Effect of Calcination Temperature on the Performance of Multi-Component Impregnated Catalysts

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Abstract. The catalyst Cu-Fe-Pd-La/γ-Al2O3 (ratio 1:1:1:3) was used to treat simulated printing and dyeing waste-water by CWAO method. The calcination temperature was set to 350, 450, 550, 650, 750, 850 °C in order. The results showed that as the calcination temperature increases, the decolorization rate of the catalyst treatment waste-water decreases, and the metal stripping concentration of the waste-water decreases. At the five temperatures set, the decolorization rate of the waste-water was 97.20%, 97.04 %, 97.92 %, 97.86 %, 95.59 %, and 98.92 % in turn. The dissolved Cu and Fe concentrations of the waste-water at 60 minutes were 0.32 mg/L and 49.15 mg/L, respectively. The catalyst has good catalytic activity and stability.

1. Introduction
Traditional reactive dye waste-water treatment includes coagulation, chemical oxidation and biological oxidation. The coagulation method has certain effects on the treatment of reactive dye waste-water, but various types of coagulants do not have a broad spectrum of decolorization of the dye, and a large amount of chemical sludge brings secondary pollution. Due to the poor biodegradability of printing and dyeing waste-water, the simple aerobic biological treatment process is difficult to meet the waste-water emission requirements, and the changes in the printing and dyeing process or dye species have a fatal impact on the dominant decolorizing bacteria in the anaerobic treatment tank [1]. How to maintain the activity of these excellent bacteria in biological treatment is the current technical difficulty in anaerobic-aerobic treatment of printing and dyeing waste-water. Chemical oxidation methods such as Fenton oxidation have a good effect in treating active printing and dyeing waste-water, but when the concentration of waste-water is high, the reaction rate decreases, and the effluent appears darker brown. Although the membrane treatment technology has been successfully used in the treatment of printing and dyeing waste-water, high-concentration liquid treatment needs further study [2].

Catalytic wet oxidation method (CWAO), which uses oxygen in the air as an oxidant under high temperature (125–320 °C) and high pressure (0.5–20 MPa) (now other oxidants are also used, such as ozone, hydrogen peroxide, etc.). It is a chemical process in the liquid phase that oxidizes pollutants to inorganic or small molecule organics such as CO2 and water [3]. The key problem of the catalytic wet oxidation method is to use a catalyst with high activity, high stability and easy to recycle. The current catalysts used in CWAO are various catalysts such as transition metals and their oxides, composite oxides and salts. According to the state of the catalyst reaction, they can be divided into homogeneous
catalysts (dissolved metal salts) and heterogeneous catalysts (metals, Oxygen, composite oxide) [4-5]. Heterogeneous catalysts appear in different phase reactions (for example, solid catalysts are mixed in liquid phase), where the catalysts are mostly solid and the reactants are liquid or gas. Homogeneous catalysts are reactions that appear in the same phase (for example, liquid catalysts are mixed in a liquid state). Homogeneous catalysts work independently at the molecular or ion level. The properties of the active center are relatively uniform, and the interaction process with the reactants is easier to study and speculate using modern detection methods. This paper studies the activity of heterogeneous supported catalysts to promote the application of CWAO technology.

Calcination is an important part of catalyst preparation. The calcination process can change the catalyst's chemical valence, crystal phase structure, and specific surface and pore structure. The precursor is obtained by impregnating and drying the active component on the catalyst, and generally exists in the form of hydrated hydroxide, nitrate, carbonate, etc. The calcination process can remove chemically bound water and volatile substances and convert them into the required chemical form or valence. At the same time, by controlling a certain calcination temperature, the size of microcrystals can be controlled, thereby changing the specific surface and pore structure of the catalyst, and improving the activity and mechanical strength of the catalyst.

2. Experimental part

2.1. Experimental materials
Catalyst: Supported Cu-Fe-Pd-La/γ-Al2O3 catalyst.
Experimental water sample: The concentration of CODCr in the methyl orange solution was 2000 mg/L. The reason why methyl orange was chosen as the simulated printing and dyeing waste-water is that the single component is convenient for the mechanism research. Methyl orange concentration: 951.6 mg/L. Absorbance: 71.4. PH: 6.41.

2.2. Detection method
PH: pH meter method. Absorbance: Spectrophotometry, Instrument: 752 spectrophotometer. Metal concentration: ICP-OES method, inductively coupled plasma emission spectrometer.

2.3. Scheme design
For the catalyst Cu-Fe-Pd-La/Al2O3, ratio: Cu:Fe:Pd:La=1.1:1:3, the total metal ion concentration was set to 6 wt%, the calcination time in the catalyst preparation is 3 hours, and the set calcination temperatures were 350, 450, 550, 650, 750, 850 °C. Six dried samples of Cu-Fe-Pd-La/Al2O3 were made in parallel, and calcined at the set temperature for 3 hours. The dyeing simulation waste-water was treated with the obtained catalyst, and the pH and decolorization activity of the catalyst were analyzed.

3. Results and discussion

3.1. Effect of catalyst calcination temperature on effluent pH of waste-water treatment
The experimental results are shown in Table 1 and Figure 1.
Table 1. PH of water samples under different calcination temperature catalysts.

| No. | Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 21# | 350 °C                  | 5.57   | 5.51   | 5.41   | 5.44   | 5.90   |
| 22# | 450 °C                  | 6.06   | 5.60   | 5.53   | 5.66   | 6.24   |
| 23# | 550 °C                  | 5.73   | 5.67   | 5.65   | 5.74   | 6.14   |
| 24# | 650 °C                  | 6.53   | 6.27   | 6.23   | 6.21   | 6.45   |
| 25# | 750 °C                  | 6.59   | 6.58   | 6.48   | 6.51   | 6.66   |
| 26# | 850 °C                  | 6.42   | 6.04   | 5.82   | 5.58   | 5.80   |

Figure 1. PH of water samples under different calcination temperature catalysts.

As can be seen from the above Table 1 and Figure 1, with the extension of the reaction time, and after the application of the catalyst, the pH of the treated water shows a trend of first decrease and then increase. At 350, 450 and 550 °C, the pH of the treated effluent is relatively low, because the organic matter is completely degraded, and the intermediate products of small-molecule organic acids appear more.

3.2. Effect of catalyst roasting temperature on absorbance and decolorization rate of waste-water

For the data of absorbance and decolorization rate of waste-water under different calcination temperature catalysts, see Tables 2 to 4 below, and Figures 2 to 4.

Table 2. Absorbance of waste-water under different calcination temperature catalysts.

| No. | Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 21# | 350 °C                  | 14.80  | 8.38   | 3.31   | 1.25   | 0.34   |
| 22# | 450 °C                  | 20.75  | 10.45  | 5.05   | 4.87   | 2.10   |
| 23# | 550 °C                  | 19.50  | 16.40  | 8.65   | 3.51   | 1.49   |
| 24# | 650 °C                  | 14.80  | 10.90  | 5.98   | 2.04   | 1.53   |
| 25# | 750 °C                  | 16.15  | 14.95  | 8.48   | 6.73   | 3.15   |
| 26# | 850 °C                  | 16.95  | 15.20  | 8.00   | 3.47   | 0.77   |
Figure 2. Absorbance of waste-water under different calcination temperature catalysts.

Table 3. Decolorization rate of waste-water under different calcination temperature catalysts.

| No. | Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 21# | 350 °C                  | 87.43  | 90.44  | 93.74  | 96.53  | 97.20  |
| 22# | 450 °C                  | 70.94  | 85.36  | 92.93  | 93.18  | 97.04  |
| 23# | 550 °C                  | 72.69  | 77.03  | 87.89  | 95.08  | 97.92  |
| 24# | 650 °C                  | 79.27  | 84.73  | 91.63  | 97.14  | 97.86  |
| 25# | 750 °C                  | 77.38  | 79.06  | 88.13  | 90.58  | 95.59  |
| 26# | 850 °C                  | 76.26  | 78.71  | 88.80  | 95.14  | 98.92  |

Figure 3. Decolorization rate of waste-water under different calcination temperature catalysts.

Table 4. Relationship between calcination temperature and catalyst activity (90 min).

| No. | 21# | 22# | 23# | 24# | 25# | 26# |
|-----|-----|-----|-----|-----|-----|-----|
| Calcination temperature | 350 °C | 450 °C | 550 °C | 650 °C | 750 °C | 850 °C |
| Absorbance | 0.34 | 2.10 | 1.49 | 1.53 | 3.15 | 0.77 |
| Decolorization rate (%) | 97.20 | 97.04 | 97.92 | 97.86 | 95.59 | 98.92 |
From the above Table 2~4, and Figure 2 to Figure 4, it can be seen that with the extension of the reaction time, the absorbance of the waste-water decreases and the decolorization rate increases. With the increase of the calcination temperature of the catalyst, the decolorization rate of the waste-water shows a trend of increasing first and then decreasing. The decolorization rate of the catalyst treated at 550 °C reaches 97.92% in 90 minutes.

3.3. Effect of catalyst calcination temperature on metal dissolution concentration of waste-water
The effect of catalyst calcination temperature on the metal dissolution concentration of waste-water is shown in Table 5.

| No. | 21# | 22# | 23# | 24# | 25# | 26# |
|-----|-----|-----|-----|-----|-----|-----|
| Calcination temperature 350 °C | 3.77 | 6.06 | 0.17 | 1.49 | 0.18 | 0.3 |
| 450 °C | 6.49 | 0.32 | 1.05 | 0.65 | 1.77 |
| 550 °C | 48.37 | 29.12 | 49.66 | 67.03 | 47.31 |
It can be seen from Table 5 that in the waste-water treated by the CWAO method, the dissolved Cu concentration is relatively low and the dissolved Fe concentration is relatively high at 60 minutes. With the increase of the calcination temperature of the catalyst, the metal dissolution concentration of the catalyst tends to decrease first. However, according to the catalyst activity experiments in Section 3.2, the increase in temperature leads to a decrease in the decolorization rate of the catalyst. When the catalyst was calcined at 550 °C, the Cu concentration and Fe concentration in the waste-water are 0.32 mg/L and 49.15 mg/L, respectively, after 60 minutes of reaction.

4. Conclusion
To investigate the effect of calcination temperature on the performance of supported catalyst Cu-Fe-Pd-La/γ-Al2O3 (ratio 1:1:1:3). The calcination temperature was set to 350, 450, 550, 650, 750 and 850 °C in turn. The results shows that as the calcination temperature increased, the decolorization rate of the catalyst treatment waste-water decreased, and the metal concentration of the waste-water decreased. At the five temperatures set, the Cu concentration of waste-water is 0.94, 2.2, 0.32, 1.05, 1.77 mg/L, and the Fe dissolution concentration is 47.47, 28.49, 49.15, 28.11, 67.03 and 47.31 mg/L. The decolorization rate of the catalyst waste-water at 550 °C reached 97.92 %. 550 °C is a suitable catalyst calcination temperature.

Acknowledgments
This work was supported by 2019 Lateral Project from Guangzhou College of Technology and Business.

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