Research Status of Enhanced Process of Nitrogen and Phosphorus Removal by Membrane Bioreactor

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Abstract. In view of the increasingly stringent sewage discharge standards, it is necessary to improve the nitrogen and phosphorus removal and the removal of refractory organic compounds in the sewage treatment process. Membrane bioreactor (MBR) as a wastewater treatment technology combined membrane bioreactor and biotechnology has a lower solid suspended solids concentration (SS) in effluent, but it is very difficult to remove nitrogen and phosphorus to meet the national emission standards. Therefore MBR intensified combination technology of nitrogen and phosphorus removal has become the main direction of our study and apply the technology to the actual sewage treatment plant. Based on the analysis of the existing MBR intensified combination technology of the removal of nitrogen and phosphorus, the principles, characteristics and treatment effects of various membrane intensified combinations technologies of the removal of nitrogen and phosphorus were introduced. It is believed that membrane fouling control, energy saving and consumption reduction are still the focus of future research through analysis.

1. Introduction
Nowadays, with the rapid economic development in our country, the discharge of industrial wastewater and urban domestic sewage is rapidly increasing. With the widespread application of fertilizers, pesticides and detergents, the nitrogen and phosphorus contents in wastewater increase significantly, and excessive nitrogen and phosphorus emissions will lead to water eutrophication, algae breeding, water quality deterioration [1]. At the same time, the problem of lack of water resources is becoming more and more prominent, and wastewater reuse is considered as an effective solution. Therefore, the research and development of economic and efficient nitrogen and phosphorus removal process has become the focus of urban sewage treatment and sewage treatment plant transformation. Membrane bioreactor (MBR) technology is a process technology that organically combines biological treatment with efficient membrane separation. Compared with the traditional biological treatment technology, MBR technology has the advantages of good effluent quality, direct effluent reuse and small equipment footprint, easy to control, high concentration of activated sludge and the remaining low yield of activated sludge [2]. MBR denitrification and dephosphorization process can be divided into a single form of MBR process and a combination of two forms of MBR process. Single-form MBR process is difficult to meet the increasingly stringent requirements of nitrogen and phosphorus
emissions. Therefore, the combined form of MBR technology is currently more common, with good prospects for development and expansion of space [3].

2. The advantage analysis of combined technology of MBR enhanced nitrogen and phosphorus removal

Almost all of the traditional nitrogen and phosphorus removal processes are combined with the MBR process, such as single-stage A/O process [4], two-stage A/O process [5], sequencing batch activated sludge process [6], A2/O process [7], intermittent activated sludge process [8] and so on. Some of the features of MBR process can strengthen the traditional biological nitrogen and phosphorus removal process. First of all, the complete interception of microorganisms by the membrane can increase the total amount of nitrifying bacteria and polyphosphate-accumulating bacteria, thereby enhancing the nitrification, denitrification and phosphorus removal ability of the system. Secondly, the gel layer on the membrane surface has a certain interception effect on colloidal phosphorus. MBR can reduce the sludge discharge and increase the phosphorus content of the remaining sludge in the premise of ensuring the effect of phosphorus accumulation. In addition, the MBR process reduces the risk of sludge denudation caused by the expansion of the nitrogen and phosphorus removal system.

MBR can not only be combined with the traditional biological nitrogen and phosphorus removal process, but also can be combined with physicochemical methods to optimize the effect of nitrogen and phosphorus removal, such as adding filler [9], carrier [10] and flocculant [11]. Compared with the MBR process alone, through physicochemical action not only can improve the efficiency of nitrogen and phosphorus removal, but also reduce membrane fouling and extend membrane life [12].

3. Combination of MBR and biological nitrogen and phosphorus removal process

3.1. Single stage A/O combined MBR nitrogen and phosphorus removal process

More than 98% of MBR applications are aerobic MBR, of which more than 55% are monolithic MBR [13]. The single-stage A/O combined MBR nitrogen and phosphorus removal process immerses the membrane module in a bioreactor to form a one-piece unit without the reflux of the mixed liquid, which reduces the equipment requirement and reduces the running cost. By limiting the operation of aeration and semi-limiting aeration, the single-stage A/O combined MBR nitrogen and phosphorus removal process achieves the combination of anoxic/aerobic time series and the appropriate time of each stage, good effect of nitrogen and phosphorus removal.

Yeom used intermittent aeration submerged MBR treatment of domestic sewage, COD removal efficiency of 96%, SS removal efficiency of 100%, TN removal efficiency of 83% [4]. It was found that the nitrification reaction proceeded very fast and completely. Denitrification was the rate limiting step. The denitrification rate ranged from 0.6 to 1.8 mg/ (g·h) and the rate of endogenous denitrification was 0.56 mg/ (g·h). Adjusting the cycle hypoxia/aerobic cycle time to study the effect of nutrient removal found that while maintaining high concentrations of MLSS can enhance nutrient removal, the length of the hypoxia period may be the key factor.

3.2. Sequencing batch membrane bioreactor

Sequencing Batch Reactor (SBR) treatment process utilizes time-advanced flow instead of spatially-pushing flow. Influent, anaerobic, aerobic, and sedimentation occur in one tank. SBR can not only provide the conditions for the biological nitrogen and phosphorus removal, but also adjust the operation mode to meet the different types of sewage treatment requirements, and it is easy to control automatically. Combining the SBR process with the MBR process helps both the membrane module itself and the SBR process. Due to the entrapment and filtration of the membrane module, the microorganisms in the reactor can be maximally increased, which is beneficial to the growth and reproduction of nitrifying bacteria with a long generation time. Therefore, the sludge has high biological activity and strong ability of adsorbing and degrading organic matter, but also has good nitrification ability. In addition, the operating mode of SBR provides the conditions for the growth of
polyphosphate bacteria, and at the same time, it can meet the needs of denitrification, making it possible to efficiently and simultaneously remove nitrogen, phosphorus and organic compounds in a single reactor.

Zhang studied the membrane bioreactor enhanced sequencing batch reactor nitrogen and phosphorus removal [6]. During the experiment, the influent C/N value was gradually decreased, the total nitrogen load was increased, and the nitrogen and phosphorus removal effect and membrane fouling status of the sequencing batch membrane bioreactor and the traditional membrane bioreactor were compared. The results showed that the traditional membrane bioreactor could not denitrification when the influent C/N decreased to 3.8 ~ 8.3 and the total nitrogen load increased to 0.22 kg·m\(^{-3}\)·d\(^{-1}\). But membrane bioreactor can make ammonia nitrogen and TN removal rates maintained at 93.1% and 67.6% by changing the cycle or improving the exchange ratio. Sequencing batch reactor mode of operation can also reduce membrane pollution.

### 3.3. A\(^2\)/O-MBR process

A\(^2\)/O process consists of anaerobic tank, anoxic tank and aerobic tank, which can achieve simultaneous nitrogen and phosphorus removal. The A\(^2\)/O-MBR process with simultaneous denitrification and dephosphorization, which is a combination of A\(^2\)/O process and membrane bioreactor, can prolong the production of MLSS concentration and improve the process of nitrogen and descaling.

Cao used A\(^2\)/O-MBR process to treat domestic sewage. The result showed that the average effluent \(\text{NH}_4^+\)-N was 0.68 mg/L and the removal rate was 98.6%, the average TN was 14.3 mg/L and the removal rate was 74.4% [7]. In the case of no sludge, the removal of TP was poor. When the biomass in the reactor reached the expected requirement and began to discharge excess sludge by SRT for 30 days, the removal rate of TP gradually increased. The average concentration of TP in steady operation was 0.98mg/L, and its average removal rate was 88.4%.

![Figure 1. Flow chart of A\(^2\)/O - MBR process](image)

### 3.4. Intermittent circulating activated sludge-MBR process

Conventional Activated Sludge Process (CASP) can be combined with MBR process by intermittent cycle to enhance its nitrogen and phosphorus removal performance. After the transformation of the process known as batch-type activated sludge cycle of a membrane bioreactor that is ICAS-MBR process. The principle of the method is to intermittently circulate the activated sludge mixture liquid between the stirring chamber and the aeration chamber so that the stirring chamber and the aeration chamber in time and space produce an oxygen-deficient, anaerobic and aerobic environment for denitrification, phosphorus release, excessive phosphorus absorption and other processes.

Zhao proposed a new batch activated carbon monolithic membrane bioreactor (ICAS-MBR) process, and applied it to transform the traditional activated sludge process to enhance nitrogen and phosphorus removal and make effluent reuse [8]. The removal efficiency of pollutants in domestic sewage by ICAS-MBR process was investigated. During the 6 months, the average removal rates of COD, TN, TP and \(\text{NH}_4^+\)-N were 93%, 70.6%, 86% and 96%, water turbidity <1 NTU, the total number of bacteria <100 CFU/mL, and it had good impact load capacity.
4. Combination of MBR and physicochemical nitrogen and phosphorus removal process

4.1. Filler-MBR combination process
Membrane fouling is a major obstacle to the widespread use of MBR. The use of aeration to form shear flow on the membrane surface is an important method to slow down the deposition of sludge flocs on the membrane surface and thus mitigate the membrane fouling. However, it consumes large amounts of power and easily leads to excess dissolved oxygen [14]. By adding fillers to MBR, the effect of padding on the membrane surface and collision can be effectively reduced and the suspended sludge concentration can be effectively reduced while keeping the effluent water quality. This can effectively reduce the deposition of sludge particles on the membrane surface and reduce membrane fouling [15]. Studies have shown that added fillers MBR can significantly improve the efficiency of nitrogen and phosphorus removal.

Cheng added polyethylene suspended filler in the membrane bioreactor and compared with no filler and filler membrane bioreactor on the removal of pollutants in the sewage. The results showed that the average removal rate of ammonia nitrogen increased from 75.85% to 97.45% after adding suspended filler and the removal efficiency was stable. The average removal rates of TN and TP increased from 45.5% and 47.2% to 57.4% and 71.8% respectively.

4.2. PAC-MBR combination process
Compared with the traditional activated sludge method, the sludge in the MBR is relatively loose, which is not conducive to the treatment of excess sludge and denitrification.

Luo added powdered activated carbon to intermittently aerated MBR for treatment of simulated domestic sewage. The comparison found that in the MBR system after adding PAC, the sludge floc size increased, an oxygen-deficient area can be formed inside the flocs, which was more conducive to the occurrence of denitrification process, can achieve better effluent quality and can be fundamentally reduce membrane resistance. The average removal rate of total nitrogen in effluent was above 96% and the highest was up to 98%, total effluent nitrogen was around 0.5mg/L. Li adopted a composite membrane bioreactor with powdered activated carbon as carrier to treat domestic sewage [16]. Without man-made sludge discharge or any treatment of the membrane, it continuously operated for 100 days. The results showed that the system was stable and the water quality was excellent. The addition of PAC increased the nitrification rate of the system and reduced the operating costs.

4.3. Flocculant-MBR combination process
Membrane fouling is an important factor hindering the development of MBR technology [17], especially the membrane module performance factors. Membrane fouling results in the deficient phosphorus removal effect of many MBR processes, and it is difficult to achieve standards only with biological phosphorus removal. In the MBR process, the flocculating agent is often added to increase the removal efficiency of phosphorus by co-precipitation mode [18]. After adding aluminum salt or iron salt in the MBR, the phosphorus in the reactor reacts with the aluminum salt or the iron salt to form a hardly soluble metal phosphate precipitate, which can not only improve the removal efficiency but also reduce the membrane fouling.

Zou intermittly added aluminum salt in the MBR process, the total phosphorus removal rate is up to 83.6% while ensuring the nitrogen removal rate. If continuously added iron salt, the total phosphorus removal rate could reach up to 89.7%. When n (A13+): n (TP) was 1.5 and TP was 4.3 ~ 5.3 mg/L, the effluent TP could be reduced to 0.5 mg/L, reaching TP <0.5 mg/L of the emission standards. Chi used aluminum salts to carry out chemical phosphorus removal in MBR. The results showed that the use of aluminum salts in chemical phosphorus removal was not easy to cause membrane fouling. When n (A13+): n (TP) was 1.5 to 2.0, the effect was better, the removal rate up to 82.1%, so that the effluent TP <0.5 mg/L. Song discusses the removal performance of pollutants by adding flocculants [19]. Results showed that the appropriate amount of flocculant dosing could effectively improve the sludge characteristics, and the removal rate of phosphorus increased from 60%
to 85% while reducing the attenuation of membrane flux. Results indicated that dosing flocculant was an effective means of prevention and control of membrane pollution.

5. Conclusion
Due to the unique technical advantages of MBR, the combination of MBR enhanced denitrification and dephosphorization technology has shown advantages and potential advantages over traditional denitrification and dephosphorization processes. It has gradually become a trend of development and provided technical support for the standardization of sewage treatment plants. Although the MBR process is relatively mature, membrane fouling affects the MBR operating flux and membrane service life, which is always the main challenge for the application of MBR technology in the field of wastewater treatment. In improving the efficiency of nitrogen and phosphorus removal should also pay attention to reducing operating costs. Therefore, studying the effective control method of membrane fouling is an important research topic to ensure the long-term stable operation of MBR process. For example, optimizing selection of membrane modules and operating conditions, studying control techniques for the filtration performance of mixed liquid membranes, improving the biochemical characteristics of sludge mixtures, determining membrane cleaning methods, developing membrane modules with anti-pollution capability and low cost, etc.

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