SYNTHESIS OF MAGNETIC BIOCHAR MATERIALS FROM CORN COBS

Ho Thi Ngoc Nhung*, Nguyen Truong Thien Y, Le Thi Huynh Nhu, Ly Minh Hien, Nguyen Minh Thong

Dong Nai Technology University

**Corresponding author: Ho Thi Ngoc Nhung, hothingocnhung@dntu.edu.vn*

GENERAL INFORMATION

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ABSTRACT

Achieving ecologically sustainable development requires utilizing the added value of waste sources to synthesize functional materials. Currently, Vietnam is a country with developed agriculture, and agricultural by-products are increasing over the years. Making the most of agricultural by-products is a difficult task for local authorities. Agricultural by-products account for a large amount of output such as straw, rice husk, and bagasse. However, the agricultural by-product that accounts for the highest proportion is corn cobs. Due to its physical characteristics, corn cobs are difficult to decompose, leaving a large output for food processing factories. This study describes the process of converting corn cobs by pyrolysis under oxygen limitation into magnetic biochar. The described magnetic biochar can be produced by an improved pyrolysis process at 500°C using iron sulfate as a magnetic precursor and limited oxygen from scavenging gas (gas mixture ratio is 4:1 nitrogen/oxygen). Iron oxide impregnation improves heavy metal ion removal efficiency and increases adsorption capacity for application in wastewater treatment processes. Results are evaluated through material analysis methods such as SEM, FTIR, BET, XRD, and TGA. This article proposes a feasible waste filtration method to turn corn cobs into valuable materials used as effective heavy metal adsorbent.

1. INTRODUCTION

Vietnam is known for its traditional sustainable agriculture, which is one of the country's economic strengths. Along with the growing agricultural output, the amount of agricultural by-products is also increasing alarmingly, such as straw, rice husks, bagasse, and corn stalks. Therefore, making the most of these by-products in the biomass production process to create biochar is a part of sustainable development. Biochar, also known as "black gold," is a carbon-rich solid material derived from the thermochemical conversion of biomass (e.g., plants, manure, and sludge) under limited oxygen conditions (Manyà et al., 2012).

Common applications of biochar include soil improvement to reduce greenhouse gas emissions, reduce soil pollution, improve soil fertility, and treat wastewater (Ghorbani et al., 2020).

The effectiveness of biochar in removing organic and inorganic pollutants depends on its surface area, pore size distribution, surface functional groups, and the size of the molecules to be removed. However, the physical structure and surface properties of biochar depend on the raw material and the synthesis process. Pyrolysis under limited oxygen is one of the most optimal methods compared to Thermal Conversion, Gasification, or Hydrothermal Carbonization (Zhao et al., 2021). High-temperature pyrolysis usually produces biochar with larger surface areas and pore volumes, making it more suitable for adsorbing organic pollutants, while low-temperature biochar has smaller pores, lower surface areas, and higher oxygen-containing functional groups, making it better for removing inorganic pollutants (Enaime et al., 2020). Thus, in the field of wastewater treatment, biochar shows potential for removing suspended solids and heavy metals due to its low cost and minimal pollution, and it has been highly regarded by many scientists.

Despite its promise in heavy metal adsorption from water, biochar use in practice is currently hindered by several challenges. Firstly, biochar has problems with recovery and regeneration, leading to ineffective use (Essandoh et al., 2017). Moreover, its small particle size and low density make it difficult to separate from water (Tan et al., 2016). A promising method to address this issue is combining biochar with magnetic materials (Wang et al., 2020; Yin et al., 2020). For example, metal materials such as iron (Fe), magnesium (Mg), cobalt (Co), nickel (Ni), and zinc (Zn) can be added to biochar's surface (Qin et al., 2017), and magnetic biochar can be prepared using metal salts or metal oxides. To evaluate the efficiency of synthesizing magnetic biochar, this study used agricultural by-product corn cobs combined with Fe ions to increase adsorption efficiency in wastewater treatment. Magnetic biochar was pyrolyzed at temperature ranges of 400ºC (BCM-400), 500ºC (BCM-500), and 600ºC (BCM-600)

2. METHODOLOGY

2.1. Chemical

The chemicals for synthesizing magnetic biochar were provided by Xilong Scientific (China), including sulfuric acid and ferric chloride hexahydrate. Corn cobs were collected from Minh Nam Co., Ltd. in Ho Chi Minh City, Vietnam. The experiment was conducted at the laboratory of Dong Nai University of Technology.

2.2. Method

The magnetic biochar synthesis process was investigated at different temperature ranges: 400ºC, 500ºC, and 600ºC. Each temperature range used 100 corn cobs, which were collected and washed several times with distilled water. The cobs were then cut into pieces approximately 3-4 cm in length to facilitate handling in the laboratory. The raw materials were soaked in 1M sulfuric acid (H_2SO_4) for 24 hours at room temperature to remove most of the hemicellulose and lignin. The materials were then rinsed several times with distilled water to completely wash away any remaining acid and then dried.

An ideal method for surface modification is the use of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$). This solution is non-toxic, can improve adsorption capacity for various pollutants, and provides strong magnetic properties. Ion exchange, complexation, electrostatic attraction, and metal–π interactions are mechanisms that make adsorption techniques suitable (Isaac et al., 2022). The biochar was soaked in ferric chloride hexahydrate

($FeCl_3 \cdot 6H_2O$) and continuously stirred at 70ºC for 24 hours. Finally, the entire material was filtered and dried before being prepared for pyrolysis at 400ºC, 500ºC, and 600ºC for 1 hour. The obtained biochar was washed with distilled water to remove ash and then dried to a constant temperature. The product was stored in desiccated bags. Before analysis, all samples were ground into fine, homogeneous powder and dried at 105ºC for 24 hours according to standard procedures before transporting the samples for analysis. The biochar samples were analyzed using material analysis methods: SEM, FTIR, EDS, VSM, and BET.

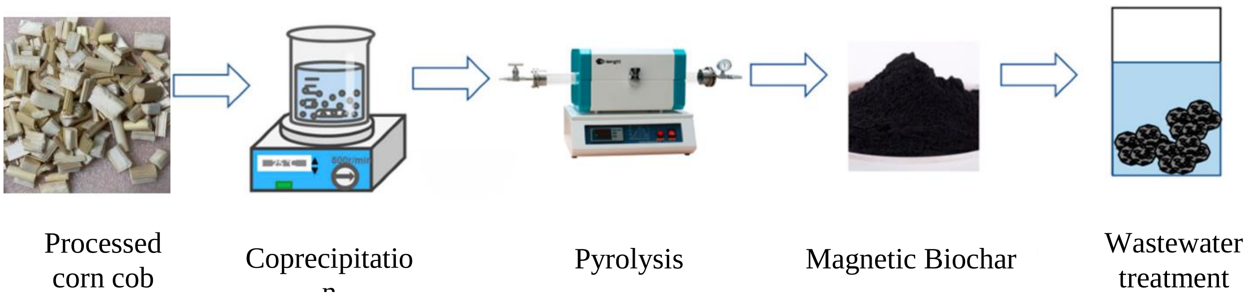

Figure 1. Process for synthesizing magnetic biochar

3. FINDINGS AND DISCUSSION

3.1. Biochar performance and ash content

Before and after pyrolysis, the biochar samples were dried to calculate the biochar yield. Drying also helps save energy and time in the carbonization process (Amalina et al., 2022). Additionally, a large amount of moisture in biomass leads to the production of liquid by-products, such as tar, which significantly affect biochar quality and yield (Al-Rumaihi et al., 2022). The experimental conditions and pyrolysis yields for the BCM samples are shown in Table 1.

Table 1. Magnetic biochar performance and ash content

Sample	Weight before pyrolysis (g)	Weight after pyrolysis (g)				Yield (%)	Ash (%)	pH
		1	2	3	Average			
BCM-400	100	35.4	35.6	35.2	35.4	35.4	11.7	7.5
BCM-500	100	32.3	32.5	32	32.2	32.2	16.4	8,9
BCM-600	100	24.5	24.8	24.6	24.6	24.6	25.3	9,8

The results in Table 1 show that as the pyrolysis temperature increases from 400ºC to 600ºC, the yield decreases from 35.4% to 24.6%, and the ash content increases from 11.7% to 25.3%. As the pyrolysis temperature rises, the mineral and residual combustion content of organic matter increases (Cao et al., 2010). Based on a comparison with Zhao et al. (2018), at a temperature of 500ºC, the author determined the ash content to be 23.27%, which is higher than the result of this study at 16.4%. This comparison shows that the overall assessment has improved the efficiency of the biochar synthesis process.

At the same time, the pH tends to increase from 7.5 to 9.8 as the temperature increases from 400ºC to 600ºC. Based on the report of Mohammad and colleagues (Al-Wabel et al., 2013), increasing the temperature not only raises the ash content from 3.18% to 8.64%, but also increases the pH from 7.37 to 12.38. It has been observed that pyrolysis temperature influences biochar by accelerating the decomposition of acidic substances and promoting the formation of ash from alkaline minerals (Zhao et al., 2018). In addition, biochar produced at lower pyrolysis temperatures may have a higher density of acidic functional groups (Keiluweit et al., 2010).

3.2. Biochar morphology and surface area

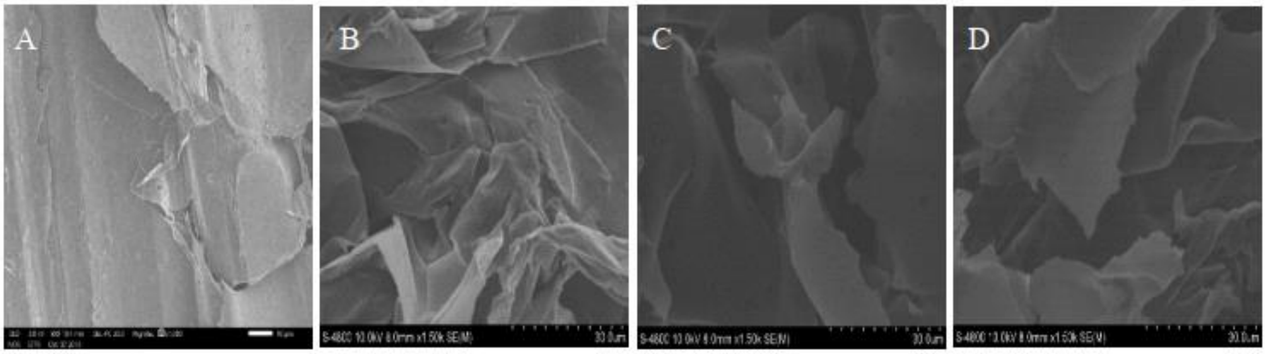

Figure 2. Surface morphology results of magnetic biochar. (A) Corn cob before pyrolysis; (B) Model BCM-400; (C) BCM-500; (D) BCM-600.

The pore distribution is an important factor affecting the adsorption behavior of biochar, as indicated in various studies (Jawad et al., 2020). SEM analysis was used to describe the morphology and surface structure of the BCM-400, BCM-500, and BCM-600 biochar samples. The structure of the material is a collection of many molecules forming microfibers, which can be arranged longitudinally within the primary cell walls. Between these microfibers are voids, where unbranched cellulose molecules join together to form a solid structure.

For the BCM-400 sample, the structure remains nearly intact compared to the original corn cob material, indicating that the pyrolysis process was not yet intense. However, as the temperature increases from 500ºC to 600ºC, the amorphous structure of the material breaks down, and numerous cracks appear. The SEM images of the samples confirm these observations (Figure 2).

The surface area of the biochar materials after pyrolysis in an oxygen-limited environment was evaluated using the BET method, which measures surface area, pore density, and pore volume by introducing nitrogen gas. The results are presented in Table 2.

Table 2. Surface area results (BET)

	S_{BET} (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)
BCM-400	58.265	20.273	0.042
BCM-500	149.743	20.641	0.067
BCM-600	97.434	20.765	0.063

To evaluate the effectiveness of the Fe metal ion addition process to biochar, EDX analysis results show the coexistence of Fe, O and C elements on the surface of ferromagnetic biochar, indicating the possibility of ferromagnetic biochar. ability to form iron oxide. This demonstrates the successful functionalization of the BCM biochar precursor with iron in solution.

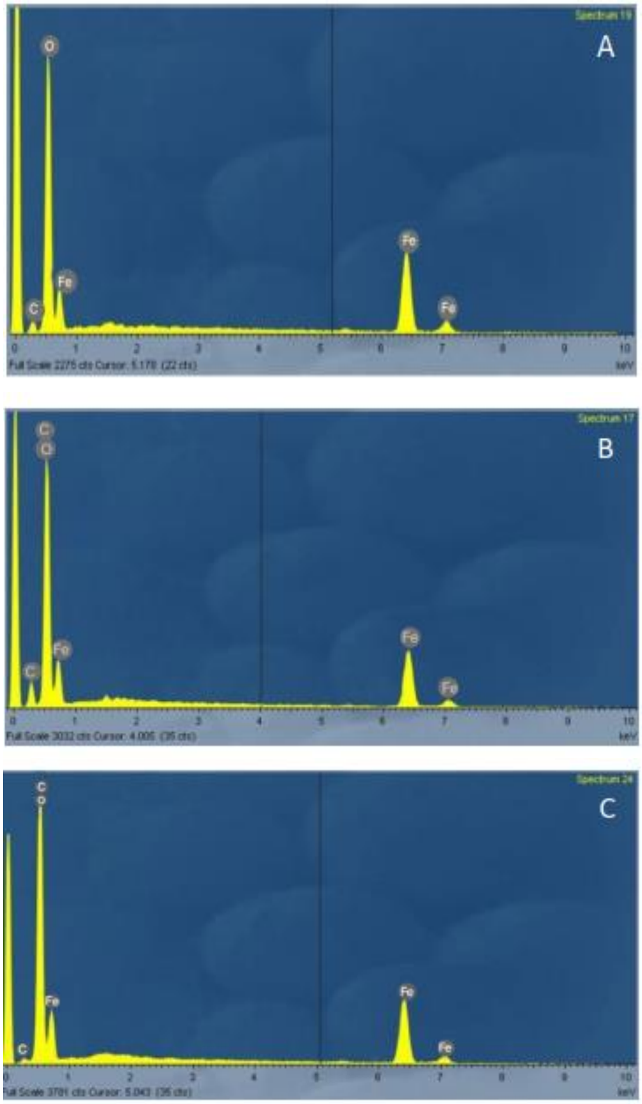

Figure 4. EDX results of biochar. (A) BCM-400; (B) BCM-500; (C) BCM-600.

3.3. Elemental Analysis

In general, the elemental composition of magnetic biochar changes with pyrolysis temperature, as shown in Table 3. Hydrogen and oxygen content decrease from 5.024% to 1.572% and from 29.643% to 10.378%, respectively, while carbon content increases from 60.541% to 81.227% as the pyrolysis temperature rises from 400°C to 600°C. The reduction in hydrogen and oxygen content in magnetic biochar is due to dehydration of organic compounds and loss of volatile components (Suliman et al., 2016). Furthermore, the H/C and O/C ratios in the magnetic biochar samples decrease significantly from 0.083 to 0.019 and 0.490 to 0.128, respectively. The (O+N)/C ratio in BCM-600 is lower than in BCM-400, likely due to the higher degree of carbonization of organic components and the removal of polar functional groups to form aromatic structures (Uchimiya et al., 2010).

Table 3. Elemental analysis of the three different biochars

	C%	H%	N%	O%	O:C	H:C	N:C	(O+N)/C
BCM-400	60.541	5.024	1.469	29.643	0.490	0.083	0.024	0.514
BCM-500	71.434	2.746	2.047	18.842	0.264	0.038	0.029	0.292
BCM-600	81.227	1.572	1.355	10.378	0.128	0.019	0.017	0.144

3.4. FTIR Analysis

FTIR spectroscopy was applied to determine the diversity of functional groups on the surface of the biochar. From the results in Figure 3, the FTIR spectra of the three types of biochar are shown. The peak intensity of CO_3^{2-} (1430 cm^{-1}) and PO_4^{3-} (1083 cm^{-1}) increased as the temperature rose, due to the decomposition of water and organic matter into minerals containing PO_4^{3-} and CO_3^{2-} at high temperatures (Cao et al., 2019). The peaks at 3385 and 2910 cm^{-1} represent the presence of phenolic-OH and methyl C-H (Sun et al., 2022), with their intensity increasing initially and then decreasing as the temperature continued to rise, peaking at 500°C. Conversely, the peak intensity at 1600 cm^{-1}, representing the carbonyl/carboxyl C=O aromatic group (Al-Wabel et al., 2013), increased as the pyrolysis temperature reached 500°C and then remained stable from 500°C to 600°C. As the pyrolysis temperature increased, the intensities of the peaks at 874 and 796 cm^{-1} (aromatic C-H vibrations) also increased (Bhuyar et al., 2019), indicating that the aromaticity of the biochar also increased, which is consistent with the results presented in Table 3. The surface functional groups of biochar did not differ significantly at the three pyrolysis temperatures, but the biochar pyrolyzed at 500°C (BCM-500) showed the highest absorption intensity for oxygen-containing functional groups.

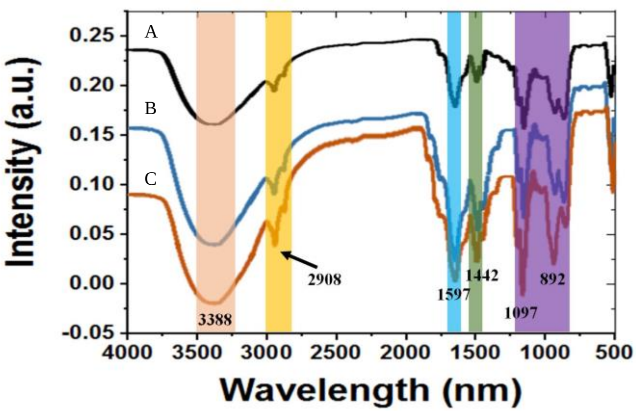

Figure 3. FTIR spectrum of magnetic biochar. (A) BCM-400; (B) BCM-500; BCM-600.

4. CONCLUSION

The study successfully synthesized magnetic biochar from corn cobs through pyrolysis at various temperatures (400ºC, 500ºC, and 600ºC). The pyrolysis process was enhanced by adding iron ions (Fe) to improve the magnetic properties of the biochar, aiming to increase the adsorption efficiency of heavy metals in wastewater treatment. Among the samples, the one pyrolyzed at 500ºC (BCM-500) showed the highest efficiency, with a surface area of 149.743 m^2/g, excellent adsorption performance due to its porous structure, and an optimal distribution of surface functional groups.

Additionally, the study indicated that as the pyrolysis temperature increases, the surface area and adsorption capacity of the biochar initially increase but then decrease after reaching a peak at 500ºC. The chemical composition of biochar changes with temperature, with a decrease in hydrogen and oxygen content and an increase in carbon content, which enhances the material's stability and its ability to remove pollutants.

The research results confirm the high potential of magnetic biochar derived from corn cobs in wastewater treatment technologies, particularly for the removal of heavy metals. This provides a sustainable and efficient solution, while also helping to utilize agricultural by-products and reduce environmental pollution.

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