

Wastewater treatment processes for industrial organosilicon wastewater

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Abstract. One organosilicon company in Jiangxi province used the major processes including iron-carbon micro-electrolytic processes-Fenton-anaerobic-aerobic-coagulation treatment processes to treat the wastewater from organosilicon production. The basis of technique selection, technological processes, technological parameter and operation effect were introduced. The results showed that, after these processes, the removal rates of chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD₅), suspended solids (SS), and ammonia nitrogen (NH₃-N) were 3.04 mg/L, 1.88 mg/L, 211 mg/L, and 3.6 mg/L, respectively. The effluent quality could reach the third grade in "Integrated Wastewater Discharge Standard" (GB8978-1996), which could meet the requirement of the inflow water of local sewage treatment plant.

Keywords: organosilicon wastewater; Fenton oxidation; iron-carbon micro-electrolysis; coagulating sedimentation.

1 Introduction

With rising living conditions, the demand of organosilicon materials such as SiHCl₃ increases gradually[1]. In 10 years, the growth rate of demand for organic silicon monomer in our country had been kept in more than 20%[2], but in the meanwhile, the wastewater produced in the processes has the characteristics such as complicated composition, high chemical oxygen demand (COD), refractory compounds, extreme acidity, high toxicity and poor biochemical ability. If the wastewater drained off directly, it could cause serious pollution in the surrounding water environment. Therefore, it was important to treat effectively this kind of wastewater. Plenty of researchers applied the physico-chemical methods and biological methods such as photo-catalysis-oxidation technique[3], membrane treatment[4], Fenton micro-electrolysis method[5,6], Fenton oxidation[7-9], contact oxidation method[10], ozone method[11], and combined processes to treat organosilicon wastewater.

One organosilicon enterprise in Jiangxi province, included the production lines of SiHCl₃, organosilicon, phenylhydrazine, chloranil and phenylhydrazine hydrochloride, the production line SiHCl₃ among them produced the sewage including acid wastewater HCl and suspended solid of SiO₂ [12]. According to the requirement of the environment ministry, to meet the influent quality of the local sewage treatment plant, the iron-carbon micro-electrolytic processes-Fenton-anaerobic-aerobic-

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coagulation treatment processes were used to treat the wastewater produced in the organic silicon production, which make COD, five-day biochemical oxygen demand (BOD₅), suspended solids (SS), and NH₃-N in the final effluent meet the third grade in table 4 in "Integrated Wastewater Discharge Standard" (GB8978-1996), that is, the values of pH, COD, BOD₅, SS, and NH₃-N were 6~9, ≤500 mg/L, ≤300 mg/L, ≤400 mg/L, and ≤50 mg/L, respectively.

2 Wastewater quality

The sewage from the production lines of SiHCl₃, organosilicon, phenylhydrazine, chloranil and phenylhydrazine hydrochloride in one organosilicon enterprise in Jiangxi province included only organic silicon, chloropropene, ethyl alcohol, aniline and inorganic salt and so on. Daily wastewater contained producing wastewater (high-concentration waste water) and non-producing wastewater (low-concentration waste water). Among them, COD, BOD₅, aniline, SS, pH, NH₃-N, and water flow in high-concentration waste water were 10000~20000 mg/L, 600~800 mg/L, 18 mg/L, 900 mg/L, 4~6, 100 mg/L, and 40 m³/d, respectively. Whereas there were mainly washing water and household wastewater in low-concentration wastewater, the main pollutants mainly included acid base and SS, and the water flow was 80 m³/d. The water quality and quantity of these two kinds of wastewater were shown in Table 1.

Table 1. The water quality of wastewater

Water quality	Water flow (m ³ /d)	COD _{Cr} (mg/L)	BOD ₅ (mg/L)	SS (mg/L)	NH ₃ -N (mg/L)	pH
high-concentration waste water	40	15000	700	900	100	4~6
Low-concentration waste water	80	600	100	1000	45	4~7

3 Process of wastewater treatment and descriptions

3.1 The process of wastewater treatment

According to the influent load and water quality, and the best optimizing process based on the results from in-situ survey and experiments in lab-scale and in pilot-scale, the combined processes of rail carbon micro-electrolytic processes-Fenton-anaerobic-aerobic-coagulation treatment were confirmed. The designed water flow in the wastewater treatment station was 120 m³/d, and the treatment process was shown in Figure 1.

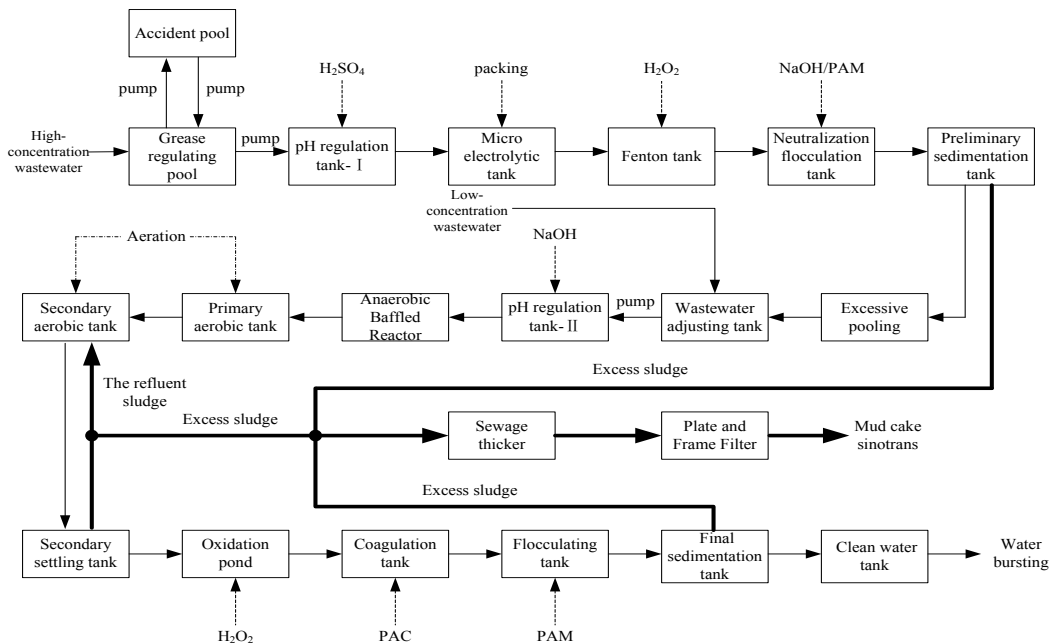


Figure 1. The process flow diagram of wastewater treatment

As shown in Fig. 1, the high-concentration and low-concentration wastewater in the entire treatment processes were separately treated. For high-concentration wastewater, it was first entered into the grease regulation pool, and then into pH regulation tank I to regulate pH value by the lifting pump, followed by the effluent enter into advanced oxidation pretreatment reactor which including the iron-carbon filter, H_2O_2 , NaOH and poly acrylamide (PAM) for sectional treatment, then the effluents were initially precipitated. After mixture in Excessive pooling, the effluent and low-concentration wastewater were together flowed into comprehensive regulation pool, and the effluents were run into pH regulation tank II by lifting pump and the pH value were adjusted by NaOH to be neutral to keep the anaerobic treatment effect of ABR. The B/C ratio value of wastewater was elevated by the ABR (Anaerobic Baffled Reactor) process, the effluents flow into first and Secondary aerobic tank in turn to further reduce COD and $\text{NH}_3\text{-N}$. After treatment by the secondary sedimentation tank, the supernatants flow into the advanced treatment reactor which included H_2O_2 , polyaluminium chloride (PAC) and PAM (the dosage of PAC and PAM et al. was depended on effluent quality). The effluents were controlled to reach the third grade in Table 4 in "Integrated Wastewater Discharge Standard" (GB8978-1996), and were discharged into the sewage treatment plant through the sewage pipe network for further treatment. The sewages from the primary, second, and final setting tank were discharged into sludge thickening tank, and then were dehydrated by the plate-and-frame filter press. The mud cakes were transported to treat safely.

3.2 Main structures of wastewater treatment

3.2.1 Regulation pool of high-concentration wastewater

One regulation pool was designed by the inflow of $2 \text{ m}^3/\text{h}$, which was within grease trap to store high-concentration wastewater from the plant, and meanwhile to homogenize the water quality and quantity in order to keep the subsequent treatment facilities operate orderly. The size of design was $4.00 \times 5.00 \times 5.00 \text{ m}$, with the effective height of 4.00 m, the effective volume of 80 m^3 , and hydraulic retention time (HRT) of 40 h. The underground steel concrete structure and the preservative treatment was applied.

3.2.2 pH regulation tank I

Two pools were designed by the inflow of $2 \text{ m}^3/\text{h}$. The pH values of the influents in these pools were adjusted by NaOH, in order to meet the conditions of micro-electrolytic reaction. The size of design is $0.90 \times 1.00 \times 3.00 \text{ m}$, with the effective height of 2.5 m, the effective volume 5.4 m^3 , and the HRT of 2.7 h. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.3 Micro-electrolytic tank

One tank, designed by the inflow of $2 \text{ m}^3/\text{h}$, was used to pretreat high-concentration wastewater, and was applied to have electrical-chemical reaction by iron scurf and carbon granule. In weak electric field, the charged colloidal particles were unstable to aggregate to precipitate. The B/C values in wastewater were improved, and then the biodegradability of wastewater was elevated. The designed size is $2.00 \times 2.00 \times 5.00 \text{ m}$, with the effective height of 4.5 m, the effective volume of 19 m^3 , and HRT of 9h. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.4 Fenton tank

Two tanks were designed by the inflow of $2 \text{ m}^3/\text{h}$. H_2O_2 and Fe^{2+} were added and their strong oxidizability was used for chemical oxidation pretreatment. Its design size is $0.90 \times 1.00 \times 3.00 \text{ m}$, with the effective height of 2.5 m, the effective volume of 5.4 m^3 , and HRT of 2.7 h. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.5 Neutralization and flocculation tank

Two tanks were designed by the inflow of $2 \text{ m}^3/\text{h}$. NaOH was added to regulate the pH values in original water to meet the necessary range of pH values in the subsequent biochemical treatment. The design size is $0.90 \times 1.00 \times 3.00 \text{ m}$, with the effective height of 2.5 m, the effective volume of 5.4 m^3 , and HRT of 2.7 h. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.6 Preliminary sedimentation tank

One tank, designed by the inflow of $2 \text{ m}^3/\text{h}$, was used to hydraulically clarify the wastewater after pretreatment, and to decrease the treatment load, and to benefit the subsequent treated processes. The design size is $2.00 \times 3.60 \times 5.00 \text{ m}$, with the effective height of 4.5 m, the effective volume of 32.4 m^3 , and the hydraulic surface loading of $0.28 \text{ m}^3/\text{m}^2 \cdot \text{h}$. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.7 Wastewater adjusting tank

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$, which was within grease trap to store high-concentration and low-concentration wastewater after pretreatment, and meanwhile to homogenize the water quality and quantity in order to keep the subsequent treatment facilities operate orderly. The size of design was $4.00 \times 7.40 \times 5.00 \text{ m}$, with the effective height of 4.00 m, the effective volume of 118.4 m^3 , and HRT of 19.7 h. The underground steel concrete structure and the preservative treatment was applied.

3.2.8 pH regulation tank II

Two tanks were designed by the inflow of $6.0 \text{ m}^3/\text{h}$. NaOH was added to regulate the pH values in original water to meet the necessary range of pH values in the subsequent biochemical treatment. The

design size is $0.90 \times 2.00 \times 3.00$ m, with the effective height of 2.5 m, the effective volume of 9.0 m^3 , and HRT of 1.5 h. The half-ground steel concrete structure and the preservative treatment was applied.

3.2.9 Anaerobic baffled reactor

One tank, designed by the inflow of $6.0 \text{ m}^3/\text{h}$, was used to have anaerobic chemistry to treat high-concentration wastewater, to decrease the subsequent treatment load, and then to improve the biodegradability of wastewater, which would benefit the subsequent aerobic treatment. The designed size is $16.60 \times 4.00 \times 5.00$ m, with the effective height of 4.5 m, the effective volume of 298.8 m^3 , and HRT of 49.8 h. The half-ground steel concrete structure was applied.

3.2.10 Primary aerobic tank

One tank, designed by the inflow of $6.0 \text{ m}^3/\text{h}$, was used to remove the organic matters in wastewater by microbial biochemical effect based on considering some mixed backflow. The designed size is $16.60 \times 4.00 \times 5.00$ m, with the effective height of 4.5 m, the effective volume of 298.8 m^3 , and HRT of 49.8 h. The half-ground steel concrete structure was applied.

3.2.11 Secondary aerobic tank (including second sedimentation tank)

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$. The biofilters were added, and the microbial biochemical effect on the surface of stuffings was used to remove organic matters based on considering some mixed backflow. On the other hand, the wastewater after aerobic treatment was hydraulically clarified through second sedimentation tank. The designed size is $16.60 \times 4.10 \times 5.00$ m, with the effective height of 4.5 m, the effective volume of 39.0 m^3 , and HRT of 1.5 h. The half-ground steel concrete structure was applied.

3.2.12 Oxidation pond

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$. H_2O_2 was added into this tank to have final treatment of chemical oxidation. The designed size is $2.00 \times 1.00 \times 5.00$ m, with the effective height of 4.50 m, the effective volume of 39.0 m^3 , and HRT of 1.5 h. The half-ground steel concrete structure was applied.

3.2.13 Coagulation tank

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$. PAC was added, and has the effect of the compression of double charge, charge neutralization and adsorption bridge and net and so on, which make the small suspended particles and gel ions to aggregate, flocculate, coagulate, sedimentate, and then reach the effect of purification treatment^[13]. The design size is $2.00 \times 1.00 \times 3.00$ m, with the effective height of 2.5 m, the effective volume of 5 m^3 , and HRT of 1.5 h. The half-ground steel concrete structure was applied.

3.2.14 Flocculation tank

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$. PAM^[14] was added and the high hydrophilic ionic groups such as amide on the molecular chain of PAM was used to realize the absorption of small molecule suspended substances in wastewaters. The design size is $2.00 \times 1.00 \times 3.00$ m, with the effective height of 2.5 m, the effective volume of 5 m^3 , and HRT of 1.5 h. The half-ground steel concrete structure was applied.

3.2.15 Final sedimentation tank

One tank was designed by the inflow of $6.0 \text{ m}^3/\text{h}$. It mainly clarifies the wastewater after coagulation and flocculation. The design size is $2.00 \times 5.00 \times 5.00 \text{ m}$, with the effective height of 4.5 m , the effective volume of 45 m^3 , and the hydraulic surface loading of $0.6 \text{ m}^3/\text{m}^2 \cdot \text{h}$. The half-ground steel concrete structure was applied.

4 The running condition of the debugging process

After completion of the system debugging in operation, and the continuous sampling test by local environmental monitoring station, the results showed that, the concentrations of COD, BOD₅, SS, and NH₃-N of the final effluents were 304 mg/L , 188 mg/L , 211 mg/L , and 36 mg/L , respectively. They were apparently better than the third grade in Table 4 in "Integrated Wastewater Discharge Standard" (GB8978-1996), and reached the requirement of influent quality of local sewage treatment plant. The monitoring data of part effluent quality were shown in Table 2.

Table 2. The main structures of treatments

Treatment units		Parameter			
		COD	BOD ₅	SS	NH ₃ -N
Regulation pool	Influent(mg/L)	15000	700	900	100
	Removal rates/%	/	/	10	/
	effluent(mg/L)	15000	700	800	100
micro-electrolytic pool/Fenton pool /neutralized flocculation pool /primary settling tank	Removal rates/%	75	25	30	10
	effluent(mg/L)	3750	525	560	90
ABR	Removal rates/%	60	15	10	5
	Effluent(mg/L)	1500	446	504	85
Primary aerobic tank / Secondary aerobic tank	Removal rate/%	55	40	20	35
	effluent(mg/L)	675	268	403	55
Secondary sedimentation tank	Removal rate/%	/	/	25	/
	effluent(mg/L)	675	268	302	55
Oxidation pond / Coagulating basin / Flocculation basin / Final setting tank	Removal rate/%	55	30	30	35
	effluent(mg/L)	304	188	211	36
Total removal rate %		98.0	73.1	76.6	64.0
Discharged requirements		500	300	400	50

5 Technical and economic analysis

The main cost of this project contained electric charge and medicament expense. According to the statistics, if the electric charge was calculated by 0.8 yuan per kilowatt hour, then 253.2 yuan per day would be paid for electric charge. That is, to treat one ton wastewater would cost 2.11 Yuan of electric

charge. The medicament expense including NaOH, PAC, PAM, and H_2O_2 , the corresponding prices of them were 4000 yuan/ton, 2200 yuan/ton, 24000 yuan/ton, and 1200 yuan/ton. One ton wastewater would consume 0.48 y uan N aOH, 0.22 y uan P AC, 0.12 y uan P AM, and 0.06 y uan H_2O_2 . The medicament expense used to treat one ton wastewater was 0.88 yuan. The total operational cost of per ton wastewater treatment would be 2.99 yuan.

6 Conclusion

For the sewage from the production lines of $SiHCl_3$, organosilicon, phenylhydrazine, chloranil and phenylhydrazine hydrochloride, the main processes of rail-carbon micro-electrolytic processes-Fenton-anaerobic-aerobic-coagulation treatment were applied. The concentrations of COD, BOD_5 , SS, and NH_3-N of the final effluents were 304 mg/L, 188 mg, 211 mg/L, and 36 mg/L, respectively, which were apparently better than the third grade standard of "Integrated Wastewater Discharge Standard (GB8978-1996)", and reached the requirement of influent quality of local sewage treatment plant. The operating cost without labor cost only contains electric charge and medicament expense, and the total cost was 2.99 yuan/ton wastewater.

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