Progress in Shale Oil Refinery Waste Water Treatment Technology

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Abstract. Shale oil refinery waste water was a kind of high-concentration organic waste water with many types of pollutants and complex components. It contained environmental pollutants such as petroleum, volatile phenols, organic nitrogen, naphthenic acid compounds and fused ring aromatic hydrocarbons. If it is discharged directly without treatment, it will cause serious harm to the environment, and it must be treated before it can be discharged. At present, the treatment methods of shale oil refinery waste water mainly include physical treatment, chemical treatment, physical and chemical treatment and biological treatment. This paper studied the treatment technology of shale oil refinery waste water.

1. Introduction

Oil shale is a kind of sedimentary rock rich in organic matter, shale oil can be generated by retorting the parent material[1]. Shale oil is a supplementary energy source for petroleum[2], which is richer than crude oil reserves. The world has more than 400 billion tons[3]. China’s oil shale resources were 719.9 billion tons, which was equivalent to 47.6 billion tons of shale oil[4-5]. The waste water produced in the production of shale oil is very complicated. The waste water contains a large amount of pollutants such as phenol, carboxylic acid, pyridine, alkane, quinoline, aldehyde, and ketone. Water causes environmental pollution[6-8], so it is necessary to study scientific and effective shale oil refinery waste water treatment methods. The current treatment methods of shale oil refinery waste water include physical treatment, chemical treatment, physical and chemical treatment and biological treatment. This article studied the progress of shale oil refinery waste water treatment technology, summarizes the advantages and disadvantages of different methods and the development direction of waste water treatment.

2. Physical treatment technology

2.1. Air floatation technology

The deoiling efficiency of the gravity separation method is only about 60%, and the deoiling efficiency of the impeller flotation method is about 80%. The effluent of these two methods does not meet the water quality requirements of the biochemical treatment. After research, the pressure dissolved air flotation method has a better treatment effect, the removal rate can reach more than 90%, and the oil content after treatment is reduced to less than 20 mg/L.

2.2. Blow off technology
The stripping method is mainly used to remove ammonia nitrogen in shale oil refinery waste water. Air stripping is used under alkaline conditions. Due to the continuous exhaust gas during the stripping process, the ammonia in the gas phase is changed. Therefore, the actual concentration is always less than the equilibrium concentration under this condition. As the pH value of the waste water rises, NH$_4^+$ in the water is gradually transformed into NH$_3$, and the air blows in NH$_3$-N.

3. Chemical treatment technology

3.1. Coagulation technology
PAC is a coagulant with good use effect and has strong hydroxyl frame adsorption performance. Its advantages include applications. It has a wide range, good sedimentation performance, and the formed flocs can settle in a short time, and have little erosion on equipment. In actual operation, a small amount of coagulant will be added to promote flocculation to improve coagulation efficiency. From an economic point of view, Fe$^{3+}$ coagulant needs to be adjusted to acidity in order to have a better treatment effect, but pH adjustment requires a lot of acid, so aluminum coagulant is more economical.

3.2. Oxidation technology
Oxidation is an effective method to transform pollutants in waste water, including chemical oxidation, photooxidation, ozone oxidation, and chlorine oxidation. Chemical oxidation is the process of adding appropriate chemicals to the water to oxidize the high-concentration organic matter in the waste water, thereby removing pollutants. Photo-oxidation is the transformation of non-degradable pollutants into degradable pollutants under ultraviolet radiation. The more important factor in the photooxidation reaction is the need for an external light source to provide energy, as well as a high-efficiency catalyst and a good immobilization method. Photooxidation has been successfully applied to the degradation of high concentrations of refractory organic pollutants. Jesús[9] and others used a variety of advanced photochemical oxidation processes to treat waste water containing p-hydroxybenzoic acid and found that the UV/H$_2$O$_2$/O$_3$/Fe$^{2+}$ system had a better removal rate. Ozone is a strong oxidant, which can oxidize organic and inorganic substances, such as phenols, aromatic compounds, etc. The reaction completely converts the oxides into O$_2$ and CO$_2$ without secondary pollution. It is a more promising method in the oxidation method. The disadvantages are large investment, high cost, and low utilization rate, which must be combined with other technologies. Chlorine can treat cyanide-containing waste water, phenol-containing waste water, and waste water decolorization. The pollutants in shale oil refinery waste water are complex. When chlorine oxidation is used to treat this waste water, excessive chlorine needs to be added, so it is usually not used to treat high-concentration, refractory industrial waste water. The Fenton reaction method is currently widely used, which can couple phenolic substances to produce phenolic polymers, which are finally converted into CO$_2$. Dincer[10] used H$_2$O$_2$/Fe$^{2+}$, UV/H$_2$O$_2$/Fe$^{2+}$ and UV/H$_2$O$_2$ to treat waste water. The result showed that the COD removal rate was 81%, and the treated water met the requirements of biochemical treatment.

3.3. Incineration technology
The incineration technology is more expensive, and requires a lot of money to be effectively treated. The amount of gas and steam contained in the outlet of Grote[11] is small, and the amount of waste water discharged from the dry distillation device is small, so it is directly introduced into the boiler for incineration and gasification after desulfurization. However, shale oil refinery wastewater contains a large amount of ammonia nitrogen, which will generate NO during combustion, causing secondary pollution, so the incineration method has not been widely used.

4. Physicochemical treatment technology

4.1. Adsorption technology
The adsorption technology uses the large specific surface area of the adsorbent to adsorb the pollutants in the waste water to the surface of the adsorbent for removal. It is mainly divided into physical adsorption caused by intermolecular force and chemical adsorption caused by molecular bonding force. Activated carbon is currently the most widely used adsorption material, which can adsorb phenolic compounds and oil compounds in shale oil refinery waste water. However, due to its small adsorption capacity, relatively high price, easy to saturate and difficult to use desorbents, it can only be used to treat low-concentration shale oil refinery waste water[12]. Fushun Petroleum Refining Research Institute used sulfonated coal to treat phenols in shale oil refining waste water. When the total phenol content in the waste water is 3-4 g/L, the phenol content after treatment drops below 0.5 g/L. The phenol content in the shale refining waste water of the Kiwitte furnace is high, and it needs to be treated[13]. The waste water of Kiwitte, Estonia contains about 0.01%-5.0% of monophenols and polyphenols. The study found that the use of urea resin as an adsorbent to remove phenols in waste water has a better treatment effect, with a dephenolization rate of 99.8% and an adsorbent dosage of 2.5 g/L, temperature 60-70°C, time 3 h[14].

4.2. Extraction technology
The most widely used extractants in industry are N-503, ethyl acetate, diisopropyl ether, tributyl phosphate and methyl isobutyl ketone. At present, many new solvents for phenol removal have been discovered. For example, Olejniczak et al.[15] found that diethyl carbonate forms hydrogen bonds between the phenolic hydroxyl group and the oxygen atom of the carbonate, which has a very high extraction rate for phenol and its derivatives. Rate, is an efficient extractant. The disadvantage of the extraction method is that the extractant will dissolve into the water phase, so that the COD in the waste water does not decrease but increases.

5. Biological treatment technology
5.1. Activated sludge technology
Activated sludge technology is the most common biological treatment method, but it is not suitable for the treatment of high-concentration shale oil refinery waste water, because the toxic substances in the waste water can destroy the cell membrane of microorganisms and cause the death of microorganisms, making it difficult to directly carry out biological treatment[16]. If the activated sludge method is used to treat shale oil refinery waste water, the cultivation and domestication of microorganisms is very important. Domesticated to be suitable for the treatment of phenols, pyridines, ketones and other non-biodegradable organic matter. Some substances can be degraded by microorganisms, but the resulting degraded derivatives have an inhibitory effect on biological treatment. The BOD removal rate reaches 90%, but the COD removal rate may be less than 50%. Therefore, the activated sludge method is not the most appropriate method to treat shale oil refinery waste water, and the effluent cannot meet the discharge standards. According to the pollution characteristics of waste water, pre-treatment is carried out first to make the water quality meet the requirements of biological treatment and then biological treatment is carried out to further degrade organic matter. The effluent after activated sludge treatment contains a lot of ammonia nitrogen compounds, which can be used as nitrogen fertilizer. Studies have shown that the use of aerobic activated sludge method to treat shale oil refinery waste water can achieve the removal rates of non-volatile phenols and volatile phenols to 85% and 95% respectively, and the volatile phenol content of effluent can be reduced to 0.5-2 mg/L[17].

5.2. Membrane separation technology
Membrane separation technology is used for the removal of organic matter in industrial water and waste water, including ultrafiltration, nanofiltration, and reverse osmosis. It uses the concentration difference on both sides of the membrane to make the macromolecules in the water pass through the exchange membrane to remove pollutants. Membrane separation method can remove the odor, color, organic matter, etc. of shale oil refinery waste water. Membrane separation is a treatment technology with simple
equipment, low energy consumption, high load, and good solid-liquid separation performance. It can be used at room temperature and has the advantages of stable chemical properties, no secondary pollution, and long generation time of activated sludge. The use time of the membrane is limited. For high-concentration waste water, it is easy to cause membrane blockage. The application of membrane technology still needs to be studied.

5.3. Immobilized biotechnology technology

Immobilized biotechnology technology uses microorganisms on the surface of the carrier to purify waste water. Because the microorganisms on the carrier have a limited generation time, some microorganisms after purifying the waste water will fall off the surface of the carrier, and new microorganisms will be generated. The advantages of immobilized biotechnology are fast reaction speed, high removal rate of pollutants, high concentration waste water treatment, and easy control.

6. Conclusion

Shale oil refinery waste water was highly concentrated and difficult to degrade waste water. For increasingly stringent water quality requirements, it was difficult to treat waste water with only one water treatment technology to meet the standards. Therefore, it was necessary to use a combination of physical and chemical methods, chemical methods, biological methods and other methods to achieve the treatment effect. For physicochemical methods and chemical methods, research and development of agents and optimization of processing equipment and processes are the development trend. For biological methods, cultivation and domestication of microorganisms suitable for the treatment of refractory waste water is the key.

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