ONE-POT PREPARATION OF MAGNETIC BIOCHAR FROM DRAGON FRUIT BRANCH FOR CATALYTIC OZONATION OF SUNSET YELLOW

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ABSTRACT

Dragon fruit branches are an abundant and underutilized waste released from the annual pruning of dragon fruit. In this study, dragon fruit branches were used for the first time as a raw material for producing magnetic biochar through one-pot pyrolysis. The results showed that zero-valent iron and magnetite particles were generated in the carbon matrix, providing a saturation magnetization of 5.92 emu/g. Due to FeCl₃ activation, magnetic biochar possessed a total pore volume of 0.15 cm³/g and a specific surface area of 203 m²/g. Subsequently, magnetic biochar was explored as a catalyst for enhanced ozonation of sunset yellow. 95% of sunset yellow (50 ppm) was treated within 80 min at pH 7.0. From the calculation results using pseudo-first-order kinetics, the sunset yellow decolorization constant was improved by 79% by using the magnetic biochar catalyst compared to ozone alone. Overall, dragon fruit branch-derived magnetic biochar is a promising material, especially as a green catalyst, because of its magnetic separability and potential catalytic activity for the treatment of sunset yellow by ozone.

Keywords: Dragon Fruit Branch, One-Pot Strategy, Magnetic Biochar, Catalytic Ozonation, Environmental Treatment, Sunset Yellow.

INTRODUCTION

Dragon fruit (Hylocereus undatus), also known as pitaya, is a tropical climbing plant.¹ Originating in the desert regions of Mexico, Central America, and South America, dragon fruits are currently cultivated in Southeast Asian nations such as Vietnam, Malaysia, Thailand, the Philippines, Indonesia, and others.²,³ To improve the productivity of harvested fruits, dragon fruit branches (DFB) are frequently cut off and discarded annually,⁴,⁵ potentially causing pollution in the surrounding environment. Numerous studies have created valuable products from lignocellulosic waste, such as carbon-based materials. For dragon fruits, several studies concentrated on their peels for the production of biochar,⁶ activated carbon,⁷,⁸ and carbon dots.⁹ However, few literature reports mention the use of DFB. Consequently, the valorization of this abundant agricultural waste could be of great interest and necessity.

Biochar (BC) is a product of the carbonization of organic resources in oxygen-free atmospheres.¹⁰ The material has received considerable notice owing to its exceptional ability to absorb heavy metals and organic contaminants from aqueous solutions.¹¹-¹³ Nonetheless, the later removal of utilized BC from aqueous media generally requires centrifugation and filtering procedures, which restricts its broad usage in wastewater treatment.¹⁴ To tackle this challenge, magnetic components such as zero-valent iron (Fe⁰), magnetite (Fe₃O₄), or maghemite (Fe₂O₃) can be loaded into BC to generate magnetic biochar (MBC).¹⁵,¹⁶ The advanced material possesses not only excellent properties of porous carbon support but also powerful separability of magnetic particles by using external magnets.¹⁷ Moreover, such reports reveal that iron-based particles in MBC could become catalytic sites for the decomposition of organic pollutants.¹⁸,¹⁹ Hence, MBC can act as both an adsorbent and an oxidation catalyst to remove organic contaminants.

To prepare MBC, biomass is first pyrolyzed into BC, then impregnated with a magnetic precursor, and finally pyrolyzed again.²⁰,²¹ Although this procedure is easy, there are numerous steps involved. Moreover,
additional magnetic particles may obstruct existing pores in BC, diminishing the properties of MBC. Recently, one-pot pyrolysis has been developed as a solution to these drawbacks. The biomass is impregnated directly with a magnetic precursor, and the mixture is subsequently pyrolyzed to yield MBC. With the generation of certain gases (like CO and H₂) from biomass carbonization, magnetic precursors can be converted into magnetic particles. According to Bedia et al., FeCl₃, a typical magnetic precursor, can not only introduce magnetic Fe-based particles into BC but also activate its porous system, resulting in better properties.

Ozone is a powerful oxidant with an electric potential of 1.25 V in basic environments and 2.07 V in acidic environments. Due to the reactivity of ozone with organic molecules, it is frequently used to decolorize wastewater and convert organic matter into one that is more biodegradable. Nevertheless, direct ozonation is ineffective at treating organic molecules with electron-withdrawing groups or saturable ring systems. To enhance degradation capabilities, catalytic ozonation has gained considerable interest. Manganese-based materials exhibit strong catalytic activity in ozonation processes. Nonetheless, manganese is a heavy metal with a drinking water guideline value of 0.4 mg/L. Although little is known about the use of cheap and non-toxic Fe-based materials as heterogeneous ozonation catalysts, this combination has the potential to be effective. Such research demonstrates that Fe₃O₄, Fe₂O₃, and FeOOH exhibit their catalytic activity during the ozonation of numerous organic compounds. However, these particles may agglomerate during use, thereby diminishing their performance. Therefore, it is preferable to disperse these particles on suitable supports, such as biochar. Recent investigations indicate that composites of Fe-based particles and carbon-based materials can serve as heterogeneous catalysts for the ozonation of organic pollutants. BC can bind Fe-based particles and induce synergistic effects that make ozonation more effective. Because MBC is composed of Fe-based particles and BC support, it is anticipated that the material could improve the ozonation process. In summary, the current research utilized dragon fruit branches to produce MBC using a single-pot pyrolysis process. The as-prepared material was then evaluated for catalytic ozonation of sunset yellow.

**EXPERIMENTAL**

**Material**

Discarded dragon fruit branches were gathered from a dragon fruit farm in Binh Thuan province, Vietnam. The biomass was cleaned using tap and distilled water, sliced into tiny pieces, and dried at 105 °C for 18 h. Following that, DFB was finely milled and sieved. The particle size range of 0.25–0.50 mm was taken and put in a plastic bag for later use. Without additional purification, all chemicals of analytical grade were utilized as received.

**One-pot Preparation of MBC from DFB**

Magnetic biochar was prepared from discarded DFB as a carbon source and FeCl₃ as a magnetic precursor. In a nutshell, 2.00 g of DFB and 0.40 g of FeCl₃ were added to a glass flask containing 100 mL of distilled water and then mixed for 24 h using a magnetic stirrer. Next, the mixture was completely dried after 24 h at 105 °C. 2.00 g of FeCl₃-loaded DFB was placed in a glass reaction tube. A constant N₂ flow of 0.2 L/min kept the environment in the tube inert. Pyrolysis was carried out at 600 °C for 2 h using a heating rate of 5.0 °C/min. After allowing the tube to cool to ambient temperature, the solid was thoroughly rinsed with distilled water to remove any remaining FeCl₃. Finally, the MBC sample obtained after drying at 105 °C for 24 h was kept in an airtight desiccator for later use.

**Characterization of MBC**

Several techniques were used to investigate the properties of MBC. A Bruker D2 Phaser XE-T diffractometer was used to acquire X-ray diffraction (XRD) patterns of MBC. The target was CuKα radiation (λ = 1.5418 Å). Fourier transforms infrared (FTIR) spectroscopy was used to explore functional groups on the MBC surface using a TENSOR 27 spectrometer. Magnetic properties were examined by the vibration sample magnetometer (VSM) at ambient temperature. Using a NOVA 2200e instrument, the nitrogen adsorption and desorption isotherms of MBC were measured at 77 K. The material was degassed at 300 °C for 3 h. The Brunauer-Emmett-Teller model was utilized to determine S_{BET}. V_{total} was determined at P/P₀ = 0.991. The average pore diameter (d_{avg}) was calculated from 4V_{total}/S_{BET}. Lastly, A JEOL JSM-
IT200 instrument was employed to examine scanning electron microscopy (SEM) images, energy dispersive X-ray (EDX) spectroscopy, and elemental mapping.

**Catalytic Ozonation of Sunset Yellow with MBC**

The catalytic performance of MBC was explored for the ozonation of sunset yellow at room temperature (30 °C). The experimental setting was based on previous studies. First, MBC was added to a glass reactor, which contained 200 mL of SY solution (50 ppm). With NaOH and H$_2$SO$_4$ solutions, the initial pH of the suspension was changed to 7.0. The mixture was continuously agitated with a magnetic stirrer. The adsorption was conducted for 10 min until it nearly reached equilibrium. Then, an airflow of 4.5 L/min containing ozone (0.52 mmol/min) generated from an ozone generator (Vina Ozone Generator model VN3) was bubbled in the reaction mixture. At appropriate points, sampling was conducted, and MBC was removed by centrifugation. A UV-VIS spectrophotometer (Spectronic Genesys 2 PC) was used to analyze the SY concentrations. Using the following formulas, the adsorption capacity and decolorization efficiency of SY over MBC were calculated:

\[
\text{Adsorption capacity (mg/g)} = \frac{(C_0^A - C_{10}^A)}{C_{\text{MBC}}} \quad (1)
\]

\[
\text{Decolorization efficiency (%) } = \frac{(C_0^O - C_{80}^O)}{C_0^O} \times 100\% \quad (2)
\]

Where $C_{\text{MBC}}$ (g/L) was MBC dosage, $C_0^A$ and $C_{10}^A$ (ppm) were the SY concentrations at the beginning and after 10 min of adsorption. $C_0^O$ and $C_{80}^O$ (ppm) were the SY concentrations at the beginning and after 80 min of ozonation. SY decolorization was calculated using pseudo-first-order kinetics. $C_t^O$ (ppm) was the SY concentration after $t$ (min) of ozonation and $k$ (min$^{-1}$) was the decolorization rate constant.

\[
k \times t = -\ln\frac{C_t^O}{C_0^O} \quad (3)
\]

**RESULTS AND DISCUSSION**

**X-ray Diffraction of MBC**

Figure-1a shows the XRD result of MBC. The noise background caused by the amorphous phase of the carbon support could partly overlap certain Fe-based crystal peaks. In this situation, careful checking found characteristic peaks at 2θ = 42.44 and 61.45°, which represent the (110) and (200) planes of zero-valent Fe crystals (JCPDS 06-0696). Moreover, peaks at 2θ = 31.90, 36.52, 58.76, and 62.45° correspond to the (311), (400), (511), and (440) planes of Fe$_3$O$_4$ crystals (JCPDS 19-0629).

Previous studies reported the existence of both Fe$^0$ and Fe$_3$O$_4$ crystals in MBC. Fe$_3$O$_4$ was formed from FeCl$_3$ precursor, then partially reduced to Fe$^0$. The proposed pathway might occur during one-pot pyrolysis of FeCl$_3$-loaded DFB as follows:

\[
\text{DFB} \rightarrow \text{C, CO, H}_2, \text{H}_2\text{O}
\]

\[
\text{FeCl}_3 + \text{H}_2\text{O} \rightarrow \text{FeO(OH)} \rightarrow \text{Fe}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{CO}_2
\]

\[
\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}
\]

(4) (5)
FTIR Spectroscopy of MBC
The FTIR spectroscopy of MBC is presented in Fig.-1b. Its surface may have a variety of functional groups, which include O-H at 3701 cm\(^{-1}\), C-H at 2882 cm\(^{-1}\), O=C=O at 2351 cm\(^{-1}\), C=O or C=C at 1530 cm\(^{-1}\), and C-O at 1048 cm\(^{-1}\).\(^{42-45}\) Notably, several studies show that a peak at 685 cm\(^{-1}\) might be a vibration of the C-Cl band, which might keep Cl in MBC.\(^{46-48}\) More specifically, Xu \ et al.\(^{49}\) reported that FeCl\(_3\)-activation of biomass could form tight C-Cl bonds. Moreover, that process might increase oxygen-rich groups in MBC.\(^{22}\) Hence, the availability of such polar groups can render the MBC surface less inert and more accessible to water-soluble organic compounds like SY.

SEM Images of MBC
Figure-2 depicts SEM images of MBC at two magnifications (x2,000 and x10,000). The results show that MBC consisted of fragments of various sizes and shapes, attributable to fine crushing and pyrolysis. Moreover, it seems that small particles were attached to the MBC surface. These particles could be Fe-based crystals trapped in the carbon matrix without forming large clusters. Such research proved that Fe-based products from one-pot FeCl\(_3\) activation of biomass could be distributed not only on the carbon surface but also inside the carbon matrix.\(^{22,50}\) A uniform and firm distribution of the Fe-based particles is expected to enhance the stability and reusability of MBC in catalytic applications.

Magnetic Properties of MBC
Figure-3a reveals that a magnet bar effectively attracted nearly all MBC powder. To learn more about the magnetic properties of MBC, VSM analysis was performed. The result shows that MBC exhibited superparamagnetic behavior with a saturation magnetization of 5.92 emu/g. As a result, MBC is instantly magnetized and demagnetized, making magnetic separation easy. Furthermore, Fe\(^0\) and Fe\(_3\)O\(_4\) particles are both typical magnetic materials.\(^{51-53}\) Consequently, their presence in MBC could contribute to its magnetic properties.

EDX Spectroscopy and Elemental Mapping of MBC
As shown in Fig.-3b, Fe (6.49 wt%) and O (12.25 wt%) were the predominant elements scattered on the carbon support (76.23 wt%). Interestingly, the atom ratio of O/Fe is 6.6, which is dramatically higher than Fe\(_2\)O\(_4\). As aforementioned, different oxygen-rich functional groups present in MBC could account for this discovery. Moreover, trace quantities of Ca, Mg, Cl, and S were identified on the MBC surface. These elements may originate from DFB or chemical impurities. In the case of Cl, careful cleaning with distilled water repeatedly removed residual FeCl\(_3\). Hence, any remaining Cl in the carbon matrix may be tightly held by strong mechanical or chemical bonds. As previously stated, this element might be kept in the carbon matrix by strong covalent C-Cl bonds. More importantly, element mapping revealed that all available elements were uniformly spread on the MBC surface. The homogeneous Fe dispersion could be attributable to the fact that FeCl\(_3\) was well-preloaded into DFB.

Porous Properties of MBC
Through FeCl\(_3\)-activation of DFB, \(S_{\text{BET}}\) for MBC was 203 m\(^2\)/g, \(V_{\text{total}}\) was 0.15 cm\(^3\)/g, and \(d_{\text{avg}}\) was 3.0 nm. With the presence of Fe-based particles in MBC, its porous properties were still favorable. Such earlier research demonstrated that FeCl\(_3\) can become an activating agent during the pyrolysis of biomass.\(^{24}\) It could...
not only eliminate the closure of existing pores by Fe-based particles but also activate them to expand the porous system.

**Fig.-3:** (a) VSM, (b) EDX Spectroscopy, and (c) Elemental Mapping of MBC

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**Catalytic Ozonation of Sunset Yellow with MBC**

The catalytic activity of MBC was investigated for the ozonation of sunset yellow. Because such reports revealed that the catalytic decolorization of sunset yellow by O\(_3\) could follow pseudo-first-order kinetics,\(^9\) that equation was used to compute the decolorization rate constant of SY. Figure-4 and Table-1 indicate that, without O\(_3\), MBC partially removed SY with a low adsorption capacity of 3.5 mg/g.

**Fig.-4:** (a) Catalytic Ozonation of SY with MBC and (b) its Pseudo-First-Order Kinetics

As discussed before, functional groups on the MBC surface might be favorable for SY adsorption on MBC. Regarding O\(_3\) alone, it is a strong oxidant that decreased 81% of SY within 80 min. The rate constant reached 0.021 min\(^{-1}\) (R\(^2\) = 0.997). When different MBC dosages were used, SY decolorization was generally enhanced. The rate constants for 0.25, 0.50, and 1.00 g/L of MBC were 0.029 min\(^{-1}\) (R\(^2\) = 0.993), 0.036...
min⁻¹ ($R^2 = 0.988$), and 0.038 min⁻¹ ($R^2 = 0.999$), respectively. As a result, the rate of catalytic SY decolorization increased from 39% to 79%. These results demonstrate that MBC accelerated SY decolorization by O₃.

Based on previous studies in the literature, the proposed mechanisms for ozonation catalyzed by Fe-based particles in MBC (denoted as C − Fe) are as follows:

\[
\begin{align*}
C - Fe^0 + O_{3} + 2H_{2}O &\rightarrow C - Fe^{2+} + O_{2} + 2OH^- \quad (6) \\
C - Fe^0 + 2O_3 &\rightarrow C - Fe^{2+} + 2O_3^- \quad (7) \\
C - Fe^0 + O_{3} + 2H^+ &\rightarrow C - Fe^{2+} + O_2 + 2H_2O \quad (8) \\
C - Fe^{2+} + O_3 &\rightarrow C - FeO^{2+} + O_2 \quad (9) \\
C - FeO^{2+} + H_{2}O &\rightarrow C - Fe^{3+} + \cdot OH + OH^- \quad (10) \\
C - Fe^{3+} + O_{3} + H_{2}O &\rightarrow C - FeO^{2+} + \cdot OH + O_2 + H^+ \quad (11) \\
SY + \cdot OH &\rightarrow \text{Intermediates} \rightarrow CO_2 + H_2O \quad (12)
\end{align*}
\]

Hence, Fe⁰ could be first converted to Fe²⁺. In neutral and basic environments, reactions (6) and (7) are predominant. In contrast, acidic media can boost the reaction (8). Next, Fe²⁺ can accelerate the formation of \cdot OH radicals from O₃. Apart from that, greater catalyst dosages may cause ineffective catalyst utilization. High Fe²⁺ site concentrations could limit the generation of \cdot OH radicals by participating in the following equation:

\[
C - FeO^{2+} + C - Fe^{2+} + 2H^+ \rightarrow 2C - Fe^{3+} + H_2O \quad (13)
\]

In the cases of 0.50 and 1.00 g/L catalyst dosages, the decolorization rate constants were quite close, and hence, increasing the catalyst dosage was regarded as insignificant. Consequently, it is possible to conclude that MBC exhibited advantageous catalytic activity for the ozonation of SY.

### Table-1: Adsorption Capacity and Catalytic Ozonation of SY by MBC

<table>
<thead>
<tr>
<th>MBC (g/L)</th>
<th>Adsorption (after 10 min)</th>
<th>Decolorization (after 80 min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SY (ppm)</td>
<td>Adsorption capacity (mg/g)</td>
<td>SY (ppm)</td>
</tr>
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<td>0</td>
<td>50.0</td>
<td>0</td>
<td>9.4</td>
</tr>
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<td>0.25</td>
<td>49.3</td>
<td>2.6</td>
<td>5.2</td>
</tr>
<tr>
<td>0.50</td>
<td>48.3</td>
<td>3.5</td>
<td>2.6</td>
</tr>
<tr>
<td>1.00</td>
<td>48.2</td>
<td>1.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### CONCLUSION

In this study, MBC was successfully synthesized via one-step pyrolysis of FeCl₃ and dragon fruit branch waste. The results show that Fe⁰ and Fe₃O₄ crystals were formed in MBC. The presence of Fe-based particles provided a saturation magnetization of 5.92 emu/g, which could support the effective magnetic separability of MBC. Moreover, FeCl₃-activation yielded MBC with a $S_{BET}$ of 203 m²/g and a $V_{total}$ of 0.15 cm³/g. Following catalytic ozonation of sunset yellow with MBC, 95% of SY (50 ppm) was removed at pH 7.0 within 80 min. The MBC catalyst improved the decolorization rate constant (calculated by pseudo-first-order kinetics) by 79% over ozone alone. In conclusion, green dragon fruit branch-derived magnetic biochar is a promisingly multifunctional material, owing to its magnetic separability and catalytic activity for the ozonation of sunset yellow.

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### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

### AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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