Treatment of Refined oil depot wastewater

Mengjie Wu1*, Zhen Liu1

1 School of Energy and Power Engineering, Wuhan University of Technology, Wuhan, Hubei, 430063, China

*Corresponding author’s e-mail: 804612350@qq.com

Abstract. In the treatment of oily wastewater, the water quality and quantity must be clarified. First, the physical form and chemical composition must be clarified, and then the drug can be treated according to the characteristics of various pollutants. The current treatment of wastewater from refined oil storage tanks is still dominated by the old three sets (sedimentation, flocculation, and biological methods). The current application research is mainly an optimization of the old three sets, such as the application of hydrocyclones, the preparation of new coagulants, the use of efficient air flotation devices and efficient microorganisms. However, the difficulty of wastewater treatment of refined oil depots is COD (Chemical Oxygen Demand). Due to the characteristics of oily wastewater, there are some limitations in biological methods. At present, the advanced oxidation method is not mature and the treatment cost is high, which restricts the advanced oxidation method to treat oily wastewater. This paper describes the source of oil products, the generation of oil-bearing wastewater and various processes of oil-bearing wastewater treatment. Finally, some ideas of advanced oxidation technology to remove COD from oil-bearing wastewater are put forward.

1. Introduction
The oily wastewater of the product oil depot mainly refers to the sewage produced in the production process of the oil depot, and specifically includes oil tank cutting water, oil tank cleaning water, equipment and ground washing water, and contaminated initial rainwater, etc.[1]. For refined oil depots, the main sewage comes from a small amount of tank bottom water and a large amount of tank washing wastewater. In the process of oil refining, storage and transportation, there will be a certain amount of water in the oil products. An aquifer is usually deposited at the bottom of a product oil tank, usually only a few to a dozen centimeters. And it aggravates the damage of oil metamorphism. When the water layer reaches a certain height, it must be drained. This is the oily waste water produced at the bottom of the tank. Compared with the wastewater from tank washing, the water content at the bottom of the tank is much less.

2. Composition of oil depot wastewater
For the treatment of wastewater from refined oil depots, we must first clarify the quality of water, especially the components of organic matter contained in the wastewater. The composition of the pollutants in the oily wastewater of the refined oil depot is relatively complicated. In terms of pollutant indicators, petroleum, COD (chemical oxygen demand) and SS (solid suspended solids) are the main pollutants[2]. Organic matter in oil depot wastewater is actually particularly complicated. As shown in Figure 1, the main pollutants of cleaning tank wastewater are generally considered to be floating oil, dispersed oil, emulsified oil, and dissolved oil with smaller particles. The floating particle size is generally greater than 100 μ m, dispersed oil is relatively unstable and easy to float to form floating oil.
The particle size is \(10 \sim 100\mu m\). Emulsified oil has a smaller particle size, less than 10\(\mu m\), most of which is between 0.1 and 2\(\mu m\). The particles of dissolved oil are smaller or even a few nanometers\[3\]. The solubility of oil in sewage is very small, about 5-15 mg / L, and it is often treated by adsorption and chemical oxidation\[4\]. However, in actual treatment, it is found that it is difficult to reduce the organic matter in the oily wastewater to the discharge standard by using only some physical methods (oil blocking, flocculation, and adsorption). We have to rethink the main reason for the high organic content in the effluent.

![Figure 1: Distribution diagram of oily waste water](image)

The pollution sources of sewage are mainly impurities on the tank wall or bottom of the refined oil tank, and pipelines, as well as some oil products. Impurity is a kind of oil product that sticks to steel plate after oxidation and deposition for many years. These impurities are no longer pure oil products, but they are oxidation products of a certain degree of hydrocarbon generation. When cleaning oil tanks, some of the oxidation products will directly dissolve in water. It is difficult to remove this part of the organic matter through oil and flocculation. If the concentration of organic matter in the activated carbon water is high, the adsorption is also easy to saturate and fail. In the process of oil processing, due to changes in the environment, some oil products are continuously oxidized, generating complex organic compounds such as alcohols, aldehydes, ketones, and acids\[5\]. Most of these dissolved organics will be removed only under normal adsorption. Therefore, the pollution components of oily sewage include not only conventional floating, dispersing oil, emulsified oil and dissolved oil, but also some organic substances (alcohols, aldehydes, acids) that are soluble in water. Under the different treatment environment and methods of different wastewater sources, the types and contents of dissolved organic matter are also different.

3. Oil depot wastewater treatment process

3.1 Oil separation

The first treatment process of washing tank waste water mixed with oil drops, solid impurities and dispersive organics is oil separation. Oil is insoluble in water, and its density is generally smaller than water. It will gradually float on the water surface to form an oil layer. The oil will be sucked away by an oil suction pump floating on the liquid surface. A water distribution device is set up to prevent the agitation of the water. The installation of the cross-corrugated board\[6\] can allow the oil to settle more stably and reduce the interference of water flow. The gravity separation method can separate oil with a particle size of more than 150 \(\mu m\). The effect is obvious and the cost is low. However, the oil trap has a large space requirement and the separation efficiency is low\[7\].

3.2 Swirl

Swirl is a combination of centrifugal and gravity separation. As shown in Figure 2, the oily wastewater treated by simple oil separation will be tangentially flushed into the conical inner wall of the cyclone at a certain flow rate. When the circular motion is performed, the dense water will adhere to the inner wall. The low-density oil content gathers in the center area and increases continuously. The oil content overflows from the upper discharge hole. When it moves to the tip, the flow rate of the liquid increases,
the centrifugal force increases, and the water is discharged from the tip. Finally, the purpose of rapid separation of oil and water is achieved. By adjusting the pressure of the fresh water outlet, the high-concentration oily sewage overflows upward. The hydrocyclone used for oily wastewater mainly treats oily wastewater with a concentration of $200 \sim 2000\text{mg/L}$. The effluent of clean water has an oil content of $30 \sim 50\text{mg/L}$. The oil content of concentrated oily wastewater is about $10 \sim 100\text{g/L}$. Then enter the oil trap for recycling.

![Figure 2. Principle diagram of swirl oil removal](image)

3.3 Coarse graining
When the oily wastewater passes through the coarse-grained packing from top to bottom at a certain flow rate, the fine oil droplets in the oily wastewater are easy to stay on the surface of the coarse-grained packing. The fine oil droplet floats finally, which promotes the demulsification process of oily wastewater.

3.4 Flocculation
There are a lot of oil in water (O/W) emulsions in the oily wastewater. Generally, the emulsion of oily wastewater is negatively charged and forms a stable double electric layer with the surrounding ions, which is difficult to be broken. The electric double layer structure of the emulsion is compressed by adding an electrolyte to break it. Then, the content of the emulsion is reduced by air flotation or flocculation sedimentation. The main purpose of flocculation is to remove emulsified oil. On the one hand, emulsion can be broken by adding charge ions opposite to the oil drop. On the other hand, the oil drop can be adsorbed and bridged to make the oil drop get closer and larger. The flocculants can be divided into inorganic flocculants, mainly iron salt and aluminum salt. The molecular weight of organic flocculants such as polyacrylamide, modified cellulose or starch can reach tens of thousands to millions.

3.5 Air flotation
Tiny oil droplets in water are hydrophobic. When there are air bubbles in the water, they are more likely to stick to the air bubbles. Then the oil droplets rise with the air bubbles and float on the water surface for easy removal. The principle of air flotation uses gravity separation. The bubbles formed by the bubble generating device are often negatively charged. A sufficient number of fine bubbles range in size from 15 to $30\mu\text{m}$, and the separated matter is suspended or hydrophobic. As shown in Table 1, the main types of air flotation include air flotation, electrolytic air flotation, dissolved air flotation and vortex air flotation.
Table 1 Comparison of the characteristics of different air flotation[8]

| Approach                        | Bubble size/mm | Removal rate | Footprint | cost   |
|---------------------------------|----------------|--------------|-----------|--------|
| Dissolved air flotation          | 0.02~0.1       | About 90%    | Big       | general|
| Electrolysis air flotation       | 0.01           | above 95     | general   | high   |
| Air floatation                   | 1~10           | 80%          | small     | low    |
| Vortex air flotation             | 1~10           | 80%          | small     | low    |

3.6 Adsorption
Adsorption is the use of activated carbon and other solid adsorbents to adsorb and store organic matters in oily wastewater, thereby removing most of the dispersed oil in the oily sewage. The efficiency of oil removal is relatively high. But when the adsorption is saturated, it cannot be recycled.

3.7 Membrane separation
Membrane separation mainly includes microfiltration, ultrafiltration, nanofiltration, osmosis, reverse osmosis and other methods. Generally, oily sewage is treated by ultrafiltration. Ultrafiltration membrane is a porous organic polymer material. Its pore size is generally dozens of nanometers to several nanometers. When the oily wastewater passes through the ultrafiltration membrane, the oil drops larger than the pore diameter are filtered into the flocculation tank and then go through the flocculation process.

3.8 Biological method
Biological method is the use of microorganisms to degrade refractory petroleum substances. Anaerobic microorganism first transforms macromolecular organics into micromolecules, and then aerobic microorganism completely degrades micromolecule organics. Through the digestion and absorption of organic matter, microorganisms provide energy for their own life activities, and continue to reproduce the next generation, so as to achieve the purpose of removing organic matter. However, there are many difficulties in the treatment of oily wastewater. The composition of organic matter in oil-bearing wastewater is relatively single, mainly carbon and hydrogen, lacking the necessary elements such as phosphorus and nitrogen. Moreover, the oily wastewater is not stable and has certain operational limitations.

3.9 Advanced oxidation method
Advanced oxidation technology is to use strong oxidation to directly and rapidly oxidize the refractory organics, mainly to reduce the COD of oily wastewater. The oxidants often used as advanced oxidation technology include Fenton reagent, potassium ferrate, ozone, sodium hypochlorite, chlorine dioxide[9].

4. Summary
According to the various components in the oily sewage, the corresponding treatment measures are put forward respectively: using oil separation or swirling flow to remove the floating oil; using flocculation, air flotation or coarse granulation to remove the emulsified oil and dispersed oil; using adsorption, biological method or advanced oxidation to remove the dissolved oil and other organic compounds, and finally meeting the discharge requirements. At present, the treatment of oil-bearing wastewater in the product oil depot is still in continuous improvement and development, and there is a big gap to achieve the goal of simple, efficient and economic. Generally speaking, the oil removal effect of each process is better, but it is difficult to deal with dissolved organic matter. The treatment of dissolved organic matter is mainly adsorption, biochemical and advanced oxidation. The adopted method should be determined according to the conditions of the oil depot itself and the development of
each method. The adsorption method is easy to absorb a large number of free organics, but it is easy to saturate and fail after a period of use. The cost of biological method of oily wastewater is low, but its disadvantages cannot be underestimated. First of all, it is necessary to cultivate microorganisms continuously and add appropriate nitrogen, phosphorus and other elements. Second, the processing speed is slow. Because of its low cost and stable effluent, it is a common method to deal with low COD, occupying most of the market. The advanced oxidation method is more efficient and rapid in the degradation of organics, and it occupies a small area, but its treatment cost is higher than that of biological method. For example, Fenton process can also produce sediment. Pure advanced oxidation can oxidize organic matters, but the cost of oxidant is large. From the current research, the treatment of organic matter with iron-containing oxidant is a technology that combines oxidation and chemical precipitation to remove COD. In the early stage, the organic matter was modified by advanced oxidation. In the later stage, the organic matter and iron precipitate will sink together by adjusting pH. At present, there are few studies in this field in the world, which may be the direction of future research.

References
[1] Shan, D. D. (2015). Existing problems and improvement suggestions for wastewater treatment process of refined oil depot J. Petrochemical Safety and Environmental Technology,31 (4): 68-70.
[2] Liu, X. M. (2017).Analysis of the status and design optimization of oily wastewater treatment process in finished oil depot J. Chemical Engineering and Equipment, (06): 303-304 + 306.
[3] Han, M. (2017).Discussion on the collection and treatment process of oily sewage in oil depot J. China Petroleum and Chemical Industry Standard and Quality,37 (17): 151-152.
[4] Cao, Q., Zhao, Y. Q. (2015).Research on Oily Wastewater Treatment of Product Oil Depot J. Science & Technology and Innovation, (16): 107 + 110.
[5] Liu, S. F. (2017). Talking about the treatment of oily sewage in the finished oil depot J. Chemical Engineering and Equipment,(09): 347-349.
[6] Ma, C. J., Zhou, Z. G., Gao, Y., Sui, L. H. (2014).Problems and Countermeasures of Oily Wastewater Treatment in Product Oil Depots J. Safety, Health and Environment,14 (04): 37-39.
[7] Wang, H. C., He, T.(2017). Brief introduction of oily wastewater treatment technology J. Chemical Engineering Design Newsletter, 43 (09): 206.
[8] Liu, H. C., Wang, H., Li, B. G., Qin, B. (2018). Advances in oil floating wastewater deaeration technology J. Guangdong Chemical Industry, 45 (01): 101-103.
[9] Lu, Q. L., Gao, Y., Zhao, S., Jiang, D. F.(2013). Study on the technology of air flotation-ozone advanced oxidation treatment of tank cleaning wastewater J. Contemporary Chemical Industry,42 (05): 611-613.