Synthesis of Composite Material Derived from Soybean Curd and Sludge Containing Fe for Removal of Paracetamol by Heterogeneous Fenton Oxidation

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ABSTRACT
In this study, a composite material (ACS) was successfully synthesized from activated carbon (AC) derived from soybean curd and sludge from the supply water treatment process using FeCl₃. Subsequently, the ACS was employed as a heterogeneous catalyst for the degradation of Paracetamol (PRC) in solutions under conditions of the Fenton process. The conditions for synthesizing composite material were evaluated under different temperatures (200 to 900°C) and AC/sludge ratios. Effects of pyrolysis temperature and of reaction parameters (pH, contacting time) were evaluated under batch conditions based on the degradation efficiency of PRC and TOC. PRC and TOC were analyzed using HPLC and TOC instrument. Results showed that the composite material synthesized at 600°C with AC/sludge = 1/1 (w/w) was of the best performance on the removal of PRC (95% after 30 min). At pH 2 and 3, the PRC removal efficiency was 89% and 18% after 15 minutes and 95% and 54% after 30 minutes, respectively, which were significantly higher than those obtained at higher pH values. After 24 hours, the PRC removal efficiency was 99% and the TOC removal efficiency reached 95%. The results indicated that high efficiency was obtained by synthesized material and most of PRC was converted to simple and non-toxic compounds such as CO₂ and H₂O.

KEYWORDS
Soybean residual;
Sludge of water treatment;
Fenton process;
Paracetamol;
Oxidation.

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1. Introduction

Pharmaceutical residues have been considered emerging contaminants (ECs) in water bodies hence medicines are extensively used around the world for human and veterinary health [1] and as the result, causing harmful threats to the aquatic environments [2]. Among the drugs frequently used, analgesics and antibiotics contributed a significant proportion of consumed medicines by both humans and farm animals. For antibiotics, an estimated 5393 tons, which accounted for nearly 97% of the medicines used for meat production, were recorded in Europe [3]. Due to misuse, improper treatment process, and overdose, their residues are widely detected in many different sources of surface water, which could make tremendously negative impacts on many aspects of our life. For instance, in Ho Chi Minh City, paracetamol (PRC) — a type of analgesics drugs — was one of the most prominent substances detected in wastewater, moreover, with the fraction of only 10% of the wastewater was treated before releasing into the environment [4], it potentially led to continuing attacking non-target organisms. Therefore, removing these harmful contaminants is crucial to prevent adverse effects.

To tackle this issue, various methods and processes have been developed to remove PRC ranging from conventional processes like adsorption [5, 6, 7] and biological processes [8], to more recent and advanced methods including advanced oxidation processes such as O₃, H₂O₂, UV/H₂O₂ [9, 10, 11], Fenton [12, 13] and Fenton-like reaction [14, 15]. However, there are several drawbacks to these processes including the costly operation price or the massive amount of toxic sludge generated during the treatment. Among all these approaches, using ACs as an adsorbent to remove antibiotic residues
seems to overcome the mentioned disadvantages due to their low cost, using eco-friendly by-product material, and simple operating conditions. Moreover, pairing this with a further degrading procedure to fully transfer pharmaceuticals into harmless substances, such as process Fenton-like oxidation [16, 17], will ensure the benefits from both the adsorption and oxidation procedure and could potentially be the right direction for PRC removal.

The adsorbent used in this study was synthesized from soybean curd, which is a by-product in the tofu production process, through a combination of physical and chemical activating methods. Based on the high surface area (151.5 to 3306 m$^2$/g) achieved from the previous study, AC derived from soybean curd residue had shown promising potential to be used as supportive material of the composite [18, 19, 20]. Furthermore, sludge released from water treatment plants contains a high level of iron which might be utilized as an iron source for the synthesis of Fenton heterogeneous material. This study utilized two types of solid waste with a simple method (pyrolysis) to synthesize a good composite material for Fenton oxidation of PRC.

2. Materials and methods

2.1. Materials and chemicals

Soybean curd (SC) from the tofu production process was collected from traditional markets in Ho Chi Minh City, Vietnam. After that, the soybean residue was dried at 105°C for 24 hours and crushed. The dried residue was then stored in a dehumidifier at room temperature and to carry out further denaturation processes. The sludge was collected from Thu Duc water treatment plant which used FeCl$_3$ as the coagulant for the treatment process. The sludge was dried at 105°C for 24 hours, crushed, and sieved through a 0.25 mm sieve before synthesis. The paracetamol (PRC) and hydrogen peroxide (30%, w/w) was purchased from Sigma Aldrich, which were of analytical grade and were used without any further purification.

2.2. Preparation of Composite Material

2.2.1. Biochar carbon preparation

To synthesize biochar from the soybean curd (SB), the SC sample was pyrolyzed in a furnace at a temperature of 500°C for 2 hours, with a heating rate of 10°C/min. The material after pyrolysis was crushed and sieved through a 0.25 mm sieve and then stored in a dehumidifier at room temperature to perform the next activation steps.

2.2.2. Activated carbon preparation

Activated carbon from soybean curd (SAC) was synthesized according to our previous publication by mixing SB with KOH. 5.0 g of SB was mixed with KOH (with the ratio of KOH:SB = 1:1 to 1:4) for 2 hours by a stirrer from the same 25 mL of distilled water in a non-humid steel beaker, then, the above mixture was dried at 150°C for 4 hours. After drying, the resulting solid mixture was crushed and heated in an airtight oven at a temperature of 800°C for 2 hours [20].

The SAC mixture obtained after the pyrolysis process was crushed and stirred with distilled water using a magnetic stirrer at 80°C. The excess OH$^-$. ions were removed by slowly adding a 1M HCl solution to it. The reaction between HCl with a mixture of K$_2$CO$_3$ (produced by the reaction between coal and KOH during pyrolysis) and residual KOH released CO$_2$, which stopped after the solution no longer bubbles form (the reaction ends). The solid mixture after treatment was subsequently washed with distilled water to reduce the pH value to 7 and remove the remaining Cl$^-$. ion in the mixture. Finally, SAC was dried at 105°C for 24 hours then crushed and sieved through a 0.075 mm sieve.

2.2.3. Preparation of composite material from Soybean activated carbon and sludge (ACS)

To create the composite material, SAC was stirred with the sludge (S) and a volume KOH, according to the SAC: S ratio consisting of 1:1; 1:2; 1:3; 1:4. The mixture was then dried at 150°C for 4 hours and heated at temperatures from 200 to 900°C. The processes of processing materials to pH 7 and storage were carried out in the same way as the processing process of SAC. In addition, composite material
from biochar and sludge (SBS) was also synthesized as control material to compare Paracetamol (PRC) decomposition performance with ACS materials. The SBS synthesis process was the same as ACS, however, at the agitation step, SAC was replaced by SB of the same ratio.

2.3. Analytical methods

In this study, Jasco's High-performance liquid chromatography (HPLC) system was used to determine PRC with the operation parameters as PDA probe with a flow rate of 1 ml/min, UV detector, Mesh solvent system: water is 6:4 ratio, wavelength 254 nm, and storage time 5.2 minutes. Pre- and post-decomposition PRC concentrations were determined so that 1ml of the pre-and post-reaction solution was added to the rated vessel along with 0.5 ml of phosphate buffer solution (KH₂PO₄ 0.05M and Na₂HPO₄ 0.05M) to eliminate factors affecting the analysis process. The solution was then rated to 25ml with distilled water and filtered through a 0.22 μm Nylon syringe filter to completely remove the remaining solids. The solution was stored in a glass jar at a temperature of 2-5°C and analyzed the PRC concentration using an HPLC and TOC instrument.

The decomposition efficiency of the PRC is defined as follows:

\[
\text{Decomposition efficiency (\%) = } \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(1)

Where \( C_0 \) (mg/L) is the initial concentration of PRC and \( C_t \) (mg/L) is the concentration of PRC at reaction time, \( t \) (min).

3. Results and discussion

3.1. Effect of and KOH: SB ratio and pyrolysis temperature on the final SAC

![Graph showing the effect of KOH: SB ratio on adsorption capacity.]

![Graph showing the effect of pyrolysis temperature on adsorption capacity.]

**Fig 3.1.** Effect of (a) KOH: SB ratio and (b) pyrolysis temperature on the final SAC.
The effect of KOH: SB ratio and pyrolysis temperature in the activation step is shown in Fig 3.1. These two factors were significantly positively correlated with the adsorption capacity of SAC, and the $q_e$ obtained by PRC increased due to the increase of the pyrolysis temperature and the increase of the amount of KOH used in the activation process. As can be seen from Fig 3.1a, the material activated with KOH: SB in a ratio of 4:1 achieved the highest adsorption capacity of 559 mg/g. This finding is consistent with the gasification effect (reaction (2) - (4)), which means that higher content of KOH may result in a better porous structure compared to the material [21 - 23].

$$6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 2\text{H}_2 + 2\text{K}_2\text{CO}_3$$ (2)
$$\text{K}_2\text{CO}_3 + 2\text{C} \rightarrow 2\text{K} + 3\text{CO}$$ (3)
$$\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2$$ (4)

Then, for the next step, SACs were prepared at different carbonization temperature ranges of 600-900°C, which help to create pore systems responsible for pollutant adsorption and attachment of other species in the synthesis of new catalyst materials. Fig 3.1b shows a clear trend in the amount of PRC adsorbed onto SAC at different pyrolysis temperatures. The material fabricated at 900°C achieved the highest $q_e$ value of 563 mg/L. Since more energy is provided with increasing temperature, the reaction between the activator (KOH) and the carbon in the biochar can be accelerated, leading to the formation of more pores, which can improve the PRC adsorption results. However, the difference in $q_e$ (about 2% during pharmaceutical removal) was neglected as the temperature increased from 800°C to 900°C. It may be assumed that at 900°C, the KOH element could get diffused into the newly-formed pore, blocked, and inhibited the adsorption of contaminant molecules into the SAC structure [24] resulting in a minor increase of the adsorption capacity. A similar pore-widening effect that occurred with the presence of chemical agents was also mentioned in earlier findings [23, 25].

3.2. Effect of pyrolysis temperature and SAC: S ratio on the final ACS

![Graph a)](image1)

$\text{Destruction efficiency (\%)}$

$\text{Pyrolysis temperatures (°C)}$

AC5-200, AC5-300, AC5-400, AC5-500, AC5-600, AC5-700, AC5-800, AC5-900

![Graph b)](image2)

$\text{Destruction efficiency (\%)}$

$\text{Time (min)}$

[PRC]$_0$ = 500mg/L, [H$_2$O]$_2$ = 70mM, m/V = 0.5 g/L, pH = 2, $t_o$ = 25°C

Fig 3.2. Effect of pyrolysis temperature (a) and ratio SAC: S (b)
The decomposition temperature that affected the PRC decomposition performance is shown in Fig 3.2a. It can be seen that the decomposition efficiency achieved by materials synthesized at 200 to 400°C was only less than 50%, while the removal efficiency increased sharply as increasing the pyrolysis temperature, accounting for 79.19% for ACS-500 and reaching 98.98% for ACS-900. It is noted that the decomposition efficiency of SAC-800 was 98.56%, which is comparable to ACS-900, therefore, the optimal pyrolysis temperature chosen for the synthesis process is 600°C.

Fig 3.2b shows the performances of different materials with different SAC: S ratios, which reveals that the ACS-1:4 performs differently from the other materials during the first five minutes of degradation. However, there was no significant difference in the performance of all materials after 15 minutes, and the removal efficiency of all materials was maintained at above 98% from 60min on.

3.3. Comparison of PRC decomposition performance of ACS composite materials and other base materials.

![Graph](image)

_Fig 3.3. Comparison of PRC decomposition performance (a) between ACS and S; (b) between ACS and SBS_

Fig 3.3a shows that, when compared to the same pyrolysis, ACS has a higher breakdown efficiency than sludge (S). In addition, the PRC breakdown efficiency of ACS reaches 96.55% in 30 minutes at a temperature of 600°C while S only reaches 9.86%. Even though sludge includes Fe and this is a factor in the Fenton process for the removal of PRC, sludge can also breakdown PRC.
Under the same synthesizing conditions, the composition efficiency achieved with SBS was significantly lower than that of ACS (Fig 3.3b). SBS only accomplishes 34.15% of PRC degradation, even when the pyrolysis is conducted at the same temperature of 600°C. This indicates that sludge and denatured activated carbon combined with KOH may have produced catalysis that is more effective at oxidizing materials than other catalysts. As we know that the surface area is critically important for a catalyst material, therefore, these results might be resulted from the higher surface area of ACS (253.14 m²/g) compared with sludge (62.25 m²/g).

3.4. Effects on the reaction parameters (pH, contacting time) of PRC.

Both homologous and heterogeneous Fenton reactions are typically advantageous and quite effective in the acidic pH range. As shown in Fig. 3.4, PRC removal efficiencies at pH 2 and 3 were 87.5% after 15 minutes, 44.9% after 30 minutes, and 95.6% and 67.4% after 60 minutes, respectively. The PRC’s removal efficiencies began to decline at pH 4, reaching only 7.9% after 15 minutes and 28.6% after 30 minutes and the removal efficiency of PRC kept the same for the higher pH values.

Since the water supply process uses a flocculant called FeCl₃, the sludge produced by the treatment process mainly contains Fe³⁺. The reaction of Fe³⁺ with H₂O₂ to form Fe²⁺ occurs according to equation (5), and then Fe²⁺ reacts with H₂O₂ to generate OH* radicals according to equation (6). According to Fig 3.4 and previous studies, Fe(OH)²⁺ forms at pH 2-4 [26, 27]. Fe(OH)²⁺ radicals have better activity than Fe²⁺, and are easy to combine with H₂O₂ to form OH* radicals. The iron ions were mainly in form of Fe(OH)₂ at pH in the range of 4 to 8, while they were mainly in the form of Fe(OH)₃ at pH > 6 [27]. At high pH, Fe³⁺ precipitates quickly to Fe(OH)₃, but the reaction of Fe(OH)₃ with H₂O₂ does not generate OH* radicals, so the treatment efficiency of the reaction decreases with increasing pH. At pH 2-3, iron exists mainly in the form of ferrous iron, which favors the formation of OH* radicals with strong oxygen activity. The oxidation potential of OH* is also 2.8 eV at pH 2-3 and 1.9 eV at pH 7, respectively, according to a study by Buxton and colleagues [28]. As the oxidation potential falls, this radical's capacity to oxidize organic molecules is diminished.

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}^\cdot + \text{H}^+ \quad (5)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{OH}^- \quad (6)$$

Within the first 15 minutes, PRC was removed quickly with an efficiency of 98.38% (Fig 3.5). When the reaction time increased to 60 min the removal efficiency only slightly increased to 98.9% subsequently, no further increase in the removal efficiency after 60 minutes. On the other hand, TOC decomposed more quickly, starting at a breakdown efficiency of 90.69% after only 5 minutes and
increasing to 92.89% after 60. During the early stages of the process, the organic chain-breaking reaction of the OH* occurs quickly and the final products or the degradation process were non-toxic compounds (CO₂ and H₂O). Due to the PRC's complete disintegration in the first 15 minutes, the PRC decomposition performance does not appear to vary after 5 minutes. The PRC breakdown performance reached its maximum at 30 minutes, indicating that the material's oxidation potential was excellent in comparison to prior research.

![Graph showing the effect of contracting time on the decomposition performance of PRC.](image)

**Fig 3.5. Effect of contracting time on the decomposition performance of PRC.**

### 3.5. Catalyst characterization

According to the SEM-EDX results (Table 1), the iron concentration of the ACS catalyst was 19.3%, compared to 30.0% in the sludge. Due to the high degree of solid hydration experienced throughout the preparation process, which made it challenging to achieve the desired iron contents, there were minor differences between the samples' determined and predicted iron contents. After the reaction, the iron concentration of the ACS catalyst was 16.9%; Only a minor quantity of iron concentration was lost. Additionally, a little amount of iron from the material was released into the reaction solution while the reaction is taking place at a low pH (2.0).

SEM morphological (Fig 3.6) observations demonstrate the surface morphology of three different types of materials (S, SAC, and ACS). The surface of SAC activated carbon (3306 m²/g) benefits the iron particles of iron-containing sludge on the surface of activated carbon, generating a large contact area to increase the catalytic process' efficiency. After the synthesis of ACS material, the surface of activated carbon was bonded to the sludge, these particles of small size coated the surface of activated carbon.

According to the results of the BET surface area analysis, the material's surface area gradually declined with pyrolysis temperature, going from 474.823 m²/g at 200°C to 27.598 m²/g at 900°C heating temperature. Additionally, a large reduction in surface area is also caused by adding more sludge to composite materials during their synthesis. Surface areas of the ACS materials including SAC: S ratios of 1:1 and 1:4 those pyrolyzed at 600°C were 253.138 m²/g and 40.715 m²/g, respectively. Additionally, SBS material had a relatively large surface area of 1292.121 m²/g, although it processes less effectively than ACS at the same temperature and percentage. However, it was demonstrated through comparison studies to establish the ideal pyrolysis temperature and evaluate the materials' processing effectiveness that the surface area had no impact on the effectiveness of the aforesaid PRC oxidation.
Table 1. Elemental composition of S and ACS before and after reaction (in wt%)

<table>
<thead>
<tr>
<th>Materials</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge (S)</td>
<td>46.8</td>
<td>17.8</td>
<td>1.26</td>
<td>3.98</td>
<td>0.52</td>
<td>30.0</td>
</tr>
<tr>
<td>ACS before reaction</td>
<td>21.3</td>
<td>26.8</td>
<td>6.34</td>
<td>10.9</td>
<td>15.4</td>
<td>19.3</td>
</tr>
<tr>
<td>ACS after reaction</td>
<td>29.0</td>
<td>29.1</td>
<td>1.20</td>
<td>3.39</td>
<td>0.58</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Fig 3.6. SEM images of (a) S, (b) SAC, and (c) ACS composite

4. Conclusions

This study utilized two types of solid waste with a simple method (pyrolysis) to synthesize a good composite material for the Fenton oxidation of PRC. The best performance on the elimination of PRC (95% after 30 min.) was demonstrated by the composite material synthesized at 600°C with AC/sludge = 1/1 (w/w). The PRC removal effectiveness at pH 2 and 3 was 89% and 18% after 15 minutes, respectively, and 95% and 54% after 30 minutes, which were significantly greater than those obtained at higher pH values. The PRC removal efficiency was 99% after 24 hours, and the TOC removal efficiency was 95%. According to the data, synthetic material performed well in the oxidation of PRC, and the majority of PRC was transformed into easily-replace substances like CO₂ and H₂O.

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