Screening of Homogeneous CWAO Catalysts for Treatment of Ceramic Printing Waste-Water

Honghua Zhang, Qinglang Zeng, Junfei Wang, Liang Shi and Yongli Zhang*
School of Environment and Chemical Engineering, Foshan University, Foshan, Guangdong, China

*Corresponding author e-mail: 1577869592@qq.com

Abstract. The ceramic printing and dyeing waste-water was treated by catalytic wet oxidation. The catalytic oxidation reaction was carried out under the conditions of 50 mg/L metal ion concentration, 180 °C of reaction temperature, 2.5 MPa of oxygen partial pressure and 500 rpm of stirring speed, and the time of catalytic oxidation was set at 90 min. Comparing the effect of structural auxiliaries and blank group on COD removal rate of effluent, the structural auxiliaries have no effect on effluent, that is, no catalytic effect; Comparing the blank group without adding catalyst, the copper nitrate has the highest COD removal rate of 72.5% for waste-water, so it can be used as the best homogeneous catalyst to treat waste-water. The order of catalytic effect from high to low is: 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$_3$)$_4$. Among the nine types of homogeneous catalysts, the most effective Cu(NO$_3$)$_2$•3H$_2$O catalyst treated the ceramic printing and dyeing waste-water, the COD decreased from 3775 mg/L to 1038 mg/L and the COD removal rate reached 72.5%, when the catalyst was not added under the same operating conditions. The COD removal rate of water samples was increased by 32.9%.

1. Introduction

The nature of ceramic printing waste-water is similar to that of printing and dyeing waste-water, which is to print colorful flower paper in the process of producing ceramic, pasting it on ceramics, burning it into one body, and forming ceramics with various color patterns. The pigment printed on ceramic flower paper is a mixture of metal oxides and various kinds of organic matter, which belongs to the difficult biodegradable organic waste-water, so it is difficult for conventional treatment to reach the level of national sewage treatment [1].

The methods for the treatment of refractory organic waste-water including:

1) Traditional wet oxidation technology, which is the chemical process of oxidizing pollutants into inorganic or small molecular organic matter, such as CO$_2$ and water in the liquid phase using oxygen in air as oxidant (Now also using other oxidants such as ozone, hydrogen peroxide, etc.) at high temperature (125~ 320 °C ) and high pressure (0.5~ 20 MPa) [2].

(2) When the reaction temperature and pressure exceed the critical point of water, it is used to be called super-critical water oxidation method, whose typical operating conditions are temperature 400~600°C, pressure 25~40 MPa, and reaction time of several seconds to several minutes. When the catalyst is added to the reaction system, the corresponding method is called catalytic wet oxidation (CWAO) and catalytic super-critical water oxidation [3].
(3) To reduce the pressure of the reaction system, hydrogen peroxide is used instead of oxygen or air, a technique called wet peroxide oxidation (CWPO). CWAO technology is effective in treating waste-water, avoiding secondary pollution. It can recycle energy, improve the comprehensive utilization of energy, make it more widely used, and play a greater role in environmental treatment [4]. For catalytic wet oxidation oxidation (CWAO), 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 [5]. 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. 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 [6].

2. Experimental part

2.1. Experimental flow path
Select a variety of catalyst types → Wet oxidation simulation waste-water → Detection of effluent and catalyst.

2.2. Experimental Materials
(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) Experimental reagents: The concentration of metal ions in the homogeneous catalyst is 50 mg/L. Details of the calculated experimental materials are shown in Table 1. According to the action of metal salts can be divided into two categories: Catalyst and structural auxiliaries (Ce(NO₃)₃ and La(NO₃)₃).

| No. | Salts          | Molecular weight | Quality of salt (g) |
|-----|----------------|------------------|---------------------|
| 1   | blank          | -                | -                   |
| 2   | Cu(NO₃)₂       | 241.63           | 0.0475              |
| 3   | CuSO₄          | 249.72           | 0.0491              |
| 4   | Fe(NO₃)₃       | 404.02           | 0.0904              |
| 5   | Fe₂(SO₄)₃      | 278.05           | 0.0622              |
| 6   | Ni(NO₃)₂       | 290.81           | 0.0619              |
| 7   | Co(NO₃)₂       | 291.03           | 0.0617              |
| 8   | Zr(NO₃)₄       | 430.24           | 0.0590              |
| 9   | Cr(NO₃)₃       | 400.15           | 0.0962              |
| 10  | AgNO₃          | 300.28           | 0.0348              |
| 11  | Ce(NO₃)₃       | 326.13           | 0.0291              |
| 12  | La(NO₃)₃       | 433.02           | 0.0390              |

Table 1. Catalyst schedule.
2.3. Evaluation method of catalyst
By detecting the COD value of waste-water before and after treatment, the COD of waste-water under the action of different catalysts was calculated, and then the COD removal rate of waste-water was calculated. Low COD removal rate leads to low catalyst activity, while high COD removal rate leads to high catalyst activity.

2.4. Analytical Methods

2.4.1. Principle. Determination of Chemical Oxygen Demand (COD), Potassium dichromate method (GB11914-89).
Chemical oxygen demand refers to the amount of oxidant consumed by oxidizing a reducing substance in a water sample under certain conditions, expressed as mg/L of oxygen. The waste-water treated in the experiment is organic waste-water, and COD is the comprehensive index of the relative content of organic matter. It was determined by potassium dichromate method (GB11914-89). In strong acid solution, the reducing substance in the water sample was oxidized with potassium dichromate, the excess potassium dichromate was used as the indicator, and the amount of oxygen consumed in the reducing substance in the water was calculated by using the standard solution of ammonium ferrous sulfate.

2.4.2. Experimental reagents. (1) standard solution of potassium dichromate (C=0.2500 mol/L): 12.258 g of standard or high quality pure heavy potassium leadate dried at 120°C for 2 hours in advance was dissolved in water.
(2) tielin indicator: 1.485g o-phenanthrene (C_{12}H_{10}N_2.H_2O) and 0.695 g FeSO_4.7H_2O were dissolved in water, diluted to 100ml, and stored in a brown bottle.
(3) standard solution of ammonium ferrous sulfate (c≈0.1 mol/L): weigh 36.5 g ammonium ferrous sulfate to dissolve in water, slowly add 20 mL concentrated sulfuric acid while stirring, cool into 1000 mL volumetric bottle, add diluted to the line, shake well. Before use, calibrate with potassium dichromate standard solution.
(4) calibration method: accurately absorb 10.00 mL standard solution of potassium dichromate in a 500mL conical flask, dilute it to about 110 mL slowly add 30 mL concentrated sulfuric acid, and mix it. After cooling, add 3 drops of ferrous spirit finger test solution (about 0.15 mL), titrate with ammonium ferrous sulfate solution, the color of the solution from yellow through blue-green to reddish-brown is the end point.
(5) silver sulfate solution: add 5 g silver sulfate to 500 mL concentrated sulfuric acid. Place 1-2 d and shake occasionally to dissolve.
(6) mercury sulfate: crystallized or powdered.

3. Result and Discussion

3.1. Effect of Structural Aids
The COD removal rate of the water sample is shown in Table 2 and Figure 1 for the application of cerium nitrate and lanthanum nitrate in the treatment of ceramic printing waste-water.

| Category of auxiliaries | 10 min | 20 min | 40 min | 60 min | 90 min |
|------------------------|--------|--------|--------|--------|--------|
| Blank (%)              | 23.8   | 33.9   | 37.0   | 43.4   | 44.4   |
| Ce(NO_3)_3 (%)         | 28.8   | 31.5   | 38.5   | 41.9   | 43.3   |
| La(NO_3)_3 (%)         | 22.9   | 35.3   | 37.4   | 41.2   | 44.3   |
3.2. Screening of Catalysts

The COD and COD removal rates of the water samples are shown in Table 3, Table 4 and Figure 2 below when the catalyst is applied to the waste-water treatment of ceramic printing.

Table 3. Effect of catalyst category on COD of waste-water.

| Metal salts   | 10 min | 20 min | 40 min | 60 min | 90 min |
|---------------|--------|--------|--------|--------|--------|
| Blank (mg/L)  | 3775   | 3775   | 3775   | 3775   | 3775   |
| Cu(NO₃)₂ (mg/L) | 1838   | 1481   | 1242   | 1194   | 1038   |
| CuSO₄ (mg/L)  | 2230   | 1844   | 1370   | 1310   | 1142   |
| Fe(NO₃)₃ (mg/L) | 2389   | 2313   | 1688   | 1629   | 1221   |
| Fe₂(SO₄)₃ (mg/L) | 2541   | 2424   | 2006   | 1812   | 1242   |
| Ni(NO₃)₂ (mg/L) | 2622   | 2507   | 2066   | 1880   | 1621   |
| Co(NO₃)₂ (mg/L) | 2690   | 2571   | 2298   | 1940   | 1706   |
| Zr(NO₃)₄ (mg/L) | 2784   | 2639   | 2333   | 1986   | 1935   |
| Cr(NO₃)₃ (mg/L) | 2835   | 2665   | 2367   | 2035   | 1981   |
| AgNO₃ (mg/L)  | 2884   | 2703   | 2408   | 2203   | 2143   |
Table 4. Effect of catalyst category on COD removal rates of waste-water.

| Metal salts     | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----------------|--------|--------|--------|--------|--------|
| Blank (%)       | 23.8   | 33.9   | 37.0   | 43.4   | 44.4   |
| Cu(NO\textsubscript{3})\textsubscript{2} (%) | 51.3   | 60.8   | 67.1   | 68.4   | 72.5   |
| CuSO\textsubscript{4} (%)            | 40.9   | 51.2   | 63.7   | 65.3   | 69.7   |
| Fe(NO\textsubscript{3})\textsubscript{3} (%) | 36.7   | 38.7   | 55.3   | 56.9   | 67.1   |
| Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} (%) | 32.7   | 35.8   | 46.9   | 52.0   | 61.5   |
| Ni(NO\textsubscript{3})\textsubscript{2} (%) | 26.3   | 30.1   | 38.2   | 47.4   | 48.7   |
| Co(NO\textsubscript{3})\textsubscript{2} (%)            | 30.5   | 33.6   | 44.7   | 50.2   | 57.1   |
| Zr(NO\textsubscript{3})\textsubscript{4} (%) | 23.6   | 28.4   | 36.2   | 41.6   | 43.2   |
| Cr(NO\textsubscript{3})\textsubscript{3} (%)            | 28.7   | 31.9   | 39.1   | 48.6   | 54.8   |
| AgNO\textsubscript{3} (%)            | 24.9   | 29.4   | 37.3   | 46.1   | 47.5   |

Figure 2. Effect of catalyst on COD removal rates of waste-water.

Comparing the blank group without adding catalyst, it can be clearly seen from Table 3, Table 4 and Figure 2 that copper nitrate has the highest COD removal rate of 72.5% for waste-water, so it can be used as the best homogeneous catalyst to treat waste-water. The order of catalytic effect from high to low is: Cu(NO\textsubscript{3})\textsubscript{2} > CuSO\textsubscript{4} > Fe(NO\textsubscript{3})\textsubscript{3} > Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} > Co(NO\textsubscript{3})\textsubscript{2} > Cr(NO\textsubscript{3})\textsubscript{3} > Ni(NO\textsubscript{3})\textsubscript{2} > AgNO\textsubscript{3} > Zr(NO\textsubscript{3})\textsubscript{4}. 
4. Conclusion

The activity of catalyst in homogeneous wet catalytic oxidation process was studied by using CWAO in the reaction kettle. Cerium nitrate and lanthanum nitrate had no catalytic activity, copper nitrate had the highest activity, treated ceramic printing and dyeing waste-water under the condition of dosage (Concentration of metal ions: 50 mg/L), reaction temperature 180 °C, reaction time 90 min, the COD removal rate reached 72.5%, which was nearly 28.1% higher than that when the catalyst was not used.

Acknowledgments

This work was supported by Water Pollution Control Engineering Technology Research Center of Guangdong, 2017 Guangdong Science and Technology Project (2017BG601622), and Environmental Pollution Catalytic Treatment Engineering Technology Research Center of Foshan, 2017 Foshan Science and Technology Project (2017BG601416).

References

[1] Dietrich, M.J. Wet air oxidation of hazardous organics in waste-water [J]. Environ. Prog., 1985, 4(3): 171-172.
[2] Ministry of Light Industry foreign light industry pollution data compilation group. Light Industrial Pollution and its Prevention and Control [M]. Beijing: Petrochemical Press, 1975, 128-177.
[3] Zhao Binxia, Han Yuying, Zhang Xiaoli. Wet oxidation catalyst for high concentration imidacloprid pesticide wastewater[J]. Journal of Northwestern University (Natural Science), 2005, 35(5): 111-114.
[4] Dong Junming, Zeng Guangming, Yang Chaohui. Study on Catalytic Wet Oxidation of Pesticide Waste-water and Catalyst [J]. Environmental Pollution Control Technology and Equipment, 2005, 6(8): 114-118.
[5] Wang Yung-yi. Study on treatment of intermediate wastewater from naphthalene yellow acid dye by catalytic wet oxidation [D]. Ph. D. thesis, Tsinghua University, 1996, 40-41.
[6] Yu Dehui, Luo Yi, Yingmin Zhao, et al. Guide to Prevention and Control of Dyeing Waste-water Pollution [M]. Beijing: China Environmental Science Press, 2002.