Facile preparation of magnetic carbon nanofiber composite from nata de coco for removal of methylene blue dye from water

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Abstract. The facile synthesis of a magnetic 3D structured carbon nanofiber composite from nata de coco was demonstrated. Nata de coco was used as a readily available and renewable source of carbon in this study because of its high cellulose content in the form of nanofibers. Fe3+ was utilized as the magnetic particle source and as a pore activating agent. Nata de coco was freeze-dried, infiltrated with Fe3+ solution, and subsequently pyrolyzed at 700 °C to prepare the magnetic carbon nanofiber composite. The resulting composite was then characterized via scanning electron microscopy, surface area and pore size analysis, X-ray diffraction, and vibrating sample magnetometry. A magnetic carbon composite with a 3D fibrous and porous structure and a high surface area of 584 m2/g was successfully obtained. When used as an adsorbent, the sample completely adsorbed 10 ppm of methylene blue (MB) dye within 1 min. The composite can be simply regenerated using ethanol and can thus be reused. The excellent magnetic properties of the sorbent allow it to be readily separated from aqueous solutions by applying an external magnet. Hence, the sorbent is practical to use in real systems.

1. Introduction
Water pollution is a serious global environmental threat because of its direct impact on human health and ecological systems.[1] Several methods for removing pollutants from contaminated wastewater have been developed.[2] Adsorption is considered as the most effective method due in part to its simplicity and inexpensive cost of operation with satisfactory results.[3] Porous carbon is one of the most promising candidates among existing adsorbent materials because of its high surface area and porosity with exceptional chemical stability. However, most porous carbon materials are in the form of fine powder that takes time to sediment and is difficult to separate. Hence, magnetic carbon composites
have become a material of choice because they offer a fast and easy separation step using only an external magnet after a complete treatment process.[4]

In this work, a magnetic carbon nanofiber composite was straightforwardly prepared via freeze-drying and pyrolysis. *Nata de coco*, a bacterial cellulose, was used as a starting material to produce the carbon nanofiber because it has high cellulose nanofiber content and can be produced in a large scale. Magnetic properties and high porosity can be simply incorporated into the material using Fe$^{3+}$ as a magnetic particle source and as an activating agent. A typically used dye in the textile industry, methylene blue (MB), was selected herein as a model for the adsorption study.

2. Methodology
Commercially available *nata de coco* (Chaokoh, Thailand) was washed in 150 mL DI water for 1 h thrice and then freeze-dried at $-80 \, ^{\circ}\mathrm{C}$. The obtained sample was then soaked with 500 ppm of FeCl$_3$ solution for 3 h, freeze-dried, and pyrolyzed under N$_2$ atmosphere at 700 $^\circ$C for 2 h at a heating rate of 2 $^\circ$C/min to obtain the magnetic carbon nanofiber composite. The resulting composite was then characterized via scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) mapping, X-ray diffraction (XRD), N$_2$ sorption analysis, and vibrating sample magnetometry (VSM).

Exactly 0.01 g of the magnetic carbon nanofiber composite was dispersed and shaken in 15 mL of the MB solution (100 ppm) at 30±2 $^{\circ}$C for 0–48 h to attain the adsorption kinetics of MB. The adsorption isotherm of MB was measured by dispersing 0.01 g of the magnetic carbon nanofiber composite and shaking it in 15 mL of the MB solution in the concentration range of 1–500 ppm at 30±2 $^\circ$C for 36 h. The sorbent was then separated using a magnet. The concentration of the MB solution before and after adsorption was examined using an ultraviolet–visible spectrophotometer, and the adsorbed amount was then calculated.

3. Results and Discussion
The morphology of the prepared composite was determined using a scanning electron microscope. As shown in Figure 1A, a nonwoven nanofibrous structure with interconnected macropores resulting from the 3D arrangement of the fibers was observed. This structure clearly confirms the successful conversion of *nata de coco* into carbon nanofibers. Furthermore, EDX mapping shown in Figure 1B-D also revealed that the nanofiber composite is composed of carbon, oxygen and iron species homogeneously distributed throughout the material.

![Figure 1](image1.png)

**Figure 1.** (A) SEM image of the magnetic carbon nanofiber composite (B-D) SEM-EDX mapping of elemental carbon, oxygen and iron in the magnetic carbon nanofiber composite.

![Figure 2](image2.png)

**Figure 2.** XRD pattern of the magnetic carbon nanofiber composite exhibiting characteristic peaks of Fe$^0$ and Fe$_3$O$_4$. 
As shown in Figure 2, the XRD pattern of the magnetic carbon nanofiber composite exhibited characteristic peaks at 30.3°, 35.7°, 43.4°, 57.4°, and 63.0° corresponding to (220), (311), (400), (511), and (440) reflections, respectively, of the face-centered cubic structure of magnetite (Fe₃O₄, JCPDS No. 01-075-0449). This result confirms that Fe³⁺ can be successfully converted into the iron magnetite phase through a one-step pyrolysis. Moreover, the XRD pattern showed a sharp peak at 44.7° and a broad signal around 20°, which were indexed as the facet (110) of Fe₀ (Fe₀, JCPDS No. 06-0696) and turbostratic carbon, respectively.

N₂ sorption analysis was conducted to monitor the development of porosity of the magnetic carbon composite. As shown in Figure 3A, a type IV isotherm with an obvious hysteresis loop that is typically found in mesoporous materials was observed. This isotherm can be further confirmed by the narrow pore size distribution (Figure 3B) with an average mesopore size of 2.11 nm. Using a t-plot method, we found that the material had a mesopore fraction of 58.7%. Furthermore, the S BET and the total pore volume were found to be 584 m²/g and 0.31 cm³/g, respectively.

![Figure 3](image1.png)

**Figure 3.** (A) N₂ sorption isotherm and (B) pore size distribution of the magnetic carbon nanofiber.

The magnetic properties of the resulting material are illustrated in Figure 4. As depicted in Figure 4A, the VSM result of the magnetic carbon nanofiber composite exhibited a hysteresis loop with a saturation magnetization value of 13.393 emu/g, which is more than sufficient to separate the adsorbent from the aqueous system. This separation can be clearly observed in Figure 4B, which shows that the magnetic carbon fiber composite was easily separated from the system using an external magnet. Furthermore, the adsorbent still exhibited excellent magnetic properties even after complete adsorption of the MB dye.

![Figure 4](image2.png)

**Figure 4.** (A) Magnetization curve obtained using a vibrating sample magnetometer at room temperature and (B) magnetic properties of the magnetic carbon nanofiber composite before and after adsorption of MB dye (10 mg/g, 20 mL).
The adsorption kinetics plot in Figure 5A shows that the adsorption reached equilibrium within 36 h. The obtained data were fitted with a pseudo-second-order model, and the calculated rate constant \( k_2 \) was found to be 2.15 g/(mg•min). Furthermore, a linear curve fitting for MB adsorption, as presented in Figure 5B, also exhibited a good correlation with \( R^2 \) of 0.9861. The adsorption isotherm of the magnetic carbon nanofiber composite toward MB was determined, and the result is shown in Figure 6A. The isotherm plot was fitted to the Langmuir adsorption model, and the correlation coefficient \( R^2 \) was found to be 0.9955, which suggested that the data were well fitted to the Langmuir adsorption model. The calculated maximum adsorption capacity and Langmuir constant were found to be 238.10 mg/g and 0.0569 L/mg, respectively. After complete adsorption, the MB dye could be simply desorbed in ethanol. This unique property is in contrast to that of most carbon-based adsorbents that are typically regenerated under harsh conditions.

![Figure 5](image1.png)

**Figure 5.** Adsorption kinetics toward methylene blue of the magnetic carbon nanofiber composite.

![Figure 6](image2.png)

**Figure 6.** Adsorption isotherm: (a) nonlinear and (b) linear plots toward MB dye of the magnetic carbon nanofiber composite.

4. Conclusion
In this study, the facile preparation of a magnetic carbon nanofiber was achieved via freeze-drying and pyrolysis. The method developed herein does not require the use of toxic chemicals and is thus environmentally friendly and sustainable. The magnetic carbon material exhibits promising properties for environmental remediation.

5. References
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