Study on the Performance of Ru Catalyst Based on the Treatment of Refractory Biodegrading Organic Wastewater

Yongxun Zhang* and Yongli Zhang
Logistics Department, Guangzhou College of Technology and Business, Guangzhou, China

*Corresponding author e-mail: 2863957925@qq.com

Abstract. Supported metal catalysts are widely used in the field of refractory biodegrading wastewater treatment because of their unique catalytic performance. The non-homogeneous CWAO process is used to treat the refractory biodegrading ceramic printing wastewater. The pH, decolorization rate and COD removal rate of water sample are used as the evaluation indexes of catalyst activity, and the metal dissolution concentration is used as the evaluation indexes of catalyst stability. Then the performance of the catalyst is evaluated comprehensively. As the reaction time goes on, decolorization rates of water samples with different groups of Ru catalyst increase. The decolorization rate of CWAO method for wastewater treatment reaches 80.4%, 78.3% and 76.7% respectively, indicating that the activity and stability of this catalyst are good. The overall trend of pH value of water sample from the first time, the second time and the third time is slightly higher, because generally printing and dyeing wastewater is alkaline, the higher the pH value of water sample indicates the lower the water sample treatment efficiency, that is, the catalyst catalytic efficiency has declined. From the first, second and third use sequence, the COD of water samples are all over 74.0%, and the COD removal rate is gradually reduced. The results show that the Ru-Fe-Co-Ce/FSC (ratio 2:0.5:0.5:3) catalyst has good catalytic activity and stability.

1. Introduction
Overview of refractory biodegrading organic wastewater, taking refractory biodegrading ceramic printing wastewater as an example [1-2]. With the development of chemical fiber fabrics, the rise of silk like fabrics and the progress of finishing technology after printing and dyeing, the content of organic compounds in printing and dyeing wastewater is increasing and the color is strong and alkaline, which makes the water quality of printing and dyeing wastewater change greatly. The traditional biological treatment technology has already received the serious challenge [3-4]. The water quality of printing and dyeing wastewater varies with different fiber types and processing technologies, and the components of pollutants vary greatly [5-6].

2. Experimental part

2.1. Equipment and instruments
The main equipment of the experiment is reactor, and its technical parameters are shown in Table 1.
Table 1. Technical parameters of reactor.

| Number | Technical parameter          | Index |
|--------|-----------------------------|-------|
| 1      | Volume                      | 0.5 L |
| 2      | Design pressure             | 12.5 MPa |
| 3      | Experimental pressure       | 1-3 MPa |
| 4      | Design temperature          | 350 ℃ |
| 5      | Rated power of heating furnace | 1.5 KW |

2.2. Preparation of catalyst

In order to improve the efficiency of wastewater treatment and save the cost, the reusable of Ru catalyst, Ru-Fe-Co-Ce/FSC (ratio 2:0.5:0.5:3), was studied. Ru catalyst Ru-Fe-Co-Ce/FSC (ratio 2:0.5:0.5:3). In the experiment, the ratio of solid to liquid is 1:2. The solid is (FSC carrier 10.0 g) and the liquid is (solution 20.0 g). The total concentration of metal ions = 6wt%, the experiment shows that the amount of immersion liquid is 10.166, if the carrier is 5 g.

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\text{Ru chemical compound: } \frac{2}{100} = \frac{10}{100} \times \frac{m}{20} \Rightarrow m = 4 \text{ g}
\]

\[
\text{Fe chemical compound: } \frac{0.5}{100} = \frac{55.845}{404.00} \times \frac{m}{20} \Rightarrow m = 0.723 \text{ g}
\]

\[
\text{Co chemical compound: } \frac{0.5}{100} = \frac{58.933}{291.03} \times \frac{m}{20} \Rightarrow m = 0.493 \text{ g}
\]

\[
\text{Ce chemical compound: } \frac{3}{100} = \frac{140.116}{434.24} \times \frac{m}{20} \Rightarrow m = 1.859 \text{ g}
\]

Among them, 255.60, 404.00, 291.03 and 434.24 are formula quantities of ruthenium nitrate, iron nitrate, cobalt nitrate and cerium nitrate respectively, 101.07, 55.845, 58.933 and 140.116 are formula quantities of ruthenium, iron, cobalt and cerium respectively, and 10.166 is the mass of nitrate solution. Accurately weigh 0.511 g ruthenium nitrate, 0.368 g iron nitrate, 0.251 g cobalt nitrate and 0.941 g cerium nitrate in 20.0-4.0.724-0.494-1.859 = 12.923 g distilled water to prepare Ru²⁺-Fe³⁺-Co³⁺-Ce³⁺ impregnating solution, immerse 7.500 g FSC carrier into the impregnating solution, and then place it in an air bath shaker, and immerse it dynamically at 35 ℃ and 150 rpm for 8 hours, take it out, drain the water, 110 Dry for 100 under the ventilation condition of ℃, and put it into muffle furnace for 3 h at 450 ℃.

3. Results and discussion

3.1. Decolorization rate

Decolorization rates: the decolorization rate was determined by 722E spectrophotometer, \( \eta = 1 - \frac{\text{water absorbance}}{\text{original absorbance}} \). The maximum absorption wavelength of methyl orange is 465 nm, and the effective absorbance should be in the best range of 0.2 ≤ 0.7. Therefore, the water sample with large chroma can only be determined after a certain multiple of dilution. The absorbance of water sample = dilution multiple \( \times a \) for determination. After adding, Table 2 and Figure 1 can be obtained.

Table 2. Decolorization rates of water samples of different groups of Ru catalyst (%).

| Frequency of use | 10 min | 20 min | 40 min | 60 min | 90 min | 120min |
|-----------------|--------|--------|--------|--------|--------|--------|

According to Table 2 and Figure 1 above, at 120 min, the decolorization rate of CWAO method for wastewater treatment reaches 80.4%, 78.3% and 76.7% respectively, indicating that the activity and stability of this catalyst are good.

3.2. pH of water sample

To determine the pH of water sample, the probe of pH meter shall be dry and clean, and the data shall be read out from the electronic display screen after the value is stable. See Table 3 and Figure 2 for the pH of water samples of different groups of Ru catalyst.

Table 3. pH of water samples of different groups of Ru catalyst.

| Frequency of use | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|-----------------|--------|--------|--------|--------|--------|---------|
| Blank           | 3.74   | 3.56   | 3.46   | 3.30   | 4.13   | 4.30    |
| First           | 3.49   | 3.33   | 3.25   | 3.19   | 3.60   | 4.05    |
| Second          | 3.53   | 3.37   | 3.30   | 3.27   | 3.66   | 4.07    |
| Third           | 3.64   | 3.48   | 3.40   | 3.29   | 3.70   | 4.14    |
Figure 2. pH of water sample at different reaction time of Ru catalyst.

It can be seen from Table 3 and Figure 2 above that the overall trend of pH value of water sample from the first time, the second time and the third time is slightly higher, because generally printing and dyeing wastewater is alkaline, the higher the pH value of water sample indicates the lower the water sample treatment efficiency, that is, the catalyst catalytic efficiency has declined. However, the overall change is very small, indicating that the catalyst stability is good.

3.3. COD and COD removal rate of water sample

Table 4, Table 5, Figure 3 and Figure 4 for COD and COD removal rates of different batches of water samples.

Table 4. COD (mg / L) of water samples with different groups of Ru-catalysts.

| Frequency of use | 10 min | 20 min | 40 min | 60 min | 90 min | 120min |
|------------------|--------|--------|--------|--------|--------|--------|
| Original         | 6800   |        |        |        |        |        |
| First            | 4454   | 3835   | 2727   | 2285   | 1707   | 1448   |
| Second           | 4808   | 4264   | 3169   | 2604   | 1938   | 1646   |
| Third            | 5066   | 4338   | 3393   | 2747   | 2142   | 1754   |
| Blank            | 5678   | 5154   | 4733   | 3924   | 3393   | 3182   |

Figure 3. COD of different groups of water samples under the action of catalysts.
Table 5. COD removal rates of water samples with different groups of Ru catalyst (%).

| Experimental group | COD (mg/L)       | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|--------------------|------------------|--------|--------|--------|--------|--------|---------|
| Blank              | 16.5             | 24.2   | 30.4   | 42.3   | 50.1   | 53.2   |
| First              | 34.5             | 43.6   | 59.9   | 66.4   | 74.9   | 78.7   |
| Second             | 29.3             | 37.3   | 53.4   | 61.7   | 71.5   | 75.8   |
| Third              | 25.5             | 36.2   | 50.1   | 59.6   | 68.5   | 74.2   |

Figure 4. COD removal rates of different water samples under the action of Ru catalyst.

From Table 4 and Table 5, Figure 3 and Figure 4, it can be seen that from the first, second and third use sequence, the COD of water samples are all over 74.0%, and the COD removal rate is gradually reduced. At the same time, the first time, the second time and the third time, the treatment effect of the latter catalyst on water samples is slightly reduced, and the COD removal rate does not change much, which shows that the catalyst has good activity and stability.

4. Conclusions
Ru-Fe-Co-Ce/FSC catalyst is used to treat organic waste-water, which is difficult to degrade. The decolorization rate and COD removal rate of water sample are very high. According to the COD removal rate, the removal rate of the first use is about 3% higher than that of the second use, and the second use is about 1% higher than that of the third use. The catalyst has good activity and stability in the CWAO treatment of refractory biodegrading organic wastewater.

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