

Synthesis of carbon dots based on corn cobs as heavy metal ion sensors using the microwave method

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Abstract: Carbon dots (CDots) are nanomaterials that can be applied as a heavy metal ion sensor. CDotss ware synthesized from corncobs which are abundant and underutilized. This study aims to determine the effect of variations in the concentration of corncobs on optical properties of CDots and their application as Fe³⁺ ion sensors. CDots were synthesized with variations of corncobs' mass 5, 10, 15, and 20 g and variations in metal ion concentrations 10⁻⁷, 10⁻⁶, 10⁻⁵, 10⁻⁴, and 10⁻³ M. The success of CDots synthesis was indicated by luminescence green when exposed to UV light. UV-Vis characterization showed that the greater the concentration of CDots could cause a shift in the absorbance peak towards longer wavelengths and peaks at wavelengths of 290, 291, 295, 298, and 323 nm, respectively. Photoluminescence (PL) characterization showed CDots emission peaks at 511, 504, 503, and 495 nm. The greater the concentration of CDots can cause a shift in the emission peak towards a shorter wavelength and increase the intensity. The PL characterization can identify the presence of Fe³⁺ metal ions with a wavelength shift that indicates a change in the CDots structure. The synthesis of CDots from corncobs have great potential to be applied as sensors.

Keywords: CDots, corn cobs, metal, microwave.

1. Introduction

Carbon Dots (CDots) are zero-dimensional carbon nanomaterials. CDots are promising materials because they have many uses in technological advancements such as those applied to chemosensing, biosensing, imaging, cancer therapy, solar cell catalysts, and sensors (Chen et al., 2019). CDots have great resistance to light. The heterogeneous size distribution of CDots results in discrete energy levels leading to very different optical, electrical, and chemical properties from other nanoparticles (Putro & Maddu,

2019). CDots have advantages such as biocompatible, inert, low toxicity, easy to modify (Sjahriza et al., 2017).

Technological developments in various aspects have positive and negative impacts. When viewed from an environmental point of view, it often brings pollution. One of the most common pollutants is heavy metal pollution. Many analytical techniques have been established to detect heavy metals such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP MS), and electrochemical methods. Although this analytical method is very accurate, it still has drawbacks such as expensive instruments, complicated operations, and long sample preparation (Zhao et al., 2019).

CDots can be applied as environmentally friendly sensors, so this material can be developed for pollution detectors because it is easy to manufacture and cheap. Salamba (2018) succeeded in researching CDots synthesized from organic materials as pollution detectors with changes in optical properties, namely shifting wavelengths. CDots can be synthesized from various organic materials, one of which is corn waste.

Corn waste is underutilized, causing pollution (Alighiri et al., 2018). Corn waste in the form of straw, cobs, and husks is a large amount of corn cropping waste. As much as 20-30% of 100 kg of corn produced is corn waste (Aziz et al., 2015). According to Muhlis (2016) the energy potential of corn cobs is 55.75 GJ. The nature of corn cobs which have a high carbon content, from the results of chemical analysis, corn cobs contain 83.7% fixed carbon (Widodo et al., 2007).

Corn cobs can be used as the main ingredient for the synthesis of CDots. CDots utilize the carbon contained in corn cobs to produce nano-sized carbon particles that can be applied as sensors. In this study CDots were developed as heavy metal sensors. Before CDots nanomaterials were developed, the sensors used were conventional quantum dot semiconductors such as CDots for metal detectors. However, this material is toxic to living things (Zhu et al., 2012) so that CDots nanoparticles were developed for metal sensors because of their low toxicity, high chemical stability, and do not pollute the environment.

In general, there are two ways to make CDots, namely bottom-up and top-down synthesis methods. The bottom-up method is to break down the carbon dot from the raw molecules. These synthesis methods include combustion, microwave, hydrothermal, ultrasonic, supported synthetic, and acid oxidation. While the top-down method is to break large particles into nanometer-sized particles. These methods include laser ablation, electrochemical synthesis, plasma treatment, and arc discharge (Chen et al., 2019). Several methods have been mentioned, the microwave method is an easy method. The microwave method is carried out by a heating process using microwaves because the resulting microwaves can simplify and speed up the synthesis process (Rahmayanti, 2015).

This research was conducted with the aim of knowing the effect of variations in the concentration of corn cobs on the optical properties of CDots and their application as metal ion sensors. Corn cobs are abundant and abundant, but they are often not managed properly so that they can be used optimally as a raw material for CDots (Zhang et al., 2019). Utilization of the optical properties of CDots as a sensor in this case is applied as

a heavy metal ion detector. To find out, characterization was carried out using UV-Vis Spectroscopy and Photoluminescence Spectroscopy (PL).

2. Experimental

2.1. Tools and Materials

The tools needed are a crusher / blender / grater, beaker, measuring cup, measuring flask, glass funnel, stirring spatula, measuring pipette, volume pipette, Ohaus scale, magnetic stirrer DLAB MS-H280-Pro, microwave SAMSUNG ME731K 2450 MHz, Centrifuge Zenthlab LC-04S 5000 rpm, and cuvette quartz. Then the 254 nm UV box was used as a visual test of the sample. UV-1800 absorbance test SHIMADZU UV Spectrophotometer and PL test using Ocean Optics MayaPro200 picosecond laser spectrometer. The materials used in this study were corn cobs and aquades. Corn cobs were used as the main material for the synthesis of CDots because of their high carbon content and FeCl_3 ($M_r = 162.204 \text{ g/mol}$) was used as metal ions Fe^{3+} .

2.2. Microwave technique CDots synthesis

Corn cobs were synthesized into CDots using a bottom-up method of microwave heating (Ng et al., 2021). The processing process begins with weighing 5 g of corn cob powder, plus 100 mL of distilled water and then using a magnetic stirrer with a rotating speed of 520 rpm for 20 minutes. The mixture was filtered and the filtrate was taken 30 mL. The filtrate solution was heated in the microwave at 450 Watt for 15 minutes. The resulting corncob crust was then dissolved with 40 mL of distilled water. The solution was centrifuged at a speed of 500 rpm for 10 minutes to separate unused carbon deposits that did not become CDots and agglomerated particles to obtain the desired CDots colloid (Fatimah et al., 2017). CDots colloid was tested visually using a 254 nm UV box to determine the optical response of CDots in the form of fluorescence which indicated that CDots had been successfully produced (Feng et al., 2017). The synthesis step was repeated for variations of 10, 15, and 20 g . corn cob powder.

2.3. Metal solution preparation

A total of 1.622 g of FeCl_3 powder was dissolved and diluted to 100 mL, resulting in a 10^{-1} M FeCl_3 solution. A 10^{-1} M FeCl_3 solution was diluted to obtain a FeCl_3 solution with concentrations of 10^{-7} , 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M. FeCl_3 solution with various concentrations is then mixed into CDots (Nurfathiya, 2017).

2.4. Preparation of CDots samples for characterization

All CDots with 4 concentration variations can be directly characterized without the addition of reagents. In addition to pure CDots, characterization was also carried out on CDots with metal solution added. CDots synthesized from 20 g of cornstarch were used as a metal ion mixture. With a ratio of 1:2 CDots 2 mL was taken and then 4 mL of metal

ion solution was added, carried out using all variations in the concentration of each metal 10^{-7} , 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M (Boobalan et al., 2020).

2.5. CDots sample characterization

Tests using a UV-Vis spectrometer were carried out to determine the optical absorption to analyze the absorbance of CDots with a UV-Vis excitation source. Tests using a PL spectrometer were carried out to determine the wavelength of the light emission produced.

3. Results and Discussion

The samples that have been successfully synthesized include CDots with four concentration variations and the application of CDots as a Fe^{3+} metal ion sensor. The heating process makes the particles become nano-sized, the color of the resulting solution is clear yellow-golden. Heating using electromagnetic wave energy causes the corncob filtrate molecules to vibrate so that the carbon chains will undergo rearrangement in the carbonization process and produce CDots like crust (Amri & Marpongahtun, 2021). In the heating process, the microwaves generated by the microwave break the chain of particles on the corn cobs so as to produce carbon chains (Prasetya, 2012).

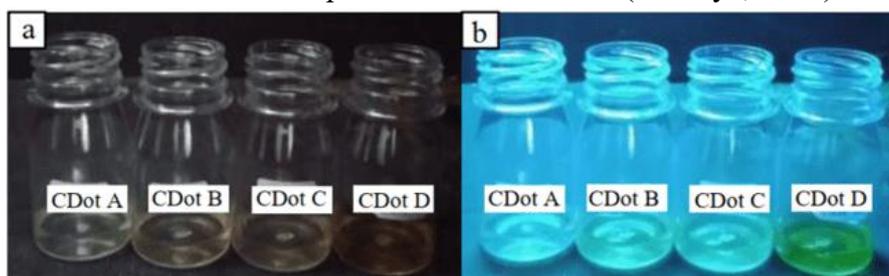


Figure 1. CDots sample (a) without UV lamp, (b) exposed to UV lamp

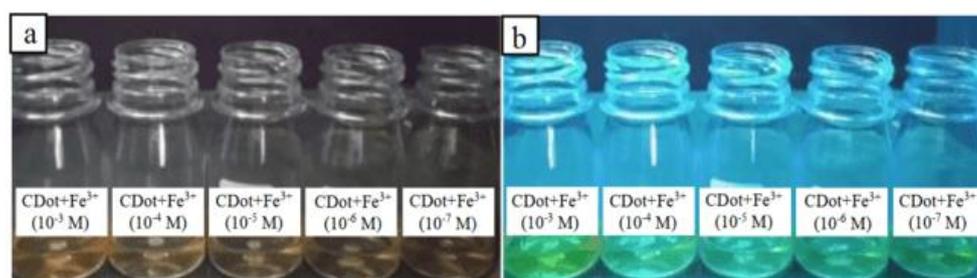


Figure 2. Sample CDots+ Fe^{3+} (a) without UV lamp, (b) exposed to UV lamp

All CDots samples were tested visually by irradiating a UV lamp with an excitation wavelength of 254 nm. When it hits the sample, CDots emit a turquoise glow as shown in Figure 1b. In contrast to the non-laser-irradiated sample shown in Figure 1a. The same thing was done on CDots samples mixed with Fe^{3+} metal ions. Based on Figure 2a, it can be seen that the sample that is not exposed to a UV lamp is brownish yellow, the greater the concentration of metal ions, the color will be darker. In Figure 2b is a sample irradiated with a UV lamp. In the picture there is a green glow. UV light is scattered by nano-sized particles. The green glow is the emission produced by these CDots. Based on references from Feng et al (2017) CDots emit light in the visible light range when excited by UV

light. So from these observations, physically all samples have become CDots material because they can emit greenish light when exposed to UV lamps (Ng et al., 2021).

The energy of UV light causes glow because it generates electrons. This energy will cause excitation and deexcitation in the form of a jump of electrons from the valence band to the conduction band under certain conditions. The electrons will then return to their ground state to fill the vacancies. The return of electrons to the ground state has excess energy which is then emitted in electromagnetic waves (Putro & Roza, 2018). In the next step, the samples were further tested using UV-Vis and PL Spectroscopy.

Characterization using UV-Vis Spectroscopy was carried out to determine the peak absorbance wavelength in each sample (Puto & Roza, 2018). Variations in the concentration of corncob solution used in the manufacture of CDots resulted in different quality of CDots. Physically, it can be seen that the higher the concentration of the cob solution used, the more concentrated the CDots produced, as shown in Figure 1a (Salamba, 2018).

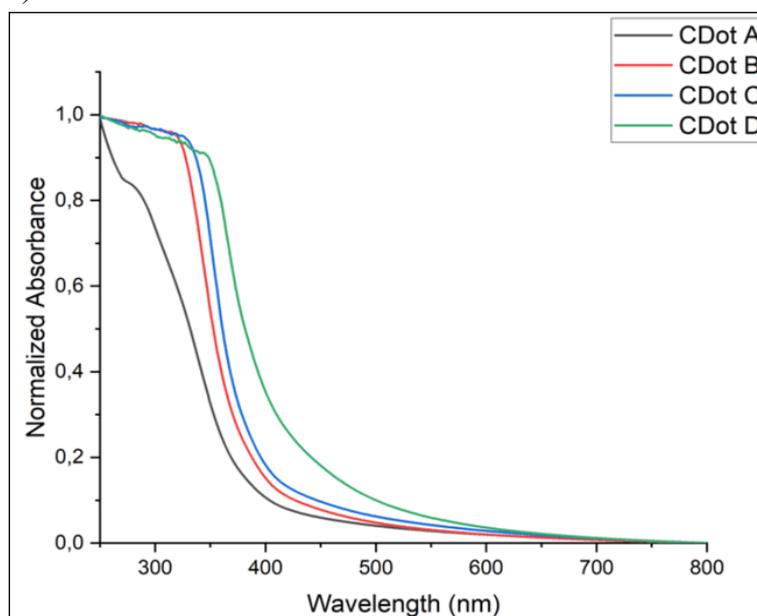


Figure 3. The results of UV-Vis spectra from CDots samples with varying concentrations of 5% (CDots A), 10% (CDots B), 15% (CDots C), and 20% m/v (CDots D)

Absorbance measurements were carried out in the wavelength range from 250 to 800 nm. The result obtained is a graph of the relationship between wavelength and absorbance. Figure 3 shows the normalized absorbance results from CDots with four concentration variations. Where CDots A, B, C, and D were CDots synthesized from 5, 10, 15, and 20 g corn cob powder, respectively. The typical peaks of these spectra were obtained at wavelengths of 278, 315, 326, and 345 nm, respectively. This is in accordance with Soni's (2016) study which showed that the absorbance spectra of CDots were measured at a wavelength of 260 – 360 nm. The absorbance spectra in the UV region are related to the presence of conjugated compounds in the CDots structure. In this region, there is an electronic transition mechanism in the orbital $\pi \rightarrow \pi^*$ of $C\equiv C$ (Alam, 2019).

Concentration variations in the synthesis of CDots affect the absorbance peak yield. Based on the absorbance results, Figure 3 shows that the higher the concentration of CDots, the higher the absorbance peak will shift to the right. The results of research conducted by Isnaeni et al (2018) stated that the absorbance spectra of CDots with variations in concentration could significantly change the absorbance spectra. The concentration of CDots is related to the amount of CDots contained in a given volume. When the concentration of CDots is high, the distance between the C atoms is getting closer, and vice versa. When the distance between the C atoms is far, the properties of the C atoms become individual, whereas when the distance between the C atoms is close together, there will be overlapping energy so that a new energy level appears which causes the wavelength to be longer.

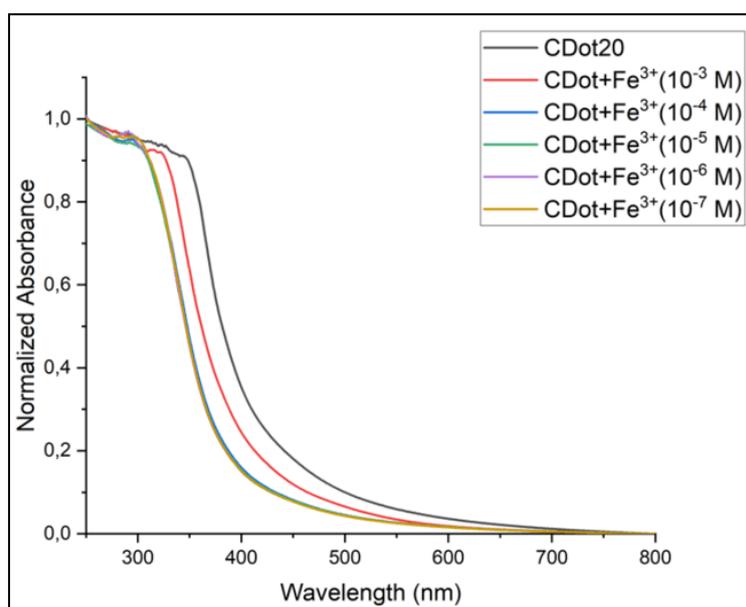


Figure 4. The results of the UV-Vis spectra of the Fe^{3+} metal ion detection sample with variations in concentrations of 10^{-7} , 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M

CDots samples made to detect Fe^{3+} metal ions were also tested for absorbance using UV-Vis spectroscopy. The metal ion concentrations used were 10^{-7} , 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M. In Figure 4 is the absorbance result of the detection of Fe^{3+} metal ions. The absorbance peaks obtained were 290, 291, 295, 298, and 323 nm, respectively. The greater the concentration mixed in the CDots will cause the absorbance peak to shift to the right.

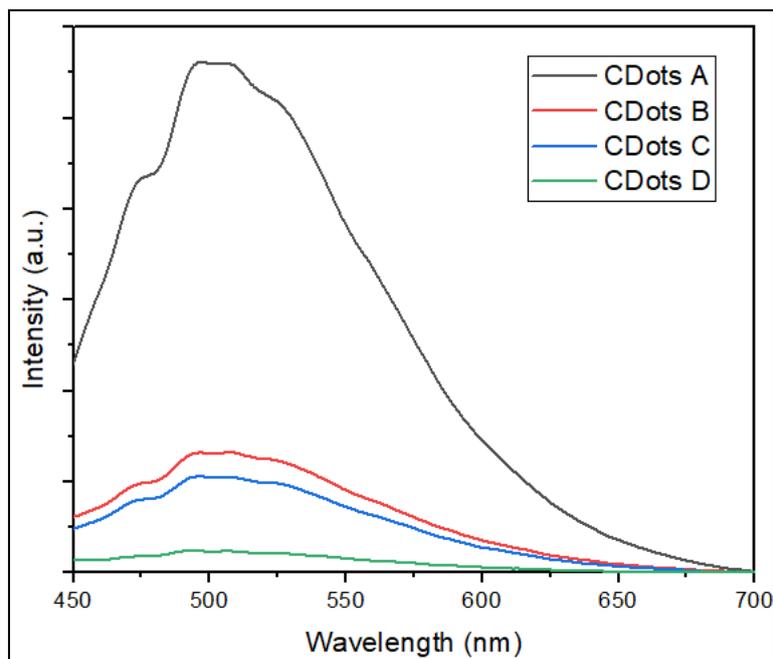


Figure 5. Results of PL spectra of CDots samples with varying concentrations of 5% (CDots A), 10% (CDots B), 15% (CDots C), and 20% m/v (CDots D)

Photoluminescence (PL) characterization was carried out to determine the emission wavelength produced by corncob-based CDots synthesized by the microwave method. The results of the PL characterization relate to the transition from the excited state to the ground state so that it will form a PL spectra consisting of the emission of the excitation wavelength on the X-axis and the intensity on the Y-axis. Intensity means the physical lightness of the dim luminescence of CDots, and the wavelength means the physical color of the luminescence (Ghifari et al., 2017). Based on Figure 5, it can be seen that the peak emission waves from the PL spectra are affected by variations in concentration. Samples of CDots A, B, C, and D have peak emission wavelengths, namely 511, 504, 503, and 495 nm, respectively. This indicates that the higher the concentration, the more shifting the peak wavelength will occur (Isnaeni et al., 2018). The addition of CDots concentration causes a shift in the emission wavelength to a shorter wavelength and increases the intensity (Alimah, 2017).

The existence of a shift in the peak emission wavelength indicates a change in the structure of the CDots caused by the bonding of the matrix molecules in the surface state (Fatimah et al., 2017). The higher intensity value indicates that the number of CDots produced is increasing. The spectral mechanism of the luminescence intensity is associated with the emission state through the energy gap, where the transition depends on the particle size and surface conditions of the smaller and more homogeneous CDots (Putro & Roza, 2018).

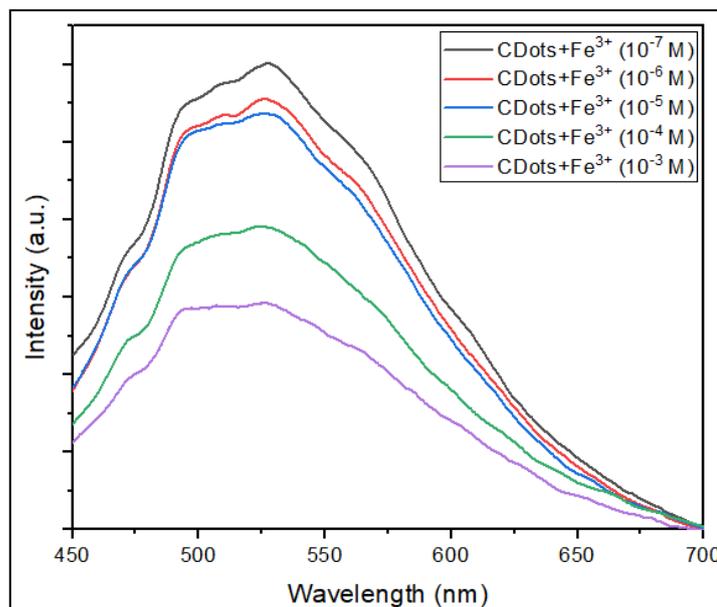


Figure 6. The results of the PL spectra of the heavy metal ion detection samples of Fe³⁺ with variations of 10⁻⁷, 10⁻⁶, 10⁻⁵, 10⁻⁴, and 10⁻³ M

This test of the ability to detect CDots heavy metal ions was carried out to determine the effect of increasing the concentration of Fe³⁺ metal ions on the luminescence intensity of CDots when a number of metal ions were added to CDots. This test shows that CDots can be used as metal ion sensors. The CDots solution mixed with metal ions experienced an increase in luminescence intensity when tested under a 254 nm UV lamp (Fig. 2b). The results of the Fe³⁺ metal ion detection spectra obtained from the PL characterization are shown in Figure 6. The emission peaks produced by the PL spectra were based on metal ion concentrations of 10⁻⁷, 10⁻⁶, 10⁻⁵, 10⁻⁴, and 10⁻³ M, respectively. also are 526, 527, 527, 528, and 528 nm. The addition of Fe³⁺ metal ions has been shown to reduce the intensity (Alimah, 2017). The greater the concentration of Fe³⁺ metal ions mixed in CDots will cause less CDots content in the solution, this indicates a decrease in the intensity of luminescence in the solution (Putro & Roza, 2018). In addition, the decrease in intensity also indicates the sensitivity of CDots as the detection of Fe³⁺ metal ions. This is in accordance with Alimah's research (2017) that the steeper the decrease in intensity with increasing concentration indicates that the more sensitive CDots are for detecting metal ions in response to Fe³⁺ ion analytes.

4. Conclusion

Based on the research that has been done, it can be concluded that variations in the concentration of corn cobs affect the optical properties of CDots. The higher the concentration of CDots causes a shift in the absorbance peak towards a longer wavelength and the emission peak towards a shorter wavelength and increases the photoluminescence intensity. The application of CDots as metal ion sensors is known from the optical properties of CDots which can be seen from the shift of the absorbance peak towards a longer wavelength and a significant decrease in photoluminescence intensity.

5. Suggestion

The use of corn cobs in the synthesis of CDots nanomaterials needs to be maximized for powder preparation in order to obtain the maximum carbon source. In addition, in this study the metal ion content cannot be known with certainty by the tests that have been carried out. Therefore, in improving the performance of the sensor with respect to its sensitivity to detect metal ions, it is possible to test the content of other metal ions besides Fe^{3+} and other tests that support it.

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