Effect of calcination time on degradation of landfill leachate by Fe-Co-Ru-Ce/γ-Al₂O₃ catalytic wet oxidation system

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Abstract. The landfill leachate was used as the target pollutant, and the degradation was carried out by catalytic wet oxidation. The heterogeneous catalyst Fe-Co-Ru-Ce/γ-Al₂O₃ was prepared by impregnation method. The calcination time was set to 1.5, 3, 4.5, 6, 7.5 h respectively, the catalyst was calcined at a constant temperature for a set time to prepare five catalysts, and the influence of the calcination time on the activity of the catalyst was investigated. The results showed that when the calcination time was 3 h, the activity of the catalyst reached the maximum. At this time, the COD removal rate and decolorization rate of the treated water were 78.1% and 60.4%, respectively.

1. Introduction

Landfill leachate is produced by the water contained in the garbage itself and the rainwater entering the landfill. It has complex water quality, many types of pollutants, high COD concentration, and contains toxic and harmful substances such as heavy metals and pathogenic bacteria, and it is also a very hot research topic [1]. The characteristics of landfill leachate are related to various factors, such as the age of landfill and the characteristics of solid waste. The COD of landfill leachate is in the range of 2000-62000 mg/L, and a biodegradability index too low to implement a biological treatment. Therefore, finding a high performance price ratio technology is demanded.

Catalytic wet oxidation technology (CWAO) refers to the oxidation of organic pollutants into inorganic substances or small substances in the liquid phase at high temperature (125~320 °C) and high pressure (0.5~10 MPa) with air or oxygen as oxidant. By adding a catalyst to shorten the reaction time and reduce the energy consumption of the reaction, it is applied to sewage with high chemical oxygen demand such as printing and dyeing, pesticide, petrochemical, leather, etc. Catalytic wet oxidation technology is widely used in the treatment of high concentration wastewater [2].

Research status of heterogeneous phase catalysts: Heterogeneous phase catalysts mainly exist in solid waste water, which has the advantages of easy separation, high catalytic activity and good stability. At present, the research hotspot of wet oxidation catalysts is a composite catalyst, which is a catalyst for supporting a combination of two or three types of metals in a noble metal, a transition metal and a rare earth metal on an active carrier. Sushma et al. [3] used a ruthenium oxide-promoted Pt/Al₂O₃ catalyst to degrade toxic pyridines in catalytic wet oxidation. The sewage was obtained at 70 °C was studied and its BOD/COD ratio was 0. The COD removal rate of catalytic wet oxidation treatment wastewater was 98.67%. Compared with a single type of catalyst, the composite catalyst combines the advantages of several other heterogeneous catalysts, and has higher catalytic efficiency, and becomes a important direction for catalytic wet oxidation.
The research contents of the project: (1) The catalyst was prepared by impregnation method, and the landfill leachate was used as the target pollutant. The effect of calcination time on the degradation of target pollutants by Fe-Co-Ru-Ce/\gamma-Al_2O_3 was studied. (2) Study on the degradation of landfill leachate by Fe, Co, Ru and rare earth metal composite catalysts.

2. Reaction mechanism of catalytic wet oxidation

Scholars at home and abroad generally believe that the reaction of wet oxidation can be divided into four stages. The mechanism formula for each reaction stage is as follows:

The first stage:

\[ RH + O_2 \rightarrow R^\cdot + HOO^\cdot \]  (RH is organic compound)

\[ 2RH + O_2 \rightarrow 2R^\cdot + H_2O_2 \]  (2)

The second stage:

\[ R^\cdot + O_2 \rightarrow ROO^\cdot \]  (3)

\[ ROO^\cdot + RH \rightarrow ROOH + R^\cdot \]  (4)

The third stage:

\[ ROOH \rightarrow RO^\cdot + HO^\cdot \]  (5)

\[ ROOH \rightarrow R^\cdot + RO^\cdot + H_2O \]  (6)

The fourth stage:

\[ R^\cdot + R^\cdot \rightarrow R - R \]  (7)

\[ ROO^\cdot + R^\cdot \rightarrow ROOR \]  (8)

\[ ROO^\cdot + ROO^\cdot \rightarrow ROH + RCOR + O_2 \]  (9)

3. Effect of Calcination Time on Activity of Fe-Co-Ru-Ce/\gamma-Al_2O_3 Catalysts

The calcination time of the catalyst at the time of preparation also has a certain influence on its activity. If the calcination time is too short, the pyrolysis of the compound is incomplete, and the crystal of the catalyst is not mature; while the calcination time is too long, the surface sintering phenomenon is easily sintered, and the activity of the catalyst is affected. Explore the appropriate calcination time by the following experiment.

Experimental scheme: Five kinds of calcination time were set to 1.5, 3, 4.5, 6, 7.5 h respectively. The Fe-Co-Ru-Ce/\gamma-Al_2O_3 impregnated with four metal salt solutions was calcinated at 450 °C. Under the calcination to the set time, five catalysts were prepared, and the adopted landfill leachate was used as the degradation target, and the pH, decolorization rate, COD removal rate and turbidity removal rate of the degraded water sample were detected. Their results were used to evaluate the activity and stability of the catalyst. Furthermore, degraded water samples were analyzed by FT-IR and UV-Vis. The experimental results are as follows:

3.1. pH of water sample after degradation

Raw water pH: 9.8, the experimental results are shown in Table 1.

| Calcination time | 10 min | 20 min | 40 min | 60 min | 90 min |
|------------------|--------|--------|--------|--------|--------|
| 1.5 h            | 9.43   | 9.69   | 9.72   | 9.56   | 9.76   |
| 3 h              | 9.41   | 9.63   | 9.53   | 9.71   | 9.86   |
| 4.5 h            | 9.47   | 9.75   | 9.74   | 9.81   | 9.92   |
| 6 h              | 9.48   | 9.66   | 9.67   | 9.62   | 9.80   |
| 7.5 h            | 9.51   | 9.72   | 9.69   | 9.82   | 9.98   |
3.2 COD and its removal rate of water sample after degradation

Raw water COD: 5983.8 mg / L, the experimental results are shown in Table 2 and Figure 1.

| Calcination time | 10 min | 20 min | 40 min | 60 min | 90 min |
|------------------|--------|--------|--------|--------|--------|
|                  | COD (mg/L) | Removal rate (%) | COD (mg/L) | Removal rate (%) | COD (mg/L) | Removal rate (%) | COD (mg/L) | Removal rate (%) | COD (mg/L) | Removal rate (%) |
| 1.5 h            | 2112.5 | 64.7   | 1736.9 | 71.0   | 1682.2 | 71.9   | 1572.6 | 73.7   | 1603.9 | 73.2 |
| 3 h              | 1655.9 | 72.3   | 1617.3 | 73.0   | 1347.1 | 77.5   | 1308.5 | 78.1   | 1308.5 | 78.1 |
| 4.5 h            | 1838.6 | 69.3   | 1916.9 | 68.0   | 1768.2 | 70.5   | 1650.9 | 72.4   | 1729.1 | 71.1 |
| 6 h              | 1885.6 | 68.5   | 1995.1 | 66.7   | 1690.0 | 71.7   | 1807.3 | 69.8   | 1807.3 | 69.8 |
| 7.5 h            | 1830.8 | 69.4   | 1807.3 | 69.8   | 1729.1 | 71.1   | 1736.9 | 71.0   | 1721.3 | 71.2 |

Figure 1. Curve of COD treatment effect of water samples under different calcination time.

3.3 Decolorization rate of water sample after degradation

Raw water absorbance: 5.67, the experimental results are shown in Table 3 and Figure 2.

Table 3. Chroma processing table for water samples at different calcination time.

| Calcination time | 10 min | 20 min | 40 min | 60 min | 90 min |
|------------------|--------|--------|--------|--------|--------|
|                  | Absorbance | Removal rate (%) | Absorbance | Removal rate (%) | Absorbance | Removal rate (%) | Absorbance | Removal rate (%) | Absorbance | Removal rate (%) |
| 1.5 h            | 4.26   | 24.9   | 3.93   | 30.7   | 3.28   | 42.2   | 2.82   | 50.3   | 2.73   | 51.9 |
| 3 h              | 4.28   | 24.5   | 3.72   | 34.4   | 3.09   | 45.5   | 2.34   | 58.8   | 2.25   | 60.4 |
| 4.5 h            | 4.31   | 24.0   | 3.86   | 31.9   | 3.29   | 42.0   | 2.94   | 48.2   | 2.83   | 50.1 |
| 6 h              | 4.76   | 16.1   | 4.15   | 26.2   | 3.44   | 39.3   | 3.15   | 44.4   | 2.95   | 48.0 |
| 7.5 h            | 4.32   | 23.8   | 3.75   | 33.9   | 2.99   | 47.3   | 2.47   | 56.4   | 2.31   | 59.3 |
Figure 2. Chroma processing effect of water samples under different calcination time.

3.4. Turbidity removal rate of water sample after degradation

Raw water turbidity: 157.36 NTU, the experimental results are shown in Table 4 and Figure 3.

Table 4. Turbidity treatment table for water samples under different calcination time.

| Calcination time | 10 min | 20 min | 40 min | 60 min | 90 min |
|------------------|--------|--------|--------|--------|--------|
|                  | turbidity (NTU) | Removal rate (%) | turbidity (NTU) | Removal rate (%) | turbidity (NTU) | Removal rate (%) | turbidity (NTU) | Removal rate (%) |
| 1.5 h            | 47.17  | 70.0   | 27.54  | 82.5   | 26.63  | 83.8   | 25.26  | 83.9   | 20.23  | 87.1   |
| 3 h              | 49.91  | 68.3   | 20.69  | 86.9   | 19.78  | 87.4   | 16.58  | 89.5   | 11.56  | 92.7   |
| 4.5 h            | 33.02  | 79.0   | 21.15  | 86.5   | 17.95  | 88.6   | 17.04  | 89.1   | 9.27   | 94.1   |
| 6 h              | 29.37  | 81.3   | 21.15  | 86.5   | 16.58  | 89.5   | 15.67  | 90.0   | 9.27   | 94.1   |
| 7.5 h            | 30.74  | 80.4   | 29.82  | 81.1   | 21.60  | 86.3   | 19.32  | 87.7   | 11.56  | 92.7   |

Figure 3. Turbidity treatment effect curve of water sample under different calcination time.
3.5. Water sample treatment results with different calcination time at 90 min reaction

The experimental results are shown in Table 5 and Figure 4.

Table 5. Water sample treatment effect table with different calcination time at 90 min reaction.

| Calcination time | COD removal rate | Decolorization rate | Turbidity removal rate |
|------------------|------------------|---------------------|------------------------|
| 1.5 h            | 73.2 %           | 51.9 %              | 87.1 %                 |
| 3 h              | 78.1 %           | 60.4 %              | 92.7 %                 |
| 4.5 h            | 71.1 %           | 50.1 %              | 94.1 %                 |
| 6 h              | 69.8 %           | 48.0 %              | 94.1 %                 |
| 7.5 h            | 71.2 %           | 59.3 %              | 92.7 %                 |

As can be seen from the above graphs, the calcination time has a certain influence on the activity of the catalyst. As the calcination time is extended, the activity of the catalyst first increases and then decreases. When the calcination time reached 3 h, the activity of the catalyst was the highest, and the COD removal rate and decolorization rate were also significantly higher than the other three times. Although the turbidity removal rate was slightly lower than 4.5 h and 6 h at 3 h, it was not obvious, since COD is the primary indicator for judging the treatment effect, the results of the three detection indexes are compared, and the calcination time of Fe-Co-Ru-Ce/γ-Al2O3 catalyst is 3 h. The reason why the calcination time affects the activity of the catalyst is mainly: when the calcination time is short (less than 3 h), the adhesion of the active component to the carrier is not enough; but when the calcination time is too long (more than 3 h), Sintering occurs and the catalyst activity is lowered.

Based on the above experiments, it can be concluded that the optimized preparation conditions of Fe-Co-Ru-Ce/γ-Al2O3 catalyst are: 00-Al2O3 carrier 5.000 g, total metal ion concentration is 6wt%, Fe:Co:Ru:Ce = 0.75: 0.75: 1.5:3 (molar ratio), the total mass of the solution was 10.166 g, dynamically impregnated at 35 °C for 8 h, ventilated at 105 °C for 8 h, and calcined at 450 °C for 3 h.

4. UV-Vis Characterization of Fe-Co-Ru-Ce/γ-Al2O3 Catalysts

The Fe-Co-Ru-Ce/γ-Al2O3 catalyst was prepared under optimized conditions and used to carry out catalytic wet oxidation reaction to treat landfill leachate. UV-Vis spectral scanning was performed on the effluent water samples with different reaction time. The results are shown in Figure 5. Shown as follows:
Figure 5. UV spectrum of different periods effluent by optimum conditions.

As shown in Fig. 5, after 90 min reaction, the maximum absorption peak at 198 nm and 301 nm in the visible region still exists, indicating that the colored dye in the landfill leachate has not been destroyed in the reaction.

5. Conclusions
(1) It has been determined that the active component and the ratio of the multicomponent impregnated Fe-Co-Ru-Ce/γ-Al₂O₃ catalyst are Fe:Co:Ru:Ce = 0.75:0.75:1.5:3 (molar ratio). The calcination temperature was 450 °C, and the optimum calcination time was determined to be: 3 h.
(2) The catalyst was treated with 250 g of landfill leachate at a dosage of 1 g, a reaction temperature of 180 °C and a reaction time of 90 min. The COD removal rate, decolorization rate and turbidity removal rate reached 78.1% and 60.4%, respectively. 92.7%.

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