Effect of calcination temperature on catalyst performance in landfill leachate treatment

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Abstract. In this study, the landfill leachate was treated by Catalytic wet air oxidation, and the heterogeneous catalyst Fe-Co-Ru-Ce/γ-Al₂O₃ was prepared. The calcination temperatures were respectively set at 300, 450, 600, 750 and 900 °C, and the Fe-Co-Ru-Ce/γ-Al₂O₃ impregnated with the four metal salt solutions was calcined at the set temperature for 3 h to study the effect of calcination temperature on the activity of the catalyst. The results showed that when the calcination temperature was 450 °C, the activity of the catalyst reached the maximum. At this time, the COD removal rate, decolorization rate and turbidity removal rate of the treated water samples were the highest, which were 78.1%, 60.4% and 92.7%, respectively.

1. Introduction

Catalytic wet air oxidation (CWAO) is the oxidative decomposition of target pollutants in water into CO₂, N₂ and H₂O at high temperature (125-320 °C), high pressure (0.5-2.0 MPa) and catalysts [1], and it is an environmentally friendly sewage treatment technology that achieves purification purposes. It is designed to overcome the shortcomings of wet air oxidation and has been developed on the basis of traditional WAO technology since the 1970s. CWAO completely converts toxic and harmful refractory organics into H₂O, CO₂, N₂ and other inorganic substances or partially oxidizes into biodegradable substances at a lower temperature than WAO and in a shorter period of time. CWAO greatly improve the efficiency of high-concentration toxic sewage treatment, reduce corrosion of equipment, expand the scope of application, and reduce the wastewater treatment process [2].

Research Status of Catalytic wet air oxidation Technology [3]: Since the development of catalytic wet oxidation technology in the 1970s, it has become one of the main development directions of hydrothermal oxidation technology. It is a suitable catalyst in the traditional wet oxidation process, by changing the reaction mileage to improve the process capacity and capacity, to reduce the reaction temperature and pressure, improve the oxidative decomposition capacity, shorten the reaction time, reduce equipment corrosion and reduce costs. The WAO method has been industrialized and achieved remarkable achievements abroad. In particular, Japan is in a leading position in this respect. Its wet
The oxidation catalyst has been implemented in industrial applications, and it has matured in the preparation and application of catalysts, but only in China. The stage is not deep enough.

2. Reaction mechanism of catalytic wet oxidation technology

At present, the research results of catalytic wet air oxidation technology generally believe that the wet air oxidation reaction is a free radical reaction, and the reaction is divided into three stages: chain initiation, chain development or transmission, and chain termination.

(1) The initiation of the chain. Free radicals are generated from the reactant molecules.

\[
RH + O_2 \rightarrow R· + HOO· (RH is organic) \\
2RH + O_2 \rightarrow 2R· + H_2O_2 \\
H_2O_2 + M \rightarrow 2OH· (M is a catalyst)
\]

(2) The development or transmission of the chain. Free radicals interact with molecules, alternating to increase the number of free radicals.

\[
RH + HO· \rightarrow R + H_2O \\
R· + O_2 \rightarrow ROO· \\
ROO· + RH \rightarrow ROOH + R·
\]

(3) Termination of the chain. Free radicals collide with each other to form stable molecules, which interrupt the growth process of the chain.

\[
R· + R· \rightarrow R-R \\
ROO· + R· \rightarrow ROOR \\
ROO· + ROO· \rightarrow ROH + RCOR + O_2
\]

3. Effect of calcination temperature on the activity of Fe-Co-Ru-Ce/γ-Al₂O₃ catalyst

Calcination is an important part of catalyst preparation. The calcination process can change the chemical valence state, crystal phase structure, specific surface and pore structure of the catalyst. After the active component is impregnated and dried, the precursor is obtained on the catalyst, and it is generally present in the form of hydrated hydroxide, anitrate, carbonate, etc. After the catalyst is loaded with the metal compound component, it is calcined to thermally decompose it, remove chemically bound water and volatile substances, and retain the desired chemical composition. At the same time, by controlling a certain calcination temperature, the size of the crystallites can be controlled, thereby changing the specific surface and pore structure of the catalyst, and improving the activity and mechanical strength of the catalyst. Since the thermal decomposition process is generally an exothermic reaction, increasing the temperature facilitates the decomposition reaction; however, too high a temperature at which the sintering is performed causes sintering, which lowers the specific surface area and lowers the performance of the catalyst. Therefore, the choice of calcination temperature has a large effect on the catalyst.

Experimental scheme: Set five kinds of calcination temperatures to 300, 450, 600,750 and 900 °C, respectively, and Fe-Co-Ru-Ce/γ-Al₂O₃ impregnated with four metal salt solutions was calcined at a set temperature for 3 h to prepare five catalysts, and the landfill leachate was used as a degradation target to detect the degraded water sample. The pH, decolorization rate, COD removal rate and turbidity removal rate were used to detect the activity and stability of the catalyst, and FT-IR and UV-V. The experimental results are as follows:
3.1 PH of the effluent treated by landfill leachate

The raw water pH was 9.8, and the results are shown in Table 1.

Table 1. PH of water samples at different calcination temperatures.

| Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-------------------------|--------|--------|--------|--------|--------|
| 300 °C                  | 9.48   | 9.62   | 9.67   | 9.51   | 9.55   |
| 450 °C                  | 9.56   | 9.83   | 9.81   | 9.71   | 9.86   |
| 600 °C                  | 9.47   | 9.58   | 9.69   | 9.55   | 9.69   |
| 750 °C                  | 9.47   | 9.66   | 9.57   | 9.62   | 9.64   |
| 900 °C                  | 9.46   | 9.57   | 9.68   | 9.56   | 9.62   |

3.2 COD removal rate of treated effluent from landfill leachate

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

Table 2. COD of water samples at different calcination temperatures.

| Calcination temperature | 10 min | 20 min | 40 min | 60 min | 90 min |
|-------------------------|--------|--------|--------|--------|--------|
| 300 °C                  | 1801.6 | 69.9   | 1702.4 | 71.6   | 1644.5 | 72.5   | 1553.6 | 74.0   | 1553.6 | 74.0   |
| 450 °C                  | 1655.9 | 72.3   | 1617.3 | 73.0   | 1347.1 | 77.5   | 1308.5 | 78.1   | 1308.5 | 78.1   |
| 600 °C                  | 1884.2 | 68.5   | 1776.8 | 70.3   | 1768.5 | 70.5   | 1760.2 | 70.6   | 1842.9 | 69.2   |
| 750 °C                  | 2173.4 | 63.7   | 1999.9 | 66.6   | 1875.9 | 68.7   | 1834.6 | 69.3   | 1884.2 | 68.5   |
| 900 °C                  | 2090.8 | 65.1   | 1966.8 | 67.1   | 1917.3 | 68.0   | 1801.6 | 69.9   | 2008.2 | 66.4   |

Figure 1. COD curve of water samples at different calcination temperatures.
3.3 Decolorization rate of treated effluent from landfill leachate

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

Table 3. Chromaticity of water samples at different calcination temperatures.

| Calcination temperature (°C) | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----------------------------|--------|--------|--------|--------|--------|
|                            | Absorbance | Decolorization rate (%) | Absorbance | Decolorization rate (%) | Absorbance | Decolorization rate (%) | Absorbance | Decolorization rate (%) | Absorbance | Decolorization rate (%) |
| 300                         | 4.60    | 18.9   | 3.86   | 3.41   | 2.75   | 51.5   | 2.55   | 55.0   |
| 450                         | 4.28    | 24.5   | 3.72   | 3.09   | 2.34   | 58.8   | 2.25   | 60.4   |
| 600                         | 4.82    | 15.0   | 4.35   | 3.80   | 2.99   | 47.3   | 2.97   | 47.7   |
| 750                         | 5.14    | 9.4    | 4.99   | 12.0   | 26.1   | 42.6   | 3.30   | 41.9   |
| 900                         | 4.39    | 22.6   | 3.93   | 30.7   | 2.86   | 49.6   | 2.73   | 51.9   |

Figure 2. Chromaticity diagram of water samples at different calcination temperatures.

3.4 Turbidity removal rate of treated effluent from landfill leachate

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

Table 4. Turbidity of water samples at different calcination temperatures.

| Calcination temperature (°C) | 10 min | 20 min | 40 min | 60 min | 90 min |
|-----------------------------|--------|--------|--------|--------|--------|
|                            | Turbidity (NTU) | Removal Turbidity rate (%) | Turbidity (NTU) | Removal Turbidity rate (%) | Turbidity (NTU) | Removal Turbidity rate (%) | Turbidity (NTU) | Removal Turbidity rate (%) |
| 300                         | 25.26  | 84.0   | 24.34  | 84.5   | 22.97  | 85.4   | 22.06  | 86.0   | 19.78  | 87.4   |
| 450                         | 49.91  | 68.3   | 20.69  | 86.9   | 19.78  | 87.4   | 16.58  | 89.5   | 11.56  | 92.7   |
| 600                         | 56.31  | 64.2   | 38.95  | 75.3   | 35.30  | 77.6   | 33.48  | 78.7   | 23.89  | 84.8   |
| 750                         | 59.96  | 61.9   | 55.85  | 64.5   | 44.89  | 71.5   | 41.69  | 73.5   | 34.85  | 77.9   |
| 900                         | 61.79  | 60.7   | 44.43  | 71.8   | 42.15  | 73.2   | 37.58  | 76.1   | 28.45  | 81.9   |
3.5. Water sample treatment results at different calcination temperatures at 90 min of reaction

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

**Table 5.** Effect of water treatment on different calcination temperatures at 90 min reaction.

| Calcination temperature | 300 °C | 450 °C | 600 °C | 750 °C | 900 °C |
|-------------------------|--------|--------|--------|--------|--------|
| COD removal rate        | 74.0 % | 78.1 % | 69.2 % | 68.5 % | 66.4 % |
| Decolorization rate     | 55.0 % | 60.4 % | 47.7 % | 41.9 % | 51.9 % |
| Turbidity removal rate  | 87.4 % | 92.7 % | 84.8 % | 77.9 % | 81.9 % |

**Figure 3.** Turbidity curve of water samples at different calcination temperatures.

It can be seen from the above graphs that the calcination temperature has a great influence on the activity of the catalyst. As the calcination temperature increases, the activity of the catalyst first increases and then decreases. The COD removal rate, decolorization rate and turbidity removal rate all show such a trend. When the calcination temperature was 450 °C, the activity of the catalyst reached the maximum. At this time, the COD removal rate, decolorization rate and turbidity removal rate of the treated water samples were the highest, which were 78.1%, 60.4% and 92.7%, respectively. At 90 min, the COD removal rate at 900 °C was 66.4%. When the calcination temperature was 750 °C, the decolorization rate and turbidity removal rate of water samples were the lowest, being 41.9 % and 77.9 %, respectively. The reason why the calcination temperature has an influence is that the catalyst undergoes a thermal decomposition reaction during the calcination process. Since the thermal decomposition process is generally an exothermic reaction, increasing the temperature is...
advantageous for the decomposition reaction; however, the excessively high temperature of the calcination may cause sintering. The catalyst is reduced in specific surface area and pore volume so that its activity is also lowered.

4. Conclusions
   (1) Fe-Co-Ru-Ce/γ-Al2O3 catalyst, the calcination temperature is set to 300, 450, 600, 750 and 900 °C, respectively. When the calcination temperature is 450 °C, and the activity of the catalyst is maximized; (2) The best catalyst treatment of landfill leachate, the COD removal rate, decolorization rate and turbidity removal rate of the effluent reached 78.1%, 60.4% and 92.7%, respectively.

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References
[1] S.K.Marttine, R.H.Kettunen. Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates[J]. Chemosphere, 2002, 46: 851-858.
[2] Lin S, Chang C. Treatment of landfill leachate by combined electro-fenton oxidation and sequencing batch reactor method [J]. Water Research, 2000, 34(17): 4243-4249.
[3] Wang Z, Zhang Z, Lin Y., et al.. Landfill leachate treatment by a coagulation-photo oxidation process [J]. Journal of hazardous materials, 2002, 95: 153-159.
[4] Trebouet D, Schlumpf J P, Jaouen P., et al.. Stabilized landfill leachate treatment by combined physicochemical-nanofiltration processes [J]. Water Research, 2001, 35(2): 2935-2942.