Original Article

Property and mechanism of phenol degradation by biochar activated persulfate

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ABSTRACT

In this study, corn stover was used to prepare biological activated carbon (BAC). First, the calcination temperature of BAC was optimized, and the calcination rate of BAC as the activator was confirmed to be maximal when the heating rate was 5.0 °C min 1 , the sample was allowed to cool naturally, and the calcination temperature was maintained at 900.0 °C for 180 min. The oxidants persulfate (PDS) and hydrogen peroxide were compared. In the case of a certain amount of BAC, the PDS was an effective as an oxidant and the dosage was small. The preferred oxidant was thus determined to be PDS. Under the PDS/BAC system, the PDS dosage (PDS/phenol molar ratio of 5:1), the initial pH value of the system (6,45), the temperature of the system (20.0 °C), and the initial concentration of phenol were optimized. The effect of BAC was explained. At the end of the experiment, the stability of BAC was verified. The degradation rate of phenol by BAC after four repetitions could still reach 80.50 % (the initial concentration of phenol was 50.00 mg L 1 ), and the degradation effect of the total organic carbon (TOC) of the system within 300 min was verified. The degradation rate of TOC was 85.94 %, and the effect was ideal. The results of a simple preliminary analysis of the degradation mechanism are presented.

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1. Introduction

With recent rapid industrial development, large amounts of organic waste discharged into surface waters and groundwater have caused serious environmental pollution. In the northeast region, oil resources are abundant, and a series of organic matter produced during the mining and smelting process has caused serious pollution to water bodies. Phenol (Ph) was discovered by the German chemist Friedlieb Runge in coal tar in 1834; it is also called carbolic acid. A Ph molecule is composed of a hydroxyl group directly attached to a benzene ring and is highly stable. Ph forms colorless needle crystals with a special odor. These physicochemical properties are responsible for the problematic environmental persistence of Ph [1]. It is widely used in chemical syntheses, the oilfield industry and

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electroplating [2–4]. The US Environmental Protection Agency (USEPA) has listed Ph as a priority contaminant, and the World Health Organization (WHO) recommends a maximum Ph concentration of 0.001 mg L⁻¹ in drinking water. Ph poses a grave risk to ecological and human health as a result of its mutagenicity and carcinogenicity, even at low concentrations [5]. Therefore, effective remediation measures for environment Ph removal are critical, with numerous physical, chemical, and biological approaches being employed globally.

At present, the treatment methods for Ph in sewage mainly include chemical methods, physicochemical methods, and biological methods. Recently, the chemical oxidation technique has received considerable attention for removing Ph [6–8]. Advanced oxidation processes (AOPs) can be successfully used for water treatment; they are based mainly on the generation of hydroxyl radicals (HO•) to oxidize organic pollutants [9]. Sulfate radical (SO₄•⁻)-based processes have shown substantial advantages over conventional AOPs because of the high redox potential (2.5–3.1 V) and long half-life (30–40 μs) of these radicals [10–12]. Peroxymonsulfate (PMS) and persulfate (PDS) are the most widely used SO₄•⁻ precursors, with sodium persulfate (Na₂S₂O₅) being preferred for water treatment applications because of its high solubility and stability [10,13].

Numerous approaches to activating the generation of SO₄•⁻ have been developed, including light-irradiation-, ultrasonication-, temperature-, microwave-, metal-, and nonmetal-catalyst-based methods [8,10,14]. Our team has used Fe³⁺ ion as an activator to oxidize Ph in a system where PDS is used as an oxidant. However, the stability of the system is strongly affected by the pH. As the reaction proceeds, the pH of the system decreases continuously, resulting in iron mud, which causes secondary pollution in water bodies [15]. The system is based on a metal catalyst that, compared with nonmetal catalysts, is both uneconomical and environmentally unfriendly; such systems are thus not suitable for practical application. Carbon materials, by contrast, are economical, environmentally friendly, and nontoxic nonmetal materials [16,17]. Since 2012, graphene has been used as a catalyst to activate PMS or PDS to degrade organic matter, and its effect is remarkable [14,16,18]. Numerous reports on graphene as an activator have appeared in the literature [6,19]. However, despite the remarkable performance of graphene as an activator, it is expensive.

Activated carbons (ACs) have been widely used in heterogeneous catalysis as both supports and catalysts because of their porous structure, high specific surface area and pore volume, low cost, and environmentally friendliness [16,19–21]. Saputra et al. reported using AC instead of graphene as an activated oxidant [22]. However, the oxidant dosage was large, which will cause secondary pollution in practical applications. In the present paper, we use corn stalk roasting to prepare a material we refer to as biological activated carbon (BAC). We compare the properties of the BAC with those of a commercial AC, use it to activate two oxidants (sodium persulfate and hydrogen peroxide), and deduce the optimum experimental conditions. The regeneration of BAC is also investigated.

2. Experimental

2.1. Samples and chemicals

Ph (99.0 % purity) was obtained from Shahid Ghazi Pharmaceutical Co. (Iran). The corn stalks were acquired from suburban farmland. Sodium persulfate (Na₂S₂O₅), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), sodium hydroxide (NaOH), ace-tonitrile (CH₃CN), methanol (MeOH), ethanol (EtOH), and other reagents for analysis were obtained from Merck (Germany). All chemicals were analytical grade and were used without further purification. Ultrapure water (resistivity =18.25 MΩ cm) was used throughout the experiments.

2.2. Preparation of biological activated carbon (BAC)

The corn stalk was collected from suburban farmland, rinsed with deionized water, and dried. Its core was removed, and it was then crushed in a crusher. After repeated crushing, the crushed corn stack was passed through 50 and 100 mesh sieves. The sieved corn stover powder was calcined at different temperatures (from 300.0 °C to 1000.0 °C) under a nitrogen atmosphere. The heating rate was 5.0 °C min⁻¹, and the target temperature was maintained for 180 min. after the temperature rise; the sample was then allowed to naturally cool to room temperature. The baked BAC was immersed in 10 % hydrochloric acid for 12 h, washed with water three times, and dried at 100.0 °C for 6 h.

2.3. Experimental procedures

The experiments were carried out in 150 mL flasks containing 100 mL of solution under constant temperature and pressure (20 ± 1 °C and 1 atm). The optimum catalyst calcination

![Fig. 1 - The SEM image of BAC.](image-url)
temperature was kept at 50.00 mg L\(^{-1}\) (0.53 mM), 40/l, and 0.50 g L\(^{-1}\), respectively. The initial Ph concentration, PDS/Ph molar ratio, and catalyst dosage were 50.00 mg L\(^{-1}\) (0.53 mM), 50/1, and 0.50 g L\(^{-1}\), respectively. However, different initial Ph concentrations, PDS/Ph molar ratios, and catalyst dosages were used in the experiments to study of the effects of these operating parameters. The solution was stirred at 400 rpm continuously to maintain a homogenous solution. MeOH was used as a free-radical scavenger. The time of reaction was 120 min; at fixed time intervals, 0.50 mL of the reaction solution was sampled using a syringe filter (0.45 mm) and then mixed with 0.50 mL of MeOH to quench the reaction. Experiments were performed in triplicate, where the percentage difference was less than 8%; the average value was reported. A few other tests were carried out with different activators (AC and BAC) and different oxidants (hydrogen peroxide and PDS) at the same concentrations. The concentration of Ph was analyzed by high-performance liquid chromatography (HPLC) with UV detection at \(\lambda_{\text{max}}=270\) nm. A C-18 column was used in conjunction with a mobile phase of 50.0% CH\(_3\)CN and 50.0% water. Fourier transform infrared (FTIR) spectroscopy was used to evaluate the chemical properties of the BAC before and after oxidation.

For catalyst recycling tests, the used BAC was washed alternately with deionized water and EtOH three times and then dried at 100.0 °C for 6 h.

### 3. Results and discussion

#### 3.1. Characterization of the BAC

The Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore radius of the AC and BAC are shown in Table 1. A substantial difference was observed in the surface areas and pore volumes. BAC has a higher surface area 693.0906 m\(^2\) g\(^{-1}\), pore volume 0.2925 cm\(^3\) g\(^{-1}\), and pore size 2.2935 nm than the commercial AC. Fig. 1 shows a scanning electron micrograph of the preparation of BAC. Due to the high temperature calcine the BAC has an irregular rod-like structure with wrinkles on the surface which provides a larger surface area and increases the adsorption site of the BAC surface. The X-ray diffraction (XRD) analysis of the materials involved in this paper was carried out by reference to the analytical methods in the following literature [23–25]. Fig. 2 shows the results of the X-ray diffraction (XRD) analyses indicate that BAC exhibits an amorphous structure and that no crystalline phases are present. The diffraction peaks at 2\(\theta\) = 22° and 43° of the two samples before and after the reaction corresponded to the (002) and (100) crystal planes of carbon, respectively, indicating that all three samples were amorphous. The appearance of diffraction peaks at 2\(\theta\) = 22° indicates that there is a parallel stacking and interconnection between portions of the graphite layer in the carbon material. The diffraction peak at 2\(\theta\) = 43° indicates that the sp\(^2\) hybridized carbon atoms in the carbon material interact to form a hexagonal lattice structure [26]. The results of the thermogravimetric analysis (TGA) show that BAC contains 94.0% of carbon.

#### 3.2. Determination of BAC roasting temperature

Fig. 3 shows that the BAC samples calcined at different temperatures and used to activate PDS differ substantially in their ability to degrade Ph. Under the condition where the initial concentration of pH was 50.00 mg L\(^{-1}\), the PDS/Ph molar ratio was 40/1 and the dosage of BAC was 0.50 g L\(^{-1}\); all of the BAC samples degraded Ph to various degrees over 120 min. When the calcination temperature was increased to greater than 800.0°C, the degradation effect of Ph was substantially improved. The efficiency of BAC degradation of Ph for BAC calcined at 900.0°C was twice that for BAC calcined at 800.0°C. The degrees of degradation with BAC calcined at 900.0°C (98.12

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Surface area (m(^2) g(^{-1}))</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC</td>
<td>693.0906</td>
<td>0.2925</td>
<td>2.2935</td>
</tr>
<tr>
<td>AC</td>
<td>465.6085</td>
<td>0.1867</td>
<td>2.1626</td>
</tr>
</tbody>
</table>

Fig. 2 – XRD of BAC before and after reaction.

Fig. 3 – Phenol degradation efficiency of BAC at different calcination temperatures.
3.3. Comparison of activators and selection of oxidants

Fig. 4 shows the orthogonal combination of the two activators, commercial activated carbon (AC) and biological activated carbon (BAC) and the two oxidants (H$_2$O$_2$ and PDS) has a significant difference in the degradation of Ph. Under the same experimental conditions, when H$_2$O$_2$ was used as an oxidant, the degradation effect of BAC as an activator on Ph was 1.34 times greater than that of AC within 120 min. However, when PDS was used as an oxidant, the degradation effect of BAC as an activator on Ph was 1.51 times that of AC within 120 min. The experiments show that BAC is a better activator than AC. In the first 30 min of the degradation reaction, the superiority of BAC is more prominent than AC, and the former is 1.87 times of the latter in terms of degradation rate. Under the conditions of BAC as an activator, the degradation of Ph by PDS as an oxidant is 1.33 times greater than the degradation of Ph by H$_2$O$_2$ within 120 min. Therefore, BAC and PDS were selected as the activator and oxidant, respectively, in subsequent experiments.

3.4. Influence of persulfate dosage

Fig. 6 shows that, when the initial concentration of Ph was 50.00 mg L$^{-1}$ and the dosage of BAC was 0.50 g L$^{-1}$, under the initial pH test conditions, the PDS/Ph molar ratio was reduced from 40/1–3/1. The degradation rates of Ph were 91.14 %, 89.04 %, 88.59 %, 77.51 %, 73.33 %, 67.52 %, and 47.24 % within 10.0 min. When the PDS/Ph molar ratio was 5/1, the degradation efficiency of Ph still reached 84.74 % within 120 min. This phenomenon has been reported by other researchers [22,27,28]. Therefore, we determined that the optimal dosage of PDS in this experimental system is a PDS/Ph molar ratio of 5/1.
3.5. Influence of initial pH value

We studied the initial pH value of the test system under the aforementioned optimal experimental conditions. The initial pH of the test system was 6.45, and the pH of the system was adjusted using dilute solutions of hydrochloric acid and sodium hydroxide. Fig. 7 shows that, under the experimental conditions of initial pH values of 4.26, 6.45, 7.96, 9.82, and 11.79, the degradation efficiencies of Ph were 92.72 %, 95.88 %, 81.22 %, 61.01 %, and 54.86 %, respectively, within 120 min. Other researchers have observed that better pollutant removal was achieved under acidic conditions in different sulfate-radical-based systems [3,29,30]. PDS has a substantially acidic nature, and the pH of the solution containing Ph and PDS was 6.45. Thus, further experiments were performed at the initial pH of the solution, with no adjustment.

3.6. Influence of temperature

Temperature is another variable that influences catalyst activity and Ph degradation. Under the aforementioned optimal experimental conditions, the initial concentration of Ph was 20.00 mg L⁻¹. Fig. 8 shows that the degradation efficiencies of Ph in 120 min. at 20.0 °C, 30.0 °C, and 40.0 °C were 95.87 %, 96.54 %, 99.08 %, respectively. As the temperature was increased, the degradation efficiency of Ph continued to increase. This result is attributed to a portion of the energy generated by the system participating in the activation of the oxidant, which produces more PDS and improves the degradation efficiency of Ph. [31]. However, the difference in degradation efficiency of Ph under different temperature conditions was not obvious. To reduce energy consumption, the experiment was carried out at room temperature with minimal adjustment of the system temperature.

3.7. Influence of initial concentration of pollutants

After the aforementioned experimental conditions were optimized, the Ph at different initial concentrations was degraded under the optimal experimental conditions. Ph solutions with initial concentrations of 10.00 mg L⁻¹, 20.00 mg L⁻¹, 30.00 mg L⁻¹, 40.00 mg L⁻¹, 50.00 mg L⁻¹, 60.00 mg L⁻¹, and 80.00 mg L⁻¹ were selected and degraded under the optimal experimental conditions previously deduced. Fig. 9 shows that the 10.00 mg L⁻¹ and 20.00 mg L⁻¹ Ph solutions were completely degraded in 30 min. and that the 30.00 mg L⁻¹ Ph solution was completely degraded in 90 min. When the initial concentration of Ph was increased to 50.00 mg L⁻¹, and the degradation rate was 84.74 % within 120 min. The initial concentration of Ph was further increased to 80.00 mg L⁻¹, and its degradation rate was 60.66 % within 120 min. This result is attributed to the added PDS being completely consumed and no more PDS being produced. Therefore, under the aforementioned optimal experimental conditions, a Ph solution with
an initial concentration of 30.00 mg L\(^{-1}\) could be completely degraded.

### 3.8. Reactivity and reusability of spent BAC catalyst

Fig. 10 shows the catalytic activity of recycled BAC for Ph degradation. The initial concentration of Ph was 50.00 mg L\(^{-1}\). The BAC was recycled using the best experimental conditions previously deduced. The BAC was rinsed with deionized water and dried after each use. In evaluating the chemical stability and reusability of the activator, BAC was tested for four consecutive cycles with the same initial experimental conditions. There was no remarkable loss of degradation performance: the degradation rate was 85.64 % for the first use and 80.50 % after the fourth use. (Fig. 10) A small amount of BAC was taken out for each sampling, BAC was cleaned with deionized water after each repeated experiment, and a small amount of BAC was lost in the cleaning process. It indicated that BAC possesses excellent chemical stability and reusability for its practical application.

### 3.9. Determination of dominant free radicals

In BAC and PDS systems, BAC can activate PDS to produce SO\(_4\)•\(^-\) and further react with water molecules to form •OH. The SO\(_4\)•\(^-\) and •OH can both degrade Ph.\(^{[32]}\) To further explore the free radicals that play leading roles, alcohol was used as a probe; specifically, MeOH and tert-BuTol (TAB) were each added to the system at an alcohol/PDS molar ratio of 500:1. The experimental conditions were as follows: the dosage of BAC was 0.50 g L\(^{-1}\), the PDS/Ph molar ratio was 5:1, the initial concentration of Ph was 50.00 mg L\(^{-1}\), the initial pH was 6.45, and the temperature was room temperature (20.0 °C). The reaction rate constants of MeOH with SO\(_4\)•\(^-\) and •OH were approximately 1.1 \times 10^7 mol L\(^{-1}\) s\(^{-1}\) and 9.7 \times 10^9 mol L\(^{-1}\) s\(^{-1}\), respectively; however, the reaction rate constants of TBA and •OH (6 \times 10^6 mol L\(^{-1}\) s\(^{-1}\)) were much larger than those of SO\(_4\)•\(^-\) (8.4 \times 10^9 mol L\(^{-1}\) s\(^{-1}\))\(^{[33]}\).

As shown in Fig. 11, after two free-radical quenchers were added, the degradation of Ph by the system was inhibited. This phenomenon indicates that both SO\(_4\)•\(^-\) and •OH participate in the Ph degradation reaction. The inhibition of Ph degradation after the addition of TBA was substantially greater than that after MeOH addition, indicating that •OH plays a major role in the activation of PDS to degrade Ph and that SO\(_4\)•\(^-\) plays a supporting role.

### 3.10. Degradation of TOC

Fig. 12 demonstrates the total organic carbon (TOC) degradation. The experimental conditions were considered to be optimal conditions, and the initial concentration of Ph was 50.00 mg L\(^{-1}\). In the first 60 min, the degree of degradation of TOC was very low, which is inconsistent with the aforementioned rate of Ph degradation. The rate of degradation of TOC increased during 60 min to 120 min, and the previously described Ph was almost completely degraded during this period. The experiment was extended to 300 min, and the degradation efficiency of TOC was only 85.94 %. This result is
likely attributable to only a single bond of Ph being destroyed at the beginning of the experiment; that is, the Ph was not immediately mineralized into carbon dioxide and water. To verify this conjecture, we further analyzed the degradation products. Fig. 13 shows the degradation process of Ph. The chemical bond connecting the hydroxyl group in the Ph is first destroyed, and then the benzene ring is opened to form a single chain connected by a single bond. As the reaction proceeds, the chemical bond between the single chains is destroyed and a single chain with a smaller number of carbon atoms is formed. The process of recombining the chains into new long chains is due to insufficient oxidant dosing; however, as the reaction progresses, intermediates such as these short chains and newly formed long chains are further degraded. The Ph is finally mineralized into water and carbon dioxide.

3.11. Reaction mechanism

Under the aforementioned optimal experimental conditions, the initial concentration of Ph was 50.00 mg L\(^{-1}\); the experiment was carried out, samples were collected every 30 min, and the degradation products were detected by gas chromatography–mass spectrometry. Fig. 10 shows the degradation process. The single bond connecting the hydroxyl groups in the Ph is first destroyed, and the benzene ring is destroyed to grow into a single chain. In this process, some single chains recombine to form a new longer single chain with increasing reaction time. As this process continues, long single chains are gradually dismembered into short chains and then mineralized into carbon dioxide and water. Fig. 14 shows the FT-IR spectra of BAC before and after activation and before and after the degradation of Ph. A distinct peak is observed at 1150 cm\(^{-1}\) before activation, and the intensity of this peak decreases after activation. This decrease in intensity is attributed to electrons being lost between CCs. After PDS is added to the system, the peak continues to decrease in intensity. When the reaction is completed, the peak increases in intensity. This increase in intensity is attributed to the electrons after the reaction returning to the BAC, thus increasing the CC and causing the peak in the FT-IR spectrum to intensify. At the same time, the intensity of the peak at 3400 cm\(^{-1}\) after activation was higher than that before activation. When PDS was added, the peak height was not substantially changed after the reaction, which indicated that activated BAC promoted the degradation of Ph. Degradation reaction formula is as follows.

\[
\text{BAC} + \text{SO}_4^{2-} \rightarrow \text{BAC}^+ + \text{SO}_4^{2-} \quad (1)
\]

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO}^- + \text{SO}_4^{2-} \quad (3)
\]

\[
\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_5^{2-} \quad (4)
\]

\[
\text{HO}^- + \text{SO}_4^{2-} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Several steps} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} \quad (5)
\]

4. Conclusion

In this study, BAC was prepared at 900.0 °C and the experiment was optimized under the condition of 0.50 g L\(^{-1}\). When the PDS/Ph molar ratio was 5:1, the initial pH value (6.45) and the degradation rate of Ph at room temperature were ideal. The degradation rate reached 84.74 % in 120 min, the degradation rate of TOC was 85.94 % in 300 min, and the degree of mineralization was ideal. The BAC exhibited high stability and reusability with the Ph degradation rate still exceeds 80 % after repeated use for 4 times. Compared with other similar systems, the system developed in this work uses a smaller amount of activator and oxidant, which has high practical value.

Conflicts of interest

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not
listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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