Research on the Performance of Pd-Catalyst Based on Chroma and COD

Liang Shi, Yukai Shen, Junfei Wang and Yongli Zhang*

School of Environment and Chemical Engineering, Foshan University, Foshan, Guangdong, China

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

Abstract. Heterogeneous CWAO process was used to treat refractory organic waste-water. The performance of Pd-catalyst (Pd-Fe-Co-Ce/FSC) was investigated. The chroma and COD removal rate of waste-water were taken as evaluation indexes. The chroma of the blank water sample is about 300 times higher than that of the first, second and third waste-water. The first use is obviously much smaller than the second and third use, while the second and third use are not very different in chroma. With the decomposement of the organic matter, COD of waste-water decreased. Therefore, under the effect of Pd-catalysts, by the method of CWAO, waste-water can be processed effectively. From the first, second and third use sequence, COD value is from low to high, COD removal rate is gradually reduced slightly, so it can be seen that the treatment effect of catalyst on water sample is increased in 120 min. The experimental results show that the chroma of the treated water sample is about 300 times lower than that without catalyst, and the COD removal rates of the water sample are 85.7%, 83.8% and 82.1% respectively in the first, second and third time of catalyst. These show that the Pd-Fe-Co-Ce/FSC catalyst has good activity and stability.

1. Introduction

Advanced oxidation technology was first proposed by glaze et al. It is a kind of treatment technology that can produce strong oxidation free radicals by transferring external energy or introducing catalyst, which can oxidize or mineralize refractory organic matters into small molecular substances. Since its development in 1980s, advanced oxidation technology has gradually shown its advantages of wide application range, fast reaction rate, strong oxidation ability and so on [1-2]. Compared with traditional biochemical and physical water treatment processes, advanced oxidation technology has a strong degradation ability for organic waste-water with high toxicity and poor biodegradability, and has obvious advantages [3-4]. Catalytic wet air oxidation technology [5] has a good prospect for the treatment of refractory organic waste-water.

2. Experimental part

2.1 Experimental scheme

Pd is the repeated utilization experiment of catalyst. For the time (take 1, 2 and 3) use of catalyst: take 1.5 g catalyst from electronic precision balance, put it into high-pressure reactor, take 250 mL experimental water sample from volumetric flask, slowly pour it into reactor, install the reactor in accordance with the operation process step by step, connect the power supply, and the reactor starts to...
run. See Table 1 for relevant technical parameters.

**Table 1.** Operation parameters of heterogeneous catalytic wet air oxidation experiment.

| Reaction temperature (℃) | reaction pressure (MPa) | Mixing speed (r/min) | COD (mg/L) |
|---------------------------|-------------------------|----------------------|------------|
| 180                       | 3                       | 500                  | 6800       |

The sampling time was 10, 20, 40, 60, 90 and 120 min respectively. After the water sample is cooled to room temperature, the water sample is put into a centrifuge tube and centrifuged,

2.2 Experimental equipment

The main equipment needed for the experiment is the pressure reaction kettle. The catalytic wet oxidation experiments were conducted in the 0.5 L-GS-type high-pressure reaction kettle, and the control instrument and reaction kettle were shown in Figure 1 and Figure 2. The main equipment of the system adopts magnetic rotary stirring autoclave (produced by Weihai chemical equipment co., LTD.), and the material of the autoclave is acid and alkali corrosion resistant 316L (Cr18Ni12Mo2-3). The reaction autoclave is composed of container, stirring device, heating furnace, control system, autoclave, motor and cooling system.

![Figure 1. Aptitude controlling apparatus.](image1)

![Figure 2. Reaction kettle.](image2)

2.3 Testing equipment

Seen in Table 2 for the operation parameters of the centrifuge required for the experiment.

**Table 2.** Operation parameters of centrifuge.

| Operation parameters | Water sampling time of reactor |
|----------------------|-------------------------------|
| Centrifugal speed (r/min) | 10 min 20 min 40 min 60 min 90 min 120 min |
| Centrifugal time (min)   | 3000                          |

Do the same experiment 3 times according to the above steps. After the experiment, put the catalyst into the oven to dry and load the catalyst for the next experiment and detection.

2.4 COD detection method

Potassium dichromate method, that's the standard method.
Chemical oxygen demand reflects the degree of pollution by reducing substances in water. In order to obtain the measured value quickly and accurately, focus on the comparison and discussion of the two analytical methods used in the determination of chemical oxygen demand.

1. Principle of method chemistry. In strongly acidic solution, a certain amount of potassium dichromate oxidized water samples with reductive substances, excessive potassium dichromate to test ferrous spirit as an indicator, with ammonium ferrous sulfate solution back drop. The oxygen consumption of reducing substances in water samples was calculated based on the amount of ammonium ferrous sulfate.

2. Interference and elimination. Chloride ions can be oxidized by dichromate and can precipitate by interaction with silver sulfate to affect the determination results. Therefore, mercury sulfate is added to the water sample before reflux to make it a complex to eliminate interference. The content of chlorine ion was higher than 1000mg/l and then determined.

3. Scope of use of the method. COD values greater than 50 mg/L can be determined by potassium dichromate solution with a concentration of 0.25mol/L. The upper limit for undiluted water samples is 700 mg/L. COD values of 5 ~ 50 mg/L can be determined by potassium dichromate solution with a concentration of 0.025 mol/L, but the accuracy is poor when less than 10 mg/L.

3. Results and discussions

3.1 Chroma
The chroma of different batches of waste-water under the action of catalyst is shown in Figure 3.

![Graph showing chroma of different batches of waste-water](image)

**Figure 3.** Chroma of different batches of waste-water under the action of catalysts.

It can be seen from Figure 3 that the chroma of the blank water sample is about 300 times higher than that of the first, second and third waste-water. The first use is obviously much smaller than the second and third use, while the second and third use are not very different in chroma. It shows that Pd catalyst has high activity and good stability.

3.2 COD and COD removal rates of different waste-water of Pd catalysts
Seen in Table 3~4 and Figure 4~5 for COD and COD removal rates of waste-water of different groups of Pd catalyst.
Table 3. COD of waste-water with different groups of catalysts.

| Frequency of use | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|------------------|--------|--------|--------|--------|--------|---------|
| First (mg/L)     | 3917   | 3196   | 2210   | 1870   | 1408   | 972     |
| Second (mg/L)    | 4094   | 3339   | 2428   | 1999   | 1516   | 1102    |
| Third (mg/L)     | 4175   | 3488   | 2523   | 2128   | 1591   | 1217    |
| Blank (mg/L)     | 5678   | 5154   | 4733   | 3924   | 3393   | 3182    |
| Original (mg/L)  | 6800   |        |        |        |        |         |

Figure 4. COD of different batches of waste-water under the action of catalysts.

Table 4. COD removal rates of waste-water of different groups of catalysts.

| Frequency of use | 10 min | 20 min | 40 min | 60 min | 90 min | 120 min |
|------------------|--------|--------|--------|--------|--------|---------|
| First (%)        | 42.4   | 53.0   | 67.5   | 72.5   | 79.3   | 85.7    |
| Second (%)       | 39.8   | 50.9   | 64.3   | 70.6   | 77.7   | 83.8    |
| Third (%)        | 38.6   | 48.7   | 62.9   | 68.7   | 76.6   | 82.1    |

Figure 5. COD removal rates of different batches of waste-water under the action of catalysts.
It can be seen from Table 3-4, Figure 4-5, COD of waste-water were presented the trend of rising, show the organic matter in waste water in the reaction are constantly decomposed, so the wastewater COD is reduced. Therefore, under the effect of Pd - catalysts, by the method of CWAO, waste-water can be processed effectively. From the first, second and third use sequence, COD value is from low to high, COD removal rate is gradually reduced slightly, so it can be seen that the treatment effect of catalyst on water sample is increased in 120min. At the same time, from the first use, the second use, the third use of the sequence, the treatment effect of the latter catalyst on the water sample is decreased, but the proportion of decline is not very large. During the first, second, and third use of the catalyst, the COD of the waste-water was 972, 1102, 1217 mg/L, respectively. Compared with the COD value of 3182 mg/L without the catalyst, the COD reduction value of the waste-water was 2210, 2080 and 1965 mg/L, respectively. The COD removal rate of waste-water was 85.7%, 83.8% and 82.1%, respectively. During the third use of the catalyst, the removal rate of COD decreased by only 3.6% compared with the first use. Based on these experiments, indicating that the Pd-catalyst has good catalytic performance.

4. Conclusions
The results show that Pd-Fe-Co-Ce/FSC catalyst can effectively remove the color and COD of simulated organic waste-water. The chroma of the treated water sample is about 300 times lower than that without catalyst. The COD removal rate of the water sample is 85.7%, 83.8% and 82.1% respectively in the first, second and third time of catalysts. These show that Pd-Fe-Co-Ce/FSC catalyst has good catalytic performance in CWAO treatment of waste-water.

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] Yang x y, jiang z p. Study on residual sludge treated by wet oxidation[J]. China water & waste-water, 2003, 19(7): 50-54. (in Chinese with English abstract)
[2] Yue Li, Qi Fu, Maria Flytzani-Stephanopoulos. Low-temperature water-gas shift reaction over Cu- and Ni-loaded cerium oxide catalysts[J]. Applied Catalysis B: Environmental, 2000, 27: 179-191.
[3] Attia A.J. Photocatalytic Degradation of Textile Dyeing waste-water Using Titanium Dioxide and Zinc Oxide[J].Journal of Chemistry, 2012, 5(2): 219-223.
[4] Soares P.A., Silva T.F., Manenti D.R., et al. Insights into real cotton-textile dyeing waste-water treatment using solar advanced oxidation processes[J]. Environmental Science & Pollution Research International, 2014, 21(2): 932.
[5] X.-h. Xia, J.-p. Tu, Y.-q. Zhang, Y.-j. Mai, X.-l. Wang, C.-d. Gu, X.-b. Zhao. Freestanding,Co3O4 nanowire array for high performance supercapacitors, Rsc Advances, 2 (2012) 1835-1841.