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Application of Anoxic-Aerobic Biological Process for Treatment of Compositive Electroplating Wastewater

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Abstract. In this paper, different physicochemical processes are used to remove heavy metals in electroplating wastewater containing nickel, chromium and fluorine. More, the three items of phosphate, NH_4^+-N and COD_{cr} are also needed to be decreased to meet discharge standards. Based on the various characteristics of electroplating wastewater, biochemistry technologies are used to improve the effluent quality after pretreatment for actual origin wastewater. Anoxic reactor and biological aerated filter are employed as biological processes (A/O process) to decrease the effluent concentration of COD_{cr} and NH_4^+-N. The results show that the system effluent meets the national standard of "Emission Standard of Pollutants for Electroplating" (GB 21900-2008), and NH_4^+-N item reaches the local standard of "Discharge Standard of Main Water Pollutants for Municipal Wastewater Treatment Plant & Key Industries of Taihu Area" (DB 32/1072-2007). The modified A/O process realizes a high denitrification removal of 80%, and the operation cost is only 2.67 Yuan/m^3.

Introduction

The emission of wastewater derived from electroplating plants has rapidly increased with growing electronic industry [1]. Electroplating wastewater contains a large amount of heavy metals, such as chromium, nickel, copper, zinc and gold, etc., and a lot of additives, such as surfactant, EDTA, citric acid, cholamine and cyanate compounds, etc., which are major causes of water and soil pollution. Heavy metals and additives pose a serious risk to both human and environment [2,3]. Therefore, it is necessary to treat electroplating wastewater prior to its discharge.

Due to the increasingly stringent environmental legislation, the treatment of electroplating wastewater laden with heavy metals has received considerable attention [4]. At present, Ministry of Environmental Protection and local government of Jiangsu province in China have established correlative laws and regulations, including "Emission Standard of Pollutants for Electroplating (State Standard, GB 21900-2008), and "Discharge Standard of Main Water Pollutants for Municipal Wastewater Treatment Plant & Key Industries of Taihu Area" (Taihu Standard, DB 32/1072-2007), respectively.

According to the discharge items in the two above standards, the item of NH_4^+-N is raised from 8 mg/L in the State Standard to 5 mg/L in the Taihu Standard. Simultaneously, the Taihu Standard enhances the control for TP and other heavy metals in effluent. The effluent items of electroplating wastewater treatment plants/stations in Taihu area (such as Suzhou, Wuxi and Changzhou in Jiangsu province, etc.) must meet the Taihu Standard besides the State Standard. However, for most these wastewater plants/stations, it is difficult and important to choose appropriate processes to treat electroplating wastewater. According to our latest investigation, most processes in electroplating wastewater treatment plants/stations employ mainly physicochemical methods [3], such as chemical precipitation, ion exchange, solvent extraction, electrodialysis, membrane filtration and so on [1,2].

Although these physicochemical methods have been widely used to treat electroplating wastewater, their drawbacks like excessive chemicals consumption, sludge production, and impossibility of directly reusing heavy metals are obvious [2,4,5].

Importantly, it is difficult that the effluent item of NH_4^+-N in most electroplating wastewater treatment plants/stations meets the State Standard with physicochemical methods, especially the Taihu Standard. Because electroplating wastewater has low biodegradation with the ratio of BOD_5 to COD_{cr} less than 0.1, resulting in difficulty with biological technologies [6,7].

In this paper, to increase the biodegradation of electroplating wastewater, domestic sewage derived from industrial district was introduced to improve the nutrition equilibrium of the wastewater. Simultaneously, a modified anoxic-aerobic (A/O) biological technology was employed as the main process for denitrification in order to meet the discharge standard for effluent NH_4^+-N. The paper used the modified A/O process and appropriate physicochemical methods to treat actual electroplating wastewater derived from a large metal manufacture enterprise in Changshu city in Jiangsu province.

Quality, Flow Rate and Discharge Standard of Wastewater

Quality and Flow Rate of Wastewater. The wastewater was mainly derived from the handling process of metal products, including pre-treatment, nickel plating, chromium plating, plating article rinsing and so on. To improve the biodegradation of the electroplating wastewater, domestic sewage was introduced. And the characteristics of the compositive wastewater were listed in Table 1.

Table 1 Characteristics of the wastewater

No.	Wastewater sorts	Discharged flow rate (m^3/d)	Pollutant factors
1	Nickel wastewater	5	Ni^{2+}<963.5 mg/L, pH=3-4, COD_{cr}<300 mg/L
2	Low concentration washing wastewater	916.4	SS<80 mg/L, NH_4^+-N<27 mg/L, P<3 mg/L, pH=3-4, COD_{cr} =100-200 mg/L
3	High concentration acidic wastewater	10	TP<11000 mg/L, pH<2, COD_{cr} <100 mg/L
4	Degreasing wastewater	58	TP<120 mg/L, pH>8, COD_{cr} <2000 mg/L
5	Chromium wastewater	150.1	Cr^{6+}<100 mg/L, pH=1-2, COD_{cr} <100 mg/L
6	Dye wastewater	40	pH=9-10, COD_{cr} <3000 mg/L
7	Fluorine wastewater	35.3	F^-<80 mg/L, NH_4^+-N <25 mg/L, pH=9-10, COD_{cr} <100 mg/L
8	Exhaust gas washing wastewater	7.5	NH_4^+-N <6 mg/L, TP<3 mg/L, SS<80 mg/L, pH=9-10, COD_{cr} <100 mg/L
9	Mixed wastewater derived from washing, up-flow regeneration and boiler	67.7	NH_4^+-N <6 mg/L, TP<3 mg/L, SS<80 mg/L, pH=3-10, COD_{cr} =100-200 mgL
10	Domestic sewage	30	NH_4^+-N <26 mg/L, TP<3 mg/L, SS<80 mg/L, pH=6-9, COD_{cr} =300-400 mg/L

According to the data shown in Table 1, the discharged flow rate of the compositive wastewater was 1320 m^3/d. The designed flow rate of the wastewater employed 60 m^3/h. The compositive concentration of NH_4^+-N was about 23.7 mg/L.

Discharge standard. According to the demand of the enterprise and local environmental protection department, the effluent must meet the NH_4^+-N item of 5 mg/L in Taihu Standard (DB 32/1072-2007), besides the State Standard (GB 21900-2008).

Choice of Treatment Processes

According to the composition and flow rate, there was great difference between the characteristics of the various electroplating wastewater. Considering treatment efficiencies and operation cost, the above wastewater should be classified to be treated. The electroplating wastewater was classified six sorts, e.g., nickel and degreasing wastewater, chromium wastewater, fluorine wastewater, high concentration acidic wastewater, dye wastewater and domestic sewage, and other wastewater (including low concentration washing, exhaust gas washing and mixed wastewater).

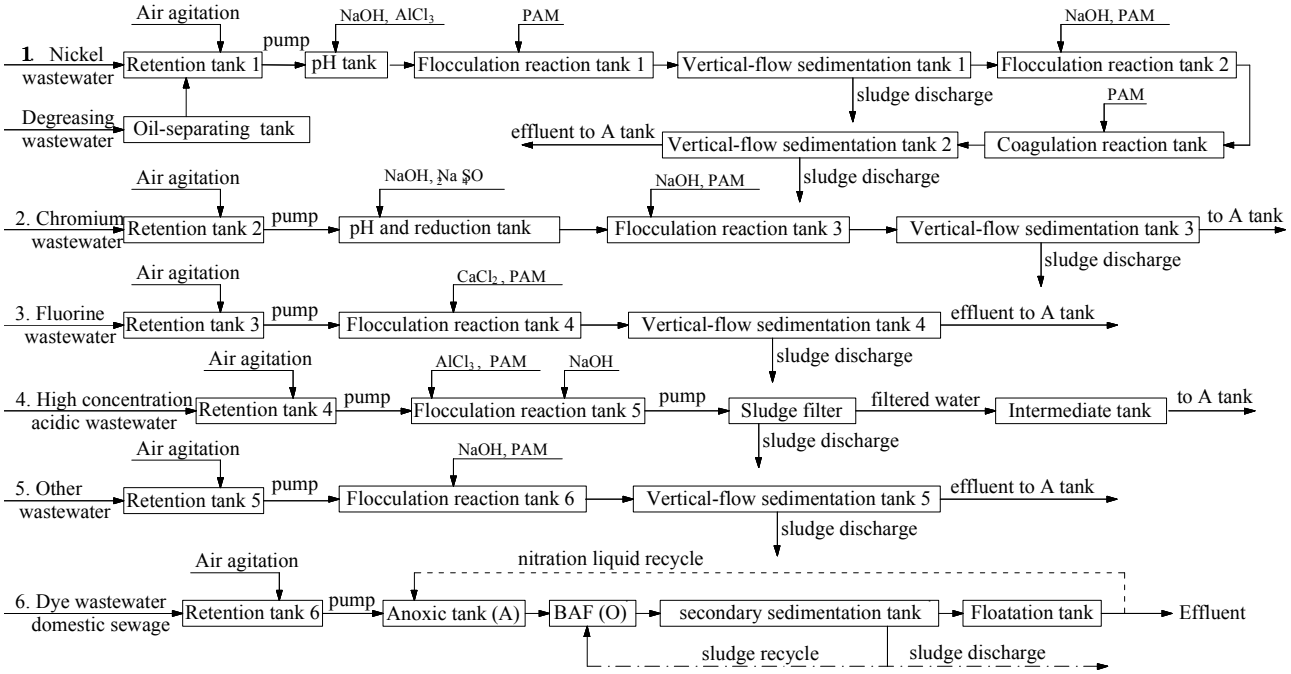

Fig. 1 Schematic flow chart of wastewater system

Due their low biodegradation, it was very difficult to treat the electroplating wastewater with biological treatment process. In order to improve the removal of COD_{cr} and NH_4^+-N, the above six wastewaters were firstly pre-treated with different physicochemical methods, and then treated with modified A/O process after mixed with domestic sewage. Among the A/O process, a hydrolysis acidification tank was used as anoxic reactor (A tank), and biological aerated filter (BAF) was used as aerobic reactor (O tank). The treatment process was shown in Fig. 1.

Wastewater Treatment Buildings and Equipments

Treatment of Nickel and Degreasing Wastewater. Considered the high concentration of Ni^{2+} in the nickel wastewater, and high TP concentration in degreasing wastewater, physicochemical methods were used to remove $Ni^{2+}$and TP with coagulation and sedimentation technologies. Also, the values of pH of the two wastewaters were great different, which was acidic and alkaline, respectively. Degreasing wastewater was introduced a retention tank of nickel wastewater after oil-separation. The two wastewaters were firstly adjusted their pH to 6-7 with addition of NaOH and $AlCl_3$. The effluent entered subsequently flocculation reaction tank 1, where a lot of fine floccules of $AlPO_4$ would be produced via the reaction of Al^{3+} and PO_4^{3-}. In order to improve the precipitation effect of floccules of $AlPO_4$, polyacrylamide (PAM) had been added before they entered vertical-flow sedimentation tank. The floccules of $AlPO_4$ were precipitated at the bottom of the sedimentation tank and the effluent entered subsequent flocculation reaction tank 2. In flocculation reaction tank 2, the value of pH of wastewater was adjusted to about 9.5 with addition of NaOH. Then a lot of fine floccules $Ni(OH)_2$ were produced and precipitated in the sedimentation tank with the addition of PAM. The effluent entered A tank.

Treatment of Chromium Wastewater. The treatment methods of chromium wastewater include mainly chemical reduction, electroanalysis, ion exchange, activated carbon adsorption and evaporation concentration and so on. The chemical reduction is generally used at home and abroad, which was also employed as the main treatment technology for the conversion of Cr^{6+} to Cr^{3+}. The precipitation of $Cr(OH)_3$ would be formed with sodium sulfite as reductants and pH of 2.5-3. The effluent entered A tank.

Treatment of Fluorine Wastewater. The treatment methods of fluorine wastewater include calcium salt precipitation, aluminium salt precipitation and biochemistry technologies. Calcium salt precipitation technology was used here. The precipitation of CaF_2 were formed under the condition of pH=9-10. The effluent entered A tank.

Treatment of High Concentration Acidic Wastewater. The characteristics of high concentration acidic wastewater were low flow rate, low pH and exceedingly high concentration TP (about 1000 mg/L). The discharge of wastewater was irregular intervals, and labor intensity was also great, so a big retention tank with hydraulic retention time (HRT) of 120 h was set. The removal of TP employed chemical method with aluminium salt ($AlCl_3$). And the appropriate pH was usually 6-7. Under the above conditions, the precipitation of $AlPO_4$ could be formed. The effluent containing trace TP entered A tank to further remove residual TP.

System of Biochemistry Treatment. The mixed wastewater of dye wastewater and domestic sewage was directly pumped into A tank, and simultaneously, other wastewater after pretreatment also entered A tank. BAF tank was used as aerobic reactor to remove most COD_{cr}.

In order to improve the drawback of conventional A/O process, A tank employed biomembrane process to fix the denitrifying bacterium. The recycled supernatant was derived from the effluent of secondary sedimentation tank to decrease the recycle rate 30%-50%. As biomembrane process was employed in A tank, the microorganism in A tank can not be discharged with the effluent, and recycled sludge only returned to O tank from secondary sedimentation tank. After pre-treated, wastewater firstly entered A tank for anoxic treatment, and then the effluent of A tank flowed into O tank for aerobic treatment and nitrification. Simultaneously, a part of the effluent of O tank flowed back A tank via a recycle pipe for denitrification. A floatation tank was used as last procedure to remove residual COD_{cr}, SS and chroma to meet State and Taihu Standards.

The main structures and size were shown in Table 2.

Table 2 Size and amount of main treatment structures

Main structures	Size (m)	Amount	Main structures	Size (m)	Amount
Retention tank 1	4.0×1.5×3.0	1	Flocculation reaction tank 6	5.0×4.0×3.0	2
Flocculation reaction tank 1	Ø 1.5×H 1.2	1	Vertical-flow sedimentation tank 5	5.0×4.0×3.0	2
Vertical-flow sedimentation tank 1	Ø1.5×H 5.5	1	Retention tank 6	5.0×2.0×4.0	1
Flocculation reaction tank 2	Ø 1.5×H 1.2	1	Anoxic tank (A)	9.0×4.0×7.0	2
Coagulation reaction tank	Ø 1.5×H 1.2	1	BAF (O)	12.0×5.0×7.0	2
Vertical-flow sedimentation tank 2	Ø 1.5×H 5.5	1	secondary sedimentation tank	12.0×3.0×3.5	2
Retention tank 5	6.0×4.5×7.0	2	Floatation tank	8.1×3.1×3.5	2

Results of Engineering Operation

After five months of commissioning and operation, the effluent quality has completely reached the design requirements. The items of COD_{cr}, SS, total chromium, F^- and TP were 44.2 mg/L, 20.7 mg/L, 0.42 mg/L, 3.9 mg/L and 0.40 mg/L, respectively.

Table 3 Measurement resluts of effluent quanlity

Items	COD_{cr} (mg/L)	SS (mg/L)	Total Cr (mg/L)	F^- (mg/L)	TP (mg/L)	NH_4^+-N (mg/L)
Influent of A tank	287.5	–	0.92-1.08	4.3-6.2	1.52-1.77	20.4-25.8
A tank	175.8	–	0.72-0.88	–	1.08-1.35	12.4-15.3
O tank	61.7	–	0.66-0.72	–	0.88-0.11	2.3-4.7
Floatation tank	32.5-48.4	18.5-26.7	0.37-0.46	2.8-4.7	0.32-0.43	2.6-4.6
State Standard	50	30	0.5	10	0.5	8
Taihu Standard	80	–	–	–	0.5	5

Simultaneously, the modified A/O process are superior to conventional denitrification and dephosphorization process, and the removal efficiency of NH_4^+-N was over 80% and superior to the limited value of 5 mg/L in the State and Taihu Standards. The measurement results were shown in Table 3.

Conclusions

The total cost of the engineering was 1.67×10^6 Yuan, containing construction (8.2×10^5 Yuan), equipments (5.1×10^5 Yuan), automatic control systems (1.6×10^5 Yuan) and other indirect cost (1.8×10^5 Yuan). The installed capacity was 92.99 kW, and power consumption was 1180 kW/h/d. Power consumption per ton wastewater was 0.66 Yuan. Considering chemical reagents and labor cost, the total operation cost was 2.67 Yuan/m^3.

At present, the discharged amounts of COD_{cr}, SS, Cr^{6+}, Ni^{2+}, TP and NH_4^+-N could be reduced about 152.35 t, 29.8 t, 5.5 t, 1.76 t, 7.67 t and 9.8 t, respectively, which showed prominent environmental benefit.

The results of operation also show that the employment of physicochemical processes ensured the healthy running of biochemistry system, the combination of hydrolysis acidification reactor and BAF filter realized the stable discharge of effluent, and the introduction of domestic sewage improved the biodegradation of electroplating wastewater.

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