Effect of Calcination Time on Catalyst’s Activity and Stability

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Abstract. Based on the catalyst Pd-Fe-Co-Ce/FSC(ratio 1:1:1:3), a catalytic wet oxidation method was used to treat organic waste-water that is difficult to biodegrade. The calcination temperature of the catalyst was set to 550 ℃, and the calcination time was set to 1 h, 3 h, 5 h, 7 h in order. From the analysis, it is found that the effluent pH first decreases and then increases. With the extension of the reaction time, the absorbance of the treated waste-water decreases, and the decolorization rate increases. With the extension of the reaction time, the COD of the treated water sample decreased and the COD removal rate increased. For catalysts No.1, No.2, No.3 and No.4, the COD of wastewater was 10851, 768, 1149 and 1238 mg/L at 120 min of catalytic wet oxidation of wastewater, and the corresponding COD removal rates was 84.1%, 88.7%, 83.1% and 81.8%, respectively. The experimental results showed that the catalyst prepared by calcining for 3 h had a COD removal rate and a decolorization rate of 88.7% and 97.9%, respectively, and the metal dissolution solubility of the treated water was relatively low. 3 h is a suitable catalyst’s calcination time.

1. Introduction
The wet oxidation method (WAO) is an effective method for the treatment of high-concentration organic waste-water invented by the American Zimmerman in the 1950s [1]. It is suitable for treating high-concentration organic waste-water that is not suitable for incineration treatment due to the low concentration of organic matter and is ineffective in biological treatment [2-3]. Such as toxic waste-water, usually organic waste-water with COD <35,000 mg/L. WAO has the advantages of wide range of application, fast processing speed, high processing efficiency, no secondary pollution, low processing cost, etc [4-5]. Since its inception, it has received much domestic and foreign scholars favor. In order to reduce the reaction pressure of the WAO process, a catalyst is introduced into the reaction system, which is a catalytic wet oxidation method (CWAO) [6-7]. Catalytic wet oxidation method is used to treat difficult biodegradable organic waste-water. This method is a treatment technology to oxidize dissolved or suspended organic matter or reduced inorganic matter in water by using oxygen as oxidant under high temperature and high pressure conditions. The temperature for wet air oxidation is 120–320 ℃, and the pressure is 0.5–20 MPa [8-9]. The CWAO has received more and more attention in the treatment of difficult biodegradable organic waste-water [10-11].

The preparation of the catalyst is the core of the CWAO, and the calcination time directly affects the performance of the catalyst [12-13]. The longer the calcination time, the more complete the calcination of the catalyst, but long time may cause the catalyst to sinter. Short time catalyst is not fully roasted, crystal formation is incomplete, and catalyst stability is poor [3]. For specific catalysts, the calcination time needs to be verified experimentally.
2. Experimental method

2.1. Experimental scheme design
Pd-based catalyst Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3), the calcination temperature was set to 550 ºC, the calcination time was set to 1 h, 3 h, 5 h, 7 h.

2.2. Experimental materials and equipment
Experimental materials: This experiment uses printing waste-water from a factory in Guangdong with a COD_{Cr} of 6800 mg/L. It is used in the research of wet oxidation and organic degradation mechanism, the development of heterogeneous catalysts. In the experiment, the volume used in each reaction vessel was 250 mL.

Experimental equipment: high-pressure reactor, with a volume of 0.5 L and a design pressure of 12.5 MPa.

(1) Determination scheme
(2) Measuring instrument
Backflow device: glass backflow device with 250 mL conical bottle. Heating device: resistance converter. 50 mL acid burette.

(3) Test reagent
Potassium dichromate standard solution, Trying ferrous spirit indication liquid, Ferrous ammonium sulfate standard solution, Sulfuric acid - silver sulfate solution, Mercury sulfate: crystallization or powder.

3. Results and discussion

3.1 Influence of calcination temperature time on effluent pH
Four drying samples of D # were made in parallel, and the four kinds of calcination time were set at 1, 3, 5, and 7 h at 550ºC; the organic waste-water was treated with a catalyst. The pH, decolorization rate, and COD removal rate at different calcination times are shown in Table 1, and Figure 1:

| No. | 0 min | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|-------|--------|--------|--------|--------|--------|---------|
| 1#  | 6.72  | 3.9    | 3.58   | 3.39   | 3.27   | 4      | 4.05    |
| 2#  | 6.72  | 3.86   | 3.6    | 3.35   | 3.22   | 3.84   | 3.89    |
| 3#  | 6.72  | 4.07   | 3.81   | 3.44   | 3.28   | 4.01   | 4.1     |
| 4#  | 6.72  | 4.09   | 3.73   | 3.43   | 3.33   | 4.12   | 4.15    |

![Figure 1. Water effluent pH at different calcination times.](image-url)
From the analysis of the figure above, it is found that the effluent pH first decreases and then increases, because the waste-water first degrades into small molecule organic acids, the pH of the waste-water decreases, then the small molecule organic acids further degrade into carbon dioxide and water, and the pH of the waste-water rises again.

3.2 Effect of calcination time on absorbance and decolorization rate of waste-water
The catalyst treated waste-water under 4 calcination times, the absorbance and decolorization rate of waste-water in different treatment time periods are shown in Table 2, Table 3 and Figure 2.

**Table 2.** Absorbance of waste-water at different calcination time.

| No. | 0 min | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|-------|--------|--------|--------|--------|--------|---------|
| 1#  | 4.31  | 2.694  | 2.474  | 2.017  | 1.276  | 0.763  | 0.315   |
| 2#  | 4.31  | 2.573  | 2.215  | 1.776  | 0.884  | 0.185  | 0.091   |
| 3#  | 4.31  | 2.875  | 2.564  | 2.03   | 1.414  | 0.914  | 0.388   |
| 4#  | 4.31  | 3.013  | 2.664  | 2.211  | 1.474  | 0.996  | 0.427   |

**Table 3.** Decolorization rates of waste-water under different calcination time .

| No. | 0 min | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|-------|--------|--------|--------|--------|--------|---------|
| 1# (%) | 0     | 37.5   | 42.6   | 53.2   | 70.4   | 82.3   | 92.7    |
| 2# (%) | 0     | 40.3   | 48.6   | 58.8   | 79.5   | 95.7   | 97.9    |
| 3# (%) | 0     | 33.3   | 40.5   | 52.9   | 67.2   | 78.8   | 91      |
| 4# (%) | 0     | 30.1   | 38.2   | 48.7   | 65.8   | 76.9   | 90.1    |

**Figure 2.** Absorbance and decolorization rates at different calcination time.
Seen from Table 2~3 and Figure 2, with the extension of the reaction time, the absorbance of the treated waste-water decreases, and the decolorization rate increases. For catalysts No. 1, No. 2, No. 3 and No. 4, the absorbance of wastewater was 0.315, 0.091, 0.388 and 0.427 at 120 min of catalytic wet oxidation of wastewater, and the corresponding decolorization rates was 92.7%, 97.9%, 91.0% and 90.1%, respectively. When the calcination time of the catalyst is 3 h, the decolorization rate is relatively highest. The decolorization rate of the water sample reached 97.9% at 120 minutes.

3.3 Effect of calcination time on COD and COD removal rate of waste-water

The COD and COD removal rate of the waste-water treated by the catalyst under 4 calcination times are shown in Table 4, Table 5 and Figure 3:

**Table 4. COD of waste-water under different calcination time.**

| No.  | 0 min  | 10 min  | 20 min  | 40 min  | 60 min  | 90 min  | 120 min |
|------|--------|---------|---------|---------|---------|---------|---------|
| 1# (mg/L) | 6800   | 4597    | 4196    | 3203    | 2298    | 1353    | 1081    |
| 2# (mg/L) | 6800   | 4223    | 3801    | 2686    | 1884    | 1136    | 768     |
| 3# (mg/L) | 6800   | 4821    | 4332    | 3298    | 2502    | 1584    | 1149    |
| 4# (mg/L) | 6800   | 4916    | 4604    | 3570    | 2863    | 1802    | 1238    |

**Table 5. COD removal rates of waste-water under different calcination time.**

| No.  | 0 min  | 10 min  | 20 min  | 40 min  | 60 min  | 90 min  | 120 min |
|------|--------|---------|---------|---------|---------|---------|---------|
| 1# (%) | 0      | 32.4    | 38.3    | 52.9    | 66.2    | 80.1    | 84.1    |
| 2# (%) | 0      | 37.9    | 44.1    | 60.5    | 72.3    | 83.3    | 88.7    |
| 3# (%) | 0      | 29.1    | 36.3    | 51.5    | 63.2    | 76.7    | 83.1    |
| 4# (%) | 0      | 27.7    | 32.3    | 47.5    | 57.9    | 73.5    | 81.8    |

**Figure 3. COD and COD removal rates of waste-water at different calcination times.**
Seen from Table 4–5 and Figure 3, with the extension of the reaction time, the COD of the treated water sample decreased and the COD removal rate increased. For catalysts No.1, No.2, No.3 and No.4, the COD of wastewater was 10851, 768, 1149 and 1238 mg/L at 120 min of catalytic wet oxidation of wastewater, and the corresponding COD removal rates was 84.1%, 88.7%, 83.1% and 81.8%, respectively. The catalyst with a calcination time of 3 h had the highest COD removal rate. The COD removal rate of the water sample reached 97.9% at 120 minutes.

4. Conclusion
Catalyst Pd-Fe-Co-Ce/FSC(ratio 1:1:1:3), at a calcination temperature of 550°C, at different calcination times of 1 h, 3 h, 5 h and 7 h, the order of decolorization rate and COD removal rate of waste-water is 3 h>1 h>5 h>7 h. Therefore, 3 h is selected as the optimum catalyst’s calcination time.

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