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Petrochemical wastewater treatment device based on ultrasonic demulsification and rotating packed bed

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Abstract: *In this paper, a device for purification of petrochemical wastewater by high gravity rotating bed is described. This paper introduces the structure and function of each module of the industrial petrochemical wastewater treatment device in detail, and finally simulates the wastewater treatment process with a mathematical model to verify the feasibility and treatment efficiency of the device. The device described in this paper has long-term significance for the treatment of industrial petrochemical wastewater, and plays a significant role in green development.*

Keywords: *industrial and petrochemical wastewater, multi-component separation, ecological environment*

1. Introduction

According to relevant statistics, by 2019, China's industrial and petrochemical wastewater discharge has exceeded 400 million tons, accounting for 28.7% of the total national wastewater discharge. The petrochemical wastewater discharge in the petrochemical industry has also increased from 10% to 18.5%[1] of the total industrial and petrochemical wastewater, causing great damage to the ecological environment.

Due to the different process flow of petrochemical industry, there are many mixed components in petrochemical wastewater with high and low content.

There are also different phenomena. To treat petrochemical wastewater innocuously, multi-component separation must be realized first. High-efficiency and environment-friendly petrochemical wastewater component separation technology has been the core technology of petrochemical wastewater treatment.

This project proposes a new petrochemical wastewater treatment device that utilizes the ultrasonic demulsification effect and the rotating packing separation effect to separate the water and various organic substances in the petrochemical wastewater. It has the characteristics of short treatment time, small floor space, high separation degree, and is expected to significantly reduce the cost of petrochemical wastewater treatment.

The research and development of this device is of great significance for reducing the discharge of petrochemical wastewater in China, improving the efficiency of China's oil refining industry and subsequent chemical industry, and promoting the healthy development of China's environment and economy.

2. Main body

2.1. Work research background

A comprehensive treatment device for petrochemical wastewater, which is characterized in that it comprises an oil-water separation mechanism and a water treatment mechanism. The oil-water separation mechanism comprises an ultrasonic demulsification component and a cyclone tube collection component arranged in sequence according to the flow direction of the wastewater;

Wherein, the ultrasonic demulsification component is used for ultrasonic demulsification treatment of waste water, and the cyclone tube collection component comprises a cyclone tube arranged in sequence

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according to the flow direction of waste water and a solid particle collection piece with adsorption materials, as shown in Figure 1. [2]

Figure 1: Diagram of petrochemical wastewater.

The demand for water and the discharge of waste water in the petrochemical industry are huge. For every ton of chemical products manufactured

It needs to discharge several tons or even dozens of tons of petrochemical wastewater. In recent years, the industrial added value and crude oil processing volume of petrochemical industry have increased year by year, and the benefits of oil refining industry and subsequent chemical industry have gradually increased. With the improvement of the level and the rapid development of the petrochemical industry, the discharge of petrochemical wastewater has increased year by year, causing great damage to the ecological environment. At the same time, due to the different technological processes in the petrochemical industry, there are many mixed components in the petrochemical wastewater, and the content is different, which makes it difficult to separate the complex organic components, sulfide, ammonia nitrogen compounds and other series of pollutants in the wastewater from the water, and the treatment cost of the wastewater is high.

2.2. Conceptual design

2.2.1. Basic principle of the project

Due to the displacement effect of water particles in petrochemical wastewater caused by ultrasonic mechanical vibration, small water droplets collide at the wave junction, merge into large water droplets, and settle down from the oil. [3] At the same time, the heat effect generated by ultrasonic vibration friction can reduce the viscosity of crude oil to a certain extent, and also has a certain auxiliary effect on water droplet settlement, as shown in Figure 2.

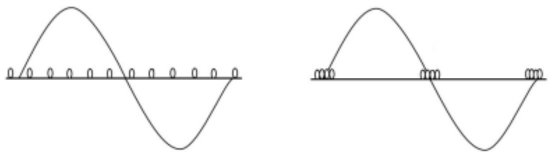

Figure 2: Schematic diagram of water particle displacement before and after ultrasonic treatment.

The hydrocyclone uses centrifugal force to separate oil and water. The stable oil-water envelope surface can be formed by stabilizing the flow rate and pressure difference ratio, thus achieving stable oil-water separation effect. Its working principle is that oily sewage enters the hydrocyclone from the feed pipe along the tangent direction, and the liquid is forced to rotate from top to bottom due to the restriction of the outer cylinder wall. The German sewage in the external cyclone is subject to the centrifugal force. If the density is greater than the density of the surrounding liquid, the centrifugal force it is subjected to will be greater. Once the force is greater than the liquid resistance generated by the movement, the sewage will overcome this resistance and move towards the wall, and separate from the sewage containing sewage. The sewage near the wall will be driven by the continuous liquid, move downward along the wall, reach the underflow port and discharge from the underflow. The hydrocyclone uses centrifugal force to separate oil and water. The stable oil-water envelope surface can be formed by stabilizing the flow rate and pressure difference ratio, thus achieving stable oil-water separation effect.

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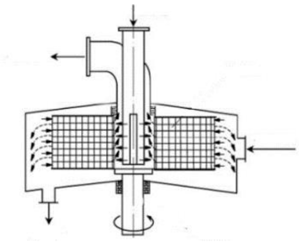

Figure 3: Schematic diagram of rotating packed bed.

2.2.2. Overall device design

The petrochemical wastewater that has been treated by static layering and filtered to remove large solid particles is introduced into the oil-water separation device. Under the barrier of its built-in wave plate and the small hole baffle at the end of the ultrasonic demulsification chamber, the flow rate of petrochemical wastewater decreases, and the ultrasonic generation device sends out ultrasonic waves of a specific frequency to demulsify the petrochemical wastewater, so that the oil-water can be preliminarily separated.

After being treated by ultrasonic demulsification module, the mixed waste water containing organic substances in the tank will enter a continuously rotating cyclone tube through the small hole on the baffle. The solid substances in the waste water will gradually gather on the pipe wall and reach the small holes arranged regularly on the pipe at the other end. After leaving the small holes, it will be adsorbed on the solid particle absorption device. [4] Due to the centrifugal force generated by the rotation of petrochemical wastewater in the hydrocyclone, the oil and water are further separated, and the stable oil-water enveloping surface is formed by the stable flow and pressure difference ratio, so as to obtain the stable oil-water separation effect. The water layer will move away from the oil layer to the pipe wall due to the high density and the centrifugal force, and the water layer near the pipe wall will receive continuous liquid propulsion, move forward along the pipe wall, reach the underflow port and discharge from the underflow port. The oil layer moves backward to the top flow port and flows out through the pipeline.

After leaving, the water enters the water treatment module from the upper port under the pressure of the water pump. When the air is introduced, the rotor rotates in the device to make the gas filler react to remove the ammonia nitrogen compound and sulfide in the waste liquid, thus making the waste water completely treated, as shown in Figure 4.

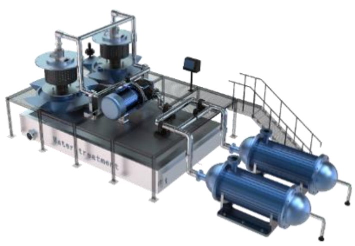

Figure 4: Overall device diagram.

2.2.3. Oil-water separation module

2.2.3.1. Ultrasonic demulsification device

The ultrasonic wave is released from the ultrasonic generator at the bottom of the temporary storage tank for petrochemical wastewater. Under the condition of 50 ℃, ultrasonic wave can spread freely in different media such as solid, liquid and gas to reach the emulsification layer of petrochemical wastewater. Ultrasonic wave will produce cavitation in waste water, and produce small bubbles that are unstable in expansion or contraction within a certain period. The small bubbles that break during this period will bring instant high heat and high pressure environment to the emulsified layer mixed with water and oil, which will break the balance of emulsified layer, and water and oil will flow relatively. In the process of

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constantly establishing new balance, water and oil will be separated to achieve the goal of demulsification of petrochemical wastewater.

Wave-shaped baffles are set in the ultrasonic demulsification chamber, and a baffle with a small hole is set at the end of the ultrasonic demulsification chamber to reduce the flow rate of petrochemical wastewater in the chamber, so as to improve the effect of ultrasonic demulsification and fully separate oil and water, as shown in Figure 5.

Figure 5: Oil collection device.

2.2.3.2. Cyclone pipe collection device

It is composed of a hydrocyclone and a solid small particle collection device. The petrochemical waste water at the opening of the hydrocyclone flows into the module along the side wall of the hydrocyclone at the tangent direction of the inlet. The cyclone tube moves around its axis, causing the wastewater to rotate from top to bottom in the pipeline. The density of small solid particles in waste water is larger than that of liquid, so the centrifugal force of small solid particles is larger than that of liquid of equal volume. The small solid particles and water phase are separated and attached to the pipe wall. Because of the device's certain taper, the small solid particles move downward along the pipe wall spiral, and concentrate at the opening of a section at the bottom of the device, and connect a cylindrical solid particle collection device with built-in adsorption material. The adsorption material is activated carbon.

Due to the centrifugal force generated by the rotation of petrochemical wastewater in the hydrocyclone, the oil and water are further separated, and the stable oil-water enveloping surface is formed by the stable flow and pressure difference ratio, so as to obtain the stable oil-water separation effect. The water layer will move away from the oil layer to the pipe wall due to the high density and the centrifugal force, and the water layer near the pipe wall will receive continuous liquid propulsion, move forward along the pipe wall, reach the underflow port and discharge from the underflow port. [5-6] The oil layer moves backward to the top flow port and flows out through the pipeline.

Small solid particles will leave the hydrocyclone and then be attracted by the adsorption device and adsorbed on it. The oil layer will flow out through the pipeline at the top of the hydrocyclone, and the petrochemical wastewater that removes small solid particles and oil layer will be transported out of the overall oil-water separation device, as shown in Figure 6.

Figure 6: Cyclone tube collecting device.

2.2.4. Water treatment module

2.2.4.1. Rotating module

It is composed of a rotating shaft and a water spray port. When the sewage after oil and water separation enters the rotating device, air is introduced from the lower port of the rotating device to react with sulfur-containing sewage to generate S2O32 - and SO42 - ions. During the rotation, the suspension passes through the filler in the rotating module by centrifugal force and is thrown to the outermost outer wall. During the process, the liquid is fully cut and dispersed, and the specific surface area is extremely expanded, which makes the gas and liquid surface contact more fully and react quickly. The liquid finally converges at the bottom of the rotating module, flows out through the outlet and flows into the sewage tank installed at the bottom of the platform, as shown in Figure 7.

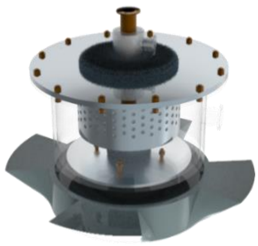

Figure 7: Rotating module.

2.2.4.2. Packing module

It is composed of solid block filler, attached with a filter screen, and has a certain space between the outer wall. When the rotating module operates, the solid fast packing does not rotate with it. The solid block filler is composed of a mixture of magnesium hydroxide and phosphoric acid, which can effectively remove ammonia nitrogen compounds in petrochemical wastewater. At the same time, the S2O32 - and SO42 - ions generated after the air oxidation of sulfur-containing wastewater will combine with the magnesium ions in the filler to form precipitation and attach to the solid filler (the solid filler is replaced regularly). Due to the existence of chemical balance, the balance will be carried out to the right to accelerate the rate of air oxidation of sulfide in the waste water, making the reaction rate faster and more complete, and the sulfide will be more complete in addition to ammonia nitrogen compounds, to promote each other, as shown in Figure 8.

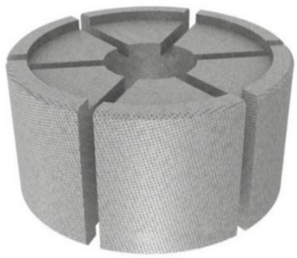

Figure 8: Packing module.

2.2.4.3. Liquid level and water quality components detection equipment

The purified petrochemical wastewater will flow through the equipment, which will monitor the ammonia nitrogen compound and sulfide content in the water in real time, as shown in Figure 9.

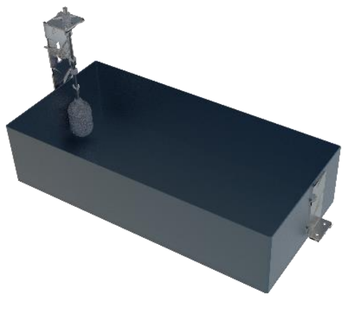

Figure 9: Water quality component detection device.

2.2.5. Intelligent control

The intelligent control module uses stm32 single-chip microcomputer to identify the oil-water ratio detected by the oil-water detector to complete the operation. The microcontroller is connected with the ultrasonic generator and the oil detector in water through USB interface. When the oil-in-water detector is working, it transmits signals to the ultrasonic generator with different pulses in different oil-water ratio of petrochemical wastewater. The ultrasonic generator adjusts the working power and frequency of the

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ultrasonic wave in real time through the received pulses.

2.3. Feasibility analysis

Drift force of water droplet due to sound pressure is:

$$F_R = \pi\rho_\omega A^2 (kr_\omega)^3 F(x) \sin 2kx_0 \quad (1)$$

Where,A represents the velocity potential amplitude of the flow field;ρ_ω is the density of the water layer, kg/m^3;ρ_0 is the density of oil layer, kg/m^3;rw is the radius of water droplet, m;F (x) is the relative density coefficient, as shown in Figure 10.

Its calculation formula is as follows:

$$F(x) = \frac{1+\frac{2}{3}\left(1-\frac{\rho\omega}{\rho_0}\right)}{2+\frac{\rho\omega}{\rho_0}} \quad (2)$$

The relevant parameters in the formula are shown in the following table 1:

Table 1: Data taken from relevant physical quantities.

Water layer density(kg/m^3)	Reservoir density(kg/m^3)	Droplet radius /m
1.0×10^3	0.9×10^3	0.001

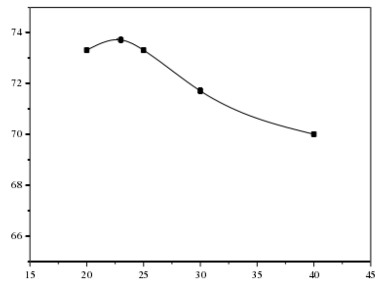

Figure 10: Effect of ultrasonic frequency on dehydration efficiency[7].

The relationship between ultrasonic wave intensity and acoustic frequency is as follows:

$$I = \frac{2\pi^2 \rho c f^2 V_m^2}{10^7} \quad (3)$$

$$\frac{P^2}{\rho_0 c} = \frac{W}{4\Pi r^2} \quad (4)$$

Where, I is the acoustic intensity, W/m^2; P represents sound pressure, Pa; c is the velocity of sound wave, m/s; f is the acoustic frequency, Hz; Vm stands for amplitude, m.

Its calculation formula is as follows:

$$V_m^2 = \frac{ZW}{4\Pi d^2}(1-a) \quad (5)$$

Where, r is the distance from the sound intensity of the measured point to the sound source, m;w is the sound source power, W;d is the distance between the sound source and the monitoring point, m;a is the reflection and absorption coefficient, 0.05;Z is the acoustic characteristic impedance. In acoustic theory, the sound absorption characteristic is expressed by acoustic impedance or sonar:

$$B = \frac{1}{Z} = \frac{1}{\rho c} \quad (6)$$

Where, B is acoustic admittance, mmho; Z is the acoustic impedance, Pa · s/m ^ 3. Air acoustic impedance is: Where, c is the sound velocity, m/s, as shown in Figure 11. [8]

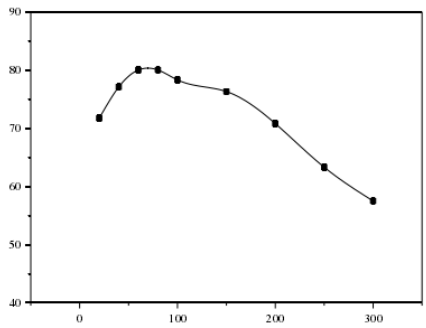

Figure 11: Effect of ultrasonic power on dehydration efficiency.

As shown above, the device adjusts the power of the ultrasonic generator and the frequency of the ultrasonic wave through the data detected by the oil-in-water detector to achieve the best effect of oil-water separation.

2.4. Purification effect of the device

The size of the orifice baffle area can be given by the following formula:

$$A_1 = \frac{Q}{K} \quad (7)$$

Where: A_1 area of filter membrane in water-oil separation device, cm^2; K is the flow constant, $m^3/(h \times cm^2)$; Q is the petrochemical wastewater flow through the cyclone pipeline, m^3/h.

$$Q = 3.6 \times 10^{-3} \times \frac{\pi}{4} \times d^2 \times V_1 \quad (8)$$

$$d \geq \sqrt{\frac{4Q}{3.6\pi V_1} \times 10^3} \quad (9)$$

Where: d is the outlet diameter of cyclone pipe, 30mm; V_1 is the flow rate of petrochemical wastewater at the outlet of cyclone pipe, unit: m/s, as shown in Table 2.

Table 2: Relevant data of benefit formula. [9]

Flow constant /($m^3 \cdot h^{-1} cm^{-2}$)	Membrane area /cm^2	Major diameter of cyclone tube /mm	Minor diameter of cyclone tube /mm
0.5	78.5	100	30

The specification data of the water pump used in this unit are shown in the following table 3:

Table 3: Relevant data of water pump used in the unit.

Rated power /W	Pumping capacity /(m^3/h)	Unit price/yuan
2200	40	500

The ultrasonic oil-water separation efficiency of the device can reach 80%; After the further layering of the hydrocyclone, the residual oil layer in the petrochemical wastewater is 0.5%, so the final efficiency can reach 99.5%.

According to the calculation of the expected treatment capacity of sewage treatment, the area of small hole baffle is about 78.5cm^2 according to the device itself. According to the speed of oil-water separation of the unit, the water pump cannot work at the rated power.

The pumping capacity of the water pump in this unit during normal operation is 30m3/h. According to the above formula, it is estimated that the average flow of petrochemical wastewater treatment is 41.6m3/h, and the water flow is 17.74m3/h after being blocked by wave-shaped baffle and small-hole baffle.

So the amount of water that can reach the standard is about 17.74 tons per hour. Compared with the existing technology for treating sulfur-containing wastewater (efficiency is 90%), according to the average concentration of sulfide is 20 mg/L, and the concentration of ammonia nitrogen is 50 mg/L, it is estimated that the amount of sulfide emissions can be reduced by 7.6 next year × 107kg, reducing ammonia nitrogen by 1.9 × 108kg.

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2.5. Research status and development trends at home and abroad

In the 1980s, ultrasonic demulsification was studied abroad. Among them, Davis Robert Michael and others used ultrasound to treat crude oil emulsion. They found that the demulsifier AQUANOX 272 was used at a frequency of 1.2kHz. Finally, the water content was analyzed to be 0 by using the Basic Separation and Water method. Teksonix Company of the United States used ultrasonic crude oil dehydration and treatment device and its process flow to carry out industrial tests in eight factories in the United States, and achieved good results. Paczynska - LahmeB used ultrasonic frequencies of 35 kHz and 45 kHz to conduct the tests, and compared with the heating demulsification method, concluded that the ultrasonic method was superior to other methods. [10]

Compared with foreign research, domestic research started late but also made brilliant achievements. Li Shuqin and others found that ultrasonic demulsification can not only improve the dehydration and demulsification rate of crude oil, but also reduce the amount of demulsifier to a large extent when treating heavy oil with viscosity greater than 5000Pa. s. Lv Xiaoping treated the waste oil of petrochemical company with ultrasonic wave, and found that 80% of free water can be removed by ultrasonic wave, and 94% of free water can be removed by adding some demulsifiers, which greatly played the role of ultrasonic demulsification. Through theoretical analysis and laboratory experiments, Chen Yonghong and others pointed out that ultrasonic demulsification technology can further realize demulsification and dehydration for some emulsified crude oil when the demulsifier cannot achieve the desired effect. It is especially pointed out that the efficiency of demulsification and dehydration can be improved to a greater extent when the chemical demulsifier is combined with ultrasonic demulsification technology.

However, the existing ultrasonic demulsification technology is mostly applied to emulsified crude oil with stable oil-water ratio, and it is used to treat the oil-water mixture when it is refined. It is rarely applied to the treatment of flowing petrochemical wastewater with extremely unstable oil-water ratio, and the accumulated experience in this field is also insufficient. The device analyzes the oil-water ratio of petrochemical wastewater in real time through online water-oil detector, then adjusts the ultrasonic frequency and power to achieve the best demulsification effect of ultrasonic on petrochemical wastewater, and finally carries out secondary separation of the oil and water that has been initially stratified through the cyclone tube.

Rotating packed bed is a new and efficient gas-liquid mass transfer equipment developed in the 1980s. Its working principle is that under the centrifugal force of hundreds to thousands of times of gravity (super gravity) in the middle ring of the packed bed, the liquid phase forms a liquid film on the surface of the packing, the liquid film flows rapidly to the outer ring, the thickness of the liquid film decreases sharply, the wetted area of the carrier increases, and the increase of the phase boundary area leads to the great enhancement of the mass transfer, heat transfer and reaction process controlled by the liquid phase. At present, the rotating packed bed is mainly used for distillation, absorption, degassing, extraction and dust removal, but it has no application in the element treatment of petrochemical wastewater.

Through the wet removal experiment of hydrogen sulfide with rotating packed bed by Du Leilei et al., it can be concluded that the rotating packed bed has certain feasibility for the treatment of liquid magazine. The packing part of the rotating packed bed module of the device is replaced by the packing that has the removal effect on the elements in petrochemical wastewater. Under the centrifugal action of the rotating packed bed supergravity, the efficient solid-liquid reaction efficiency makes the sulfur, nitrogen Phosphorus and other major elements can combine with the filler to form a precipitated solid attached to the filler. The device has a development trend for the application of rotating packed bed.

2.6. Innovation points and project characteristics

2.6.1. Structural innovation

A temporary storage tank loaded with ultrasonic generator was designed to demulsify the petrochemical wastewater, and a wave-shaped baffle and a small-hole baffle were designed to block the petrochemical wastewater and fully pretreat the petrochemical wastewater.

2.6.2. Principle innovation

At present, the high gravity rotating packed bed has not been applied to the treatment of petrochemical wastewater in industry. The project applies the high gravity rotating packed bed to the treatment of sulfur and ammonia nitrogen compounds in petrochemical wastewater, which improves the removal rate of pollutants, reduces the time required for reaction, and saves site space.

The principle of ultrasonic demulsification technology is applied to the oil-water separation step of petrochemical wastewater treatment, which solves the difficulty of incomplete oil-water separation of petrochemical wastewater treatment by existing technology.

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2.6.3. Project features

The innovative application of ultrasonic demulsification technology and high gravity rotating packed bed in the treatment of petrochemical wastewater can greatly reduce the time and space of petrochemical wastewater treatment, and has certain economic benefits. Compared with the current petrochemical wastewater treatment technology, the project increases the efficiency of wastewater treatment and has a wider application.

3. Conclusions

The research of this device is beneficial to improve the oil-water separation rate of petrochemical wastewater, improve the removal rate of pollutants in petrochemical wastewater, and reduce the treatment cost of petrochemical wastewater. It is of great significance to reduce the discharge of petrochemical wastewater in China, improve the efficiency of China's oil refining industry and subsequent chemical industry, and promote the healthy development of China's environment and economy. Through the innovation of ultrasonic demulsification technology and rotating packed bed in petrochemical wastewater treatment, the core technology of petrochemical wastewater separation is broken, the current situation of wastewater treatment technology is changed, and the industrial transformation and upgrading is led.

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