Effect of Precious Metals on the Activity of Multi-Component Supported Catalysts

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Abstract. Organic waste-water is treated by catalytic wet oxidation method (CWAO). The catalysts are prepared by the same amount of impregnation method. Fe and Co are used as active components of the catalyst, and Ce is used as the catalytic assistant, and the precious metal Pd is added to prepare a multi-component composite catalysts. When the Pd-based catalyst is added to the waste-water, the pH decreases and then increases. The process of organic matter degradation is first converted to small molecule organic acids, the pH is reduced, and then the small molecule organic acids are gradually decomposed. In the proportion of Pd-catalyst, as the Pd content in the catalyst increases, the treatment effect of the waste-water is enhanced; Effect of different ratios on the stability of Pd-Fe-Co-Ce/FSC catalysts showed that, CODCr removal rate increased from 65.7% to 84.7%, and decolorization rate increased from 72.5% to 97.2%. The average concentration of Pd3+, Fe3+, Co2+ and Ce3+ dissolved is 0.0015, 2.2519, 0.2281 and 0.2300, respectively. The Pd-catalyst Pd-Fe-Co-Ce/FSC with metal ion ratio Pd-Fe-Co-Ce=1:1:1:3 has the highest activity in waste-water treatment, and CODCr removal rates and decolorization rates reach 88.7% and 97.9%, respectively.

1. Introduction
In recent years, with the rapid development of the world's industry, the types and quantities of synthetic organic matter have been increasing. There are currently more than 7 million types of organic matter known, and they increase at the rate of 2000 kinds per year [1]. The number of synthetic organic compounds in the world has reached 250 million tons. These organic compounds have entered the environment through various channels, causing a series of water pollution and ecological degradation, threatening human survival and hindering the development of relevant industries and social progress, especially in developing countries.

Printing waste-water treatment status: waste-water discharged from the ceramic printing industry is a major source of industrial water pollution. waste-water often contains a large amount of organic matter and darker colors [2,3]. Ceramic printing companies produce various kinds of flowers and papers, glazed and printed porcelain, and then fired in a kiln. The colorful patterns consist of a variety of heavy metal compounds, glazes, adhesives, thickeners, etc. Ceramic printing waste-water includes waste-water from the production process of flower paper, printing plate washing water, floor washing water, and mixed sewage. The COD Cr is 10,000~20,000 mg/L, the BOD 5 is about 1000 mg/L, the chroma is more than 10,000 times, and the biodegradability index B/C of the waste-water is 0.05~0.1, which is less than the critical value 0.3, so the ceramic printing waste-water is a typical high concentration of hardly biochemical organic waste-water.
The catalysts for the catalytic wet oxidation technology can be divided into two types: homogeneous catalysts and heterogeneous catalysts. Heterogeneous catalysts have the advantages of high activity, easy separation, and good stability, so they have become the focus of the development of wet catalytic oxidation [4,5].

2. Experimental method

2.1 Experimental water samples
The high-concentration organic waste water used in this experiment came from the printing waste-water of a ceramic factory in Guangdong. Its COD$_{Cr}$ is 6800 mg/L. It is used in catalytic wet oxidation treatment. The amount of water sample charged into the reactor each time in the experiment is 250 mL.

2.2 Experimental reagents
The main reagents used in the experiment: palladium nitrate, 98% sulfuric acid, mercury sulfate, ferrous ammonium sulfate, potassium dichromate, 1.10-phenanthroline, ferrous sulfate, concentrated nitric acid, and a series of nitrates.

2.3 Test analysis method
Chroma: Spectrophotometric method.
pH: pH meter method.
Determination of chemical oxygen demand (COD$_{Cr}$): national standard, Cr method.
Determination of metal ion concentration: ICP method.

3. Results and discussion

3.1 Proportion of catalytic agent
It is concluded from the references that most heterogeneous catalytic wet oxidation catalysts are soluble transition metal salts, including: metal chlorides, metal sulfates and metal nitrates, and the active ingredient is transition metal ions. Because the atomic valence layer of the transition metal is partially filled with d orbitals or f orbitals, it can be bonded to the reaction matrix in various forms, and various unique reactions occur in the coordination field of the transition metal. These become important elementary reactions for homogeneous catalytic reactions. However, since the material of the reactor is Cr$_{18}$Ni$_{12}$Mo$_3$, it has been proved in practice that the compounds containing chlorine will corrode the equipment during the wet oxidation process. And both sulfate and nitrate are soluble salts, which meet the requirements of homogeneous catalytic wet oxidation. which meets the requirements of homogeneous catalytic wet oxidation. In addition, under high temperature conditions, NO$_3^-$ is easily decomposed into NO$_2^-$, which reduces the secondary pollution of water samples by homogeneous catalysts. Meanwhile, many literatures show that chloride and sulfate have no higher catalytic activity than nitrate. Therefore, nitrate was selected as a homogeneous catalyst component by experiments. Various metal salts constituting the catalyst component, Pd(NO$_3$)$_2$ + Fe(NO$_3$)$_3$ + Co(NO$_3$)$_2$ + Ce$_2$(NO$_3$)$_3$, The total concentration of its constituent metal ions in the configured dipping solution is 6wt%. The mass distribution of each metal ion is shown in Table 1:
Table 1. Various preparation parameters of Pd-Fe-Co-Ce/FSC catalysts.

| No. | Element ratio | Carrier (g) | Palladium nitrate (g) | Iron nitrate (g) | Cobalt nitrate (g) | Cerium nitrate (g) | Water (g) |
|-----|---------------|-------------|-----------------------|------------------|--------------------|--------------------|-----------|
| A1  | Fe-Co-Ce=1.5:1.5:3 (Fe1Co1Ce2) | 10.00 | 0 | 2.1703 | 1.4815 | 1.8590 | 14.4865 |
| A2  | Pd-Ce=3:3 (Pd1Ce1) | 10.00 | 4.0000 | 0 | 0 | 1.8593 | 14.1407 |
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3 (Pd4Fe1Co1Ce6) | 10.00 | 2.6667 | 0.7263 | 0.4938 | 1.8593 | 14.2566 |
| A4  | Pd-Fe-Co-Ce=1:1:1:3 (Pd1Fe1Co1Ce3) | 10.00 | 1.3333 | 1.4472 | 0.9877 | 1.8593 | 14.3725 |
| A5  | Pd-Fe-Co-Ce=1.5:0.75:0.75:3 (Pd2Fe1Co1Ce4) | 10.00 | 2.0000 | 1.0854 | 0.7407 | 1.8593 | 14.3146 |
| A6  | blank | 6.72 | 3.74 | 3.56 | 3.46 | 3.3 | 4.13 | 4.30 |

3.2 Effect of Pd catalyst ratio on catalyst performance

The pH, absorbance and decolorization rate, COD and COD removal rate of waste water treated with ceramic printing waste water added with Pd-based catalyst are shown in Tables 2 to 6, as shown in Figure 1, Figure 2, and Figure 3, respectively.

Table 2. pH of treated water under different proportion of catalysts.

| No. | Element ratio | pH | 0 | 10 | 20 | 40 | 60 | 90 | 120 |
|-----|---------------|----|---|----|----|----|----|----|-----|
| A1  | Fe-Co-Ce=1.5:1.5:3 (Fe1Co1Ce2) | 6.72 | 3.96 | 3.71 | 3.42 | 3.34 | 4.06 | 4.24 |
| A2  | Pd-Ce=3:3 (Pd1Ce1) | 6.72 | 3.88 | 3.66 | 3.42 | 3.34 | 3.67 | 4.18 |
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3 (Pd4Fe1Co1Ce6) | 6.72 | 3.91 | 3.61 | 3.4 | 3.32 | 4.15 | 4.30 |
| A4  | Pd-Fe-Co-Ce=1:1:1:3 (Pd1Fe1Co1Ce3) | 6.72 | 4.03 | 3.73 | 3.7 | 3.44 | 4.20 | 4.49 |
| A5  | Pd-Fe-Co-Ce=1.5:0.75:0.75:3 (Pd2Fe1Co1Ce4) | 6.72 | 3.94 | 3.45 | 3.4 | 3.36 | 4.19 | 4.36 |
| A6  | blank | 6.72 | 3.74 | 3.56 | 3.46 | 3.3 | 4.13 | 4.30 |

Figure 1. pH of treated effluent under different catalyst ratios.
### Table 3. Absorbance of treated effluent under different catalyst ratios.

| No. | Element ratio                                      | 0    | 10   | 20   | 40   | 60   | 90   | 120  |
|-----|---------------------------------------------------|------|------|------|------|------|------|------|
| A1  | Fe-Co-Ce=1.5:1.5:3 (Fe1Co1Ce2)                     | 4.31 | 3.237| 2.81 | 2.371| 1.991| 1.396| 1.185|
| A2  | Pd-Ce=3:3 (Pd1Ce1)                                 | 4.31 | 1.806| 1.371| 0.944| 0.500| 0.047| 0.013|
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3 (Pd4Fe1Co1Ce6)             | 4.31 | 2.069| 1.720| 1.220| 0.616| 0.203| 0.086|
| A4  | Pd-Fe-Co-Ce=1:1:1:3 (Pd1Fe1Co1Ce3)                 | 4.31 | 2.573| 2.276| 1.690| 0.884| 0.336| 0.181|
| A5  | Pd-Fe-Co-Ce=1.5:0.75:0.75:3 (Pd2Fe1Co1Ce4)         | 4.31 | 2.332| 2.060| 1.496| 0.711| 0.259| 0.121|
| A6  | blank                                             | 4.31 | 3.500| 3.103| 2.896| 2.345| 2.008| 1.892|

### Table 4. Decolorization rate of treated effluent under different proportion of catalysts.

| No. | Element ratio                                      | 0    | 10   | 20   | 40   | 60   | 90   | 120  |
|-----|---------------------------------------------------|------|------|------|------|------|------|------|
| A1  | Fe-Co-Ce=1.5:1.5:3 (Fe1Co1Ce2)                     | 0    | 24.9 | 34.8 | 45.0 | 53.6 | 67.6 | 72.5 |
| A2  | Pd-Ce=3:3 (Pd1Ce1)                                 | 0    | 58.1 | 68.2 | 78.1 | 88.4 | 98.9 | 99.7 |
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3 (Pd4Fe1Co1Ce6)             | 0    | 52.0 | 60.1 | 71.7 | 85.7 | 95.3 | 98.0 |
| A4  | Pd-Fe-Co-Ce=1:1:1:3 (Pd1Fe1Co1Ce3)                 | 0    | 40.3 | 47.2 | 60.8 | 79.5 | 92.2 | 95.8 |
| A5  | Pd-Fe-Co-Ce=1.5:0.75:0.75:3 (Pd2Fe1Co1Ce4)         | 0    | 45.9 | 52.2 | 65.3 | 83.5 | 94.0 | 97.2 |
| A6  | blank                                             | 0    | 18.8 | 28.0 | 32.8 | 45.6 | 53.4 | 56.1 |

![Figure 2](image-url). **Figure 2.** Absorbance and decolorization rates of treated effluent under different catalysts.
Table 5. COD of treated effluent under different catalysts.

| No. | Element ratio          | 0  | 10 | 20  | 40  | 60  | 90  | 120 |
|-----|------------------------|----|----|-----|-----|-----|-----|-----|
| A1  | Fe-Co-Ce=1:5:1.5:3     | 6800 | 5331 | 5018 | 4046 | 3244 | 2591 | 2332 |
|     | (Fe1Co1Ce2) (mg/L)     |    |     |     |     |     |     |     |
| A2  | Pd-Ce=3:3             | 6800 | 3706 | 3040 | 2244 | 1374 | 945  | 714  |
|     | (Pd1Ce1) (mg/L)       |    |     |     |     |     |     |     |
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3| 6800 | 3828 | 3475 | 2428 | 1618 | 1034 | 938  |
|     | (Pd4Fe1Co1Ce6) (mg/L) |    |     |     |     |     |     |     |
| A4  | Pd-Fe-Co-Ce=1:1:1:3    | 6800 | 4298 | 3917 | 2734 | 1829 | 1258 | 1156 |
|     | (Pd1Fe1Co1Ce3) (mg/L) |    |     |     |     |     |     |     |
| A5  | Pd-Fe-Co-Ce=1:5:0.75:0.75:3| 6800 | 4134 | 3720 | 2482 | 1707 | 1136 | 1040 |
|     | (Pd2Fe1Co1Ce4) (mg/L) |    |     |     |     |     |     |     |
| A6  | Blank (mg/L)           | 6800 | 5678 | 5154 | 4733 | 3924 | 3393 | 3182 |

Table 6. COD removal rates of waste-water under different proportion of catalysts.

| No. | Element ratio          | 0  | 10 | 20  | 40  | 60  | 90  | 120 |
|-----|------------------------|----|----|-----|-----|-----|-----|-----|
| A1  | Fe-Co-Ce=1:5:1.5:3     | 0  | 21.6 | 26.2 | 40.5 | 52.3 | 61.9 | 65.7 |
|     | (Fe1Co1Ce2) (%)        |    |     |     |     |     |     |     |
| A2  | Pd-Ce=3:3             | 0  | 45.5 | 55.3 | 67.0 | 79.8 | 86.1 | 89.5 |
|     | (Pd1Ce1) (%)          |    |     |     |     |     |     |     |
| A3  | Pd-Fe-Co-Ce=2:0.5:0.5:3| 0  | 43.7 | 4839 | 64.3 | 76.2 | 84.8 | 86.2 |
|     | (Pd4Fe1Co1Ce6) (%)    |    |     |     |     |     |     |     |
| A4  | Pd-Fe-Co-Ce=1:1:1:3    | 0  | 36.8 | 42.4 | 59.8 | 73.1 | 81.5 | 83.0 |
|     | (Pd1Fe1Co1Ce3) (%)    |    |     |     |     |     |     |     |
| A5  | Pd-Fe-Co-Ce=1:5:0.75:0.75:3| 0  | 39.2 | 45.3 | 63.5 | 74.9 | 83.3 | 84.7 |
|     | (Pd2Fe1Co1Ce4) (%)    |    |     |     |     |     |     |     |
| A6  | Blank (%)             | 0  | 16.5 | 24.2 | 30.4 | 42.3 | 50.1 | 53.2 |

Figure 3. COD and COD removal rates of treated effluent under different catalysts.

It can be seen from Figure 2 that when the Pd-based catalyst is added to the waste-water, the pH decreases and then increases. The process of organic matter degradation is first converted to small molecule organic acids, the pH is reduced, and then the small molecule organic acids are gradually decomposed. The pH rises. According to the analysis in Figure 2 and Figure 3, under the same treatment conditions, the addition of different catalysts can increase the decolorization rate and COD removal rate. From the decoloration rates and COD perspective, the treatment effect of Pd1Ce1 catalyst is the best. Therefore, in the proportion of Pd- catalyst, as the Pd content in the catalyst...
increases, the treatment effect of the waste-water is enhanced; the dissolution concentrations of Pd, Fe, Co, and Ce ions are shown in Table 7 as shown in Table 7.

| Catalyst type | A1 | A2 | A3 | A4 | A5 | blank |
|---------------|----|----|----|----|----|-------|
| COD\(_\text{Cr}\) removal rate (%) | 65.7 | 89.5 | 86.2 | 83.0 | 84.7 | 53.2 |
| Decolorization rate (%) | 72.5 | 99.7 | 98.0 | 95.8 | 97.2 | 56.1 |
| C[Pd\(^{3+}\)]/(mg/L) | 0.0000 | 0.0024 | 0.0019 | 0.0014 | 0.0017 | - |
| C[Fe\(^{3+}\)]/(mg/L) | 3.4782 | 1.6378 | 2.0044 | 2.1267 | 2.0180 | - |
| C[Co\(^{2+}\)]/(mg/L) | 0.3895 | 0.2321 | 0.1429 | 0.2145 | 0.1613 | - |
| C[Ce\(^{3+}\)]/(mg/L) | 0.2156 | 0.2315 | 0.2371 | 0.2306 | 0.2351 | - |

4. Conclusion
After the addition of Pd-based catalysts, the dissolution concentrations of Pd, Fe, Co, and Ce in the water samples were small, and the stability of the five types of catalysts was good. When the molar ratio of the Pd-Ce catalyst was 3:3, its decolorization rate and the COD removal rate is the most ideal, but considering the prime cost of Pd, comprehensive consideration of catalyst cost and performance, the catalyst with Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) is selected.

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