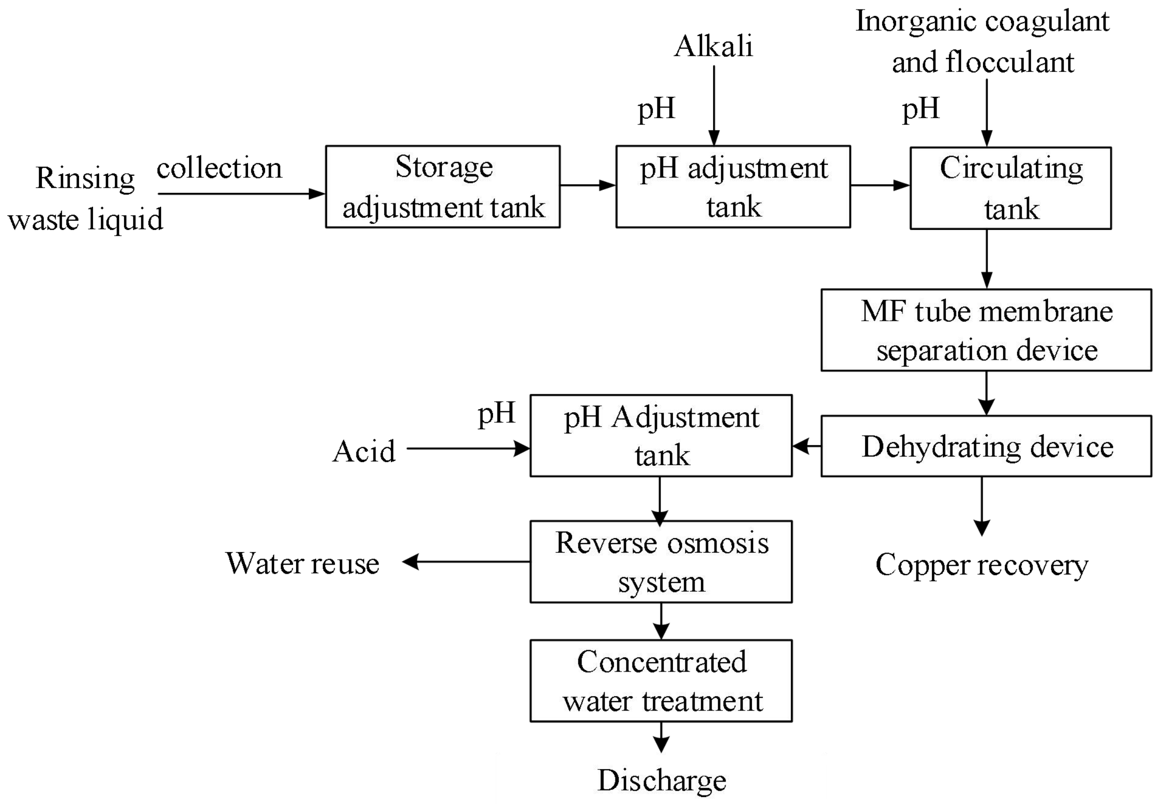

Figure 3 — Process flow diagram of chemical coagulation-microfiltration-reverse osmosis for electroplating copper-bearing wastewater treatment

5.2.3 Ion exchange-electrolysis

The rinsing wastewater enters the ion exchange resin after filtration, the effluent from ion exchange and wastewater from resin regeneration can be reused or discharge after advanced treatment. The acid liquid from resin regeneration can be directly reused, and can also enter the electrolytic equipment for recovery of copper. The process flow diagram is given in Figure 4.

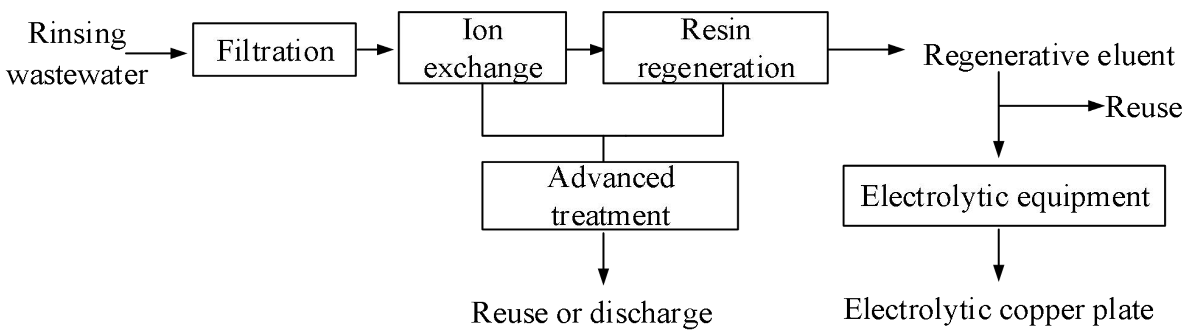

Figure 4 — Process flow diagram of ion exchange-electrolysis for electroplating copper-bearing Wastewater treatment

5.3 Design Requirements

5.3.1 Electrolysis

5.3.1.1 The selection of electrolysis equipment shall be determined according to the concentration of copper ions in the wastewater and the scale of treatment.

5.3.1.2 The electric current I (A) is determined by the current density DK (A/m^2) and the cathode plate area M (m^2). The current density is determined by the current efficiency and the mass of the deposited copper. Generally, when the concentration of copper in wastewater is not less than 0.7 g/L, the cathode current density should be 0.5 A/dm^3 to 1.0 A/dm^3. When the concentration of copper in wastewater is less than 0.7 g/L, the cathodic current density should be 0.1 A/dm^3 to 0.5 A/dm^3.

5.3.1.3 The fluctuation range of the power supply voltage is not more than 5% of the rated value.

5.3.2 Ion exchange

5.3.2.1 The exchange capacity of the unit volume resin and the selectivity of the resin should meet the requirements of the separation process, and the weak acid cation ion exchange resin or chelating resin should be adopted.

5.3.2.2 The application of ion exchange method to the treatment and recovery of copper-bearing wastewater should be selected in series with multi-resin columns. It is regenerated when one resin column reaches saturation, and the influent enters to another resin column for exchange. The regenerated resin column is connected to the last resin column for the exchange reaction, and the regenerated resin column is repeated alternately.

5.3.2.3 The resin shall have the ability of resistance to abrasion, damage, mass loss, acid and alkali, oxidization and pollution. The density, grain size and pore structure of resin shall meet the technological requirements.

5.3.2.4 Ion exchange regeneration treatment process should be determined according to the characteristic of regenerated liquid, and the concentration of regenerated liquid is determined by concentration of regenerated agent, resin adsorption rate, regeneration efficiency and so on.

5.3.2.5 The amount of ion exchange resin regeneration agent shall be determined according to the amount of ions adsorbed on the regenerated resin functional group and the concentration of regeneration agent.

5.3.2.6 The copper sulfate solution produced by the regeneration of the exchange column can be reused to previous electroplating process as replenisher, and also can be send to electrolysis equipment for copper recovery.

5.3.3 Chemical condensation-microfiltration-reverse osmosis

5.3.3.1 The process system consists of storage adjustment tank, pH adjustment tank, circulation groove, tubular MF membrane separation equipment, pH adjustment tank, reverse osmosis equipment, dehydration equipment and concentrated water treatment equipment.

5.3.3.2 The operation mode of the wastewater treatment system is designed to be automatic and manual and can be switched at any time according to the needs. The control room of the wastewater treatment system is connected with the equipment scientifically and reasonably, which can intuitively understand the operation of the equipment and monitor automatically.

5.3.3.3 The operation process diagram of the wastewater treatment system should real-time display the operation state of wastewater treatment station, including equipment operation state of all pump, draught fan, the measured value and the set value of all monitoring instruments, the liquid level in each collection tank, the liquid level in the medicine tank, etc.

5.3.3.4 Control the working state of the wastewater lifting pump from each wastewater conditioning tank and the subsequent treatment units. The control system should conduct consistently forming into a loop.

5.3.3.5 Wastewater treatment shall rationally utilize resources, reduce investment in drugs, decrease the costs of operation, and can automatically add drugs and automatically continuously reaction under instrument monitoring to reduce human-induced interference and ensure the stability of water quality.

5.3.3.6 The amount of alkali is determined according to the content of Cu^{2+} in the electroplating copper-bearing wastewater. Generally, the molar ratio of OH^- to Cu^{2+} is 2:1 and the amount of OH^- is over 1% to 5%.

5.3.3.7 The design flux of the membrane module shall not exceed the maximum flux value specified by the manufacturers of membrane modules, and a reasonable design flux shall be selected to ensure the normal operation of the membrane module and a reasonable cleaning cycle.

5.3.3.8 Membrane modules chemical cleaning agents are selected based on the quality of the feedwater and the characteristics of the selected membrane module.

5.3.3.9 Membrane equipment should be equipped with an on-line backwash system, and the backwashing period, backwashing time and backwashing strength should be designed according to the properties of the wastewater.

5.3.4 Advanced treatment and reuse of wastewater

5.3.4.1 Electroplating copper-bearing wastewater can be treated by physicochemical and biochemical methods after being treated by ion exchange-electrolysis or ion exchange-membrane technology, and the treated water quality shall meet the requirements of Table 3 in GB 21900-2008.

5.3.4.2 Select an appropriate process to meet the reuse standard for reusing the effluent if it is needed.

5.4 Technological parameter

5.4.1 Before the rinsing wastewater enters into the ion exchange resin, the suspended solids in the wastewater shall be removed through a filter, and the content shall no more than 2 mg/L. After the treatment of ion exchange resin, the concentration of copper ions in the effluent shall less than 0.3 mg/L.

5.4.2 The technical performance parameters are given in Table 3.

Table 3 — The technical performance parameters

Technical parameters	Electrolysis section	Ion exchange section	Microfiltration
Recovery rate of copper	≥90%	——	——
The purity of reclaimed copper	≥99%	——	——
Concentration of copper ion in effluent	——	≤0.3 mg/L	≤0.3 mg/L

5.5 Analytical detection and control

5.5.1 General requirements

5.5.1.1 Electroplating companies should be equipped with laboratories and equipped with corresponding copper ion concentration test equipment.

5.5.1.2 The copper ion concentration in rinsing waste liquid and rinsing wastewater needs to be tested during the commissioning and daily operation of the equipment.

5.5.1.3 The current of the direct current power is regulated according to the concentration of copper ions to ensure the best effect of the electrolysis.

5.5.1.4 The determination of copper content in water shall be carried out in accordance with the provisions of GB/T 7475.

5.5.1.5 The recovery rate of copper is calculated according to Annex A.

5.5.1.6 The determination of copper purity is carried out in accordance with the provisions of GB/T 5121.1.

5.5.2 Control of ion exchange

5.5.2.1 Ion exchange efficiency should be increased as much as possible to reduce operating costs.

5.5.2.2 The regeneration efficiency of the ion exchange resin can be improved by optimizing the amount of regenerant, concentration, flow rate, flow direction and other parameters.

5.5.2.3 The series or parallel connection of ion exchange resin shall be selected according to the requirements of the design document. Parallel connection is for treating large amount of wastewater. Series connection is for achieving high quality of effluent.

5.5.2.4 When copper ion content in the effluent of ion exchange resin is higher than 0.3 mg/L, ion exchange resin shall be regenerated.

5.5.2.5 When the copper ion content in the effluent of the ion exchange resin after regeneration is equivalent to the influent, the ion exchange resin shall be resuscitated. If the exchange capacity is still not restored, the ion exchange resin shall be replaced.

5.5.3 Control of chemical coagulation - microfiltration - reverse osmosis

5.5.3.1 The pH in the pH adjustment tank shall be 10~11, and the pH in the pH adjustment tank shall be 7.0~8.5.

5.5.3.2 The hydraulic retention time of the circulation tank is not less than 30 mins to ensure adequate reaction.

5.5.3.3 Sludge concentration of the tubular MF membrane separation equipment shall be maintained at 1% to 5%, and when it is between 2% and 5%, the sludge can be sent to the dehydration equipment.

5.5.3.4 When the concentration of copper ions in the permeate of microfiltration membrane is higher than 0.3 mg/L, the permeate shall be returned to the circulation tank.

5.5.3.5 The flux of tubular microfiltration membranes should be in the range from 200 $L\cdot m^2/h$ to 400 $L\cdot m^2/h$, and the flux of reverse osmosis membranes should be in the range from 13 $L\cdot m^2/h$ to 19 $L\cdot m^2/h$.

5.5.3.6 The turbidity of reverse osmosis water inflow shall be less than 0.2 NTU and the water pollution index SDI shall less than 5.

5.5.3.7 If the organic membrane element is used for the microfiltration membrane, the inlet water temperature shall be controlled between 5 °C and 35 °C. During the operation, the membrane flux shall be monitored. When the flux decays by 30% to 50%, the membrane element should be shut down for cleaning and regeneration.

6 Process Equipment

6.1 Electroplating copper-bearing wastewater treatment and recovery equipment should be composed of three main parts: electrolysis unit, ion exchange unit and membrane filtration unit.

6.2 The main components of the electrolytic unit include electrolytic cell, circulating water tanks, and circulating pumps. The main materials are electrolytic cathode and anode plates. The anode should be titanium mesh coated with an insoluble noble metal, and the cathode should be stainless steel or copper plate. The control unit of the electrolytic unit mainly includes a direct current power supply and a voltage regulator.

6.3 The main components of the ion exchange unit include circulation pumps, filters, ion exchange columns, ion exchange resins and regeneration equipment.

6.4 The main components of the membrane filtration process unit include circulation pumps, pressure pumps, membrane modules, control cabinets, switches, valves and pipelines.

6.5 The auxiliary facilities include ventilation, drainage trenches, and waterproof enclosures.

7 Acceptance Inspection

7.1 Project acceptance

7.1.1 The key technical documents such as overall process flow, equipment layout and overall design shall be implemented in accordance with the design documents.

7.1.2 The parts and equipment in the project are all new and industrial.

7.1.3 The treatment equipment of electroplating copper-bearing wastewater shall be accepted strictly in according to this acceptance standard.

7.1.4 Electronic drawings, mechanical drawings, purchased parts data, backup procedures and other materials shall be submitted.

7.2 Acceptance of process performance

7.2.1 Acceptance of environmental protection complies with regulations of HJ 2002.

7.2.2 The treated wastewater quality meets the standards in Table 3 of GB 21900-2008.

7.2.3 In the wastewater treatment process, the copper recovery rate shall not be lower than 90% and the copper purity shall not be lower than 99%.

7.2.4 The effluent of the system shall meet related standards within three months of pilot run.

7.3 Labor safety and occupational health

Labor safety and occupational health shall meet the regulations of HJ 2002.

8 Operation and Maintenance

8.1 General provisions

8.1.1 A operation and maintenance manuals or specification shall be established for the equipment operation, and all the facilities and equipment shall be used in accordance with the design requirements.

8.1.2 The on-line monitoring instrument is calibrated every two weeks and the thermal control instrument is calibrated every two months.

8.1.3 The operation, maintenance and safety of electroplating copper bearing wastewater treatment and recovery equipment shall meet the relevant national standards.

8.2 Operation management

8.2.1 The operation and management personnel and operators shall be trained to master the knowledge of treatment and recycling process of electroplating copper bearing wastewater, the operation regulations of the equipment and various design indicators.

8.2.2 Each post shall have safe operating procedures, etc., and shall be listed in obvious locations.

8.2.3 The operators of each post shall make record of their operations on time. The data shall be accurate. When unnormal operation is found, shall be handled or reported to relevant personnel in time.

8.2.4 The inspection shall be conducted periodically to ensure the normal operation of the equipment according to the requirements of different equipment.

8.2.5 During the electrolysis process, the waste liquid shall be sampled periodically to detect the concentration of copper ions, and the DC power supply current shall be adjusted according to the concentration change.

8.2.6 For ion exchange effluent, it is necessary to be sampled periodically and detect the concentration of copper ions. If it meets standard, discharge directly. If not, it shall be treated with ion exchange resin.

8.3 Maintenance

8.3.1 The operator shall strictly implement the equipment safety operation regulations, and regularly check whether the equipment operation is normal. If problems are found, they shall be checked and eliminated as soon as possible.

8.3.2 The lubrication status of each operating part of the equipment shall be maintained, adding the lubricating oil and de-rusting in time; if any oil leakage or oil leakage is found, it shall be resolved promptly.

8.3.3 Records of the equipment maintenance shall be made.

8.3.4 The control system shall be maintained, and the automatic control system shall be improved.

Annex A
（Normative annex）
The calculation formula of copper recovery of copper-bearing wastewater

A.1 The calculation of copper recovery rate

A.1.1 Electrolytic process

Calculate the recovery rate of electrolysis, expressed as a percentage, of the electrolytic process, η_e, using the formula (A.1):

$$\eta_e = \left(m_e / m_0 \right) \times 100 \quad \text{(A.1)}$$

Where:

η_e—— Recovery rate of electrolysis (%);

m_e—— The weight of recovered copper in the process of electrolysis (kg);

m_0—— The weight of copper in electrolysis influent (kg).

A.1.2 Ion exchange process

Calculate the ion exchange recovery, expressed as a percentage, of the ion exchange process, η_i, using the formula (A.2):

$$\eta_i = \left(1 - \rho_1 / \rho_e \right) \times 100 \quad \text{(A.2)}$$

Where:

η_i—— Ion exchange recovery (%);

ρ_1—— Copper ion concentration in ion exchange effluent (g/L);

ρ_e—— Copper ion concentration in ion exchange influent (g/L).

A.2 Calculation of unit power consumption during electrolysis

Calculate the DC power consumption of unit weight cathode copper, expressed as a kW·h/kg, of the unit power consumption during electrolysis, *WD*, using the formula (A.3):

$$WD = Wt / m \quad \text{(A.3)}$$

Where:

WD—— DC power consumption of unit weight cathode copper (kW·h/kg);

Wt —— The amount of direct current consumed in a given metering period (usually one year) (kW·h);

m—— The total amount of cathode copper in the same metering time (usually one year) (kg).