

# Nitrogen-doped Carbon Dots Derived from Green Algae and Ammonia as Photocatalyst Material

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**ABSTRACT** – Carbon dots are a novel carbon-based material with the appealing properties of inexpensive nanomaterials, low toxicity, environmental tolerance, abundance, photostability, and simplicity of synthesis. Carbon dots (CDs) have effectively distinguished themselves from other materials due to their superior properties, such as ultra-small size, good photostability, excellent biocompatibility, and tunable fluorescence properties. This study synthesized carbon dots from green algae and ammonia solution as the nitrogen dopant precursor using a hydrothermal method at 180°C. Green algae contain carbohydrates, proteins, and poly-unsaturated fatty acids, allowing them to produce more carbon and be used as a precursor in synthesizing carbon dots. The Fourier transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectra reveal the distinct functionalization and energy gap between the surface states of CDs and nitrogen-doped carbon dots (N-CDs). The carbon nanoparticles were then used as photocatalysts to degrade methyl red. The results indicate that nitrogen doping is superior for reducing methyl red and has tremendous potential for environmental applications.

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## INTRODUCTION

Green algae is a low-level organism that has adapted to various environments by evolving distinct growth habits. Green algae are abundant in the freshwater ecosystem of Indonesia [1]. Green algae had the highest crude carbohydrates (22.5–42%) than other algae [2]. Due to its high carbon content, green algae biomass is an acceptable option for carbon production. The biological characteristics of the carbon source influence the elemental composition of the ultimate product. As an illustration, the protein functions as a nitrogen source, whereas the presence of chlorophyll contributes to magnesium/nitrogen in the natural product in addition to carbon [3]. The utilization of algae as a carbon source is a sustainable waste recovery strategy since it can prevent waste accumulation and is a cost-effective option.

Carbon dots (CDs) are newly developed fluorescent carbon nanomaterials among the most important members of the carbon nanomaterials family [4]. CDs are three-dimensional clusters composed of carbon atoms and trace amounts of molecules. The inner parts of the three-dimensional clusters are mostly made up of  $sp^3$  hybridization carbon atoms, with a small amount of  $sp^2$  hybridization carbon atoms [5]. CDs are currently a widely researched topic in science due to their unique size and benefits [6]. CDs consist of core and functional groups on their surface. The most common functional groups are hydroxyl groups ( $-OH$ ), carboxyl groups ( $-COOH$ ), carbonyl groups ( $-CO$ ), and amino groups ( $-NH_2$ ). Functional group manipulation and doping can be used to change the properties of the CDs surface and the core, respectively, that have an impact on optical characteristics [7].

The controllable synthesis of carbon dots is still in its early stages of development. Bottom-up synthesis methods can create CDs from various organic acids and biomass sources [8]. The bottom-up method is a synthesis method in which CDs are formed from precursor molecules. Bottom-up approaches include the microwave-assisted method, pyrolysis, ultrasonic method, and hydrothermal method [9]. They have the advantages of low cost, simple operation, and low equipment requirements and have thus been widely used in the synthesis of C-dots [10]. Organic domestic garbage and residues from agriculture, fishery, poultry, animal, forestry, and related industries have been used to synthesize CDs from biomass [11].

The hydrothermal method is one of the most commonly used procedures in CDs synthesis because the setup is simple, and the result particle is almost uniform in size and has a high quantum yield [12]. The organic or inorganic carbon source is dissolved in an aqueous solution and transferred to a Teflon-lined stainless steel autoclave. After continuous heating, the raw carbon source will be converted to CDs under high temperature and pressure conditions [12]. The hydrothermal method has the advantages of being environmentally friendly, low cost, simple to operate, and requiring only basic equipment [13].

Many researchers have used heteroatom doping to improve the properties of CDs. The majority of these substances were doped with non-metal heteroatoms, including nitrogen (N), sulfur (S), boron (B), or phosphorus (P) [14].

Incorporating heteroatoms into the carbon atom framework can effectively control the electrical, internal, and surface chemical properties of CDs [15]. The nitrogen atom is commonly doped into carbon materials due to its similar atomic size to a carbon atom, five outermost orbital electrons, and higher electronegativity than carbon. Nitrogen doping at carbon resulted in a high quantum yield and a red emission wavelength shift [16].

CDs can be used in various ways, including as photocatalysts for managing textile industry waste. High concentrations of dyes discarded carelessly and without proper treatment can contaminate the ecosystem, kill aquatic life, and endanger humans and other animals if swallowed or inhaled [17]. Methyl red is a common textile coloring agent. Because methyl red is a mutagenic dye, efforts must be made to reduce its toxicity and environmental pollution [18]. The photocatalytic degradation method has the advantage of being simple to implement and inexpensive [19].

This paper presents the synthesis of novel nitrogen-doped carbon dots (N-CDs) by a one-pot hydrothermal process, utilizing green algae and ammonia as precursors. The N-CDs from ammonia solution as a nitrogen source are discovered to be uniformly sized spherical nanoparticles with significant optical characteristics [20]. The impact of ammonia concentration on the synthesis of N-CDs was investigated through several analytical techniques, including Fourier-transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, and UV-light irradiation. Furthermore, CDs and N-CDs from green algae were carried out as an application to degrade methyl red. It is hoped that CDs from green algae can effectively degrade methyl red contained in industrial waste to assistance overcome environmental problems.

## EXPERIMENTAL METHOD

### Materials and Instruments

Green algae used as raw materials was obtained from a local market. Aquades, alcohol, ammonia (NH<sub>3</sub>), and methyl red (MR) used in our experiment were analytical reagents without further treatment. The Fourier transform infrared (FTIR) spectra of materials were measured using an FTIR spectrometer (FTIR, FT 1000 Varian) to determine the functional groups of carbon dots (CDs) and nitrogen-doped carbon dots (N-CDs) in the scanning range of 4000–400 cm<sup>-1</sup>. UV-visible absorption spectra were determined using a UV-visible spectrophotometer (Varian Cary 50), observed between 200–800 nm. The light fluorescence generated by UV-Light 395 nm obtains the luminescence color of CDs and N-CDs.

### Method and Procedure

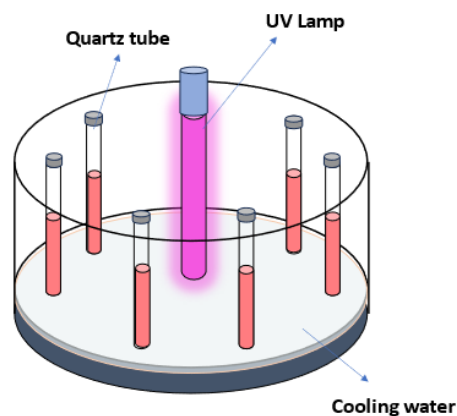
Synthesis of CDs from green algae using the hydrothermal method with various doping nitrogen. A total of 6 grams of green algae were mashed and added with 60 mL aquades for CDs and various ammonia concentrations of 1, 2, and 3% (v/v) for nitrogen doping for N-CDs samples with sample code of NCD-1, NCD-2, and NCD-3, respectively. Afterward, the green algae were transferred into a 100 mL Teflon-lined autoclave and heated at 180°C for 5 hours. After completion of the reaction, the autoclave was cooled naturally to room temperature, and CDs and N-CDs samples were centrifuged at 1000 rpm for 10 minutes to remove the larger particle. The obtained brown liquid phase was filtered through a 0.22 μm filter membrane and stored in a refrigerator for the following process.

The FTIR technique is used to determine functional groups in the sample. At room temperature, the spectra were obtained within the wave number range of 4000 to 400 cm<sup>-1</sup>. The sample spectrum was compared to standard and reference data from previous journals to conduct the analysis.

Degradation methyl red (MR) solution under UV-light irradiation. In detail, the experiment was carried out at room temperature using a homemade reactor (Figure 1). The CDs were added to 10 ppm MR solution with a ratio of 2:3 (vol) and irradiated with UV lamps. The absorbance intensity of the MR solution was measured every 30 minutes with a visible spectrophotometer AMTAST AMV01, and the degradation efficiency of the MR was calculated using the following equation [21].

$$\eta(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

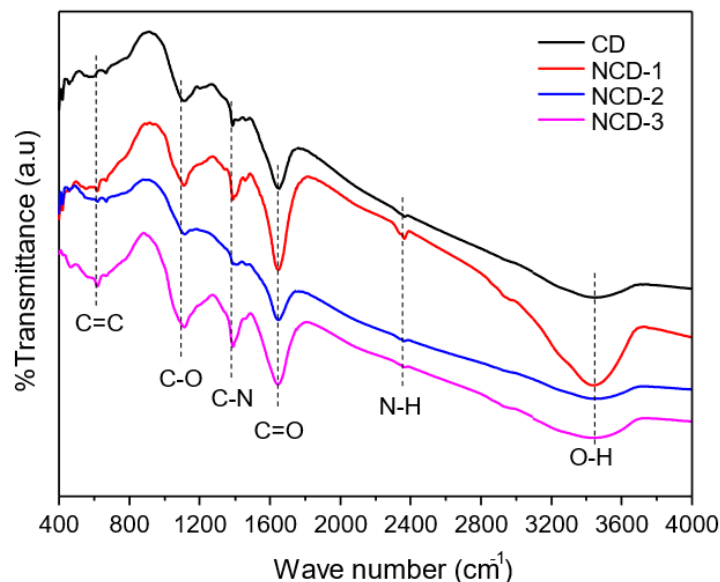
where  $C_0$  is the initial concentration of MR and  $C_t$  is the concentration after  $t$  min reaction.



**Figure 1.** Design of reactor photocatalyst

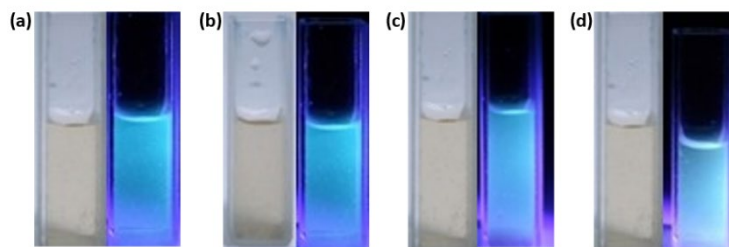
## RESULT AND DISCUSSION

Figure 2 illustrates the Fourier transform infrared (FTIR) spectra of each sample used to determine the identification of the functional groups present in the samples. The FTIR results of carbon dots (CDs) and nitrogen-doped carbon dots (N-CDs) are consistent with previous research [22], [23]. In the range of  $3400$  to  $3500\text{ cm}^{-1}$ , there were absorption peaks assigned to the OH vibration (hydroxyl group). The absorption peak at  $2360\text{ cm}^{-1}$  was attributed to  $\text{-NH}$  and  $\text{-OH}$  stretching vibrations, whereas the strong peak at  $1640\text{--}1690\text{ cm}^{-1}$  was attributed to  $\text{C=O/C=N}$  stretching vibrations of the amide group [24]. The  $1300\text{--}1450\text{ cm}^{-1}$  peak was attributed to  $\text{C-N}$  stretching (carbonyl group) [25]. These results confirmed that the N-containing groups were formed through a hydrothermal process between green algae and ammonia [26]. The increasing of dopant concentration, increased the peak intensity of  $\text{C-N}$  functional group. The  $\text{C-O}$  vibrations of carboxyl groups are responsible for the  $1100\text{--}1150\text{ cm}^{-1}$  peak, while the peak at  $670\text{ cm}^{-1}$  corresponds to the  $\text{C=C}$  bond [27].



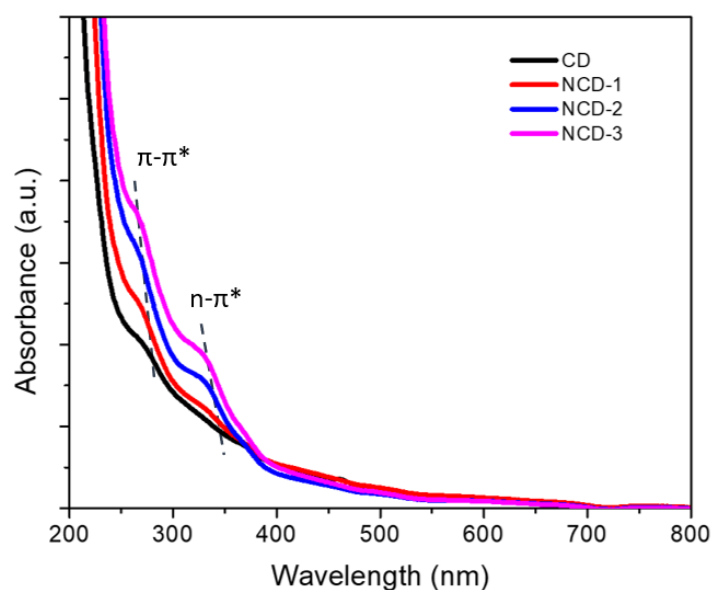
**Figure 1.** FTIR spectra of the CDs and N-CDs from green algae

Furthermore, UV-light testing with a wavelength of  $395\text{ nm}$  was conducted to analyze the luminescence of light produced by CDs from green algae. The process of forming CDs from green algae is successful when the CDs samples from green algae showed fluorescent blue-green when irradiated with UV light [28]. This indication is based on the fact that CDs have photoluminescence properties when irradiated with UV light around the wavelength of  $330\text{--}460\text{ nm}$ , as shown in Figure 3. Blue emissions are seen to be excitation-dependent, which is linked to the carbon core. Stronger blue fluorescence is supported by simultaneously excited carbon nuclei at  $\lambda_{\text{exc}} \leq 460\text{ nm}$  and lower excitation wavelength. This is because blue fluorescence results mostly from electron-hole recombination in the carbon core state of carbon dots [29].



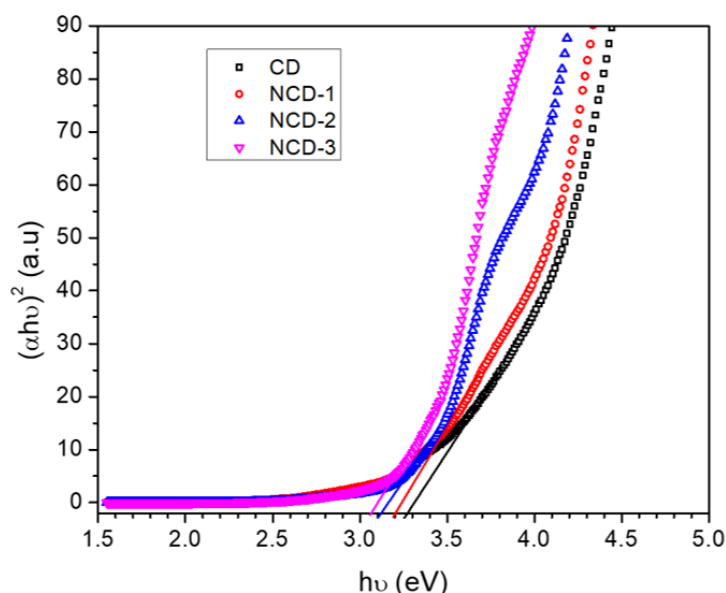
**Figure 2.** UV illumination of the CDs from green algae: (a) CD; (b) NCD-1; (c) NCD-2; and (d) NCD-3

The UV-vis characterization results are shown in Figure 4 as a graph of the relationship between wavelength and absorbance. Figure 4 shows the two different absorption peaks with various N doped. In the far UV, the absorption peaks of CD, NCD-1, NCD-2, and NCD-3 are 279, 276, 267, and 268 nm, respectively, which could be attributed to the  $\pi-\pi^*$  transition of C=C. While in the near UV, the absorption peaks at 339, 334, and 333 nm for NCD-1, NCD-2, and NCD-3 would be attributed to the  $n-\pi^*$  transition of the C=O bond in the molecular band due to the  $n-\pi^*$  transitions of N or O containing structures at the edge of the carbon structure [30]. The energy absorption increased with the gradual addition of nitrogen, indicating a change in the functional groups on the CD surface and proving that the doping process was successful [24].



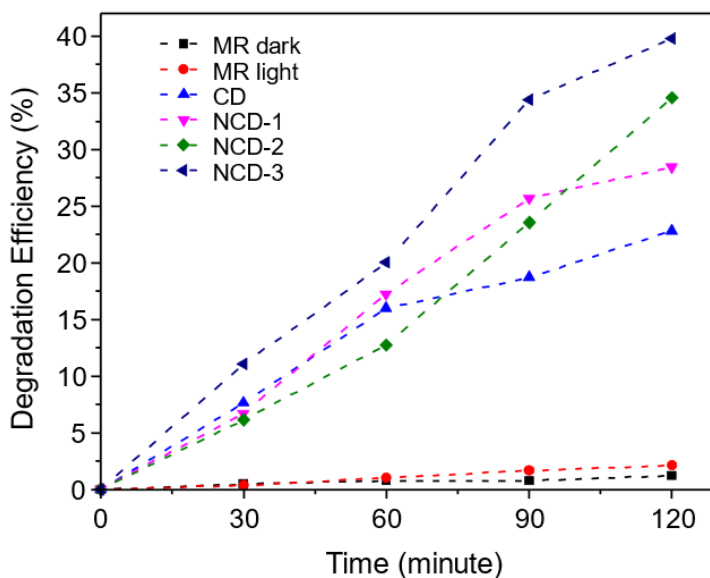
**Figure 3.** UV-vis spectra of the CDs from green algae

The energy gap ( $E_g$ ) of CDs and N-CDs of green algae, as determined by the Tauc Plot method and their absorbance spectra, is illustrated in Figure 5. N-doping further decreased the  $E_g$  values for CD, NCD-1, NCD-2, and NCD-3 by 3.28, 3.20, 3.10, and 3.05 eV, respectively. The addition of nitrogen atoms leads to a reduction in the value of the energy gap. A reduced gap energy value facilitates the excitation of electrons from the valence band to the conduction band [5]. In addition, the gap energy value calculation reveals that the green algae CDs and N-CDs samples are semiconductor materials; thus, they are employed as photocatalyst materials in the degradation of methyl red.



**Figure 4.** Band gap spectra of the CDs and N-CDs from green algae

In order to assess the photocatalytic efficiency of CDs and N-CDs samples when exposed to visible light, the target pollutant employed was methylene red (MR) for 120 minutes. The degradation efficiency of N-CDs over MR is considerably greater than that of the controlled pure CDs, as illustrated in Figure 6. The percent degradation value of methylene red in light and dark conditions without CDs has a degradation value of 2%. The addition of CDs sample (without doping) in MR solution increases the percentage degradation value of 22%. C-dots can absorb UV-vis light due to the  $\pi$ - $\pi^*$  transition of  $sp^2$  C=C double bonds in their inner core [31].



**Figure 6.** Degradation efficiency for methylene red

Interestingly, the degradation efficiency increased linearly with the concentration of nitrogen dopant. The outer layer of N-CDs comprises functional groups such as COOH, OH, and  $NH_2$ . These functional groups respond to excitation light sources due to  $n$ - $\pi^*$  transition [31]. The maximum degradation efficiency is 40% with the addition of N-CDs, which is two times greater than that of the CDs sample. It is noteworthy that the photocatalytic activity of N-CDs increased significantly as the ammonia concentration was added to the synthesis process. This nitrogen-doped can be attributed to the enhanced absorbance of visible light and the improved separation efficiency of charge carriers generated by photons. The N-CDs have higher photocatalytic activity than CDs because they have a smaller band gap. Narrowing the band gap of N-CDs leads to increased efficiency, as it facilitates the excitation of electrons, generating more hydroxyl radicals. The hydroxyl radical is employed as an oxidizing agent to facilitate the conversion of the methylene red molecule into a neutral chemical. Moreover, the presence of hydroxyl radicals ( $\cdot OH$ ) suggests that the photoinduced holes generated upon exposure to visible light can interact with absorbed  $H_2O$ , resulting in the formation

of hydroxyl radicals [22]. These radicals are responsible for the degradation of organic pollutants attached to the surface of CDs.

## CONCLUSION

Green algae were successfully synthesized into carbon dots (CDs) and nitrogen-doped carbon dots (N-CDs) using a hydrothermal method by utilizing nitrogen-doped green algae, employing ammonia as a dopant. The characteristic of CDs and N-CDs derived from green algae is their ability to exhibit a fluorescent blue-green emission upon exposure to UV radiation at a wavelength of 395 nm. Additionally, these compounds display absorption peaks at around 270 nm and 333 nm. The chemical composition of these compounds includes functional groups of hydroxyl, carbonyl, amide, and carboxyl that indicate the characteristics of carbon dots. As a result of the reduction in band gap energy caused by the presence of ammonia, the photodegradation kinetics of methyl red are altered. The specimen designated as NCD-3 exhibited the highest degradation efficiency, with a precise measurement of 40%.

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