Heat Pump Evaporation Crystallization Technology of Salt-containing Phenol Wastewater

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Abstract: China is a large country in the production and use of pesticides, and the production and use of pesticides are among the highest in the world. According to statistics, the ratio of wastewater from pesticide production to wastewater discharged is about 1:100. Arbitrary discharge of a large amount of pesticide wastewater has caused serious environmental problems. The main way of pesticide wastewater treatment is to optimize emission reduction and control emissions. At present, treatment is the main way. There are many kinds of pesticide wastewater, which need targeted treatment, greatly increasing the difficulty of treatment. This paper takes the salty waste phenol wastewater discharged from a pesticide factory as the carrier, through basic physical property analysis, thermal property detection, crystallization kinetics research, basic small test, pilot scale amplification, research and development for the evaporation of this wastewater, crystallization processing equipment. In order to optimize the process route, it is preferable to use MVR compressor technology in comparison with multi-effects. Under the conditions of evaporation temperature 75°C to 90°C, compare the parameters of compressor power, cooling water volume, total energy consumption of evaporation crystallization device, total area, etc., and determine the evaporation temperature to be 90°C. In order to improve the energy utilization rate, the heat such as condensed water, crystal slurry output, and mother liquor reflux is rationally utilized. The multi-stage plate preheater and plate evaporator are used in the equipment design. The separator and condensed water vapor-liquid separation device adopt the patented structure to improve the operation efficiency.

Keywords: Wastewater Treatment, Crystallization Kinetics, Wastewater Physical Properties

1. Introduction

China country has more than 1400 pesticide factories and the second largest pesticide output in the world, with about 400,000 tons. Due to unreasonable structure and supervision, environmental pollution is very serious. According to statistics, China's pesticide industry produces up to 1 billion cubic meters of wastewater [2], only one tenth of the wastewater is treated and only one percent of the water reaches the eligible discharge standards. Essentially, the solution to the problem of wastewater pollution lies in the development and use of new production processes that can reduce the generation and discharge of pollutants. However, due to many factors, it is still in the process of solving pollution control. The main wastewater in this paper is herbicide 2,4-sodium salt (full name 2,4-dichlorophenoxyacetate) wastewater.

MVR (Mechanical Vapor Recompression), the Chinese name of mechanical recompression technology [3], is the use of impeller rotation to compress the steam body, so that the steam from low temperature and low pressure to high temperature and high pressure can be used for heating steam [3], improve the enthalpy of steam, reuse. In the 1960s, Germany and France in Europe have used it in chemical production, pharmaceutical industry, seawater treatment and other industries [4].

In this study, the basic physical properties of wastewater were studied and the evaporative crystallization and chemical characteristics of saline wastewater containing phenol were obtained by means of experiments [5]. A key parameter was the increase of boiling point, which was the consumption of evaporative heat transfer temperature difference. In this paper, the MSMPR model was used to carry out the related experiments on the crystallization kinetics of wastewater, the
2. Study on Characteristics and Crystallization Kinetics of Salinated Phenol Wastewater

2.1. Determination of Basic Parameters of Physical Properties

The salty wastewater to be treated comes from a pesticide manufacturer [6]. A mixture of wastewater from an acidification phenol removal plant, a neutralization plant, and a vacuum distillation plant. The pH value of wastewater is between 6 and 7. The apparent color is brown. The main components are: 20~22% sodium chloride, phenol 100-150ppm, trimethylamine 0.8-1.0%, and other impurities. The initial density of the wastewater is 1109 kg/m3, and the COD value is 40,000ppm [7]. Most of the wastewater is complex and contains inorganic, organic and other unidentified impurities. Therefore, directly checking the physical property data obtained from the literature may not be able to reflect the physical properties of the wastewater well, and experiments must be carried out.

Through experimental analysis, the boiling point of the wastewater in the initial state was increased to 2.8°C, and the boiling point was increased to 9.5°C in the saturated state. Through the above experimental analysis, the boiling point of the wastewater in the initial state was increased to 2.8°C, and the boiling point was increased to 9.5°C in the saturated state [8]. The evaporation temperature and boiling point of this wastewater are known by simulated evaporation and vacuum evaporation. Elevated boiling point is an important parameter in evaporation and crystallization design.

2.2. Wastewater Crystallization Kinetics Experiment

a) Experimental principle and device

The principle of the experiment is as above, the configured saturated solution is placed in the system, and the cycle is started. The material passes through the high level tank and the preheater enters the saturation tank [9]; the saturated tank is provided with the solid waste water crystal particles, and the saturated solution after passing through the saturation tank ensures that there is no crystal grain in the circulating liquid through the crystal killing tank; the saturated liquid enters the crystallizer, the crystallizer The MSMPR type is used; the suspension from the crystallizer enters the bath to ensure that there are no grains in the circulating liquid. In order to simulate crystallization under different vacuum levels, the crystallizer operates with an adjustable negative pressure.

b) Experimental steps

1) using the solid particles after crystallization and evaporation of the wastewater, and arranging a saturated solution at a temperature of 85°C;
2) Put the configured saturated solution into the experimental device and start the cycle;
3) vacuuming, using a constant temperature water bath circulating water to control the saturator, the crystallizer temperature is 90±1°C;
4) controlling the crystal killer and the crystallizer temperature of 92±1°C;
5) The solution in the crystallizer is kept at 5000±200ml, and the stirrer in a container is opened;
6) When crystals appear in the crystallizer, 500 ml samples are taken at intervals of 10 minutes;
7) filtering and drying the suspension, sieving, and weighing 100, 154, 200, 250, 315, 400, 500, 630, 800, 1000 microns, respectively;
8) Data processing.
c) Experimental results and data processing

Make the following picture based on data analysis:

![Figure 2. Number density and particle size.](image)

![Figure 3. Growth rate and nucleation rate.](image)

![Figure 4. Relationship between grain density growth rate.](image)

As can be seen from the above figure, the crystallization kinetic index of wastewater is $i = 1.790$, and the kinetic model is $B = 4.57 \times 10^7 G^{1.790}$ [10].


3.1. Process Parameters

- Feeding amount (F): 5,000kg/h
- Feed concentration (f X): 15%
- Feed temperature (f T): 30°C
- Main components: sodium chloride, phenols, trimethylamine, other impurities
- Evaporation type: MVR evaporation
- Evaporation discharge temperature: 28%
- Evaporation amount (D): 4250kg/h
- Solid output (S D): 750kg/h

3.2. Process Design

![Figure 5. Waste water evaporation crystallization process diagram.](image)

Z101—MVR compressor; E101—plate evaporator; E102—plate condenser; E103—dissolved heat exchanger; E104—spiral heat exchanger; E105—tubular heat exchanger; E106—tubular heat exchanger; E107—multi-stage plate preheater; G101—flash separation tank; G102—crystallization tank; G103—cyclone concentration tank; G104—solution crystal tank; Z102—double stage pusher centrifuge; P101—condensate pump; P102—material pump; P103—screw pump; P104—mother liquor pump; P105—crystallization circulating pump.

The process consists of MVR as a heat source, which consists of an evaporation section and a crystallization section. The evaporation section mainly changes the unsaturated material to near saturation by evaporation, and the crystallization section provides a place for crystallization of the material [11].

The material waste water enters the multi-stage preheater through the pretreatment through the flow meter and the variable frequency feed pump. The heat source of the preheater adopts the evaporated condensed water, and the other part comes from the excess steam after the compression and the fresh steam; In order to ensure that the steam and fresh steam at the outlet of the compressor do not affect each other, it is best to set it to two sections. The pre-heated material bubble point enters E101, and is evaporated by heat in the evaporator. The vaporized liquid mixture enters G101 and is flash-separated [12]. If the separated material is 28%, it can
enter G102 for evaporation and crystallization [13]. When it is low, it needs to be circulated and evaporated; the material of G102 is heated by E105, P105 and E106, and then evaporated into the evaporation zone of G102. The liquid is supersaturated, and the crystal grains gradually nucleate and grow during the process of supersaturation disappearing; suitable grains And the suspension is pumped out through P103, cooled to near room temperature by E104, into G103 cyclone concentration and Z102 centrifugal separation; the separated solid particles are discharged from the package, and the mother liquor enters G104 for crystallization; the mother liquor can be returned to the feed tank, or through 104 Suspension heat exchange (the centrifuge is mostly operated at atmospheric pressure, in contact with the atmosphere), and then heated to the crystallization temperature by E103, a route to the washing legs to enter, all the way directly into the crystallization tank [14]. The secondary vapors evaporated by G101 and G102 are compressed by the pipeline into the compressor, and the high-temperature steam at the outlet is used as the heat source for E101, E105, and E106, and a small portion is used for the heat source of E107 and E103 [15].

After evaporation, the condensed water is used as a heat source for the preheater because of its high temperature and heat. A small amount of secondary non-condensable gas and steam are condensed through the condenser to about 40°C for discharge [16].

4. Industrial Operation Results and Analysis

The MVR evaporative crystallization unit involves a compressor and evaporative crystallization. The design and configuration of the compressed steam line and the design and formulation of the crystallization part of the slurry transfer line are key [17].

Compressor inlet and outlet steam lines should consider the loss of steam and the condensation of steam during the transportation process. Condensate collection and drainage devices should be installed in the pipeline [18]. The water spray cooling device designed for the compressor outlet usually has a large amount of water spray, and the design of the condensed water and excess cooling water collecting and discharging device here is more important. The pipeline should also fully consider the pressure drop problem to ensure that the temperature difference loss provided by the compressor to the evaporator is as small as possible. The steam line is also not as large as possible, considering the cost [19].

The design of the crystallization part of the pipeline. Due to the presence of solid crystal slurry, this pipeline has more difficult factors in transportation. Flow rate problems, temperature problems, flow problems, and welding interface problems should all be considered. Excessive flow rate has a good effect on solids transport, but high flow rate requires high energy consumption. The wear and impact of solid particles on the inner wall of the pipe will also increase, which requires the design of the pipe wall thickness and pump power to increase [20]. The flow rate is small, the crystal grains are easily deposited, and the possibility of clogging is increased. Temperature is one of the important factors in the design of this pipeline. It is necessary to consider whether it is heat preservation or heat tracing. Temperature affects the solubility of organic and inorganic materials in most wastewaters. Temperature also affects the viscosity of wastewater. Temperature changes can cause changes in grain size and changes in the form of wastewater flow, which can change the likelihood of sediment plugging. Proper insulation and heat tracing design [21]. The transport of the slurry suspension is preferably carried out obliquely or vertically. The usual crystallization apparatus is designed to be vertically oriented from the top to the bottom, which can effectively prevent clogging due to grain deposition. The welding interface and the inner surface of the pipe are also factors that cause grain deposition or even blockage. The inner surface is as smooth as possible, the weld is as smooth as possible to reduce the presence of welding slag, the elbow of 90° and acute angle is reduced, the elbow is made of long radius elbow, the valve is smooth and open, and the ball valve is used as much as possible. The transfer line should also consider steam purge and water purge, used when the line is clogged. Pipes should be kept as many as possible, and can be processed in stages [22].

The effect of the evaporator on evaporation is mainly due to the material properties and equipment characteristics. Material properties determine the corresponding structure of the equipment. In the plate evaporator, the plate evaporator of the corrugated structure, the heat transfer coefficient and the pressure drop may play different roles in the evaporation process.

The structural plate spacing and corrugation angle of the evaporator plate type affect the heat transfer coefficient and pressure drop. In the evaporation of materials with easy structure, the flow rate should be increased so that the pressure drop should be as small as possible. The evaporator should also consider the structural dead angle and the flow rate as consistent as possible. In the relatively simple material handling, it may be necessary to pay attention to the improvement of heat transfer.

The operation of the crystallizer is to reduce the possibility of fouling, and the equipment needs a smooth transition to reduce the dead angle. The Oslo crystallizer has a chunky and slim design. Under the same circulation amount, the sedimentation speed of the chunky grain is slow, and the stratification is not obvious. Due to the large diameter, the material liquid extraction port may have to be designed more, otherwise the extracted grain may have uneven particle size distribution. The high and thin shape, the sedimentation speed is fast, the stratified height of the same particle size is relatively thick, the material extraction design can be relatively small, and the extracted grain size distribution is relatively uniform. The design of the crystallizer outlet should ensure the stability and uniformity of the discharge as much as possible.
5. Conclusion

In this paper, an MVR evaporation crystallization device for a salt-containing wastewater is designed. Through the experimental method, some thermal parameters needed to facilitate the design of the device were determined, and the physical properties of the wastewater were comprehensively understood. Through the small test and on-site operation, understand the law of evaporation and crystallization of this wastewater. This wastewater has a lower solubility than pure sodium chloride and a lower supersaturation than pure sodium chloride. Evaporation, heat transfer to salty wastewater, the boiling point should be fully considered, in the calculation of heat transfer temperature difference to subtract the boiling point rise value is the actual temperature difference of the actual heat transfer. The boiling point rise value of wastewater will increase with the increase of concentration. In the MVR evaporation crystallization design calculation, the temperature rise of MVR should be limited, and sufficient effective temperature difference should be ensured. The crystallization constant of this wastewater is 1.790, and the supersaturation increases the nucleation and growth rate. When the degree of supersaturation is small, the growth rate is greater than the nucleation rate, indicating growth. When the degree of supersaturation is large, since the secondary nucleation is much larger than one nucleation, and the secondary nucleation due to factors such as collision increases, the grain size is usually not large. The evaporation crystallization device of MVR should consider the evaporation amount of the evaporation part and the crystallization part. If the concentration of the evaporation part is too high, it will increase the boiling point and increase the possibility of crystallization. On the other hand, if the concentration is too high, it may force the MVR to choose an increase in the temperature difference, which may also cause the evaporator to be blocked. Usually, the evaporation portion is brought to near saturation, and the crystallizer can achieve supersaturation while ensuring a certain amount of evaporation, and the supersaturation formed is also reasonable. If it is too large, the grain is large but not large; if it is too small, there will be no grain growth. Therefore, the supersaturation should be chosen reasonably, usually 30% of the experimental supersaturation is used as the design supersaturation. The actual operation of the site must ensure the continuous supply of water, electricity and gas. The crystallization conveying pipeline should be as inclined as possible. The installation and welding should not leave a dead angle. The valve is a ball valve. The pump uses a pump head with small cutting and welding should not leave a dead angle. The valve is a ball such as heat preservation, heat tracing and purging.

References


