Research on the Stability of Pd-Catalysts Based on the Treatment of Refractory Biodegrading Organic Wastewater

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Abstract. The non-homogeneous CWAO method was used to treat refractory biodegrading organic wastewater. The re-usability of Pd-catalyst was investigated. The pH and decolorization rate of waste-waters were used as evaluation indexes. The results showed that the pH of waste-water did not change obviously in the first, second and third use of catalyst. The absorbance difference between the second and third use of catalyst waste-waters is approximately equal, but they are both larger than that of the first use and smaller than that of blank waste-waters. The decolorization rate of the first use is obviously higher than that of the second and third use, and the second use is higher than that of the third use, but the difference is not great, which shows that the catalyst has good re-usability. Compared with the last application of catalyst, the decolorization rate of waste-water decreased 3.8% and 1.6% respectively in the second and third application. Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) catalyst has good catalytic stability.

1. Introduction
Refractory biodegrading wastewater, taking printing and dyeing wastewater as an example, it has the characteristics of a amount of waste-water, high concentration of organic pollutants, deep chroma, great alkalinity, and large change of waste-water quality [1-2]. It is difficult to treat industrial wastewater. Printing and dyeing wastewater is a complex organic wastewater with organic pollution as the main component. The main objects of treatment are COD, BOD, organics which are not easy to be biodegraded or whose bio-degradation speed is slow, dye pigment and a small quantity of toxic content [3-4]. Despite the biodegradable property of printing and dyeing waste-water is greatly weak, it is a kind of biodegradable organic waste-water. Biological treatment is the main treatment method, and the necessary physical and chemical advanced treatment is also needed. In order to improve the treatment efficiency of printing and dyeing waste-water, there have been many in-depth studies on wastewater treatment at home and abroad, and some results have been achieved [5].

2. Experimental part

2.1. Experimental equipment
In order to further improve the efficiency of wastewater treatment and save the cost of treatment, the re-usability of Ru catalyst Pd-Fe-Co-Ce/FSC (ratio 1:1:1:3) was tested. The purpose was to study the re-usability stability of the catalyst under certain experimental conditions.
Main experimental instruments: 250 mL autoclave, electronic precision balance, 752
spectrophotometer, electric blast drying oven, electric heating furnace.

FSC: it is a catalyst carrier from a chemical plant in Liaoning province, China. It is made of SB powder imported from the United States, added with sesbania powder made in China and some additives. Through a series of technological processes, it is pressed into shamrock shaped particles with a length of 0.5-1 cm and a particle size of 0.3 cm.

2.2. Preparation of catalysts

Pd-catalyst Pd-Fe-Co-Ce/FSC (ratio:1:1:1:3). The solid-liquid ratio was 1:2 by impregnation. Solid is (FSC carrier 10.0 g). Liquid (solution 20.0g). Total metal ion concentration = 6wt%.

Ru compound quality: \[ \frac{1}{100} = \frac{15}{20} \Rightarrow m = 1.333 \text{ g} \] (1)

Fe compound quality: \[ \frac{1}{100} = \frac{55.845}{20} \Rightarrow m = 1.447 \text{ g} \] (2)

Co compound quality: \[ \frac{1}{100} = \frac{58.933}{20} \Rightarrow m = 0.988 \text{ g} \] (3)

Ce compound quality: \[ \frac{3}{100} = \frac{140.116}{20} \Rightarrow m = 1.859 \text{ g} \] (4)

Among them, 404.00, 291.03, 434.24 is the formula quantity of iron nitrate, cobalt nitrate and cerium nitrate respectively, 55.845, 58.933 and 140.116 are the formula quantity of iron, cobalt and cerium respectively. 4.0 g is the mass of nitrate solution. Accurately weigh 0.221 g of palladium nitrate, 0.289 of iron nitrate, 0.197 g of cobalt nitrate and 0.372 g of cerium nitrate in 20.0 g of distilled water to prepare Pd$^{2+}$-Fe$^{3+}$-Co$^{3+}$-Ce$^{3+}$ impregnating solution, immerse 2.0 g of FSC carrier in the impregnating solution, 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, and 110 ℃ Dry for 10 hours under ventilation condition, and put into muffle furnace for 3 hours at 450 ℃.

2.3 Absorbance determination method

2.3.1. Spectrophotometry. Detection principle: when a bunch of monochromatic light intensity for $I_0$ vertical irradiation after solution of A substance, as a part of light is absorbed, so the strength of the transmitted light down to I, the solution of the transmittance T as follows Formula 5:

\[ T = \frac{I_0 - I}{I_0} \times 100\% \] (5)

Detection spectrophotometry is a method for qualitative and quantitative analysis of a substance by measuring its absorbance or luminescence intensity at a specific wavelength or within a certain wavelength. In a spectrophotometer, the absorption intensity corresponding to different wavelengths can be obtained when different wavelengths of light are continuously irradiated to a certain concentration of the sample solution. If the wavelength $\lambda$ is the abscissa and the absorption intensity, A is the ordinate, and the absorption spectrum curve of the substance can be plotted. This curve is used for qualitative and quantitative analysis of substances, called spectrophotometry, also known as absorption spectroscopy. A is the absorption coefficient. The absorption coefficient is related to the solution nature. The absorbance A of A series of solutions with known concentrations c can be measured as the light source, and the a-c working curve can be made. When analyzing the unknown solution, the corresponding concentration can be determined according to the measured absorbance A and the working curve. This is the basic principle for measuring concentration by spectrophotometry.
2.3.2. Calculation of decolorization rates. Spectrophotometer determination of wastewater absorbance \( A \), in different variables using the following Formula 6 to calculate the decolorization rate.

\[
Y = \frac{A_0 - A_t}{A_0} \times 100\% 
\]  

Where \( Y \) represents the decolorization rate of the wastewater, \( A_0 \) represents the original absorbance of the wastewater, and \( A_t \) represents the absorbance of the treated wastewater.

3. Results and discussion

3.1. pH of waste-water

Table 1 and Figure 1 for the effluent pH of waste-water under the action of catalysts.

| Experimental group | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|--------------------|--------|--------|--------|--------|--------|---------|
| First              | 3.66   | 3.44   | 3.18   | 3.13   | 3.93   | 4.08    |
| Second             | 3.70   | 3.45   | 3.27   | 3.14   | 3.98   | 4.18    |
| Third              | 3.73   | 3.48   | 3.31   | 3.18   | 4.02   | 4.19    |

Figure 1. pH of waste-water under the action of catalysts.

It can be seen from Table 1 and Figure 1 that the overall trend of pH value of waste-water after treatment is increased from the first use, the second use and the third use. The results show that the first treatment is better than the second and the third, because the printing and dyeing wastewater is usually alkaline, the higher the pH of the waste-water, the lower the efficiency of the waste-water treatment, that is, the catalyst efficiency has decreased.

3.2. Absorbance and decolorization rate

The absorbance of waste-waters of different groups of Pd catalyst is shown in Table 2, Table 3 and Figure 2, Figure 3.

| Experimental group | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|--------------------|--------|--------|--------|--------|--------|---------|
| First              | 2.379  | 1.909  | 1.310  | 1.073  | 0.767  | 0.422   |
| Second             | 2.487  | 2.017  | 1.444  | 1.164  | 0.858  | 0.586   |
Table 3. Decolorization rates of waste-water under the action of catalysts.

| Experimental group | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|--------------------|--------|--------|--------|--------|--------|---------|
| First              | 44.8   | 55.7   | 69.6   | 75.1   | 82.2   | 90.2    |
| Second             | 42.3   | 53.2   | 66.5   | 73.0   | 80.1   | 86.4    |
| Third              | 41.5   | 50.9   | 65.1   | 71.7   | 79.3   | 84.8    |
| Blank              | 18.8   | 28.0   | 32.8   | 45.6   | 53.4   | 56.1    |
| Original           | 6.72   |        |        |        |        |         |

Figure 2. Absorbance of different groups of waste-water.

Figure 3. Decolorization rates of waste-water under the action of catalysts.
It can be seen from Table 2 and Table 3, Figure 2 and Figure 3 that the absorbance difference between the second and third use of catalyst waste-waters is not very big, but they are both larger than that of the first use and smaller than that of blank waste-waters. The decolorization rate of the first use is obviously higher than that of the second and third use, and the second use is higher than that of the third use, but the difference is not great, which shows that the catalyst has good re-usability.

4. Conclusions
When Pd-Fe-Co-Ce/FSC catalyst was used to treat waste-waters, the pH of waste-waters did not change significantly, and the removal effect of waste-waters was significant. In the first, second and third use of the catalyst, 90.2%, 86.4% and 84.8% of the waste-waters showed a downward trend, but the difference was very small. The experimental results show that the Pd-catalyst has good catalytic stability.

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