Facile preparation of lotus seedpod-derived magnetic porous carbon for catalytic oxidation of Ponceau 4R

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Abstract. In this research, magnetic porous carbon was directly synthesized through one-step pyrolysis of FeCl3 – lotus seedpod mixture. Properties of the obtained material were analysed by X-ray powder diffraction, SEM image, nitrogen adsorption isotherm and vibrating sample magnetometer. The results showed that magnetic Fe3O4 particles were successfully formed over the material template in 1 hour. The magnetic porous carbon possessed the specific magnetization of 7.13 emu/g, high specific surface area of 288 m²/g and total pore volume of 0.18 cm³/g. The material was subsequently applied as a potential catalyst for Ponceau 4R degradation by H2O2. Parameters including pH, H2O2 concentration, and different types of catalysts were investigated. At pH 3, 200 ppm H2O2, and 0.40 g/L magnetic porous carbon, 83% Ponceau 4R 50 ppm was removed after 120 minutes treatment. Moreover, the catalyst powders were separated from the treated mixture easily by a magnet. Summarily, magnetic porous carbon can promise to be an efficient catalyst in decomposition of Ponceau 4R.

1. Introduction

Lotus (Nelumbo nucifera) is an aquatic plant, which is widely grown in ponds and lakes throughout Asia [1]. Lotus is world famous for its multitude of purposes [2]. Its seeds, rhizomes, roots, stems can be used as food. Parts of the lotus plant are utilized as a traditional medicine to treat many diseases. Lotus leaves can be used to wrap foods as an environmentally friendly packaging. In addition, many studies show its protective effects in human health in the prevention of diabetes, neurotic, obesity and cancer [3]. Lotus flowers are collected on a large scale because they contain alkaloids, flavonoids, steroids and polysaccharides [2, 4]. Lotus roots and seeds are regarded as a popular nutritious source of food, since they provide β-sitosterol, palmitic acid and glucose [5]. However, lotus seedpods (LSPs) are under-utilized. They are often discarded or bulked into mounds, causing environmental pollution. The conversion of surplus agricultural residues like LSPs into porous carbon (PCs) can be described as a “green” solution to produce a new material of outstanding environmental value, contributing to environmental protection and meets the requirements for sustainable development.

PCs possess high specific surface area, large pore size, and diverse surface functional groups [6, 7]. Therefore, they are mainly used as adsorbents [6-8]. Nevertheless, PC powders are difficult to separate from mixtures. To overcome this situation, magnetic particles such as Fe, Co, γ-Fe2O3, Fe3O4, MnFe2O4 are recently attracting the attention of scientists [9-12]. Dispersing magnetic particles on PCs not only
supports magnetic recoverability but also prevents magnetic nanoparticles from aggregating into larger species. Due to its strong magnetic properties [13], magnetite Fe3O4 has gotten the most attention. Moreover, Fe3O4 particles can be an oxidation catalyst for the degradation of organic pollutants in wastewater. The dispersion of magnetic particles as Fe3O4 on porous carbon material can open new applications. The composite is known as magnetic porous carbon (MPC). Normally, MPC can be prepared by salt precipitation on the surface of an existing carbon material [14]. However, the conventional method is not only complicated, but also causes adverse effects on the capillary of the resulting material. More recently, an advanced method has been introduced for the synthesis of MPC. It is only one-step pyrolysis of biomass with a magnetic precursor [15]. This convenient method can form carbon-based magnetic particles simultaneously during a one-step pyrolysis process. That makes the material easy to recover after use. In recent years, there have been a few studies related to the catalytic activity of magnetic particles of this material. On that account, the research will provide a method to formulate magnetic porous carbon from lotus seedpods and iron (III) chloride that also has catalytic activity to decompose organic pollutants in water. Therefore, it potentially has eco-friendly utilization as a catalyst for Ponceau 4R (P4R) degradation by H2O2.

2. Materials and method

2.1. Materials
Lotus seedpods were collected from Thanh Binh district, Dong Thap province, Vietnam. The biomass was washed with distilled water and dried in an oven at 110 °C within 24 hours. The dried material was then crushed and sieved to obtain smooth flour.

2.2. Preparation of magnetic porous carbon
4.00 g dried lotus seedpods were added into the FeCl3 solution. The mixture was stirred for 18 hours and dried at 110 °C for 24 hours. The dried sample was then pyrolyzed under a continuous nitrogen flow of 200 mL/min at 600 °C at different time. The obtained material was washed with distilled water until pH became neutral. Samples are denoted by MPC-Rx-yh (x: the mass ratio of FeCl3 to lotus seedpods (w/w), y: pyrolytic time (h)).

2.3. Characterization
The crystalline structure of MPCs was characterized by X-ray powder diffraction (XRD) using Brucker AXS D8 diffractometer over the 2θ range of 10 – 80° and the scan rate of 0.02°/min. Cu-Kα radiation was used as the target (λ = 1.5418 Å). Scanning electron microscope (SEM) images were recorded with a FE-SEM S-4800. Nitrogen adsorption and desorption isotherms of MPC were conducted at 77 K on a NOVA 2200e Surface Area & Pore Size Analyzer. Magnetic measurements of MPC were performed by a vibrating sample magnetometer (VSM).

2.4. Degradation of Ponceau 4R by magnetic porous carbon
P4R removal was performed in a glass cylinder 500 mL at room temperature (31 °C). 0.1 g MPC was added into 250 mL P4R solution with its initial concentration of 50 ppm. Initial pH values of the mixture were adjusted by H2SO4 0.5 M and NaOH 0.1 M solutions. A magnetic stirrer was used to mix the suspension continuously. After 10 minutes of adsorption, various H2O2 concentrations were rapidly poured into the mixture. At different time intervals, 1.0 mL suspension was withdrawn from the mixture and added into a solution of Na2S2O3 and phosphate buffered solution to remove excess H2O2 and adjust pH value to around 7. P4R concentration was subsequently measured by a UV-Vis Spectronic Genesys 2 PC at 508 nm. Important parameters including pH value, H2O2 concentration, MPC catalyst with different synthesis conditions and dose of catalyst were investigated.
3. Results and discussion

3.1. Effects of various parameters on characterization of magnetic porous carbon

Figure 1 shows the effects of pyrolysis time and the mass ratio of FeCl\textsubscript{3} to lotus seedpod on XRD patterns of samples. Peaks at 2\(\theta\) = 18.18°, 29.96°, 35.33°, 42.98°, 53.25°, 56.82°, 62.44°, 73.83° correspond to (110), (220), (311), (400), (422), (511), (440), (622) of crystal Fe\textsubscript{3}O\textsubscript{4} [16, 17]. Almost characteristic peaks of Fe\textsubscript{3}O\textsubscript{4} appear in all samples. According to Bedia J et al. [18], forming Fe\textsubscript{3}O\textsubscript{4} crystals from iron (III) chloride on biomass raw materials includes the following reactions:

\[
\begin{align*}
\text{FeCl}_3 + 2\text{H}_2\text{O} &\rightarrow \text{FeOCl}_\text{H}_2\text{O} + 2\text{HCl} \\ 
\text{FeOCl}_\text{H}_2\text{O} &\rightarrow \text{FeOOH} + \text{HCl} \\ 
\text{FeOOH} &\rightarrow \gamma\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O} \\ 
3\gamma\text{-Fe}_2\text{O}_3 + \text{H}_2 &\rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \\ 
3\gamma\text{-Fe}_2\text{O}_3 + \text{C} &\rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}
\end{align*}
\]

As shown in Figure 1a, the intensities of peaks increased when pyrolysis time increased from 0.5 h to 1.0 h. However, similar intensities of peaks were observed for MPC samples which were prepared from 1.0 h and 2.0 h pyrolysis. The carbonization and activation processes could almost complete after 1.0 h. In addition to pyrolysis time, the mass ratio of FeCl\textsubscript{3} to LPSs significantly influenced XRD patterns of MPC (Figure 1b). At the same pyrolysis time of 1.0 h, the peak intensity and number of peaks appeared gradually decreased with increasing the mass ratio. The lack of carbon produced from biomass could decrease the reduction of FeCl\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}.

![Figure 1](image-url) **Figure 1.** Effects of (a) pyrolysis time and (b) the mass ratio of FeCl\textsubscript{3} to lotus seed pods on XRD patterns of MPC samples.

Figure 2a shows the surface of MPC-R0.2-1.0h. The sample seems to be fragmented into pieces, due to carbonization and activation. The activation process contributed a specific surface area of 288 m\textsuperscript{2}/g and a total pore volume of 0.18 cm\textsuperscript{3}/g for MPC.

To demonstrate the magnetism of the material, MPC is easily attracted to the bar magnet in air or water (Figure 2b). In addition, the magnetic hysteresis curve of MPC-R0.2-1.0h described superparamagnetic properties with the saturation magnetization of 7.13 emu/g, thanks to the existence of Fe\textsubscript{3}O\textsubscript{4} particles on MPC [19-21]. Therefore, in the process of using MPC, it will be easily separated from the solution. However, MPC in this study will be used as an oxidation catalyst based on a heterogeneous Fenton.
3.2. Catalytic activity of magnetic porous carbon

The investigation process consists of two steps: adsorption and oxidation. As presented in Figure 3a and Table 1, MPC-R0.2-1.0h sample could adsorb P4R with its capacities of 4.4 – 6.5 mg/g. After 10 minutes, adsorption almost reached equilibrium, H$_2$O$_2$ was added into the mixture for further oxidation step. Parameters including pH, H$_2$O$_2$ concentration, MPC dosage, MPC prepared from different conditions were explored.

Figure 3b showed that pH strongly affected the catalytic activity of MPC. At low pH 2, 3, the decolorization occurred strongly [22]. When pH increased from 3 to 9, the decolorization decreased gradually. These results are consistent with previous Fenton research [23-25]. In acid environment, the transition between Fe (II) and Fe (III) occurs more easily, thus it is favorable for the formation of hydroxyl radicals •OH. In a high pH, this transition is limited. Hence, the amount of hydroxyl radicals •OH decreases. To limit the leakage of ferric ions as well as reduce a part of chemicals, pH 3 was selected for further experiments.

Hydro peroxide is a source of oxidizing agents •OH. According to equation (6) [26], the minimum H$_2$O$_2$ concentration is 150 ppm to completely degrade P4R (50 ppm) to CO$_2$ and H$_2$O. Therefore, H$_2$O$_2$ concentrations from 100 to 300 ppm were investigated.

$$C_{20}H_{11}N_2O_{10}S_3Na_3 + 51H_2O_2 \rightarrow 20CO_2 + 2NH_3^+ + 3SO_4^{2-} + 3Na^+ + 5H^+ + 54H_2O \tag{6}$$
Figure 3. Effect of (a) pH values and (b) \( \text{H}_2\text{O}_2 \) concentration on P4R degradation

When \( \text{H}_2\text{O}_2 \) concentration increased from 100 to 200 ppm, the decolorization rate increased gradually. However, the decolorization rate decreased slightly when \( \text{H}_2\text{O}_2 \) concentration increased from 200 to 300 ppm. On the surface of MPC, \( \text{H}_2\text{O}_2 \) react with \( \text{Fe}_3\text{O}_4 \) particles to create \( \cdot\text{OH}, \cdot\text{OOH} \) radicals. Therefore, the higher the amount of \( \text{H}_2\text{O}_2 \), the more \( \cdot\text{OH} \) free radicals are generated, enhancing the reaction rate. However, these radicals could react with \( \text{H}_2\text{O}_2 \) and also itself, leading to their decrease, according to the following reaction equations (7) – (9) [27]:

\[
\begin{align*}
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OOH} + \text{H}_2\text{O} \\
\cdot\text{OH} + \cdot\text{OOH} & \rightarrow \text{O}_2 + \text{H}_2\text{O} \\
\cdot\text{OH} + \cdot\text{OH} & \rightarrow \text{H}_2\text{O}_2
\end{align*}
\] (7) (8) (9)

Figure 4 indicated catalytic activities of MPC samples synthesized at different pyrolysis time and ratio of \( \text{FeCl}_3/\text{LSPs} \). The MPC sample with 1.0 h pyrolysis showed high decolorization rate, as compared with the sample with 0.5 h and 2.0 h pyrolysis (Figure 4a). These results demonstrate that \( \text{Fe}_3\text{O}_4 \) structure could strongly affect its catalytic activity. MPC provides active sites \( \text{Fe(II)}, \text{Fe(III)} \) to generate \( \cdot\text{OH} \) as heterogeneous Fenton mechanism [28]:

\[
\begin{align*}
\text{C-Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{X-Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\text{C-Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{X-Fe}^{2+} + \cdot\text{OOH} + \text{H}^+
\end{align*}
\] (10) (11)

Figure 4. Effect of MPC: (a) pyrolysis time and (b) the mass ratio \( \text{FeCl}_3/\text{LSPs} \) (w/w) on P4R degradation
Figure 4b shows that H$_2$O$_2$ could not decompose P4R effectively in the absence of MPC. With porous carbon, P4R removal occurred very slowly. When the mass ratio of FeCl$_3$/LSPs increased from 0.1 to 0.2, the decolorization efficiency increased significantly from 58.8% to 83.0% after 120 min (Table 1). Increasing active sites on the MPC might explain this result. However, the efficiency decreased for MPC with the ratio 0.5. Low intensities of Fe$_3$O$_4$ peaks might lead to low catalytic activity.

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**Figure 5.** Effect of MPC dosage on P4R degradation

The results of P4R degradation of MPC-R0.2-1.0h at different MPC dosage are presented in Figure 5 and Table 1. When the MPC dose increased from 0.1 g/L to 0.6 g/L, the decolorization rate increased, owing to increasing active sites on the surface material, in order to form more •OH from H$_2$O$_2$. However, similar decolorization rates were observed for doses of 0.4 and 0.6 g/L, due to excessive Fe$^{2+}$ concentration interferes with the process according to the equation (12) /29, 30/:

$$\text{Fe}^{2+} + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$$

(12)

**Table 1.** Summary of conditions to investigate the catalytic activity of MPC

| Samples        | pH | H$_2$O$_2$ (ppm) | MPC (g/L) | Adsorption (after 10 min) | Oxidation (after 120 min) |
|----------------|----|------------------|-----------|--------------------------|---------------------------|
|                |    |                  |           | P4R (ppm) | Adsorption capacity (mg/g) | P4R (ppm) | P4R removal (%) |
| MPC-R0.2-1.0h  | 2  | 150              | 0.4       | 47.4       | 6.5                        | 20.3       | 59.5            |
|                | 3  | 150              | 0.4       | 47.8       | 5.4                        | 28.2       | 43.5            |
|                | 7  | 150              | 0.4       | 48.0       | 4.9                        | 38.4       | 23.2            |
|                | 9  | 150              | 0.4       | 48.1       | 4.7                        | 39.1       | 21.8            |
|                | 100| 150              | 0.4       | 48.1       | 4.8                        | 34.8       | 30.3            |
|                | 200| 150              | 0.4       | 48.5       | 3.7                        | 26.1       | 47.8            |
|                | 300| 150              | 0.4       | 48.3       | 4.4                        | 20.6       | 58.8            |
| MPC-R0.2-0.5h  | 3  | 200              | 0.4       | 48.1       | 4.7                        | 30.1       | 39.8            |
| MPC-R0.2-1.0h  | 3  | 200              | 0.4       | 48.1       | 4.8                        | 8.5        | 83.0            |
| MPC-R0.2-2.0h  | 3  | 200              | 0.4       | 48.0       | 5.0                        | 23.4       | 53.2            |
| MPC-R0.1-1.0h  | 3  | 200              | 0.4       | 48.1       | 4.8                        | 8.5        | 83.0            |
|                | 0.1| 49.4             | 1.5       | 35.0       | 30.0                      |
|                | 0.2| 48.9             | 2.8       | 17.1       | 65.7                      |
|                | 0.4| 48.1             | 4.8       | 8.5        | 83.0                      |
|                | 0.6| 49.0             | 2.5       | 10.4       | 79.3                      |
4. Conclusion

Magnetic porous carbon was prepared successfully from one-step pyrolysis of lotus seedpods – FeCl₃ mixture. XRD results reveal that Fe₂O₃ particles were formed on the carbon base. The obtained material shows good magnetic recoverability with the saturation magnetization of 7.13 emu/g and high specific surface area of 288 m²/g. For Ponceau 4R treatment, the experimental results demonstrated that MPC was not only a practical adsorbent but also an effective catalyst. At pH 3, 200 ppm H₂O₂, 0.4 g/L magnetic porous carbon, 83% Ponceau 4R 50 ppm was removed after 120 minutes treatment. Moreover, MPC powders could be separated from the treated mixture easily by a magnet bar. Overall, eco-friendly, sustainable and cheap MPC can potentially be an effective catalyst for Ponceau 4R treatment in wastewater.

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