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A Case Study of Dye Intermediate Production Wastewater Treatment Project

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Abstract: Dye intermediates are indispensable chemical raw materials and play an important role in global industrial production. In the production process of dye intermediates, a large amount of wastewater is produced, which will cause serious pollution to the environment, and ultimately harm human health. Dye intermediate production wastewater is characterized by high organic matter concentration, complicated pollutants and poor biodegradability. The traditional treatment process has limited ability to purify wastewater and can not effectively degrade the organic pollutants. In this project, a novel combined process of "ozone catalytic oxidation + biochemical degradation" was adopted to treat the dye intermediate production wastewater, and the process mechanism and treatment effect were analyzed. The results showed that the key process unit of this project was heterogeneous ozone catalytic oxidation. Due to the high activity, low cost, easy recovery and strong adsorption capacity of heterogeneous ozone catalysts, a large amount of organic matters in wastewater could be adsorbed on the surface to improve the treatment effect. Through the oxidation process, the biodegradability of wastewater was improved to facilitate subsequent advanced treatment. Ultimately, the effluent water quality could meet the three-level limit requirements in the "Integrated Wastewater Discharge Standard" (GB8978-1996), with the water index as follows: CODcr≤450 mg/L, BOD_5≤200 mg/L, SS≤200 mg/L, chromatic value≤32 times. This operational process was manifested to be economical and reliable, possessing a broad development prospect in wastewater treatment of dye intermediates related industries.

Keywords: Dye intermediate, Ozone, Catalytic Oxidation, Biochemical Degradation

1. Introduction

Dye intermediates generally refer to various aromatic derivatives used in the production of dyes and organic pigments, which are widely used in textile, medicine, chemical and other industries. The production process of dye intermediates involves a series of chemical unit operations such as sulfonation, nitration, reduction, halogenation, amination, and oxidation of basic organic raw materials such as benzene and naphthalene to generate complex organic compounds, including benzidine, some toxic substances such as pyridine, ammonia and phenol. These toxic substances will be discharged into the production wastewater, which are not only more difficult to degrade, but also inhibit the growth of bacteria [1]. Therefore, the dye intermediate production wastewater is low in biodegradability and difficultly treated. Traditional technology is difficult to meet the standard treatment, and it will have a greater negative impact on the environment if it is directly discharged [2].

Recently, some advanced technologies have been developed to treat the dye intermediate wastewater, including electrically assisted Fenton, UV-based oxidation, sonication, and membrane filtration [3-5]. For example, Menon et al. [5] have succeeded in removing organic nitrogen from the dye intermediate wastewater through a combined process of electro-Fenton and sonication. However, most of these reported technologies were implemented in the laboratory and had defects such as unstable operation or high cost. The information on the application of dye intermediate wastewater treatment with advanced technologies is limited.

In this project, the wastewater from the production of dye intermediates in a chemical enterprise in Jiangxi province was pre-treated by the process of "coagulation sedimentation + ozone catalytic oxidation" to improve the biodegradability, then the "hydrolysis acidification + contact oxidation" system was used for biochemical treatment. Also, the effluent indicators are stable to meet the management requirements in the "Integrated Wastewater Discharge Standard" (GB8978-1996). This case can provide a reference for the industry to treat wastewater.

2. Water Quantity and Quality Design

The designed wastewater treatment capacity of the project is 180 m^3/d. The discharge after treatment should meet the requirements of class III limit in “Integrated Wastewater Discharge Standard” (GB8978-1996) and be incorporated into the sewage pipe network of the local industrial park. The inlet and outlet water quality is shown in Table 1 below.

Table 1. *Actual inlet water quality and designed outlet water quality.*

Project	pH	COD_{cr} (mg/L)	BOD_5 (mg/L)	SS (mg/L)	Chroma (times)
Influent water quality	2~14	≤8500	≤820	≤160	≤600
Discharge standard	6~9	≤500	≤300	≤400	/

3. Process Flow

3.1. Process Flow Description

According to the characteristics of wastewater quality and treatment requirements, "coagulation chemical precipitation + ozone catalytic oxidation" is mainly adopted in the wastewater pretreatment process, which can greatly improve the biodegradability of wastewater and reduce the pollution load of subsequent biochemical facilities. The technological process is shown in Figure 1.

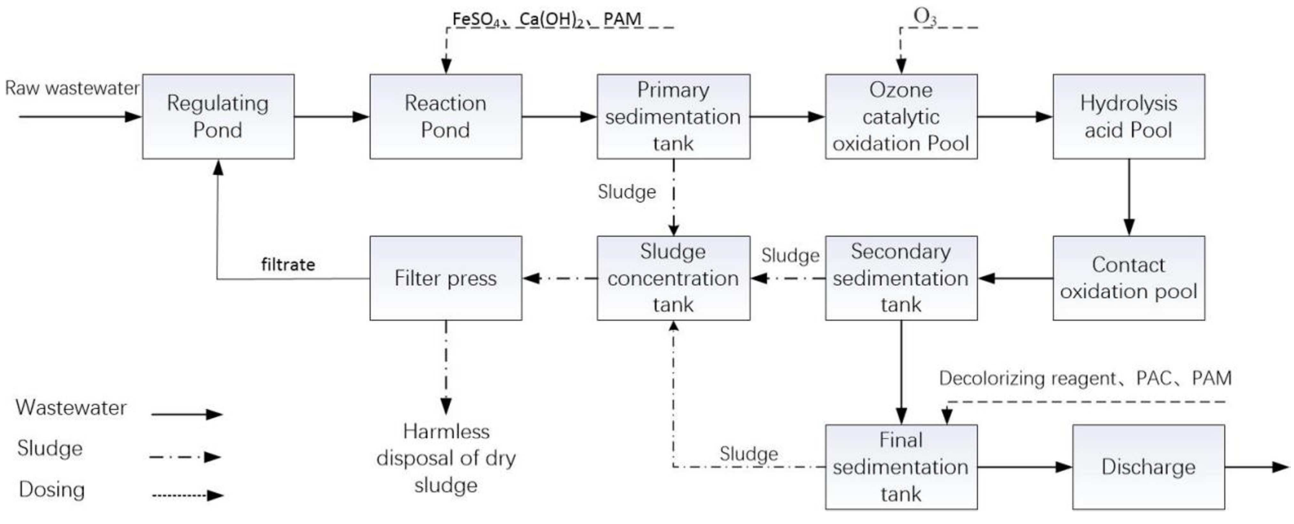

Figure 1. *Process flow chart.*

The collected wastewater in the plant area flows into the regulating tank where the water quality and volume are adjusted to achieve the effect of homogeneity and uniformity. The wastewater from the adjustment tank is lifted by a pump to the reaction tank, then ferrous sulfate and lime solution are added so that the pH of the reaction system can be adjusted to about 8.0. Later, the fine suspended particles in the wastewater are flocculated into larger flocculent particles by adding PAM so as to enter the primary sedimentation tank to separate the mud and water. Since the raw water contains a certain amount of suspended matter, and most of the organic matters and salt are attached to the suspended matters while removing the suspended matter, it can also reduce the concentration of pollutants such as organic matters and salt in the wastewater.

The supernatant in the primary sedimentation tank automatically flows into the ozone catalytic oxidation tank. Under the action of the heterogeneous catalyst, the O_3

generated by the ozone generator oxidizes the soluble organic matters that are difficult to biodegrade, interrupts the organic macromolecular chain, and greatly improves the biodegradability of the wastewater, while reducing the chromaticity and CODcr of the effluent. The effluent enters the hydrolysis acidification tank to hydrolyze organic pollutant molecules and enhance the adaptability of microorganisms [6]. The effluent from the hydrolysis acidification tank flows into the contact oxidation tank for aerobic biochemical treatment. Most of the small molecular organic matters in this unit are decomposed into CO_2 and H_2O under the action of the microbial membrane, and the remaining small part is assimilated into bacteria. The effluent from the biochemical tank enters the secondary sedimentation tank to separate the mud and water, and remove the suspended solids such as aging and dead bacterial membranes. The effluent from the secondary sedimentation tank finally enters the reaction final sedimentation tank where the water color, residual organic pollutants and suspended solids and other pollution indicators are further removed by adding decolorizers, PAC, PAM and other agents, hence the effluent is discharged through the standard discharge outlet.

3.2. Process Characteristics

3.2.1. Analysis of Chemical Oxidation Process

Since many heterocyclic pollutants in the wastewater of this project are the organic pollutants that are difficult to biochemically degrade, it is necessary to set up a chemical oxidation unit for pretreatment to improve the biodegradability of the wastewater. Considering the factors such as the scale of wastewater of this project, water quality characteristics, operating costs and control requirements, Fenton oxidation and ozone oxidation are regarded as the more suitable chemical oxidation processes. The comparison of the two oxidation processes is shown in Table 2.

Table 2. *Comparison of Fenton oxidation and ozone oxidation.*

Project	Fenton oxidation	Ozone oxidation
Oxidation-reduction potential	2.80V	2.07V
Major equipment	Dosing system, Fenton oxidation pool	Ozone generator, oxidation pond
Oxidation effect	Strong	Stronger
Usage of medicament	Iron salt, hydrogen peroxide, acid, alkali	Air or liquid oxygen
Secondary pollution	Sludge	Nothing
Advantage	Good oxidation effect and low equipment investment cost	Simple operation, does not affect subsequent desalination
Shortcoming	Good oxidation effect and low equipment investment cost	Higher operating costs and large equipment investment

It can be seen from the above table that both Fenton oxidation and ozone oxidation can oxidize and destroy the organic molecular structure, thereby improving the biodegradability of wastewater. However, Fenton oxidation will increase the salt concentration such as iron ions in the wastewater, and produce a large amount of sludge, which not only causes secondary pollution but also increases operating costs. In addition, the remaining Fenton reagent easily affects the normal growth of microorganisms in the subsequent biochemical processing unit, which results in the risk of paralysis of the biochemical system existing [7]. The ozone oxidation process can effectively avoid the occurrence of the above situation and has less impact on the subsequent biochemical units. Therefore, the ozone oxidation process was adopted for chemical oxidation pretreatment of wastewater in this project.

3.2.2. Reaction Mechanism and Advantages of Heterogeneous Catalysts

Reasonable use of catalysts can improve the efficiency of ozone oxidation. Metal ions are used as catalysts in homogeneous ozone catalytic oxidation, which are difficult to recover and easy to cause secondary pollution of water bodies, leading to higher water treatment costs, so heterogeneous ozone catalytic oxidation has attracted increasing attention [8]. In heterogeneous ozone catalytic oxidation, the catalyst exists in solid form, and the reaction can be carried out in water or on the surface of the catalyst. When ozone and organic pollutant molecules are adsorbed on the surface of the catalyst alone or at the same time, they can promote the occurrence of heterogeneous ozone catalytic oxidation [9]. The specific reaction mechanism is shown in Figure 2.

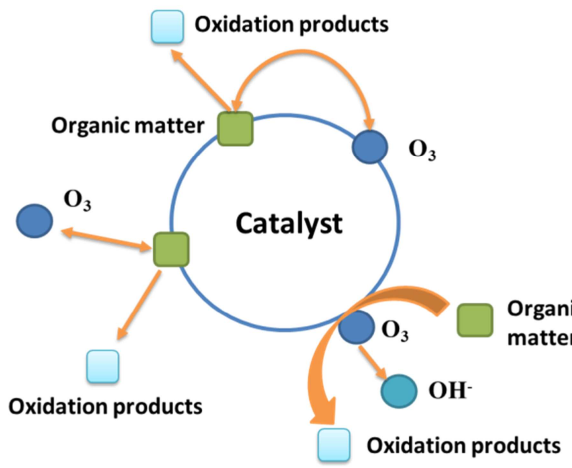

Figure 2. *Catalytic mechanism of heterogeneous ozone.*

Due to the high activity, low cost, easy recovery and strong adsorption capacity of ozone heterogeneous catalysts, a large amount of organic matters in wastewater can be adsorbed on the surface to improve the treatment effect [10]. Compared with pure ozone oxidation, it overcomes the traditional ozone's shortcomings, low utilization rate and weak oxidizing ability, and also possess extremely strong oxidizing ability to mineralize organic matters completely. Ren et al. [11] used

NdFeB magnetic activated carbon to catalyze ozone degradation of methyl orange in water, and the reaction rate constant was three times that of ordinary activated carbon. The permanent magnet powder with high magnetic properties was adopted in this project to be loaded on granular activated carbon. It was used as a heterogeneous catalyst in the ozone oxidation pretreatment process unit, which can achieve fast reaction speed, low catalyst dosage, high decomposition rate of organic pollution [12-15].

4. Main Structures and Design Parameters

4.1. Regulating Pond

One pond used for uniforming quality and quantity of wastewater; 4.0 m × 5.0 m × 3.5 m in size, 60 m^3 in effective volume and 8h hydraulic retention time; equipped with underground steel concrete structure; anti-corrosive treatment by epoxy resin with clothing three layers and smearing five times.

Auxiliary equipment: 2 lifting pumps with 10 m^3/h single flow rate, 15 m head and N=1.1 kW; 1 for use and 1 for standby; 1 set of ultrasonic level gauge; 1 set of electromagnetic flow meter.

4.2. Reaction Pond

Three reaction ponds used for coagulation reaction; 2.0 m × 1.5 m × 2.0 m in size, 5 m^3 in effective volume and 0.6 h reaction time; equipped with the above-ground steel concrete structure; anti-corrosion treatment by epoxy resin with clothing three layers and smearing five times.

Auxiliary equipment: 3 sets of mechanical agitators with 1.1 kW per set; 3 sets of dosing devices including 3 PE dosing barrels with 1 ton each, 3 sets of chemical agitators with 0.75 kW each and 3 sets of 200 L/h metering pumps; 1 set of online pH meter.

4.3. Primary Sedimentation Tank

One primary sedimentation tank used for solid-liquid separation; 6.0 m × 2.0 m × 4.0 m in size, 11 m^2 effective flow area and 0.68 $m^3/m^2 \cdot h$ surface load; equipped with semi-ground steel concrete structure.

Auxiliary equipment: 2 mud pumps with 10 m^3/h flow rate, 15 m head and N=1.1kW; 1 for use and 1 for standby; honeycomb inclined plate 11 m^2.

4.4. Ozone Catalytic Reaction Pool

One ozone catalytic reaction pool used to oxidize organic pollutants and improve the biodegradability of wastewater; 3.0 m × 5.0 m × 4.0 m in size, 53 m^3 in effective volume and 7 h reaction time; equipped with the semi-ground steel concrete structure; anti-corrosion treatment by epoxy resin with clothing three layers and smearing five times.

Auxiliary equipment: 1 set of aeration and stirring system made of UPVC; 2 sets of ozone generator with 55 kW each; 15 m^3 permanent magnet loaded activated carbon.

4.5. Hydrolysis Acidification Tank

One hydrolysis acidification tank used to further decompose macromolecular organic pollutants and promote the adaptability of microorganisms; 5.0 m × 5.0 m× 4.0 m in size, 88 m^3 in effective volume and 11h the residence time; equipped with the semi-ground steel concrete structure.

Supporting materials: D150 combined packing and 88 m^3 support; 12 sets of rotary mixing aerator.

4.6. Contact Oxidation Pool

One contact oxidation pool used for biological absorption and degradation of organic pollutants; 4.0 m × 8.0 m × 4.0 m × 2 cells in size, 224 m^3 in total effective volume and 0.6 kg CODcr/$m^3 \cdot h$ volumetric load; equipped with semi-ground steel concrete structure.

Auxiliary equipment: 2 Roots blowers with air volume 2.44 m^3/min, P=39.2 kPa and N=3.0 kW; 1for use and 1 for standby; D150 combined packing and 224 m^3 support; 128 sets of rotary mixer aerators; 2 reflux pumps with 20 m^3/h flow; 15 m head and 1.5 kW in power; 1 for use and 1 for standby.

4.7. Secondary Sedimentation Tank

One secondary sedimentation tank used for solid-liquid separation to remove suspended particles such as dead and aging bacteria; 6.0 m × 2.0 m × 4.0 m in size, 11 m^2 effective flow area, and 0.68 $m^3/m^2 \cdot h$ in surface load; equipped with the semi-ground steel concrete structure.

Auxiliary equipment: 2 mud pumps with 10m^3/h flow rate, 15 m head, rand 1.1 kW in power; 1 for use and 1 for standby.

4.8. Final Sedimentation Tank of Reaction

One final sedimentation tank of the reaction used for coagulation reaction to further remove residual organic pollutants and suspended solids; 8.0 m × 2.0 m × 4.0 m in size, in which 2.0 m × 2.0 m × 4.0 m for the reaction zone and 6.0 m × 2.0 m × 4.0 m for sedimentation area; 1.8 h reaction time, 11m^2 effective overflow area, and 0.68 $m^3/m^2 \cdot h$ surface load; equipped with the semi above-ground steel concrete structure.

Supporting equipment: 3 mechanical agitators with a single power of 1.1 kW; 3 sets of dosing devices, including 3 sets of 1-ton PE dosing barrels, 3 chemical agitators with power of 0.75 kW, and 3 metering pumps with measuring range of 200 L/h; Two sludge pumps with flow of 10 m^3/h. Lift 15 m, power 1.1 kW, one for use and one for standby.

5. Operation Effect and Economic Analysis

After the completion of the project, the system has operated stably through 4-5 months' commissioning. Monitored repeatedly by the local third-party testing agency, the effluent quality is as follows: pH=6.5~7.5, CODcr≤450 mg/L, BOD_5≤200 mg/L, SS≤20 mg/L, chromaticity≤32 times, stably meeting the relevant requirements of "Integrated Wastewater Discharge Standard" (GB8978-1996). Table 3 shows the monitoring results of the inlet and outlet water of each process unit. Among them, the CODcr removal rate of the wastewater stayed above 95% stably after the combined process of "ozone catalytic oxidation + biochemical degradation". Through the ozone catalytic oxidation, the wastewater BOD/COD value could be stably maintained above 0.32, and the biodegradability was significantly improved. The improvement of the biochemical degradation unit effectively guaranteed the stable operation of the subsequent biochemical degradation unit.

Table 3. *Monitoring results of effluent quality of each process unit.*

Process unit	pH	COD_{cr} (mg/L)	BOD_5 (mg/L)	SS (mg/L)	Chroma (times)
Regulating tank	2~14	7350~8370	524~812	136~152	256~512
Primary sedimentation tank	6~9	6223~6885	618~675	26~38	64~128
Ozone catalytic oxidation	6~9	5590~5688	1945~1832	35~48	16~32
Biochemical-Secondary Sedimentation Tank	6~9	423~472	189~197	25~33	32~64
Final sedimentation tank of reaction	6.5~7.5	372~420	152~176	10~16	16~32

The total investment of this project is about 2.7 million yuan, including about 2.13 million yuan used for equipment and materials investment, and about 570,000 yuan used for civil engineering investment. The direct operating cost of wastewater facilities is about 9.33 yuan/m^3, among which the power consumption of the equipment calculated at 80%, consuming 1380.79 yuan per day, which is equivalent to 7.67 yuan per ton of water treatment; the daily chemical fee is about 65.60 yuan, which is equivalent to 0.36 yuan per ton of water treatment; and there are 2 operators with 1.30 yuan/m^3 wastewater.

6. Conclusion

The combined process of "coagulation precipitation-ozone catalytic oxidation-biochemical degradation" was used in this project to treat dye intermediate production wastewater, and the effluent index could stably meet the requirements of the third-level limit in the "Integrated Wastewater Discharge Standard" (GB8978-1996).

The key process unit of this project is heterogeneous ozone catalytic oxidation. This technology has high treatment efficiency without secondary pollution. During the reaction process, the biodegradability of wastewater can be improved to facilitate subsequent advanced treatment. Due to the advantages of the process, such as low cost, high efficiency, stable operation, etc., the process can provide a reference for the standard treatment of high-concentration refractory organic wastewater such as dye intermediate production wastewater. In the future, the operation parameters of the catalytic process should be further optimized, which will lead to broad application prospects.

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