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Magnetic Carbon Nanofibers from Horse Manure via Hydrothermal Carbonization for Methylene Blue Adsorption

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Abstract. Disposal and recycle of waste biomass is of great concern. Thermochemically converting the waste biomass to carbon nanomaterials is an interesting because of environmental friendly, low cost and local availability. In this work, magnetic carbon nanofibers have been synthesized by hydrothermal and carbonization of the magnetite preloaded on horse manure which is controllable temperature and additive of catalyst. It was found that Fe is able to form magnetic carbon nanofibers (M-CNFs). Furthermore, magnetic carbon nanofibers were used as an adsorbent for methylene blue adsorption. Synthesized magnetic sorbents exhibited high performance on methylene blue adsorption and it is successfully separated from the water by magnetic separation.

1. Introduction

The manures from livestock sections have been traditionally used for increase the crop production as an organic fertilizer providing high organic nutrients, nitrogen, phosphorus and potassium. However, animal manure utilization reveals the negative impacts to surrounding environment. The air pollution as an odour nuisance is the main influence on environmental concerns. On one hand, the organic substances such as carbon, nitrogen, hydrogen, etc. compounded of livestock manure can be converted to a high value products. Based on energy production, the production of biogas from manure has been widely investigated recently because of energy and environment issues concerns [1]. Biogas production is employed using anaerobic digestion process can be used in several uses for heat production such as cooking in household, direct combustion to generate electricity [2, 3]. On the other hand, carbon material produced from organic materials has received a much attention since it is abundance of carbon source. Hence, it become a favourable raw feedstock for carbon material production due to alternative precursor with huge availability in nature [4-6]. The development of animal manure to a carbon materials such as biochar, activated carbon, carbon fiber, etc. is extensively effective due to its potential such as the reduction of greenhouse gases emission, cost effective solution, and carbon sequestration [7]. Animal manures developed to porous carbons have some significances such as adsorption performance, high mechanical property, high thermal stability for novel applications. It was widely applied in the fields of environmental technologies such as adsorbent and soil amender. Also, energy utilizations such as electronic devices, catalyst supporter and even



alternate solid fuel [8]. For these reasons, the several technologies have been applied for its manufacturing.

Currently, several thermochemical conversion technologies have been applied for the carbon material manufacturing [9]. Hydrothermal treatment and carbonization is the most effective thermal techniques for carbon production from organic substances [10]. In hydrothermal treatment, the chemical structure of biomass materials have been developed by temperature and pressure during the reaction leads to high carbon content and rising in hydrophobic property obtaining at relatively low temperature (140-260 °C) [11]. While, the carbonization provides the pore formation and also increases in carbon percentage from devolatilization during high temperature operation [12]. Carbonization of organic substances to carbon is normally conducted at moderate temperature ranges between 400 to 900 °C. Vast recent studies reported the process variables such as treatment temperature, holding time in HT process has a significant impact on the specific surface area. A small number of micropores results in a small surface area is only generated from HT process compared to activated carbon. Also, the pores of HT by-product can be blocked via the repolymerization of water soluble compound at long residence time conditions leads to the decrease of specific surface area. In this respect, further carbonization at higher temperatures, the surface areas could be elevated dramatically due to an increase in micropore structure. The HT process combined carbonization can be suitable for the production of adsorbent or catalyst supporter [13-15]. In this study, horse manure (HM) is a famous residue with natural fibrous characteristics was selected as a raw feedstock for synthesis of magnetic carbon nanofibers (M-CNFs) using hydrothermal treatment combined carbonization. The effects of magnetic precursors (*i.e.* iron nitrite and iron oxide) has been investigated on 10 wt.% of magnetic precursor using various impregnation ratios of 10:0 to 0:10 (iron nitrate and iron oxide, wt./wt.) to optimize and serve the magnetic characteristic. The prepared M-CNFs were comprehensively characterized by scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM), respectively. The produced M-CNFs produced from optimum condition was tested to remove methylene blue. Also, the M-CNFs is successfully abled to separate by magnetic characteristic.

2. Experimental

2.1 Magnetic carbon nanofibers preparation

Horse manure (HM) were collected as raw precursor for synthesis of magnetic carbon nanofibers (M-CNF). Before the experiments, the feedstocks were crushed and sieved into the size of 800 µm. In M-CNF synthesis experiment, M-CNF was completely obtained via two-step process which is a hydrothermal treatment followed by carbonization. 30 g prepared horse manure was mixed with 60 ml deionized water. Then, the suspension was transferred into a stainless steel autoclave and it was directly heated in an electrical oven at constant temperature of 200 °C under 24 h controlled holding time to reach hydrothermal treatment which has been reported elsewhere [7]. Afterwards, the effects of iron precursor types and impregnation ratios on the magnetic feature of M-CNF were comprehensively investigated. the solid char from HT process was impregnated with 10 wt.% of magnetic precursor using a various impregnation ratios of 10:0 to 0:10 (iron nitrate and iron oxide, wt./wt.) to optimize and serve the magnetic characteristic. The impregnated samples were dried at 90 °C for overnight before carbonization. Finally, carbonization was conducted in a tubular furnace system, the samples were carbonized at the temperature of 900 °C using a ramping rate of 10 °C/min for 2 h and then cooled to ambient under the nitrogen surrounding. The prepared M-CNF was washed several times with deionized water for cleaning up impurities and then dried and kept for further characterization. The physical morphology and surface functional characteristics of as-prepared M-CNFs were characterized by Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), respectively. While, X-ray diffractometer (XRD) was analyzed to reveals the crystallography of as-prepared M-CNF. While, the magnetic spectra was determined using vibrating sample magnetometer (VSM).

2.2 Methylene blue adsorption study

The adsorption studies were conducted in 100 mL flasks. The methylene blue (MB) solution of 30 mL with the different initial concentrations 25 – 100 mg/L used as an adsorbate were placed in this flask. Then, 0.1 g of as-prepared M-CNFs was added into the MB solution and each sample was kept in an isothermal shaker (30 °C) for 12 h to reach equilibrium of the solution. Another flask containing the same concentration of MB solution without M-CNFs was set to analyze as a blank. Then, the final concentration of MB solutions were directly filtered and analyzed rapidly. The amount of adsorption at equilibrium, Q_e (mg/g), was calculated by:

$$Q_e = (C_0 - C)V / W \quad (1)$$

Table 1. Proximate and elemental analysis of horse manure.

Parameter	
Proximate analysis (wt.%)	
Moisture	7.79
Ash	13.54
Volatile matter	63.34
Fixed carbon*	15.33
Ultimate analysis (wt.%)	
C	45.9
H	6.4
N	1.0
O*	35.8

*calculated by different

where C_0 and C (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

3. Results and discussion

3.1. M-CNFs characteristic

3.1.1 Chemical composition of M-CNFs

Proximate analysis, was analyzed followed standard technique, [16] demonstrated the chemical composition of biomaterials which composes of moisture, volatile matter, fixed carbon and ash. While, the ultimate analysis was used to determine percentage of carbon, hydrogen using CHN elemental analyzer [17]. The oxygen was calculated by the different of 100 percent. The result on proximate analysis of horse manure shows in table 1. It found that horse manure contains 15.33 wt.% of fixed carbon content and ash content about 13.54 wt.%. Furthermore, moisture is lower than 8.0% in weight. The volatile matter content is approximately 64 wt.%. In addition, elemental analysis carried out to examine the C, H, N, O elemental composition. The ultimate analysis obtained on C, H, N, O is approximately 45.9%, 6.4%, 1.0%, 35.7%, respectively.

3.1.2 SEM micrographs of M-CNFs

Physical morphology of M-CNFs samples was observed by scanning electron microscope at the magnificant of 1000X. Figure 1. (A) displays the surface of raw horse manure. Whereas, Figure 1. (B)-(L) displayed SEM images of MCNF samples produced by hydrothermal processes at 200 °C for 24 hours and carbonization at 900 °C for 2 h, and add the iron nitrate and iron oxide ($\text{Fe}(\text{NO}_3)_3$: Fe_2O_3) in a ratio of (0:10) to (0:10). The rough surface and cavities characteristic were found because of high temperature process during pyrolysis. The volatile substances was completely decomposed leaves the carbon matrix representing the pore formation [17, 18]. It is also noticeable that the iron oxide distribution on the surface of the carbon causes the carbon to be magnetized.

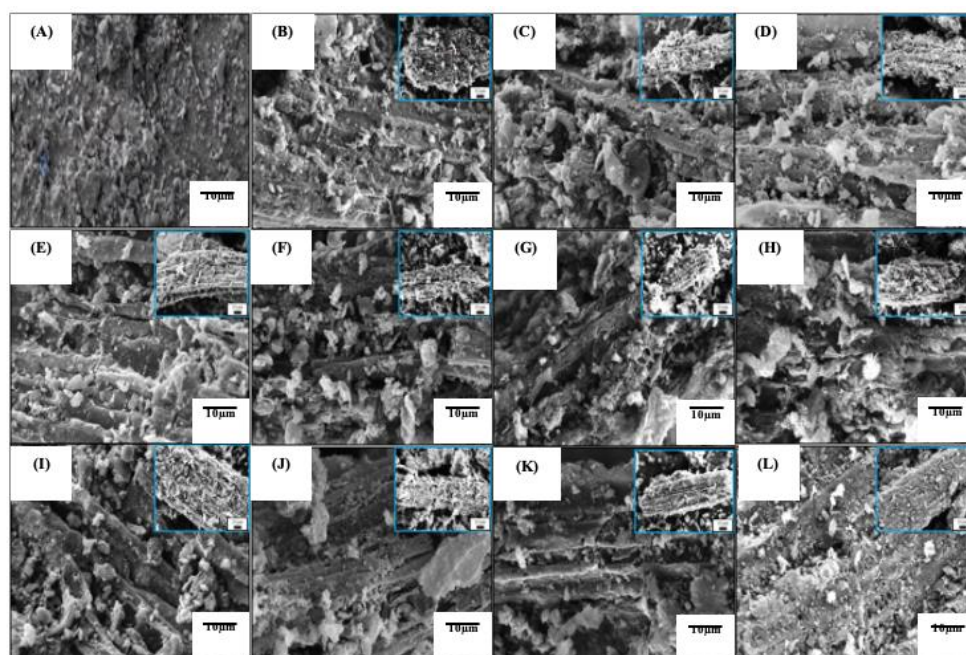


Figure 1. Scanning Electron Microscope (SEM) of (1000x) and (300x) (A). horse manure, the horse manure through hydrothermal processes at 200 °C for 24 h and carbonization at 900 °C for 2 h, and add the iron nitrate and iron oxide($\text{Fe}(\text{NO}_3)_3$: Fe_2O_3) in a ratio of (B). 10:0, (C). 9:1, (D). 8:2, (E).7:3, (F).6:4, (G).5:5, (H). 4:6, (I). 3:7, (J). 2:8, (K). 1:9 and (L). 0:10.

3.1.3 FTIR spectra

The FTIR spectra of a M-CNFs performed with impregnation ratio of magnetic precursors of 10:0 to 0:10 has shown in figure 2. The dominant bands of the products at $525\text{--}575\text{ cm}^{-1}$ and $400\text{--}425\text{ cm}^{-1}$ are the characteristics of Fe_2O_3 [5]. The presence of C–O bond stretching of the C–O–C group at $1,096\text{--}1,121\text{ cm}^{-1}$, respectively [6]. It can be seen that the FTIR spectra situated at 1387 cm^{-1} revealed the characteristic of $\text{Fe}(\text{NO}_3)_3$, where this band was converted due to the carbonization process resulting the $\text{Fe}(\text{NO}_3)_3$ to change into Fe_2O_3 in Peak $400\text{--}425\text{ cm}^{-1}$ and $525\text{--}575\text{ cm}^{-1}$.

3.1.4 XRD patterns

The pattern of the diffraction peak of M-CNFs at the position theta (theta; θ) in figure 3 shows the positions of the peaks in the 26° and 43° of MCNFs that are characteristic of crystalline graphite [7]. The peaks in these positions are low and wide in the range of $20\text{--}30^\circ$ and $40\text{--}50^\circ$, respectively. Amorphous carbon could be explained between the heating process of the arrangement and it is the graphite form, and during carbonization there is a distribution of graphite structure. Higher carbonization heating results in smaller crystals of graphite [8]. However, the peak located at 27° , 32° , 37° , 45° correspond to Fe_2O_3 , which appears in each spectra of M-CNFs and there are any peaks of $\text{Fe}(\text{NO}_3)_3$, therefore, it can be implied that the carbonization process causing the development of $\text{Fe}(\text{NO}_3)_3$ into Fe_2O_3 [18].

3.1.5 VSM analysis of M-CNFs

The magnetic properties of prepared M-CNFs was determined using a vibrating sample magnetometer is displayed in figure 4. M-CNFs was induced in magnetic field to collect the voltage signal which shows the relationship between magnetic moment and applied field [7]. It can be seen that M-CNFs performed at the impregnation ratio of 5:5 magnetic precursors (Fe_2O_3 and $\text{Fe}(\text{NO}_3)_3$) has a magnetic property approximately 0.2 emu.

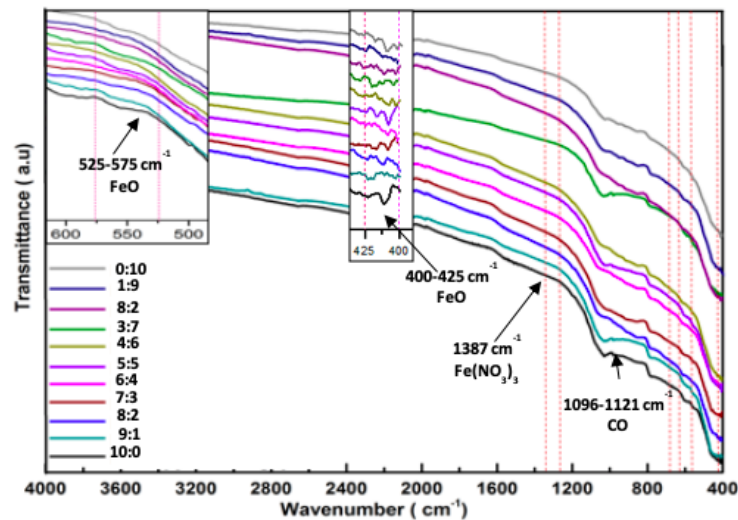


Figure 2. FTIR spectra of a MCNFs and add the iron nitrate and iron oxide ($\text{Fe}(\text{NO}_3)_3$: Fe_2O_3) in a ratio of (10:0) to (0:10).

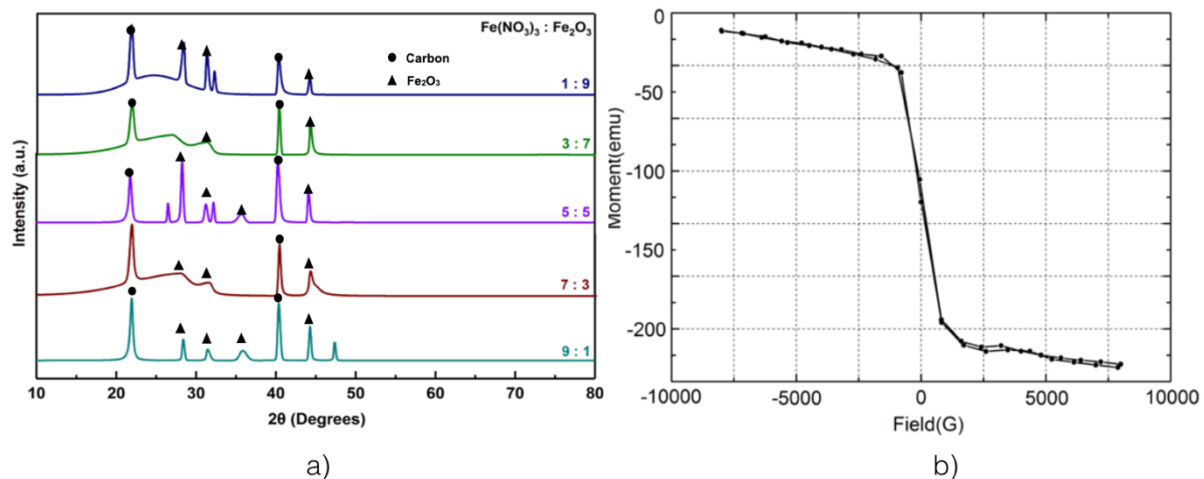


Figure 3. (a) XRD curves of the MCNFs and add the iron nitrate and iron oxide ($\text{Fe}(\text{NO}_3)_3$: Fe_2O_3) in a ratio of (9:1), (7:3), (5:5), (3:7), (1:9) and (b) VSM curve of M-CNFs performed at magnetic precursor impregnation ratio of 5:5.

3.2 Methylene blue adsorption

The results on methylene blue adsorption using as-prepared M-CNFs is shown on figure 4(a). It can be seen that the adsorption curves is linear relationship shows the gradual adsorption at the beginning until 5 min of adsorption time. That is because the adsorption on the pores is occurred rapidly due to the fresh active site on surface of M-CNFs leads to high adsorption rate. After 5 min, the adsorption is slightly decreased until equilibrium at the adsorption time of 15 min. The adsorption performance of M-CNFs is over 98 %. Nonetheless, M-CNFs can be separated conveniently by using a magnet as seen in figure 4(b).

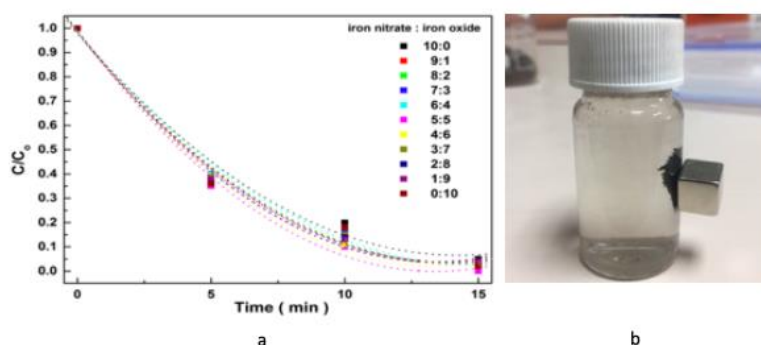


Figure 4. (a) Adsorption capacity of M-CNFs on MB solution at the concentration of 100 mg/L and (b) separation of M-CNFs using a magnetic property.

4. Conclusions

In this study, the carbon nanofibers with magnetic feature (M-CNFs) have been prepared from horse manure via employing the optimum condition of hydrothermal treatment and carbonization processes. The resulting M-CNFs shows the magnetic property. This study reveal that the horse manure is perfectly alternative precursor to develop a carbon nanofiber because of its nature which can provide effective production cost and eco-friendly. Nonetheless, the M-CNFs can be applied as favourable adsorbent providing some prominent characteristics such as high carbon content and high specific surface area. The prepared M-CNFs with the impregnation ratio of 5:5 magnetic precursor shows a paramagnetic properties of 0.2 emu and the methylene blue adsorption is above 98%. It could be implied that animal manures is one of alternative precursors for a carbon-based adsorbent manufacturing.

5. Acknowledgment

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