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Study on the dispose of landfill leachates over tombarthite catalyst by catalytic wet air oxidation

Heng Gao[1], Junpeng Jin[1], Yanbo Zhou[1], Yongli Zhang[1,*]

[1]Foshan University, Foshan, Guangdong, China
670511263@qq.com
[*]Corresponding author

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Abstract: Experimental use of catalytic wet air oxidation of landfill leachates treatment simulation, catalyst preparation by impregnation method of Cu, Fe, Co as a catalyst active component, La, Ce for the catalytic agent. Experiments were conducted to comprehensively assess the activity and stability of a catalyst developed with varying component ratios of composite supported catalysts. Various parameters including water pH, decolorization rate, COD removal, as well as the detection rates of Cu^{2+} and Fe^{3+} dissolution, were evaluated. Based on the experimental results: Choose Fe-Co=3:3 as the best catalyst, Ce is the best catalytic additives. Based on this premise, research was conducted on the active component Pt, utilizing the Fe-Co-Ru-Pt-Ce/FSC composite catalyst support. The ratio Fe-Co-Ru-Pt-Ce =0.75:0.75:0.75:0.75:3 was determined as the optimal ratio for the catalyst. Modern testing technology, such as atomic absorption, is utilized to determine the performance of catalysts in testing. Through many experiments, from the treatment effect and the stability of both the comprehensive analysis of the catalyst, to determine the best catalyst agent is Ce. Under the same conditions dealt with landfill leachates, reaction time conditions for 90min, landfill leachates processing wastewater. The turbidity removal rates of Fe Co catalyst and Cu Ce catalyst reached 93.8 % and 94.4 %, respectively.

1. Introduction

With the increase in population, the development of socio-economic levels, the improvement of residents' living standards, and the accelerating urbanization process, the production of urban garbage is increasing day by day. Currently, the main disposal methods for urban garbage at home and abroad include incineration, sanitary landfill, surface stacking, and composting[1]. Sanitary landfill is one of the main garbage disposal methods in China. The treatment of leachate generated during the landfill process poses a major challenge and has become a major research focus. Currently, the main methods for treating leachate include biological and physicochemical methods[2]. When the BOD_5/COD value of leachate is greater than 0.3, the leachate has good biodegradability and can be treated using biological methods. For leachate with a small BOD_5/COD ratio (0.07-0.2), which is difficult to treat biologically, and for organic components with relatively high toxicity that

are difficult to remove by biological methods, physicochemical methods are more effective, with shorter operation cycles but higher treatment costs[3]. Catalytic wet air oxidation (CWAO), which has better efficiency and lower costs, has become the mainstream in recent years. This study focuses on exploring the application of rare earth catalysts in CWAO and the optimal catalyst ratio[4].

2. Experimental part

2.1 Experimental materials

The leachate samples used in this experiment were obtained from the Xigang municipal solid waste landfill site in Chaozhou city.

The catalysts used in heterogeneous catalytic wet oxidation are soluble transition metal salts, including metal chlorides, metal sulfates, and metal nitrates, with the active component being transition metal ions[5]. Transition metals have partially filled d or f orbitals in their valence shell, allowing them to form various bonds with reaction substrates and undergo unique reactions within the coordination field of transition metals[6]. These interactions form the fundamental basis for key elementary reactions in homogeneous catalysis.The noble metal series catalysts exhibit high activity but are expensive, which limits their application[7]. Therefore, in this experiment, most of the homogeneous catalysts selected are nitrates.

2.2 Experimental methods

The original leachate is poured into the reaction vessel, along with the predetermined amount of homemade catalyst. The reaction vessel is then sealed with its cover and secured with a nut to ensure good air tightness of the equipment. Once the reaction temperature is reached, the valve of the oxygen cylinder is opened to oxygenate the system to the set pressure. The magnetic stirrer and timer are started, marking this as the zero point of the reaction time. Subsequently, water samples are taken at appropriate intervals according to the experimental plan using a sampling tube for water sample analysis tests. During sampling, the oxygen supply valve is opened to maintain a constant total pressure in the reaction system[8]. The collected water samples are then tested for pH, turbidity removal rate, and decolorization rate to infer the optimal catalyst formulation.

3. Results and Conclusion

3.1 Preparation parameters of each catalyst

Using the given parameters, we set the total percentage content of metal ions in the finished catalyst to wt6 %, with a carrier dosage of 5.000 grams. Subsequently, a Wt6 % $Cu^{2+}Fe^{3+}La^{3+}Ce^{3+}$ impregnation solution was prepared according to the ratios outlined in Table 1.

Among them, 241.60, 291.03, 404.00, 434.24, and 433.01 represent the formula quantities of copper nitrate, cobalt nitrate, iron nitrate, cerium nitrate, and lanthanum nitrate, respectively. 63.546, 58.933, 55.845140.12138.9 represent the formula quantities of copper, cobalt, iron, cerium, and lanthanum, respectively. 15 is the mass of nitrate solution.

After the catalyst preparation is completed, take 1.00 g and place it in a reaction kettle (180 ℃, 2.5 MPa, 500 rpm) to react with the leachate for 90 minutes. The sampling time is taken every 10 minutes, 20 minutes, 40 minutes, 60 minutes, and 90 minutes, each time about 30 ml. And we conducted an experiment in our laboratory to measure and record the decolorization rate, turbidity removal rate, and pH of the water sample.

Table 1: Preparation parameters of each group of rare earth catalysts

CAT number	Element proportion	Copper nitrate	Cobalt nitrate	Iron nitrate	Cerium nitrate	Lanthanum nitrate	water
		Reagent content(g)					
A-1	Cu	3.422	0	0	0	0	11.578
A-2	Co	0	4.444	0	0	0	10.556
A-3	Fe	0	0	6.511	0	0	8.489
A-4	Cu-Ce=3:3	1.711	0	0	1.395	0	11.894
A-5	Fe-Ce=3:3	0	0	3.255	1.395	0	10.35
A-6	Co-Ce=3:3	0	2.222	0	1.395	0	11.383
B-1	Cu-Co=3:3	1.711	2.222	0	0	0	11.067
B-2	Cu-Fe=3:3	1.711	0	3.255	0	0	10.034
B-3	Fe-Co=3:3	0	2.222	3.255	0	0	9.523
B-4	Cu-La=3:3	1.711	0	0	0	1.403	11.886
B-5	Fe-La=3:3	0	0	3.255	0	1.403	10.342
B-6	Co-La=3:3	0	2.222	0	0	1.403	11.375

3.2 The pH of each catalyst treated water sample

When measuring the pH value of the sample, a PHs-3D pH meter is used for measurement, and the pH values of different catalysts in each group are recorded in Table 2. At the same time, we ensure that the pH meter probe is dry and clean, and read the data from the electronic display screen after the value stabilizes.

Table 2: The pH of each catalyst treated water sample

CAT number	Element proportion	10min	20min	40min	60min	90min
A-1	Cu	9.41	9.35	9.20	9.55	9.63
A-2	Co	9.35	9.77	9.75	9.68	9.60
A-3	Fe	9.41	9.78	9.74	9.72	9.65
B-1	Cu-Co=3:3	9.36	9.56	9.46	9.47	9.49
B-2	Cu-Fe=3:3	9.38	9.76	9.72	9.66	9.61
B-3	Fe-Co=3:3	9.30	9.60	9.50	9.46	9.41
A-4	Cu-Ce=3:3	9.55	9.67	9.76	9.78	9.91
A-5	Fe-Ce=3:3	8.22	8.38	8.40	8.29	8.33
A-6	Co-Ce=3:3	9.35	9.79	9.76	9.71	9.61
B-4	Cu-La=3:3	8.87	9.10	9.09	9.01	9.20
B-5	Fe-La=3:3	8.84	9.15	9.17	9.03	9.14
B-6	Co-La=3:3	8.92	9.18	9.20	9.03	9.20
	No CAT	9.50	9.61	9.65	9.66	9.32

From the above table, it can be concluded that the pH of the leachate from garbage is around 9.5. As the treatment time increases, the pH of the effluent shows an upward trend.

3.3 The decolorization rate of water samples treated with each catalyst

By comparing the decolorization rates of single component catalysts and composite catalysts, the specific decolorization rates of each group of catalysts are shown in Table 3.

Table 3: The decolorization rate of water samples treated with each catalysts

CAT number	Element proportion	10min	20min	40min	60min	90min
		decolorization (%)				
A-1	Cu	48.7	62.4	76.8	83.7	84.5
A-2	Co	28.8	31.6	46.0	52.2	57.3
A-3	Fe	17.1	27.0	37.2	43.4	42.5
B-1	Cu-Co=3:3	24.7	35.6	54.7	63.2	69.2
B-2	Cu-Fe=3:3	19.9	21.7	30.9	32.5	46.0
B-3	Fe-Co=3:3	18.8	21.3	31.2	32.0	46.6
A-4	Cu-Ce=3:3	47.7	63.9	77.6	82.1	84.8
A-5	Fe-Ce=3:3	49.0	52.4	57.3	59.6	70.0
A-6	Co-Ce=3:3	45.0	56.9	63.5	68.3	72.2
B-4	Cu-La=3:3	60.7	77.4	80.4	81.0	82.0
B-5	Fe-La=3:3	63.5	62.8	77.4	78.3	78.8
B-6	Co-La=3:3	63.3	77.5	79.5	80.8	81.2
	No CAT	39.9	42.0	47.0	49.9	59.3

By comparing the two different data sets in Figure 1, it can be clearly seen that when rare earth metals are added as additives to each group of metal catalysts, the decolorization rate increases significantly.

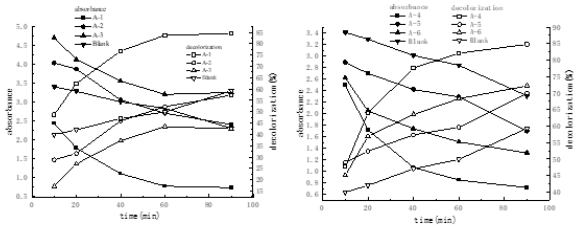

Figure 1: The decolorization rate of single component catalysts and combination catalysts

3.4 The turbidity removal rate of water samples treated with each catalyst

Table 4: The turbidity removal rate of water samples treated with various catalysts

CAT number	Element proportion	10min	20min	40min	60min	90min
		Turbidity removal rate(%)				
A-1	Cu	37.8	77.6	78.4	88.0	88.9
A-2	Co	53.5	56.4	73.5	79.0	89.5
A-3	Fe	56.7	85.1	87.7	88.3	89.5
B-1	Cu-Co=3:3	65.4	73.5	85.4	90.0	93.0
B-2	Cu-Fe=3:3	39.3	51.7	72.9	81.1	88.0
B-3	Fe-Co=3:3	59.6	84.5	89.2	91.2	93.8
A-4	Cu-Ce=3:3	37.8	86.0	86.9	92.1	94.4
A-5	Fe-Ce=3:3	---	---	---	---	---
A-6	Co-Ce=3:3	---	---	---	---	---
B-4	Cu-La=3:3	74.4	84.5	88.6	89.8	90.0
B-5	Fe-La=3:3	66.0	77.0	83.7	89.5	90.9
B-6	Co-La=3:3	80.5	90.0	90.0	91.2	91.8
	No CAT	68.3	74.4	75.0	77.0	81.6

From the table 4, it can be seen that when the reaction time is 90 minutes, the turbidity removal rate of the treated effluent increases significantly with the addition of catalyst. Among the metal composite catalysts, the turbidity removal rate of Fe-Co catalyst is the highest, reaching 93.8 %. Among the rare earth metal composite catalysts, the turbidity removal rate of Cu-Ce catalyst reaches 94.4 %.

4. Conclusion

The results indicate that the catalyst with a Co:Fe ratio of 3:3 exhibited better activity.At 90 minutes of reaction time, the turbidity removal rate of the effluent treated with catalysts significantly increased. Among the metal composite catalysts, the Fe-Co catalyst exhibited the highest turbidity removal rate, reaching 93.8 %. In the rare earth metal composite catalysts, the Cu-Ce catalyst achieved a turbidity removal rate of 94.4 %.This indicates that cerium plays a role in enhancing the catalyst's activity and increasing the reaction rate.

Additionally, the CWAO (Catalytic Wet Air Oxidation) process is particularly suitable for treating high-concentration, biologically resistant wastewater[9-10]. Addressing the issues of harsh reaction conditions, high treatment costs, stringent equipment requirements, and ineffective equipment performance associated with conventional processes, this study systematically investigates the high-temperature, high-pressure CWAO process. Rare earth series catalysts were prepared and characterized, and the degradation process of dyes in the catalytic wet oxidation process was explored, laying a theoretical foundation for the industrial application of these catalysts. Moreover, through comparison with several catalyst groups for treating leachate, ideal treatment results were achieved. Hence, it can be observed that this study holds significant theoretical significance and practical value, providing assistance for future research endeavors.

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