The utilization of vehicle waste-oil as a material source for preparing carbon dots

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Abstract. Synthesis of carbon dots (c-dots) from vehicle waste-oil is one of the alternatives for reducing the burden of environmental pollution. This study aimed to develop a green and economical strategy to produce C-dots by using motor oil waste. C-dots were synthesized by heating motor oil waste in the various percentage of sulfuric acid solution (95, 70, 30, and 0% H₂SO₄). The synthesized C-dot was characterized by UV-Vis spectrophotometry and Fourier Transform Infrared (FT-IR) spectroscopy. The result showed that the carbon dot produces blue color at 365 nm of UV light. This color was attributed to the oxidation of chemical content in motor oil waste. Therefore, four peaks were obtained at 203 nm, 204 nm, 215 nm, and 210 nm for all samples. Based on FT-IR spectra, the most prominent sample difference was observed at peak 1630 cm⁻¹. The characteristic band of the carbonyl group was identified at the c-dot concentration (70 and 95%) but was not observed in the c-dot concentration (0 and 30%). The presence of carbonyl groups caused the fluorescent color to gradually shift from dark blue to light blue.

1. Introduction

Every year, more than 30 billion liters of oil waste is produced by vehicles [1]. This waste includes high pollutant materials which are explosive, flammable, reactive, corrosive, and toxic [2]. The careless disposal of motor oil waste can damage the environment because it contains polychlorinated biphenyl compounds, acid phosphorus esters, and alkyl benzene which act as contaminants for soil and water [3]. Currently, handling this waste is difficult to do because of the relatively expensive processing costs. So, an innovative, easy, low-cost, environmentally friendly new method of handling waste is needed. The presence of chlorinated hydrocarbons and organic substances in motor oil waste can be utilized as one of the sources of carbon-dot formation' C-dot is a ~10 nm material with a carbon sp² framework, which has low toxicity, biocompatibility, chemical inertia, water-soluble, low cost, and environmentally friendly [4]. Several methods have been developed for the synthesis of c-dot-based materials including chemical vapor deposition, soft and hard templating, and hydrothermal carbonization [5]. The use of sappan wood extract to prepare c-dot using a hydrothermal treatment has reported by Hasrudin et al. [6]. Not only for preparing c-dot, the

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hydrotermal treatment is also used to prepare zeolite materials from different sources [7, 8]. However, chemical synthesis processes such as polymerization and carbonization require a long time, are expensive, lower yields, and are not environmentally friendly [9]. Therefore, the method used in this study is the heating process by using a hotplate. The advantages of this method are non-toxic producing samples, simply used apparatus, and environmentally friendly [10].

Different synthesis methods lead to differences in the carbogenic core and the surface structure of C-dot. The C-dot surface contains functional groups (−OH, −COOH, and -C=O) with high surface area, low toxicity, and a stable redox process on photo induction [11]. Mechanically, the photo-excreted C-dot functions as both an electron donator and acceptor. This indicates that there are different species in the solution, which influence the fluorescence properties [5]. The oxidation process in the fluorescent mechanism causes defects in the c-dot surface by the low oxygen groups. It results a shorter space (bandgap) between the valence band (HOMO) and the conduction band (LUMO), so that when electrons are excited from the ground state (\(\pi\)) to the higher state (\(\pi^*\)), it does not consume a lot of energy. This process will increase the fluorescence, it is often known as a red shift [12]. Therefore, in this study, the synthesis of c-dot synthesis from motor oil waste was carried out using the hotplate method to develop an environmentally friendly and economical strategy to produce carbon-dot by utilizing motor oil waste from various solvent concentrations. The role of solvent concentration is to damage the chemical structure of the waste oil, resulting in defects on the c-dot surface. These surface defects can enhance the fluorescence properties when irradiated with a UV 365 lamp as a sign that c-dot has formed.

2. Experimental

2.1. Materials
The vehicle waste-oil was obtained from a motorbike and car repair shops around Dramaga, Bogor. All chemicals purchased from inorganic chemistry laboratory, IPB University.

2.2. Synthesis of c-dots
The C-dot synthesis was carried out by preparing 5 mL of motor oil waste in a 50 mL beaker and heating it at temperature up to 100 °C by using a hotplate. Then 1 mL of sulfuric acid (95%) was dropped into the waste oil while stirring using a magnetic stirrer for 5 minutes. After being cooled at room temperature, 20 mL of distilled water was added to the solution and then reheated at 100 °C while being stirred for 1 minute [13]. The precipitate that is formed was then filtered using filter paper.

2.3. Characterization of c-dots
These CD solutions were further irradiated under a UV lamp (365 nm) and then analyzed by using a UV-Vis spectrophotometer. Measurements were conducted at a wavelength of 200-600 nm. To get the solid phase, 1 mL of CD solutions that contain 0, 30, 70, and 95 % of \(\text{H}_2\text{SO}_4\) were dried at 100 °C and characterized by FTIR spectroscopy using a Perkin Elmer Spectrum One spectrometer, which recorded from 500 – 4,000 cm\(^{-1}\).

3. Result and discussion

3.1. Effect of solvent concentration on the intensity of fluorescent carbon dot
Carbon-dots (c-dots) was synthesized from motor oil waste by a heating process using a hotplate. The synthesis process begins with a chemical ablation process that uses \(\text{H}_2\text{SO}_4\) to carbonize small organic molecules into carbonated materials. At this stage, the molecule undergoes a hydrolysis process where sulfuric acid breaks the long-chain into simpler molecules [14]. The heating process caused the movement of atoms which will produce energy in the form of heat resulting in further oxidation and carbonization. The oxidation process caused the carbon chains to rearrange into c-dot particles. The advantage of heating by using a hotplate is a shorter time compared to the hydrothermal method. The result is a dark brown liquid, which indicated that the c-dot solution has been successfully synthesized. The synthesis of c-dots in this study was carried out by varying the concentration of \(\text{H}_2\text{SO}_4\) to get the
difference in hydrolysis from the carbonization results. The general scheme of c-dot’s synthesis is shown in Figure 1.

Motor oil waste as a carbon source is divided into four different samples based on sample treatment, they are c-dots that contain 0, 30, 70, and 95 % of H₂SO₄ named as C0, C3, C7, and C9 respectively. The sample C0 was synthesized by diluting motor oil waste with distilled water and then heated using a hotplate for 5 minutes at 100 °C. The result of the synthesized C0 was a yellowish clear solution with the lowest density than the other samples. The resulting solution was then filtered with filter paper to separate the precipitate from the solution. The synthesis of C3, C7, and C9 samples was carried out by the same method. The result of the synthesis of a C3 sample is a dark brown solution with a concentration that is more concentrated than the C0 sample. The concentration of the solution increases with increasing H₂SO₄ concentration. These results indicate that the higher the concentration of H₂SO₄, the more fluorescent intensity of c-dots, which is shown by the increase in crystallinity (Figure 2).

![Figure 1. General scheme of synthesis of c-dots from motor oil waste by using heating process](image)

The C9 sample had more crystals (0.4 g) compared to the obtained mass of other samples, namely 0.09; 0.1; 0.3 g for C0, C3, and C7 respectively. The synthesized samples of c-dots were determined by visual analysis using a 365 nm UV lamp. The analysis was carried out by irradiating the negative control solution and each sample as shown in Figure 3. It showed the color of the c-dot solution under visible and UV light with H₂SO₄ as the control solution at room temperature. All c-dot samples produced a clear color in solution under normal light, while the sample under UV light produced blue fluorescence. The higher the solvent concentration, the better the resulting fluorescence. This is because the high concentration of solvent caused the larger defects of the c-dots surface, which can increase the excitation process. According to previous reports, motor oil waste containing aromatic molecules such as
polycyclic aromatic hydrocarbon (PAHs) [2] is recommended for c-dot synthesis because it can be polymerized and carbonized to form a carbon backbone under high-temperature conditions.

![Figure 3. C-dot fluorescence at different concentration of H₂SO₄, (A) under visible light and (B) under UV](image)

3.2. Absorbance properties of c-dots

The results of the c-dots synthesis were characterized using a UV-Vis spectrometer to observe the absorbance peaks of each sample. Figure 4 shows the spectrum of the c-dot solution from motor oil waste under different H₂SO₄ concentration conditions.

![Figure 4. The C-Dot absorbance peak from motor oil waste using H₂SO₄](image)

The change in concentration based on measurement shows that there are differences in absorbance peak. Absorption peak will increase with the increase in H₂SO₄ concentration due to the interaction between particles and photons. The highest absorption peaks of each sample are at 203 nm, 204 nm, 215 nm, and 210 nm of wavelengths, respectively. The c-dots sample has maximum absorption peak at 2,672; 2,606; 3,203 and 3,112 for C0, C3, C7, and C9 respectively. The higher the concentration of H₂SO₄ solvent in the sample, the greater the number of particle constituents of c-dots.

3.3. Characteristics of C-dots Infrared Absorption Functional Groups

The FTIR spectrum was used to identify functional groups of C-dots at each sample concentration as shown in Figure 5. The results obtained are not significant changes. The FT-IR spectrum of the four
samples showed that the c-dots have an OH bond at a wavenumber of 3429 cm\(^{-1}\). Also, there was C=\(\text{N}\) absorption at 1384 cm\(^{-1}\), C-H absorption at 1155-1118 cm\(^{-1}\), and Fe absorption at 594 cm\(^{-1}\). One of the most notable differences from this sample was the presence of carbonyl groups peak at 1630 cm\(^{-1}\) (C7 and C9) that did not appear in the c-dot spectrum of C0 and C3. This result indicated that the carbonization reaction at the c-dot has been successful.

4. Conclusion
C-dots have been successfully synthesized from motor oil waste oil by adding an H\(_2\)SO\(_4\) solution through the heating process. All the c-dot solution samples showed blue fluorescence under a UV lamp. The difference in concentration percentage of H\(_2\)SO\(_4\) in the c-dot synthesis results in different optical characteristics. The higher the concentration percentage of H\(_2\)SO\(_4\), increasing the absorption peak. The C0, C3, C7, and C9 samples have wavelengths of 203 nm, 204 nm, 215 nm, and 210 nm, respectively.

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