Effect of Composition and Mass Ratio on the Catalytic Wet Air Oxidation Catalyst Cu–Fe–La/FSC

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Abstract. The catalytic wet air oxidation (CWAO) technology is used for the treatment of the simulated printing and dyeing wastewater and also for investigating the catalyst performance indicators such as catalyst activity and stability. The catalyst activity is mainly reflected from the water decolorization and COD_{Cr} removal rates, and the stability of the catalyst is mainly reflected by the quantity of metal dissolution. The experimental results showed that the prepared Cu–Fe–La/FSC catalyst with a 1:1:2 ratio of Cu–Fe–La by the impregnation method exhibited good activity for the treatment of the simulated printing and dyeing wastewater by the CWAO method, and the decolorization and COD_{Cr} removal rates using this catalyst were 98.7% and 78.6%, respectively, with a higher catalytic activity, lower concentration of metal dissolution, and good stability.
Keywords: Cu–Fe–La/FSC; CWAO; Printing and dyeing wastewater; Decolorization rate; COD_{Cr} removal rate

1 Introduction

The printing and dyeing wastewater at higher concentrations, big chromaticity, complexly composition and difficulty to biodegrade is a big problem in the industrial wastewater treatment, and it is also a very interesting issue to study [1]. The core technology of the catalytic wet air oxidation (CWAO) is the selection of catalyst, and the catalyst activity depends on the types of catalyst and the ratio between the types of catalyst and cocatalyst [2]. The CWAO process was used for the treatment of the simulated dyeing and printing wastewater by the immersion type catalysts, using active Cu and Fe as the cost-effective metals [3], and at the same time, La cocatalyst with special physiochemical properties was added [4]. In this study, we developed a treatment of printing and dyeing wastewater with a high COD_{Cr} removal rate of the catalyst, and this study could provide a scientific basis for the printing and dyeing wastewater CWAO process. Moreover, the preparation of transition metal and rare earth catalysts, and their CWAO performance were investigated in this study [5].

2 Materials and Methods

2.1 Samples and materials

Methyl orange simulated printing and dyeing wastewater (COD_{Cr}: 2,000 mg/L), copper nitrate, nitric acid, iron, cerium nitrate, lanthanum nitrate, methyl orange, potassium dichromate, ammonium ferrous sulfate, and 98% sulfuric acid were purchased from Sigma-Aldrich (St. Louis, USA) and were of analytical grades.

2.2 Equipment and instruments

GS type permanent magnet rotating stirred autoclave (Material 316L, $Cr_{18}Ni_{12}Mo_{2-3}$), the detection of COD_{Cr} all-glass distillation unit, atomic absorption spectrometer (AAS), spectrophotometer, pH meter, electronic precision balance, and muffle furnace were used.

2.3 Analysis method

Chemical oxygen demand (COD_{Cr}) was determined by the GB dichromate method. Turbidity was determined by spectrophotometric method.

Decolorization rate $\eta = \dfrac{A0 - A}{A0} \times 100\%$.

where A0: the absorbance of raw water and A is the absorbance of water after the processing

2.4 Preparation of catalysts

The load type multicomponent catalysts were prepared by the impregnation method. To ensure full immersion, the excessive impregnation method was used, and the required amounts of the active substances were accurately weighed and dissolved in a certain ratio of distilled water and the impregnation liquid by mass fraction. The FSC dipping was placed in the corresponding impregnation liquid, and after a period of impregnation and drying, the resulting materials were roasted at 450 °C in a muffle furnace for 3 h to afford the corresponding catalysts.

3 Results and Discussion

3.1 Methyl orange blank experiment

The effect of catalysts was investigated by first performing blank experiment using methyl orange to ensure whether it had an impact on the decolorization rate of water and COD_{Cr} after adding the catalyst, and the experimental data are shown in Table 1.

Fig. 1 shows that the pH of water first decreases and then increases. The initial amounts of organic matter rapidly decomposed into small molecular organic components. At higher temperatures, pH first decreased, and later the oxidation of small organic molecules led to further oxidative decomposition, reducing the acidity of the solution, thereby increasing the water pH. After 90 min of the reaction, at equilibrium, the decolorization and COD_{Cr} removal rates of methyl orange blank liquid were 78.8% and 56.8%, respectively.

Table 1 Methyl Orange Blank Experiment

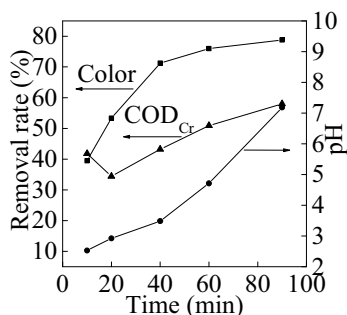| Sampling time （min）	10	20	40	60	90
Dilution ration	100	100	50	50	50
Decoloring rate η(%)	39.5	53.4	71.2	76	78.8
Removal rate of COD_{Cr} η(%)	206	484	496	642	1136
pH	5.68	4.94	5.82	6.59	7.3

Fig.1 Methyl orange blank experiment

3.2 Experimental results and analysis of the catalysts

3.2.1 Choice of transition metal catalysts

The catalyst activity and stability largely depend on its composition. At first Fe, Cu, and composite Cu–Fe catalysts were chosen for comparison. The experimental data are shown in Table 2.

As shown in Table 2, after adding the catalyst, the decolorization and COD_{Cr} removal rates increased significantly, as shown in Fig. 2(a) for the treatment of the simulation of the printing and dyeing wastewater. The decolorization rate of the catalyst containing Cu was better than that containing only Fe catalyst. After 60 min, the decolorization rate of Cu–Fe/FSC catalyst was same as that of Cu/FSC catalyst. Fig. 2(b) shows that the catalysts containing only Fe did not show significant COD_{Cr} removal rate, and the COD_{Cr} removal rates of the catalysts with only Cu were significantly higher than that of the catalysts with Fe. The COD_{Cr} removal rate of the catalyst with only Cu was better than that of the catalyst with Cu–Fe. In general, in the first 40 min the reaction rate increased; after 60 min, the reaction rate decreased slowly; after 90 min, it reached to equilibrium state and the decolorization rate (η) was as high as 99.8%, and the COD_{Cr} removal rate was 91.2% with a high catalyst performance.

The atomic absorption spectroscopy (AAS) showed that higher the impregnation liquid concentration, greater the effluent concentration, because of metal dissolution, which could cause secondary pollution to the environment. Therefore, the Cu-Fe/FSC catalyst was chosen based on the catalytic activity, cost-effectiveness, environmental protection, and relatively higher decolorization and COD_{Cr} removal rates.

Table 2 Transition Metal Catalyst For Experimental Data Processing

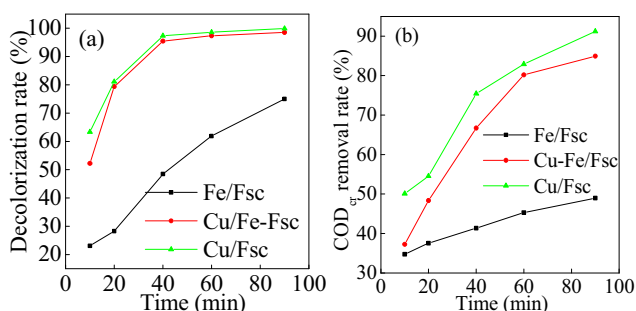|	Sampling time（min）	Fe/FSC	Cu-Fe/FSC	Cu/FSC
Decoloring rate η(%)	10	23.1	52.2	63.3
	20	28.2	81.3	81
	40	48.4	97.4	97.3
	60	61.9	99.3	99.5
	90	75	99.5	99.7
Removal rate of COD_{Cr} η(%)	10	34.7	37.2	50
	20	36.5	48.3	54.5
	40	41.3	66.7	75.4
	60	45.3	80.1	82.8
	90	48.9	84.9	91.2

Fig. 2 The curve of the transition metal catalyst performance with time

3.2.2 Choice of rare earth elements in catalytic system

After determining the composition of the Cu–Fe–FSC catalyst, to increase the stability of the catalyst, the rare earth elements Ce and La were added to the catalyst, and their compositions were determined. The experimental data are listed in Table 3.

Fig. 3(a) shows that the addition of Ce or La to the catalyst increased the decolorization rate with increasing reaction time, and the catalyst with La exhibited obviously better decolorization rate than the catalyst with Ce, and with both Ce and La, the catalyst decolorization effect was between the two separate catalytic effects.

The change in the COD_{Cr} removal rate had a similar trend to that of the decolorization rate. The Cu–Fe–La/FSC catalyst obviously had significantly better effect on the simulated printing and dyeing wastewater treatment than the other two types of catalysts and was measured by AAS. The Cu–Fe–La/FSC catalyst was chosen, because the dissolution of metal was not significant, thereby it poses less pollution to the environment.

Table 3 Rare Earth Metal Catalysts Experimental Data Processing

	Sampling time(min)	Cu-Fe-Ce=1:1:2	Cu-Fe-La=1:1:2	Cu-Fe-Ce-La=1:1:1:1
Decoloring rateη(%)	10	17.5	35	21.7
	20	44.3	54.9	46.4
	40	74.9	81.7	77.2
	60	85.7	97.4	91.3
	90	91.3	98.9	96.9
Removal rate of	10	640	706	682

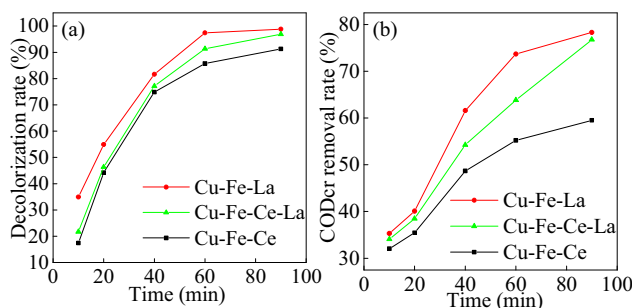| COD_{Cr} η(%)	20	710	802	770
	40	974	1232	1086
	60	1104	1474	1276
	90	1190	1566	1536

Fig.3 Rare earth catalyst performance and the curve of time

3.2.3 Ce quality formula of catalytic agent selection

After determining the concentrations of three types of metals Cu, Fe, and La, different proportions of La element were chosen for the optimization of the catalysts for better catalytic activity, and the experimental data are listed in Table 4.

Fig.4 shows that when the proportion of La in the catalyst is smaller, the decolorization and COD_{Cr} removal rates of the catalyst are higher. Different proportions of (Cu–Fe):La were used for the optimization of the performance of the catalysts, and the order of catalytic effects of the catalysts with different proportions of (Cu–Fe):La is as follows: 3:1 > 2:1 > 1:1 > 1:2 > 1:3. A 1:1:2 ratio of Cu–Fe–La was selected, because of a better catalytic effect and high stability. The decolorization and COD_{Cr} removal rates of the catalyst with 1:1:2 ratio of Cu–Fe–La were 98.7% and 78.6%, respectively, together with a lower metal dissolution rate, thus exhibiting better catalytic activity, cost-effectiveness, and environmental protection. Therefore, a 1:1:2 ratio of Cu–Fe–La metals in the catalyst was used for the subsequent experiments of the simulated dyeing and printing wastewater treatment.

Table 4 The La In Different Proportions Catalyst

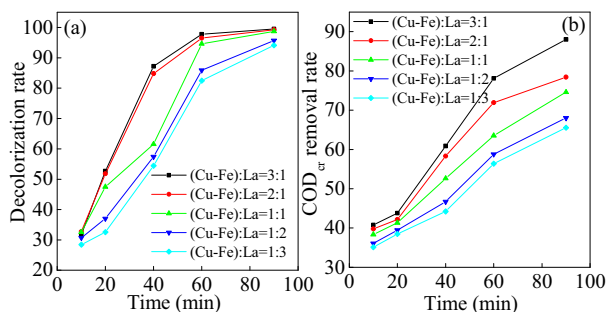|	Sampling time(min)	(Cu-Fe)-La 3:1	(Cu-Fe)-La 2:1	(Cu-Fe)-La 1:1	(Cu-Fe)-La 1:2	(Cu-Fe)-La 1:3
Decoloring rateη(%)	10	33.7	32.7	32.5	30.7	28.4
	20	52.6	51.8	47.4	37	32.5
	40	87.2	84.8	61.5	57.4	54.4
	60	97.7	96.5	94.6	85.9	82.4
	90	99.4	99.2	98.7	95.7	94.1
Removal rate of COD_{Cr} η(%)	10	814	794	766	722	702
	20	874	842	826	788	768
	40	1218	1166	1052	932	884
	60	1562	1438	1270	1176	1126
	90	1760	1568	1488	1360	1310

Fig. 4. Different proportion (Cu-Fe)-La catalyst performance and the curve of the time

4 SEM And TEM

The SEM images of the impregnated catalyst after the roasting are shown in Figs. 5a–5c, indicating that the carrier FSC at 450 °C after dipping, and calcination exhibited a uniform distribution, porous structure, and the catalyst active component is ~500 μm particle aggregates covering on the surface of the carrier; therefore, the carrier offers a porous surface structure. Comparison of the SEM images before and after the adsorption shows that the surface has a small amount of material, and the material structure slightly changed but the stability was good. The TEM image of the catalyst FSC shows the catalyst's particles in the diameter range 10–30 nm with a higher dispersion and less load (Fig. 5(d)).
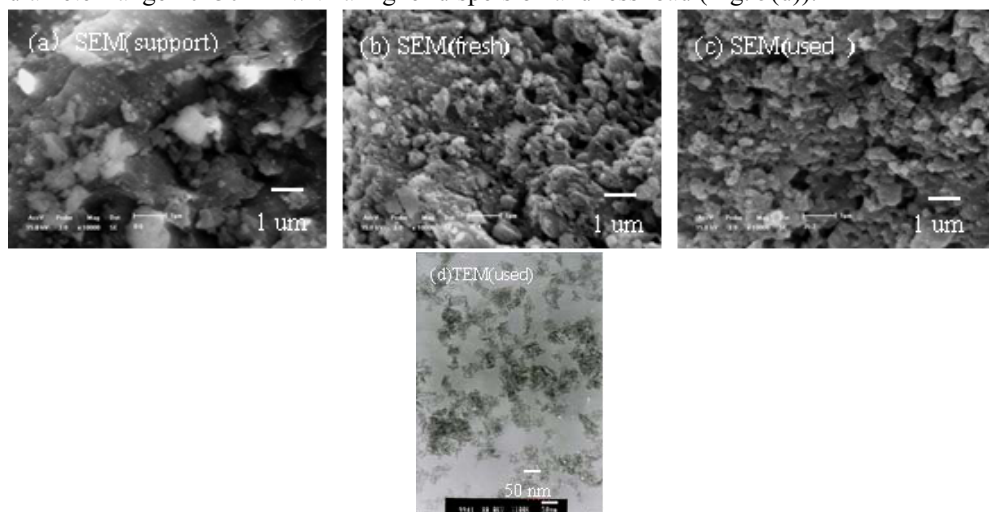

Fig. 5 SEM and TEM photos of fresh and used Cu-Fe-La/FSC

5 Conclusions

The single factor variable method was used to determine the metal concentration. According to the proportion of La in the catalysts, five types of catalysts were tested for (Cu–Fe):La ratios of 3:1, 2:1, 1:1, 1:2, and 1:3. With increasing proportions of La, the catalysts exhibited a poor decolorization effect, and the COD_{Cr} removal effect was not significant; however, less metal was dissolved. In conclusion, a 1:1 ratio of (Cu–Fe):La was selected as it exhibited a remarkable decolorization effect, COD_{Cr} removal rate, and lower dissolubility of metal. As the reaction reached to the equilibrium state, the water

decolorization rate increased gradually, the COD_{Cr} removal rate also increased, and the pH decreased slowly. A 1:1 ratio of (Cu, Fe):La was used for the treatment of the simulated printing and dyeing wastewater, and the decolorization and COD_{Cr} removal rates were 98.7% and 78.6%, respectively, with a higher catalytic activity, less metal dissolution, and good stability.

Acknowledgments

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