

# A Case Study of Dyestuff Chemical Wastewater Treatment Project

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**Abstract:** The wastewater treatment engineering design scale of a certain dye group co., LTD in Xuzhou is 3000m<sup>3</sup>/d. According to the characteristics of dyestuff wastewater, the combined treatment process of "physicochemical + biochemical" was adopted. The engineering operation results show that the removal rate of COD, NH<sub>3</sub>-N and chroma is 93.1, 80.5 and 90.7 percent, and the effluent water quality is stable and meets the design requirements.

**Keywords:** Dyestuff Wastewater, Hydrolytic Acidification, SBR, The Test and Operation

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## 1. Introduction

Jiangsu Xuzhou dyestuff Group co. LTD. located in the east development area of Xuzhou city, is a joint-stock enterprise engaged in the production and export of reducing series of dyestuff, dyestuff intermediates, building paint, industrial paint and industrial glue. The company has more than 1200 employees, with annual capacity of about 3500 tons. The main products are: reducing olive T primary dye, reducing brown BR primary dye, reducing blue RSN primary dye, synthetic anthraquinone, 1-amino anthraquinone, etc. It is the largest and most comprehensive anthraquinone reduction dye production base in China and one of the domestic military camouflage dye production enterprises.

The company is equipped with sewage treatment plant. In 2013, the company improved the wastewater treatment process and carried out comprehensive remediation on the sewage pipe network of the plant, which improved the treatment level of pollutants and ensured the stable and standard discharge of water quality. The treated tail water through kui river to a 20,000-ton daily urban sewage treatment plant about 7 kilometers south of the company for comprehensive treatment [1].

## 2. General Situation of Sewage Treatment Project

The waste water mainly comes from the production process: first, the mother liquor water, mainly composed of waste acid and waste alkali mother liquor, contains water and some unreactive substances, reactants [2], organic solvents, inorganic salts and a small amount of products; The second is the water washing liquid, which is mainly produced when the product is washed, and this part of waste water is directly discharged into the waste treatment workshop.

As most of the waste water comes from dye production workshops, the waste water produced by them is highly concentrated and contains a large amount of dye, which is one of the wastewater that is difficult to degrade [3]. These high concentration of wastewater contain a large number of unreacted chemicals, solvents and generated by-products, with high concentration of COD, various organic chemicals and great toxicity. Among them, polyphenyl pollutants are difficult to be degraded by microorganisms, and their entry into the environment has a great impact on human health and ecological environment [4].

In view of the water quality characteristics of the above wastewater, the treatment of dyestuff wastewater should

adopt the comprehensive treatment technology which is mainly based on biological treatment and supplemented by physical and chemical treatment [5]. In order to ensure the effective collection of waste water, the company carries out the classification collection and quality treatment of waste water according to the principle of waste separation and separation. High concentration wastewater and low concentration wastewater are individually collection of transportation network, laid in the mother liquor discharge port set high concentration wastewater collection pool, collect mother liquor concentration [6], burned by the

incinerator and the rest of the wastewater collected by the special network, enter the pretreatment +micro electrolysis + hydrolytic acidification + SBR + air flotation + sand filtration and activated carbon combination process.

### 2.1. Design Scale and Water Quality of Inlet and Outlet

According to the test data provided by the company and the field investigation, the production process and discharge water quality and quantity are analyzed as follows.

#### 2.1.1. Shop Displacement

**Table 1.** Table of the amount of waste water produced.

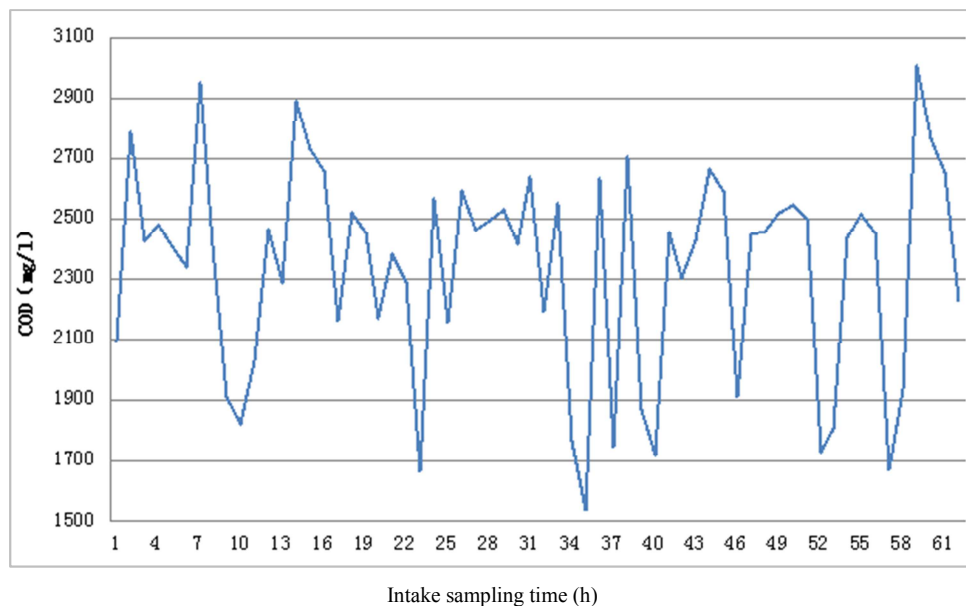
| project                                    | 1 workshop | 2 workshop | 3 workshop | 4 workshop | 5 workshop | 6 other | 7 The total |
|--|------------|------------|------------|------------|------------|---------|-------------|
| Mother liquor quantity (m <sup>3</sup> /a) | 16000      | 13000      | 6000       | 21000      | 7200       | 65000   | 624400      |
| $\rho$ (CODCr) (mg/L)                      | 11200      | 12100      | 1700       | 980        | 1200       | -       | -           |
| Rinse water (m <sup>3</sup> /a)            | 130000     | 98000      | 6200       | 192000     | 70000      | -       | 496200      |

According to the analysis in table 1, the annual waste water is about 624400m<sup>3</sup>, in which the mother liquid volume is 63200m<sup>3</sup>, the amount of flushing water is 496,200m<sup>3</sup>, and the other amount of water (including uncounted water

amount, living water amount, etc.) is 65000m<sup>3</sup>.

The company produces about 300d/a, and the discharge volume is about 2081m<sup>3</sup>/a, The design coefficient is 1.44. Therefore, the design scale of this project is 3000m<sup>3</sup>/d.

#### 2.1.2. Design Standards for Water Quality of Inlet and Outlet Water



**Figure 1.** Trend of COD data in water inflow.

Production of the company is affected by the season and the market, the determination of the quality of inflow water shall refer to similar dyestuff production enterprises, and the effluent water quality shall comply with the water quality standard of sewage discharge into urban sewage discharge,

which is second to grade B of cj343-2010. According to the requirements of the water environment in the region where the enterprise is located, the water quality of effluent shall be subject to the standards approved by the local environmental protection bureau.

**Table 2.** Design water quality of inlet and outlet water Unit: mg/L.

| Project name | PH      | $\rho$ (CODCr) | Chroma   | $\rho$ (BOD <sub>5</sub> ) | $\rho$ (SS) | $\rho$ (NH <sub>3</sub> -N) | Sulphide |
|--------------|---------|----------------|----------|----------------------------|-------------|-----------------------------|----------|
| Influent     | 4-9     | 3500-5000      | 500-1000 | 1920-2000                  | ≤1500       | 40                          |          |
| effluent     | 6.5-9.5 | ≤500           | ≤70      | ≤350                       | ≤400        | ≤45                         | 1.0      |
| effluent     | 6-9     | ≤350           | ≤80      | ≤100                       | ≤150        | ≤25                         | 1.0      |

## 2.2. Wastewater Treatment Process

Dye wastewater is characterized by large chroma, high COD, complex composition and difficult degradation. At present, domestic treatment of this kind of wastewater mainly adopts the combination process of "pretreatment + biochemical treatment". Including: physical chemistry method, chemical method, biochemical method, SCWO, ozone [7] etc. This project adopts the combined process of "pretreatment + micro-electrolysis + hydrolytic acidification + SBR + air flotation + sand filtration and activated carbon" [8] according to the actual situation in the field.

The mother liquid is discharged from the production workshop, which is collected and sent to the incinerator for incineration treatment or recycling. The remaining waste water flows into the adjustment tank through the elevated sewage collection pipe for the first regulation of PH value, which controls the PH value of about 4.5-6.5. The ferrous sulfate liquid agent is pumped into the pipeline, and enters the micro-electrolysis device through the DN125 pipeline

mixer [9], and then flows into the regulating pool for the second regulation of PH value, controlling the PH value about 7.5-8.5. The reaction precipitates in the two regulating pools were introduced into two plate and frame filter press for dewatering treatment. The waste water of the final stage regulating tank is pumped into the inclined plate sedimentation tank by the lifting pump, and the supernatant after precipitation flows into the hydrolysis acidification tank for treatment, and then flows into the secondary biochemical tank (SBR treatment process) for biological treatment. Decanting the precipitated supernatant into the intermediate tank by decanter with the private equipment decanter, and then lifting the pump to the shallow gas floatation according to the monitoring data and drainage requirements, decolorizing and removing SS, etc., which then flow into quartz sand and activated carbon devices, and then discharge up to standard after filtration. The treated sludge is partly sanitary landfill and partly transported to the brick factory as raw material for burning bricks [10].

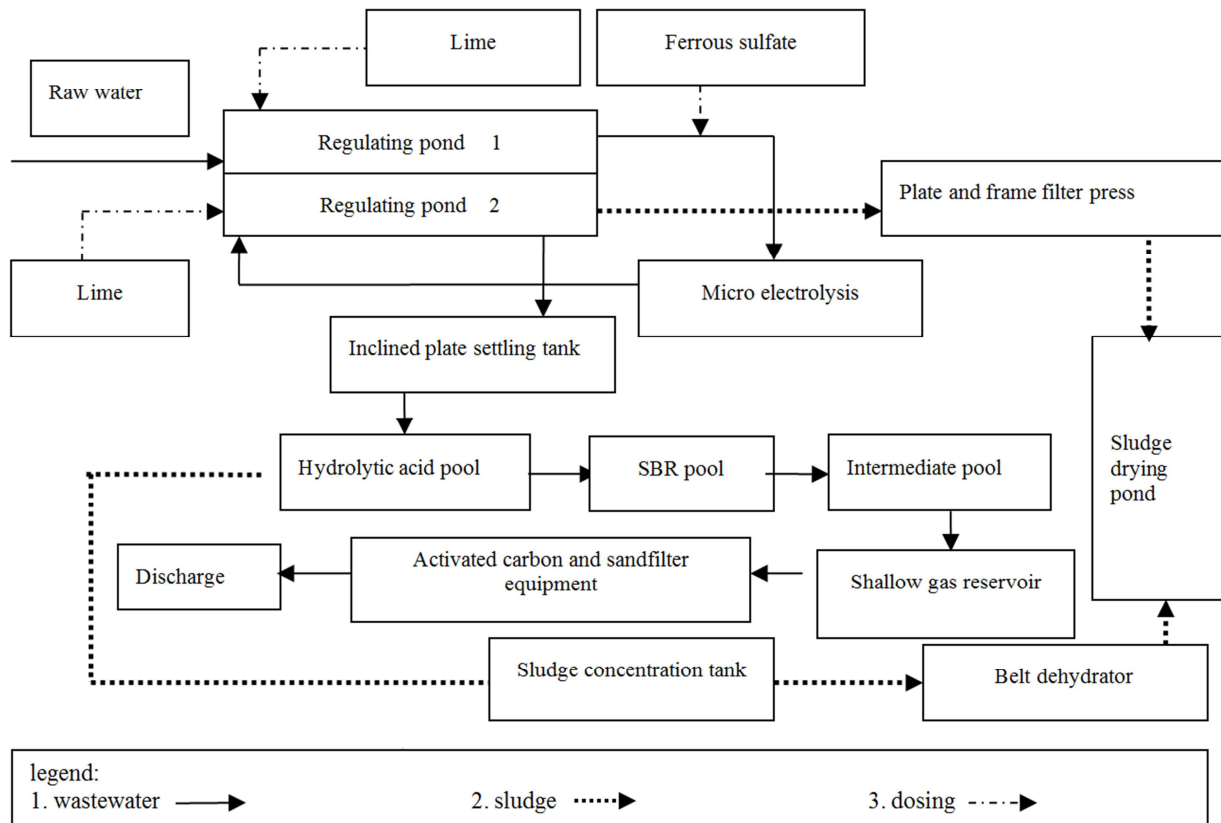


Figure 2. Sewage treatment flow chart.

## 2.3. Mainly Deals with Structures and Design Parameters

### 2.3.1. Regulating Pond: Underground Steel Concrete Structure

Size: 30m × 12.5 m × 5.5m, effective volume 1875m<sup>3</sup>.

The adjustment pool is designed to be 2 grids. Each cell design is divided into three parts: 1 neutralization reaction area, contact reaction time 5.76h; 2 Precipitation area,

precipitation time 9.6h; 3 Buffer, stay at 3.84h. The discharge water in the sediment area is designed as overflow discharge, and the bottom is modified with an enhanced sludge discharge device. The model of the suction pump is zws65-65-190.

One roots fan, model: nsr-200h. Q26.62m<sup>3</sup> / min; 73.5 kPa pressure; 30 kw power. The gas-water ratio is 12.8: 1.

### 2.3.2. Micro Electrolysis Device: Concrete Structure of Ground Steel

Size: 5.0 m×4.0 m×5.0 m.

The iron carbon packing layer is 1.5m high, with aeration stirring device on the bottom. According to the pilot test results, the quality ratio of iron filings to coke was 0.8: 1.1. Iron source steel processing plant raw materials, coke source plant procurement self-processing: particle size is more than 5mm.

### 2.3.3. Inclined Plate Settling Tank: Concrete Structure of Ground Steel

Size: 13.0 m×5.5 m×4.5m.

Rising velocity in clear water area  $V=3.0\text{mm/s}$ . Use hexagonal plastic sheet, 1m long, 66 degrees horizontal inclination. To facilitate the uniform water distribution, the installation method is retrograde compression. The bottom volume was 169 m<sup>3</sup>, and the perforated pipe was used to discharge mud.

### 2.3.4. Hydrolysis Acidification Pool [11]: Concrete Structure of Ground Steel

Size: 32.0 m×6.0m×5.5m.

Effective volume: 960m<sup>3</sup>, residence time: 7.68h. The pool is filled with semi-soft filler: H=2.7m; The volume rate is 70 times 1 liter.

### 2.3.5. SBR Pool: Concrete Structure of Ground Steel

Size: 30.0 m×8.0m×5.0m.

Effective volume: 1080m<sup>3</sup>, residence time is 8.64h. Volume load: 0.5kgCOD/m<sup>3</sup>·d.

4 roots fans: Type of NSR – 125A. Q = 13.60 m<sup>3</sup>/ min; 58.8 kPa pressure; Power 15 kw. The gas-water ratio is 26.1: 1.

### 2.3.6. Shallow Air Flotation Device [12]: Complete Equipment on the Ground

Model no.: zcqh-30. Effective pool depth: 400mm; Residence time: 3.5-5.5min.

### 2.3.7. Upflow Sand Filter

Size: Φ 3.0 m by 2.0 m. Filter velocity: 10m/h. Lower power backflush.

Table 3. List of filling dimensions of sand filter packing layer.

| Layer Number       | 1    | 2   | 3   | 4   | 5     |
|--------------------|------|-----|-----|-----|-------|
| particle size (mm) | 8-10 | 5-6 | 2-3 | 1-2 | 0.5-1 |
| Fill Height (mm)   | 100  | 100 | 100 | 200 | 300   |

### 2.3.8. Activated Carbon Installation

Size: Φ 2.6 m by 2.5 m. Design parameters: the flow rate of the empty tank is 10m/h; Water rate: 5.5m<sup>3</sup>/kg; Carbon layer density is 0.42t/m<sup>3</sup>.

## 2.4. Engineering Design Features

In order to ensure the continuous and stable operation of the wastewater treatment unit, the treatment method combined with the special pollution factors is adopted.

Engineering design:

### 2.4.1. Mother Liquor Recycling and Incineration Process

Main function: 1. The raw slag which has not been fully reacted is extracted and used for production; High concentration of waste residue and waste liquid will be incinerated to relieve the pressure of subsequent treatment units.

### 2.4.2. Lime Installation [13]

The main function of the original injection of caustic soda is to adjust the PH value of the waste water in the workshop and adjust it to be lime neutralization according to the actual situation. The adjustment pool is divided into two parts to improve the mobility and flexibility of operation.

The first lime is mainly used to adjust the PH value of raw water. The role of the second channel is: the elastomer regulates the PH value of the micro-electrolysis water; Removal of sulfide from the reduction wastewater by curtailing; Broken benzene ring and long chain compound.

### 2.4.3. Ferrous Sulfate Casting Device

Main function: use Fe<sup>2+</sup> to replace Cu<sup>2+</sup> from the complex, and then add lime to remove Cu; 2. The excessive reaction of iron salt and lime can produce iron hydroxide precipitate, which can absorb other pollutants at the same time. In this project, the amount of water input is adjusted according to the discharge condition of the regulating pool 1, which is generally 12%.

### 2.4.4. Adjust the Direction of Water Intake in the Hydrolysis Acidification Tank

The direction of water intake in the original hydrolysis acidification tank is the longitudinal water inflow along the length of the pool.

### 2.4.5. Adding Agents to Shallow Air Flotation

According to the actual situation of the effluent from SBR pool, adjust the type and variety of adding agents to shallow air flotation [14].

Table 4. Empirical data of drug combinations.

| Drug combination     | PAC+PAM | PAM+Al <sub>2</sub> (SO <sub>3</sub> ) | PAM+FeCl <sub>3</sub> |
|----------------------|---------|--|-----------------------|
| COD Removal Rate (%) | 90.2    | 80.1                                   | 99.3                  |
| Decolorizing Effect  | general | Better                                 | good                  |

The selected potion in this project is "PAM+FeCl<sub>3</sub>". PAM and FeCl<sub>3</sub> add 3 to 5 per thousand.

### 2.4.6. Sand Filter and Activated Carbon Device

According to the requirement of local water environment, the effluent of shallow air floatation is treated in depth. Make use of the original waste cans in the factory. Sand filter tank 1, size: 3000 X Φ 2000; 1, activated carbon tank size Φ X 2500 2600. According to the characteristics of dyestuff wastewater, the packing in activated carbon canister was combined. Arrangement: supporting layer: 8-10mm quartz sand; The second layer: 1-2mm lignite; The third layer: 1.40-1.70mm and 0.425mm bituminous coal. Each layer is laid with a stainless steel grating with different apertures.

## 2.5. Analysis of Operation Results

The rectification of the waste water treatment station was completed from March 1 to the end of July, and the commissioning and operation of the new system began on August 1.

### 2.5.1. Wastewater Quality

In the initial debugging operation stage, the first step is mainly the linkage of the whole system. At this stage, it was found that the workshop wastewater fluctuated greatly due to the particularity of production, but the water intake could be regulated through the emergency pool and the first adjustment pool.

### 2.5.2. Debugging Operation Management

#### i. Nutrient addition [15]

According to the characteristics of dye wastewater and the changes of water quality of intake, the nutrition ratio should be adjusted timely:

1. Add flour: 4.5-7.5kg/100m<sup>3</sup> water;
2. Potassium dihydrogen phosphate added: 0.07 to 0.21kg/100m<sup>3</sup> of water;
3. Urea addition: 0.9-2.7kg/100m<sup>3</sup> water.

#### ii. Regulate the control of the pool

Due to the use of lime neutralization, more sediment, so to add 2 plate frame filter press. The pH value of the first adjustment pool is controlled at 4.5-6.5. The pH value of the second adjustment pool is controlled at 7.5-9.0.

#### iii. Control of micro electrolytic devices

Pay attention to the bubbles on the surface of the micro-electrolysis cell, and add coke or iron scraps according to the number of bubbles and the frequency of the bubbles.

#### iv. Running adjustment

Features of SBR operation mode [16]: The operation mode of time division replaces the operation mode of space division. If by water time, reaction time, precipitation time, decanting time, mud discharge time and idle time, can be adjusted appropriately and flexibly. During the operation, it was found that the automatic control device of SBR pool could not meet the requirement of nitrification, so the operation time of SBR pool was adjusted according to the field conditions: aeration time was greater than 10h; Precipitation time: 3.5h; Water inflow time is 3.5h. The entire operating cycle is greater than or equal to 18h. Operation mode: adopt 4 pool linkage step operation.

#### v. Maintenance of processing system during shutdown

When enterprises stop production in a seasonal manner, the SBR system can be maintained in a normal operation by applying aeration and adding nutrients.

### 2.5.3. Engineering Efficiency

The project has been in stable operation since December 1. SBR discharge water was basically up to standard during operation, so the sand filter and activated carbon device were not activated. The removal rate analysis of processing units is shown in table 5.

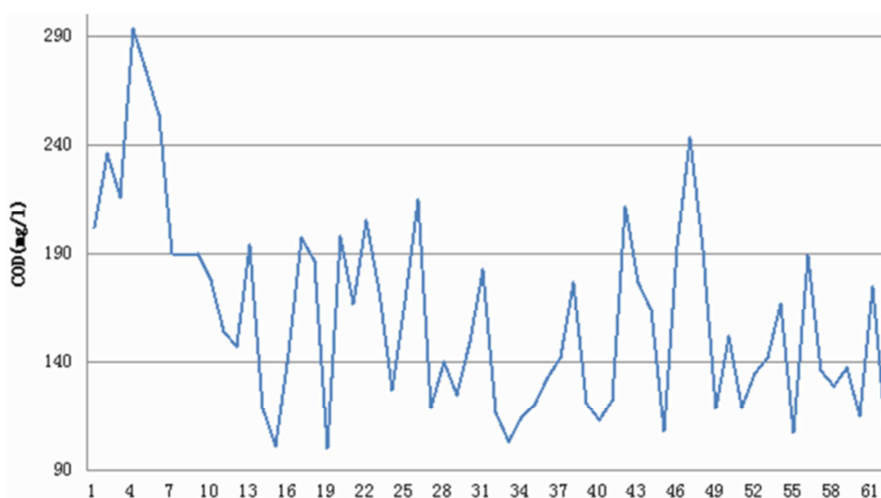


Figure 3. Effluent trend diagram.

Table 5. Removal rate analysis of processing units (mg/L).

| Processing unit               | CODcr | BOD  | SS   | NH3-N | Chroma (degree) | p (sulphide) |
|-------------------------------|-------|------|------|-------|-----------------|--------------|
| Adjustment Pool               | 2337  | 362  | 1480 | 52    | 800             | 1.5          |
| Hydrolysis Acidification Pool | 1389  | 432  | 240  | 36    | -               | -            |
| SBR Pool                      | 258   | 80.0 | -    | 14    | -               | -            |
| Shallow Air Floating Pool     | -     | -    | -    | -     | -               | -            |
| Middle Pool                   | 162   | 30.0 | 78   | 12    | 60              | 0.08         |
| Removal Rate (%)              | 93.1  | 91.7 | 94.7 | 77.0  | 92.5            | 94.7         |
| Standard                      | 350   | 100  | 150  | 25    | 80              | 1.0          |

The combined process adopted in this project is used to treat this kind of dye wastewater. The effluent quality is

relatively stable and the impact load is strong.



### 3. Conclusion

This process rectification investment is about 1.5 million Yuan. At present, although the operating cost is reduced from 15.8 Yuan /m<sup>3</sup> to 7.5 Yuan /m<sup>3</sup>, the burden is still heavy for the enterprise. How to absorb investment and reduce costs and increase efficiency will become the focus of the next step. Through the operation of nearly half a year, it is shown that the process operation is stable after rectification, the water outlet is stable and up to standard, and the environmental protection acceptance is passed. In the past year, the most prominent problem is that there are many lime residues. Although the enterprise does everything possible to find solutions, such as burning bricks to the brick factory and adding plate and frame filter press, how to choose a good neutralizer and consider the operation cost of the enterprise will still be the future research direction.

To sum up: the design of dye wastewater should take into account the actual situation of the enterprise and the seasonal production. How to combine the process, how to simplify the operation mode of the process and reduce the operation cost of the enterprise need further research and discussion.

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### Biography



**Xianglin Wu** (1970-), male, Han nationality, undergraduate, senior environmental engineer, invention of pre-denitrification A2/O process patent, mainly engaged in sewage treatment process rectification and commissioning.



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