Current Situation and Problems of MBR Treatment Process in Dye Wastewater

Qin Li¹, Kun Dong¹, Yue Tu¹, Lei Jiang¹, Xiangmin Li¹, Haixinag Li¹

¹College of Environmental Science and Engineering, Guilin University of Technology, Guilin, Guangxi Province, 541006, China

Abstract. In most areas in China, the poor quality of printing and dyeing wastewater discharged from dyeing, papermaking and silk factories have caused a series of environment pollution and health problems. So the optimization of the dyeing wastewater effluent process has become imminent. MBR is a new type of wastewater treatment technology in recent years, MBR can efficiently treat printing and dyeing wastewater. The paper introduces several basic types of MBR treatment process in terms of the working principle, advantages and current situation of treatment in the dye wastewater applications, including AO-MBR Process, Coagulation Sedimentation-Micro electrolysis-MBR Process, MBR-RO Process, MBR Gravity Drain Process, Submerged Membrane Bioreactor (SMBR) Process and Direct Contact Membrane Distillation Process. Through analysis and summary, the MBR treatment process in dye wastewater should focus on solving the problem of removal of the final product. The effective combination of MBR technology and other chemical and physical treatment processes can provide important guiding significance for the future dye wastewater from the end treatment to the control of source pollution.

1. introduction
With the rapid development of China’s economic level, the discharge of wastewater from the printing and dyeing industry is increasing. The annual dye production in China is as high as 1.5×10⁵ t, of which about 10%–20% is directly discharged into the water body by the printing and dyeing plant without treatment, causing water pollution[1]. Due to the different raw materials used in the printing and dyeing industry, the processes used to process cotton, hemp, chemical fiber and its blended products, silk, etc. Make the difference in the types and concentrations of pollutants different. Moreover, printing and dyeing wastewater is highly polluting. Some developed countries have more restrictions on it. Since the cheap labor force in Asia, it has become a concentrated place in the printing and dyeing industry[3], and the complexity and tenacity of dyes make a single treatment method is not enough to remove dyes in industrial wastewater[4]. As a new type of high-efficiency treatment process, MBR (membrane bioreactor) process can retain organic matter and macromolecular substances, and has a good development prospect[5]. The combination of dye wastewater and MBR treatment process can treat the pollutants in the wastewater through the characteristics of the biofilm, so that the effluent of the printing and dyeing wastewater can reach the standard[6]. Printing and dyeing wastewater can be used as an industrial and municipal water reuse process through advanced treatment processes[7]. Today, most areas of China do not have strict control over the discharge of printing and dyeing wastewater, and a series of pollution problems and environmental problems brought about by the direct discharge of printing and dyeing wastewater are worrying. In October 2017, General Secretary Xi’s research in Zhejiang Province, China’s printing and dyeing textile province, once again proposed that “lucid waters and lush mountains are better than invaluable assets”, it is necessary to focus on rectifying illegal wastewater discharge in
industries such as printing and dyeing, and establish an environmental supervision mechanism\cite{8}.

2. **Type of MBR treatment process in dye wastewater**

2.1 **A/O-MBR process**

Process flow (Figure 1), That is, the printing and dyeing wastewater first intercepts some macromolecules and hairs through the action of the grid to ensure the normal operation of the subsequent system. The sewage is pumped into the anoxic tank through the peristaltic pump, and then enters the aerobic tank from the upper end of the anoxic tank. The aerobic tank and the membrane tank adopt a joint construction method, and the filler in the anoxic tank can increase the removal of total nitrogen, and the There is a submerged agitator in the tank to make the sludge in the reactor mix and stir. At the same time, a diffuser is provided at the bottom of the reactor to provide ventilation to ensure uniform distribution of oxygen concentration in the mixture and reduce the degree of membrane fouling\cite{9}. At the same time, due to the excess of phosphorus and the lack of carbon source, the steps of adding carbon source and polyaluminum chloride (PAC) were added to achieve the purpose of nitrogen and phosphorus removal\cite{10}. Moreover, in order to ensure that the dye wastewater has sufficient residence time in the membrane pool to achieve a higher removal rate, the water discharge index is strictly controlled in accordance with the requirements of the 《Textile Dyeing and Finishing Industry Water Pollutant Emission Standard》 (GB4287-2012).

![Figure 1. Flow chart of MBR integrated equipment.](image)

The A/O-MBR process is not complicated, and the MBR can withstand a certain amount of load and is resistant to organic matter and ammonia-nitrogen shock loads. The removal rate of NH3-N is close to 95%, the removal rate of COD fluctuates greatly, but the highest can reach 80%, the removal rate of TN is about 80%, and the removal rate of TP can only reach 59%, so it is needed. Adding PVC medicine for dosing and removing phosphorus can reach 90% after adding medicine\cite{11}. This process has been promoted in China, but as the A/O-MBR process is used more and more in practical applications, its problems are more and more significant. For example, the process has a large fluctuation in the removal rate of COD and TN. The reason is mainly that the raw water quality has a great influence on the removal of pollutants. Moreover, membrane fouling on MBR is also a problem that cannot be ignored\cite{12}. Adding medicine and removing phosphorus will speed up the film pollution, and will cause secondary pollution to the treated water. In addition, the raw water contains a large amount of waste residue, which affects the residence time and makes the water discharge effect bad. Hong Junming\cite{13} et al used A/O-MBR to remove COD from different reactive dye wastewaters, which can achieve a removal rate of 90% and a certain removal of chromaticity.

2.2 **Coagulation-micro electrolysis-MBR process**

The coagulation-micro electrolysis-MBR process mainly includes several parts such as a coagulation sedimentation tank, a pH adjustment tank, a micro electrolysis tower, a middle sedimentation tank, a hydrolysis acidification tank and an MBR reactor. The process flow chart is shown in figure 2. First, the printing and dyeing wastewater enters the first coagulation sedimentation tank, and the coagulant Poly Aluminum Chloride (PAC) and Polyacrylamide (PAM) are added for coagulation and sedimentation, which is generated in the reactor. After a certain amount of flocculent substance, it was allowed to stand.
for 2h, until it was fully precipitated and reflected completely, the upper and lower liquids were separated, and the supernatant liquid entered the pH pool for acid-base regulation.

In the pH tank, it is controlled by adding sulfuric acid to about 4-5, and the adjusted pH enters the third electrolysis tower of the reaction device. The micro-electrolysis tower contains Fe, C mixed filler, and the tower is an inverted triangular structure. Under aeration, it is fully reacted. The water and lime substances entering the secondary settling tank form Fe$^{3+}$ and Fe$^{2+}$ precipitates, and the flocculation effect is strong. Then the effluent enters the hydrolysis acidification tank, and under acidic conditions, the macromolecular substance is decomposed, and finally the wastewater enters the MBR reactor and reacts on the surface of the membrane, so that the effluent can be used for the reuse of the water[14].

![Figure 2. Micro-electrolysis coupled with MBR process for treatment of dyeing wastewater.](image)

The COD removal rate of this process can reach 96%[15], while the removal rate of NH3-N is 93.3%, and the chromaticity is almost undetectable in the effluent. After treatment, the water quality can meet the requirements of the 《Sewage Integrated Emission Standard》 GB8978-1996 standard. However, this process also has its own problems. After the addition of sulfuric acid in the pH adjustment tank, the residual sulfuric acid is difficult to remove and the flocculation of Fe$^{3+}$ in the intermediate sedimentation tank is difficult to control the dosage, which is a place to be noted in the future.

2.3 MBR reverse osmosis process

MBR reverse osmosis process Also known as MBR-RO process. The characteristic of this process is that due to the fact that the COD of the printing and dyeing wastewater is not very high, and the NH3-N content is low, it can be deeply treated by the MBR process, and the reverse osmosis process is added after the MBR process, in order to stabilize the water quality of the effluent. The water quality of the recycled water meets the requirements of the enterprise and the factory. The flow chart of the process is shown in figure 3.

![Figure 3. MBR-RO process flow chart.](image)

The process MBR membrane module adopts a polyvinyl chloride hollow fiber membrane, the raw water is pumped into the pretreatment tank for catalytic oxidation, and then enters the MBR to react on the surface of the membrane, and the reaction water enters the clear water pool to adjust the water quality and quantity. Then the water in the clear water pool is pumped into the reverse osmosis process by the peristaltic pump, and after reverse osmosis treatment, the reverse osmosis water can be directly used back and forth[16]. The parameters of each part of the process are: membrane bioreactor volume 80 liters,
pre-oxidation tank volume 40 liters, water intake 25 liters / hour, clear water tank volume 40 liters, the raw water quality and return water indicators of the reaction as shown in Table 1 Show:

| item                  | COD (mg/L) | Conductivity (μ S/cm) | pH | Chroma / multiple | NH3-N (mg/L) |
|-----------------------|------------|-----------------------|----|-------------------|---------------|
| Raw water quality     | 105~120    | 4000~5000             | 6~9| 50                | 0.7~0.9       |
| water quality         | ≤10        | ≤20                   | 6~9| ≤5                | ≤1            |

After the MBR effluent water quality is stabilized, reverse osmosis treatment means that the effluent of the reactor passes through the reverse osmosis membrane by using the difference between the internal and external pressure difference of the biofilm, so that the water is discharged after the standard is reached, and the conductivity of the effluent is 15-20μS/cm, pH is 6.5-7.5, the chromaticity is 0-5 times, and the NH3-N content is 0.3-0.5mg/L, which has reached the national textile dyeing and finishing industry water pollution discharge standard[17].

For the advanced treatment process of MBR-RO, Xing Wei[18] et al found that the MBR-RO process can remove most of the COD, NH3-N and chromaticity, but does not contribute to the removal of hardness and salinity, and in actual operation. There is also a need to pay attention to the problem of membrane fouling to extend the life of the reactor. Xiao[19] and others also found that if the reverse osmosis membrane RO is not chemically cleaned, the RO membrane will rapidly accumulate membrane fouling in a short time. At the same time, Wu et al[20] also confirmed that in the MBR-RO process, improving the operation of MBR is the key to slowing the membrane fouling of RO.

3. Analysis and discussion
As mentioned above, the common feature of the A/O-MBR process, the coagulation-micro electrolysis-MBR process, and the MBR-RO process is that it can remove certain NH3-N and COD. The removal of various substances by AO-MBR process, coagulation-micro electrolysis-MBR process and MBR-RO process is shown in Table 2.

| item                                | COD (mg/L) | NH3-N (mg/L) | TN | TP     | Chroma/ multiple |
|-------------------------------------|------------|--------------|----|--------|------------------|
| A/O-MBR                             | 80%        | 95%          | 80%| 90%    | -                |
| coagulation-micro electrolysis-MBR  | 96%        | 93.3%        | 50%~60% | 50%~60% | 99.1%            |
| MBR-RO                              | 95.2%~95.8%| 80%          | -  | -      | ≥90%             |

From Table 2, we can find that the removal rate of COD by A/O-MBR is lower than that of the other two methods in the process of treating printing and dyeing wastewater, but the removal rate of ammonia nitrogen is high, and the removal rate of TN and TP is also Better, while coagulation-micro electrolysis-MBR and MBR-RO can remove most of COD, ammonia nitrogen and chromaticity. The three methods for treating printing and dyeing wastewater have their own advantages and disadvantages. The advantage of A/O-MBR is that it can be compared. Achieve stable ammonia nitrogen removal in a fast time[21], and the operating cost is low, easy to operate[22], the disadvantage is that A / O-MBR will form a thick cake layer, leading to serious fouling behavior[23]. The advantage of the coagulation-micro electrolysis-MBR process is that it can effectively degrade ammonia nitrogen, color and COD content. The disadvantage is that the removal rate of TN and TP is not high. The advantages of the MBR-RO process are small footprint, simple operation, and considerable economic benefits, and can be promoted in the treatment of printing and dyeing wastewater[24]. The disadvantage is that the MBR and reverse osmosis processes are reused in printing and dyeing wastewater. The operating costs are too high and it is necessary to allocate the costs of each part[25].

In addition, membrane fouling is always at the core, whether it is A/O-MBR process, coagulation-micro electrolysis-MBR process, MBR-RO process. However, in the above three processes, there is a
widespread contamination of the membrane due to poor management. The main reasons and improvement measures are as follows: (1) There are many characteristic pollutants in printing and dyeing wastewater, which can solve the problem of printing and dyeing wastewater by membrane distillation, and further improve the surface properties and modification of the membrane, which can reduce the printing and dyeing wastewater: Membrane fouling caused by surfactants and other contaminants; (2) In the MBR-RO process, the membrane fouling of the RO membrane is caused by the desalination process of printing wastewater containing high COD, so it can be set before entering the joint process. The pre-process removes part of the COD. Therefore, we need to improve the efficiency of the process by controlling membrane fouling.

4. Conclusion

① Due to the current severe transformation of dyeing wastewater standard, dyeing wastewater pollution concentration is high. The selection of MBR process in printing and dyeing factory needs to be adapted to local conditions. According to the actual situation, the most suitable type can be selected to maximize the role of MBR in the printing and dyeing wastewater process.

② Printing and dyeing wastewater treatment is a long-term process. We should use different quality of wastewater according to the MBR process of printing and dyeing wastewater, and reuse different degrees of wastewater in different process steps to achieve the best technical goal.

③ In the application of MBR process in printing and dyeing wastewater, the biggest problem at present is the membrane fouling problem in the process operation. In operation, the biofilm will be polluted to different degrees. Therefore, when the MBR process is used as the treatment process of printing and dyeing wastewater, Membrane flux can be restored by optimizing membrane module and membrane material modification, periodic membrane cleaning, and optimized operating conditions to improve the efficiency of MBR process in printing and dyeing wastewater.

References

[1] Zhang, Z. L. (2017) Status and development of dye wastewater treatment technology. J. Sci. Commun., 43(3): 205.
[2] Gao, Q. G. (2016) Characteristics of Wastewater Pollution in Typical Printing and Dyeing Industry and Application of Treatment Process. J. Sci. Commun., 17: 134-136.
[3] Wang, T. N., Zu, G., Yang, L. (2015) Research progress on printing and dyeing wastewater at home and abroad. J. Sci. Commun., 04: 28-31.
[4] Su, C. X., Low, L. W., Teng, T. T. (2016) Combination and hybridisation of treatments in dye wastewater treatment: A review. J. Sci. Commun., 4(3): 3618-3631.
[5] Gao, H. P. (2017) Comparative Study on MBR Process and Its Application in Reclaimed Water Reuse. J. Sci. Commun., 12: 45.
[6] Zhang, Y. H. (2017) Application of MBR membrane in the treatment of printing and dyeing wastewater. J. Sci. Commun., 03: 23-24.
[7] Li, Y. X., Nan, G. Y, Dai, X. M. (2016) Research Status and Development Trend of Advanced Technology of Printing and Dyeing Wastewater in China. J. Sci. Commun., 02: 69-72.
[8] Wang, J. N., Su, J. Q., Wan, J. (2017) The Theoretical Connotation of “The green is property” and Its Innovation of Implementation Mechanism. J. Sci. Commun., 11: 13-17.
[9] Xia, S., Jia, R., Feng, F. (2012) Effect of solids retention time on antibiotics removal performance and microbial communities in an A/O-MBR process. J. Sci. Commun., 106: 36-43.
[10] Zhang, Y. W., Peng, X. F., Wang, B. (2018) AO+MBR integrated equipment for commissioning operation of wastewater containing printing and dyeing wastewater. J. Sci. Commun., 04: 114-118.
[11] Feng, M. L. (2014) Study on A/O-MBR Process for Printing and Dyeing Wastewater. J. Sci. Commun., 07: 34-35.
[12] Niu, Z., Zhang, Z., Liu, S. (2016) Discrepant membrane fouling of partial nitrification and
anammox membrane bioreactor operated at the same nitrogen loading rate. J. Sci. Commun., 214: 729-736.

[13] Hong, J. M., Hong, H. S., Xiong, X. J. (2004) A/O MBR combined process for treating reactive dye wastewater. J. Sci. Commun., 214: 729-736.

[14] Chen, C. G.(2016) Study on Advanced Treatment of Printing and Dyeing Wastewater by Coagulation and Sedimentation-Micro electrolysis-MBR. J. Sci. Commun., 12: 118-128.

[15] Zhai, J. (2009) Accelerator M Wastewater Treatment by Coagulating Sedimentation-Micro-electrolysis-Catalytic Oxidation Process. J. Sci. Commun., 35(10): 12.

[16] Zhu, Z. L., Cui, S., Ge, X. X. (2017) Advanced Treatment of Printing and Dyeing Wastewater by Preoxidation-MBR-Reverse Osmosis Process. J. Sci. Commun., 05: 79-82.

[17] Zhong, G. H. B. W. Z. (2015) GB 4287—2012 Elimination of Water Pollutant Emission Standards for Textile Dyeing and Finishing Industry. J. Sci. Commun., 02: 38

[18] Xing, Y., Lu, A. H., Hong, C. (2011) Experimental Study on Advanced Treatment of Printing and Dyeing Wastewater by Membrane Bioreactor (MBR)-Reverse Osmosis (RO) Process. J. Sci. Commun., 11: 2583-2586.

[19] Xiao, Y., Cheng, Y., Hu Y. (2014) Advanced treatment of semiconductor wastewater by combined MBR – RO technology. J. Sci. Commun., 336: 168-178.

[20] Wu, B., Kitade, T., Chong, T. H. (2013) Impact of membrane bioreactor operating conditions on fouling behavior of reverse osmosis membranes in MBR – RO processes. J. Sci. Commun., 311: 37-45.

[21] Sun, X. F., Zhang, Y., Li, R. G. (2012) Experimental study on short-range nitrification treatment of high ammonia nitrogen wastewater by AO-MBR process. J. Sci. Commun., 06(1): 24-27.

[22] Li, F. F., Zhang, Y., Chen, L. J. (2013) Design and operation of A/O-MBR process for water reuse project in campus domestic sewage. J. Sci. Commun., 10: 4015-4020.

[23] Zhou, L., Zhuang, W., Ye, B. (2017) Inorganic characteristics of cake layer in A/O MBR for anaerobically digested leachate from municipal solid waste incineration plant with MAP pretreatment. J. Sci. Commun., 327: 71-78.

[24] Guo, L. H., Zhou, Y. S., Li, L. (2016) MBR+Reverse Osmosis Double Membrane Process for Printing and Dyeing Wastewater and Its Reuse Project. J. Sci. Commun., 03: 132-135.

[25] Sun, G. F., Shen, L. H.(2016) Reduce the operating costs of MBR and reverse osmosis processes in the recycling of printing and dyeing wastewater. J. Sci. Commun., 15: 68-69.

[26] Li, F., Huang, J., Xia, Q. (2018) Direct contact membrane distillation for the treatment of industrial dyeing wastewater and characteristic pollutants. J. Sci. Commun., 195: 83-91.

[27] Tan, Y., Sun, L., Li, B. (2017) Fouling characteristics and fouling control of reverse osmosis membranes for desalination of dyeing wastewater with high chemical oxygen demand. J. Sci. Commun., 419: 1-7.

[28] Wu, B. B. (2016) Current situation and trend of reformation of printing and dyeing wastewater under the new situation. J. Sci. Commun., 09: 100.

[29] Chen, H., Li, X., Xue, Z. (2015) Key issues in the current printing and dyeing wastewater treatment. J. Sci. Commun., 35(10): 16-19.

[30] Liu, C., Li, L., Qian, G. S. (2017) Research progress on membrane fouling and control of membrane bioreactor. J. Sci. Commun., 10.