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PETROCHEMICAL WASTEWATER AND ITS TREATMENT

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ABSTRACT

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In the petrochemical industry, water is a necessity in the process of petroleum processing. The refining process of petroleum products is long, and the production equipment and process are complex, which will produce a lot of petrochemical wastewater. Generally, the water quality of petrochemical wastewater is complex, which not only contains residual oil but also contains a lot of dissolved toxic substances. The direct discharge of these wastewater without treatment will cause serious damage to air, water and organisms.

Petrochemical wastewater is very harmful, so people use specific indicators to demarcate the pollution components in petrochemical wastewater. In order to deal with harmful petrochemical wastewater, protect water resources and reduce the harm of petrochemical wastewater to biology, many effective technologies have been developed. But many traditional technologies have the problems of large area, high cost, and low treatment efficiency, and the simple use of a wastewater treatment technology will cause a lot of waste of resources. Therefore, it is an important research direction to study the wastewater treatment process combined with various technologies and improve the efficiency of traditional wastewater treatment methods.

This thesis work describes the characteristics of petrochemical wastewater, the source, harm and the importance of treatment. It introduces the Membrane bioreactor (MBR), and more efficient catalytic wet air oxidation (CWAO).

Key words Catalytic wet air oxidation, membrane bioreactor, petrochemical wastewater

CONCEPT DEFINITIONS

List of abbreviations

AC	Activated carbon
$Al(OH)_3$	Aluminium hydroxide
Al_2O_3	Aluminium oxide
BOD_5	Biochemical oxygen demand (Oxygen consumed in five days)
Cl^-	Chloride ion
CO_2	Carbon dioxide
COD	Chemical oxygen demand
COD_{cr}	Chemical oxygen demand determined by potassium dichromate
Cu-cat	Copper system catalyst
CuO	Cupric oxide
CWAO	Catalytic wet air oxidation
DO	Dissolved oxygen
FCC	Fluid catalytic cracking
FCCU	Fluid catalytic cracking unit
H_2O	Water, product or reactant
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
HRT	Hydraulic retention time
Ir	Iridium
$K_2Cr_2O_7$	Potassium dichromate
$KAl(SO_4)_2 \cdot 12H_2O$	Aluminum potassium sulfate dodecahydrate
$KMnO_4$	Potassium permanganate
MBR	Membrane bioreactor
MF	Microfiltration
N_2	Nitrogen gas
$NaAlO_2$	Sodium aluminate
NaOH	Sodium hydroxide
NF	Nanofiltration
NH_3	Ammonia gas
NH_3-N	Ammonia nitrogen content index

NH$_4$SCN	Ammonium thiocyanate
O$_2$	Oxygen gas
Pb	Palladium
pH	Hydrogen ion concentration
Pt	Platinum
Ru	Ruthenium
S^{2-}	Sulfur ion
SRT	Sludge residence time
SS	Suspended Solids
TiO$_2$	Titanium Dioxide
TOC	Total organic carbon
UF	Ultrafiltration
WAO	Wet air oxidation
ZrO$_2$	Zirconium dioxide

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1. INTRODUCTION

Petroleum, known as "industrial blood", is important energy and industrial raw material, as well as an important production and daily necessities of human beings. With the rapid development of economy and society, oil and its products have been widely used in various fields of the national economy and people's daily life, and their use and demand are gradually increasing. In the refining process, petroleum will produce by-products that have an impact on the environment, including petrochemical wastewater. As one of the main sources of petroleum pollution, petrochemical wastewater has a serious negative impact on economic development and the ecological environment. (Wang 2007.)

After the petrochemical wastewater enters the water body, it causes water pollution, changes the local ecological environment, causes the death of aquatic organisms, and brings a lot of losses to water supply resources, biological resources, aquaculture, and tourism. The harm of petrochemical wastewater to the ecological environment and human health has gradually attracted people's attention. Therefore, corresponding measures should be taken to solve the problem of petrochemical wastewater treatment, to prevent petrochemical wastewater from causing great harm to soil, water, biology, thus affecting people's health. (Wang 2007.)

Many countries in the world pay great attention to environmental protection. Take China for example. In 1979, China passed the first environmental protection law, the environmental protection law of the People's Republic of China. In 1983, environmental protection became one of the seven basic national policies of China. As the most populous country in the world, China has a large demand and consumption for oil, which will produce a lot of petrochemical wastewater in the process of refining oil. Therefore, it is of great significance to analyze the composition of petrochemical wastewater and choose a reasonable wastewater treatment method. (Yang & Cao 2011, 57-62.)

Water plays an important role in economic development. Water is an important part of human beings. Protecting water resources is the responsibility of all mankind. But in fact, the sewage treatment facilities of petrochemical enterprises are not balanced. Large petrochemical plants not only have more mature production process but also have more comprehensive sewage treatment facilities. They can also reuse some polluted water to maximize the use value of water. However, some small-scale petrochemical plants will not be able to effectively treat petrochemical wastewater due to the cost or production area, Causing a lot of pollution. (Wang 2012, 192.)

Due to the limitation of space and time, it is hard to give a comprehensive introduction to all petrochemical wastewater treatment technologies. The purpose of this paper is to describe the source and harm of petrochemical wastewater, improve people's attention to petrochemical wastewater, and further study new technologies with higher efficiency, more energy saving, and environmental protection, and apply these new technologies to practice. This paper is divided into three parts. The first part introduces the common characteristic indexes of petrochemical wastewater to help understand the data of petrochemical wastewater treatment results. The second part describes the definition, classification, harm of petrochemical wastewater and the importance of petrochemical wastewater treatment. The third part introduces the membrane bioreactor (MBR), and more efficient catalytic wet air oxidation (CWAO).

2. CHARACTERISTIC INDEX OF WASTEWATER

The characteristics of refinery sewage quality can be expressed by some physical and chemical indicators, including water color, water temperature, pH value, degree of acid or alkali, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), Total organic carbon (TOC) , etc. Through the analysis of these indicators, people can have a more comprehensive understanding of the nature of sewage. (Fushun Petroleum Research Institute 1974.)

The temperature of sewage is an important indicator, especially for refineries. Most of the freshwater or circulating water is used to cool the hot oil products so that the temperature of the discharged sewage is higher than the normal water temperature. The rise of water temperature has disadvantages for reuse (industrial and agricultural water) or discharge into the water body. When it is used as cooling water source, the water consumption will increase due to the rise of temperature, sometimes it cannot even cool to the required temperature. When used for farmland irrigation, too high temperature will also destroy the normal growth of crops. As for the discharged water, due to the increase of water temperature, dissolved oxygen (DO) will be reduced, the chemical reaction will be accelerated, and biological metabolism will be accelerated. If the temperature is too high, the survival of aquatic organisms will be endangered. (Fushun Petroleum Research Institute 1974.)

The color of the water is usually directly related to the condition of the water. Transparent and colorless indicates the water is clean and it will change color in case of pollution. Although the color of sewage is not necessarily harmful, if the sewage in the refinery has color, it often means that there are several pollutants that cause color change. For example, alkali washing water is milky white, sulfur-containing sewage is green-yellow, and the color of sewage can help people quickly identify the source of pollution. (Fushun Petroleum Research Institute 1974.)

The definition of pH value is the reciprocal negative logarithm of hydrogen ion concentration in the solution, its range is 0-14, the solution with pH value of 7 is neutral, below 7 is acid, above 7 is alkaline. Because the pH value can effectively represent the chemical and biochemical characteristics of the solution, many emission standards have specified the range of pH value. Most organisms can only live normally when the pH is close to neutral, and beyond a certain range (for example, pH = 3) will cause damage or even death to organisms. (Fushun Petroleum Research Institute 1974.)

Acidity and alkalinity change the nature of the water. Acidity is the quantitative value of compounds in solution that can dissociate and produce hydrogen ions. Basicity is the quantitative value of the compound in solution which can dissociate and produce hydroxyl ion. When pH is low, the water is acidic and corrosive, which destroys the purification of the water body and leads to biological death. When the pH is high, the water is alkaline, which will also cause the above problems. (Fushun Petroleum Research Institute 1974.)

BOD_5 is the representative value of the organics in sewage that can be biodegraded. It is the oldest and most common method to measure the degree of organic pollution in water. It has been adopted by many countries in the world as the standard method of wastewater quality. It is expressed in terms of the oxygen (O_2) (unit: mg/L) consumed by the sewage for five days under the constant temperature of 20 °C. Its disadvantage is that the analysis time is as long as 5 days. Nevertheless, it is still an important standard to measure the pollution degree of sewage. (Fushun Petroleum Research Institute 1974.)

COD is the oxygen consumption of organic matter which can be oxidized by a certain chemical oxidant in sewage during oxidation, usually use potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$) as oxidants. $KMnO_4$ method is commonly used to determine oxygen consumption of clean water, is simple and fast. However, the value of this method is relatively low when it is used to measure sewage or industrial sewage because there are many complex organic substances in these waters, it is difficult to oxidize them with $KMnO_4$. COD_{cr} is a chemical oxygen consumption determined by using $K_2Cr_2O_7$ as an oxidant. $K_2Cr_2O_7$ as oxidant can oxidize most organic substances, but the aliphatic straight chain, aromatic hydrocarbons, benzene and other compounds are not easy to oxidize. When silver sulfate is added as a catalyst, straight-chain compounds can be oxidized, but not for aromatic hydrocarbons. Generally, COD value is higher than COD_{cr} value. (Fushun Petroleum Research Institute 1974.)

TOC is a method developed to measure the degree of organic pollution in industrial sewage in order to overcome the shortcomings of BOD and COD analysis, such as longer testing time, many influencing factors and large consumption of chemicals. It converts organic matter in sewage into carbon dioxide (CO_2), and then uses infrared gas analyzer for determination. The analysis time of TOC is only 1-3 minutes, and its operation is simple. (Fushun Petroleum Research Institute 1974.)

3. PETROCHEMICAL WASTEWATER

Petrochemical wastewater is a general term for wastewater related to the petroleum industry. Petrochemical wastewater comes from different sources. Fuel production units, olefin process units, cooling units and oil field exploitation in refineries all produce wastewater. Wastewater from different sources has different compositions and shows different toxicity and degradability in biological treatment. Refinery wastewater is usually produced during the refining process. It comes from cooling systems, distillation, hydrotreating and electrical desalting units. (Wang & Nirmal 2018.)

Petrochemical wastewater contains many components due to various processing technologies of petroleum products. The concentration of phenol, sulfur and other hydrocarbons in wastewater from different treatment technologies and equipment will vary. The production process of the petrochemical industry generally needs high temperature and pressure conditions, and most of the production process is in direct or indirect contact with water, which pollutes the water quality and generates chemical wastewater. (Wang & Nirmal 2018.)

COD of wastewater from petroleum refinery production ranges from 150-1000 mg/L. Phenolic compound content is 20 - 200 mg/L. Free hydrocarbon in water produced in desalting process is 100 - 300 mg/l, oil content is 5000 mg/L at the bottom of individual tower tank. Organic matter level of desalting wastewater (taking benzene as an example) is 5 - 15 mg/L. Petroleum refineries also produce solid waste and sludge (about 0.75 - 3 tons per ton of crude oil processed), 80 % of which may contain toxic organic substances and heavy metals. The above contents are shown in TABLE 1. (Shafiuddin 2016.)

TABLE 1. Contaminants Produced During Refining Process. (from Shafiuddin 2016.)

Contaminants		COD	Free Hydrocarbons	Suspended solid	Phenol
Unit		(mg/L)	(mg/L)	(mg/L)	(mg/L)
Process water	Desalter effluent	400-1000	<1000	<500	10-100
	Sour water	600-1200	<10	<10	<200
	Tank bottom draws	400-1000	<1000	<500	/
Cooling water		150	<5	<200	/

TABLE 1. (continues) Contaminants Produced During Refining Process. (from Shafiuddin 2016.)

Contaminants		Benzene	Sulphide	Ammonia
Unit		(mg/L)	(mg/L)	(mg/L)
Process water	Desalter effluent	5-15	<100	<100
	Sour water	0	<10	<100
	Tank bottom draws	/	<100	/
Cooling water		/	/	/

3.1 Classification of petrochemical wastewater

The pollutants in petrochemical wastewater are complex, so it is difficult to classify petrochemical wastewater accurately. However, some pollutants will make the wastewater have specific properties, which can be used to classify petrochemical wastewater. According to the water characteristics of petrochemical wastewater, petrochemical wastewater can be divided into the following categories: oily wastewater, sulfur-containing wastewater, alkali wastewater, phenol wastewater. (Fushun Petroleum Research Institute 1974.)

With the development of industry, the use of petroleum products increases, but a large number of oil products enters the water body due to the lag of the development of various technologies and imperfect management. The source of oily wastewater is very wide. In the process of oil production, oil refining, oil storage, transportation and production in the petroleum industry, large quantities of oily wastewater will be produced. It is a kind of wastewater with the largest drainage capacity in the refinery. The oil in oily wastewater generally exists in five forms: floating oil, dispersed oil, emulsified oil, dissolved oil, and oil solid. (Zhang, Yu, Bi & Zhang, 1155-1160.)

The oil floating on the water is called the oil slick.it will form an oil film or oil layer. The diameter of the oil drop is generally larger than 100 μm. The oil droplets of the dispersed oil are usually dispersed in water in a suspended state. After standing for a period, they gather together into large oil drops and float up to the water surface to form floating oil. The diameter of the dispersed oil is generally 10 - 100 μm. Emulsified oil will form a stable emulsion with water, its stability depends on the dispersion of oil particles of water. The greater the dispersion, the more stable it will be. The diameter of emulsified oil is generally less than 10 μm, most of which is 0.1 - 2 μm. The form of dissolved oil is the molecular state. Currently molecules form a stable system in water. Compared with emulsified oil, its particle size

is smaller, and some of them reach nanometer level. Oil in water adheres to solid suspension to form oil solid. (Zhang, Yu, Bi & Zhang, 1155-1160.)

Sulfur content plays a very important role in refineries. According to the classification method of sulfur content, crude oil with mass composition less than 0.5 % is low sulfur crude oil, and crude oil with mass composition greater than 2 % is high sulfur crude oil. Sulfur water is highly toxic and mainly exists in the form of hydrogen sulfide (H_2S), it is very toxic. It can form explosive mixture when mixed with air. It is a strong neurotoxin and has a strong stimulating effect on mucous membrane. (Zhao, Ndisang & Wang 2003, 848-853.)

There are many sources of sulfur-containing sewage. Its sources are as follows: fluid catalytic cracking (FCC) fractionator separation water, catalytic rich gas water washing water, circulating liquid hydrocarbon storage tank cutting water, stripper separation water, pre hydrogenation reactor separation water, lubricating oil hydrofining low-pressure separation water, coking fractionator oil-water separator, cracking fractionator tower top oil-water separator. TABLE 2 shows the source of sulfur-containing sewage and quality of water. This is a wastewater with a small amount of drainage but a high concentration of pollutants. Sewage contains a large amount of H_2S, ammonia, nitrogen, volatile phenols, and has a strong odor, which is corrosive to the equipment. When pH value is low, sulfide easily decomposes, releasing H_2S gas, which affects air quality. (Chang, Zhou & Gao 2012, 187-190.)

TABLE 2. Source of sulfur-containing sewage and quality of water. (from Chang, Zhou & Gao 2012, 187-190.)

Source of sewage	Flow of water	Sulfide	Volatile phenol	Ammonia, Nitrogen
Unit	m³/h	mg/L	mg/L	mg/L
FCC separator water	4	200	400	300
Catalytic rich gas washing water	10	200	40	550
Cut water of circulating liquid hydrocarbon storage tank	0.5	1300	/	400
Stripper separation water	0.5	18400	/	8000
Pre hydrogenation reactor separate water	1	19300	/	6000
Lubricating oil hydrofining low pressure separation water	2	20000	/	/
Coker fractionator oil water separator	1.8	2300	149	1200
Oil water separator on the top of Cracking Fractionator	0.02	150	300	2000

In the production of gasoline, diesel, aviation fuel and liquefied gas, atmospheric and vacuum distillation, FCC and other units are used. In the process of alkaline washing, harmful alkaline waste liquid including sulfide, naphthenic acid and free caustic soda will be produced. The COD concentration in wastewater is more than 20000 mg/L, and the pH value is higher, usually more than 12. The wastewater with this component has the characteristics of high alkaline strength and high pollutant concentration, which is similar to the definition of solid pollutants and is called refining alkali residue. Its discharge is usually small (5 % - 10 % of refinery sewage), but its pollutant contents is very high (20 % - 50 %). TABLE 3 shows the composition of several refining alkali residues. (Guo, Zhong & Wen 2007, 10-14.)

TABLE 3. Composition of several refining alkali residues. (from Guo, Zhong & Wen 2007, 10-14.)

Types of alkali residue	FREE NaOH	Sulfide	Volatile phenol	COD	Neutral oil
Unit	%	mg/L	mg/L	mg/L	%
Alkali residue on top of atmospheric tower	6	3375	835	2320	0.45
	3.5	2800	4370	20333	2
	1.4	15000	1110	43000	0.01
Alkali residue of catalytic gasoline	10.7	8100	90500	34000	0.2
	8	26450	100000	535750	
	5	22000	1160000	300000	
Catalytic diesel alkali residue	13	4000	5370	515000	1
	6.4	5040	52410	180000	1.35
	1.9	1345	53000	100000	1.2
Liquid hydrocarbon alkali residue	10	1190	2130	33070	0.19
	4.5	120230	10	52620	
	4	40000	100	300000	

The wastewater containing phenol will be produced in the processes of fluid catalytic cracking unit (FCCU), delayed coking and electrorefining. The wastewater discharged from the top oil-water separator of the fractionator in the FCCU has a high phenol content. The phenol content of all the wastewater discharged from the refinery exceeds 50 %. The phenol concentration of the wastewater discharged from other units is low, but the water content is huge. Phenol pollution will bring serious harm to the ecosystem. (Rodríguez, Santana, Palazon, Diez & Marsh 1998, 105-116.)

3.2 Hazards of petrochemical wastewater

Petrochemical wastewater directly discharged into the water will affect the water body. Free hydrogen in petrochemical wastewater causes the pH value of water to rise, inhibits the growth of microorganisms in water, reduces the self-purification capacity of water, corrodes buildings and ships, and increases the hardness of water. When sulfur-containing wastewater flows into the water containing iron metal, the water will turn black and produce peculiar smell. Sulfur ion (S^{2-}) in the water has strong corrosiveness to metal equipment. The COD of phenol wastewater is very high, and the water oxygen balance will be broken when it is discharged into water. When the content of phenolic compounds in water is 0.002 - 0.015 mg/l, the traditional water disinfection and chlorination will cause the odor of chlorophenol, which cannot be used as drinking water. When the content of phenol in water is 0.1 - 0.2 mg/l, phenol compounds will be detected in fish, when the concentration of phenol compounds is high, a large number of fish will die. If the petrochemical wastewater seeps into the soil, it will affect the drinking water and groundwater. (Ren & Zhang 2014, 46-68; Yang 2013; Poulo, Voutsas & Grigoropoulou 2005, 135-139; Yao 2010, 88-89.)

After the petrochemical wastewater is discharged into the water body, in addition to being diluted, the organic matter can also be oxidized and decomposed under the action of microorganism, which needs to consume a certain amount of O_2. When the decomposition of organic matter is near to completion, the former decomposition product ammonia compounds is further oxidized to nitrite and nitrate, which also consumes the DO in the water. When the sediment and sludge deposited at the bottom of the water decompose, O_2 also is drawn from the water. When photosynthesis stops at night, DO is also required for aquatic plant respiration. In addition, reducing substances such as sulfides, sulfites, thiosulfates in sewage also react with DO in water, so as to reduce the amount of small DO in the water. Because of the above reasons, DO in water is often consumed, which is called the oxygen consumption process. (Fushun Petroleum Research Institute 1974.)

In the process of oxygen consumption, O_2 is constantly replenished. There are generally three sources of O_2 consumed in the above processes. O_2 originally contained in the water body and sewage. O_2 in the atmosphere diffuses and dissolves to the water body with insufficient O_2 until the DO in the water body reaches saturation. Aquatic plants reproduce in water bodies, release O2 by photosynthesis during the day, and dissolve in water to saturate O_2 in water bodies. As a result, the DO in water is consumed and gradually replenished and recovered. This process is called reoxygenation process. It is found that the reaeration process of river is slow. There are many pollution sources besides petrochemical wastewater,

so in densely populated areas or industrial concentrated areas, DO in rivers is rarely saturated. (Fushun Petroleum Research Institute 1974.)

Petrochemical wastewater is a threat to biological health. Phenolic compounds are prototype toxicants, which have toxic effects on all organisms. Phenol can react with human skin and mucous membrane to form insoluble protein, which makes cells lose their vitality. High concentration phenol solution can also make protein coagulate. Phenol can also penetrate into the deep layer, causing deep tissue damage and necrosis, and even systemic poisoning. Drinking water polluted by phenol for a long time can cause dizziness, anemia and various nervous system diseases. Direct use of phenol containing wastewater to irrigate farmland will wither crops and reduce yield. H_2S volatilized from sulfur-containing wastewater will react with ozone in the atmosphere, forming acid rain. H_2S is also a kind of nerve gas, which will pose a threat to human health. (Ren & Zhang 2014, 46-68; Yang 2013; Poulo, Voutsas & Grigoropoulou 2005, 135-139; Yao 2010, 88-89.)

Petrochemical wastewater also has an impact on the environment. Petrochemical wastewater will worsen the ecological health of a region and the living environment of people by affecting the water body. This is a report on the pollution of petrochemical sewage without treatment in a news survey in China: a petrochemical group turns a blind eye to the problem of pollution, or even says there is no water pollution. The untreated petrochemical sewage is directly discharged into the river. The river water can no longer be used, and even the groundwater is seriously polluted and cannot be used. The wastewater from the factory emits a strong pungent smell, which is slightly worse in the daytime. At night, many people cannot sleep because of exhaust gas choking. It is more harmful to villagers suffering from rhinitis, tracheitis, pneumonia and other respiratory diseases. It is very difficult for crops to survive if they are irrigated with this water (Xi & Liu 2012, 66-68). Petrochemical wastewater will damage the overall image of the environment, and the floating oil in the oily wastewater will float on the water surface, which will cause safety problems in case of open fire combustion. (Ren & Zhang 2014, 46-68; Yang 2013; Poulo, Voutsas & Grigoropoulou 2005, 135-139; Yao 2010, 88-89.)

3.3 The importance of petrochemical wastewater treatment

The production process of petrochemical products is complicated, which makes the water quantity, water temperature and water quality of wastewater fluctuate widely. If petrochemical wastewater is not directly discharged without treatment, the self-purification ability of the water body will be totally lost, which will destroy the ecological balance. Meanwhile, the volatile gas in the water will further cause exhaust gas pollution far beyond the scope of the plant. Petrochemical wastewater has more impact on the environment than other wastewater. (Gao, Li & Shan 2010, 11-16.)

After excessive consumption of DO in water, organisms will die after hypoxia, which will lead to other pollution problems (such as water body odor, algae blooms). The nutrients in the wastewater will make the lake eutrophic. In addition, many pollutants may have toxic effects on aquatic organisms and humans. Due to the industrial nature of the refinery, once the production plant is started, it will be difficult to stop (production safety accidents and a large number of potential economic losses may occur during the shutdown process), which will produce a large amount of petrochemical wastewater. Due to the release of toxic pollutants (organic matter, phenol and soluble heavy metals), if not properly handled, it will affect the marine environment and the whole ecosystem. As the top organism of the food chain, all pollutants return to the human body and cause damage. Benzenes increase the risk of carcinogenesis in humans, and phenolic compounds and dissolved minerals are toxic, causing severe damage to the kidney, lung and vascular system. Therefore, after using water in refineries, it is necessary to ensure that pollutants are removed from the water to protect the environment and public health. (Attiogbe, Glover & Nyadziehe 2009, 11; Min 1998, 207-214.)

4. PETROCHEMICAL WASTEWATER TREATMENT TECHNOLOGY

Petroleum is an important energy material in the world. With the increasing demand for oil, more petrochemical wastewater will be produced, which will have a greater impact on the environment. The effective treatment of petrochemical wastewater is the prerequisite of modern industrial development. The effective treatment of petrochemical wastewater has become one of the main problems facing petrochemical enterprises. In order to effectively improve the efficiency of petrochemical wastewater treatment, it is necessary to analyse the characteristics of petrochemical wastewater. On this basis, effective technology should be adopted to improve the treatment effect of petrochemical wastewater, so that petrochemical wastewater can meet the discharge standard and minimize the impact of wastewater. (Qin 2015, 219.)

Petrochemical wastewater treatment technology can be generally divided into three categories, physical method, chemical and biological methods. Physical method refers to the treatment technology of analyzing the water in suspended substances by physical and mechanical action, which usually acts to remove floating substances in wastewater, and can also remove sand, suspended solids (SS), oil and other substances in wastewater. Common methods include gravity precipitation, membrane separation, and air flotation. The principle of gravity precipitation is that there is a large gap between the density of solid suspensions in water and that of water. The solid suspensions are precipitated under the action of gravity to remove the solid suspensions with larger density in the water. Membrane separation is based on the principle of selective permeability of membranes to filter small particle suspensions, macromolecular organics, etc. Air flotation treatment refers to the rational separation of water and suspended substances by adhering to suspended substances in wastewater with the help of small bubbles with higher dispersion. This treatment technology is usually applied in the treatment of oil separation and suspended substances. Physical methods are relatively simple, but physical methods are difficult to remove dissolved substances from petrochemical wastewater. (Cui 2018, 244,255.)

Chemical method refers to a change in the function of a substance through a chemical reaction, so as to effectively treat the colloidal substance and soluble substance in sewage. Oxidation is one of the typical methods. The specific principle is to add oxidants to the wastewater and remove the pollutants in the dissolved state by oxidation reaction, such as metal ions. Biological treatment is mainly to play the role

of microbial metabolism, so as to decompose the organic matter in wastewater. In the process of petro-chemical wastewater treatment, the three methods are often used together to effectively treat petrochemical wastewater. FIGURE 1 shows the treatment process of oily wastewater. (Yi 2020, 100.)
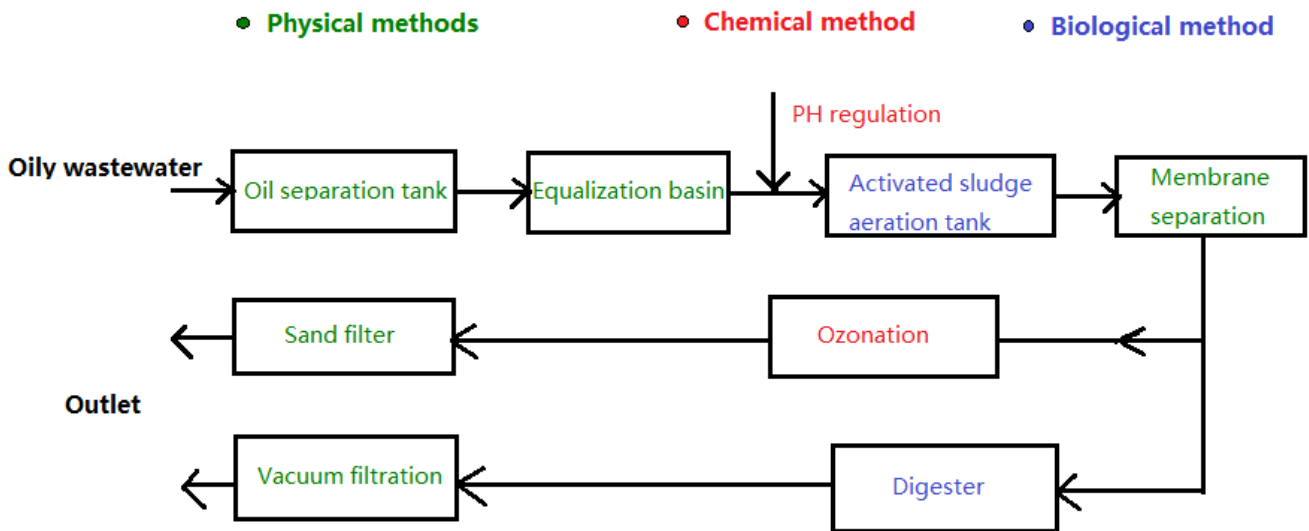

FIGURE 1. Treatment process of oily wastewater. (adapted from Yi 2020.)

Due to the limitation of the length of the thesis it is not possible to give a detailed description of all technologies. The following sections mainly introduce the MBR and catalytic CWAO technology with high efficiency, elaborate their processes and reaction mechanisms, and give a brief outlook on the development prospects of the two technologies.

4.1 Membrane bioreactor

The MBR device usually consists of a membrane module and a bioreactor. It effectively utilizes the biochemical effect of high concentration microorganism in the bioreactor and the filtration effect of microporous biofilm. It makes use of the pressure difference to make the wastewater pass through the membrane and retain the microorganism in the bioreactor. It can degrade the pollution factors by the way of recycling treatment, so that the wastewater can be purified. There are two types of combinations of reactors：Split type MBR and Integrated MBR. (Ma 2007.)

The split type MBR (FIGURE 2) is usually composed of a bioreactor, a membrane module and a booster pump. The separated system is a system form in which the bioreactor and membrane module are set separately. The air compressor pushes the air from the bottom of the bioreactor to make the microorganism and wastewater fully react. The mixed liquid enters the membrane module for solid-liquid separation after being lifted by the pressurized booster pump. The macromolecular substances and solid substances in the mixed liquid are trapped by the membrane, and the water passing through the membrane becomes the output water, and the reflux liquid returns to the bioreactor for further reaction. The advantages of the split type MBR mainly lie in the strong stability and reliability of operation, the convenience of cleaning and replacement of membrane, and generally it can operate under a large membrane flux. The disadvantage of this system is that it needs high liquid flow rate, which results in high energy consumption during operation. (Ma 2007.)

The integrated MBR (FIGURE 3) is generally composed of a bioreactor, a membrane component and a negative pressure suction pump. The membrane module is immersed in the bioreactor. After a certain period of microbial action in the bioreactor, the sewage can directly enter into the membrane module for separation, and the separated water is pumped out into the output water under the action of the suction pump. The advantages of the integrated MBR are that the energy consumption is lower than that of the split bioreactor, and the floor area is more compact. The disadvantage is that the membrane flux is low, the membrane pollution is serious, and it is not easy to clean and replace membrane components. (Ma 2007.)
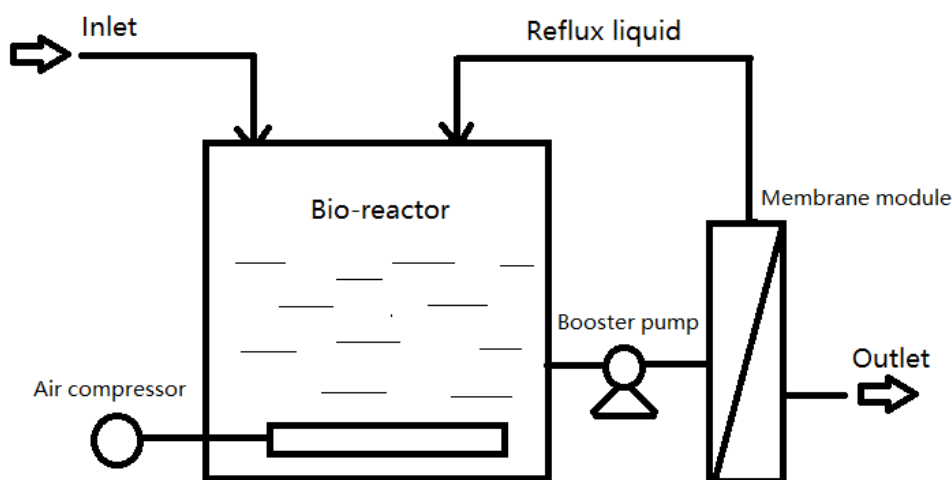

FIGURE 2. Split type membrane bioreactor. (adapter from Ma 2007.)

The main feature of MBR process is to combine the bioreactor with high sludge concentration with the membrane module with high efficiency of interception. The activated sludge in the bioreactor has a strong adsorption and oxidation capacity for the organics in the wastewater. At the same time, under the effect of membrane filtration, all the pollutants and microorganisms whose particle size is larger than the membrane pore diameter are trapped in the membrane tank to obtain good effluent quality and high treatment efficiency. (Ma 2007.)
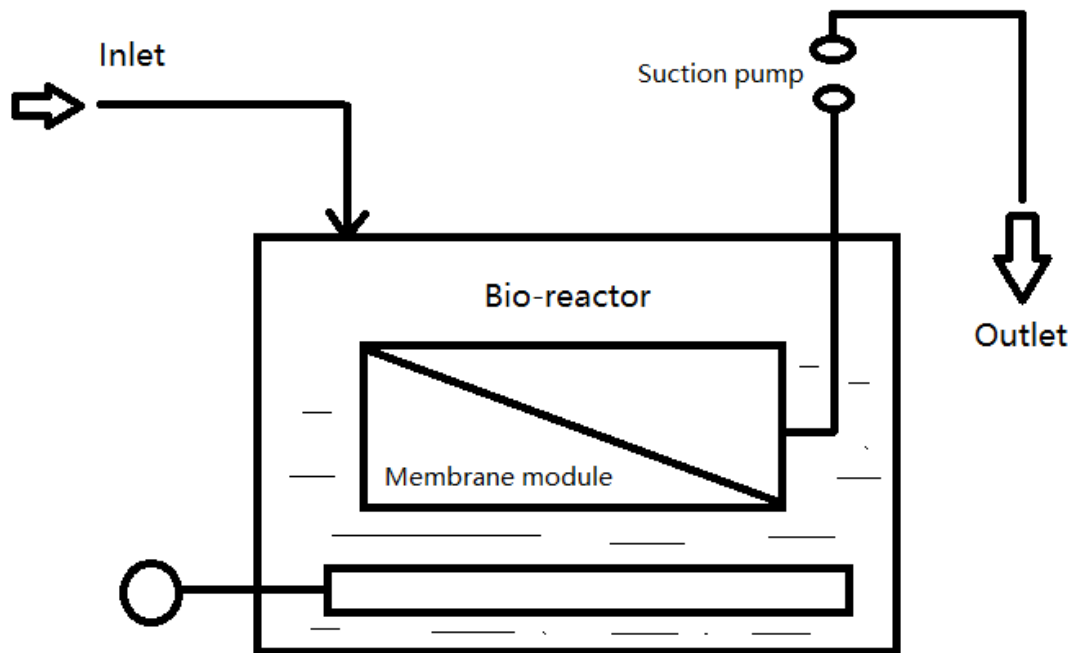
FIGURE 3. Integrated membrane bioreactor. (adapted from Ma 2007.)

4.1.1 Activated sludge

Activated sludge process is an aerobic biological treatment of sewage, which was invented and applied by Clark and Gage in England in 1913 at Laurence sewage test station in Manchester. It can remove the soluble and colloidal biochemical organics, SS and other substances that can be adsorbed by activated sludge, as well as a part of phosphorus and nitrogen. It is a general term for various methods of wastewater biological treatment of suspended microorganisms. (Tabata, Suzuki, Hamamoto, Hayakawa & Watanabe 1987, 655,925.)

The activated sludge is mainly composed of four parts: the active microbial community with metabolic function; the residues of internal respiration and self-oxidation of microorganisms; the refractory organics adsorbed by sludge flocs; the inorganic substances adsorbed by sludge flocs. The bacteria in the activated sludge is a mixed group, which often exists in the form of bacterial micelles, with less free state. Bacterial micelle is a kind of sticky mass which is made up of polysaccharides secreted by bacteria, which makes bacteria have the ability to resist external adverse factors. Microbial micelles are the main components of activated sludge flocs. (Gao 1978.)

The basic principle of the activated sludge process is as follows: in the first stage, the organic pollutants in the sewage are adsorbed on the surface of the microbial micelles by the activated sludge particles, which is due to the large surface area of the microbial micelles and the polysaccharide viscous substances. At the same time, some macromolecular organics are decomposed into small molecular organics under the action of bacterial extracellular enzyme. In the second stage, under the condition of sufficient O_2, aerobic microorganisms absorb these organics, oxidize and decompose them to form CO_2 and water, and some of them provide necessary energy for their own reproduction. In the other part, the excessive organics in the wastewater are removed by the reaction because of the consumption of organics in the oxidation reaction. Activated sludge can grow through the consumption of organic matter in sewage and make sewage purification. (Reyes & Raskin 2002, 445-459.)

The technological process of the activated sludge process is shown in FIGURE 4. It is generally composed of aeration tank, sedimentation tank, air compressor, sludge return system and excess sludge removal system. The mixed liquid formed by sewage and return sludge enters the aeration tank together. The air compressor pushes the air into the air diffusion device at the bottom of the aeration tank to make the air enter the sewage in the form of small bubbles, so as to increase the content of DO in the sewage. Due to the addition of air, the mixed liquid is in a violent state of motion. Through the air diffusion device, the DO and activated sludge in the sewage are mixed with the sewage and contacted completely, so that the activated sludge reaction can be carried out normally. After the mixed liquid passes through the sedimentation tank and sludge settles, one part of sludge enters the sludge reflux device for reflux, the other part of excess sludge is discharged through the excess sludge removal system, and the purified water becomes the output water. (Wang 2014, 1-3.)
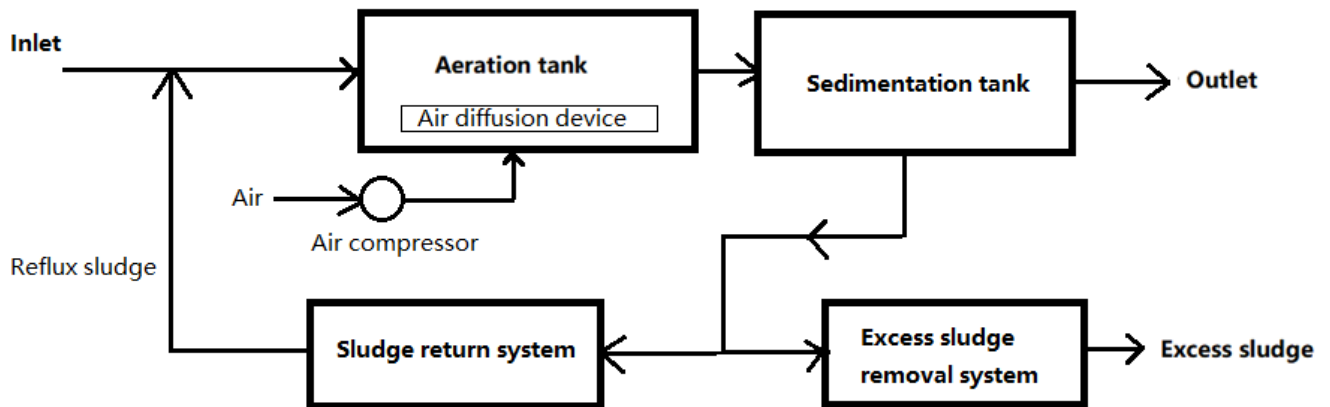
FIGURE 4. Process flow of activated sludge process. (adapted from Wang 2014.)

4.1.2 Membrane assembly

Membrane is a kind of material with selective separation function. Membrane separation is a process of separation, purification and concentration of different components in feed solution by membrane selective separation. Different from traditional filtration, membrane can separate substances at molecular level, which is a physical process without phase change and additives. Compared with the traditional water treatment method, membrane separation method has a good treatment effect, which can realize the recycling of wastewater and the recovery of useful substances. (Xu, Xiang, Shao & Li 2006, 7-10.) This can be reflected in the membrane intercepting the activated sludge and leaving it in the bioreactor.

The key equipment of MBR process is membrane module. The performance of membrane directly affects the quality and operation of produced water cost. According to the microporous pore size and designed filtration precision, the biofilm can be divided into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Membrane separation function is shown in FIGURE 5. (Wang 2016.)
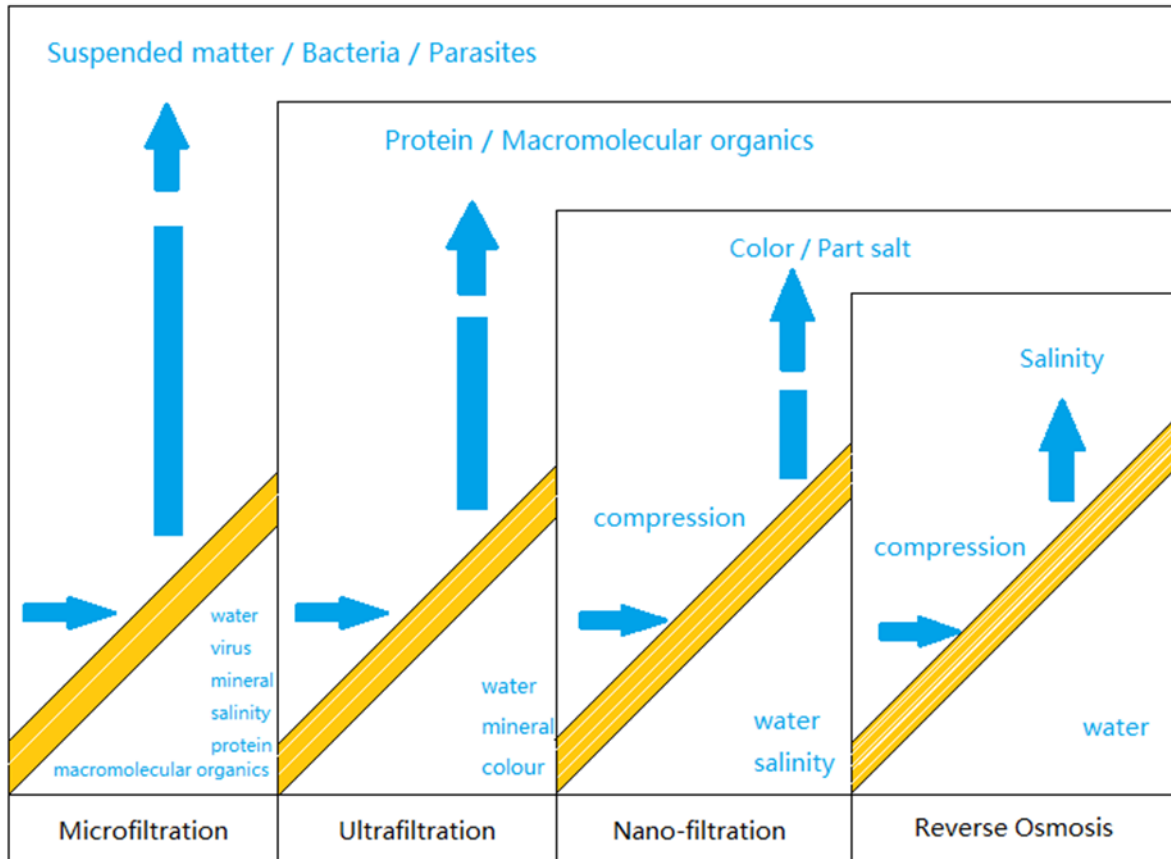
FIGURE 5. Membrane separation function. (adapted from Wang 2016.)

In MF, the membrane surface pore size is from about 0.1 μm to several μm. MF membrane can make macromolecules and soluble solids (inorganic salts) pass through, but it can intercept SS, active bacteria and macromolecular colloids. The operating pressure of MF is generally between 0.01 and 0.2 MPa. In UF, the pore diameter of membrane surface is about 0.002 - 0.1 μm. UF membrane can make small molecules and soluble solids (inorganic salts) pass through, but it can intercept micelles, proteins, microorganisms and macromolecular organics. The cutting molecular weight used to represent the pore size of UF membrane is generally between 1100 and 500000. The operating pressure of UF is generally between 0.05 and 0.6 MPa. (Wang 2016.)

In NF，the pore size of the membrane surface is about 0.001 μm (1 nm). The operation range of NF membrane is between UF membrane and reverse osmosis membrane. The molecular weight of organic matter retained by NF membrane is about 210 - 805, and the capacity of soluble salts retained is between 21 % - 97 %. The removal rate of soluble monovalent particles is higher than that of high valence ions. NF membrane is generally used to remove organic matter and pigment in surface water, hardness of

groundwater and some dissolved salts, food and medicine production to extract, concentrate, etc. with substances. The operating pressure of NF is generally between 0.5 and 1.5 MPa. (Wang 2016.)

In RO, the pore size of the membrane surface is smaller than 0.001 μm (1 nm). Reverse osmosis has the highest separation accuracy, which can effectively intercept all dissolved salts and organics with molecular weight greater than 100. At the same time, it allows water molecules to pass through. It is mainly used for desalination of industrial water, desalination of brackish water and seawater, boiler make-up water, production of industrial pure water and drinking pure water, wastewater treatment, etc. The operating pressure of reverse osmosis is generally between 1 and 10 MPa. (Wang 2016.)
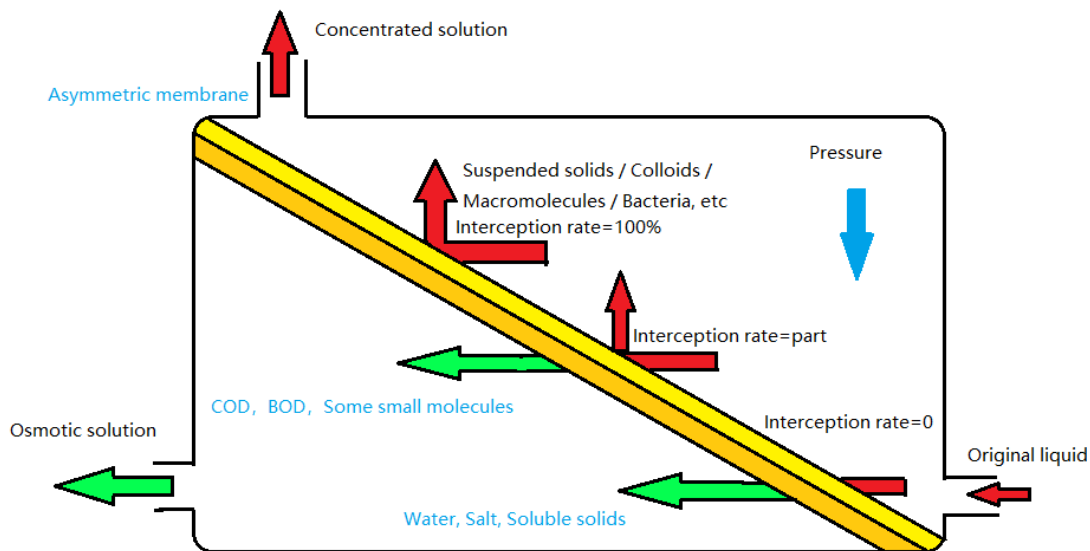

FIGURE 6. Ultrafiltration membrane filtration process. (adapted from Wang 2016.)

Membrane used in MBR process is a kind of UF membrane. There is a certain pressure difference between the inner side and the outer side of the UF membrane, and the original liquid moves from the high-pressure side to low pressure side. The pore diameter of the membrane surface screened the components of the fluid and finally formed the permeate to flow out. The low-pressure side of the UF membrane is called the water purification side (left side). The liquid inside is the permeate after removing all kinds of macromolecular particles. The high-pressure side is called the concentrated water side (right side). The liquid inside contains some small molecules and SS, bacteria, macromolecular substances, etc., which means the origin liquid have been successfully filtered. UF cannot filter water, salt and soluble solids. FIGURE 6 shows UF membrane filtration process. Among them, macromolecular organics

are good for the reproduction of microorganisms and the degradation of pollutants. In this process, macromolecular organic matter is intercepted, which is beneficial to the proliferation of microorganisms and improve their ability to degrade pollutants in water. (Wang 2016.)

4.1.3 Process research

Hydraulic Retention Time (HRT) is one of the factors affecting MBR device. The high-efficiency interception of membrane in MBR greatly improves the concentration of activated sludge in the bioreactor and enhances the removal ability of microorganisms to pollutants, thus reducing the hydraulic residence time of the system. Therefore, for the design of MBR, the size of the bioreactor volume and the water yield of MBR are also determined by HRT after the selection of the membrane components with a certain filtration area. Excessive long HRT will directly increase the volume of bioreactor, too short HRT will lead to the accumulation of soluble organic matter in the system and trigger the rapid fouling of membrane and the decline of membrane flux. The calculation formula of HRT can be simplified as follows (1):

$$HRT = \frac{1.1 \times \left(\frac{1}{\beta}-1\right)(K_S+L)}{KS_0} \tag{1}$$

In the formula, β is the concentration ratio of effluent and influent organics; K_S is the saturation constant, the unit is (mg/L); L is the concentration of effluent organics, the unit is (mg/L); K is the maximum specific degradation rate constant of substrate, the unit is (h^{-1}); S_0 is the concentration of reflux sludge, the unit is (mg/L). From the above formula, it can be seen that the main factors affecting HRT are the water quality of the inlet and outlet water and the sludge concentration of the bioreactor. Therefore, for the split type MBR system, the amount of reflux sludge should be increased appropriately to shorten HRT and improve the removal rate of organic matter. (Ye 2005.)

MBR can realize the separate control of sludge residence time (SRT) and HRT, as well as the simultaneous interception of microbial and macromolecular pollutants by membrane, making the choice of sludge in MBR more free than ordinary activated sludge process. It was found that with the increase of SRT, the removal efficiency of COD increased, and the sludge yield decreased. Because the sludge yield

is reduced and the effective removal ability of organic matter is improved under longer SRT, the selective function of the membrane also ensures the effluent water quality. According to the material balance equation, the relationship between SRT and biological concentration is derived as follows (2) and (3):

$$X = Y \times SRT[\frac{(C_i - C_c)}{HRT} + \frac{(C_i - C_s)}{SRT}] \qquad (2)$$

$$Y = \frac{Y_s}{1 + K_d \times SRT} \qquad (3)$$

In the formula, X is the biological concentration, the unit is (mg/L). y is the actual yield coefficient. C_i, C_C, C_S are respectively the COD concentration of influent, effluent and sludge supernatant, the unit is mg/L. SRT is the sludge residence time, the unit is (hour). HRT is the hydraulic retention time, the unit is hour; Y_s is the general activated sludge biological kinetic constant. K_d is the microbial decay constant, the unit is (d^{-1}). It can be seen from the formula that the sludge concentration X is not only related to the inlet and outlet water quality, HRT and SRT, but also to the COD concentration of the supernatant of the MBR. The formula has certain significance for judging the operation of MBR. Too long SRT is harmful to the activity of microorganisms. Because with the increase of SRT, the sludge concentration also increase leading to the extreme lack of nutrients, which will cause a large number of microorganisms to die and release a large number of non-biodegradable cell residues, and increase the endogenous respiration of microbial cells to produce a large number of difficult-to-degrade soluble microbial metabolites, thus destabilizing the COD of the effluent water and reducing the removal rate of ammonia and nitrogen. (Ye 2005.)

For organic wastewater with low COD content, most MBR processes use aerobic microorganisms to degrade organic matter in water, so sufficient DO must be maintained to maintain sludge activity. The increase of DO will promote the proliferation of microorganisms, and the interception effect of the membrane also makes the microbiota aggregate, further improving the pollutant removal efficiency. Membrane – bubble free oxygenation method appeared after the 1980s, and the efficiency was almost 100% because O_2 diffused into the water in molecular form. (Wang, Shi & Chai 2002, 355-56.)

In the sewage treatment operation, the sludge volume will generally remain at a certain level, and the volume of the reactor (aeration tank, anaerobic reactor, etc.) will not change. But if the water quality of the influent changes a lot (COD increases or decreases dramatically), the sludge load and volumetric load will change a lot, this impact on sludge microorganisms is called impact load. The MBR effluent has stable water quality and strong resistance to COD load impact. The reasons for the stability of MBR

effluent can be summarized as follows: longer SRT enhances the biochemical ability of refractory organic matter; effective separation of the membrane ensures the stability of effluent quality; the high concentration of sludge in the reactor has a dynamic balance with the change of influent COD; and large specific surface of activated sludge. (Fan, Wang & Jiang 1997, 68-74.)

The operating pressure will affect the membrane flux. Membrane flux refers to the amount of material passing through the membrane area per unit time. The size of membrane flux is directly related to the processing capacity of the MBR process. The calculation formula of membrane flux is as follow (4):

$$J = \frac{\Delta P}{\mu R_m} \qquad (4)$$

J is the membrane flux, the unit is (L/m^2·d); P is the operating pressure, the unit is (MP); μ is the mixed liquid viscosity, the unit is (Pa·S); R_m is the total resistance of membrane filtration. The operating pressure is proportional to the membrane flux, and the greater the pressure, the higher the membrane flux. The relationship between membrane flux and operating pressure can be referred to the following TABLE 4. (Ye 2005.)

It can be seen from the TABLE 4 that the membrane flux changes in a positive proportion with the increase of pressure when the temperature, sludge concentration, and membrane surface flow rate are unchanged, but there is a critical pressure. When the critical pressure is increased, the increase of membrane flux is not obvious, indicating that the effect of pressure on membrane flux becomes smaller and smaller. Usually, Rm is a fixed value, but under excessive operating pressure, the sludge will form a gel layer attached to the surface of the membrane, which will aggravate the membrane pollution and improve the filtration resistance of the membrane. Therefore, when designing the MBR process device, the appropriate operating pressure should be selected through the test. (Ye 2005.)

TABLE 4. Relationship between operating pressure and membrane flux. (from Ye 2005.)

Project	Numerical value						
Operating negative pressureΔP (MP)	0.007	0.009	0.013	0.015	0.018	0.019	0.023
Membrane flux Q (L/h)	4.8	5.7	6.8	7.9	8.65	9.6	9.7

4.1.4 Membrane pollution and control measures

Membrane fouling is one of the important problems faced by membrane separation technology. The introduction of membrane separation makes the treatment effect of the technology superior to the traditional technology, but membrane fouling is a prominent problem, which will affect the stable operation of the membrane and determine the frequency of membrane replacement. The material source of membrane pollution is activated sludge mixture. Membrane fouling refers to the phenomenon that suspended particles, colloidal particles or dissolved macromolecular organic matter in the mixed liquid in the bioreactor adsorb and deposit on the membrane surface and in the membrane pore, resulting in the decrease or blockage of the membrane pore size and the decrease of the membrane flux. There are many reasons for the attenuation of membrane flux, mainly the resistance of mass transfer during operation. The generalized membrane fouling includes not only the irreversible pollution caused by adsorption and clogging, but also the concentration of polarization and the formation of gel layer (reversible pollution), and the interaction between the two causes the attenuation of membrane flux during operation. (You, Jiang, Han, Liu & Wan 2009, 232-235.)

During continuous filtration, narrowing or blocking of membrane pores is irreversible contamination. Even if the membrane is cleaned after long-term use, the membrane permeability will decrease. If strong corrosive sewage is used to pass through the membrane, the structure and function of the membrane will be seriously affected. Irreversible contamination cannot be removed by physical cleaning, so new membranes need to be replaced regularly to maintain the operation of the device. (You et al. 2009.)

In the bioreactor, the mixed liquid passes through the membrane assembly under pressure driving. Under the action of the membrane, the solute is trapped and accumulated on the membrane surface. The solution concentration on the right side of the membrane is much higher than that on the left side of the membrane. Under the action of the concentration gradient, the solute will diffuse to the solution on the right side of the membrane to form a boundary layer, which increases the fluid resistance and local osmotic pressure and reduces the membrane flux. This process is called concentration polarization. Under the action of concentration polarization, with the entrapment of solute on the right side of the membrane, a boundary layer will gradually be formed, and the material in the boundary layer will further accumulate to form a gel layer. Concentration polarization and causes of gel layer formation shows in FIGURE 7. In the FIGURE 7, C_m is the solute concentration on the surface of the membrane, C_g is the

gel layer concentration, C_b is the solute concentration in the reactor, C_p is the solute concentration on the left side of the permeable membrane assembly, and C_p is much smaller than C_m and C_g. (Ma 2007.)
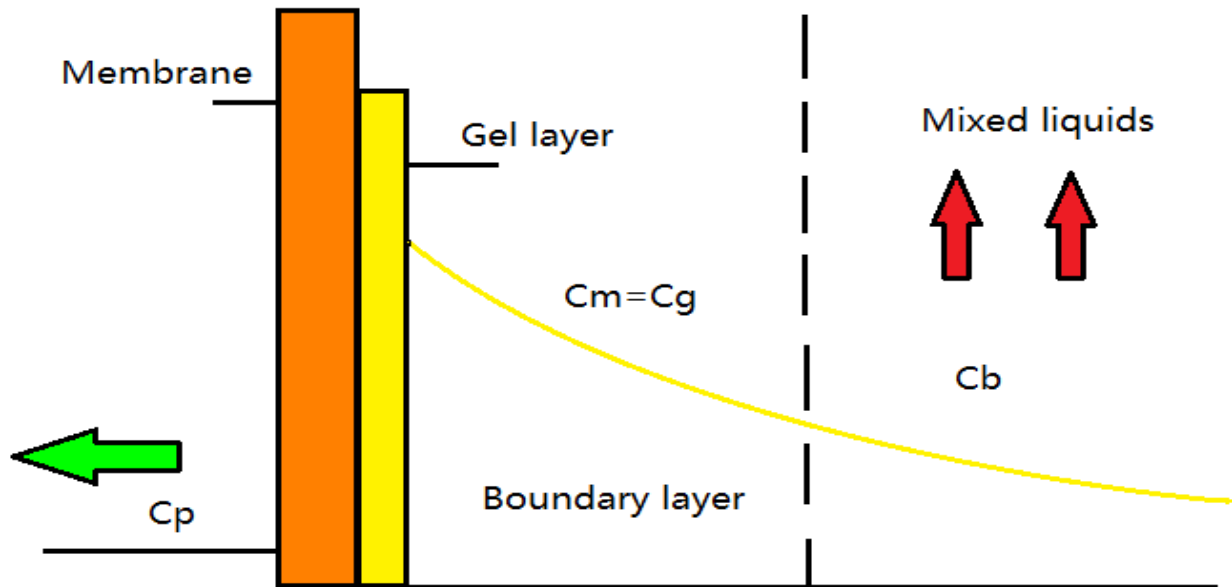

FIGURE 7. Concentration polarization and causes of gel layer formation. (adapted from Ma 2007.)

The specific form of membrane pollution can be seen in Li Weimin's experiment (FIGURE 8). It can be clearly seen in the figure that in the initial stage, large granular sludge rarely accumulated on the surface of the membrane, and the surface was white. At this time, the increase of membrane resistance was mainly due to the adsorption and adhesion of the membrane, and the gel layer was gradually formed on the surface of the membrane. On the fourth day, the surface of the membrane began to darken. After six days of operation, a small amount of sludge began to accumulate on the membrane surface, mainly from the root of the membrane. This was due to the suction effect. The pressure inside the membrane gradually decreased with the distance from the outlet, and the suction pressure near the root was high. The pollution took this as a breakthrough, and continuously developed into the middle of the membrane. On the eighth and tenth days, the sludge accumulated on the membrane surface is in the middle. It is clear that this form of pollution is consistent with the description above. (Li 2007.)

Membrane surface after two days of operation   Membrane surface after four days of operation

Membrane surface after six days of operation   Membrane surface after ten days of operation

Membrane surface after eight days of operation

FIGURE 8. Change of membrane contamination with days. (adapted from Li 2007.)

At present, there is no general mathematical model for estimating the nature and extent of membrane fouling. It is generally believed that the classical model for characterizing the fouling resistance during membrane filtration is up to the Darcy equation (5) and (6). Darcy's formula can establish a variety of mathematical models based on different membrane experiments. For example, Choo et al. studied the effect of microbial organic load on membrane pollution in 2000 and established a model between pressure, flux and filtration resistance. (Choo, Kang, Yoon, Park, Kim & Adiya et al 2000, 363-371.)

$$J = \frac{\Delta p}{\mu R_t} \tag{5}$$

$$R_t = R_M + R_v + R_f \tag{6}$$

J is the membrane flux, the units is $(m^3/m^2 \cdot d)$. P is the pressure difference between the two sides of the membrane, the units is (Pa). u is the viscosity of the filtrate, the units is (Pa·S). Rt is the total resistance, the units is (m^{-1}). Rm is the resistance of the new membrane, the units is (m^{-1}). Rv is the resistance

generated by the gel layer deposited on the membrane surface, the units is (m^{-1}). Rf is the membrane fouling resistance, the units is (m^{-1}). (Choo, Kang, Yoon, Park, Kim & Adiya et al 2000, 363-371.)

The control methods of membrane contamination are as follows. Pretreatment of wastewater can effectively change water quality, and the common method of sewage pretreatment is flocculation. Its principle is that the surface of the particles has the same charge, and they are mutually exclusive and stable under certain conditions. The thicker the electric double layer is, the greater the force of mutual exclusion and the more stable the particles are. The more stable the particles are, the more a certain amount of electrolyte is added to the system to reduce the surface charge and the thickness of the electric double layer, so that the repulsion between the particles decreases and flocculent aggregation occurs, it can be re-dispersed uniformly after shaking. This phenomenon is called flocculation, and the added electrolyte is called flocculant. Common flocculants include aluminum potassium sulfate dodecahydrate ($KAl(SO_4)_2 \cdot 12H2O$), etc. It can also be considered to directly inject flocculant into the mixed liquid to make the sludge and flocculant form larger flocs, which is helpful to form a mud cake layer easily falling off on the surface of the membrane and prevent the fine particulate matter from blocking the membrane. (Wang 2017.)

The pollution can be effectively reduced by improving the conditions of membrane hydrodynamics. Improve the local structure of the reactor and reducing the concentration polarization, the occurrence of membrane pollution can be reduced. Or by improving the inlet flow rate or using staggered flow of water, water flow can timely take away the solutes trapped on the membrane surface. This method increasing the sweeping force on the membrane surface through aeration, reducing the residence time of mud cake on the membrane surface. Control the critical pressure value of membrane flux filtration and stop the pressure increase when the critical pressure is reached. (Wang 2017.)

4.1.5 Removal effect and Application

The efficiency of MBR water treatment is high. The maximum removal efficiency of BOD_5, SS and turbidity in petrochemical wastewater is higher than 98 %, and the average removal efficiency of COD is 91 % from 78 % to 98 %. The maximum treatment efficiency of petroleum and ammonia nitrogen content index (NH_3-N) reached 100 %. MBR effluent water quality and water treatment efficiency have high stability. Pure water is colorless, tasteless and has the same appearance as tap water, and can be

directly reused as medium water or used as non-drinking water. TABLE 5 shows MBR treatment effect. (Zhao, Fan & Wang 1997, 69-73.)

TABLE 5. Membrane bioreactor treatment effect. (From Zhao et al. 1997.)

Water quality index		COD	BOD$_5$	SS	Petroleum	NH$_3$-N	Turbidity
Statistics		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Inlet	Maximum value	900	368	399	56.6	91.1	74
	Minimum value	135	120	26	2.24	14.5	7
	Average value	542	2257	118	19.6	58.5	45
	Sample variance	318	108	83	13	96	15
Outlet	Maximum value	68.6	8	7.9	10.7	39.8	0.61
	Minimum value	15.8	2.4	1.2	0.04	0.05	0.11
	Average value	26.7	5.9	4.6	1.93	7.3	0.37
	Sample variance	9.5	2.6	1.7	1.99	9.5	0.15
Efficiency	Maximum value	98	99	99	100	100	100
	Minimum value	78	96	80	24	35	98
	Average value	91	98	93	87	86	99
	Sample variance	5	1	6	14	16	1

The area occupied by an integrated MBR with a treatment scale of 50 m^3/d and 40 m^3/d in 2002 was 5.6 m^{3}and 3.36 m^2. The converted area is about 1 m^2/m^3. If the treatment scale is 240 m^3/d, it needs to cover an area of about 240 m^2. The total floor area of pumps, blowers, control panels, etc. required for the equipment is 240 m^3/d, and the total floor area is 260 m^2. The floor area of the building area is 234 €/m^2, and the cost of the integrated MBR is 6 0937 €. In summary, the total investment of this project is 12 3436 €, the unit treatment investment is 514 /m^3, while the equipment investment using the traditional biological treatment process is 325 - 390 /m^3 (activated sludge tank). (Fu & Feng 2002, 53-55.)

In terms of cost, membrane components usually have a shelf life of 3 to 5 years. In UF/MF membrane components, especially on membranes used in MBR, most international companies claim a membrane life of 5 to 10 years. When both UF and reverse osmosis membranes are used simultaneously, the cost price of the membranes is nearly doubled. However, from experience, the service life of the membrane can be extended from the original 3 years to 5 to 6 years. If better maintenance and cleaning can improve the service life of the membrane for 1 year. (Guo, Li, Yang, Cao, Du & Liu 2014, 95-98.)

Due to the extremely poor water and land resources in Japan, special attention has been paid to the research and development of MBR process, so MBR process has been greatly developed in Japan. For example, in the mid-1970 s, Japan took the lead in successfully applying the MBR process to a sewage reuse system in a high-rise building. In the early 1980s, Japan built two small-scale sewage treatment plants using the MBR process. In the late 1980 s, Japanese scholars successfully pioneered an integrated MBR process that placed membrane components in a biochemical tank. With the development and improvement of membrane materials, membrane manufacturing technology, and membrane cleaning methods, by the mid-1990s, more than 100 high-rise building wastewater reuse systems in Japan used the MBR process to treat wastewater. About 40 small-scale wastewater treatment plants used MBR process to treat wastewater. (Wang 2017.)

MBR has been widely concerned and applied in industrial wastewater, domestic wastewater, and wastewater reuse due to its outstanding characteristics such as high treatment efficiency, good effluent quality, simple process, compact equipment, small footprint, easy to realize automatic control, simple operation and management. It has incomparable advantages over conventional treatment processes. With the development and improvement of MBR technology, the gradual solution of membrane pollution, the improvement of membrane quality, and the reduction of membrane manufacturing cost, the equipment investment of MBR will also be reduced. It is reasonable to believe that with the increasing shortage of water resources, the application of MBR in sewage treatment, especially in sewage reuse, will be more extensive and have a broader prospect. (Liu & Zhang 2003, 9-12.)

4.2 Catalytic wet air oxidation

CWAO is an advanced technology for treating high concentration organic wastewater. CWAO technology is a new technology developed based on conventional wet air oxidation (WAO) in the mid-1980s. Compared with WAO technology, CWAO technology incorporates catalyst and reduces harsh reaction conditions. Under the action of catalyst, the requirement of CWAO for temperature and pressure is further reduced and the oxidation efficiency is higher. The catalytic wet oxidation process can utilize the heat generated by the reaction, so the energy consumption is lower. (Cheng & Yi 2005, 79-80.)

According to the existing research, it is generally accepted that WAO belongs to free radical reaction. The reaction usually consists of three stages: initiation of the chain; transmission of the chain; and termination of the chain (in this reaction peroxy radicals and peroxides are taken as examples).
During the initiation of the chain, the production of free radicals by breaking active molecules requires a certain amount of energy. Under the combined action of high temperature and high pressure and O_2, organic substances generate the initial free radical (7). Hydroxyl radicals can also be generated directly from hydrogen peroxide (H_2O_2) and catalysts (8). The initiation reaction of the chain is as follows. (Cai, Li & Zhang 2004, 107-112.)

$$RH + O_2 \rightarrow R\cdot + HOO\cdot \quad \text{(High temperature and high pressure)} \tag{7}$$
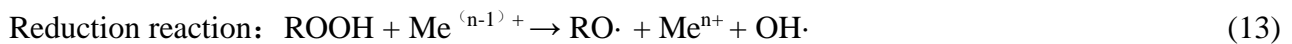$$H_2O_2 + M \rightarrow 2\cdot OH \quad \text{(M as catalyst)} \tag{8}$$

In the process of chain transfer, the alternating process of the interaction between free radicals and molecules. For example, organic compounds and hydroxyl groups form free radicals and water (H_2O) (9). Free radicals and O_2 combine to form peroxy radicals (10). During the interruption of the chain, free radicals produce stable molecules after collision, which interrupts the chain growth process and stops the reaction. For example, two free radicals collide to form a new covalent molecule. (11). Peroxy radicals and other free radicals react to form peroxides (12). (Cai, Li & Zhang 2004, 107-112.)

$$RH + \cdot OH \rightarrow R\cdot + H_2O \tag{9}$$
$$R\cdot + O_2 \rightarrow ROO\cdot \tag{10}$$
$$R\cdot + R\cdot \rightarrow R - R \tag{11}$$
$$ROO\cdot + R\cdot \rightarrow ROOR \tag{12}$$

It was found that H_2O_2 was detected when WAO was used to treat phenolic wastewater, and it was believed that O_2 in the molecular state was involved in the formation of various free radicals during the induction and proliferation phases. The wet oxidation of organic matter first generates oxygen radical, which reacts with water to generate hydroxyl radical, and then with organic compound to generate low-level acid, which is further oxidized to CO_2 and H_2O. (Qian 2006.)

Because catalyst is added to catalytic wet oxidation technology, the reaction speed can be accelerated. This principle can be explained from two aspects: one is to reduce the activation energy of the reaction; the other is to change the reaction process. CWAO is similar in the reaction mechanism of WAO. Taking metal catalyst as an example, free radical oxidation reaction was found during the oxidative degradation of polyethylene glycol, including three periods: initiation period, propagation period, and termination period. During the initiation period, organic compound and O_2 generate free radicals. During the propagation period, free radicals combine with O_2 to produce peroxide radicals, a reaction identical to WAO. During the termination period, free radicals meet to produce low molecular alcohols, ketones, acids and CO_2. (Qian 2006.)

Metallic catalysts cause the decomposition of peroxide through the following oxidation-reduction catalytic cycles. Metal catalyst $Me^{(n-1)+}$ reduces peroxide to generate Me^{n+}, alkoxyl radical, and hydroxyl radical (13). Me^{n+} and oxidized alcohols generate peroxyl radicals, $Me^{(n-1)+}$ and hydrogen ion (14). (Qian 2006.)

Reduction reaction： $ROOH + Me^{(n-1)+} \rightarrow RO\cdot + Me^{n+} + OH\cdot$ (13)

Oxidation reaction： $ROH + Me^{n+} \rightarrow ROO\cdot + Me^{(n-1)+} + H^+$ (14)

4.2.1 Operating process and influencing factors

The operating conditions of the wet oxidation method are generally as follows: temperature $150 - 350\,°C$, pressure 2 - 15 MPa. Under this condition, the organic pollutants in wastewater are oxidized by using O_2-rich gas or O_2 as oxidant and catalytic action of catalyst to increase the oxidation reaction rate between organic matter and oxidant in wastewater. As can be seen from FIGURE 9, one part of the macromolecular organic pollutants reacts to produce CO_2 and H_2O, the other part reacts to produce small molecular organic compounds, and then further generates CO_2 and H_2O. The final products of this reaction are CO_2 and H_2O. Thiocyanate compounds in wastewater, such as ammonium thiocyanate

(NH4SCN), react with O_2 to produce nitrogen (N_2) and CO_2 gases (15). Ammonia (NH_3) generated from ammonia-containing compounds reacts with O_2 to produce H_2O and N_2 (16). The reaction formula is as follows (Yuan 2020.):

$$2NH_4SCN + 7O_2 = 2N_2 + 2H_2O + 2H_2SO_4 + 2CO_2 \tag{15}$$
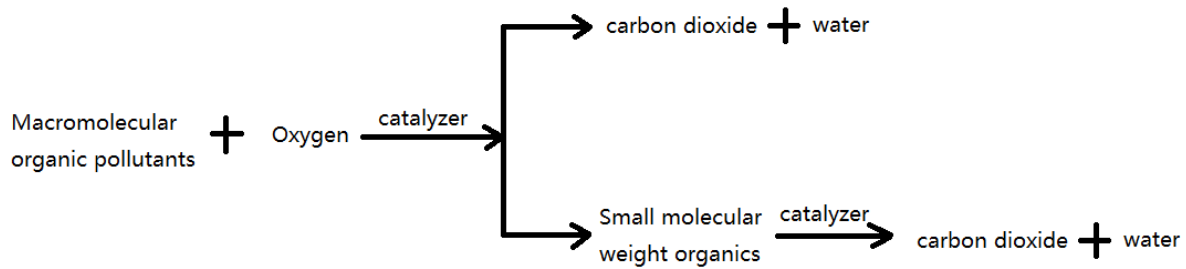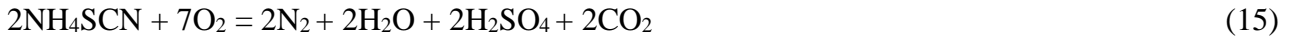$$4NH_3 + 3O_2 = 6H_2O + 2N_2 \tag{16}$$

FIGURE 9. Reaction process of organic substances. (adapted from Yuan 2020.)

The basic process flow of CWAO is shown in FIGURE 10. The wastewater is pumped into heat exchanger (2) by high-pressure pump (1) for heating, and the air is compressed by the compressor (5) and enters reactor (3) together with the heated wastewater. The compressed O_2 entering reactor (3) undergoes an oxidation reaction with the organic matter in the wastewater (the CWAO reactor is filled with catalyst). Most of the organic matter is oxidized to CO_2 and H_2O, and a small part is converted to small molecule organic matter, which is oxidized to CO_2 and H_2O in the subsequent process. The treated water enters the heat exchanger (2) through a circuit for cooling while preheating the untreated wastewater. The cooled gas-liquid mixture feeds into the gas-liquid separator (4) for separation of gas phase and liquid phase. After separation, the liquid phase can enter the next microbial treatment facility or discharge up to standard, and the gas phase mainly contains CO_2 and N_2 (tail gas). Tail gas can enter the turbogenerator to generate electricity to further reduce energy consumption. This type of CWAO process can utilize the heat generated by the reaction. When COD is more than 20,000 mg/L, the energy generated by the reaction can maintain the normal operation of the reaction without additional energy input. At this time, the running energy consumption is mainly provided by the air compressor and high-pressure water pump. (Chen & Shen 2005, 79-80.)
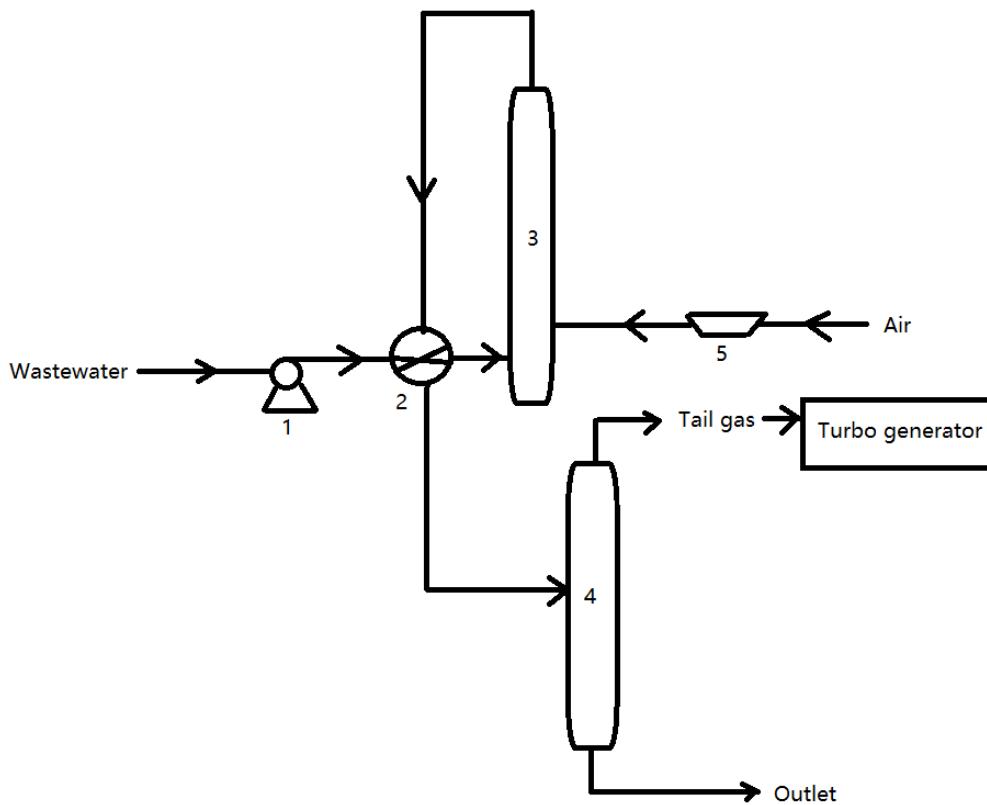
(1). High pressure pump; (2) Heat exchanger; (3) CWAO reactor; (4) Gas-liquid separator; (5) Air compressor

FIGURE 10. Basic process flow of catalytic wet reaction. (adapted from Chen & Shen 2005, 79-80.)

The materials of wet oxidation reactor 3 mainly include stainless steel 316 L, nickel-based alloy C - 276 and 625, cobalt-based alloy, titanium alloy, and ceramics. The results of a large number of studies show that the higher the chloride ion (Cl^-) content in water, the stronger the corrosiveness. Therefore, the main basis for selecting materials is the concentration of Cl^-. When the temperature is below 290 °C and $Cl^- <$ 300 mg/L, stainless steel is sufficient. When $Cl^- <$ 3000 mg/L, nickel-based alloys C - 276 and 625 are recommended. Nickel-based alloys are corrosion resistant. The addition of molybdenum to stainless steel 316 gives it a special corrosion-resistant structure. The microstructure of stainless steel 316 is shown in FIGURE 11. (Qian 2006.)
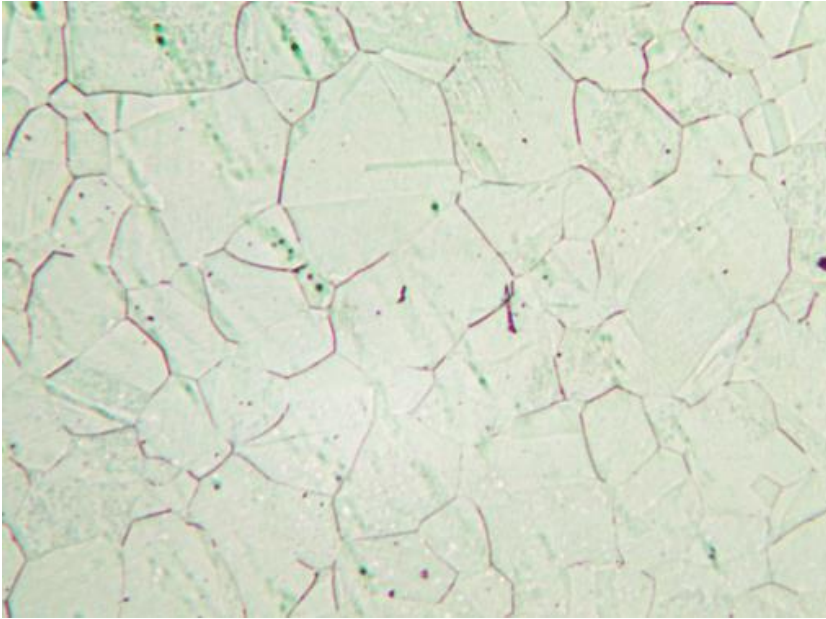
FIGURE 11. Microstructure of stainless steel 316. (adapted from Qian 2006.)

The value of pH will affect the reaction. It can be seen from FIGURE 10 that wastewater enters reactor (3) after passing through the heat exchanger, so the pH value of wastewater will have a certain effect on the oxidation effect, and the pH value directly affects the existence form of substances in wastewater and then the effect of reaction. A variety of experiments and studies have found that too high pH value will affect the water quality of the final effluent, and too low pH value will lead to the acidic state of the wastewater, which will cause corrosion to the reactor and other materials. When homogeneous catalysts are used, low pH value easily makes the active components of catalysts dissolve and lose, resulting in secondary pollution. (Qian 2006.)

Temperature is an important factor in the catalytic wet oxidation reaction. In the normal range, the oxidation rate increases with the increase of temperature, but the temperature cannot be raised blindly. The higher the temperature, the higher the pressure of the reaction will be, and the greater the power consumption of water and air, and the resulting high pressure has a higher requirement on the temperature resistance and pressure resistance of the reactor. (Qian 2006.)

4.2.2 Classification

Catalytic wet oxidation techniques can be classified according to the type of catalyst. Catalysts are divided into homogeneous catalysts and heterogeneous catalysts. When catalysts and reactants are in a

homogeneous gas or liquid phase, they are called single-phase catalysis; when catalysts and reactants are in different phases, they are called heterogeneous catalysis. Heterogeneous catalysts present in reactions of different phases (e.g., solid catalysts in liquid mixing reactions), while homogeneous catalysts present in reactions of the same phase (e.g., liquid catalysts in liquid mixing reactions). (Zhou 2007.)

Catalytic wet oxidation using homogeneous catalysts has milder reaction temperature and more specific reaction performance, which can be finely formulated and designed through the selection of ligands, solvent conversion, increase of promoters and other factors. Its principle is that by adding soluble catalysts in the reaction solution, the catalysts play a catalytic role in the oxidation reaction of organic matter in the water at the molecular or ionic level under high temperature and pressure (such as copper ion Cu^{2+} iron ion Fe^{2+} in the mixture of copper nitrate and ferrous chloride has oxidative catalytic activity). Because the catalyst is miscible in water, it needs to be recovered through the follow-up treatment of the ionic catalyst, otherwise it will produce secondary pollution, this process is more complex. Therefore, from the late 1970s, the research focused on catalytic wet oxidation has shifted to the heterogeneous catalytic wet oxidation reaction, mainly the heterogeneous catalytic wet oxidation reaction system. (Zhou 2007.)

The heterogeneous CWAO catalyst exists in solid-state, and the catalyst is simple and easy to separate from the wastewater. Because transition metal oxides have a strong ability to absorb and activate O_2, most catalysts in wet oxidation reactions catalyzed by multiphase catalysis are transition metal oxides. Such catalysts can be divided into two categories: noble metal catalysts and non-noble metal catalysts. Among them, the active components of noble metal catalysts include platinum (Pt), palladium (Pb), rhodium (Rh), ruthenium (Ru), and iridium (Ir), etc., because of their high catalytic activity and long lifetime, they have practical application prospects. However, the expensive price of precious metal catalysts limits their wide use. (Zhou 2007.)

4.2.3 Carrier of catalyst

The role of catalyst support is generally to disperse active components on the surface of the support to obtain a higher surface area and improve the catalytic efficiency of active components per unit mass. Because of the harsh industrial conditions of catalytic wet oxidation reaction, the catalyst should be immersed in high temperature and high-pressure wastewater for a long time, and because of the characteristics of wet catalytic oxidation reaction, the intermediate product of the reaction is small molecule
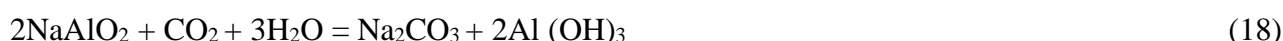
carboxylic acid, which has strong acidity and is also unaffordable to many common catalyst supports. (Yang 2007.)

Activated carbon (AC) can be used as catalyst carrier. Substances containing carbon (such as coal, wood or petroleum pitch) are heated in the absence of air to volatilize large amounts of material, leaving carbon with a porous structure. This heated substance usually also contains some hydrogen. Then the substance is further enlarged and the total surface area is increased by the controlled oxidation of water vapor or carbon dioxide to achieve the purpose of activation. AC can contain up to about 10% mass fraction of oxygen, which covers most of the surface in the form of chemical adsorption of ketones, hydroxyl groups, or carboxylic acids. These oxygen-containing species can make the adsorption characteristics of AC very different from those of carbon heated in inert gas or under reducing conditions, and the surface area can be as high as 1200 m^2/g. (Lei & Jiang 2001, 133.)

Considering that AC has a large specific surface area and relatively low price, there are some research works on the preparation of catalysts using AC as a carrier to carry out the study of the catalytic wet oxidation reaction. However, because AC is easy to be oxidized and decomposed under the condition of the catalytic wet oxidation reaction in the presence of long-term aerobic, the AC catalyst has not the possibility of practical application at present. (Yang 2007.)

The basic morphology of alumina is shown in FIGURE 12. Aluminium oxide (Al_2O_3) has many morphologies, different morphologies, and different properties. Even with the same morphology, its macrostructure, density, porosity, pore size distribution, specific surface area, etc., can also be different due to its different manufacturing methods. Alumina can be prepared by sodium hydroxide (NaOH) dissolves aluminium hydroxide (Al(OH)$_3$) to form sodium aluminate (NaAlO$_2$) and H_2O (17), and then reacts with CO_2 and H_2O to produce Al(OH)$_3$ and sodium carbonate (Na$_2$CO$_3$) (18), followed by heating Al(OH)$_3$ to produce Al_2O_3 (19). The reaction formula is as follows (Lei & Jiang 2001, 133.):

$$NaOH + Al(OH)_3 = NaAlO_2 + H2O \tag{17}$$
$$2NaAlO_2 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3 \tag{18}$$
$$2Al(OH)_3 = Al_2O_3 + 3H_2O \qquad (Heating) \tag{19}$$

Al_2O_3 has been widely used because of its mature preparation process, low price, large specific surface area and good strength, it belongs to acid-base amphoteric oxides, and special surface acidity and alkalinity. However, because Al_2O_3 belongs to amphoteric oxides, it cannot exist stably for a long time under

strong acidic conditions, so it is not easy to apply it in the treatment of organic wastewater by catalytic wet oxidation. However, in the treatment of wastewater containing ammonia and nitrogen, Ru/Al_2O_3 can be used as catalyst for wet oxidation reaction because the pH value of such wastewater is generally about 10 - 12 and Al_2O_3 can exist stably for a long time. The use of alumina as catalyst support should be selected according to the specific conditions. (Yang 2007.)
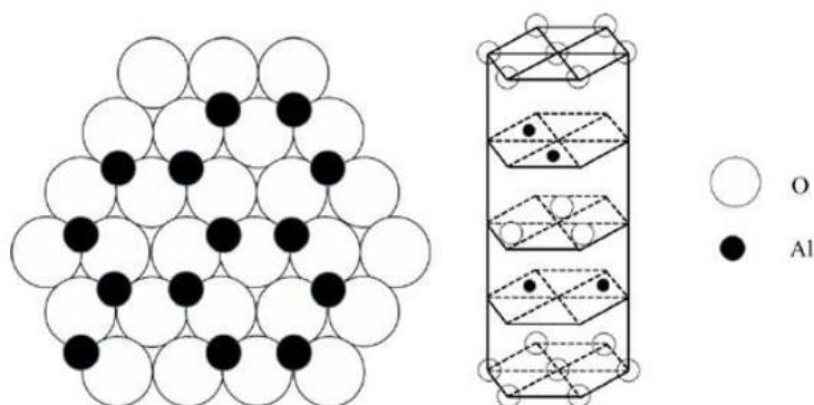

FIGURE 12 . Basic morphology of alumina. (adapted from Lei & Jiang 2001.)

At present, titanium dioxide (TiO_2) is the main catalyst carrier with practical application prospects (FIGURE 13), because it has good stability under acidic and alkaline conditions, and the price is relatively cheap. However, it also has some problems such as small specific surface area and immature forming process. Zirconium dioxide (ZrO_2) has similar properties to that of TiO2, but its higher price also makes it impossible for large-scale practical applications. However, the addition of a small amount of ZrO2 in TiO2 can improve the structural properties of the TiO2 support, increase the specific surface area of the support, and improve the strength. Therefore, the composite support of TiO2-ZrO2, which is used as ZrO2 modification assistant, is most likely to be the support of catalytic wet oxidation reaction catalyst for practical application at the present stage. (Yang 2007.)

FIGURE 13. Catalyst carrier made of titanium dioxide. (adapted from Lei & Jiang 2001.)

4.2.4 Mechanism of treating phenolic wastewater

In the experiment of treating phenol-containing wastewater, phenol was treated with supported cupric oxide (CuO) catalyst. It was found that there was an induction period for the reaction, and the effect of free radical inhibitors on the reaction rate was the same as that on the homogeneous free radical oxidation reaction. The reaction rate was affected by pH, and at pH is 4.0, the reaction rate is the highest, and the intermediate products formed to support the free radical reaction theory. (Hao 2004.)

During the initiation of the chain, phenol reacts with a copper system catalyst (Cu-cat) to produce phenoxy radical (20). In the process of chain transfer, phenoxy (ROH·) and O_2 generate phenol peroxy radical (21), phenol peroxy radical and phenol generate peroxide (22). Peroxide decomposition is a two-way reaction to form intermediate complexes (23).

$$HO\text{-}R\text{-}H + Cu\text{-}cat \rightarrow ROH\cdot + \cdot H\text{-}Cu\text{-}cat \tag{20}$$
$$ROH\cdot + O_2 \rightarrow ROOOH\cdot \tag{21}$$
$$ROOOH\cdot + HO\text{-}R\text{-}H \rightarrow ROOOH + ROH\cdot \tag{22}$$
$$ROOOH + 2Cu\text{-}cat \longleftrightarrow Cu\text{-}cat\ldots R(OH)\text{-}O\cdot + OH\ldots Cu\text{-}cat \tag{23}$$

Chain termination: peroxides and phenols produce phenol compound and phenoxy groups, further generate H_2O termination chains. (24)(25). In this reaction (20-25), it was found in the experiment that

phenolic salt ions did not work and free radicals were mainly formed by dehydrogenation. The addition of copper ions is mainly through the formation of intermediate complexes, dehydrogenation to initiate the oxidation reaction radical chain. (Hao 2004.)

$$\text{Cu-cat}\ldots\text{R(OH)-O}\cdot + \text{HO-R-H} \rightarrow \text{HO-R-OH} + \text{ROH} + \text{Cu-cat} \tag{24}$$

$$\cdot\text{OH}\ldots\text{Cu-cat} + \text{HO-R-H} \rightarrow \text{ROH} + \text{H2O} + \text{Cu-cat} \tag{25}$$
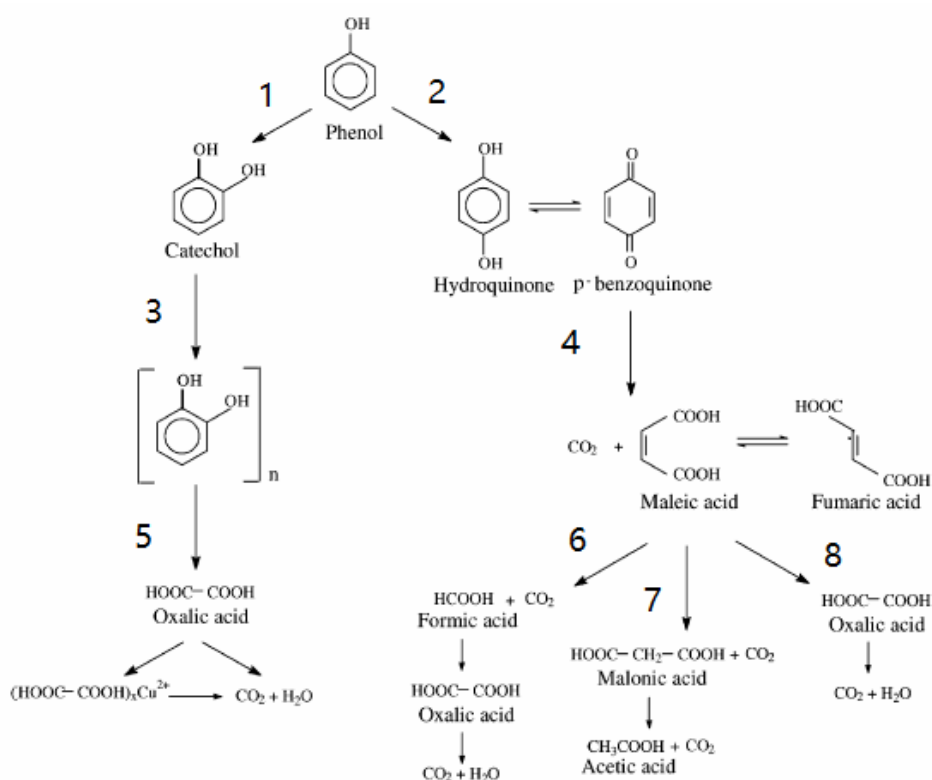

FIGURE 14. Pathway for the phenol oxidation in aqueous phase proposed. (from Santos et al. 2004.)

The oxidation pathway of phenol is shown in the following FIGURE 14: phenol generates Catechol by reaction 1 and hydroquinone by reaction 2, which is reversible. Catechol in reaction 5 reacts to form oxalic acid, which further reacts to produce CO_2 and H_2O. In reaction 4, benzoquinone reacts to form maleic acid, which is reversible and fumaric acid does not participate in the next stage of the reaction. In reaction 6, maleic acid reacts to form formic acid, which in the following reaction forms oxalic acid, which further reacts to form CO_2 and H_2O. Maleic acid was reacted in reaction 7 to produce malonic acid, which was further reacted to produce acetic acid. Oxalic acid is produced in reaction 8, which in

turn generates CO_2 and H_2O. In this process, phenol undergoes a series of transformations to form two harmless substances, CO_2 and H_2O. (Hao 2004.)

4.2.5 Application prospect

Japan Osaka Gas Company adopted heterogeneous catalytic wet air oxidation technology to treat coking wastewater. The facility scale is 6 tons/day. The catalyst is supported by TiO_2 or ZrO_2, and the catalyst shape is honeycomb. The coking wastewater treated with this catalyst has chemical COD of 5870 mg/L and TOD of 17500 mg/L, and the removal efficiency reaches 99.9 % and 99.8 %, respectively. (Chen & Shen 2005, 79-80.)

CWAO has high efficiency due to the addition of catalysts, which has a wide range of applications. CWAO technology is very efficient in the treatment of various high concentration organic wastewater, especially suitable for wastewater treatment in petrochemical, pharmaceutical, coking gas, papermaking, synthetic fibers, and other industries, with high toxicity and difficult to treat with conventional methods. However, from a technical and economic point of view, the range of COD is 8000 - 20 0000 mg/L. Processing efficiency is high. More than 95 % of organic matter can be removed by choosing appropriate temperature, pressure, and catalyst. The oxidation speed is fast, the device is small, the occupied area is small (compared with the traditional method), and the reaction time is short. (30 - 60 minutes) CWAO technology can also recover energy. The reaction heat of the system can be used to heat the feed. The higher the inflow concentration, the more heat is recovered. (Jiang, Ai & Min 2004, 326-331.)

CWAO has higher requirements for equipment. High-quality humidified oxidation reactor and heat exchanger will improve the efficiency of this method. With the continuous improvement of environmental protection standards, more priority has been given to the treatment of harmful substances, which has become a hot and difficult point in environmental research. CWAO is a better way to treat this waste. Under the same conditions, this method is more suitable for large enterprises and has broad industrial application prospects. (Tan, Jiang & Yu 1998, 64-67; Gao & Zhang 2006, 8-16.)

5. CONCLUSION

Petrochemical wastewater is a very complex pollutant. The pollutants in petrochemical wastewater are not a single substance, but a mixture of many substances. A single treatment method cannot completely and effectively purify the petrochemical wastewater, which often requires a combination of multiple methods to reach the discharge standard. The cost of petrochemical wastewater treatment is not small for small petrochemical enterprises. Therefore, reasonable distribution of social resources can make petrochemical wastewater more effectively treated.

The damage of petrochemical wastewater to the environment is very significant. People who do not understand the harm of petrochemical wastewater will be hurt when they use the water polluted by petrochemical wastewater. Some refineries may be built close to the city for various reasons, and the discharged wastewater needs to be treated strictly, which requires more advanced technology to make the discharged wastewater meet the discharge standard.

At the same time, people should pay more attention to petrochemical wastewater treatment technology. Water is not only the source of life but also a precious resource. For industrial wastewater with complex pollutants, it should be treated in time to avoid irreversible pollution due to its long-term un-controlled discharge. At the same time, it should be noted that the treatment measures of wastewater are often universal. The MBR method and catalytic oxidation method for petrochemical wastewater treatment can also be used in the treatment of urban sewage. The key is to develop mature, stable, simple operation and low energy consumption new technologies to reduce the impact of wastewater on the environment.

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