Catalytic wet oxidation treatment of landfill leachate

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Abstract. The landfill leachate was treated by catalytic wet oxidation. The catalysts were prepared by impregnation method, and FSC was used as catalyst carrier. Fe and Co were used as catalyst active components and Ce was used as catalyst auxiliary, and noble metal ruthenium was added to prepare supported multi-component composite catalyst of Fe-Co-Ru-Ce/γ-Al₂O₃. The water sample pH, decolorization rate, COD removal rate and turbidity removal rate were used as evaluation indexes of catalyst activity. The catalysts were prepared under the conditions of calcination temperature of 450 °C and calcination time of 3 h. Under the same conditions, for the Landfill Leachate, the COD removal rate, decolorization rate, turbidity removal rate of the water samples reached 78.1%, 60.4% and 92.7%, respectively.

1. Introduction

With the increase of the number of urban construction, the expansion of scale and the increase of population, people's living standards are increasing day by day, and urban garbage is also growing rapidly. The amount of urban garbage generated in China has exceeded 140 million tons, with an annual growth rate of 8% to 10%. There are quite a lot of methods for urban garbage disposal. At present, the most common ways of harmless disposal in the world are: composting disposal method, incineration disposal method, sanitary landfill method and comprehensive utilization. Among them, the sanitary landfill disposal method has been widely adopted in countries all over the world due to its advantages of low investment, low operating cost, wide application range, remarkable environmental protection effect and thorough disposal. However, in the landfill process, solids (mainly degraded waste), liquid (leachate), gas (landfill gas) and other pollutants are produced [1], and landfill leachate is one of the concentrations of organic wastewater that recognized as the most difficult to handle in the world.

Landfill leachate has the following characteristics: high concentration of pollutants, long duration, uneven flow, unstable water quality, and large variation. The harm of landfill leachate pollution is as follows: Landfill leachate is a high-concentration organic wastewater with complex composition. The pollution to the environment is mainly caused by the pollution of groundwater and surface water, and its pollution to groundwaters is also characterized by imperceptibility and persistence. Since the 1960s, countries around the world have gradually realized the pollution of leachate on surface water and groundwater and have conducted research [2-4]. Leachate can cause serious pollution to natural water bodies.

At present, the separate treatment methods for landfill leachate mainly include biological methods, physical and chemical methods, land methods and a combination of different types of methods. The catalytic wet oxidation method is an effective treatment method for landfill leachate.
2. Experimental part

2.1. Experimental equipment and materials
See Table 1 for details.

| Serial number | Name                        | Model          | Manufacturer                                      |
|---------------|-----------------------------|----------------|--------------------------------------------------|
| 1             | Visible spectrophotometer    | 722N           | Shanghai Nuclear Light Technology Co., Ltd.       |
| 2             | pH meter                    | PHS - 3C       | Shanghai Jingke                                  |
| 3             | COD full glass distillation equipment | Assembly | Shenyang Dongke Scientific Equipment Co., Ltd. |
| 4             | Electronic universal furnace | Guangming      | Beijing Yongguangming Medical Instrument Co., Ltd. |
| 5             | Electronic precision balance | AB - 204S     | METTLER Instruments                              |
| 6             | Digital display electric blast drying oven | DGF30/14 - II A | Shanghai Boxun Industrial Co., Ltd. Medical Equipment Factory |
| 7             | Muffle furnace              | KSW            | Beijing Yongguangming Medical Instrument Factory  |
| 8             | Air bath thermostat         | ET - Q         | Changzhou Rongguan Experimental Analytical Instrument Factory |
| 9             | High speed centrifuge       | TDL - 40B      | Shanghai Anting Scientific Instrument Factory    |
| 10            | Fourier transform infrared spectrophotometer | WQF - 510 FTIR | Beijing Ruili Analytical Instrument Co., Ltd. |
| 11            | Dual beam UV-visible spectrophotometer | TU - 1900 | Beijing Pu analysis |
| 12            | Atomic absorption spectrophotometer | TAS - 990 | Beijing Pu analysis |
| 13            | High pressure reaction       | GSH            | Weihai Jixin Chemical Machinery Co., Ltd.        |

Experimental material details: analysis of pure grade hydrated antimony trichloride, cobalt nitrate, copper nitrate, ferric nitrate, barium nitrate, barium nitrate, silver sulfate, phenanthroline, ammonium ferrous sulfate, ferrous sulfate, potassium dichromate, 98% sulfuric acid, mercury sulfate, concentrated nitric acid.

2.2. Experimental device
The core equipment of this experiment was a high pressure reactor apparatus, and the catalytic wet oxidation test was carried out in an autoclave. The device includes a control unit and two parts of the reactor. The reactor consists of a kettle body, a heating furnace, a magnetic stirrer, a cooling system, and the like.

2.3. Blank analysis of raw water from landfill leachate
The water samples of this experiment were collected from the domestic waste sanitary landfill. The parameters of the landfill leachate are as follows:
2.4. Determination of process conditions

Based on a variety of literatures and preliminary research, the experimental conditions are determined as shown in Table 3. The catalyst is directly added to the wastewater. The catalytic activity is mainly characterized by the removal rate of COD and the decolorization rate. The higher the COD removal rate and the decolorization rate, the better the catalytic activity.

| Parameter | Test results |
|-----------|-------------|
| pH        | 9.8         |
| Absorbance| 5.67        |
| Turbidity (NTU) | 157.36 |
| COD<sub>cr</sub> (mg/L) | 5983.8 |

Table 3. Heterogeneous Catalytic Wet Oxidation Test Operation Parameter.

| temperature reflex (℃) | Total reaction pressure (MPa) | Stirring speed (r/min) | Influent COD<sub>cr</sub> (mg/L) |
|-------------------------|-------------------------------|------------------------|----------------------------------|
| 180                     | 2.5                           | 500                    | 5983.8                           |

3. Raw water analysis

250 mL of landfill leachate was taken and reacted in the oxygen partial pressure reaction system of the above process parameters without catalyst, and the reaction time was 1.5 h. The pH, decolorization rate, COD removal rate and turbidity removal rate were sampled at 10 min, 20 min, 40 min, 60 min and 90 min respectively. After the effluent was dried, the solid waste leachate was taken for infrared spectrum analysis.

The effluent test is shown in Table 4, and the experimental results are shown in Figure 1.

Table 4. Table of results of effluent test for landfill leachate blank test.

| Test items          | Raw water | 10 min | 20 min | 40 min | 60 min | 90 min |
|---------------------|-----------|--------|--------|--------|--------|--------|
| pH                  | 9.8       | 9.50   | 9.61   | 9.65   | 9.66   | 9.32   |
| Absorbance          | 5.67      | 3.41   | 3.29   | 3.01   | 2.84   | 2.12   |
| Decolorization rate | —         | 39.9%  | 42.0%  | 49.9%  | 59.3%  | 62.7%  |
| COD (mg/L)          | 5983.8    | 1887.5 | 1904.0 | 1907.6 | 1626.5 | 1586.3 |
| COD removal rate    | —         | 68.5%  | 68.2%  | 68.1%  | 72.8%  | 73.5%  |
| Turbidity (NTU)     | 157.36    | 49.91  | 40.32  | 39.41  | 36.22  | 28.91  |
| Turbidity removal rate | —        | 68.3%  | 74.4%  | 75.0%  | 77.0%  | 81.6%  |
From Fig. 1, during the process of degradation of the blank landfill leachate, the pH is lowered and then picked up again. During the reaction period of 90 min, COD removal rate, decolorization rate and turbidity removal rate all showed a trend of increasing with the extension of reaction time, reaching the maximum at 90 min, which were 73.5%, 62.7% and 81.6% respectively.

4. Preparation and Properties of Ru Series Catalysts

4.1. Determination of load

Accurately weigh 5.000 g of the treated carrier FSC, and test the quality of the Cu-Ce solution used in the micro-excess with a solution of 6 wt% Cu-Ce (Cu:Ce = 3:3, total solution mass 15 g) that is the loading of 10.000 g of carrier. After several parallel experiments, the loading of 10.000 g of carrier FSC was finally determined to be 20.332 g.

4.2. Preparation of Fe-Co-Ru-Ce/γ-Al₂O₃ catalyst

The total percentage of metal ions in the finished catalyst was set to 6 wt%, and the amount of carrier FSC was 10.000 g. In the first half of the experiment, the best active components and ratios (molar ratios) of the four metal salts were determined. ) is Fe:Co:Ru:Ce = 0.75:0.75:1.5:3, then the formulation of 6 wt% Fe-Co-Ru-Ce impregnation solution is as follows:

- Ferric nitrate,
- Cobalt nitrate,
- Antimony trichloride (hydration):
- Barium nitrate,
Distilled water,
Among them, 404.00, 291.03, 434.24 are the formula of ferric nitrate, cobalt nitrate and lanthanum nitrate respectively; 55.845, 58.933, 140.116 are the formula of iron, cobalt and bismuth respectively; 38.75% are the content of bismuth in antimony trichloride (hydration) ;20.332 is the mass of the nitrate solution.
Accurately weigh 1.1032 g of ferric nitrate, 0.7530 g of cobalt nitrate, 0.787 g of lanthanum trichloride (hydrated), 1.8904 g of lanthanum nitrate in 15.78984 g of distilled water, and then add appropriate amount of nitric acid (about 70 drops) to completely hydrate ruthenium trichloride Dissolved and made into a Ru-Fe-Co-Ce impregnating solution. 10.000 g of FSC carrier was immersed in the immersion liquid, and then placed in an ET-Q type air bath thermostat shaker, dynamically immersed for 8 hours at 35 °C and 150 rpm, taken out, washed twice with distilled water, and drained. It was dried at 105 °C for 8 h under ventilation conditions, and finally placed in a KSW muffle furnace at a constant temperature (the following experiment was conducted with the temperature and time of calcination of the catalyst as the main research object).

4.3. Use of catalyst
After the catalyst was prepared according to the above method, 1.000 g was weighed into a GS-0.5 high pressure reactor (180 °C, 2.5 MPa, 500 rpm) and reacted with landfill leachate for 90 min. The sampling time was taken once every 10 min, 20 min, 40 min, 60 min, and 90 min, about 30 mL each time.

4.4. Study on the factors affecting the activity of Ru series catalysts
The calcination temperature and calcination time of the catalyst intermediate affect the structure and activity of the catalyst. Therefore, the effects of the above two factors on the activity of the catalyst were examined by the following experiments, as shown in Table 5 and Figure 2.

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

Figure 2. Water sample treatment effect chart under the action of a 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, but the difference is not obvious. In addition, since COD is the primary indicator for judging Therefore, the results of these three detection indexes were weighed, and the calcination time of the Fe-Co-Ru-Ce/γ-Al₂O₃ catalyst was selected to be 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. The treatment effect.

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

4.5. UV-Vis analysis
The Fe-Co-Ru-Ce/γ-Al₂O₃ catalyst was prepared under optimized conditions, and the host was subjected to catalytic wet oxidation reaction to treat landfill leachate. UV-Vis spectral scanning was performed on the effluent water samples with different reaction time. The result is shown in Figure 3:

![Figure 3. Ultraviolet spectrum of effluent treated by landfill leachate under the catalyst](image)

As shown in Figure 3, after the landfill leachate is reacted for 90 minutes. The maximum absorption peak at 198 nm and 301 nm in the visible light region has not disappeared, indicating that the colored dye in the landfill leachate has not been destroyed in the reaction.

5. Conclusions
(1) Fe and Co are the active components of the catalyst, Ce is a catalytic aid, and a noble multi-component composite catalyst Fe-Co-Ru-Ce/γ-Al₂O₃ is prepared by adding noble metal ruthenium.

(2) The catalyst prepared under the conditions of calcination temperature of 450 °C and calcination time of 3 h, treated with landfill leachate, the COD removal rate, decolorization rate and turbidity removal rate of the water samples reached 78.1%, 60.4% and 92.7% respectively.

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