Studies on Catalyst Activity Based on Organic Wastewater Treated by Homogeneous CWAO Method

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Abstract. High concentration organic waste-water was treated with nine homogeneous catalysts, such as Cu(NO$_3$)$_2$, CuSO$_4$, Fe(NO$_3$)$_3$, using the pH and decolorization rate of the treated effluent as the evaluation index. The results show that the order of catalytic effect from high to low is as follows: Cu(NO$_3$)$_2$ > CuSO$_4$ > Fe(NO$_3$)$_3$ > Fe$_2$(SO$_4$)$_3$ > Co(NO$_3$)$_2$ > Cr(NO$_3$)$_3$ > Ni(NO$_3$)$_2$ > AgNO$_3$ > Zr(NO$_3$)$_4$. The most effective Cu(NO$_3$)$_2$·3H$_2$O catalyst, the absorbance of the treated waste-water decreased from 2.465 to 0.283, and the decolorization rate reached 88.5%, which was 28.1% higher than that of the water sample without the catalyst under the same operating conditions. The pH of the treated effluent was also similarly lower than that of other homogeneous catalysts.

1. Introduction
Nowadays, water pollution is a global problem, especially the pollution of organic matter is more serious. Since the 1950s, with the development of new industries such as chemical industry, the variety and quantity of synthetic organic matter have increased day by day. These organisms have entered and are entering the environment through various means, causing a series of water pollution and deterioration of the ecological environment, which threaten the survival of mankind and hinder the development and social progress of related industries, especially in developing countries. Therefore, the treatment of high-concentration organic waste-water, especially toxic and harmful organic wastewater, has become a difficult problem to be solved in the field of environmental protection at home and abroad [1].

It is to add suitable catalyst to the traditional wet oxidation process to achieve the improvement of process capacity and capacity by changing the reaction mileage to reduce the reaction temperature and pressure, improve the oxidation decomposition ability, shorten the reaction time, reduce the corrosion of equipment and reduce the cost [2]. The initial study of catalytic wet oxidation focuses on homogeneous catalysts, which catalyze the reaction process at molecular or ionic levels by adding soluble catalysts to the reaction solution [3-4]. The reaction temperature of homogeneous catalysis is milder, the reaction performance is more specific. There is a specific selectivity, the activity and selectivity of homogeneous catalysis can be determined by the selection of ligands, the transformation of solvents, the addition of accelerators, and the fine blending and design. The mechanism of homogeneous catalysis is clear and easy to study and grasp [5].
2. Experimental Methods

2.1. Experimental Flow
Select a variety of catalyst types→ Wet oxidation simulation waste-water→ Effluent and catalyst detection.

2.2. Experimental Flow
(1) Selection of water samples: In this experiment, a ceramic printing and dyeing waste-water was selected, CODCr 3775 mg/L of raw water, absorbance A =2.465.
(2) The instruments required for the experiment are shown in Table 1.

Table 1. Detailed list of experimental instruments.

| No. | Name Said                          | Type No. | Health Factory Home           |
|-----|-----------------------------------|----------|-------------------------------|
| 1   | Visible spectrophotometer          | 722N     | Shanghai Spectral Instruments Co., Ltd. |
| 2   | Acid estimation apparatus          | Sartorius PB-10 | Serdolis Instruments, Germany |
| 3   | COD All Glass Distillation Equipment | Assemble | Shenyang Dongke Scientific Equipment Co., Ltd. |
| 4   | Electronic Multi-Raster            | Guangming | Beijing Yongguang Medical Instrument Factory |
| 5   | Electronic precision balance       | AB-204S  | Mettler Instruments           |
| 6   | Electric drying oven with forced convection | DGF-30/14-II | Nanjing Experimental Instruments Factory |
| 7   | Circulating water vacuum pump      | SHZ-D (III) | Gongyi Yuhua Experimental Instruments Co., Ltd. |
| 8   | High-speed centrifuge              | W800     | Shanghai Experimental Instruments Company |
| 9   | High Pressure Heating              | GS-0.5   | Weihai Chemical Equipment Medical Co., Ltd. |

2.3. Analytical Methods
(1) Determination of pH: Glass Electrode Method (GB6920-86)
(2) The pH value is obtained by measuring the electromotive force of the battery. The cell usually consists of a saturated calomel electrode and a glass electrode as an indicator electrode.
(3) Determination of decolorization rate
(4) The decolorization rate was determined by spectrophotometry. The chromaticity was determined by GB11903-89 and the decolorization rate was determined by 722N spectrophotometer, \( \eta = \frac{\text{Water sample absorbance}}{\text{Original absorbance}} \).

3. Results and Discussions

3.1. Effect of structural aids on pH and decolorization rates of waste-water
Ce(NO\(_3\)_3) and La(NO\(_3\)_3) are used as structural aids for the catalyst, compared with the blank water samples without the catalyst.

Table 2. Effect of structural aids on effluent pH.

| Category of auxiliaries | 10 min | 40 min | 60 min | 90 min |
|-------------------------|--------|--------|--------|--------|
| blank                   | 3.74   | 3.56   | 3.46   | 3.23   |
| Ce(NO\(_3\)_3)          | 3.31   | 3.30   | 3.22   | 3.16   |
| La(NO\(_3\)_3)          | 3.35   | 3.31   | 3.29   | 3.21   |
As can be seen from the above Table 2, Table 3 and Figure 1, Figure 2, it indicated that the ceramic printing and dyeing waste-water continuously produces small molecular organic acids during the decomposition process with the increase of reaction time, the effluent pH gradually decreases. After 60 min, the effluent pH increased mainly because of the decomposition of small organic acids. Comparing the effect of structural auxiliaries and blank groups on the pH and decolorization rate of waste-water, it can be seen that structural auxiliaries have no catalytic performance on waste-water treatment.
3.2. Screening of Catalysts
Nine metal salts such as Cu(NO₃)₂ were used as catalytic treatment of ceramic printed waste-water, compared with treated water samples without catalyst, the experimental results are shown in Table 4–Table 6, Figure 3–Figure 4.

**Table 4.** Effect of catalysts on effluent pH.

| Metal salts | 10 min | 20 min | 40 min | 90 min |
|-------------|--------|--------|--------|--------|
| blank       | 3.74   | 3.56   | 3.46   | 4.13   |
| Cu(NO₃)₂    | 3.91   | 3.74   | 3.42   | 3.45   |
| CuSO₄       | 3.76   | 3.68   | 3.43   | 3.52   |
| Fe(NO₃)₃    | 3.70   | 3.63   | 3.59   | 3.58   |
| Fe₂(SO₄)₃   | 3.85   | 3.62   | 3.46   | 3.63   |
| Ni(NO₃)₂    | 3.62   | 3.52   | 3.41   | 3.80   |
| Co(NO₃)₂    | 3.82   | 3.66   | 3.44   | 3.70   |
| Zr(NO₃)₄    | 3.33   | 3.32   | 3.30   | 3.94   |
| Cr(NO₃)₃    | 3.67   | 3.54   | 3.41   | 3.76   |
| AgNO₃       | 3.57   | 3.43   | 3.31   | 3.88   |

**Table 5.** Effect of catalysts on absorbance of waste-water.

| Metal salts | 10 min | 20 min | 40 min | 60 min | 90 min |
|-------------|--------|--------|--------|--------|--------|
| blank       | 1.624  | 1.366  | 1.269  | 1.136  | 1.094  |
| Cu(NO₃)₂    | 0.714  | 0.575  | 0.441  | 0.360  | 0.283  |
| CuSO₄       | 0.895  | 0.590  | 0.493  | 0.441  | 0.365  |
| Fe(NO₃)₃    | 1.057  | 1.006  | 0.833  | 0.806  | 0.562  |
| Fe₂(SO₄)₃   | 1.316  | 1.183  | 1.040  | 0.895  | 0.683  |
| Ni(NO₃)₂    | 1.474  | 1.267  | 1.104  | 0.956  | 0.784  |
| Co(NO₃)₂    | 1.528  | 1.338  | 1.198  | 1.003  | 0.853  |
| Zr(NO₃)₄    | 1.555  | 1.368  | 1.245  | 1.050  | 0.991  |
| Cr(NO₃)₃    | 1.597  | 1.388  | 1.272  | 1.094  | 1.026  |
| AgNO₃       | 1.624  | 1.444  | 1.299  | 1.163  | 1.065  |

**Table 6.** Effect of catalysts on decolorization rates of waste-water (%).

| Metal salts | 10 min | 20 min | 40 min | 60 min | 90 min |
|-------------|--------|--------|--------|--------|--------|
| blank       | 34.1   | 44.6   | 48.5   | 53.9   | 55.6   |
| Cu(NO₃)₂    | 71.0   | 76.7   | 82.1   | 85.4   | 88.5   |
| CuSO₄       | 63.7   | 76.1   | 80.0   | 82.1   | 85.2   |
| Fe(NO₃)₃    | 57.1   | 59.2   | 66.2   | 67.3   | 77.2   |
| Fe₂(SO₄)₃   | 46.6   | 52.0   | 57.8   | 63.7   | 72.3   |
| Ni(NO₃)₂    | 36.9   | 44.5   | 49.5   | 57.4   | 59.8   |
| Co(NO₃)₂    | 40.2   | 48.6   | 55.2   | 61.2   | 68.2   |
| Zr(NO₃)₄    | 34.1   | 41.4   | 47.3   | 52.8   | 56.8   |
| Cr(NO₃)₃    | 38.0   | 45.7   | 51.4   | 59.3   | 65.4   |
| AgNO₃       | 35.2   | 43.7   | 48.4   | 55.6   | 58.3   |
It can be seen from the above table and figure that the oxidation efficiency of water sample is obviously higher than that of no catalyst when using catalyst, and the decolorization rate of waste-water increases with the increase of reaction time. As a catalyst, the pH of the treated effluent was the lowest at 60 min, indicating that the organic acid produced by the waste-water degradation reached the most at this time, and then there was a rise in 90 min, indicating the organic acid decomposition. The decoloration rate of waste-water using copper nitrate is the highest, reaching 88.5%, so it can be used as the best homogeneous catalyst for the treatment of waste-water.

4. Conclusion
(1) The catalytic aids cerium nitrate and lanthanum nitrate have no catalytic activity.
(2) The catalytic activity of the homogeneous copper nitrate is the highest, and the pH of the treated waste-water is low, which indicates that the catalytic effect is good. The decolorization rate of the treated waste-water reached 88.5%, and the decolorization rate of the waste-water without adding catalyst increased by 32.9%.
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