Study on the Performance of Pd-Catalyst Based on Decolorization Rate

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Abstract. The simulated azo dye waste-water was treated by Catalytic Wet Oxidation. The catalyst was prepared by impregnation method, and FSC (main component: γ-Al₂O₃) was used as the catalyst carrier, and 6wt%Cu, Fe, Pd and La were added. The catalyst was dynamically impregnated at 35 °C for 8 h, dried at 110 °C for 10 h, and roasted at 450 °C for 3h to prepare the supported catalyst. Based on the decolorization rate of treated waste-water, the effect of component composition on catalyst performance was investigated. In the CWAO treatment of waste-water, the pH of the treated effluent first decreased and then increased with the extension of reaction time; with the extension of reaction time, organic matter degrades continuously, the absorbance of waste-water decreases and the decolorization rate increases. Cu-Fe-Pd-La/FSC (ratio 0.75:0.75:1.5:3) has the best treatment effect; the metal dissolution concentration of the waste-water increases with the reaction time. Cu and Al are relatively stable, and the dissolution concentration in treated effluent is between 0.5 and 3.0 mg/L. The results showed that the Cu-Fe-Pd-La/FSC catalyst composed of Cu: Fe: Pd: La=1:1:1:3 had good catalytic activity and stability.

1. Introduction
There are eight basic processes in the printing and dyeing industry, including desizing, refining, bleaching, mercerizing, dyeing, finishing, drying and finished products. The main pollution sources are difficult to biodegrade, and conventional water treatment methods cannot effectively treat high-concentration printing and dyeing waste-water, while according to literature, catalytic wet oxidation technology can effectively treat printing and dyeing wastewater [1].

Catalytic wet oxidation technology was developed in the 1970s. At present, hydrothermal oxidation technology has become one of the main development directions. It is in the traditional wet oxidation process to add the appropriate catalyst, by changing the reaction mileage to achieve the process capacity and capacity increase, in order to reduce the reaction temperature and pressure, improve the oxidation decomposition capacity, shorten the reaction time, reduce equipment corrosion and reduce the cost [2, 3]. Japan is leading the way, with its wet oxidation catalysts already in industrial use and with a life span of up to 10,000 hours. The wet catalytic oxidation process is much cheaper to treat coking waste-water than the traditional non-catalytic process in terms of both infrastructure cost and operation cost, and the treatment effect is good and the speed is fast [4]. The catalyst speeds up the reaction mainly because: first, it reduces the activation energy of the reaction; Second, it changes the course of the reaction.
Because the catalysts are selective and the waste-water contains many kinds and structures of organic matter, the catalysts need to be screened and evaluated. According to the phase state of catalysts used, catalysts can be divided into homogeneous catalysts and heterogeneous catalysts. Homogeneous catalyst and reaction material are in the same phase; The heterogeneous catalyst is solid and is in a different phase from the reaction material. Heterogeneous CWAO method has received more and more attention in the treatment of high concentration refractory organic waste-water [5].

The core of catalytic wet oxidation technology is catalyst. This paper studies the performance of catalyst in CWAO technology.

2. Experimental Section

2.1. The water samples
The $\text{COD}_{Cr}$ concentration of methyl orange solution is 2000 mg/L, and the relevant calculation is as follows:

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\begin{align*}
\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S} & \rightarrow \frac{43}{2} \text{O}_2 \\
327.34 \text{ g/mol} & \times \frac{43}{2} \times 32 \text{ g/mol} \\
\text{c} & = 2000 \text{ mg/l} \\
\end{align*}
\]

\[
c = 2000 \times 327.34 \times \left(\frac{43}{2} \times 32\right) = 0.952 \text{ g/L}
\]

The relevant indicators of simulated wastewater are shown in Table 1.

| Table 1. Parameters of simulated printing and dyeing waste-water. |
|---------------------------------------------------------------|
| **Methyl orange concentration** (mg/L) | **$\text{COD}_{Cr}$** (mg/L) | **Absorbance** | **pH** |
|--------------------------------------|-------------------------------|----------------|--------|
| 951.6                                | 2000                          | 71.4           | 6.41   |

2.2. Detection method
pH: pH meter method.
Absorbance: Spectrophotometry, instrument 752 scenery photometer.
Metal concentration: Icp-oes method, inductively coupled plasma emission spectrometer.

2.3. Catalyst composition
Cu-Fe-Pd-La/FSC catalyst was prepared based on copper nitrate, iron nitrate, palladium chloride and lanthanum nitrate.

3. Experiment Results and Discussion

3.1. Influence of catalyst components on pH of treated effluent
As shown in table 2, in terms of the mass percentage of Cu, Fe, La and Pt, the total amount of metal ions in the prepared impregnation solution was 6wt %. The preparation conditions of the catalyst were dynamic impregnation at 35 °C for 8 h, drying at 110 °C for 10 h and roasting at 450 °C for 3 h.
The change in the concentration of the impregnating solution may have an impact on the activity of the catalyst and the dissolution concentration of Cu and Fe out of the water. Part of the experimental results are shown in table 2, Figure 1.

**Table 2.** pH of water samples under different components of catalysts.

| No. | Elements ratio      | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|---------------------|--------|--------|--------|--------|--------|
| 1#  | Pd-La=3:3           | 5.06   | 4.96   | 4.80   | 4.64   | 5.01   |
| 2#  | Cu-Fe-Pd-La =1.1:1:3| 6.06   | 5.60   | 5.45   | 5.43   | 6.24   |
| 3#  | Cu-Fe-Pd-La=0.75:0.75:1.5:3 | 5.68 | 5.42 | 5.11 | 4.99 | 6.09 |
| blank| Without catalyst    | 6.20   | 6.10   | 5.84   | 5.26   | 4.48   |

**Figure 1.** pH of water samples under different components of catalysts.

In the CWAO treatment of waste-water, the pH of the treated effluent first decreased and then increased with the extension of reaction time. The faster the pH drops, the better the waste-water is treated. Therefore, the higher the content of noble metal Pd, the better the treatment effect of waste water.

### 3.2. Influence of catalyst components on absorbance and decolorization rate of waste-water

The experimental results are shown in Table 3~5 and Figure 2~5.

**Table 3.** Absorbance of waste-water under different components of catalysts.

| No. | Elements ratio      | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|---------------------|--------|--------|--------|--------|--------|
| 1#  | Pd-La=3:3           | 8.98   | 6.83   | 4.47   | 2.48   | 2.00   |
| 2#  | Cu-Fe-Pd-La =1.1:1:3| 19.50  | 16.40  | 8.65   | 3.51   | 1.49   |
| 3#  | Cu-Fe-Pd-La=0.75:0.75:1.5:3 | 10.70 | 5.48 | 2.17 | 1.39 | 0.53 |
| blank| Without catalyst    | 66.40  | 60.51  | 54.25  | 41.13  | 24.70  |
Figure 2. Absorbance of waste-water under catalysts of different components.

Table 4. Decolorization rates of waste-water under different components of catalysts.

| No. | Elements ratio          | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|-------------------------|--------|--------|--------|--------|--------|
| 1#  | Pd-La = 3:3 (%)         | 87.43  | 90.44  | 93.74  | 96.53  | 97.20  |
| 2#  | Cu-Fe-Pd-La = 1.1:1:3 (%) | 72.69  | 77.03  | 87.89  | 95.08  | 97.92  |
| 3#  | Cu-Fe-Pd-La = 0.75:0.75:1.5:3 (%) | 85.01  | 92.32  | 96.96  | 98.05  | 99.26  |
| blank | Without catalyst (%)     | 7.000  | 15.25  | 24.02  | 42.39  | 65.40  |

Figure 3. Decolorization rates of waste-water under different component catalysts.
Table 5. Activity of catalysts with different components.

| No. | 1#  | 2#  | 3#  | blank |
|-----|-----|-----|-----|-------|
| Absorbance (90 min) | 2.000 | 1.485 | 0.361 | 24.64 |
| Decolorization rate (%), 90 min | 97.20 | 97.04 | 99.49 | 65.40 |

Figure 4. Activity of catalysts with different components based on absorbance.

Figure 5. Activity of catalysts with different components based on decolorization rates.
As can be seen from Table 3–5 above and Figure 2–5 above, with the extension of reaction time, organic matter degrades continuously, the absorbance of waste-water decreases and the decolorization rate increases. Cu-Fe-Pd-La/FSC (ratio 0.75:0.75:1.5:3) has the best treatment effect. At the reaction time of 90 min, the absorbance of the waste-water decreased from 71.4 to 1.485, and the decolorization rate reached 97.04%.

3.3. Influence of catalyst components on its stability

The influence of catalyst components on its stability is shown in Table 6.

| Table 6. Stability of catalysts with different components. |
|-----------------------------------------------------------|
| No. | 1# | 2# | 3# | blank |
|----------|----------|----------|----------|----------|
| Concentration of Cu (mg/L, 90 min) | 1.43 | 2.1 | 2.64 | — |
| Concentration of Fe (mg/L, 90 min) | 51.45 | 50.28 | 58.44 | — |
| Concentration of Al (mg/L, 90 min) | 1.20 | 0.51 | 0.64 | — |

It can be seen from the table that the metal dissolution concentration of the waste-water increases with the reaction time. Cu and Al are relatively stable, and the dissolution concentration in treated effluent is between 0.5 and 3.0 mg/L. The dissolution concentration of metallic Fe is slightly higher, between 50 and 60 mg/L. Among the three catalysts, Cu-Fe-Pd-La/FSC (ratio 0.75:0.75:1.5:3) has the strongest stability.

4. Conclusion

For the three catalysts selected for the study, Pd-La/FSC (ratio 3:3), Cu-Fe-Pd-La/FSC (ratio 1:1:1:3), and Cu-Fe-Pd-La/FSC (ratio 0.75:0.75:1.5:3), the activity and stability of the catalysts increased with the increase of Pd content in the precious metal. Considering the performance and cost of the catalyst, Cu-Fe-Pd-La/FSC (ratio 1.1:1:3) is elected as the suitable catalyst.

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