Effect of Calcination Temperature on the Performance of Pd-Based Catalysts

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Abstract. It is difficult to biodegrade organic waste-water, which is treated by catalytic wet oxidation method. The catalyst Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3), and the calcination time was 3 h, and the calcination temperatures were set to 400, 550, 700, and 850 °C, respectively. When the calcination temperature was 550 °C, the experimental results show that: when Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) is added with , the pH of wastewater is reduced, and then the pH will rise again ; the Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalyst has good decolorization effect at 4 calcining temperatures, which can reach 92.7% - 97.9%, and 36.6% - 41.8% higher than the blank without catalyst; the best treatment effect is when the calcination time is 3 h and the calcination temperature is 550 °C. The addition of Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) after treatment of printing waste-water, its COD removal rate increased significantly, and the final effluent percentage reached 71.7% - 88.8%.

1. Introduction
Printing and dyeing waste-water has the characteristics of large amount of water, high content of organic pollutants, deep chroma, large alkalinity, and large changes in water quality. The electrolytic method, biological activated carbon method and chemical oxidation method are also sometimes used in the treatment of printing and dyeing waste-water. Coagulation method is the most widely used method in the treatment of printing and dyeing waste-water, and it is a physical and chemical advanced treatment method [1]. Chemical oxidation methods such as Fenton oxidation method for the treatment of active printing and dyeing waste-water. When the ambient pH is 3-4, Fenton reagent produces highly oxidative hydroxyl radicals (HO•), which can completely destroy the molecular structure of reactive dyes, but cannot effectively remove COD [2]. The use of reverse osmosis membrane separation technology to treat waste-water has the characteristics of no secondary pollution, low energy consumption, and recyclability. However, there are also major problems in membrane treatment technology that need to be improved. For example, clogging will occur during use, and the problems of acid resistance, corrosion resistance, film pollution, and film cleaning of film materials need to be further improved [3]. Because the raw materials used in the printing and dyeing (printing) process vary greatly, the alkalinity is high, and the water quality changes quickly and violently. Most dyes and pigments are macromolecular substances that are difficult to biodegrade, and the colored groups are firm and difficult to destroy. Therefore, the traditional biological decolorization process faces new challenges.
Overview of wet oxidation catalysts: CWAO catalysts can be divided into homogeneous catalysts and heterogeneous catalysts. Temperature plays a particularly important role in the reaction process. High temperature can accelerate the oxidation reaction and increase the solubility in the liquid phase of oxygen and oxygen. When the temperature is higher than 150 °C, the solubility of water increases with increasing temperature. Increasing temperature can also generate oxygen radicals, which can form HO• with water [4]. The addition of the catalyst can increase the degradation rate of organic matter. The nature and amount of the catalyst are the key factors affecting CWAO. At present, CWAO has been widely used in the treatment of various high-concentration organic waste-water, but the research and improvement of catalysts have always been the focus of research [5-6].

2. Experimental method

2.1. Experimental water samples
In this experiment, printing waste-water from a ceramic factory in Guangdong Province was used. Its COD$_{cr}$ was 6800 mg/L, which was used for catalytic wet oxidation treatment. The amount of each time it was charged into the reactor was 250 mL.

2.2. Experimental equipment
The main technical parameters of the reactor are shown in Table 1.

| No. | Technical Parameters   | index  |
|-----|------------------------|--------|
| 1   | Volume                 | 0.5 L  |
| 2   | Design pressure        | 12.5 MPa |
| 3   | Test pressure          | 3.0 MPa |
| 4   | Design temperature     | 180 °C |
| 5   | Heating furnace rated power | 1.5 KW |

Take 250 mL of organic waste-water with an initial COD value of 6800 mg/L, pour it into the reactor, and add a set amount of homemade catalyst. Close the lid of the reactor and fix it with nuts to ensure the airtightness of the equipment. Otherwise, when the temperature rises and the pressure rises, there will be air leakage or liquid leakage at the grinding mouth of the kettle, which affects the test. Turn on the power to set the reaction temperature and heating power, and heat up. Setting parameters of Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) calcination temperature are shown in Table 2.

| No. | Element ratio           | calcination time | calcination temperature |
|-----|-------------------------|------------------|------------------------|
| D1  | Pd-Fe-Co-Ce/Al$_2$O$_3$=1:1:1:3 | 3 h              | 400 °C                 |
| D2  | Pd-Fe-Co-Ce/Al$_2$O$_3$=1:1:1:3 | 3 h              | 550 °C                 |
| D3  | Pd-Fe-Co-Ce/Al$_2$O$_3$=1:1:1:3 | 3 h              | 700 °C                 |
| D4  | Pd-Fe-Co-Ce/Al$_2$O$_3$=1:1:1:3 | 3 h              | 850 °C                 |

3. Results and discussion

3.1. Effect of catalyst calcination temperature on pH of treated water
Dry samples of 4 Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalysts were made in parallel, and the four kinds of calcination temperatures were set to 400, 550, 700, and 850 °C, respectively, and the calcination time was 3 h. Treat the printing waste-water with the obtained catalyst, and test the catalyst activity and stability. The pH of the treated water sample is shown in Table 3 and Figure 1:
Table 3. pH of catalyst treated effluent at different calcination temperatures.

| No. | 0   | 10  | 20  | 40  | 60  | 90  | 120 |
|-----|-----|-----|-----|-----|-----|-----|-----|
| D1  | 6.72| 3.82| 3.50| 3.31| 3.25| 3.97| 4.08|
| D2  | 6.72| 3.86| 3.60| 3.35| 3.22| 3.84| 3.89|
| D3  | 6.72| 3.90| 3.70| 3.38| 3.45| 4.19| 4.18|
| D4  | 6.72| 4.18| 3.91| 3.73| 3.28| 3.99| 4.34|

Figure 1. pH of effluent from catalyst treatment at different calcination temperatures.

It can be seen from Figure 1 that when organic waste-water is added with Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3), the process of organic matter degradation is first converted into small molecule organic acids, the pH is reduced, and then small molecule organic acids are gradually decomposed again. After the decomposition is complete, the pH will rise again.

3.2. Effect of catalyst calcination temperature on absorbance and decolorization rate of treated effluent

The effect of Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalyst on the absorbance and decolorization rate of treated effluent is shown in Tables 4-5, and Figure 2.

Table 4. Absorbance of catalyst treated water at different calcination temperatures.

| No. | 0  | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|----|---------|--------|--------|--------|--------|---------|
| D1  | 4.31| 2.711   | 2.353  | 2.039  | 1.034  | 0.293  | 0.151   |
| D2  | 4.31| 2.573   | 2.215  | 1.776  | 0.884  | 0.185  | 0.091   |
| D3  | 4.31| 2.836   | 2.474  | 2.129  | 1.276  | 0.422  | 0.224   |
| D4  | 4.31| 3.004   | 2.638  | 2.267  | 1.496  | 0.547  | 0.315   |

Table 5. Decolorization rates of waste-water treated at different calcination temperatures (%).

| No. | 0  | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|----|--------|--------|--------|--------|--------|---------|
| D1  | 37.1| 45.4   | 52.7   | 76.0   | 93.2   | 96.5   |         |
| D2  | 40.3| 48.6   | 58.8   | 79.5   | 95.7   | 97.9   |         |
| D3  | 34.2| 42.6   | 50.6   | 70.4   | 90.2   | 94.8   |         |
| D4  | 30.3| 38.8   | 47.4   | 65.3   | 87.3   | 92.7   |         |
Figure 2. Absorbance and decolorization rates of waste-water at different calcination temperatures (%).

It can be seen from the figure that the Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalyst has good decolorization effect at 4 calcining temperatures, which can reach 92.7%~97.9%, and 36.6%~41.8% higher than the blank without catalyst.

3.3. Effect of catalyst calcination temperature on COD and COD removal rate of treated effluent
The effects of Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalyst on the COD and COD removal rate of treated effluent are shown in Tables 6~7, and Figures 2~3.

Table 6. COD (mg/L) of waste-water treated effluent at different calcination temperatures.

| No. | 0   | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|-----|--------|--------|--------|--------|--------|---------|
| D1  | 6800| 4359   | 4046   | 3475   | 2645   | 1326   | 932     |
| D2  | 6800| 4223   | 3801   | 2686   | 1884   | 1136   | 768     |
| D3  | 6800| 4706   | 4168   | 3808   | 2924   | 1639   | 1312    |
| D4  | 6800| 4984   | 4338   | 3910   | 3046   | 2312   | 1952    |

Table 7. COD removal rates of waste-water treated at different calcination temperatures (%)

| No. | 0 | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----|---|--------|--------|--------|--------|--------|---------|
| D1  | 0 | 35.9   | 40.5   | 48.9   | 61.1   | 80.5   | 86.3    |
| D2  | 0 | 37.9   | 44.1   | 60.5   | 72.3   | 83.3   | 88.7    |
| D3  | 0 | 30.8   | 38.7   | 44.0   | 57.0   | 75.9   | 80.7    |
| D4  | 0 | 26.7   | 36.2   | 42.5   | 55.2   | 66.0   | 71.3    |

From the analysis of the above tables and figures, it is concluded that the catalytic effect of the mixed catalyst is obvious, which can fully degrade the waste water. The best treatment effect is when the calcination time is 3 h and the calcination temperature is 550 °C. The addition of Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) after treatment of printing waste-water, its COD removal rate increased significantly, and the final effluent percentage reached 71.7% -88.8%.
4. Conclusion
For Pd-Fe-Co-Ce/FS C (ratio 1:1:1:3) catalyst, during the preparation of the catalysts, select a calcination time of 3 h. For the set calcination temperatures of 400, 550, 700, and 850 °C, as the calcination temperature increases, the stability of the catalyst increases and the activity decreases. At the calcination temperature of 550 °C, for the water samples after the catalyst treatment, the COD removal rates and decolorization rates both increases, reaching 88.7% and 97.9%, respectively, and the leaching concentrations of the effluent Pd, Fe, Co, and Ce were also low. Weighing the activity and stability of the catalyst, a calcination temperature of 550 °C was chosen.

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References
[1] Li Jiazhen. Treatment of dyestuff and dyeing industrial wastewater [M]. Beijing: Chemical Industry Press, 1997.
[2] Du Guirong, Song Zhanxue, Huang Keling, et al. Study on Fenton Oxidation-Coagulation Treatment of Reactive Dye Wastewater [J]. Journal of East China Institute of Geology, 2002, 25 (4): 306-307.
[3] Zhang Xin, Cao Yingwen. Reverse osmosis membrane treatment and reuse technology of printing and dyeing wastewater [J]. Printing and Dyeing. 2008, 14: 36-38.
[4] Lee Dong-Keun, Kim Dul-Sun. Catalytic wet air oxidation of carboxylic acids at atmospheric pressure [J]. Catalysis Today, 2000, 63: 249-255.
[5] Seftel E M, Puscasu M C, Mertens M, et al. Assemblies of nanoparticles of CeO$_2$–ZnTi-LDHs and their derived mixed oxides as novel photocatalytic systems for phenol degradation[J]. Applied Catalysis B: Environmental, 2014,150-151:157-166.
[6] Catrinescu C, Arsene D, Teodosiu C. Catalytic wet hydrogen peroxide oxidation of para-chlorophenol over Al/Fe pillared clays (AlFePILCs) prepared from different host clays[J]. Applied Catalysis B: Environmental, 2011,101:451-460.