Research on the performance of Cu-Fe-Pd-La/FSC catalyst based on COD

Yongli Zhang*

Logistics Department, Guangzhou College of Technology and Business, Guangzhou, China

*Corresponding author e-mail: 670511263@qq.com

Abstract. The catalysts were prepared by impregnation method, and the simulated printing and dyeing waste-water was treated by CWAO method. Based on the COD rates of treated waste-water, the influence of composition of Cu, Fe, Pd and La on catalyst activity and stability was investigated. The results showed that Cu-Fe-Pd-La/FSC catalyst, composed of Cu: Fe: Pd: La = 1:1:1:3 catalyst, had a COD removal rate of 85.43%, and the Cu and Fe concentrations of the treated waste-water were 0.54 mg/L and 51.96 mg/L, respectively. The catalyst has good catalytic activity and stability.

1. Introduction

Waste-water discharged by textile printing and dyeing industry is a major source of industrial water pollution. Physical, chemical and biological methods can not effectively treat dyeing waste-water. Catalytic wet oxidation can treat printing and dyeing waste-water. At present, it is generally believed that CWAO reaction belongs to free radical reaction, which can be divided into three stages, namely: chain initiation, chain development or transfer, and chain termination [1-2]. In the initiation and development stage of the chain, molecular oxygen is involved in the formation of various free radicals, but Yang (1986) [3] believed that molecular oxygen only participates in the formation of free radicals in the development stage of the chain. The generated free radicals, such as HO-, RO- and ROO-, attack the organic compound RH, triggering a series of chain reactions to generate carbon dioxide and low molecular acid, thus effectively degrading the waste-water [4].

Initial research on catalytic wet oxidation focused on homogeneous catalysts, which catalyze the reaction process at the molecular or ionic level by adding a soluble catalyst to the reaction fluid [5]. The advantages of CWAO technology are shown in Table 1.
Table 1. Cost and effect of coking waste-water treatment by different processes.

| Process types               | Operating cost/yuan | Capital expenditure/yuan | The relative velocity | Concentration of NH₃ (mg/L) | Export COD concentration (mg/L) |
|-----------------------------|---------------------|--------------------------|-----------------------|----------------------------|---------------------------------|
| The traditional process     | 2425                | 1170                     | 1                     | 5000                       | 1000                            |
| Wet catalytic oxidation process | 1140               | 855                      | 100                   | 20                         | 10–20                           |

The catalyst is an important part of CWAO technology. In this paper, the activity of multi-component catalysts based on COD₅₇ was studied to promote the industrialization of CWAO technology.

2. Experimental part

2.1. Experimental materials
Catalyst: Cu-Fe-Pd-La/FSC catalyst.
Experimental water sample: methyl orange solution with COD₅₇ concentration of 2000 mg/L. On the one hand, only methyl orange is used as a single component, and methyl orange belongs to pure analysis, compared with the industrial dye can be more accurate and easier to grasp the law and nature of the reaction; Methyl oranges, on the other hand, are complex and contain N, S, dimethylamino (CH₃)₂N- and azo groups. Azo dyes are also the most variety of synthetic dyes. Methyl orange is similar to most dyes in chemical composition and properties and has certain representativeness.

2.2. Detection method
COD: Potassium dichromate method (GB11914-89)
Metal concentration: ICP method, Inductively coupled plasma emission spectrometer.

3. Results and discussion

3.1. The activity of component catalysts to waste-water was not investigated
The influence of different catalysts on COD degradation and COD removal rate of wastewater is shown in Table 2~4, and Figure 1~4.

Table 2. COD of wastewater under different components of catalysts.

| No. | Elements ratio | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----|----------------|--------|--------|--------|--------|--------|
| 1#  | Pd-La=3:3 (mg/L) | 566.08 | 489.84 | 365.95 | 341.17 | 245.87 |
| 2#  | Cu-Fe-Pd-La=1.1:1:3 (mg/L) | 1595.9 | 1388.91 | 994.95 | 627.12 | 291.4 |
| 3#  | Cu-Fe-Pd-La=0.75:0.75:1.5:3 (mg/L) | 498.74 | 511.00 | 388.36 | 333.13 | 301.20 |
| blank | Without catalyst (mg/L) | 1875.6 | 1794.4 | 1603.2 | 1357.8 | 1255.2 |
Figure 1. COD of wastewater under different components of catalysts.

Table 3. COD removal rate 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 (mg/L)               | 71.70  | 75.51  | 81.70  | 82.94  | 87.71  |
| 2#  | Cu-Fe-Pd-La=1.1:1:3 (mg/L)     | 45.73  | 61.11  | 74.17  | 82.71  | 85.43  |
| 3#  | Cu-Fe-Pd-La=0.75:0.75:1.5:3 (mg/L) | 59.84 | 69.28  | 76.31  | 77.51  | 84.94  |
| blank | Without catalyst (mg/L)       | 6.22   | 10.28  | 19.84  | 32.11  | 37.24  |

Figure 2. COD removal rate of wastewater under different components of catalyst.

Table 4. Performance of catalysts of different components.

| No. | 1#   | 2#   | 3#   | blank |
|-----|------|------|------|-------|
| COD (mg/L, 90 min) | 245.87 | 305.5 | 306.3 | 1255.2 |
| COD removal rate(%, 90 min) | 87.71 | 85.43 | 85.94 | 37.24 |
According to the tables and figures analysis, with the increase of reaction time, methyl orange simulated printing and dyeing waste-water in the decomposition process, continuously produce small molecules of organic acid, waste-water COD continued to decline, COD removal rate continued to increase. After three catalysts with different proportions were used to treat the waste of simulated printing and dyeing, COD removal rate of 1# was the highest, followed by that of 2#. This catalyst treated methyl orange simulated dye waste-water under the same conditions, COD removal rate of water sample reached 84.72 %, 24.04 % higher than that of water sample without catalyst.

3.2. Stability of catalysts with different components
The stability of catalysts with different components is shown in Table 5, Figure 5~6.

| No. | 1#   | 2#   | 3#   |
|-----|------|------|------|
| Concentration of Cu (mg/L, 60 min) | 1.31 | 0.54 | 5.39 |
| Concentration of Fe (mg/L, 60 min)  | 48.04| 51.96| 50.63|
As shown in the tables and figures above, it was found by atomic absorption testing that the dissolution concentrations of Cu, Fe and Al in the 2# catalyst (Cu-Fe-Pd-La=1.1:1:3) were smaller than those in the 3# catalyst (Cu-Fe-Pd-La=0.75:0.75:1.5:3) and 1# (Pd-La=3:3). Since the higher the dissolution concentration of metal ions was, the more unstable the catalyst was, so the 2# was more stable than the 1# and 3#.

Considering the cost, secondary utilization, loss and environmental protection, when the molar ratio of Cu:Fe:Pd:La is 1:1:1:3, the COD removal rate and metal dissolution rate are the most ideal catalysts for component composition.

3.3. XRD characterization of the catalysts
The experimental results are shown in Figure 7.
The XRD pattern of the catalyst, which is composed of three components in Figure 7, is characterized by fixed peak phase pairs, indicating that the catalyst has certain relative stability.

4. Conclusion
Three catalysts of Pd-La/FSC (ratio 3:3), Cu-Fe-Pd-La/FSC (ratio 1.1:1:3), Cu-Fe-Pd-La/FSC (ratio 0.75:0.75:1.5:3) were used to treat the printing and dyeing waste-water, and the COD removal rates were 87.71%, 85.43% and 85.94%, respectively. Cu dissolution concentrations were 1.31, 0.54 and 5.39 mg/L, respectively, and Fe dissolution concentrations were 48.04, 51.96 and 50.63 mg/L, respectively. Cu-Fe-Pd-La/FSC (ratio 1.1:1:3) was selected as the suitable catalyst based on the activity and stability of the catalyst.

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