Engineering Chemistry
ISSN: 2813-6535, Vol. 11, pp 1-6
doi:10.4028/p-esjRg1
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Submitted: 2024-12-15
Revised: 2025-03-18
Accepted: 2025-05-05
Online: 2025-09-10

Enhancing Sponge Absorbency with Carbon Dots for Cost-Effective Oil Spill Remediation

Ismawati Putri[1,a], Isnaeni[2,b*], Mochamad Zainuri[3, c] and Widyastuti[1,d]

[1]Department of Materials and Metallurgical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, Indonesia

[2]Research Center for Photonics, National Research and Innovation Agency, Tangerang Selatan, Indonesia

[3]Department of Physics, Sepuluh Nopember Institute of Technology, Surabaya, Indonesia

[a]puputisma98@gmail.com, [b]isnaeni@brin.go.id (corresponding author), [c]zainuri@physics.its.ac.id, [d]wiwid@mat-eng.its.ac.id

Keywords: Carbon Dots, Environmental Remediation, Oil absorption, and Oil-spill

Abstract. Marine oil spills negatively impact human health and aquatic ecosystems, causing biodiversity loss and reduce water quality. A range of mechanical, chemical, and biological methods have been employed to address oil spills in marine environments. As science and technology advance, there is a high demand for affordable and effective oil-absorbing materials. Oil absorbers using sponges with solar heat can be a solution to overcome the problem of oil spills at low cost and can be recycled. In this study, we combined the sponge with carbon dots from graphite pencils to improve the sponge's ability to absorb oil. The electrochemical method successfully synthesized carbon dots with particle sizes ranging from 1 to 5 nm. UV-Vis absorption, photoluminescence intensity, and FTIR spectra have revealed transition energies, peak intensities, and functional groups characteristic of carbon dots, respectively. We used sponges with and without carbon dots to compare their performance in absorbing oils. In addition, we also compared sponge performance when exposed to temperatures of 60 to 65 ºC. Sponges with carbon dots have high absorbency. The absorbency of the sponge increases by 28% when combined with a carbon dot. A higher temperature can also increase the absorbency of the sponge.

Introduction

Oil spills are one of the main causes of marine water pollution. Oil spills in the ocean negatively impact human health and aquatic ecosystems, as well as loss of biodiversity and reduced water quality [1]. Efforts to effectively clean up oil spills are necessary to prevent harm to the public and preserve the environment's health. Several methods have been used to overcome the problem of marine oil spills, including skimmers [2], oil dispersants [3], biodegradation and in situ burning [4]. However, these methods are expensive, time consuming and cause secondary pollution. With the development of science and technology, there is great demand for low-cost and efficient oil-absorbent materials. Oil absorbers using sponges that utilize solar heat can be a solution to overcome the problem of oil spills at a low cost and can be recycled.

Sponge are porous materials that can be used as oil absorbers. To increase the absorbency, we combined the sponges with carbon dots. Carbon dots are zero-dimensional nanomaterials with a particle size of less than 10 nm [5]. Carbon dots were initially discovered in 2004 while purifying single-walled carbon nanotubes [6–8]. Carbon dots have good optical properties [9], non-toxicity [5], biocompatibility [10], good chemical stability and low cost [7]. Carbon dots can be synthesized from materials containing carbon elements. Their unique properties make them widely used as photocatalysts [11], solar cells [12], drug delivery [13], sensor and oil-absorbing material [1, 14].

Sunlight oil absorption is a promising method for increasing the absorbency of sponges. Sunlight lowers the oil's viscosity, allowing the sponge to absorb the oil easily [1]. Previous studies have shown the outstanding performance of carbon dots conjugated with several types of sponges to absorb water and oil [15]. Polyvinyl alcohol sponges have better absorbency than other sponges. Therefore,

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we combined the polyvinyl alcohol sponges with carbon dots derived from pencil graphite. This research aims to increase the absorbency of sponges combined with carbon dots to absorb oil. Besides, we used a halogen lamp as an irradiation source.

Methods

Carbon dots were made from 2B pencil graphite using a simple electrochemical process. Two graphite pencils were used as anode and cathode electrodes for the electrochemical process. The electrolyte solvent was 0.5 sodium hydroxide (NaOH) mixed with 100 ml of ethanol. The electrodes were connected to a 45 mA DC power supply for 2 hours. The solution was kept at room temperature for 24 hours until a brown solution appeared. The appearance of a brown color indicates that the carbon dots were successfully synthesized.

We made a 1 cm^2 sponge with a thickness of 0.5 cm. The sponge used is polyvinyl alcohol from local distributor and engine oil from shell HX6. The sponge was manually dipped in the carbon dots solution and dried for 24 hours at room temperature. We tested each sponge's oil absorption (with and without carbon dots). We put 3 ml of oil in a glass with 30 ml of seawater. Then, manually dip a sponge into the glass until all sponge parts are submerged. We measured the mass of the sponge after and before dipping to determine the absorbency of the sponge based on the following equation.

$$absorbency\ (\%) = \frac{M_b - M_a}{M_a}\ x\ 100\% \qquad (1)$$

M_a is the mass of the sponge before dipping, and M_b is the mass of the sponge after dipping. We tested the absorbency of the sponge with carbon dots when irradiated with a halogen lamp. The halogen lamp was placed 30 cm from the sample. Then the absorbency results with and without irradiation were compared. In addition, we characterize the synthesized carbon dots using UV-Vis absorbance, photoluminescence, fourier transform infrared spectroscopy (FTIR) and transmission electron microscope (TEM).

Results and Discussion

Carbon dots have been successfully synthesized from 2B pencil graphite using a simple electrochemical method. The brown color indicates that the carbon dots have been successfully synthesized. In addition, we perform various characterizations such as UV-Vis, photoluminescence, FTIR and TEM. The UV-Vis absorption spectrum (Fig. 1a) shows that carbon dots exhibit two peaks at 263 and 364 nm. The first peak is thought to represent the π→π* energy transition at the core of the carbon dots. Meanwhile, the second peak is assumed to be the carbon dots peak' n→π* energy transition. These two transition peaks are characteristic of carbon dots [16]. Photoluminescence characterization was performed, and the characterization result (Fig. 1b) shows that carbon dots have the highest luminescence intensity at a wavelength of 527 nm when excited using a laser diode with a wavelength of 420 nm.

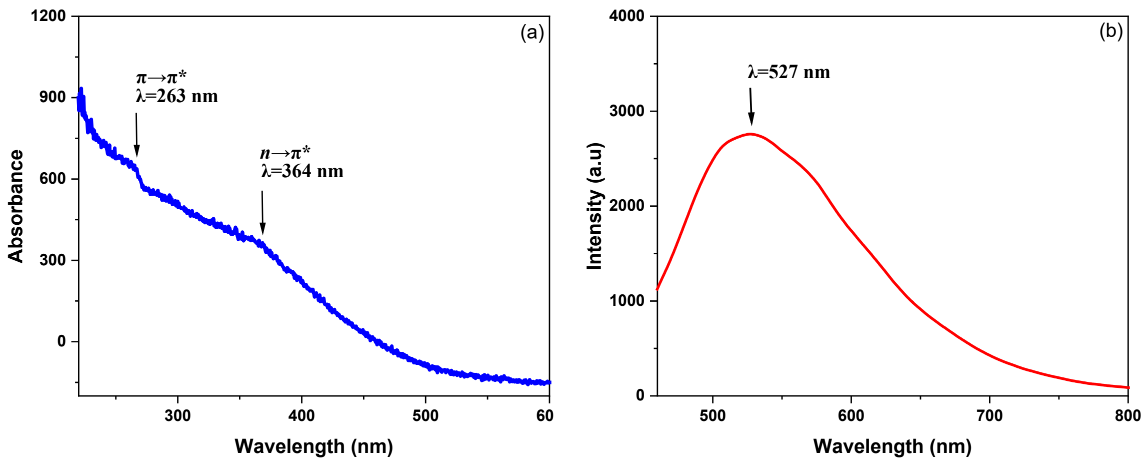

Fig. 1. Absorption spectrum of carbon dots (a) and photolinescence spectrum (b) of carbon dots

We performed FTIR characterization to determine the functional groups of carbon dots. FTIR characterization results show that carbon dots have the same peaks as ethanol, except for three peaks (Fig. 2a). H−O, C=O and C−N stretching vibrations that were detected at wave numbers 3317, 1740 and 1274 cm^{-1} respectively [17]. These three functional groups originated from the surface of carbon dots. Additionally, we conducted TEM characterization to determine the size and morphology of carbon dots. Carbon dots were quasi-spherical in shape with uniform particle size and distributed from 1 nm to 5 nm. The dominant particle size of carbon dots is 3 nm (Fig. 2b). This size is consistent with previous research indicating that carbon dots have a particle size of less than 10 nm [18]. Since the carbon dots are small (less than 5 nm), the synthesized carbon dots can be called carbon quantum dots [15].

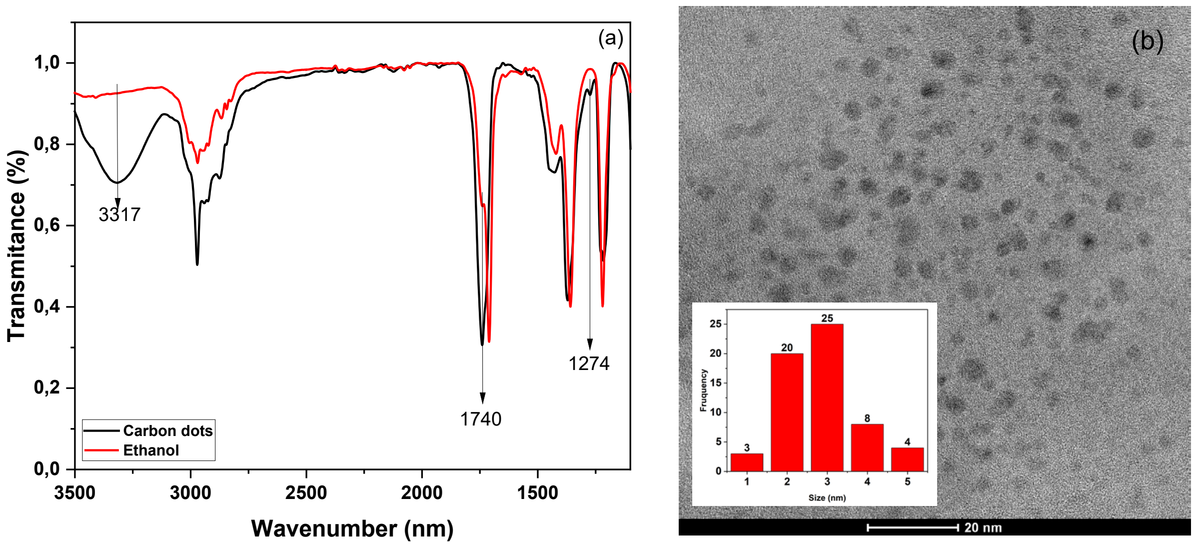

Fig. 2. FTIR spectra of carbon dots and ethanol (a) and TEM image of carbon dots (b)

The next phase of this research involved testing the absorbency of sponges with and without carbon dots. The sponges combined with carbon dots turned brown (Fig. 3). Next, the sponge is used to test the oil absorbency. We dipped the sponge in a glass filled with sea water and oil, and let it soak for 10 minutes at room temperature. The absorbency of sponge is calculated using Equation 1 to determine the performance of the sponge in absorbing oil.

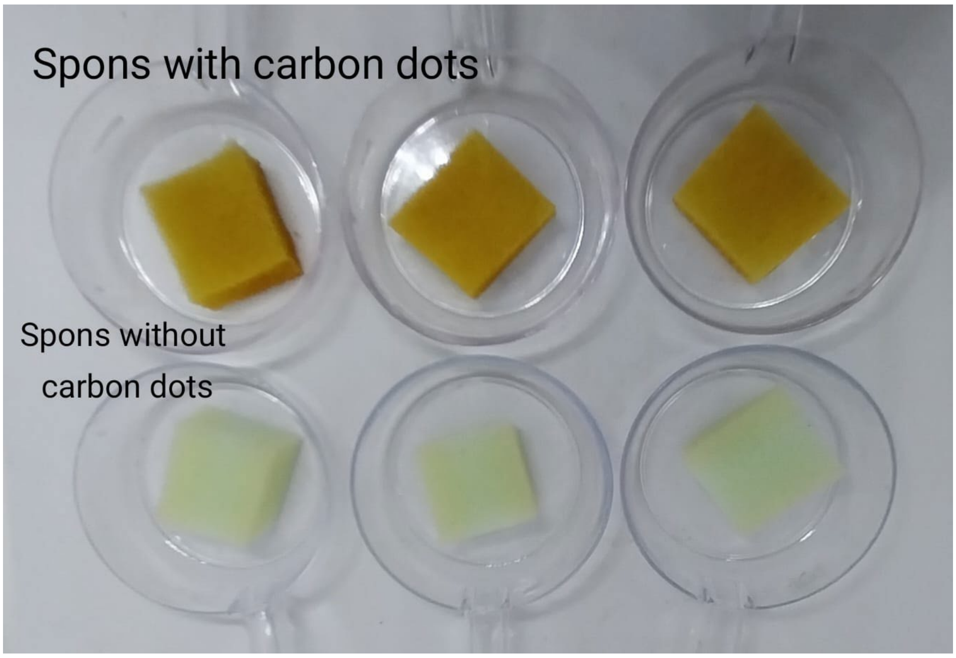

Fig. 3. Sponges image with and without carbon dots

This research results show that sponges with carbon dots have a greater absorbency than sponges without carbon dots (Fig. 4a). The research was conducted at room temperature with normal light from a ceiling lamp. The first and second experiments showed increased absorbency of sponges with carbon dots. Meanwhile, the third experiment showed that the sponge without carbon dots had higher absorbency. The sponge without carbon dots had a 1.95% higher absorbency than the sponge with carbon dots, it is thought to be due to the difference in the initial mass of the sponge and the low amount of carbon dots conjugated in the sponge. In addition, we tested the absorbency using halogen lamp irradiation (temperature at 60-65 ºC). Sponge with carbon dots compared their absorbency when irradiation and non-irradiation. Sponge increased absorbency when given irradiation (Fig. 3b). The absorbency of sponges increased by 5.4 to 8.63% under the influence of the irradiation process. The irradiation process can increase the surface polarity of sponge, so that it easily absorbs oil. Furthermore, the irradiation process can help decrease the oil's viscosity so that it is easily absorbed into the sponge.

In this study, we evaluated the effectiveness of sponges infused with carbon dots for absorbing oil (Fig.4c). The results indicate a progressive decline in absorbency with repeated use, suggesting that several factors contribute to this degradation. One primary factor is structural damage to the sponges' porous. Over time, repeated exposure to oil, mechanical stress during use, and irradiation may cause compression, collapse, or fragmentation of the pores, reducing the available surface area for absorption. Additionally, the loss of carbon dots embedded within the sponge matrix could significantly impact its performance. Carbon dots are known for their ability to enhance surface wettability and interaction with hydrophobic substances, so their depletion may lead to reduced oil affinity. Furthermore, degradation of the sponge material itself is another critical consideration. Prolonged exposure to oil, grease, and irradiation could alter the chemical and physical properties of the polymeric structure, leading to embrittlement, swelling, or oxidative degradation. These changes may not only weaken the sponge but also alter its oil-absorbing capability. Lastly, surface modifications induced by irradiation may also play a role. Irradiation can lead to crosslinking, oxidation, or surface roughness changes, which might influence the sponge's interaction with oil molecules. Depending on the irradiation type and intensity, it may cause beneficial modifications initially but contribute to long-term deterioration of the material's effectiveness. Future work could explore strategies to improve the durability of such sponges, such as optimizing carbon dot adhesion, enhancing the stability of the sponge matrix, or developing protective coatings to minimize structural degradation. Investigating alternative irradiation methods or lower-energy treatments may also help in maintaining sponge performance over extended use cycles.

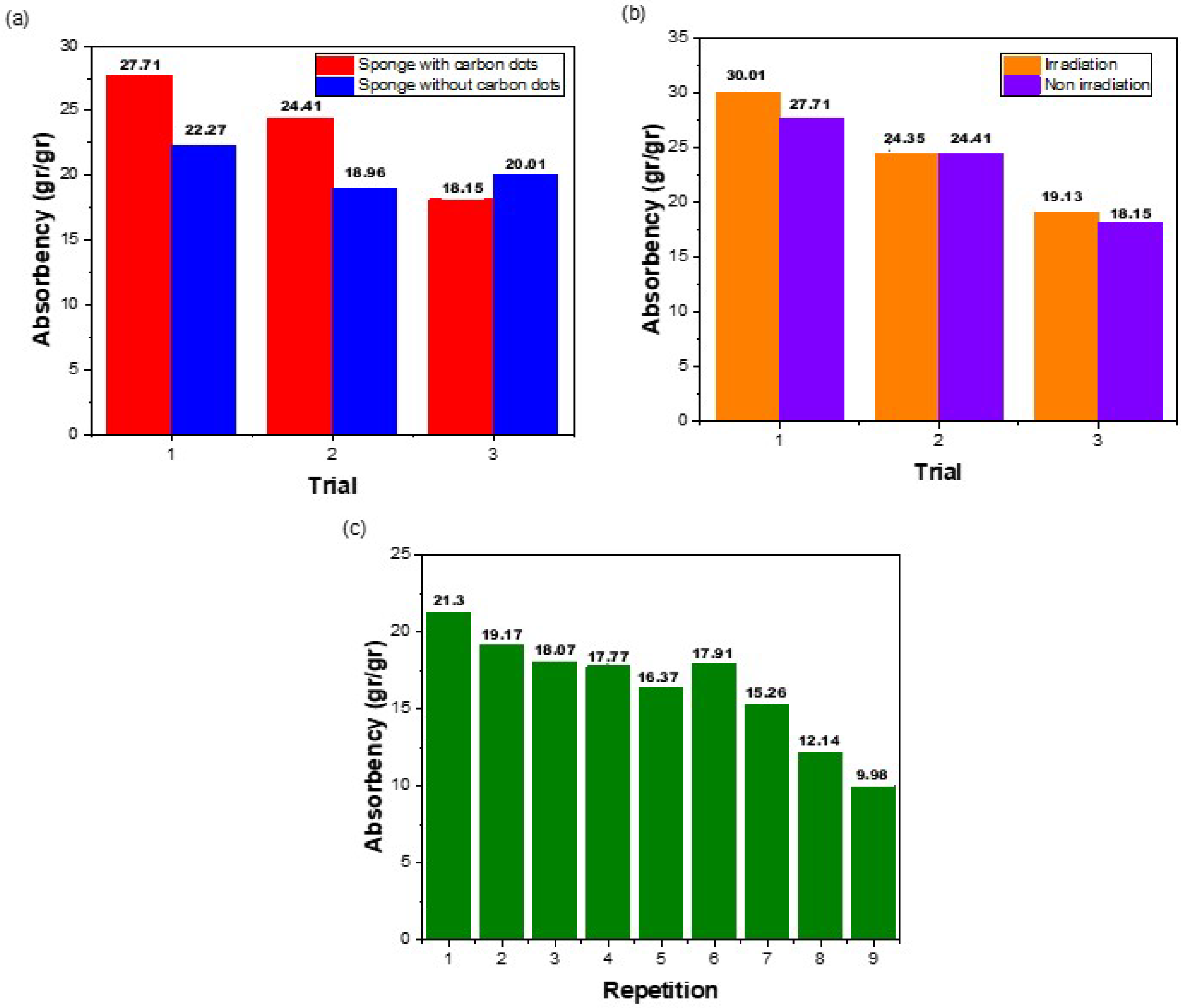

Fig. 4. Absorbency of sponges with and without carbon dots (a), absorbency of sponge when given irradiation and non-irraditation process (b), and the effectiveness of sponge in absorbing oil

Summary

Carbon dots have been successfully synthesized from 2B pencil graphite using a simple electrochemical method. The results of UV-Vis, photoluminescence, FTIR and TEM show that carbon dots have been synthesized. The particle size of carbon dots ranged from 1 to 5 nm. Carbon dots conjugated into the sponge can increase the absorbency up to 28%. The irradiation process can help the sponge to increase its absorbency. Sponge with carbon dots showed a decrease in absorbency with repeated use. Separating oil using a sponge with carbon dots is simple, low-cost and time consuming. However, for broader practical applications, future research should explore several key areas such as testing the sponge's performance with different types of oils and assessing the sponge's durability and absorbency under real-world spill conditions. Further studies could also investigate strategies to enhance sponge longevity, such as optimizing carbon dot adhesion, using more resilient sponge materials, or incorporating protective coatings.

Acknowledgment

All experiments were conducted in the Research Center for Photonics BRIN with characterization tools fully facilitated by BRIN’s e-Science Service (ELSA).

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