Sriplai, N., Mongkolthanaruk, W., Eichhorn, S. J., & Pinitsoontorn, S. (2020). Magnetic bacterial cellulose and carbon nanofiber aerogel by simple immersion and pyrolysis. *Journal of Materials Science*, 55(9), 4113-4126. <https://doi.org/10.1007/s10853-019-04295-w>

Peer reviewed version

Link to published version (if available):
[10.1007/s10853-019-04295-w](https://doi.org/10.1007/s10853-019-04295-w)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via Springer Nature at <https://link.springer.com/article/10.1007/s10853-019-04295-w> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

Magnetic Bacterial Cellulose and Carbon Nanofiber Aerogel by Simple Immersion and Pyrolysis

Nipaporn Sriplai¹, Wiyada Mongkolthanaruk², Stephen J. Eichhorn^{3,*}, Supree Pinitsoontorn^{1,4,**}

¹*Materials Science and Nanotechnology Program, Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, THAILAND.*

²*Department of Microbiology, Faculty of Science, Khon Kaen University, Khon Kaen 40002, THAILAND.*

³*Bristol Composites Institute, CAME School of Engineering, University Walk, University of Bristol, Bristol, BS8 1TR, UK.*

⁴*Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), NANOTEC-KKU RNN on Nanomaterials Research and Innovation for Energy, Khon Kaen University, Khon Kaen 40002, THAILAND.*

Corresponding authors

*Stephen J. Eichhorn (s.j.eichhorn@bristol.ac.uk), **Supree Pinitsoontorn (psupree@kku.ac.th)

Abstract

Bacterial cellulose (BC)/Fe₃O₄ aerogels were fabricated by a simple immersion of BC hydrogels in commercially available ferrofluid solution followed by freeze-drying. The BC/Fe₃O₄ aerogels were converted into carbon nanofiber (CNF)/Fe₃O₄ aerogels by pyrolysis at 600 °C. With our fabrication methods, the Fe₃O₄ nanoparticles (NPs) were effectively impregnated and homogeneously distributed in the nanostructures of BC and CNF. The average diameters of the BC and CNF nanofibers were found to be about 79.3 ± 14.1 nm and 56.7 ± 13.6 nm, respectively. Increasing the ferrofluid concentration resulted in a non-linear increase of Fe₃O₄ NPs loaded into the BC and CNF structure but the functional groups were not affected. The saturation magnetization (M_s) of CNF/Fe₃O₄ were larger than those of BC/Fe₃O₄ and increased with the amount of impregnated Fe₃O₄ NPs. The maximum magnetization in our work was larger than literature values, with the highest M_s of 82.9 emu/g approaching the bulk value of Fe₃O₄. The materials presented could be used as pollutant absorbers for wastewater treatment. We have demonstrated the capability of using magnetic CNF aerogels in absorbing a common dye pollutant from water. The dye was absorbed efficiently, and the aerogels were easily magnetically removed from the solution and reusable.

Keywords: bacterial cellulose; carbon nanofiber; iron oxide; pyrolysis; magnetic property; absorption;

1. Introduction

Iron oxide nanoparticles (NPs) are of great importance and interest for many research groups because of the wide range of possible applications including biomedical applications/diagnostics [1], catalysis [2], environmental remediation [3], data storage [4], magnetic resonance imaging [5], and electrochemical energy storage [6]. They can exist in several phases, including Fe_3O_4 (magnetite), $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), $\alpha\text{-Fe}_2\text{O}_3$ (hematite), FeO (Wüstite), $\epsilon\text{-Fe}_2\text{O}_3$ and $\beta\text{-Fe}_2\text{O}_3$ [7]. Among them, magnetite and maghemite are the most popular candidates for utilization due to their ferromagnetic behavior, low toxicity, chemical inertness, and biocompatibility [8]. However, one major drawback of using iron oxide NPs is their aggregation, because of the inter-particle magnetic forces. To avoid aggregation, composites between nanofibers and iron oxide NPs were developed [9, 10]. The nanofibers help to separate the magnetic NPs [9, 10].

Carbon nanofibers (CNFs) are an important form of carbon because of their unique physical properties. For example, they are known to have low density, high conductivity, high strength, high surface area, high porosity, and chemical and environmental stabilities. They have become promising materials to use as catalysts [11], pollutant absorbers [12], water filtration [13], electron field emitters [14], and for supercapacitors [15]. Conventionally, CNFs are produced by electrospinning of polymer solutions, followed by thermal treatment [16]. Precise control of processing parameters, *e.g.* viscosity, voltage, distance between tip and collector, flow rate, temperature, humidity, are crucial. The use of expensive or toxic chemicals are also required [17, 18]. Alternatively, CNFs can be derived from renewable natural materials (*e.g.*, wood, sugarcane bagasse, palm, kenaf, hemp, cotton,) *via* carbonization [19]. The advantage of this route is the abundant resource of raw materials [20].

Recently, much research has focused on studies of natural polymeric fibers produced by bacteria *e.g.* bacterial cellulose (BC). BC has a nano-scale fiber structure with a three-dimensional network [21] and several advantages over other polymeric fiber forms, such as high crystallinity, numerous -OH groups, a high degree of polymerization, high water holding capacity, low density, and high surface area [22]. In addition, BC also exhibits excellent biocompatibility, non-toxicity, biodegradability, low-cost, ease of fabrication and abundance [22, 23]. With these unique properties, it is an interesting material for hosting many different types of guest molecules [24], including iron oxide NPs.

In 1994, Raymond *et al.* was the first group to prepare BC/iron oxide composites by using a lumen loading method [25, 26]. Since then, there have been several published articles reporting the fabrication of BC/iron oxide NPs composites by a variety of approaches. These

methods have included, microwave-assisted thermal decomposition [27], *in situ* synthesis combined with ultrasonic treatment [28], ammonia gas-enhancing *in situ* co-precipitation [29], and reduction–precipitation [30]. These BC composite systems have potential applications in electronic devices, for neuro-endovascular treatment, catalytic, wastewater treatment, and as antibacterial materials.

BC/iron oxide composites can be transformed into CNF/iron oxide composites *via* a carbonization process. For microwave absorption applications, for example, Ren *et al.* prepared CNF/Fe₃O₄ composites by mixing carbonized BC and Fe₃O₄ solutions before subjecting them to vacuum filtration and annealing (VFA method) [31]. Luo *et al.* presented the controlled dispersion of Fe₃O₄ NPs on the surfaces of CNF derived from BC [32]. The CNF was surface treated in HNO₃ solution to generate carbonyl groups prior to the synthesis of Fe₃O₄ NPs *via* a co-precipitation method. For other applications, CNF/Fe₂O₃ and CNF/Fe₃O₄ nanocomposite systems have been used in energy storage devices. Nanocomposites have been prepared using several approaches including carbonization, impregnation, a direct thermal treatment process [9], and *via* a hydrothermal method [33]. However, the preparation of CNF/iron oxide composites in the research mentioned above is complicated and requires specific tools and chemicals.

The novelty of our work is that we propose a much simpler process route to prepare BC/Fe₃O₄ composite materials by immersion of BC pellicles in a commercially available ferrofluid, without using any chemical activation agents. Moreover, our BC/Fe₃O₄ composites are then transformed to CNF/Fe₃O₄ aerogels by pyrolysis at a relatively low temperature under an inert gas atmosphere. The Fe₃O₄ NPs exhibit a uniform dispersion in the nanostructure of both BC and CNF, resulting in very high magnetisation values, exceeding previously published values. Moreover, we have demonstrated the potential use of the fabricated materials as a dye absorbent for wastewater treatment. The unique properties of the fabricated aerogels make them capable of absorbing dye as well as being magnetically removable.

2. Materials and methods

2.1 Preparations of BC/Fe₃O₄ and CNF/Fe₃O₄ aerogels

BC pellicles used in this work were obtained from coconut gel cubes ($2 \times 2 \times 2$ cm³, supplied by Chaokoh, Thailand). The cubes were cut in half before being thoroughly washed several times in deionized water to remove other components. After that, they were thinned again to a thickness of 2.5 mm. For the source of Fe₃O₄ NPs, we used a commercial ferrofluid solution (supplied by Weistron Co. Ltd., Taiwan). The characteristics of this ferrofluid are shown in Table S1 and

Fig. S1 (Supplementary Information). The wet BC pellicles were immersed in the ferrofluid solution which allowed a simple diffusion process of Fe_3O_4 NPs into the nanostructure of BC. The immersion was carried out at 80 °C with continuous stirring for 1 h to accelerate the diffusion process. To study the effect of the Fe_3O_4 concentration in the composites, the BC pellicles were immersed in different concentrations of ferrofluid ($x = 1, 3, 5, 10$, and 20 vol. %) [34]. The BC/ Fe_3O_4 hydrogels were subsequently freeze dried to obtain the BC/ Fe_3O_4 aerogels. The samples in this group are denoted as BC- $x\%$.

To prepare the CNF/ Fe_3O_4 nanocomposites, the BC/ Fe_3O_4 aerogels were pyrolyzed by annealing in an Ar atmosphere. In brief, the samples were heated from room temperature to 300 °C, with a heating rate of 1 °C min⁻¹., and then held at that temperature for 1 h. They were then heated to 600 °C using a rate of 2 °C min⁻¹., and maintained at that temperature for 2 h, before cooling down to room temperature. This set of samples was called CNF- $x\%$. The fabrication processes for both BC/ Fe_3O_4 and CNF/ Fe_3O_4 aerogels are summarized in Fig. 1.

Fig. 1. Schematic for the preparation process of BC/ Fe_3O_4 and CNF/ Fe_3O_4 aerogels.

2.2 Characterization methods

The thermal stability of the BC/ Fe_3O_4 nanocomposites was investigated by using thermogravimetric analysis (TGA) (Hitachi, STA7200, Japan), within a temperature range of 30 to 800 °C, and a heating rate of 10 °C min⁻¹. in a N_2 atmosphere. The functional groups involved in the formation of the BC and Fe_3O_4 NPs composites were investigated using Fourier transform infrared (FTIR) spectroscopy (Bruker, TENSOR27, Germany) within a wavenumber range of 4000 to 600 cm⁻¹. The crystalline structures of the samples were investigated using an

X-ray diffraction (XRD) technique with a diffractometer employing Cu-K α radiation (PANalytical, Empyrean, USA) in a 2θ range of 10-80°. The surface morphology of the samples was studied using a scanning electron microscope (SEM) (LEO 1450VP, UK). The morphology and formation of CNF/Fe₃O₄ nanocomposites was examined using transmission electron microscopy (TEM) (ThermoFisher Scientific, Talos F200S, USA). The magnetic property measurements were carried out using a vibrating sample magnetometer (VSM) option in the VersaLab instrument (Quantum Design, USA) with a maximum applied field of 30 kOe.

3. Results and Discussion

TG analysis of the pristine BC and the BC/Fe₃O₄ composites show a significant weight loss at 300 – 360 °C (Fig. 2a), which was assigned to the degradation of BC including decomposition, dehydration and depolymerization of the glycosidic units [22, 35]. Beyond this point, the weight of the samples appears stable. Hence, a pyrolysis temperature of 600 °C was chosen, which is thought to be sufficiently high to transform BC into CNF.

The residual weight of the BC composites at 600 °C as a function of ferrofluid concentration is shown in Fig. 2b. These residual weights represent the amount of the loaded volume of the Fe₃O₄ NPs in the nanocomposites. From Fig. 2b the residual weight increased rapidly initially (at ferrofluid <5 vol.%) but the slope decreased for higher ferrofluid concentrations. At a low content of ferrofluid, the Fe₃O₄ NPs are thought to easily diffuse into the BC nanostructure network and anchor at the nanofiber surfaces. However, when the ferrofluid concentration was increased above 5 vol.%, excessive amounts of NPs caused difficulties in the diffusion process, whereby the anchoring sites for NPs become saturated, resulting in a decreasing rate of NP loading.

Fig. 2. (a) Typical TG curves of the BC- $x\%$ aerogels, and (b) the residual weight at 600 °C.

The solid line in (b) is a ‘guide for the eyes’ only.

Typical FTIR spectra for the pristine BC and BC/Fe₃O₄ aerogels are shown in Fig. 3a. All the samples show nearly the same spectra regardless the concentration of magnetic NPs (MNPs). Hence, the incorporation of the MNPs did not affect the functional groups of the original BC [34]. Typical FTIR spectra of the CNF and the CNF/Fe₃O₄ aerogels are shown in Fig. 3b which are also very similar, independent of MNP concentration. However, the spectra for CNF are significantly different from BC aerogels. The main peaks observed for BC at ~1055 cm⁻¹ and ~3360 cm⁻¹ are absent after the pyrolysis process, indicating that the C-O-C bonds are broken due to decarboxylation [36] and the hydroxyl groups are decomposed. However, additional peaks are observed at ~1570 cm⁻¹ and ~1230 cm⁻¹, which may be associated with stretching vibrations of C=C and C-O, respectively [37-39]. A number of peaks representing

several characteristic functional groups of BC and the CNFs are identified in Fig. S2 (Supplementary Information).

Fig. 3. FTIR spectra of (a) BC-x% and (b) CNF-x% aerogels.

The XRD patterns indicate a high crystallinity of the pristine BC (Fig. 4a). Three main diffraction peaks were observed at 14.0° , 16.5° and 22.4° , indexed as the $(1\bar{1}0)$, (110) and (200) reflections of BC [40]. For the BC composites, the characteristic diffraction peaks of Fe_3O_4 gradually appeared as the concentration of the ferrofluid solution increased. The main characteristic diffraction peaks for the Fe_3O_4 NPs are observed at 2θ angles of 30.2° , 35.8° , 43.2° , 57.25° and 62.6° corresponding to the (220) , (311) , (400) , (511) and (440) planes, respectively, based on a magnetite structure (ICCD 01-089-0950). On the other hand, the peak intensities from the BC gradually decrease with increasing Fe_3O_4 concentrations. The pristine CNFs exhibit an amorphous carbon phase (no crystalline peaks) (Fig. 4b), in agreement with other reports [41, 42]. For the CNF-x% nanocomposites, the XRD peaks of Fe_3O_4 NPs are similar to the BC-x% composites. This result shows that the Fe_3O_4 NPs are highly thermally stable, and do not change phase up to a pyrolysis temperature of 600°C .

Fig. 4. XRD patterns of (a) pristine BC and BC-x%, and (b) pristine CNF and CNF-x% aerogels.

The morphologies of the BC and CNF samples were investigated using SEM, as shown in Fig. 5. The diameter of fibrils within the pristine BC aerogel were found to be 79.3 ± 14.1 nm (Fig. 5a), reducing to 56.7 ± 13.6 nm for the CNF (Fig. 5g) due to the loss of oxygen, hydrogen and some carbon in the pyrolysis process. Nevertheless, the 3D network of the nanofibril structure was observed in both samples. For both BC/ Fe_3O_4 and CNF/ Fe_3O_4 aerogels, the MNPs were coated only on the surfaces of the fibers without any obvious aggregation in the pores. As a result, the porous structure was observed in both cases. An exception was found in the case of BC-20% (Fig. 5f) where the nanopores seem to collapse as the fibers aggregate. For the CNFs with $>10\%$ Fe_3O_4 (Fig. 5k and 5l), the nanofiber structure breaks down due to the excessive amount of MNPs. The excessive MNPs create additional surface area and van der Waal's forces between particles encourage aggregation [43, 44]. MNP agglomeration occurs when subjected to high temperatures. This process in turn disrupts the nanofiber network structure.

Fig. 5. Typical SEM images of (a) pristine BC, (b-f) BC- $x\%$, (g) pristine CNF, and (h-l) CNF- $x\%$ aerogels.

For a more detailed investigation of the MNPs in the nanocomposites TEM images were taken; these are displayed in Fig. 6. Widespread separation of the Fe_3O_4 nanoparticles on the surface of BC nanofibers is clearly observed. The Fe_3O_4 NPs are homogeneously distributed on the surface of the BC nanofibers without any obvious agglomeration (Fig. 6a & 6b). From the high resolution TEM (HRTEM) images (Fig. 6c), both the lattice fringes of Fe_3O_4 and the amorphous carbon structure of BC are clearly observed, confirming the encapsulation of the MNPs in the amorphous carbon. Chemical analysis using the EDS elemental mapping shows the distribution of each element confirming the distribution of Fe_3O_4 NPs on the surface of BC nanofibers (Fig. 6d).

Fig. 6. TEM images of the BC-1% nanocomposites: (a) bright field, (b) dark field (c) HRTEM images and (d) EDS elemental mapping images of the BC-1% nanocomposites.

TEM images of CNF- $x\%$ aerogels are shown in Fig. 7. The pristine CNFs show a weaving structure of amorphous carbon nanofibers. At low concentrations of Fe_3O_4 ($<10\%$), the MNPs are evenly distributed without obvious aggregation. However, for CNF concentrations of 10% and above, agglomeration of MNPs begins to occur. The average diameters of Fe_3O_4 NPs measured from the TEM images show that the particle sizes were in the range of 16 – 18 nm for both BC/ Fe_3O_4 and CNF/ Fe_3O_4 samples. This indicated that the pyrolysis did not have an influence on the sizes of MNPs.

Fig. 7. TEM images of (a) pristine CNF, (b) CNF-1%, (c) CNF-3%, (d) CNF-5%, (e) CNF-10%, (f) CNF-20%.

Typical room temperature M-H curves are shown in Fig. 8. The pristine BC and CNFs exhibit non-magnetic behavior as expected. Incorporating Fe_3O_4 nanoparticles induces ferromagnetic responses of the composites but due to the nano-size of Fe_3O_4 particles the width of the hysteresis loops is very small approaching superparamagnetic behavior. The saturation magnetization (M_s) increased with the MNP concentration in a non-linear fashion for both BC- $x\%$ and CNF- $x\%$ composites as shown in Fig. 9. Above 5 vol% of ferrofluid, the rate of increasing M_s is flattened as it approaches the limit of the loaded amount of Fe_3O_4 NPs. The trend of M_s against ferrofluid concentration is similar to the residual weight at 600 °C in Fig. 2b. In addition, the M_s values for the CNF- $x\%$ series are considerably higher than those of the BC- $x\%$ series for all ferrofluid concentrations as a result of their much lighter weight. The highest M_s values were 49.2 emu g^{-1} and 82.9 emu g^{-1} for BC-20% and CNF-20%, respectively. The M_s of CNF-20% nearly approaches the M_s of the bulk Fe_3O_4 (92 emu g^{-1}) [45].

Fig. 8. M-H curves of (a) pristine BC and BC-x%, and (b) pristine CNF and CNF-x% aerogels.

Fig. 9. Saturation magnetization (M_s) versus ferrofluid concentration of BC-x% and CNF-x% aerogels. The solid lines represent a ‘guide for eyes’ only.

For comparison, the maximum magnetization from the present work and previously published data are summarized in Table 1. It is notable that both BC- $x\%$ and CNF- $x\%$ nanocomposites in the present work have a much higher M_s compared to literature values. Even for the magnetization normalized to the weight of Fe_3O_4 particles, our samples still show a very high magnetization, especially for the CNF/ Fe_3O_4 sample, for which the normalized magnetization is nearly double compared to the highest values reported in the literature. Moreover, our synthesis method is facile by simply immersing BC in the commercially available ferrofluid solution and allowing diffusion to occur. The BC/ Fe_3O_4 was transformed to CNF/ Fe_3O_4 by pyrolysis at relatively low temperatures, but achieving large magnetization. The large value of M_s was due to the effective impregnation of Fe_3O_4 NPs and homogeneous distribution of MNPs which allows a large portion of MNPs in the BC structure. The higher magnetization provides the better sensitivity of BC or CNF aerogels to external magnetic fields.

For demonstration of the potential applications of the fabricated materials, we applied the magnetic CNF aerogels as a dye absorbent for water treatment. Fig. 10a shows a series of images demonstrating dye absorption capability of the magnetic CNF aerogel. The vivid blue color was clearly observed after a drop of blue dye was added in water. By immersing the magnetic CNF aerogel in the solution, the blue color gradually faded and the solution became clear just like before the dye was added. After the process was completed, the aerogel was magnetically removed by applying an external magnetic force. The UV-Vis spectroscopy was employed to measure the absorbance spectra of the solution before and after the dye removal using the magnetic CNF aerogel. As clearly shown in Fig. 10b, the UV-Vis absorbance of the solution after dye removal by CNF aerogel was totally suppressed, indicating the efficient dye absorption capability of the CNF aerogel. This demonstration thus shows the unique ability of the CNF/ Fe_3O_4 aerogels for wastewater treatment and the reusability by magnetic extraction. In addition, the saturated CNF/ Fe_3O_4 aerogels can be regenerated simply by immersing the aerogels in ethanol for the desorption of dye. Then, they are dried in an oven for the evaporation of ethanol, which requires an energy of ~ 54 kJ/g. The details of the calculation can be found in the Supplementary Information.

Table 1. Comparison between the maximum magnetizations of the BC/Fe₃O₄ and CNF/Fe₃O₄ in the present work and published data.

Materials	Synthesis method	Maximum magnetization (emu g ⁻¹)	Fe ₃ O ₄ content (wt.%)	M _{max} (emu g ⁻¹) /Fe ₃ O ₄ (wt.%)	Reference
BC/Fe ₃ O ₄	BC grown in MNP-dispersed culture medium	~10	60	0.17	[46]
	Co-precipitation	13.68	N/A	-	[47]
	Gas-enhancing <i>in situ</i> co-precipitation	26.2	57.23	0.46	[29]
	Ultrasonic-assisted <i>in situ</i> synthesis	40.57	65.69	0.62	[28]
	Ultrasonic-assisted <i>in situ</i> synthesis	40.58	38	1.07	[10]
	Simple immersion	49.2	61.1	0.81	Present work
CNF/Fe ₃ O ₄	Pyrolysis and co-precipitation	~10	51.7	0.19	[48]
	Surface-treated and co-precipitation	28	65.1	0.43	[32]
	Vacuum filtration and annealing	56.5	95	0.59	[31]
	Simple immersion and pyrolysis	82.9	90	0.92	Present work

Fig. 10. (a) a series of images demonstrating dye absorption using magnetic CNF aerogel, which was magnetically retracted afterwards. (b) UV-Vis spectra of the solution before and after dye removal using magnetic CNF aerogel, with corresponding images of the solution.

Results from more detailed experiments for the dye (methylene blue, MB) absorption effect are shown in Fig. 11 and 12. Fig. 11a shows the effect of the initial dye concentration on the amount of MB absorbed per unit mass of the absorbent at time t , q_t (mg/g), defined as [49, 50]:

$$q_t = \left(\frac{C_0 - C_t}{m} \right) \times V$$

where C_0 and C_t are concentrations of MB in the solution at the initial state and at any time t , respectively, m is the mass of the absorbent used, and V is the initial volume of the MB solution.

Increasing the initial MB concentration from 10 mg/L to 20 mg/L increases the absorbed dose. However, when the initial MB concentration reaches 50 mg/L, the absorption decreases, probably due to the spatial blockade of MB molecules in concentrated solutions, which restricts the absorption process [51]. It is interesting to note that the CNF with Fe_3O_4 , CNF-5%, (open symbols) exhibits a faster absorption rate than the pristine CNF (solid symbols). This effect is attributed to the different densities of the samples. The CNF/ Fe_3O_4 aerogel is more dense than the pristine CNF aerogel, which means that the CNF/ Fe_3O_4 sample is submerged in the MB solution, whereas the pristine CNF floats on the surface. The data in Fig. 11a are fitted to theoretical models to quantify the absorption isotherm as shown in Fig. 11b (for CNF) and Fig. 11c (for CNF-5%). The linearized Langmuir model [52] fits well to both sets of data, according to the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \left(\frac{1}{q_m}\right)C_e$$

where q_e is the amount of MB absorbed per unit mass of the absorbent, C_e is the equilibrium concentrations of MB in the solution, q_m (mg g^{-1}) is the maximum absorption capacity, and K_a (L mg^{-1}) is the isotherm constants for the Langmuir model.

Fig. 12 shows the effect of temperature on the MB absorption capacity. It is clearly shown that the absorption rate of the pristine CNF strongly depends on temperature; the absorption rate increases with temperature. On the other hand, the absorption of MB is nearly temperature independent for the CNF/ Fe_3O_4 aerogel. These samples can absorb MB almost instantly (within 5 minutes). The data in Fig. 12 are fitted with theoretical models to quantify the absorption kinetics as shown in Fig. 12b (for CNF) and Fig. 12c (for CNF-5%). The linearized-integral form of the pseudo-second-order model [52] is more precise in fitting the data for both samples, using the equation:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \left(\frac{1}{q_e}\right)t$$

where k_2 is the second-order rate constant of absorption.

Fig. 11. (a) The absorption capacity versus time at different initial MB concentrations for CNF and CNF-5%, and Langmuir absorption isotherm for (b) CNF and (c) CNF-5%.

Fig. 12. (a) The absorption capacity versus time at different temperatures for CNF and CNF-5%, and pseudo-second-order absorption kinetics for (b) CNF and (c) CNF-5%.

4. Conclusion

In summary, we have successfully produced BC/Fe₃O₄ nanocomposite aerogels by a simple diffusion method of wet BC in a ferrofluid solution. The BC/Fe₃O₄ aerogels were converted to CNF/Fe₃O₄ aerogels by a pyrolysis process. The formation of the composite phases for the BC/Fe₃O₄ and CNF/Fe₃O₄ aerogels was confirmed by XRD analysis. The amount of the retained Fe₃O₄ NPs in BC and CNF aerogels were not linearly dependent on the concentration of ferrofluid. At higher concentrations (>5 vol.%), Fe₃O₄ NPs were so concentrated that it retarded the diffusion process. However, the ferrofluid concentration did not affect the functional groups of BC or CNF aerogels since the FTIR spectra were not different amongst the samples. For low ferrofluid concentrations, Fe₃O₄ NPs were homogeneously distributed on the surface of the fibres. NPs were found to be encapsulated by amorphous carbon on the surface of the nanofibers, thereby preserving the three-dimensional porous structure of the carbonized bacterial cellulose. However, at higher ferrofluid concentrations, the MNPs were found to be aggregated, and filling the pores. The pyrolysis process affected the size of the nanofibers but not the MNPs. The nanofibers had smaller lateral dimensions after pyrolysis due to weight loss whereas the size of MNPs were not significantly changed. The magnetic measurements were found to be in agreement with the materials characterization. M_s increased non-linearly with ferrofluid concentration. The magnetic CNF aerogels showed higher M_s compared to the BC nanocomposites. The maximum magnetization in the present work is higher than literature values for both the magnetic BC and magnetic CNF. Higher magnetization implies better sensitivity which could be exploited in various applications, such as electronic devices, microwave absorption, energy storage, or wastewater treatment. For wastewater treatment, the magnetic CNF aerogel was demonstrated to show the pollutant absorption capability. The pollutant was totally removed from water and the aerogel was easily recovered using a magnet.

Acknowledgements

This work was supported by the Thailand Research Fund (TRF) in cooperation with Synchrotron Light Research Institute (public organization) and Khon Kaen University (RSA6280020), the Royal Society-Newton Advanced Fellowship (NA160147) in partnership with the Thailand Research Fund (TRF) (DBG6080002), the Royal Golden Jubilee PhD Programme (PHD/0063/2558), and the Research Network NANOTEC (RNN) program of the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Higher Education, Science, Research and Innovation and Khon Kaen University, Thailand.

References

- [1] Mandal M, Kundu S, Ghosh S K, Panigrahi S, Sau T K, Yusuf S M, Pal T (2005) Magnetite nanoparticles with tunable gold or silver shell. *J. Colloid Interface Sci* 286: 187-194. Doi:<https://doi.org/10.1016/j.jcis.2005.01.013>
- [2] Gawande M B, Branco P S, Varma R S (2013) Nano-magnetite (Fe₃O₄) as a support for recyclable catalysts in the development of sustainable methodologies. *Chem. Soc. Rev.* 42: 3371-3393. Doi:10.1039/C3CS35480F
- [3] Tang S C N, Lo I M C (2013) Magnetic nanoparticles: Essential factors for sustainable environmental applications. *Water Res.* 47: 2613-2632. Doi:<https://doi.org/10.1016/j.watres.2013.02.039>
- [4] Turcheniuk K, Tarasevych A V, Kukhar V P, Boukherroub R, Szunerits S (2013) Recent advances in surface chemistry strategies for the fabrication of functional iron oxide based magnetic nanoparticles. *Nanoscale* 5: 10729-10752. Doi:10.1039/C3NR04131J
- [5] Sun C, Lee J S H, Zhang M (2008) Magnetic nanoparticles in MR imaging and drug delivery. *Adv. Drug Deliv. Rev* 60: 1252-1265. Doi:<https://doi.org/10.1016/j.addr.2008.03.018>
- [6] Xie K, Li J, Lai Y, Lu W, Zhang Z a, Liu Y, Zhou L, Huang H (2011) Highly ordered iron oxide nanotube arrays as electrodes for electrochemical energy storage. *Electrochem. Commun.* 13: 657-660. Doi:<https://doi.org/10.1016/j.elecom.2011.03.040>
- [7] Wu W, He Q, Jiang C (2008) Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. *Nanoscale Res. Lett* 3: 397-415. Doi:10.1007/s11671-008-9174-9
- [8] Xu P, Zeng G M, Huang D L, Feng C L, Hu S, Zhao M H, Lai C, Wei Z, Huang C, Xie G X, Liu Z F (2012) Use of iron oxide nanomaterials in wastewater treatment: A review. *Sci. Total Environ* 424: 1-10. Doi:<https://doi.org/10.1016/j.scitotenv.2012.02.023>
- [9] Huang Y, Lin Z, Zheng M, Wang T, Yang J, Yuan F, Lu X, Liu L, Sun D (2016) Amorphous Fe₂O₃ nanoshells coated on carbonized bacterial cellulose nanofibers as a flexible anode for high-performance lithium ion batteries. *J. Power Sources* 307: 649-656. Doi:<http://dx.doi.org/10.1016/j.jpowsour.2016.01.026>
- [10] Zheng Y, Yang J, Zheng W, Wang X, Xiang C, Tang L, Zhang W, Chen S, Wang H (2013) Synthesis of flexible magnetic nanohybrid based on bacterial cellulose under ultrasonic irradiation. *Mater Sci Eng C Mater* 33: 2407-2412. Doi:<http://dx.doi.org/10.1016/j.msec.2013.02.007>
- [11] De Jong K P, Geus J W (2000) Carbon Nanofibers: Catalytic Synthesis and Applications. *Catal. Rev.* 42: 481-510. Doi:10.1081/CR-100101954

- [12] Han S, Sun Q, Zheng H, Li J, Jin C (2016) Green and facile fabrication of carbon aerogels from cellulose-based waste newspaper for solving organic pollution. *Carbohydr.* 136: 95-100. Doi:<https://doi.org/10.1016/j.carbpol.2015.09.024>
- [13] Faccini M, Borja G, Boerrigter M, Martin D M, Crespiera S M, Vazquez-Campos S, Aubouy L, Amantia D (2015) Electrospun Carbon Nanofiber Membranes for Filtration of Nanoparticles from Water. *J. nanomater.*: 9. Doi:10.1155/2015/247471
- [14] Yang X, Guillorn M A, Austin D, Melechko A V, Cui H, Meyer H M, Merkulov V I, Caughman J B O, Lowndes D H, Simpson M L (2003) Fabrication and Characterization of Carbon Nanofiber-Based Vertically Integrated Schottky Barrier Junction Diodes. *Nano Lett.* 3: 1751-1755. Doi:10.1021/nl0346631
- [15] Xu J, Zhang L, Xu G, Sun Z, Zhang C, Ma X, Qi C, Zhang L, Jia D (2018) Facile synthesis of NiS anchored carbon nanofibers for high-performance supercapacitors. *Appl. Surf. Sci.* 434: 112-119. Doi:<https://doi.org/10.1016/j.apsusc.2017.09.233>
- [16] Liu Y, Teng H, Hou H, You T (2009) Nonenzymatic glucose sensor based on renewable electrospun Ni nanoparticle-loaded carbon nanofiber paste electrode. *Biosens. Bioelectron* 24: 3329-3334. Doi:<https://doi.org/10.1016/j.bios.2009.04.032>
- [17] Bhardwaj N, Kundu S C (2010) Electrospinning: A fascinating fiber fabrication technique. *Biotechnol. Adv.* 28: 325-347. Doi:<https://doi.org/10.1016/j.biotechadv.2010.01.004>
- [18] Li D, Wang Y, Xia Y (2004) Electrospinning Nanofibers as Uniaxially Aligned Arrays and Layer-by-Layer Stacked Films. *Adv. Mater* 16: 361-366. Doi:10.1002/adma.200306226
- [19] Faruk O, Bledzki A K, Fink H-P, Sain M (2012) Biocomposites reinforced with natural fibers: 2000–2010. *Prog. Polym. Sci.* 37: 1552-1596. Doi:<https://doi.org/10.1016/j.progpolymsci.2012.04.003>
- [20] Zhu H, Luo W, Ciesielski P N, Fang Z, Zhu J Y, Henriksson G, Himmel M E, Hu L (2016) Wood-Derived Materials for Green Electronics, Biological Devices, and Energy Applications. *Chem. Rev* 116: 9305-9374. Doi:10.1021/acs.chemrev.6b00225
- [21] Lee S-H, An S-J, Lim Y-M, Huh J-B (2017) The Efficacy of Electron Beam Irradiated Bacterial Cellulose Membranes as Compared with Collagen Membranes on Guided Bone Regeneration in Peri-Implant Bone Defects. *Materials* 10: 1018.
- [22] Vasconcelos N F, Feitosa J P A, da Gama F M P, Morais J P S, Andrade F K, de Souza Filho M d S M, Rosa M d F (2017) Bacterial cellulose nanocrystals produced under different hydrolysis conditions: Properties and morphological features. *Carbohydr.* 155: 425-431. Doi:<http://dx.doi.org/10.1016/j.carbpol.2016.08.090>

- [23] Wu Z-Y, Liang H-W, Chen L-F, Hu B-C, Yu S-H (2016) Bacterial Cellulose: A Robust Platform for Design of Three Dimensional Carbon-Based Functional Nanomaterials. *Acc. Chem. Res* 49: 96-105. Doi:10.1021/acs.accounts.5b00380
- [24] Shah N, Ul-Islam M, Khattak W A, Park J K (2013) Overview of bacterial cellulose composites: A multipurpose advanced material. *Carbohydr.* 98: 1585-1598. Doi:http://dx.doi.org/10.1016/j.carbpol.2013.08.018
- [25] Raymond L, Revol J F, Ryan D H, Marchessault R H (1994) In Situ Synthesis of Ferrites in Cellulosics. *Chem. Mater.* 6: 249-255. Doi:10.1021/cm00038a025
- [26] Raymond L, Revol J F, Marchessault R H, Ryan D H (1995) In situ synthesis of ferrites in ionic and neutral cellulose gels. *Polymer* 36: 5035-5043. Doi:http://dx.doi.org/10.1016/0032-3861(96)81633-8
- [27] Zeng M, Laromaine A, Feng W, Levkin P A, Roig A (2014) Origami magnetic cellulose: controlled magnetic fraction and patterning of flexible bacterial cellulose. *J. Mater. Chem. C* 2: 6312-6318. Doi:10.1039/C4TC00787E
- [28] Yingkamhaeng N, Intapan I, Sukyai P (2018) Fabrication and Characterisation of Functionalised Superparamagnetic Bacterial Nanocellulose Using Ultrasonic-Assisted In Situ Synthesis. *Fiber. Polym.* 19: 489-497. Doi:10.1007/s12221-018-7738-6
- [29] Katepetch C, Rujiravanit R (2011) Synthesis of magnetic nanoparticle into bacterial cellulose matrix by ammonia gas-enhancing in situ co-precipitation method. *Carbohydr.* 86: 162-170. Doi:http://dx.doi.org/10.1016/j.carbpol.2011.04.024
- [30] Marins J A, Soares B G, Barud H S, Ribeiro S J L (2013) Flexible magnetic membranes based on bacterial cellulose and its evaluation as electromagnetic interference shielding material. *Mater Sci Eng C Mater* 33: 3994-4001. Doi:https://doi.org/10.1016/j.msec.2013.05.035
- [31] Ren Y, Dai B, Wang G H, Zhang X W, Zhu P, Li S R (2015) Preparation and Microwave Absorption Properties of Novel Carbon Nanofiber/Fe₃O₄ Composites. *J Nanosci Nanotechnol* 15: 2845-2849.
- [32] Luo H, Zhang Y, Yang Z, Xiong G, Wan Y (2017) Constructing superior carbon-nanofiber-based composite microwave absorbers by engineering dispersion and loading of Fe₃O₄ nanoparticles on three-dimensional carbon nanofibers derived from bacterial cellulose. *Mater. Chem. Phys.* 201: 130-138. Doi:https://doi.org/10.1016/j.matchemphys.2017.08.048
- [33] Lv X, Li G, Zhou H, Li D, Zhang J, Pang Z, Lv P, Cai Y, Huang F, Wei Q (2018) Novel freestanding N-doped carbon coated Fe₃O₄ nanocomposites with 3D carbon fibers network

- derived from bacterial cellulose for supercapacitor application. *J. Electroanal. Chem.* 810: 18-26. Doi:<https://doi.org/10.1016/j.jelechem.2017.12.082>
- [34] Sriplai N, Mongkolthanaruk W, Eichhorn S J, Pinitsoontorn S (2018) Magnetically responsive and flexible bacterial cellulose membranes. *Carbohydr.* 192: 251-262. Doi:<https://doi.org/10.1016/j.carbpol.2018.03.072>
- [35] Varma A J, Chavan V B (1995) Thermal properties of oxidized cellulose. *Cellulose* 2: 41-49. Doi:10.1007/bf00812771
- [36] Puig-Gamero M, Fernandez-Lopez M, Sánchez P, Valverde J L, Sanchez-Silva L (2017) Pyrolysis process using a bench scale high pressure thermobalance. *Fuel Proc. Tech.* 167: 345-354. Doi:<https://doi.org/10.1016/j.fuproc.2017.07.020>
- [37] Yue Z R, Jiang W, Wang L, Gardner S D, Pittman C U (1999) Surface characterization of electrochemically oxidized carbon fibers. *Carbon* 37: 1785-1796. Doi:[https://doi.org/10.1016/S0008-6223\(99\)00047-0](https://doi.org/10.1016/S0008-6223(99)00047-0)
- [38] Gomez-Serrano V, Pastor-Villegas J, Perez-Florindo A, Duran-Valle C, Valenzuela-Calahorra C (1996) FT-IR study of rockrose and of char and activated carbon. *J. Anal. Appl. Pyrol.* 36: 71-80. Doi:[https://doi.org/10.1016/0165-2370\(95\)00921-3](https://doi.org/10.1016/0165-2370(95)00921-3)
- [39] Nasibulina L I, Anoshkin I V, Nasibulin A G, Cwirzen A, Penttala V, Kauppinen E I (2012) Effect of carbon nanotube aqueous dispersion quality on mechanical properties of cement composite. *J. Nanomaterials* 2012: 35-35. Doi:10.1155/2012/169262
- [40] Czaja W, Romanovicz D, Brown R M (2004) Structural investigations of microbial cellulose produced in stationary and agitated culture. *Cellulose* 11: 403-411. Doi:10.1023/B:Cell.0000046412.11983.61
- [41] Shen Y-D, Xiao Z-C, Miao L-X, Kong D-B, Zheng X-Y, Chang Y-H, Zhi L-J (2017) Pyrolyzed bacterial cellulose/graphene oxide sandwich interlayer for lithium–sulfur batteries. *Rare Metals* 36: 418-424. Doi:10.1007/s12598-017-0906-9
- [42] Dursun B, Sar T, Ata A, Morcrette M, Akbas M Y, Demir-Cakan R (2016) Pyrolyzed bacterial cellulose-supported SnO₂ nanocomposites as high-capacity anode materials for sodium-ion batteries. *Cellulose* 23: 2597-2607. Doi:10.1007/s10570-016-0966-2
- [43] Korobeinyk A V, Whitby R L D, Niu J J, Gogotsi Y, Mikhlovsky S V (2011) Rapid assembly of carbon nanotube-based magnetic composites. *Mater. Chem. Phys.* 128: 514-518. Doi:<https://doi.org/10.1016/j.matchemphys.2011.03.038>
- [44] Ozaki M, Suzuki H, Takahashi K, Matijević E (1986) Reversible ordered agglomeration of hematite particles due to weak magnetic interactions. *J Colloid Interface Sci.* 113: 76-80. Doi:[https://doi.org/10.1016/0021-9797\(86\)90207-9](https://doi.org/10.1016/0021-9797(86)90207-9)

- [45] Cullity B D, Graham C D (2009) Introduction to magnetic materials. IEEE/Wiley, Hoboken, N.J.
- [46] Park M, Cheng J, Choi J, Kim J, Hyun J (2013) Electromagnetic nanocomposite of bacterial cellulose using magnetite nanoclusters and polyaniline. *Colloid Surface B*. 102: 238-242. Doi:<http://dx.doi.org/10.1016/j.colsurfb.2012.07.046>
- [47] Zhang W, Chen S, Hu W, Zhou B, Yang Z, Yin N, Wang H (2011) Facile fabrication of flexible magnetic nanohybrid membrane with amphiphobic surface based on bacterial cellulose. *Carbohydr*. 86: 1760-1767. Doi:<http://dx.doi.org/10.1016/j.carbpol.2011.07.015>
- [48] Liu Z, Wan Y, Xiong G, Guo R, Luo H (2015) Three-dimensional porous nanocomposite of highly dispersed Fe₃O₄ nanoparticles on carbon nanofibers for high-performance microwave absorbents. *Mater. Express* 5: 113-120. Doi:10.1166/mex.2015.1216
- [49] Ai L, Zhang C, Chen Z (2011) Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite. *J Hazard Mater*. 192: 1515-1524. Doi:<https://doi.org/10.1016/j.jhazmat.2011.06.068>
- [50] Tan I A W, Hameed B H, Ahmad A L (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chem. Eng. J*. 127: 111-119. Doi:<https://doi.org/10.1016/j.cej.2006.09.010>
- [51] Roufegari-Nejhad E, Sirousazar M, Abbasi-Chiyaneh V, Kheiri F (2019) Removal of Methylene Blue from Aqueous Solutions Using Poly(vinyl alcohol)/Montmorillonite Nanocomposite Hydrogels: Taguchi Optimization. *J. Environ. Polym*. 27: 2239-2249. Doi:10.1007/s10924-019-01514-y
- [52] Yagub M T, Sen T K, Afroze S, Ang H M (2014) Dye and its removal from aqueous solution by adsorption: A review. *Adv Colloid Interface Sci*. 209: 172-184. Doi:<https://doi.org/10.1016/j.cis.2014.04.002>