Research Progress of Membrane Bioreactor in Organic Industrial Wastewater Treatment

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Abstract. The paper expounds the membrane bioreactor (MBR) working principle, process type and technical characteristics, and reviews the application of membrane bioreactor in the treatment of petrochemical wastewater, petroleum wastewater, pharmaceutical wastewater, printing wastewater in recent years, and summarizes and analyzes the problems in the application of the MBR and the solutions. Finally, the future research on the membrane bioreactor treatment of organic industrial wastewater is prospected.

1. Introduction
Today, with the rapid development of the economy, the industrial economy is also booming, and there are more and more industrial types. Industrial wastewater has become an important factor in environmental hazards. For high-concentration refractory organic industrial wastewater, the traditional treatment process cannot fully meet the emission requirements, and research and development of new treatment technology has become a hot issue. Among them, Membrane Bioreactor (MBR) provides a promising treatment technology for organic industrial wastewater treatment with its high biodegradability and good effluent quality[1]. This paper summarizes the working principle, process characteristics and process types of MBR, summarizes the MBR treatment of chemical wastewater, petroleum wastewater, pharmaceutical wastewater, and analyzes the membrane fouling problems occurring during the treatment process, and carries out the future development trend.

2. Membrane bioreactor

2.1. MBR’s working principle
MBR, also known as Membrane Bio-Reactors, is a new water treatment technology combined with membrane separation unit and biological treatment unit[2]. It is mainly composed of a membrane separation module and a bioreactor. The working principle is to firstly use the activated sludge in the reactor to degrade the biodegradable organic matter in the sewage. At the same time, the ammonia nitrogen in the sewage is converted into nitrate nitrogen by using nitrifying bacteria, and finally, the membrane module is used for efficient solid-liquid separation[3].
2.2. MBR’s process classification
Due to different classification standards, MBR can be mainly divided into the following types:

2.2.1. According to different film materials, it is divided into organic film and inorganic film. Organic film materials include PVDF (polyvinylidene fluoride), PP (polypropylene), polyolefin film, cellulose derivative film, polyester film, polysulfone film, etc., which are cheaper but more susceptible to fouling; The membrane has a ceramic membrane, a porous glass membrane, a metal oxide membrane, etc., has a long service life, and can work in a harsh environment, but the price is relatively expensive. According to the pore size of the membrane, the membrane can be divided into microfiltration, ultrafiltration, nanofiltration and reverse osmosis membranes, among which microfiltration and ultrafiltration membranes are used more[4].

2.2.2. According to the different oxygen demand of the bioreactor, it is divided into aerobic MBR (mainly treating urban wastewater and domestic sewage) and anaerobic MBR (mainly treating high concentration organic wastewater).

2.2.3. According to the type of membrane module, it is divided into tubular, plate, coil and hollow fiber membranes.

2.2.4. According to the different functions of the membrane module in MBR, it is divided into membrane separation MBR (for separation and retention of the same body), aeration type MBR (bubble-free aeration, suitable for wastewater treatment with high oxygen demand), extraction MBR (for the extraction of priority pollutants from industrial wastewater). Among them, membrane separation MBR is the most widely used.

2.2.5. According to the relative position of the membrane module and the bioreactor, it is divided into a split type (also called cross-flow type) MBR and an integrated type (also called submerged type) MBR, of which more than 55% use an integrated MBR.

2.3. MBR process features
Membrane bioreactors have obvious advantages that many other biological treatment processes cannot match. The main features are as follows[1]:

- The device is more compact and has a small footprint. The MBR medium has a high concentration of activated sludge, so the volumetric load is increased and the device is more compact. In addition, the membrane module replaces the traditional secondary sedimentation tank and also reduces the footprint[5].
- The effluent water quality is excellent and stable. It can efficiently perform solid-liquid separation, and the effluent is not affected by factors such as sludge expansion in the bioreactor[6].
- MBR is beneficial to the retention, growth and reproduction of slow-increasing nitrifying bacteria. The system has high nitrification efficiency and high sludge concentration (MLSS).
- The microorganisms are completely trapped in the reactor, and the complete separation of the reactor hydraulic retention time (HRT) and sludge retention time (SRT) is achieved, which makes the operation control more flexible and stable.
- The reactor has high mass transfer efficiency and the oxygen transfer efficiency is as high as 26% ~ 60% [1].
- Easy to maintain management. Compared with the traditional activated sludge method, the sludge concentration in MBR is easy to control, and the influent flow rate and water quality change little[7].

3. Application of MBR in organic industrial wastewater treatment
In recent years, the MBR process technology has been continuously improved and developed, and the
COD and NH$_3$-N of various high-concentration organic wastewaters and refractory wastewaters can achieve good removal effects[2]. It is widely used in the treatment of organic industrial wastewater and some refractory wastewater.

3.1. Treatment of stone chemical wastewater
The wastewater of petrochemical enterprises is characterized by large fluctuations in water volume, frequent fluctuations in water quality, and complex pollutants. It contains a large amount of toxic and hazardous substances such as oil, sulfides and volatile phenols. Direct discharge will cause great harm to the environment[8]. Xiangdong Yan et al.[9] used the membrane bioreactor (MBR) to conduct industrial experiments on the refinery wastewater of Guangzhou Petrochemical. When the influent COD concentration was 275.0~921.0 mg/L, the removal rate of COD Cr was 98%; When the concentration is 8.2~72.1 mg/L, the removal rate of effluent NH$_3$-N can reach over 99%; when the concentration of influent oil is 10.1~87 mg/L, the degradation rate of MBR to oil is as high as 90%, the oil content is less than 5 mg/L, which meets the national first-class emission standards. The process has good effects on COD, ammonia nitrogen, oil and other pollutants, but there is a certain limit on the maximum concentration of influent pollutants. After exceeding the limit value, the growth of microorganism’s changes, resulting in poor treatment. Lihua Lin et al.[10] studied the production of wastewater from petrochemical enterprises in an industrial park in Jiangsu Province. The average removal rates were COD Cr 86.4%, BOD$_5$ 97.6%, NH$_3$-N 99%, TP 68%, petroleum class 86.7%. Liu Fengping et al.[11] used a hydrolysis acidification-membrane bioreactor process to treat sewage in an oilfield in the “Golden Triangle” zone of Beijing-Tianjin-Tangshan. The experimental results show that under the optimal operating conditions, the combined process is cod, volatile phenol and petroleum in oily wastewater. Contaminants such as organic matter, ammonia nitrogen and turbidity have good decontamination effects, and the removal rates are 95.82%, 99.86%, 98.82%, 98.86% and 99.82%, respectively. The effluent quality fully meets the national first-level standard for comprehensive wastewater discharge (GB8978-1996). Yuzhi Li et al.[12] used the immersion membrane bioreactor (MBR) was to treat chemical wastewater with a treatment capacity of 60 m$^3$/h, and the influent COD, NH$_3$-N, and SS concentrations were 533, 182, and 86 mg/L, respectively. After treatment, the effluent COD, NH$_3$-N, and SS were 8.0, 28.5, and 6.0 mg/L, respectively, and the removal rates were 94.6%, 95.6%, and 93%, respectively, and the effluent was clear and stable, and can be reused to circulating cooling water system.

3.2. Treatment of pharmaceutical wastewater
The pharmaceutical wastewater has complex composition, high concentration of pollutants, contains a large amount of toxic, harmful and refractory substances. In addition, it has color and odor, and the suspended matter content is high, which is easy to produce foam. Thanh Tran et al.[13] used MBR and nanofiltration (NF) technology to conduct experimental research on medical wastewater in 175 military hospitals. The three organic loading rates (OLR) were operated at 0.5, 1.5 and 2.5 kgCOD/m$^3$.d. The average COD removal rates were 94%, 93.3%, and 92.7%, respectively. In terms of nitrogen removal, the three-phase efficiencies of the system were 75%, 79%, and 83%, respectively; the log removal values of E. coli and coliforms (LRV) is higher than 4; the average removal rate of color and total iron is 98% and 99%, respectively, and the treated water reaches the Vietnamese Class A standard. Zhou Li et al.[14] transformed a pharmaceutical wastewater plant by using the MBR membrane combined with activated sludge method and the activated sludge method. The removal rate of COD$_{Cr}$ and SS is 96% and 80%, which effectively solves the shortcomings of traditional activated sludge effluent water quality instability, operational difficulties, etc. It makes the effluent water quality reach the recycling standard. Guanglei Qiu et al.[15] adopted the upflow anaerobic sludge bed-membrane bioreactor combined process to treat simulated berberine wastewater, with a hydraulic retention time (HRT) of 24 h, influent $\rho$(COD$_{Cr}$), and $\rho$(NH$_4$+-N), $\rho$(berberine) are 1 717–4 393, 91.8–158.7 and 64.4–276.8 mg/L, the contribution rate of $\rho$(COD$_{Cr}$) in wastewater is 7.5%–25.0% of the conditions, the combination process can achieve $\rho$(COD$_{Cr}$) d), $\rho$(NH$_4$+-N) and $\rho$(berberine)
removal rate of 92.5%–95.9%, 67.0%–98.9% and more than 99%. However, with the increase of MBR influx $\rho$ (berberine), under the microbial toxicity of berberine, the transition of sludge from dispersed to aggregated state in MBR. Zhaopeng Chen et al.[16] used a composite membrane bioreactor (CMBR) to study the effluent of anaerobic reactor of chemical synthesis pharmaceutical wastewater in a pharmaceutical factory. The feasibility of CMBR treatment of chemical synthesis pharmaceutical wastewater was investigated. The experimental results show that when the HRT is 10h and 5h, the influent COD concentration fluctuates between 915.9 mg/L and 1937.5 mg/L. The effluent COD of the composite MBR is 62.5~141.7 mg/L and 76.2~149.7 mg/L, COD removal rates were 88.7%–96% and 85.7%–94.3%, respectively, can meet the requirements of the standard discharge standards (150 mg/L). When the HRT is 3h, the effluent COD concentration is 176.2~ 291.7 mg/L, which cannot meet the requirements of the discharge standard. The optimal HRT for the treatment of chemically synthesized pharmaceutical wastewater by compound MBR should be controlled at 5h. The relationship between sludge mass concentration (MLSS) and COD removal indicates that in order to obtain better COD removal rate, the optimal MLSS of composite MBR should be controlled at about 7000 mg/L.

3.3. Treatment of printing and dyeing industrial wastewater

Printing and dyeing wastewater has complex composition, deep color, strong alkalinity, and contains many toxic and harmful substances, which are seriously polluted by the environment[17]. In the papermaking, printing and dyeing wastewater treatment, Zhejiang University of Technology[18] used MBR to treat papermaking wastewater (mixture of black liquor mid-stage wastewater and white water) and compared with traditional activated sludge method and biological contact oxidation method. The experimental results show that the treatment of papermaking wastewater with MBR increases the sludge concentration and effluent COD Cr can be reduced to less than 100 mg/L (system hydraulic retention time is 18 h), and the total removal rate of the entire reactor can be up to 90%. Lan Ding et al.[19] designed a hypoxia/aerobic MBR treatment device. The 165-day operation test showed that the removal rate of COD in the stationary phase of the system could reach 95.0%, and the average removal rate of ammonia nitrogen could reach 96.5%, the removal rate of reactive brilliant red dye X-3B is between 60% and 73%, and the effluent contains a small amount of color. Yunqing Li[20] treated printing and dyeing wastewater with hollow fiber membrane MBR. The results showed that the change from volumetric load and sludge load had no significant effect on the removal rate from sludge inoculation to acclimation for 21 days. Sludge activity (MLVSS/MLSS) reached a maximum at day 61, and the COD and chromaticity removal rates of the system were both above 90%. Yanxia Sun[21] used the coupling method of manganese sand catalyzed sponge iron internal electrolysis and membrane bioreactor (MBR) to treat the simulated printing and dyeing wastewater, the original printing and dyeing wastewater COD is 700~800 mg/L, BOD$_5$ is 230~250 mg/L, color is 1 000~1 200 times. When it is pretreated by manganese sand catalytic sponge iron internal electrolysis, COD can be reduced to 570~670 mg/L, BOD$_5$ is reduced to 200~320 mg/L, color reduced to 4~150 times. Subsequent biological treatment with MBR, the COD value of effluent can be reduced to 3~31 mg/L, the average COD value is 8 mg/L, and the decolorization rate of MBR biological segment is 66.94%. The removal rate of chromaticity in the whole MBR was 76.29%.

4. Problems and countermeasures in the MBR processing

4.1. Membrane fouling

Membrane fouling refers to the physicochemical action of particles, colloidal particles or solute molecules in the sewage with the membrane during membrane filtration, or because of the concentration polarization causes certain solutes to exceed the solubility and mechanical action on the membrane surface. Adsorption and deposition in the surface and pores of the membrane, resulting in a small pore size or blockage of the membrane, resulting in changes in membrane flux and separation characteristics[22].
4.2. Membrane fouling formation mechanism

There is no unified conclusion on the mechanism of membrane fouling[23]. In the literature, it is agreed that colloidal particles, solute macromolecules, microparticles and membranes in the raw material liquid have different effects (physical, chemical, biochemical or mechanical), which are adsorbed on the surface of the membrane for a long time or deposited in the pores of the membrane, resulting in membrane water production. It is generally believed that membrane fouling is mainly divided into three parts: concentration polarization, membrane surface contamination (formation and compression of the filter cake layer), adsorption and clogging in the pores of the membrane. Concentration polarization will increase the solute concentration on the surface of the membrane, causing the osmotic pressure to increase, thereby reducing the mass transfer dynamics; the deposited layer or gel layer formed on the surface of the membrane will change the separation characteristics of the membrane; severe concentration polarization leads to crystallization, blocking the passage, making the operation worse[24]. Particle material smaller than the pore size of the membrane is adsorbed in the pores of the membrane, and the membrane pores are clogged with different degrees by concentration, crystallization, precipitation and growth or due to concentration polarization, so that some solute exceeds its solubility and mechanical action on the membrane surface. Membrane produced by the flow rate and separation characteristics change, resulting in membrane fouling[25].

4.3. Control measures

Changing the nature of raw water can delay membrane fouling to varying degrees, and researchers at home and abroad have done a lot of research[23]. The raw water is modified by adding a coagulant, activated carbon, pre-oxidation, biological pretreatment, ultrasonic, MIEX and other treatment units in front of the membrane. Operating conditions that affect ultrafiltration membrane fouling are membrane flux, filtration cycle, backwash time, and strength. As the filtration time increases, contaminants in the water gradually form a thicker layer of mud cake on the surface of the membrane, and once the layer of mud cake is compacted, it is difficult to clean. Membrane fouling can be mitigated by adding suspension carriers, shortening the filtration cycle, extending the backwashing time, and increasing the backwashing strength. Ziliang Xiao et al.[26] added a columnar suspension carrier to the integrated MBR. Under the condition of low sludge concentration, the 20% dosage reduced the membrane fouling effect. Under the condition of high sludge concentration, the 20% dosage is good, but the system of 30% dosage is not as stable as the 20% dosage. The suspension carrier is used to reduce the membrane fouling of MBR mud cake. Applicable to high sludge concentration conditions, the treated COD removal rate of wastewater is 95.1%, and the NH$_3$-N removal rate is 97.3%. Jing Zhang et al.[27] took a 10×10$^4$ m$^3$/dMBR process reclaimed water plant in Beijing as an example. Chemical cleaning and off-line cleaning are used. The membrane blowing fan is opened to 4 and 2, and the air volume per unit membrane is increased to 0.25 m$^3$/(m$^2$·h), membrane fouling is controlled in a timely and effective manner. The hydrophilicity of the membrane has a certain effect on membrane fouling. Jonsson et al.[28] studied the effect of different membrane materials on membrane fouling, it is concluded that the hydrophobic membrane is faster than the membrane of the hydrophilic membrane. By comparing the UF and MF films, Lee et al.[29] found that the surface roughness of UF is more likely to cause pollution. At the same time, the smaller the contact angle, the stronger the hydrophilic property of the film. The larger the contact angle, the stronger the hydrophobic property of the film. The study found that finding the optimal cross-flow velocity of the system, as well as the critical flux under this condition, and the low-pressure constant-current operation, controlling the reasonable aeration amount, intermittent suction time, maintaining a suitable reaction temperature, can reduce the membrane resistance. Improve membrane permeability, slow membrane fouling and extend membrane life. In addition, the latest research uses quorum induction quenching technology to inhibit biofilm formation with good application prospects[30]. Kappachery et al.[31] applied vanillin as a quenching (QQ, quenching quenching) quencher in the reactor, which successfully inhibited the growth of biofilm on the reverse osmosis membrane (inhibition rate of 97%), thus demonstrating that vanillin can be the natural QQ quenching compound that effectively reduces
membrane fouling in membrane filtration systems. Xu et al. [32] investigated the effects of D-tyrosine on bacterial QS system and biofilm formation. It was found that D-tyrosine significantly reduced the production of bacterial signaling molecules (AI-2), promoted biofilm exfoliation and reduced membrane fouling.

5. Conclusions
This paper mainly introduces the working principle, type and characteristics of membrane bioreactor, its application in organic industrial wastewater such as petrochemical, pharmaceutical and printing and dyeing, and further discusses membrane fouling, control measures and research prospects. In recent years, membrane bioreactors have been developed rapidly in the treatment of organic industrial wastewater. Many domestic and foreign scholars have developed a combination of MBR technology for advanced treatment and initial effects. However, membrane bioreactors have limitations in the field of high-concentration organic industrial wastewater treatment. Therefore, the future should focus on the following aspects:

- Research and development of low-cost, high mechanical strength, pollution-resistant new membrane materials.
- A targeted new MBR process is used for industrial wastewater of different types and different processing requirements.
- Strengthen the research on membrane fouling mechanism and solutions.
- Optimize the pretreatment technology of industrial wastewater to achieve the highest quality of effluent water.

References
[1] Xu, B.H., Zhu, G.S., Huang, C. (2016) Research progress in the treatment of light industrial wastewater by membrane bioreactor. J. Anhui Chemical Industry, 42: 12-17.
[2] Li, S., Zhou, X.C., Zhang, J.H., et al. (2013) Progress in the application of membrane reactor (MBR) in industrial wastewater treatment. J. Contemporary Chemical Industry, 42: 1465-1468.
[3] Chu, X.J. (2015) Application status and development prospects of MBR in water treatment in China. J. Science and Technology Forum, 30: 20-21.
[4] Li, X.B. (2014) Research and application of MBR process in wastewater treatment. J. Guangdong Chemical Industry, 41: 168-170.
[5] Pierre, I.C. (2010) Membrane bioreactors and their uses in wastewater treatments. J. Applied Microbiology and Biotechnology, 88: 1253-1260.
[6] Zakir, M.H., James, F.D., Samer, S. A., et al. (2010) Peak flux performance and microbial removal by selected membrane bioreactor systems. J. Water research, 44: 2431-2440.
[7] Cui, Z.G., Wang, X.L., Shan, B.T. (2005) Research and application of membrane bioreactor in industrial wastewater treatment. J. Water Treatment Technology, 31: 7-10.
[8] Yin, Y.Q., Deng, X.Y., Liu, R.H., et al. (2006) Research progress in petrochemical wastewater treatment technology. J. Environmental Pollution and Control, 28: 356-360.
[9] Zhai, W.B., Qi, X.D., Li, L., et al. (2005) Membrane bioreactor (MBR) treatment of refinery wastewater. J. Water Treatment Technology, 31: 79-81.
[10] Lin, L.H. (2015) Application of MBR in advanced treatment of petrochemical industry wastewater. J. Journal of Xihamen University of Technology, 23: 105-110.
[11] Liu, F.P. (2012) Feasibility study on the treatment of oily wastewater by hydrolysis acidification membrane bioreactor process. North China Electric Power University, Beijing.
[12] Li, Y.Z., Yang, Q.H. (2008) Treatment of high concentration chemical wastewater by MBR process. J. Industrial Water Treatment, 28: 89-91.
[13] Thanh, T., Thanh, B.N., Huu, L.H. (2019) Integration of Membrane Bioreactor and Nanofiltration for the Treatment Process of Real Hospital Wastewater in Ho Chi Minh City, Vietnam. J. Processes, 123: 1-14.
[14] Zhou, L., Yan, H.L. (2017) Application of MBR membrane in pharmaceutical wastewater treatment. J. Engineering Equipment and Materials, 3: 104-105.
[15] Qiu, G.L., Song, Y.H., Zeng, P., et al. (2010) Simulation of berberine wastewater by UASB-MBR combined process. J. Environmental Science Research, 23: 942-947.
[16] Chen, Z.P., Li, Z., Chen, Z.B., et al. (2008) Study on compound MBR treatment of chemical synthesis wastewater. J. Journal of Harbin University of Commerce, 24: 678-694.
[17] Li, S., Zhou, X.C., Zhang, J.H., et al. (2013) Progress in the application of membrane reactor (MBR) in industrial wastewater treatment. J. Contemporary Chemical Industry, 42: 1465-1467.
[18] Han, H.F., Jin, M.Z. (2001) Membrane Bioreactor Technology for Treatment of Papermaking Water. J. Water Treatment Technology, 27: 96-98.
[19] Ding, W., Xie, Y.H., Zhong, S.J., et al. (2013) Membrane bioreactor treatment of simulated printing and dyeing wastewater. J. Environmental Protection Science, 39: 6-10.
[20] Li, Y.Q. (2010) Development of a new hollow fiber membrane and its application in the treatment of printing and dyeing wastewater. Donghua University, Shanghai.
[21] Sun, Y.X. (2009) Study on the treatment of printing and dyeing wastewater by manganese sand catalyz-ed sponge iron internal electrolysis and membrane bioreactor. Ocean University of China, Shandong.
[22] Xie, J. (2018) Mechanism of activated sludge properties on MBR membrane fouling and research progress of membrane cleaning agent. J. Guangdong Chemical Industry, 45: 113-114.
[23] Li, M., Wei, W., Li, X.F. (2017) Discussion on the pollution mechanism and prevention measures of ultrafiltration membrane. J. Resource Conservation and Environmental Protection, 4: 30-31.
[24] Li, Y.S. (2006) Membrane pollution factor identification and gel layer structure analysis. Dalian University of Technology, Liaoning.
[25] Li, L., Wang, Z.Q., Chen, W.Q. (2012) Progress in the formation mechanism of MBR membrane fouling and control membrane fouling. J. Anhui Agricultural Sciences, 40: 284-286.
[26] Xiao, Y.L., Li, Y.F., Song, W. (2018) Effects of Suspension Carriers on Membrane Fouling of MBR mud cakes. J. Environmental Science and Management, 43: 100-104.
[27] Zhang, J., Zhang, Z.Y. (2019) Optimization of MBR process operation and membrane pollution control. J. China Water Supply and Drainage, 35: 117-122.
[28] Jonsson, C., Jonsson, A.S. (1995) Influence of the membrane material on the adsorptive fouling of ultrafiltration membranes. J. Journal of Membrane Science, 108: 79-87.
[29] Lee, N., Gary, A., Croué, J.P., et al. (2004) Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). J. Water Research, 38: 4511-4523.
[30] Ni, L.F., Wang, Y.Y. (Journal of Harbin Institute of Technology), (2019). Research progress of MBR membrane pollution control technology based on quorum sensing annihilation theory. http://kns.chki.net/KCMS/detail/23.1235.T.20190306.1703.002.html
[31] Sajeesh, K., Diby, P., Jeyong, Y., et al. (2010) Vanillin a potential agent to prevent biofouling of reverse osmosis membrane. J. Biofouling, 26: 667-672.
[32] Xu, H.J., Liu, Y. (2011) Reduced microbial attachment by D-amino acid-inhibited AI-2 and EPS production. J. Water Research, 45: 5796-5804.