Study on the treatment of caprolactam wastewater by electrocatalytic oxidation process

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Abstract. Aiming at the caprolactam wastewater discharged from a chemical enterprise, the electrocatalytic oxidation technology was used for advanced treatment. When the current is 450 A and the inflow flow is 3 m³/h, the COD value of the effluent is reduced from 100 mg/L to below 50 mg/L, the ammonia nitrogen is reduced from 10 mg/L to below 4 mg/L, and the chroma is reduced from 50 times to below 30 times. The effluent quality meets the class A standard in Table 3 of 《Discharge standard of pollutants for municipal wastewater treatment plant》 (GB 18918-2002).

1. Introduction

The wastewater from caprolactam production contains cyclohexanone, cyclohexane, benzene, cyclohexanone fat, organic acid, caprolactam, ammonia nitrogen, etc., which is characterized by large amount of water, complex and variable water quality, poor biodegradability and difficult treatment[1]. In recent years, with the continuous expansion of the production capacity of caprolactam plant, its wastewater discharge exceeds the capacity of sewage treatment plant, and the national and local sewage discharge standards continue to improve. Traditional anaerobic aerobic (A/O) - membrane bioreactor (MBR) process continues to be used for treatment. There are many refractory organics left in the effluent, and the color of the water body is dark, so it is unable to meet the discharge requirements of class A standard COD less than 50 mg/L, NH₃ less than 5 mg/L and chroma less than 30 in Table 3 of 《Discharge standard of pollutants for municipal wastewater treatment plant》 (GB 18918-2002)[2].

Scholars have carried out in-depth research on all kinds of advanced treatment technologies as the technical guarantee method for achieving emission standards. Some researchers used micro electrolysis Fenton, O₃/O₂/BAF, O₃/H₂O₂ and electrocatalytic oxidation as advanced treatment technologies to treat wastewater, and achieved good results[3-6]. Among them, electrocatalytic oxidation water treatment technology is to make the pollutants react directly on the electrode or use the strong oxidizing active species on the surface of the electrode to make the pollutants undergo oxidation-reduction transformation, so as to degrade the pollutants in the wastewater. The electrocatalytic oxidation method has the advantages of no addition of any additives, strong oxidation capacity, no secondary pollution and simple equipment [7-9]. It is considered to be an efficient, low-consumption and environmentally friendly advanced treatment technology.

After pretreatment + multi-stage A/O + physicochemical treatment, the COD of caprolactam wastewater is 100-120 mg/L, the ammonia nitrogen is 10-12 mg/L, the chroma is 45-55 times, and the pH value is 7.5-8. The current sewage treatment process can not meet the increasingly strict national
discharge standards. In this paper, the electrocatalytic oxidation method is used to treat caprolactam wastewater, and the removal effect of COD, ammonia nitrogen and chroma of the wastewater is investigated. At the same time, the operation cost of the advanced treatment is summarized.

2. Materials and methods

2.1. Main equipment
One PP electrolyzer with an effective volume of 1t; Two DC stabilized power supplies with a total power of 15kw; One self-priming pump with a total power of 2KW; Ti/Iro₂RuO₂ coated anode with pure titanium electrode; Several copper bars and PVC pipelines.

2.2. Pilot process
The waste water is lifted from the self-priming pump to the electrolytic cell, and the flow is regulated to 3m³/h by the valve. After reaction, it is discharged from the outlet of the electrolytic cell. Samples are taken at the water inlet and outlet for analysis every other period of time, and the electric energy consumption is recorded.

2.3. Test principle
Electrocatalytic oxidation can be divided into direct electro oxidation and indirect electro oxidation according to different action principles.

Generally, electrochemical oxidation process includes the following three steps:

(1) Transfer of electroactive substances: organic substances in direct electrochemical oxidation or O₂ in indirect electrochemical oxidation, etc., are transferred from solution to electrode surface.

(2) The electroactive substance adsorbs on the surface of the electrode and reacts with the electrode in different phases. The organic substance is degraded by direct electrochemical oxidation, and the intermediate products such as ·OH radical with strong oxidation are produced by indirect electrochemical oxidation.

(3) In direct electrochemical oxidation, the degradation products of organics are desorbed and transferred to the bulk phase or deposited on the electrode surface; in indirect electrochemical oxidation, the reaction products with strong oxidizability are desorbed and transferred to the bulk phase to oxidize the organics in the bulk phase or react with the organics directly adsorbed on the electrode surface.

2.4. Analysis method
Chemical oxygen demand (CODcr) shall be determined in accordance with 《The dichromate method for the determination of chemical oxygen demand of water quality》 (GB 11914-1989).

The mass concentration of NH₃ (ρN) shall be determined in accordance with HJ535-2009 《Determination of NH₃ in water: Nessler's reagent spectrophotometry》.

The chromaticity shall be determined in accordance with GB/T 11903-89 《Determination of water quality chromaticity》.

The pH value shall be determined in accordance with GB6920-86 《Determination of pH value of water quality glass electrode method》.

3. Results and discussion

3.1. Pilot operation effect

3.1.1. COD degradation effect.
According to the continuous operation of the electrocatalytic oxidation device, the data of COD value of caprolactam wastewater treated by the device for three months are plotted as shown in Figure 1. It can be seen from the figure that the COD of influent water fluctuates between 100-120mg/L, the COD
of effluent water can be reduced to 30-50mg/L by electrocatalytic oxidation, and the removal rate is about 50% - 75%. After electrocatalytic oxidation, the COD of effluent water can be stable below 50mg/L.

![Data diagram](Figure 1. Removal of COD from caprolactam wastewater by electrocatalytic oxidation process)

3.1.2 NH₃ degradation effect.
In the mechanism of electrocatalytic oxidation, the direct and indirect electrochemical oxidation of ammonia nitrogen may take place on the anode. The direct oxidation process of ammonia nitrogen includes the direct loss of electrons on the anode surface and the removal of the adsorbed state of ammonia nitrogen by radical oxidation. Indirect oxidation refers to the reaction of chloride ion in water at the anode to generate ClO⁻, and then oxidation ClO⁻ with strong property reacts with ammonia nitrogen to remove ammonia nitrogen. The NH₃ value of caprolactam wastewater treated by the unit has been operated for 3 months, as shown in Figure 2. It can be seen from the figure that the influent NH₃ fluctuates between 10-12mg/L, the effluent NH₃ can be reduced to 2-4mg/L by electrocatalytic oxidation, and the removal rate is about 60% - 83%. After electrocatalytic oxidation, the effluent NH₃ can be stable below 4mg/L.

![Data diagram](Figure 2. Removal of NH₃ from caprolactam wastewater by electrocatalytic oxidation process)
3.1.3 Chroma degradation effect.
According to the continuous operation of the electrocatalytic oxidation device, the chromaticity operation data of caprolactam wastewater treated by the device for three months are plotted as shown in Figure 3. It can be seen from the figure that the chroma of the influent fluctuates between 45-55, and the chroma of the effluent from electrocatalytic oxidation can be reduced to 20-30, with a removal rate of about 45%. After electrocatalytic oxidation, the chroma of the effluent can be stable below 30. The data of wastewater quality after electrocatalytic oxidation are summarized in Table 1. It can be seen from Table 1 that the effluent quality meets the class a standard in Table 1 of 《Discharge standard of pollutants for municipal wastewater treatment plant》(GB 18918-2002).

![Data diagram](image_url)

Figure 3. Removal of chroma from caprolactam wastewater by electrocatalytic oxidation process

| Analysis item     | Control index | Maximum  | Minimum  | Average  |
|-------------------|---------------|----------|----------|----------|
| Influent COD      | ≤120          | 119.32   | 100.76   | 109.98   |
| Effluent COD      | ≤50           | 49.34    | 30.32    | 39.27    |
| Influent NH₃      | ≤12           | 11.98    | 10.12    | 11.01    |
| Effluent NH₃      | ≤4            | 3.98     | 2.12     | 2.92     |
| Influent chroma   | ≤55           | 54.98    | 43.21    | 49.56    |
| Effluent chroma   | ≤30           | 29.55    | 21.01    | 24.11    |

3.2. Operation cost analysis
Operation cost is an important part of the total cost of a project. The daily treatment capacity of caprolactam wastewater in the chemical plant is 50m³/L, and the main cost in the operation of electrocatalytic oxidation system is the consumption of electricity. According to the results of three months of continuous experimental operation, the operation cost of advanced treatment of caprolactam wastewater is as follows:

1. Electric energy consumption
   Electric energy consumption per ton of hydropower catalytic oxidation = 2.8/(KWh).
   Power consumption of water pump=0.2/(KWh).
   If the electric charge is 0.51yuan/KWh, then 3.0×0.51=1.53 yuan/ton.

2. Labor cost
   There are 3 persons in the sewage treatment plant, and the monthly wage is 5000 yuan/person.
Labor cost: $5000 \times \frac{3}{(30 \times 1200)} = \text{yuan/ton}.

(3) Total operating cost per ton of water

The total operating cost per ton of water is: power consumption + labor cost = 1.53 + 0.42 = 1.95 yuan.

4. Conclusion

After the advanced treatment of caprolactam wastewater by electrocatalytic oxidation technology in a chemical plant, the COD, NH$_3$ and chroma of effluent reach the first class a standard of 《Discharge standard of pollutants for municipal wastewater treatment plant》(GB 18918-2002), and the operation cost is low, only 1.95 yuan/ton. The successful pilot test of electrocatalytic oxidation technology in caprolactam wastewater has proved that the technology is stable and reliable. It is an effective means to implement the advanced treatment and reuse of caprolactam wastewater, provides a new reliable way for the advanced treatment of this kind of wastewater, and is an effective means for chemical enterprises to cope with increasingly strict environmental protection pressure.

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