Valorization of Tropical Almond (*Terminalia catappa*) Leaves into Iron-Containing Activated Carbon for Rapid Catalytic Degradation of Methylene Blue with Hydrogen Peroxide

Nhi Thi Kieu Nguyen¹,², Duong Thi Thuy Le¹,², Khang Dinh Vo¹,², Linh Tung Huynh¹,², Hung Minh Nguyen¹,², Tuyet-Mai Tran-Thuy¹,², Long Quang Nguyen¹,², Dung Van Nguyen¹,²*

¹ Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam
² Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc City, Ho Chi Minh City, Vietnam
* Corresponding author’s e-mail: nvdung@hcmut.edu.vn

**ABSTRACT**

This study sought to use tropical almond leaves (TALs) for the simple fabrication of iron-containing activated carbon (IAC). Iron precursor (FeCl₃) and activating agent (KOH) were sequentially preloaded in TALs. One-pot pyrolysis then generated iron-based particles (8.7 wt%), mainly metallic iron crystals, within AC support. The specific saturation magnetization of IAC was measured to be 48.9 emu/g, highlighting its ability to be efficiently separated using external magnetic fields. Moreover, the activation process yielded IAC with a large total volume of 0.28 cm³/g and a high specific surface area of 463 m²/g. Accordingly, IAC was investigated as an oxidation catalyst to degrade methylene blue (MB) by H₂O₂. At pH 3.0, 800 ppm H₂O₂, and 0.10 g/L IAC, 95.3% of MB (200 ppm) was removed after 30 min of adsorption and 60 min of oxidation. Altogether, iron-containing activated carbon from fallen leaves of tropical almonds proved its potential for robust methylene blue degradation by H₂O₂.

**Keywords:** zero-valent iron, activated carbon, tropical almond leaves, one-pot strategy, Fenton-like process, methylene blue.

**INTRODUCTION**

Tropical almond (*Terminalia catappa*) is a sizable tree that is widely found in tropical and subtropical areas [1]. The tree is considered decorative as its enormous leaves offer extensive shade [2]. During the dry season, TALs undergo a color change, turning pinkish-reddish or yellow-brown before eventually dropping to the ground [3, 4]. Although TALs can be used to create herbal medicines [5, 6], this demand is very limited. Indeed, a substantial volume of fallen leaves is normally left for natural decomposition or gathered as urban waste. Thus, TALs are an abundant and underutilized biomass resource. Due to their large size, TALs can be collected with less effort than other small leaves. Their soft structure might also be advantageous for further processes.

Currently, water contamination caused by organic compounds originating from diverse manufacturing processes is a notable ecological issue [7]. Wastewater commonly contains organic contaminants such as pesticides, medicines, detergents, solvents, and colorants [8, 9]. These chemicals persist in the environment, leading to bioaccumulation in the food chain and detrimental impacts on aquatic organisms [10, 11]. They also pose possible concerns for human health through contaminated water sources [12]. In order to mitigate these impacts, it is necessary to properly treat organic pollutants before releasing them into water bodies. Nevertheless, conventional treatment methods have such limitations,
especially for recalcitrant organic contaminants [13, 14]. Thus, it necessitates the development of advanced treatment techniques. Fenton and Fenton-like advanced oxidation processes are a promising solution for the treatment of organic pollutants in wastewater [15, 16]. These processes convert hydrogen peroxide (H$_2$O$_2$) into highly reactive hydroxyl radicals (•OH), which can degrade a wide variety of organic contaminants into less harmful substances like water and carbon dioxide [17]. For that purpose, the classical Fenton process employs ferrous ions (Fe$^{2+}$), while Fenton-like processes extend the utilization of ferric ions (Fe$^{3+}$) or other transition metal ions [18]. Although these homogeneous processes are simple and effective, the handling and disposal of solid sludge pose challenges [19]. Therefore, heterogeneous Fenton-like processes using solid catalysts are more favorable. In recent years, metallic iron (Fe(0)) has been increasingly explored as a potential heterogeneous catalyst due to its high reactivity, low cost, and environmental friendliness [20, 21]. Indeed, Fe(0) particles can continuously provide Fe(II) to produce hydroxyl radicals from H$_2$O$_2$ [22]. However, Fe(0) particles are easily agglomerated, causing a decline in their catalytic performance during use [23, 24]. To overcome this shortcoming, Fe(0) particles could be immobilized on proper supports.

Activated carbon (AC) is widely recognized as a highly effective support for Fe(0) particles, offering numerous advantages such as a highly porous structure, excellent adsorption properties, chemical stability, cost-effectiveness, and eco-friendliness [25, 26]. These properties improve the catalytic activity, stability, and reusability of Fe(0) catalysts [27]. To immobilize Fe(0) particles in AC, different methods have been developed. In previous studies, direct FeCl$_3$ activation of biomass mainly forms Fe$_3$O$_4$ crystals within biochar base [28, 29]. To obtain Fe(0) and AC simultaneously, an improved procedure was introduced recently [30]. Biomass is loaded consecutively with an iron precursor (FeCl$_3$) and KOH. One-pot pyrolysis can then form IAC. In addition to the properties mentioned before, the new composite possesses magnetic properties for convenient separation. Because of these advantages, the current study applied the procedure to fabricate IAC from TALs. The catalytic activity of IAC was explored for methylene blue degradation with H$_2$O$_2$.

**MATERIALS AND METHODS**

**Materials**

Fallen leaves of tropical almonds were gathered at Ly Thuong Kiet campus, HCMUT, Ho Chi Minh City, Vietnam. After being cleaned with tap water and distilled water, the leaves were dried at 110 °C for 24 h. The raw material was pulverized into a fine powder and stored in a jar for later use.

**Fabrication of iron-containing activated carbon from tropical almond leaves**

First, 4.00 g of TAL powder, 1.333 g of FeCl$_3$·6H$_2$O, and 50.0 mL of distilled water were put together in a 250 mL beaker. After agitating for 2 h at room temperature, 50.0 mL of an aqueous solution containing 12.00 g of KOH was poured into the beaker. Another 2 h of continuous mixing was kept before the sample was dried for 24 h at 110 °C. The dried material was pulverized into a fine powder before being placed in a tube furnace with a heating rate of 5 °C/min. The pyrolysis was then carried out at 600 °C for 1 h under a nitrogen atmosphere. Lastly, the pyrolyzed product was rinsed carefully and evaporated to obtain IAC. For comparison, AC was prepared using the same procedure but without FeCl$_3$·6H$_2$O.

**Characterization of iron-containing activated carbon**

The crystalline structure of IAC was studied by X-ray diffraction (XRD) using a Bruker AXS D8 diffractometer. The 20 range was 10–80°, and Cu-Kα radiation (λ = 1.5418 Å) was used as the target. Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-IT200 instrument. Functional groups present on the surface of IAC were explored by Fourier transform infrared (FTIR) spectroscopy using a Bruker VERTEX 70 spectrometer. Nitrogen adsorption and desorption isotherms of IAC were measured at 77 K on a Micromeritics Tristar II Plus instrument. The sample was outgassed at 150 °C for 12 h. The BJH method was used to express pore size distribution. Specific surface area was calculated by the BET equation. Total pore volume was obtained at P/P$_0$ = 0.997. Micropore and mesopore volumes were estimated using the t-plot method. A PerkinElmer Optima 7300 DV ICP-OES instrument was used for the compositional analysis.
of IAC. Iron was extracted from IAC using concentrated HNO$_3$ at 50 °C for 1 h. The magnetic measurement of IAC was examined using a VSM at room temperature.

**Degradation of methylene blue using iron-containing activated carbon**

Catalytic degradation of MB was performed in 250-mL flasks at room temperature (30 °C). In a typical experiment, a specific IAC dosage was added to 100 mL of MB solution (200 ppm). Initial pH values were altered with NaOH (0.10 M) and HCl (0.10 M) solutions. The mixture underwent continual stirring throughout the treatment. After the adsorption step took 30 min, H$_2$O$_2$ (800 ppm) was promptly added to the suspension to commence the oxidation step. At specified times, each 1.00 mL of suspension was withdrawn from flasks and added to 9.00 mL of an aqueous solution containing Na$_2$S$_2$O$_3$ (2.00 g/L) and phosphate buffer. IAC was separated from treated mixtures and MB concentrations were analyzed using a spectrophotometer at 664 nm. The MB adsorption capacity and total MB removal were computed as follows:

\[
\text{MB adsorption capacity (mg/g)} = \frac{200 - C_a}{C_0} \times 100\% \quad (1)
\]

\[
\text{Total MB removal (\%)} = \frac{200 - C_{a_6}}{200} \times 100\% \quad (2)
\]

where: $C_a$ (g/L) was AC or IAC dosages, while the initial MB concentration was 200 ppm. $C_0$ and $C_{a_6}$ (ppm) were MB concentrations after 30 min of adsorption and after 60 min of oxidation, respectively.

**RESULTS AND DISCUSSION**

**Properties of iron-containing activated carbon**

Figure 1 illustrates the XRD pattern of IAC. Distinct peaks were observed at 2θ = 44.6 and 65.0° oriented along the (110) and (200) planes of metallic iron crystals (ICDD 00-001-1262). In contrast, other peaks lacked sufficient clarity to discern certain crystals. Hence, iron loaded in AC predominantly existed in the form of Fe(0) crystals. Their formation pathway is proposed as follows:

\[
\text{FeCl}_3 + 3\text{KOH} \rightarrow \text{Fe(OH)}_3 + 3\text{KCl} \quad (3)
\]

\[
\text{TAL} \rightarrow \text{Fe(OH)}_3 + \text{C}, \text{CO}, \text{H}_2\text{O} \quad (4)
\]

\[
\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + \text{C}, \text{CO}, \text{H}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{C}, \text{CO}, \text{H}_2 \rightarrow \text{Fe(0)} \quad (5)
\]

As previously presented, FeCl$_3$ was initially impregnated into TAL powder. This process could disperse Fe$^{3+}$ ions within vacant spaces of TAL biomass. Subsequently, the addition of KOH could generate Fe(OH)$_3$ precipitate in TAL structure. During pyrolysis, the biomass could be carbonized and emit such gas-phase compounds, while Fe(OH)$_3$ was dehydrated. Consecutive reactions have the potential to convert Fe$_2$O$_3$ into Fe(0). At 600 °C, excess KOH could also activate the carbon framework. As a result, carbonization, reduction, and activation could occur simultaneously, leading to the generation of Fe(0) particles within AC support. This innovative approach differs from previous methodologies, which commonly involve multiple steps and costly reducing agents like NaBH$_4$.

The nitrogen adsorption and desorption isotherms of IAC are presented in Figure 2. The dramatic increase in the adsorbed volume when P/P$_o$ grew from 0.0004 to 0.05 revealed the existence of micropores in IAC. Next, the hysteresis loop in P/P$_o$ range from 0.38 to 0.99 affirmed capillary condensation in mesopores. In detail, BJH pore size distribution demonstrated that IAC developed a hierarchically microporous and mesoporous structure with a typical mesopore size of 4.1 nm. Furthermore, total pore volume of IAC was 0.28 cm$^3$/g, including 50% of micropore volume (0.14 cm$^3$/g) and 50% of mesopore volume (0.14 cm$^3$/g). The hierarchically porous structure might improve mass transfer, while a high specific
surface area of 463 m$^2$/g might enhance surface interaction during IAC use. Figure 3 shows the FTIR spectroscopy of IAC. The stretching vibration of O–H bonding could be determined at 3436 cm$^{-1}$, while the vibrating peaks at 1436 and 874 cm$^{-1}$ are predicted to belong to C–H bonding. Moreover, the vibrating bands at 1617 cm$^{-1}$ could be present for C=C bonding and a peak of 1024 cm$^{-1}$ affirmed the existence of C–O bonding. Hence, the pyrolysis condition still kept some polar functional groups on the IAC surface. Their existence could potentially strengthen the interaction of IAC with organic contaminants and oxidizing agents.

Figure 4 illustrates that IAC consisted of small fragments with various shapes and sizes, possibly as a result of the fine grinding process. In each fragment, such empty spaces with thin walls were observed. At the microscale, these cavities...
may originate from the natural structure of TALs rather than being formed through activation. In general, the spacious cavities might be advantageous for surface interaction during IAC use.

The magnetic properties of IAC were studied with VSM (Figure 5). The narrow hysteresis found indicates that IAC was susceptible to magnetization and demagnetization by the alteration of external magnetic fields. Furthermore, the specific saturation magnetization of IAC reached 48.9 emu/g, whereas iron only accounted for 8.7 wt% of IAC. This result could be derived from the powerful magnetic properties of Fe(0) particles in IAC. The composite is therefore capable of magnetic separation and recovery.

Degradation of methylene blue using iron-containing activated carbon

MB can be removed by IAC through not only oxidation but also adsorption pathways. Hence, adsorption was carried out in the first 30 min, and then H$_2$O$_2$ was added for further oxidation. In general, MB concentration slightly declined and almost reached equilibrium after 30 min of adsorption. At pH 3.0, the MB adsorption capacities of IAC and AC were 55 and 140 mg/g, respectively. Accordingly, only 2.8–7.0% of MB was removed in the first step, which was suitable for the evaluation of the next catalytic oxidation step.

Figure 6 shows that H$_2$O$_2$ alone (no catalyst) was almost incapable of directly degrading MB during 60 min. To improve MB degradation, an appropriate catalyst must be used. In the case of AC, MB concentration generally remained in the oxidation step. On the contrary, the presence of IAC provided rapid MB elimination. The comparison revealed that AC served as a support, while Fe(0) particles acted as catalytic sites for MB degradation. According to the Fenton-like process, organic pollutants can be oxidized by reactive ·OH radicals [31]. The existence of Fe(0) particles in IAC could enhance the production of ·OH radicals from H$_2$O$_2$ as follows:

\[
\begin{align*}
\text{Fe}(0) + \text{H}_2\text{O}_2 + 2\text{H}^+ & \rightarrow \text{Fe}(II) + 2\text{H}_2\text{O} \\
\text{Fe}(II) + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}(III) + \bullet\text{OH} + \text{OH}^- \\
\text{Fe}(III) + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}(II) + \text{H}^+ + \bullet\text{OOH} \\
\text{Fe}(0) + 2\text{Fe}(III) & \rightarrow 3\text{Fe}(II) \\
\bullet\text{OH} + \text{MB} & \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} 
\end{align*}
\]

Under acidic media, Fe(0) could be corroded into Fe(II) [32]. Fe(II) could then form ·OH radicals from H$_2$O$_2$. Notably, Fe(II) could be regenerated from Fe(III) via Equation 8. Furthermore, Fe(0) is capable of rapidly reducing Fe(III) to Fe(II) [33, 34]. As a result, Fe(0) is served as the source of Fe(II).

The effect of IAC dosage on MB degradation is illustrated in Figure 7. As previously presented, H$_2$O$_2$ without IAC could not directly eliminate MB during 60 min. As IAC was employed, MB degradation was accelerated drastically. In addition, the degradation rate improved gradually when IAC dosage rose from 0.05 to 0.20 g/L.
A higher IAC dosage could provide more active sites, thereby accelerating the production of ·OH radicals. However, too much IAC dosage might cause wasting and negative effects. In detail, excessive Fe(II) might consume ·OH radicals [35, 36], as follows:

\[ \text{Fe(II)} + \cdot \text{OH} \rightarrow \text{Fe(III)} + \text{OH}^- \]  

\[ \text{(11)} \]

Figure 8 demonstrates that pH significantly influenced MB degradation, with the highest rate occurring at pH 3.0. High proton concentration at low pH could accelerate the corrosion of Fe(0) into Fe(II), thereby significantly improving the rate of MB degradation [20]. Nonetheless, MB degradation at pH 2.0 was weaker than that at pH 3.0. Very low pH greatly enhanced the loss of ·OH by the scavenging effect [18, 37]:

\[ \cdot \text{OH} + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} \]  

\[ \text{(12)} \]

On the contrary, as pH increased from 3.0 to 4.0, total MB removal decreased remarkably from 95.3% to 54.3%. Even MB degradation became negligible at pH 6.0. The decrease in the oxidation potential of ·OH could be attributed to the decline in MB degradation at higher pH values [18, 20]. In addition, higher pH values may promote H₂O₂ decomposition into O₂ rather than ·OH [22, 37]. Notably, the corrosion of Fe(0) into Fe(II) could be weakened at high pH. Fe(II) and Fe(III) ions may create precipitates located on IAC surface, resulting in further corrosion prevention [31]. Thus, pH 3.0 was favorable for IAC catalyst, similar to previous studies for the Fenton-like reaction catalyzed by metallic iron [18].

**CONCLUSION**

Fallen leaves of tropical almonds are regarded as municipal waste with limited use. TALs were therefore valorized for the simple fabrication of iron-containing activated carbon using FeCl₃ as an iron precursor and KOH as an activating agent. As a result, metallic iron crystals were identified as the primary iron-based ones. With 8.7 wt% of iron introduced into IAC, its specific saturation magnetization was enhanced to 48.9 emu/g, providing robust support for magnetic separation. In addition, the activation process yielded IAC with a total volume of 0.28 cm³/g and a specific surface area of 463 m²/g. Accordingly, IAC was explored for catalytic MB degradation by H₂O₂. In the first 30-min adsorption, 0.10 g/L of IAC at pH 3.0 slightly eliminated 2.8% of MB (200 ppm) with an adsorption capacity of 55 mg/g. As 800 ppm H₂O₂ was added, a total of 95.3% of MB was treated after 60 min of oxidation. Overall, iron-containing activated carbon prepared from tropical almond leaves is favorable for the expeditious Fenton-like degradation of methylene blue.

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