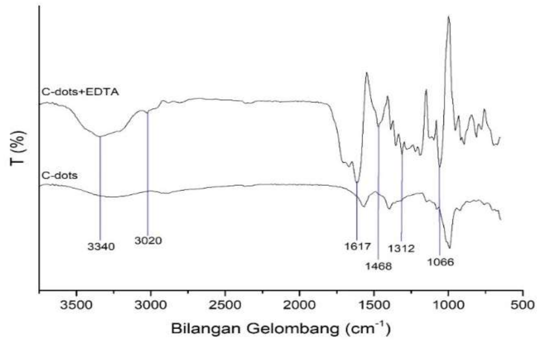

Fig.-7: FTIR Spectrum of Carbon Dots Based on Molasses Without Passivation Agent and with Passivation Agent

Based on the FTIR spectrum above, it can be seen that carbon dots with the addition of a passivation agent have differences from carbon dots without the addition of a passivation agent. There is absorption at a wavenumber of 3340 cm^{-1} that shows an OH group, a wavenumber of 3020 cm^{-1} shows a CH stretching group, a wavenumber of 1617 cm^{-1} shows a C=O group, a wavenumber of 1468 cm $^{-1}$ shows a C=C group, a wavenumber 1312 cm^{-1} shows a CN group and a wave number 1066 cm-1 shows of a COC group. The presence of C-N groups is assumed to come from EDTA so it can be said that the carbon dots produced are already passivated. The results of the FTIR analysis show that there are C=C groups that make up the core of the carbon dots and O-H, C-H, and C-O-C groups which are part of the surface carbon dots.[16,17]

Analysis of the Average Size Distribution with TEM

Analysis of the average diameter size on carbon dots molasses was characterized by TEM JEOL JEM 1400 at 100 kV with various magnifications. The results of the TEM analysis of molasses-based carbon dots with the addition of an EDTA passivation agent can be seen in Fig.-8.

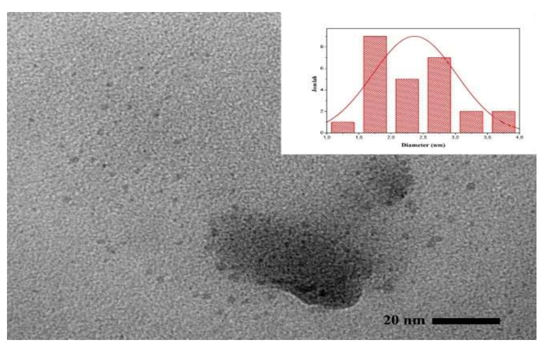

Fig.-8: Results of TEM Carbon Dots with the Addition of a Passivation Agent

Based on the calculation of the diameter of the Carbon dots using the Image J application, the average diameter of the carbon dots with a passivation agent was 1.8 nm. The average diameter size of the carbon dots obtained is by statement [2] which states that Carbon dots are a class of nanomaterials of dimension 0, with a particle size of less than 10 nm. So, the results obtained prove that carbon dots with the addition of a passivation agent have been successfully carried out. In this study, the average diameter measurement was only performed on carbon dots with the addition of a passivation agent. This is related to the results of the UV-Vis test that has been carried out on both samples, which shows that the peak UV-Vis wavelength for carbon dots with the addition of a passivation agent is longer than that without a passivation agent. This shows that the size of the carbon dots with the addition of a passivation agent is greater than that without a passivation agent so the size test is carried out only on carbon dots with the addition of a passivation agent as a sample which proves that both carbon dots have been successfully synthesized with an average size below 8 nm.

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CONCLUSION

From the research that has been done, it can be concluded that carbon dots made from molasses without a passivation agent and with the addition of EDTA as a passivation agent using the microwave method have been successfully carried out. EDTA as a passivation agent has been proven to be able to change the carbon dots' physical properties by a test under a 366 nm UV lamp which is characterized by a change in the carbon dots' luminescence, which initially is green with a faint intensity then after the addition of a passivation agent, there is an increase in luminescence to the bright green solution. Carbon dots with the addition of EDTA have also been proven to be able to improve the optical properties of carbon dots which are indicated by an increase in absorbance intensity along with a shift in the wavelength peak towards red. Changes in the carbon dots' optical properties with the addition of a passivation agent were also proven by photoluminescence analysis which was characterized by a significant increase in the carbon dots' emission intensity after the addition of EDTA as a surface passive agent. From the results obtained, it can be concluded that the role of EDTA in improving optical properties and changing the molasses carbon dots' physical properties as a carbon source has been successfully carried out.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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