A Treatment Design and Operation Effect of Membrane Material Production Wastewater Treatment Project

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Abstract: Classification treatment was applied for the fluorine-containing membrane material production wastewater, which was low biodegradability with high concentration of fluoride and salinity. Salinity wastewater was collected and pretreated by three-effect evaporation and ozone oxidation for desalting and improving the biodegradability, then mixed with other production wastewater with low concentration. Mixed wastewater was treated by hydrolysis acidification, AO biological treatment and modified Fenton treatment process. The operation results of stable operation showed that when the influent concentrations of COD, NH₃-N, fluoride, TN and TP were 5000mg/L, 50mg/L, 5000mg/L, 60mg/ and 1mg/L, the effluent mean concentrations were 32mg/L, 1.2mg/L, 1.1mg/L, 13.5mg/L and 0.12mg/L, which could meet the discharge standards.

1. Introduction
In the direction of low-carbon and clean, the development mode of energy industry are undergoing profound changes. With the advantages of high energy conversion efficiency, safe and reliable, greenness and environmentally friendly, fuel cell is one of the most promising new green renewable energy to replace the traditional fossil energy[1~3]. The rapid development of fuel cells has promoted the continuous growth of related fluorine-containing membrane material fields, and the fluorine-containing wastewater has been produced constantly. The discharge of fluorine-containing wastewater will cause serious ecological pollution, local fluorine exceeding and threatening human health[4]. The wastewater from a fuel cell membrane material company is low biodegradability with high concentration of fluoride and salinity. According to the water quality, the treatment process was selected and designed, and the actual operation effect of the project was tracked to provide reference for the design of similar wastewater treatment plants.

2. General situation
2.1 Wastewater quality and quantity
According to the production information provided by the company, the main production wastewater could be divided into two types. Wastewater from post-treatment, vacuum displace and neutralization was high-concentration with fluoride and salt content, while wastewater from material washing, vacuum tank washing and domestic sewage in plant area was low-concentration. Quality and quantity of different kinds of wastewater is shown in table 1.
Table 1 Wastewater quality and quantity.

| Item                 | pH  | COD (mg·L⁻¹) | Fluoride (mg·L⁻¹) | TDS (mg·L⁻¹) | NH₃-N (mg·L⁻¹) | TN (mg·L⁻¹) | TP (mg·L⁻¹) | Quantity (m³·d⁻¹) |
|----------------------|-----|--------------|-------------------|--------------|----------------|-------------|-------------|-------------------|
| High-concentration   | 10~12 | 3800~4600 | 2900~4200 | 15000~20000 | 4.7~6.2 | 13.1~23.9 | 0.3~0.6 | 68.5 |
| wastewater           |     |             |                   |              |                |             |             |                   |
| Low-concentration    | 6~8 | 300~500      | 5.8~10.1          | 900~1500     | 26.6~34.9     | 32.1~50.7  | 0.4~0.9     | 371               |
| wastewater           |     |             |                   |              |                |             |             |                   |

According to the wastewater quantity and requirements of subsequent production expansion, the design process scale of high-concentration wastewater was 84 m³/d and 558 m³/d of low-concentration wastewater. The effluent quality of the treatment project should meet the first class A standard of discharge standard of pollutants for urban sewage treatment plants (GB 18918-2002), and the fluoride concentration of the effluent should be lower than 1.5mg/l according to the local section water quality control requirements. The design influent and effluent quality is shown in table 2.

Table 2 Design influent and effluent quality.

| Item   | pH  | COD (mg·L⁻¹) | Fluoride (mg·L⁻¹) | NH₃-N (mg·L⁻¹) | TN (mg·L⁻¹) | TP (mg·L⁻¹) | TDS (mg·L⁻¹) |
|--------|-----|--------------|-------------------|----------------|-------------|-------------|-------------|
| Influent | 6~9 | 5000         | 5000              | 50             | 60          | 1           | 20000       |
| Effluent | 6~9 | 50           | 1.5               | 5              | 15          | 0.5         | --          |

3. Wastewater treatment

Related studies have shown that the biodegradability of fluoride chemical wastewater was significantly enhanced after desalination and heavy metal removal. Therefore, the wastewater treatment system of this project was designed to collect high concentration wastewater separately and desalt by three-effect evaporation. After being desalted, it was pretreated with ozone oxidation to reduce the biological toxicity. The pretreated condensation was then discharged to the condensate storage tank and then pumped into the low-concentration regulating tank, mixed with other low concentration wastewater, and then treated in the subsequent biochemical treatment system.

The low-concentration production wastewater was designed to be collected and discharged to the low-concentration regulating tank to be mixed with the pretreated condensate, after adjusted the pH and balanced the water quality, the mixed wastewater was discharged into the subsequent “Hydrolysis acidification + AO treatment” process. Functional bacteria and microbial carriers was applied into the biochemical treatment to enhance the treatment efficiency. Functional microorganism technology is a hot issue in chemical wastewater treatment research [6,7]. By putting compound functional microbial agents and carriers into the AO biochemical system, a high concentration microorganism system would be quickly formed, and the mass transfer rate and degradation rate of refractory pollutants in wastewater would be greatly improved, so as to the removal efficiency of pollutants in the wastewater.

Due to the high requirement for discharge standards, advanced treatment was needed. "Modified Fenton" catalytic oxidation treatment technology was settled, and fluoride removal agent was added into the flocculation stage to achieve the synergistic and efficient removal of COD, fluoride and chromaticity. The flow chart of wastewater treatment process is shown in figure 1.
4. Main structures and design parameters

4.1 High-concentration wastewater pretreatment

4.1.1 High-concentration regulating tank
The structure of the tank body was reinforced concrete, inner wall was made of FRP for anti-corrosion, the overall dimension was 10m×4m×4.5m and designed residence time was 48h. It was equipped with agitators and four lifting pumps (Q=5m³/h, H=20m, W=1.5kW), two for use and two for standby.

4.1.2 Three-effect evaporation system
The overall dimension of triple effect evaporation equipment was 10m×5m×12m and the evaporation capacity was 3385kg/h, the consumption of steam was 1370kg/h, and the total power is 123.7kW. The main control parameters of three-effect evaporation system is shown in table 3.

Table 3 Main control parameters of three-effect evaporation system.

| Parameter               | One-effect evaporation | Two-effect evaporation | Three-effect evaporation |
|-------------------------|------------------------|------------------------|--------------------------|
| Heater temperature (℃)  | 100                    | 85±1                   | 70±1                     |
| Heater vacuum (MPa)     | 0                      | -0.045                 | -0.07                    |
| Separator temperature (℃)| 85±1                   | 70±1                   | 55±1                     |
| Separator vacuum (MPa)  | -0.045                 | -0.07                  | -0.086                   |

4.1.3 Ozone oxidation tank
The structure of the tank body was reinforced concrete and the overall dimension was 3m×1.5m×4.5m. The tank was equipped with agitators and titanium plate aerator. A 0.5kg/h gas production ozone generator system was equipped, as well as ozone exhaust breaker.
4.1.4 Condensate storage tank
The structure of the tank body was reinforced concrete and the overall dimension was 5m×4m×4.5 m.

4.2 Biochemical treatment

4.2.1 Low-concentration regulating tank
The structure of the tank body was reinforced concrete, the overall dimension was 10m×5m×4.5m and the designed residence time was 24h. The tank was equipped with agitators and two lifting pumps (Q=30m³/h, H=8.5m, W=1.5kW), one for use and one for standby.

4.2.2 Hydrolysis acidification tank
The structure of the tank body was reinforced concrete, the overall dimension was 6m×6m×6.5m and the designed residence time was 24h. It was equipped with jet mixer and two circulating pumps (Q=30m³/h, H=8.5m, W=1.5kW), one for use and one for standby.

4.2.3 AO biochemical tank
The structure of the tank body was reinforced concrete, the overall dimension was 31m×10m×6.5m. The effect volume of anoxic tank was 300m³ and 1560m³ for aerobic tank. The design sludge concentration was 4000mg/L and the sludge loading rate was 0.50 kgCOD/m³·kgMLSS. Submersible water impeller was equipped and 36t of biological carriers composited with functional microbial agents were added into the aerobic tank to improve the removal efficiency of refractory pollutants in the wastewater.

4.2.4 Secondary sedimentation tank
The structure of the tank body was reinforced concrete, the overall dimension was 8.0×4.5×5.5m and the design surface loading is 0.7m³/(m²·h). Two sludge recirculation pumps (Q= 30m³/h, H=8.5m, W=1.5kW) and two dredge pumps (Q= 10m³/h, H=10m, W=0.75kW) were equipped. Both of them are one for use and one for standby.

4.3 Advanced treatment

4.3.1 Fenton reaction tank
The structure of the tank body was reinforced concrete, inner wall was made of FRP for anti-corrosion and the overall dimension was 5m×3m×4m. The reaction tank was equipped with hyperboloid stirrer, which power is 1.5kW.

4.3.2 Tertiary sedimentation tank
The structure of the tank body was reinforced concrete, the overall dimension was 10m×3.8m×4.5m, and the surface loading was 0.7m³/(m²·h). Non-metallic sludge collection system (W=0.75kW) and sludge pump (Q=10m³, H=10m, W=0.75kW) were equipped to collect and discharge the chemistry sludge.

4.4 Sludge treatment

4.4.1 Sludge thickening tank
The structure of the tank body was reinforced concrete, the overall dimension was φ5.0m×3.5m and the design surface loading was 50kg/(m²·d), while both belt sludge thickener and sludge pump were equipped.

5. Operation effect and economic benefit analysis
In May 2021, the wastewater treatment station was completed and put into use. The cost of three-effect evaporation system was 79.1 yuan/m³ (excluding the waste salt treatment and disposal), and the wastewater treatment cost was 3.21 yuan/m³, including electricity cost of 1.63 yuan/m³, labor cost of
0.20 yuan/m³, reagent cost of 1.23 yuan/m³ and sludge treatment reagent cost of 0.15 yuan/m³. After commissioning, the treatment system operation was stable and effective. The effluent quality of each unit of the treatment system was tested and the results are shown in table 4.

Table 4 Effluent quality of each treatment unit.

| Item                        | pH   | COD (mg·L⁻¹) | NH₃-N (mg·L⁻¹) | TN (mg·L⁻¹) | TP (mg·L⁻¹) | Fluoride (mg·L⁻¹) |
|-----------------------------|------|--------------|----------------|-------------|-------------|------------------|
| High-concentration regulating tank | 10–12 | 3652–4228 | 4.6–6.5 | 11.4–18.2 | 0.3–0.6 | 3317–4182 |
| Condensate storage tank     | 6.2–8.8 | 1280–2450 | 4.7–6.2 | 10.8–17.9 | 0.3–0.5 | 10.44–32.98 |
| Low-concentration regulating tank | 7.5–8.4 | 680–1100 | 5.39–6.16 | 17.75–52.06 | 0.4–0.8 | 5.71–9.25 |
| Hydrolysis acidification tank | 6.1–7.2 | 558–906 | 17.5–44.7 | 17.68–49.71 | 0.4–0.8 | 3.11–7.32 |
| Secondary sedimentation tank | 7.3–8.2 | 62–88 | 0.08–2.25 | 8.7–15.1 | 0.2–0.3 | 2.88–7.12 |
| Tertiary sedimentation tank | 6.2–7.6 | 25–40 | 0.10–2.23 | 8.3–14.6 | 0.1–0.2 | 1.1–1.5 |
| Clear water tank            | 6.1–7.5 | 21–36 | 0.10–2.23 | 8.3–14.6 | 0.1–0.2 | 0.8–1.3 |
| Mean concentration of effluent | 6–7.5 | 32 | 1.2 | 13.5 | 0.12 | 1.1 |
| Emission standards          | 6–9 | ≤40 | ≤5 | ≤15 | ≤0.5 | ≤1.5 |

According to the results shown in table 4, the biochemical treatment process design is relatively reasonable. After actual operation, the removal efficiency of COD, ammonia nitrogen and total nitrogen reached more than 80%, and after advanced treatment, the fluoride concentration in the clear water tank was less than 1.5mg/l. The effluent quality could meet the discharge requirements.

6. Conclusion
Classification treatment was applied for the fuel cell membrane material production wastewater. Salinity wastewater was collected and pretreated by three-effect evaporation and ozonation for desalting and improving the biodegradability, then mixed with other production wastewater. Mixed wastewater was treated by the following biochemical and advanced treatment. After commissioning, the treatment system operation was stable and effective. The effluent mean concentrations of COD, NH₃-N, fluoride, TN and TP were 32mg/L, 1.2mg/L, 1.1mg/L, 13.5mg/L and 0.12mg/L, which could meet the discharge standards.

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