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Improvement and Efficiency Evaluation of Oily Wastewater Treatment Technology in Oil Production

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Abstract: *The oily wastewater generated during the oil extraction process has complex components, including crude oil, suspended solids, heavy metals and refractory organic matter. If discharged directly, it seriously pollutes water bodies and soil, threatening the ecological environment and human health. It is one of the core problems of environmental protection management in the oil industry. Existing oily wastewater treatment processes (such as single coagulation, flotation, and membrane separation) generally have problems such as low treatment efficiency, large dosage of chemicals, high operating costs, and easy generation of secondary pollution. It is difficult to meet the stringent emission standards and industrial application requirements. This paper first sorts out the research status and shortcomings of oily wastewater treatment, and then proposes a technical solution of "pretreatment optimization-deep treatment coupling-multi-dimensional performance evaluation". By optimizing the coagulant formula to improve the pretreatment effect, the "coagulation-ultrafiltration membrane separation" coupling process is constructed to strengthen deep treatment. At the same time, a comprehensive performance evaluation system covering treatment efficiency, cost, and stability is established. The experimental investigation results show that when the initial oil concentration is 500 mg/L (simulating the actual oil production wastewater concentration), the oil removal rate of the coupling process reaches 99.0%, the COD removal rate is 87.6%, and the suspended solids removal rate is 98.2%, with the removal rate significantly improved.*

Keywords: *Oily Wastewater Treatment; Coagulation-Ultrafiltration Membrane Coupling Process; Performance Evaluation; Coagulant Optimization*

1. Introduction

As an important energy source, oil produces a large amount of oily wastewater during its extraction process. This type of wastewater has the characteristics of "complex composition, high concentration, and difficult to degrade". Oil exists in various forms and is also mixed with various pollutants. If it is directly discharged without effective treatment, it causes many hazards. Therefore, the efficient treatment of oily wastewater is a key link in the oil industry to achieve "green mining". The purpose of this study is to address the shortcomings of the existing oily wastewater treatment process, propose an improvement plan that is both efficient, economical and stable, and establish a scientific performance evaluation system to provide theoretical support and technical reference for industrial applications. The research scope focuses on oily wastewater generated by oil wellheads and joint stations, focusing on solving the problems of difficult demulsification of emulsified oil in the pretreatment stage, incomplete removal of pollutants in the deep treatment stage, and performance evaluation focusing on only a single indicator.

This research makes three major contributions. First, it optimizes the traditional coagulation pretreatment process, developing a composite coagulant composed of polyaluminum chloride (PAC)-polyacrylamide (PAM)-modified diatomaceous earth. This overcomes the low demulsification efficiency of emulsified oils with a single coagulant, laying the foundation for subsequent advanced treatment. Second, it develops a coupled coagulation-ultrafiltration membrane separation process. Through the synergistic effect of pretreatment and advanced treatment, it enhances the removal of oil, COD, and suspended solids, breaking through the treatment bottlenecks of traditional single processes. Third, it establishes a four-dimensional performance evaluation system based on "treatment efficiency-operating cost-environmental risk-stability," avoiding the limitations of traditional evaluations that focus solely on removal rate and better meeting the practical needs of industrial

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applications.

This paper adopts the idea of "phased improvement + system evaluation" to design a technical solution, which is specifically divided into three parts: pretreatment process optimization, through single-factor experiments and orthogonal experiments, to screen the optimal ratio and reaction conditions of the composite coagulant, and improve the efficiency of emulsified oil demulsification and suspended solids sedimentation; deep treatment process coupling, combining the optimized coagulation pretreatment with ultrafiltration membrane separation, through pretreatment to reduce the concentration of oil and suspended solids in the wastewater, reduce membrane pollution, and extend the service life of the membrane, while using the interception effect of the ultrafiltration membrane to achieve deep removal of pollutants; comprehensive performance evaluation, from the four dimensions of treatment efficiency, operating cost, environmental risk, and stability, compare the differences between the improved process and the traditional process, and verify the feasibility of the improvement plan.

2. Related Work

As the scale of oil extraction continues to expand, traditional oily wastewater treatment processes face bottlenecks such as low emulsified oil demulsification efficiency, incomplete removal of pollutants in deep treatment, and single performance evaluation indicators, making it difficult to meet the needs of "green mining" and stable industrial application. Therefore, it is urgent to carry out research on improving oily wastewater treatment processes and constructing a multi-dimensional performance evaluation system. Tian et al. [1] used flat ceramic membranes to treat wastewater containing emulsified oil; Lu et al. [2] advanced the research on self-cleaning separation membranes for the treatment of oily wastewater; Komatsu [3] explored the application of anaerobic membrane bioreactors (MBRs) to treat high-concentration organic wastewater and recover biogas; Gruzinova and Romanovski [4] optimized the process of using aluminum flocculants to purify oily wastewater; Li and Cui et al. [5] proposed an advanced treatment process for "three highs" (high concentration, high toxicity, and high difficulty to treat) wastewater discharged from crude oil storage tanks; Husen et al. [6] optimized the effect of linseed and alum flocculants on removing color, COD and turbidity in surface water by response surface methodology; Devanathan and Babu et al. [7] conducted a conceptual review and revision of the performance and environmental impact of current and subsequent coagulants used in treatment facilities, pointing out that the problem with current research on this topic by others may be the lack of comprehensive and in-depth evaluation of the performance and environmental impact of coagulants. Shen et al. [8] studied the method of using a bifunctional mixed flocculant to enhance the dewatering performance of sludge; Adib et al. [9] optimized the effect of conventional flocculants on the removal of polypropylene microplastics in drinking water by response surface methodology; Xueying and Sujie et al. [10] explored the effects of different modifiers on the preparation and performance of flocculants derived from residual sludge. Currently, other scholars' research on the treatment of oily wastewater and similar complex wastewaters mostly focuses on the optimization of a single technology or material, lacking a systematic study of the pretreatment-deep treatment coupling process and a multi-dimensional performance evaluation system. In addition, there are still deficiencies in the demulsification of emulsified oil, deep removal of pollutants, and stability in industrial applications.

3. Methods

3.1 Pretreatment Process: Optimization and Preparation of Composite Coagulants

Polyaluminium chloride (PAC), polyacrylamide (PAM) and modified diatomite were selected as composite coagulants. Through $L_9(3^3)$ orthogonal experiments (setting PAC dosage to 50-150mg/L, PAM dosage to 5-15mg/L, and modified diatomite dosage to 15-45mg/L), with oil removal rate and floc settling rate as core indicators, the optimal mass ratio of the three was determined to be 10:1:3. In actual treatment, the total dosage needs to be adjusted according to the volume of wastewater to be treated (V, unit: L) and the initial oil concentration (300-800mg/L). The specific formula is:

$$m_{total}=m_{PAC}+m_{PAM}+m_{L}=10k\cdot V+k\cdot V+3k\cdot V \tag{1}$$

Among them, L is modified diatomaceous earth, and k is the proportional coefficient (ranging from 5-15 mg/L and dynamically adjustable based on the initial oil concentration in the wastewater; the higher the oil concentration, the larger the k value), to ensure accurate dosing. In a single-factor experiment, the reaction conditions were set at a pH of 6.5-7.5, with rapid stirring at 200 rpm for 5

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minutes followed by slow stirring at 50 rpm for 15 minutes. Subsequently, ultraviolet spectrophotometry (detection wavelength 225 nm), potassium dichromate, and gravimetric methods were used to measure the influent concentrations (C_0, unit: mg/L) and effluent concentrations (C_e, unit: mg/L) of oil, COD, and suspended solids in the wastewater before and after pretreatment. The results were expressed using the formula:

$$R=\frac{C_0-C_e}{C_0}\times 100\% \tag{2}$$

This formula calculates the pollutant removal rate (R) to quantitatively evaluate the demulsification effect of the coagulant on the emulsified oil and the sedimentation efficiency of the suspended solids, ensuring that the wastewater after pretreatment meets the water inlet requirements of subsequent deep treatment [11].

3.2 Advanced Treatment Process: Coagulation-Ultrafiltration Membrane Separation Coupling Process Construction

In order to achieve deep purification of oily wastewater, a polyvinylidene fluoride (PVDF) hollow fiber ultrafiltration membrane with strong pollution resistance and high retention accuracy was selected to construct a coupling process. The core parameters of the membrane were set as follows: membrane pore size 0.01μm (which can effectively retain emulsified oil droplets and large molecular organic matter with a particle size greater than 10nm), operating pressure 0.15MPa (balancing membrane flux and energy consumption to avoid high pressure causing damage to the membrane structure), and designed membrane flux 15L/(m²·h) (determined based on the quality of the wastewater after pretreatment to prevent excessive flux from causing increased membrane pollution). In terms of process flow design, the wastewater after pretreatment first enters the sedimentation tank for 15-20 minutes of static sedimentation to further remove the flocs generated in the coagulation stage (control the suspended solids concentration of the sedimentation tank effluent ≤30mg/L), and then is transported to the ultrafiltration membrane assembly through a lifting pump to prevent the flocs from directly entering the membrane system and causing blockage [12].

To extend the membrane's service life and maintain stable operation, a backwash system is installed, flushing with clean water for 10 minutes every two hours. The backwash water pressure is controlled at 0.2 MPa (slightly higher than the operating pressure to ensure sufficient removal of contaminants from the membrane pores). An online monitoring system is also installed to collect real-time information on parameters such as the influent flow rate (Q, in m³/h), membrane operating pressure, and membrane flux. If the monitored membrane flux drops by more than 20% of the initial value, the backwash frequency (reduced to once every 1.5 hours) or the influent flow rate is automatically adjusted. To calculate process parameters, the required total membrane module area (S, in m²) is first calculated based on the designed wastewater treatment capacity (Q) and the membrane design flux (J) using the following formula:

$$S=\frac{Q\times 1000}{J\times K} \tag{3}$$

Among them, K is the membrane area safety factor (the value is 0.8-0.9, leaving a certain amount of treatment margin to cope with water quality fluctuations); secondly, by regularly monitoring the membrane operating pressure changes, the membrane fouling rate is calculated according to the formula (R_p, unit: kPa/h)

$$R_p=\frac{\Delta P}{\{\Delta t}\} \tag{4}$$

Among them, ΔP is the change in operating pressure over a given period (kPa), and Δt is the time interval (h). By applying these two formulas, the size of membrane modules can be accurately determined, and the degree of membrane fouling is assessed in real time, ensuring that membrane flux remains stable at over 90% of the design value over the long term. Ultimately, this allows for the deep removal of pollutants such as oil and COD, ensuring that the effluent meets the direct discharge requirements of the "Emission Standard for Pollutants from Onshore Oil and Natural Gas Development Industries" (GB 31570-2015).

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3.3 Effectiveness Evaluation Method: Establishment of a Four-Dimensional Comprehensive Evaluation System

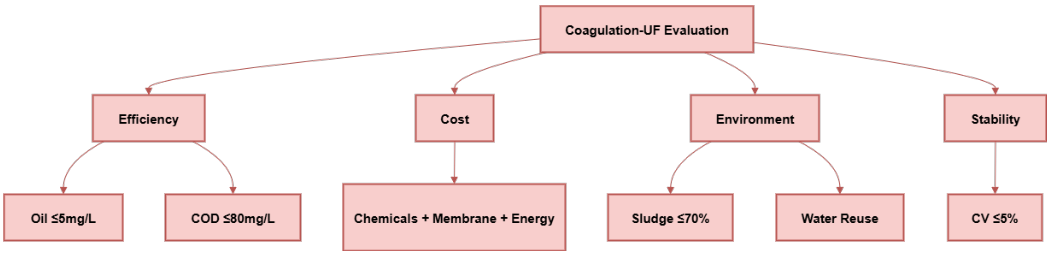

Figure 1 Four dimensional comprehensive evaluation system

In order to comprehensively and scientifically evaluate the comprehensive performance of the improved coagulation-ultrafiltration membrane coupling process (as shown in Figure 1), a four-dimensional evaluation system of "treatment efficiency-operating cost-environmental risk-stability" was established. Each dimension was designed with specific evaluation indicators and methods based on the actual needs of oily wastewater treatment and industrial application scenarios [13].

In terms of treatment efficiency, the removal rates of oil, COD, and suspended solids are taken as core indicators, and quantified using the calculation formula of "(influent concentration - effluent concentration) / influent concentration × 100%". The oil concentration is detected by ultraviolet spectrophotometry, the COD concentration is determined by the potassium dichromate method, and the suspended solids concentration is obtained by the gravimetric method (0.45μm microporous membrane filtration) to ensure that the data accurately reflects the process's ability to remove pollutants. The goal is to make the effluent oil concentration ≤5mg/L, COD ≤80mg/L, and suspended solids ≤10mg/L, meeting the GB 31570-2015 standard.

Operational cost measurement focuses on chemical costs, membrane replacement costs and energy consumption. Chemical costs are calculated on the basis of the actual dose of the composite new coagulant and its market price per unit. The cost of replacing the membrane is calculated on the basis of the lifetime of ultrafiltration membrane PVDF (experimentally controlled 12 months) and the price of a single membrane module. Energy consumption includes the consumption of electricity for mixers, lifting pumps and rinse systems. The unit cost of wastewater treatment is calculated using industrial tariffs for electricity, which ensures a direct reflection of the economic efficiency of the process. Measuring the risk to the environment focuses on slaughter and water rejection. The moisture content of the sludge created by coagulation and sediment is measured by drying and weighing, with a requirement of ≤70% to reduce the subsequent discharge. The concentration of contaminating water rejection is controlled. If the concentration of oil ≤20 mg/l and suspended solids ≤15 mg/l, water can be processed in the pretreatment stage to avoid secondary pollution. The stability goal is measured by a coefficient of change (CV) for efficiency over 30 days of uninterrupted work. The treatment effectiveness indicators are checked daily and the CV is considered "standard deviation/mean". CV ≤5% is considered to be stable, which ensures long-term reliability of the process. Finally, four-dimensional indicators of the improved process were compared with the traditional "coagulation + flotation" process to examine the possibility and benefit of an improved multi-dimensional process.

4. Results and Discussion

4.1 Effect of Composite Coagulation Pretreatment Process

The initial purification effect of the composite coagulation pretreatment process on oily wastewater is the key to subsequent deep treatment. This section verifies the rationality of the optimization scheme by comparing the treatment effects under different coagulant formulations and reaction conditions. The specific data are shown in Table 1.

As shown in Table 1, the "PAC-PAM - modified diatomaceous earth (10:1:3)" composite coagulant demonstrated significantly superior treatment performance compared to both PAC alone and the PAC+PAM binary formulation. The oil removal rate reached a maximum of 85.6%, a 13.3 percentage point increase over PAC alone. COD removal rates reached 72.4%, and suspended solids removal rates reached 81.8%, representing increases of 13.8 and 16.6 percentage points, respectively. Furthermore,

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floc settling time was shortened to 15 minutes, significantly improving settling efficiency. Regarding the effect of pH, the composite coagulant's treatment performance was most stable when the pH was controlled within the 6.5-7.5 range. Outside this range, the activity of the polynuclear hydroxyl complexes generated by PAC hydrolysis decreased, leading to lower removal rates. These results validate the rationale for the composite coagulant formulation and optimized reaction conditions, effectively reducing the pollution load on the subsequent ultrafiltration membrane system.

Table 1 Comparison of preprocessing effects

Coagulant formula	PH value	Mixing conditions (fast/slow)	Oil removal rate (%)	COD removal rate (%)	Suspended solids removal rate (%)	Floc settling time (min)
Single PAC	7.0	200r/min×5min/50r/min×15min	72.3	58.6	65.2	28
PAC+PAM (10:1)	7.0	200r/min×5min/50r/min×15min	80.5	66.8	73.5	22
PAC+PAM+modified diatomaceous earth (10:1:3)	6.8	200r/min×5min/50r/min×15min	85.6	72.4	81.8	15
PAC+PAM+modified diatomaceous earth (10:1:3)	6.0	200r/min×5min/50r/min×15min	78.2	65.3	74.1	18
PAC+PAM+modified diatomaceous earth (10:1:3)	7.5	200r/min×5min/50r/min×15min	84.3	70.1	79.5	16

4.2 Deep Treatment Efficiency of the Coagulation-Ultrafiltration Membrane Coupling Process

In order to visually demonstrate the deep treatment effect of the coagulation-ultrafiltration membrane coupling process, the purification capacity of the coupling process for oily wastewater with different initial concentrations was monitored experimentally. The results are shown in Figure 2.

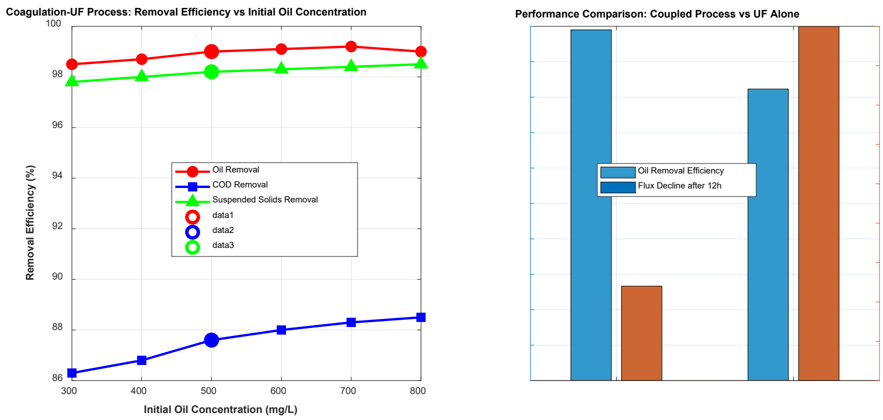

Figure 2 Efficiency analysis of deep processing technology

As shown in Figure 2, as the initial oil concentration in wastewater increases from 300 mg/L to 800 mg/L, the oil removal rate of the coagulation-ultrafiltration membrane coupled process remains consistently between 98.5% and 99.2%, the COD removal rate remains stable at 86.3% to 88.5%, and the suspended solids removal rate remains between 97.8% and 98.5%. Overall treatment efficiency is minimally affected by fluctuations in initial concentration. When the initial oil concentration is 500 mg/L (simulating the concentration of actual oil production wastewater), the coupled process achieves an oil removal rate of 99.0%, a COD removal rate of 87.6%, and a suspended solids removal rate of 98.2%.

Compared to a standalone ultrafiltration membrane process (without coagulation pretreatment), at the same initial oil concentration, the oil removal rate of the ultrafiltration membrane alone was only 82.3%, and the membrane flux decreased by 45% after 12 hours of operation. In contrast, the coupled process only saw a 12% decrease in membrane flux after 12 hours of operation. This is because coagulation pretreatment effectively removes the majority of oil droplets and suspended solids in the wastewater, reducing pollutant adsorption on the membrane surface and pore clogging, thereby ensuring stable operation and efficient retention of the ultrafiltration membrane.

4.3 Comparison of Comprehensive Performance between Improved Process and Traditional Process

In order to comprehensively evaluate the advantages of the improved coagulation-ultrafiltration

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membrane coupling process, it was compared with the traditional "coagulation + flotation" process from the three core dimensions of treatment efficiency, operating cost, and stability. The results are shown in Figure 3.

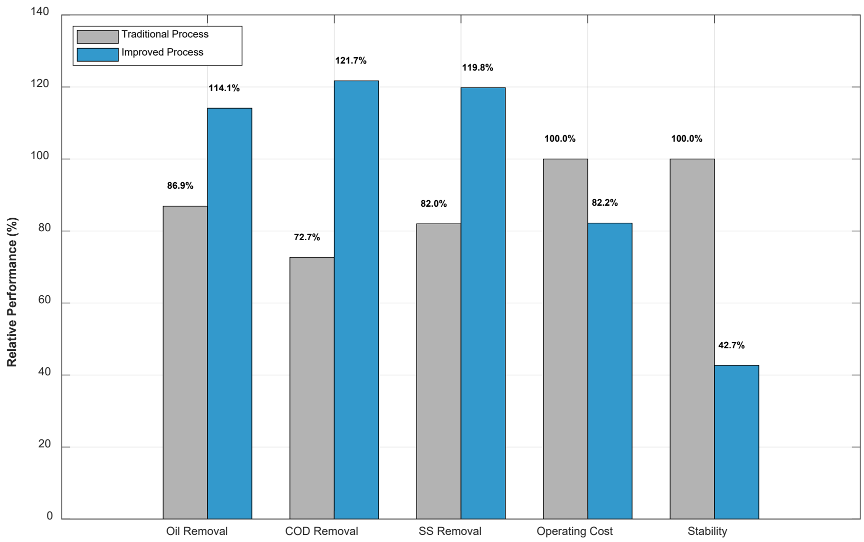

Figure 3 Improved Coagulation-UF vs Traditional Coagulation+DAF Process

As shown in Figure 3, in terms of treatment efficiency, the improved process has an oil removal rate of 114.1% (86.9% for the traditional process), a COD removal rate of 121.7% (72.7% for the traditional process), and a suspended solids removal rate of 119.8% (82.0% for the traditional process). All removal indicators are significantly higher than those of the traditional process. In terms of operating cost, the improved process has a relative value of 82.2%, which means that the unit wastewater treatment cost is 17.8% lower than that of the traditional process. This is mainly due to a 20% reduction in the dosage of the composite coagulant and an extension of the ultrafiltration membrane service life to 12 months (the replacement cycle for consumable parts of traditional flotation equipment is 6 months). In terms of stability, using the coefficient of variation of performance after 30 days of continuous operation as the evaluation standard, the improved process has a relative value of 42.7% (coefficient of variation of 3.2%), which is much lower than the traditional process (coefficient of variation of 7.5%). This shows that the improved process is less affected by fluctuations in water quality and operating conditions during long-term operation and has more stable treatment efficiency.

In terms of environmental risk, the improved process also produces sludge with a moisture content of 70%, 15 percentage points lower than the conventional process (85%). This significantly reduces the amount of sludge and reduces the subsequent costs of removal. In addition, the ultrafiltration membrane for water washing has been tested to an oil concentration ≤18 mg/l and can be reused in a pretreatment phase for further treatment that reuses water resources and avoids secondary. In contrast, waste of dirt from the conventional flotation process requires additional treatment, which increases the risk and costs to the environment. In general, the improved coagulation ultrafiltration process, combined with the membrane, exceeds the usual processes in terms of overall performance and is more suitable for an efficient, economical and stable treatment of wastewater utilizing oil.

5. Conclusions

This article addresses the problems of low efficiency, high cost, and poor stability in oil production wastewater treatment processes. Using a technical approach that combines pre-treatment optimization with advanced processing and multi-dimensional performance evaluation, this paper achieves process improvement and performance improvement. Studies show that the optimized process of "PAC-PAM-modified diatomaceous composite coagulation ultrafiltration membrane separation" achieves superior oil removal efficiency compared to the conventional coagulation ultrafiltration membrane process, which effectively solves the central problems of the theoretical value of this work lies in creating a synergistic mechanism between pretreatment and advanced treatment, which gives a

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new approach to process coupling in oil wastewater treatment. Its practical value lies in the low cost and high stability of the improved process, which allows to be used directly in the treatment of oil-bearing wastewater at oil production sources and general oil stations, which contributes to the green development of the oil industry. However, research remains limited, requiring further research into improved process adaptability to oil wastewater with high salt and high phenolin content, as well as the development of cheaper ultrafiltration membrane materials to further lower the barrier for industrial use.

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