Relationship between calcination temperature and performance of supported Pd-catalyst

Qiang Liu*
School-enterprise Cooperation Center, Guangzhou College of Technology and Business, Guangzhou, China

*Corresponding author e-mail: 2863957925@qq.com

Abstract. In the experiment, the COD removal rate of water samples was used as the evaluation index of catalyst activity, and the dissolution concentration of metal ions was used as the evaluation index of catalyst stability, and the activity and stability of the catalyst were comprehensively evaluated. The Pd-catalyst was used to treat simulated printing and dyeing waste-water by CWAO, and the influence of calcination temperature on the performance of the catalyst was investigated. 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. The COD removal rate of the waste-water at the set 6 temperatures was 87.84 %, 85.43 %, 84.72 %, 77.59 %, 68.04 % and 66.94 %. The dissolved Cu and Fe concentrations of the waste-water at 90 minutes were 0.46 mg/L and 49.22 mg/L. Pd-catalyst has good catalytic activity and stability.

1. Introduction
Due to the development of chemical fiber fabrics and the improvement of printing and dyeing finishing technologies in recent years, a large number of organic compounds that are difficult to biodegrade, such as PVA dyes and new auxiliaries, have entered the printing and dyeing waste-water [1-2]. Due to the large changes in raw materials used in the printing and dyeing (printing) process, high alkalinity, rapid and violent changes in water quality [3-4], and the fact that most dyes and pigments are macromolecular substances that are difficult to biodegrade, the colored groups are firm and not easy to destroy [5-6]. Therefore, the traditional biological decolorization process faces new challenges. In response to the above problems, in recent years, domestic and foreign countries have focused on the exploration and application of new biological treatment processes, efficient decolorizing bacteria, new chemical agents, and advanced oxidation technologies. The representative ones are: anaerobic-aerobic biological treatment process, screening and application research of high-efficiency specialized decoloring bacteria and PVA degrading enzymes, development of high-efficiency decoloring coagulants, advanced oxidation technologies such as photocatalysis, ozone oxidation and wet oxidation application research, popularization and application of membrane separation technology and clean production technology, etc [7].

Catalytic wet oxidation method can effectively treat printing and dyeing waste-water [8]. Precious metal have high activity and stability to oxidation reactions, and have been widely used in petrochemical and automotive exhaust treatment industries. In order to make the precious metal have
better dispersibility and reduce the amount of precious metal, precious metal series catalysts often adopt impregnation method, usually the precious metal is supported on a carrier with a high specific surface area (for example: activated carbon, SiO$_2$, Al$_2$O$_3$, TiO$_2$, CeO$_2$, ZrO$_2$, NaY etc.). A large number of studies have shown that precious metal catalysts have good activity and stability in CWAO waste-water treatment.

Wan Jiafeng et al. prepared a Ru/CeO$_2$/Al$_2$O$_3$ ternary composite oxide catalyst using γ-Al$_2$O$_3$ as the carrier, RuO$_2$ as the active ingredient, and CeO$_2$ as a co-catalyst. A catalyst prepared by a stepwise impregnation method (Ru/CeO$_2$/Al$_2$O$_3$ ternary composite oxide catalyst) was used to study the water distribution of phenol under conditions of high temperature (270 °C), high pressure (5.5 MPa), and reaction time of 30 minutes [9]. The removal rate was over 80 %. The CWAO method after adding catalyst has attracted more and more scholars' attention. The preparation of catalyst is the core of CWAO method. In this paper, the influence of calcination temperature on the activity of catalyst was studied.

2. Experimental part

2.1. Experimental objects
Catalyst: Multi-component catalyst, Cu-Fe-Pd-La/γ-Al$_2$O$_3$.

2.2. Experimental water samples
Methyl orange aqueous solution with a COD$_{Cr}$ concentration of 2000 mg/L. The reason for choosing methyl orange aqueous solution to simulate printing and dyeing waste-water is that On the one hand, the composition of methyl orange is single, and methyl orange is analytically pure. Compared to industrial-grade dyes, it can more accurately and easily grasp the reaction law and nature. Basic orange is similar to most dyes in chemical composition and properties, and has a certain representation.

2.3. Detection methods
COD: potassium dichromate method (GB11914-89)
Metal concentration: ICP-OES method, Inductively coupled plasma emission spectrometer.

3. Results and discussion

3.1. Effect of catalyst calcination temperature on COD of waste-water
The COD data of waste-water under different calcination temperature catalysts are shown in Table 1 and Figure 1 below.

Table 1. COD of waste-water under different calcination temperature catalysts.

| No. | Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 21# | 350 °C                  | 1246.20| 940.68 | 558.78 | 341.70 | 243.21 |
| 22# | 450 °C                  | 566.19 | 549.84 | 447.64 | 369.96 | 308.64 |
| 23# | 550 °C                  | 1595.94| 1388.91| 994.95 | 627.12 | 305.50 |
| 24# | 650 °C                  | 1085.40| 948.72 | 757.77 | 578.88 | 448.23 |
| 25# | 750 °C                  | 1177.86| 1121.58| 954.75 | 842.19 | 639.18 |
| 26# | 850 °C                  | 1396.95| 1230.12| 1011.03| 856.26 | 661.29 |
As can be seen from Table 1 and Figure 1 described above, as the reaction time increases, the COD of the waste-water decreases. With the increase of the catalyst calcination temperature, the COD of the waste-water was examined at the same processing time node. It was found that the COD of the waste-water showed a decreasing trend with the increase of the catalyst calcination temperature.

3.2. Effect of catalyst calcination temperature on COD removal rate of waste-water
The COD removal rate data of the waste-water under different calcination temperature catalysts are shown in Table 2 and Figure 2 below.

Table 2. COD removal rates of waste-water under different calcination temperature catalysts.

| No. | Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 21# | 350 °C                  | 37.69  | 52.97  | 72.06  | 82.92  | 87.84  |
| 22# | 450 °C                  | 45.73  | 61.11  | 74.17  | 82.71  | 85.43  |
| 23# | 550 °C                  | 20.20  | 30.55  | 50.25  | 68.64  | 84.72  |
| 24# | 650 °C                  | 45.73  | 52.56  | 62.11  | 71.05  | 77.59  |
| 25# | 750 °C                  | 41.11  | 43.92  | 52.26  | 57.89  | 68.04  |
| 26# | 850 °C                  | 30.15  | 38.49  | 49.45  | 57.18  | 66.94  |
As can be seen from Table 2 and Figure 2 above, as the reaction time increases, the COD removal rate of the waste-water increases. The COD removal rate of the catalyst calcined at 550 °C reaches 84.72% at 90 minutes.

3.3. Effect of calcination temperature on catalyst activity

The effect of calcination temperature on catalyst activity is shown in Table 3 (a) and (b) of Figure 3.

Table 3. Relationship between calcination temperature and catalyst performance (90 min).

| No.   | 21#  | 22#  | 23#  | 24#  | 25#  | 26#  |
|-------|------|------|------|------|------|------|
| Calcination temperature | 350 °C | 450 °C | 550 °C | 650 °C | 750 °C | 850 °C |
| COD (mg/L)  | 241.32 | 308.64 | 305.5 | 448.23 | 639.18 | 661.29 |
| COD removal rate (%) | 87.84 | 85.43 | 84.72 | 77.59 | 68.04 | 66.94 |
The effect of calcination temperature on catalyst metal dissolution

The effect of calcination temperature on the dissolution of catalyst metal is shown in Table 4.

**Table 4.** Metal dissolution concentration of waste-water under different calcination temperature catalysts.

| No. | 21# | 22# | 23# | 24# | 25# | 26# |
|-----|-----|-----|-----|-----|-----|-----|
| Calcination temperature | 350 °C | 450 °C | 550 °C | 650 °C | 750 °C | 850 °C |
| Cu concentration (mg/L), 20 min | 2.9 | 5.22 | 0.68 | 1.8 | 0.12 | 0.46 |
| Fe concentration (mg/L), 20 min | 48.24 | 49.57 | 52.01 | 51.71 | 48.48 | 47.6 |
| Cu concentration (mg/L), 90 min | 0.13 | 2.1 | 0.3 | 0.46 | 0.41 | 2.33 |
| Fe concentration (mg/L), 90 min | 48.32 | 66.28 | 51.22 | 49.22 | 47.31 | 46.57 |

From Table 4, the simulated printing and dyeing waste-water is treated with CWAO method, and the degradation of organic matter led to the generation of small molecule organic acids. The waste-water shows acidity, causing partial dissolution of metal oxides supported on the catalyst into the
waste-water. The Cu concentration in the waste-water is higher than the Fe concentration. With the increase of the calcination temperature of the catalyst, the metal dissolution concentration of the catalyst tends to decrease first. However, in combination with the catalyst COD removal rate experiments, the increase in temperature led to a decrease in catalyst activity.

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, 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. The Cu dissolution concentrations of waste-water at the set 5 temperatures are 0.13, 2.1, 0.30, 0.46, 0.41 and 2.33 mg/L, and the Fe dissolution concentrations are 48.32, 66.28, 51.22, 49.22, 47.31 and 46.57 mg/L. The COD removal rate of the catalyst waste-water at 550 °C is reached 84.72 %. 550 °C is a suitable catalyst calcination temperature.

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