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Application of the membrane bioreactor process in upgrading a norfloxacin pharmaceutical wastewater treatment system

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ABSTRACT

A norfloxacin pharmaceutical factory in Henan Province, China, uses a metal-based electrochemical redox pretreatment step followed by anaerobic hydrolytic acidification and the anoxic/oxic (A/O) process for biological treatment. The effluent chemical oxygen demand (COD) does not meet the limit of 120 mg L^{-1} in the national "Discharge Standards of Water Pollutants for Pharmaceutical Industry Chemical Synthesis Products Category" (GB21904-2008, in Chinese) and therefore needs to be improved. In this study, influent from the hydrolytic acidification tank and a built-in membrane bioreactor are used to determine the effects of operating parameters such as the sludge load (Ns), sludge concentration (mixed liquor suspended solids, MLSS), dissolved oxygen (DO) and sludge age (sludge retention time, SRT) on the effluent COD and NH_3–N. The results show that the optimal operating ranges of each parameter are as follows: MLSS, 8,000~12,000 mg L^{-1}; Ns, 0.14~0.33 kg COD/kg MLSS d; DO, 2.0~3.0 mg L^{-1}; and SRT, 15~50 d. The actual operational results after optimization of each parameter show that effluent COD is between 60 and 130 mg L^{-1}, effluent NH_3–N is less than 5 mg L^{-1}, and 90% and 100% of the effluent COD and NH_3–N measurements, respectively, meet the discharge standard. Through kinetic analysis of the reactor, the kinetic parameters of sludge degradation are found to be V_{max} = 0.32 d^{-1} and K_s = 270.36 mg L^{-1}.

Keywords: NH_3–N; Chemical oxygen demand; Dynamic analysis; Membrane bioreactor; Norfloxacin wastewater; Optimization

1. Introduction

Norfloxacin is a quinolone antibiotic, and antibiotics have made great contributions to the treatment of diseases and protection of people's health. However, wastewater from the production of antibiotics is characterized by high biotoxicity, a high concentration of organic matter, a complex composition, multiple types of pollutants, a low ratio of BOD_5 to COD_{cr} and large fluctuations, which makes antibiotic wastewater difficult to treat [1,2].

The treatment process adopted in the sewage treatment station of the norfloxacin pharmaceutical factory considered herein is shown in Fig. 1.

The technological process in the sewage treatment station is designed to first adjust the water quality and quantity to ensure that the pipes, canals and structures are not affected by changes in wastewater flow rate or concentration. Then, through electrochemical redox, toxic and harmful substances are transformed. Next, neutralization, flocculation and precipitation are carried out to reduce the inorganic matter and a small amount of organic matter in

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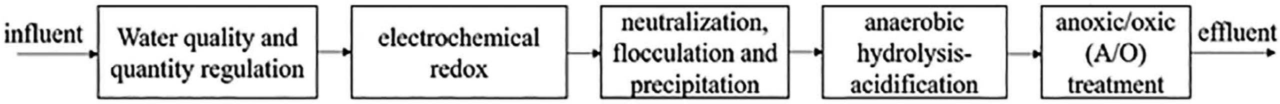

Fig. 1. Sewage treatment process of the norfloxacin pharmaceutical factory.

the wastewater, after which anaerobic hydrolysis-acidification is applied to improve the biodegradability of the wastewater to create a good environment for subsequent aerobic biochemical treatment. Finally, anoxic/oxic (A/O) treatment takes place to decrease the chemical oxygen demand (COD) and NH_3–N. The COD in the effluent from the A/O aerobic pool generally ranges from 150~250 mg L^{-1}, and the NH_3–N ranges from 5~15 mg L^{-1}. COD and NH_3–N are the main pollutants causing water pollution. Excessive discharge of COD affects the water balance and leads to black and smelly water; too high NH_3–N leads to eutrophication and smelly water and has some toxicity for aquatic organisms. Therefore, these two indicators receive more attention, and COD fail to meet the requirements in the national "Discharge Standards of Water Pollutants for Pharmaceutical Industry Chemical Synthesis Products Category" (GB21904-2008, in Chinese); therefore, according to the effluent pollutant concentrations, it is necessary to upgrade the wastewater treatment process of this pharmaceutical factory.

Various processes have been adopted for treating pharmaceutical wastewater, such as advanced oxidation, adsorption and biological processes. Although these processes can save costs and produce fewer by-products than physical-chemical methods, some require large areas and added equipment. At the same time, the complex nature and fluctuation of pharmaceutical wastewater compositions leads to great challenges to treatment [3]. The norfloxacin pharmaceutical factory produces conventional pollutants such as COD, BOD, and ammonia nitrogen, as well as residual products (fluochloroaniline and norfloxacin) and by-products (cyanide, phenol, and polycyclic aromatic hydrocarbons). These pollutants are characterized by high concentrations and wide fluctuation ranges, and some of the pollutants are biotoxic. Therefore, the treatment requirements are further increased, and a more appropriate treatment method is needed.

Membrane bioreactor (MBR) technology has the characteristics of a high removal efficiency, high treatment concentration, strong anti-shock loading capability, stable effluent, etc., and MBRs can effectively improve the purification efficiency of refractory organic compounds without the need for additional civil engineering facilities [4–6]. Liu and Dang [7] used MBR technology to upgrade the second sewage treatment plant in Changsha City, Hunan Province, China, according to certain characteristics. The original effluent values (COD ≤ 60 mg L^{-1} and NH_3–N ≤ 20 mg L^{-1}) met the "Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant" (GB18918-2002, in Chinese) and now meet the "Environmental Quality Standards for Surface Water" (GB3838-2002, in Chinese) (COD ≤ 30 mg L^{-1} and NH_3–N ≤ 1.5 mg L^{-1}). Echevarria et al. [8] used an MBR combined with ozonation and UV technology for the modification of organic micropollutants (OMPs) in a wastewater treatment plant, and the removal rate of OMPs increased to 85% ± 2%. Kim et al. [9] replaced the sequencing batch reactor (SBR) used to treat the wastewater generated by the toilets and restaurants of a hotel and resorted with an MBR to accommodate the increased flow rate and the overall hotel expansion construction schedule and achieved a 100% water recovery rate.

Although there are many cases of MBR being used for upgrading, there are few cases of MBR applied to norfloxacin pharmaceutical wastewater. Therefore, this study applied MBR to norfloxacin pharmaceutical wastewater. In the process of transformation, Kim et al. [9] modified the SBR process by converting two existing SBR chambers into preanoxic, aerobic and postanoxic tanks and added a 40-foot container as an MBR storage tank. In this study, MBR can directly replace the A/O process without additional civil engineering projects. To compare the effluent quality of the MBR process with the original A/O process, the same influent water as the original A/O process is used, that is, the effluent from the anaerobic hydrolysis acidification pool. Therefore, this study adopted MBR technology to treat the effluent from the anaerobic hydrolysis acidification pool of the plant under study to prepare for upgrading the norfloxacin pharmaceutical plant. When using membrane treatment methods to treat pharmaceutical wastewater, most studies focus on the study of membrane characteristics, such as the rejection rate, permeate flux and membrane fouling, while the influence of the change in operating conditions on the membrane treatment effect has been less studied. Therefore, the operational effect of the process under different conditions was explored and analysed, and the best operation parameters were determined, providing technical support for upgrading the plant. To further understand the MBR treatment of norfloxacin pharmaceutical wastewater, the degradation kinetics model of the substrate was also studied.

2. Materials and methods

2.1. Experimental setup and operation

In this experiment, a built-in MBR was adopted. The membrane was installed inside the reactor, and the separation of sludge and water was achieved through membrane filtration and interception. Then, an aeration device below the membrane was used to drive the mixture up to generate shear force on the membrane surface to achieve membrane cleaning and reduce membrane fouling [10,11].

The size of the test device was 1,000 mm × 970 mm × 1500 mm, the effective volume was 1.2 m^3, and microporous aeration was performed. The polyvinylidene fluoride (PVDF) hollow-fibre sheet ultrafiltration membranes were purchased from Litree, a company in Hainan, China.

The membrane size was 721 mm × 70 mm × 1,222 mm, the pore diameter was 0.02 μm, and membrane fibre inner diameter 1.00 mm outer diameter 1.80 mm, the effective area was 13 m^2, maximum operating temperature 40°C, pH range 1–12. Two sheet membranes were prepared—one for reserve and one for use. The experimental results show that when the membrane flux was 15 L m^{-2} h^{-1}, the membrane pressure increased from the initial 0.014 to 0.048 MPa for 7 d, and when the membrane flux was 10 L m^{-2} h^{-1}, the membrane pressure increased from 0.018 to 0.048 MPa for 16 d, and the membrane pressure increased faster when the membrane flux was higher. Therefore, attention should be given to the change in membrane pressure in the experiment to avoid membrane contamination, and the membrane components should be replaced in time to avoid affecting the experimental results. In this experiment, the membrane flux was approximately 11.5 L m^{-2} h^{-1}.

The test procedure was as follows. Pretreated pharmaceutical wastewater from the wastewater treatment station was extracted by a self-priming pump and transferred to the two-stage high water tank of the device, where the water inflow was adjusted through an inlet valve and return valve. The inlet water sank through gravity precipitation in the first tank, and the sludge was discharged through the sludge discharge pipe at the bottom of the tank. The supernatant overflowed into the second tank, which was mainly used for water storage. Effluent water was introduced into the main test device (MBR) by a water pipe, and the influent water flow was monitored by valves and flow metres. The sewage in the reactor was aerobically biodegraded, and the effluent was filtered through the membrane and discharged or returned by the suction pump. The discharge and return flows were controlled through the valve. The bottom hole of the test reactor was connected to pipes and valves to control the sludge discharge and emptying of the reaction tank.

The operational mode included pumping for 8 min and air aeration for 2 min. The main purpose of air aeration was to wash the surface of the membrane and suppress membrane fouling. The starting and stopping of the pump were controlled by a time relay.

The detailed test device diagram is shown in Fig. 2.

2.2. Experimental methods

Temperature has a great influence on microorganisms, mainly affecting their physiological activities, generation cycle time, enzyme activity and species. Most of the activated sludge is medium-temperature bacteria, and the most suitable temperature is 25°C~37°C, while other bacteria (nitrifying bacteria) have the most suitable temperature of 15°C~38°C. pH also has a great influence on the removal rate, mainly affecting the growth and metabolism of nitrifying bacteria, as well as the effectiveness and toxicity of nitrifying substrates and products. The normal physiological activities of activated sludge range from pH 6.5 to 8.5. When the pH of the MBR membrane tank is controlled between pH 7.0 and 8.5, the growth of nitrifying bacteria is inhibited. When the pH is controlled between 6.0 and 7.0, nitrifying bacteria grow well and are the most vigorous, and the removal effect of ammonia nitrogen is the best. Therefore, after the device was started, the temperature was maintained at approximately 25°C, and the pH was 6.5~7.0. Different treatment effects were obtained by changing the operating parameters, and the best range of operating parameters was determined by taking COD and NH_3–N as the index. The test range of each operating parameter and the operating conditions were as follows:

Under the conditions of an sludge load (Ns) of 0.2 ± 0.05 kg COD/kg MLSS d, dissolved oxygen (DO) of 3.0~4.0 mg L^{-1} and sludge retention time (SRT) of 25 d, the effluent COD and ammonia nitrogen of different mixed liquor suspended solids (MLSSs) were measured to determine the appropriate range of MLSS, which was controlled in the range of 5,000~18,000 mg L^{-1}. Under certain suitable MLSS conditions, DO of 3.0~4.0 mg L^{-1} and an SRT

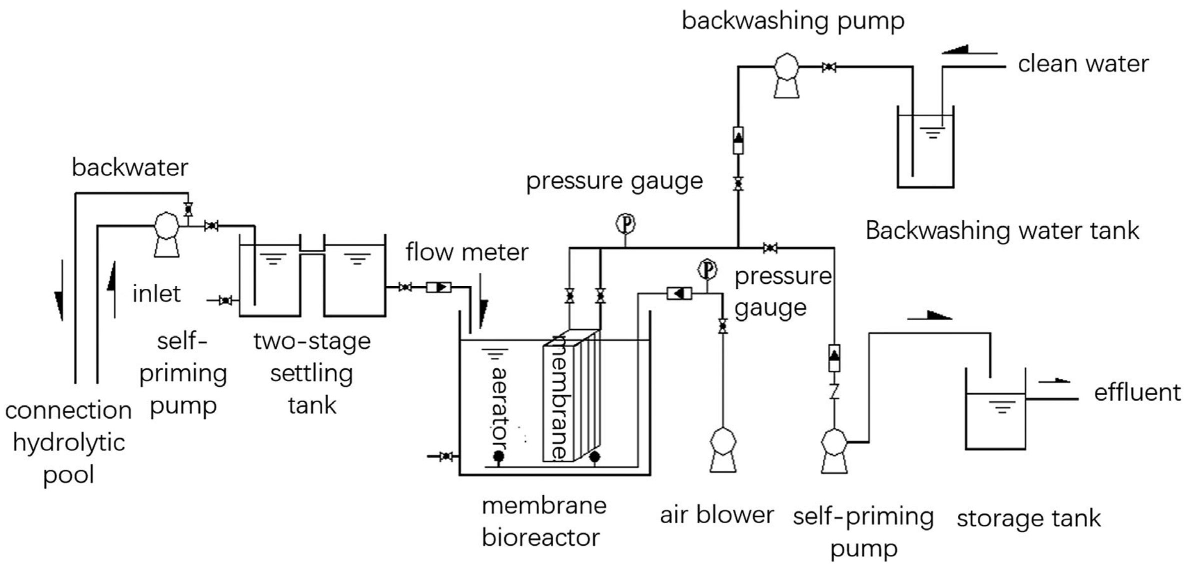

Fig. 2. Experimental device.

of 25 d, the influent COD concentration was changed to adjust the Ns range from 0.05 to 0.45 kg COD/kg MLSS d, and the effluent COD at different Ns values was measured to determine the appropriate Ns range. Under appropriate MLSS and Ns conditions, the SRT was controlled at 25 d, and the DO was varied between 0.5 and 6.0 mg L^{-1}. The effluent COD and NH_3–N at different DO levels were measured to determine the appropriate DO range. Under the conditions of the determined appropriate MLSS, Ns and DO, the SRT was adjusted within the range of 8~112.5 d by changing the amount of sludge discharge, and the effluent COD and NH_3–N at different SRTs were measured to determine the appropriate SRT range.

Under the optimized conditions, the temperature was maintained at approximately 25°C, the pH was maintained at 6.5~7.0, the influent flow rate (1.25~3.87 m^3 d^{-1}) was changed to obtain different hydraulic retention times (HRTs), and the influent and effluent COD concentrations and MLSSs under different HRTs were measured. A substrate degradation kinetics model was established after these data were obtained and verified by comparison with actual measured values.

The MBR reactor was operated under optimized conditions, and the pollutant removal effect was compared with that before the modifications.

2.3. Influent water quality

The influent water was the effluent of the anaerobic hydrolysis acidification pool, and the main water quality conditions are shown in Table 1. The influent water quality fluctuated greatly.

2.4. Start-up of the device

To achieve good sludge adaptation and wastewater treatment effects, the sludge in this test was obtained from the secondary settling tank of the sewage treatment plant. After further precipitation and concentration, sludge was added to the test device. This approach greatly shortened the incubation and acclimation times. The added MLSS was approximately 10,000 mg L^{-1}, mixed liquor volatile suspended solids (MLVSS)/MLSS was approximately 0.7, and the sludge volume was 1/3 of the reactor volume. The sludge had certain adaptability to the wastewater; thus, continuous inflow was used from the beginning of the culture. The initial inflow rate was 60 L h^{-1}, and the inflow quantity gradually increased with increasing MLSS. The COD of the influent and effluent, sludge settling ratio (SV_{30}), MLSS, etc. were measured every day, and the sludge discharge quantity was controlled to keep the MLSS value stable in the reactor. The DO in the unit was in the range of 2~4 mg L^{-1} to maintain good sludge activity and settling properties. The MLSS, SV_{30} and other indicators were monitored, and the quality of the influent and effluent were observed. The system continued to operate until the effluent water quality was stable, at which point the main test stage, which lasted for approximately 20 d, began.

The inflow of water increased from 1.44 m^3 d^{-1} at the beginning of the start-up period to 3.6 m^3 d^{-1} at the end, and the MLSS increased linearly over the 20 d, from a minimum of 3,200 to 9,130 mg L^{-1} at the end, with no sludge discharged during this period. When the COD in the influent water was 400~900 mg L^{-1}, the effluent quality decreased from approximately 200 mg L^{-1} in the first week to 90~130 mg L^{-1} at approximately 15 d and remained stable, and the COD removal rate increased from 60% in the initial stage to more than 80%. At the same time, the effluent NH_3–N (initial value of 10 mg L^{-1}) stabilized below 5 mg L^{-1}. Due to the high MLSS, a certain influent flow rate was needed to maintain a certain MLSS. According to the equipment starting, MLSS reached 9,130 mg L^{-1}, the influent flow rate was 3.6 m^3 d^{-1}, the calculated HRT was 8 h (HRT = V/Q, V: reactor effective volume, Q: influent flow rate), and the general activated sludge method HRT was 4~8 h. Therefore, when exploring the influence of different factors on effluent water, the influent flow rate was maintained at 3.6 m^3 d^{-1}, and the hydraulic residence time was maintained at 8 h.

Table 1
Inlet water quality conditions

Parameter	Scope
pH	5.5~6.5
COD_{cr} (mg L^{-1})	300~2,800
NH_3–N (mg L^{-1})	10~60
SS (mg L^{-1})	50~200

2.5. Test methods

The main parameters tested included the COD, NH_3–N, temperature, MLSS of the mixed liquid in the test MBR, etc., and the data were measured three times in parallel samples. Monitoring of each pollutant index was performed according to the monitoring methods stipulated in the "Industrial Standards for Environmental Protection of the People's Republic of China" issued by the Ministry of Environmental Protection of the People's Republic of China. The specific detection and analysis methods are shown in Table 2.

2.6. Analysis methods

To evaluate the results, one-way analysis of variance (ANOVA) was used to analyse whether the removal rates of MLSS in different intervals were statistically significant. A 95% confidence level was applied, and the software used was SPSS (IBM SPSS Statistics Version 20).

3. Results and discussion

3.1. Optimization of MBR operating parameters

3.1.1. Effects of MLSS

Due to the interception of the membrane, complete separation of HRT and SRT was realized, which allowed the MLSS to easily obtain more than 10,000 mg L^{-1} and eliminated the harm caused by sludge bulking. The increase in MLSS was conducive to the removal of refractory organic matter. Therefore, the MLSS was controlled at 5,000~18,000 mg L^{-1}

to explore the influence of MLSS on the COD and NH_3–N in the effluent. According to the changes in the influent COD concentration, the influent flow rate was controlled to keep Ns at approximately 0.2 kg COD/kg MLSS d. The results are shown in Fig. 3.

Fig. 3a shows that the COD removal rate exhibited a trend of first increasing and then decreasing. The ANOVA results for the average COD removal rates of the three groups with different sludge concentrations show that there were significant differences among the three groups ($P < 0.05$). When the MLSS was less than 8,000 mg L^{-1}, the effluent COD concentration was significantly higher, and the removal rate was lower. When the MLSS ranged from 8,000~12,000 mg L^{-1}, the effluent COD was maintained at approximately 100 mg L^{-1} at best, and the removal rate exceeded 80%. When the MLSS was higher than 12,000 mg L^{-1}, the COD removal rate was reduced to approximately 75%, and the effluent COD was maintained at approximately 200 mg L^{-1}.

System substrate was abundant when the sludge concentration was too low. Among the components of soluble microbial products (SMPs), the amount of utilization-associated products (UAPs) increased, and the accumulation of UAPs led to an increase in the total amount of SMPs. However, UAP is easy to decompose. With increasing sludge concentrations, UAP decreased, the total amount of SMPs decreased and the effluent quality improved. However, with increasing sludge concentrations and microbial biomass, the number of biomass-associated products (BAPs) in SMPs increased, and BAPs are macromolecular organic matter that is difficult to decompose, thus leading to an increase in SMPs and a deterioration in the effluent water quality. Brookes et al. [12] studied sustainable flux fouling in a membrane bioreactor, wastewater brought to the surface during oil and gas production, and wastewater containing varying salinities and dissolved hydrocarbons such as benzene, toluene, ethylbenzene, xylene and

Table 2
Water quality detection methods

Number	Parameters	Test method	Test frequency
1	COD	Standard potassium dichromate method	Twice a day (morning, evening)
2	MLSS	Weight method	Three times a week
3	DO	Portable tester	Once a day
4	MLVSS	Weight method	Once a week
5	Ammonia nitrogen	Acid titration	Twice a day (morning, evening)
6	Water temperature	Thermometer	Twice a day
7	pH	Test paper	Twice a day (morning, evening)
8	SV_{30}	100 mL measuring cylinder for field measurement	Twice a day

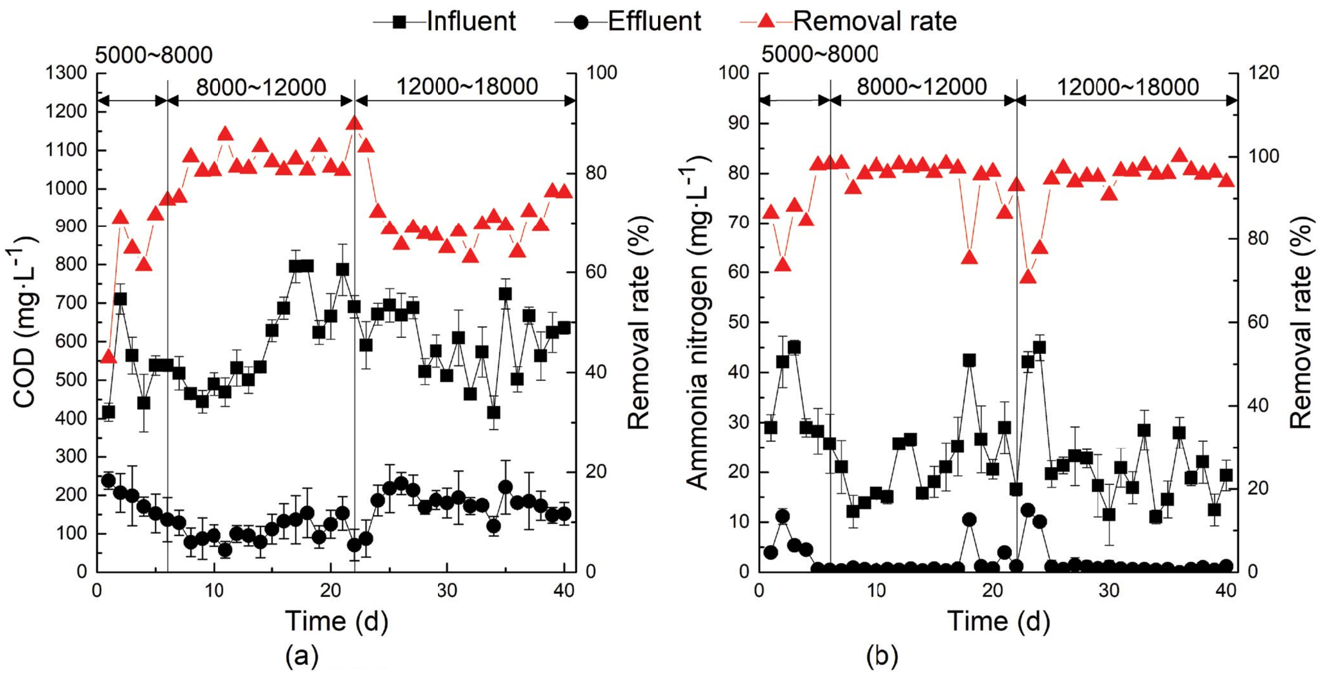

Fig. 3. Effects of MLSS on (a) COD and (b) NH_3–N (Ns, 0.2 ± 0.05 kg COD/kg MLSS d; DO, 3.0~4.0 mg L^{-1}; SRT, 25 d).

polycyclic aromatic hydrocarbons. When the sludge concentration increased from 6,000 to 18,000 mg L^{-1}, SMPs increased from 11.35 to 22.7 mg L^{-1}, indicating that the increase in sludge concentration led to an increase in the SMP content. In addition, sufficient DO is needed to maintain microbial activity. When the MLSS is too high, the mass transfer rate of oxygen will be reduced, and to maintain a stable Ns, the inflow of water must be increased, which will lead to a decrease in the HRT. A reduction in the HRT can enhance the growth of biomass, and accumulated SMPs inhibit microbial activity, resulting in a reduction in the removal rate [13,14]. Poojamnong et al. [15] used an MBR to treat pollutants in eucalyptus pulp papermaking wastewater. When the MLSS increased from 3,985 to 7,280 mg L^{-1}, the COD removal rate increased from 47% to 73%. Moreover, when the MLSS reached 6,940 mg L^{-1}, the chroma removal value met the discharge standard, indicating that MLSS should be maintained at a high level to achieve a good treatment effect in an MBR.

Fig. 3b shows that overall, the effluent NH_3–N concentration remained low, and the removal rate was relatively high. The main reason for the reduction in the NH_3–N removal rate is related to the higher NH_3–N in the influent. Moreover, DO decreased and SMPs accumulated when the MLSS increased, which affected the growth activity of nitrifying bacteria and led to a decrease in the removal rate; however, the NH_3–N in the effluent was maintained at a good level most of the time, which was related to the long SRT in the plant and the retention of nitrifying bacteria by the membrane. The removal rates obtained with three different MLSS values were analysed by ANOVA, and the P value between the groups was 0.164, which is greater than 0.05, indicating that there was no significant difference between the data. Therefore, MLSS has little influence on NH_3–N removal from the perspective of MLSS alone.

Therefore, MBR treatment of norfloxacin wastewater with an MLSS of 8,000~12,000 mg L^{-1} is considered effective.

3.1.2. Effects of Ns

Ns refers to the amount of COD removed by a certain amount of sludge per unit time. Ns was a major parameter affecting the process and was directly related to the treatment efficiency and sludge settling performance of the system. In activated sludge treatment, the COD load of sludge was generally 0.3~0.5 kg COD/kg MLSS d. Low Ns led to insufficient microbial nutrition, low microbial activity and concentration, and low sewage treatment efficiency. High Ns led to partial adsorption but did not absorb organic pollutants in cells discharged with the remaining sludge, resulting in effluent that was not easy to qualify. At the same time, due to strong microbial activity, sludge did not easily settle, water separation was poor, and Ns values that were too high or too low easily caused sludge bulking. Therefore, it was necessary to determine the appropriate Ns. Because of the high MLSS, the Ns of the MBR was lower than that of the conventional activated sludge process. In the above comparison of the influence of MLSS on the effluent, Ns was approximately 0.2 kg COD/kg MLSS d. To further study the influence of Ns on the effluent quality, the MLSS was controlled at approximately 8,000 mg L^{-1}. The change in Ns was calculated from the change in the influent COD concentration (400~1,400 mg L^{-1}). The influence of Ns on the effluent was analysed and compared for Ns values ranging from 0.05~0.55 kg COD/kg MLSS d. The results are shown in Fig. 4.

Fig. 4 shows that with increasing Ns, the COD removal rate gradually increased and remained stable, and then it decreased as the load continued to increase. When Ns was lower than 0.14 kg COD/kg MLSS d, and especially when it was lower than 0.08 kg COD/kg MLSS d, the effluent COD concentration was higher, and the removal rate was lower. This result occurred because when Ns was low, the activity of microbial nutrients decreased, and the microorganisms themselves decomposed to produce soluble metabolites, leading to an increase in COD and a decrease in the COD removal rate. In the range of 0.14~0.45 kg COD/kg MLSS d, the COD removal rate was higher, and the effluent quality and removal rate were the most stable at 0.24~0.33 kg COD/kg MLSS d. However, as the COD concentration in the influent increased and Ns increased to 0.33 kg COD/kg MLSS d, the effluent COD concentration increased, and the COD removal rate decreased. The main reason for this result is that as the COD concentration increases, pollutants cannot be effectively degraded, and microorganisms are not in the endogenous respiration period; thus, the pollutant decomposition ability of microorganisms decreases, but the overall change is not obvious, which is related to the higher MLSS in the MBR [16].

Therefore, when using an MBR to treat norfloxacin pharmaceutical wastewater, the reasonable interval of Ns values is 0.14~0.33 kg COD/kg MLSS d, and the COD volumetric load of the system should be 2.0 kg COD m^{-3} d^{-1}. Chtourou et al. [17] used an MBR to remove triclosan, carbamazepine and caffeine from industrial wastewater from the production of pharmaceutical and medical products. When the MLSS was 4 g L^{-1}, the volume load of the

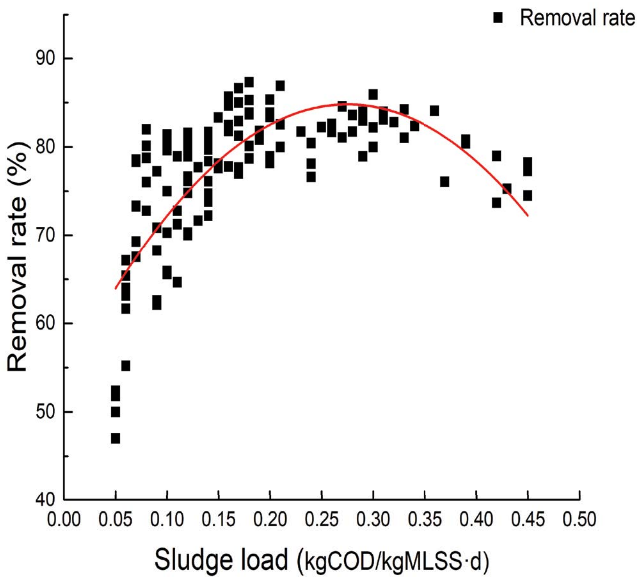

Fig. 4. Effects of Ns on COD (MLSS, 8,000 mg L^{-1}; DO, 3.0~4.0 mg L^{-1}; SRT, 25 d).

system reached 1.38 kg COD m^{-3} d^{-1} (according to the calculation, Ns was 0.345 kg COD/kg MLSS d, which is close to the current results).

3.1.3. Effects of DO

MBR mainly uses aerobic bacteria to decompose COD and NH_3–N. Dissolved oxygen is a necessary condition for the survival of aerobic bacteria. Generally, the DO should be kept above 2 mg L^{-1}, the activated sludge can be kept in a good state, and the treatment effect will be in the best state. Nitrification stopped when the dissolved oxygen was less than 0.5 mg L^{-1}. Therefore, an appropriate dissolved oxygen condition was very important for the treatment effect of the system. The MLSS in the MBRs was more than 2–3 times that in the ordinary activated sludge process, and according to the above analysis, MLSS should be kept within the range of 8,000~12,000 mg L^{-1}. An MLSS that is too high may lead to a poor mass transfer effect of oxygen and affect removal, so the oxygen supply will need to be increased. However, blindly increasing the oxygen supply or improving the original oxygen supply equipment will increase the system energy consumption and operating cost. Therefore, this experiment studied the influence of DO values from 0.5~6.0 mg L^{-1} on COD and NH_3–N in the effluent of the system when the MLSS was approximately 9,000 mg L^{-1}. The results are shown in Fig. 5.

Fig. 5a shows that the effluent COD of the system was stable. When the system DO was maintained above 1.0 mg L^{-1}, the COD removal rate was relatively high, typically more than 82%. However, when the DO was less than 1.0 mg L^{-1}, the COD removal rate dropped to less than 80%. The main reason for these results is that aerobic bacteria could not obtain enough oxygen, and their growth was affected; thus, COD could not be effectively degraded, but a high removal rate could still be maintained, proving that the system can operate under the condition of low DO. Such operation is possible mainly because the MLSS is high and Ns is low, and a DO value that is too high has little effect on COD removal [18].

Fig. 5b shows that when the DO was lower than 1.0 mg L^{-1}, the NH_3–N removal rate was significantly reduced. A comparison with the MLSS data (Fig. 2.1b) shows that the main factor affecting the NH_3–N removal rate was the DO rather than the MLSS. The main reason for this effect is that a low DO environment strongly affects the activity of nitrifying bacteria, but when the DO was at 1.0 mg L^{-1}, the NH_3–N removal rate was high. This relationship was observed because the SRT in the MBR system is high and suitable for the growth of nitrifying bacteria, and membrane filtration can trap nitrifying bacteria within the reactor. Therefore, compared with the traditional activated sludge method, the MBR treatment of norfloxacin wastewater can better adapt to environments with low DO [19].

Therefore, the DO during system operation should be greater than 1.0 mg L^{-1} and maintained between 2.0~3.0 mg L^{-1} considering membrane fouling concerns and operating costs. Yao et al. [20] used a submerged MBR to treat pig farm sewage. The authors found that when the DO was increased to 1.5~3.0 mg L^{-1}, the removal rates of COD and NH_3–N in the system increased to more than 90%, and excessively low DO had a great influence on the removal of NH_3–N. These findings are consistent with the conclusion of the current study.

3.1.4. Effects of SRT

SRT was the ratio of the total amount of activated sludge in the aeration tank to the residual sludge discharged every day. Due to the small amount of sludge discharge, a notable

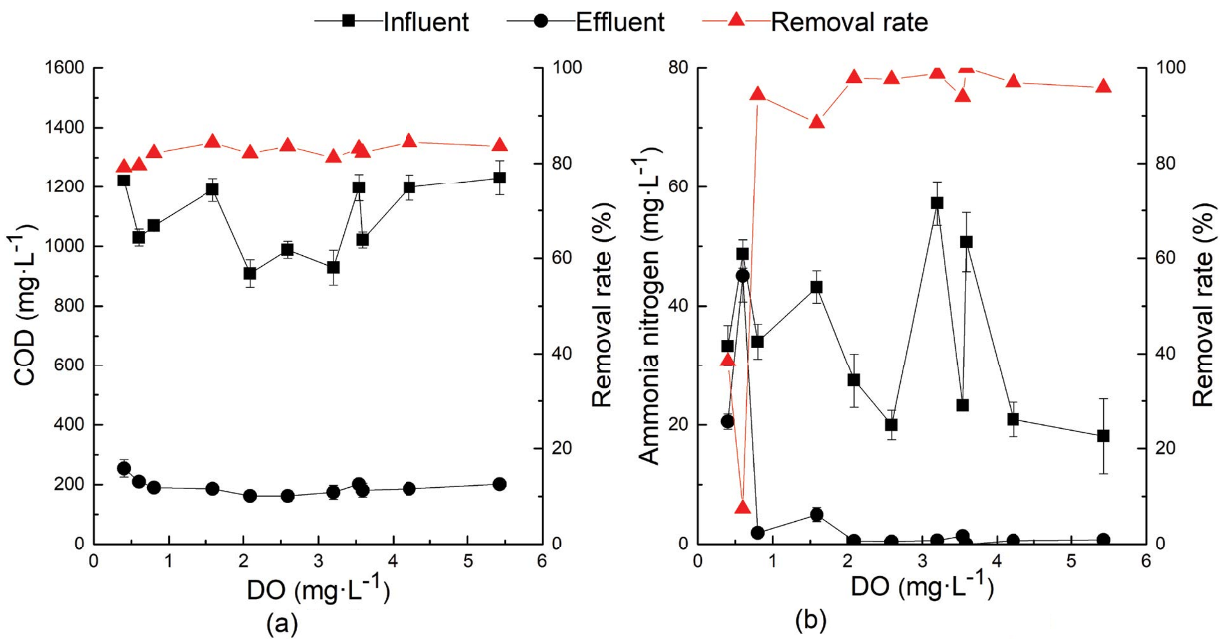

Fig. 5. Effects of DO on (a) COD and (b) NH_3–N (MLSS, 9,000 mg L^{-1}; Ns, 0.2~0.3 kg COD/kg MLSS d; SRT, 25 d).

feature of the MBR was its ability to operate under long SRTs. Appropriate SRT played a key role in the degradation of pollutants and sludge settlement. Generally, with the increase in SRT, the decomposition ability of microorganisms to organic pollutants became weaker, but the sludge settlement performance became stronger. At the same time, considering the generation cycle of microbial flora, the SRT should be longer than the generation cycle so that it can reproduce and ensure the treatment effect. Generally, the generation cycle of nitrifying bacteria was approximately 10 d, so SRT should be at least approximately 10 d. Therefore, in this experiment, the SRT was modified by adjusting the sludge volume through sludge discharge, and the influence of SRTs of 8~112.5 d on the COD and NH_3–N of the system effluent was studied. The results are shown in Fig. 6.

Fig. 6a shows that when the SRT was 8~112.5 d, the removal rates of COD were all higher than 76%. However, with increasing SRT, the removal rate first increased and then decreased, but the change was not great. The removal of COD was the best at approximately 45 d, reaching 84.84%, and the effluent concentration was 104.72 mg L^{-1}. The COD removal rate began to decline after 50 d. An SRT that is too low or too high will lead to an increase in COD in the effluent, resulting in COD values up to 234.58 mg L^{-1}. A short SRT will lead to a short residence time for microorganisms, which will not be able to effectively multiply and degrade COD, and the removal rate of COD will decrease when the amount of sludge discharged is greater than the amount used for microbial reproduction. A long SRT leads to a reduction in the amount of sludge discharged, sludge ageing and a decrease in microbial activity. The aged sludge remains in the reactor and decomposes to form SMPs, which affects the effluent quality, resulting in a higher effluent COD [21].

Fig. 6b shows that after 20 d, the effluent NH_3–N concentration was the best (maintained below 5 mg L^{-1}), and the average removal rate reached 97%. An excessively low SRT led to an increase in NH_3–N, and the effluent NH_3–N rose to a maximum of 36.86 mg L^{-1}. When the SRT was less than 10 d, the removal rate decreased significantly because the generation cycle of nitrifying bacteria was longer than 10 d. A shorter SRT is not enough to provide a stable environment for the multiplication of nitrifying bacteria, and therefore, the SRT needs to be maintained at more than twice the generation cycle time of nitrifying bacteria [22].

Considering the removal of COD and NH_3–N, the optimum SRT should be maintained at 15~50 d. Teck et al. [23] used a three-stage submerged MBR to treat highly concentrated industrial wastewater under long SRT conditions (over 800 d). Throughout the experiment, the COD removal rate remained above 98%. After approximately 100 d of operation, the total nitrogen concentration was reduced to 0.3 mg L^{-1}, and a longer SRT was required to achieve a better nitrogen removal effect. Therefore, the previous results are consistent with the conclusion of the current study.

3.2. Kinetic model of substrate degradation

3.2.1. Analysis of the kinetic model of substrate degradation

In biological wastewater treatment systems, the degradation and removal of organic pollutants are the most important tasks. The Monod equation ($V = V_{max}$ $(S/K_s + S)$)

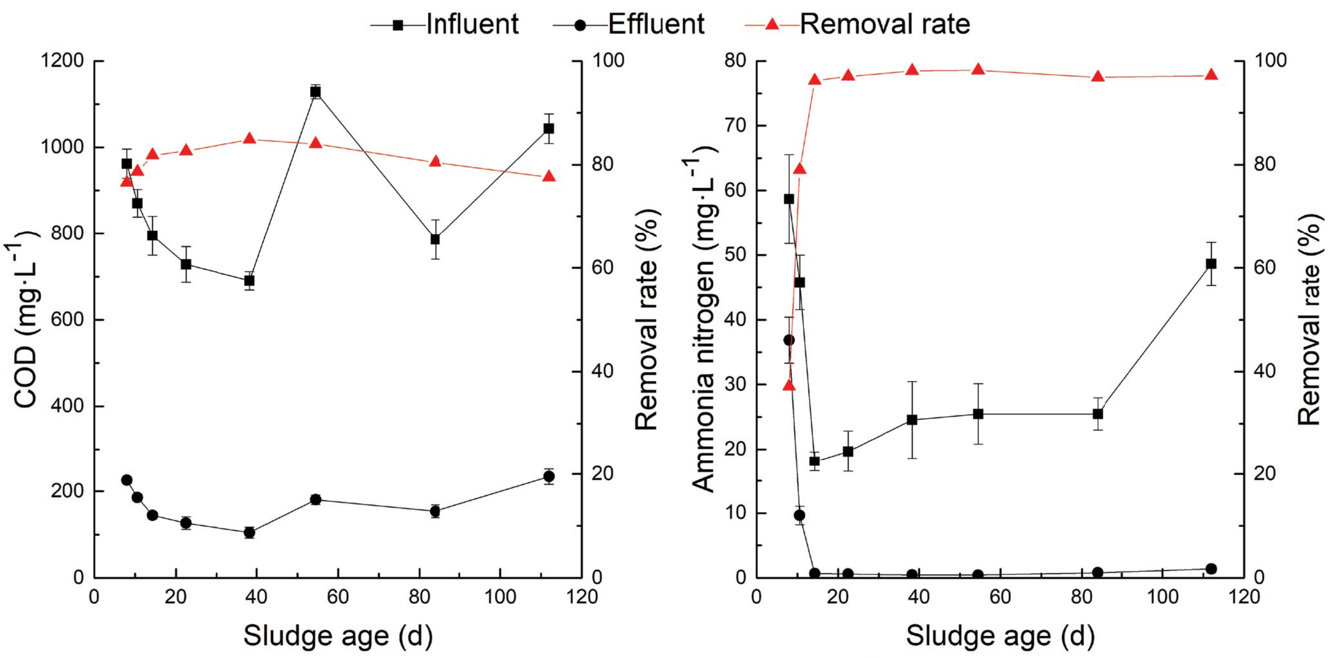

Fig. 6. Effects of SRT on (a) COD and (b) NH_3–N (MLSS, approximately 10,000 mg L^{-1}; Ns, 0.3 ± 0.05 kg COD/kg MLSS d; DO, 2.0~3.0 mg L^{-1}).

can be solved by applying the double-reciprocal method and the material balance in the reactor, which yields the following formula for the degradation kinetics of the system substrate:

$$\frac{\mathrm{HRT}\cdot X}{S_0-S_e}=\frac{K_s}{V_{\max}}\cdot\frac{1}{S_e}+\frac{1}{V_{\max}} \quad (1)$$

This formula can be solved by taking HRT $X/S_0–S_e$ as the vertical axis and $1/S_e$ as the horizontal axis and substituting the data in Table 3.

The regression curve is shown in Fig. 7.

V_{max} = 0.32 d^{-1}, and K_s = 270.36 mg L^{-1}. The kinetic model of organic substrate degradation can be expressed as follows:

$$\frac{S_0-S_e}{\mathrm{HRT}\cdot X}=\frac{0.32S_e}{270.36+S_e} \quad (2)$$

Engineering practice and research show that the saturation constant K_s is usually in the range of 2.5~180 mg L^{-1}. In the current study, K_s = 270.36 mg L^{-1}, which is much higher than the conventional values. The larger K_s is, the higher the concentration of the growth-limiting matrix is, indicating that the MBR process is more suitable for the treatment of wastewater with a high matrix concentration [24,25].

3.2.2. Validation of the kinetic model

By introducing the operating parameters under different operating conditions, the practical application of the established substrate degradation kinetic model was verified, and the simulated values of the kinetic model were calculated. The theoretical simulated values were then compared with the measured values. The results are listed in Table 4.

The simulated and measured values in the above table are plotted in Fig. 8.

Fig. 8 shows that the difference between the simulated and measured values is relatively small and that the kinetic model can reliably predict the changes in the organic matter concentration in the MBR during the treatment of norfloxacin pharmaceutical wastewater. From these values, the effluent water quality of the plant can be predicted, which can be used for reference in practical engineering.

3.2.3. Actual operation effect

In the final stage of the test, to verify the accuracy of the conclusions drawn in the previous stage, the test device was operated under the reasonable operating range determined in the previous stage, and the effluent COD and NH_3–N and their removal rates were analysed. The operation lasted for approximately one month. The operating conditions were an MLSS of 7,000~9,000 mg L^{-1}, Ns of 0.16~0.28 kg COD/kg MLSS d, DO of 2.0~4.0 mg L^{-1}, and temperature of ~25°C. The results are shown in Figs. 9 and 10.

As shown in Fig. 9, the overall effluent COD was stable during actual operation. Furthermore, when the influent COD was between 400 and 1,200 mg L^{-1}, the effluent value was maintained at approximately 100 mg L^{-1}, and the COD removal rate was maintained above 80%. According to the calculated guarantee rate, 90% of the effluent COD values were lower than 120 mg L^{-1} and met the discharge standard in the "Discharge Standards of Water Pollutants for Pharmaceutical Industry Chemical Synthesis Products Category" (GB21904-2008, in Chinese).

Fig. 10 shows that the overall effluent NH_3–N was stable during actual operation. When the influent NH_3–N was between 20 and 60 mg L^{-1}, the NH_3–N removal rate was generally above 90%. According to the calculated guarantee rate, 100% of the effluent had a concentration lower than

Table 3
Calculation of the model parameters for the degradation kinetics of the organic substrate

HRT (d)	$S_0–S_e$ (mg L^{-1})	X (mg L^{-1})	$\frac{\mathrm{HRT}\cdot X}{S_0-S_e}$	$1/S_e$
0.31	407.89	6,315	4.80	0.0022
0.42	425.35	6,045	6.04	0.0045
0.57	431.14	6,610	8.74	0.0059
0.68	437.17	5,836	9.14	0.0060
0.82	437.24	5,192	9.76	0.0071
0.96	435.32	4,524	9.93	0.0091

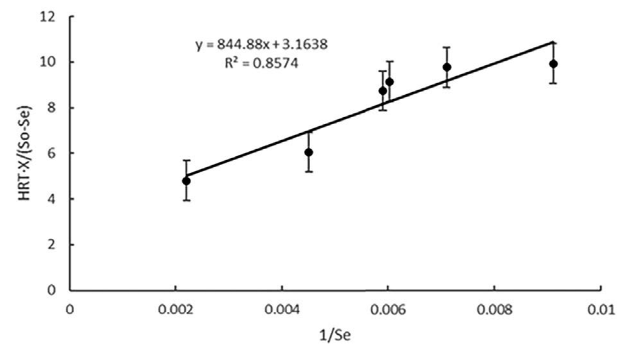

Fig. 7. Regression curve of the kinetic model parameters of substrate degradation.

Table 4
Kinetic parameters for the degradation of organic substrates

HRT (d)	X (mg L^{-1})	S_0 (mg L^{-1})	S_e (mg L^{-1})/simulated value	S_e (mg L^{-1})/measured value
0.28	4,400	416.89	234.13	238.22
0.63	3,580	440.71	166.33	170.73
0.63	4,930	562.80	173.77	172.86
1	4,760	703.46	152.95	150.18

5 mg L^{-1} and met the discharge standard in the "Discharge Standards of Water Pollutants for Pharmaceutical Industry Chemical Synthesis Products Category" (GB21904-2008, in Chinese).

In contrast, during normal operation, the COD of the effluent from the aerobic pool of the sewage treatment station was approximately 150~250 mg L^{-1}, and the NH_3–N was in the range of 5~15 mg L^{-1}. It can be seen from the comparison of the two systems that the treatment effect of the MBR test device was better. Compared with the values in the effluent from the aerobic tank of the sewage station, the effluent COD concentration was reduced by approximately 50%, and the effluent NH_3–N concentration was reduced by approximately 70%. Moreover, the MBR operation was more stable, the effluent water quality fluctuated little, and the system showed a strong ability to resist load shock.

According to the treatment effect on COD and NH_3–N, when the MBR process was used to treat norfloxacin pharmaceutical wastewater, the effluent quality was better and more stable than that in the existing plant process. These results therefore provide a reference for upgrading and transforming sewage stations.

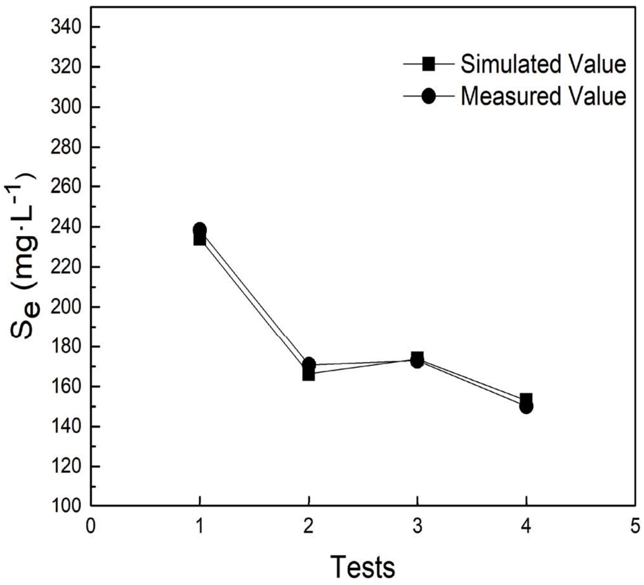

Fig. 8. Comparison of simulated and theoretical values.

4. Conclusions

The characteristics of MBRs, such as a high sludge concentration, long sludge age and low sludge load, have a good treatment effect on many kinds of pollutants, high concentrations, high fluctuations and biological toxicity in pharmaceutical wastewater. Therefore, treatment of norfloxacin pharmaceutical wastewater by the MBR process can further improve the effluent quality. The optimum conditions for the treatment of norfloxacin pharmaceutical wastewater are as follows: Ns, 0.14~0.33 kg COD/kg MLSS d (COD volumetric load, 2.0 kg COD/m^3 d); MLSS, 8,000~12,000 mg L^{-1}; DO, 2.0~3.0 mg L^{-1}; and SRT, 15~50 d.

The kinetic model parameters for substrate degradation are V_{max} = 0.32 d^{-1} and K_s = 270.36 mg L^{-1}. A comparison of the obtained K_s value with that of the traditional activated sludge process (2.5~180 mg L^{-1}) indicates that the MBR system is more suitable for the treatment of high-concentration wastewater.

The actual operation results show that 90% of the effluent COD values were below 120 mg L^{-1}, meeting the discharge standard. NH_3–N was kept below 5 mg L^{-1}, thus meeting the

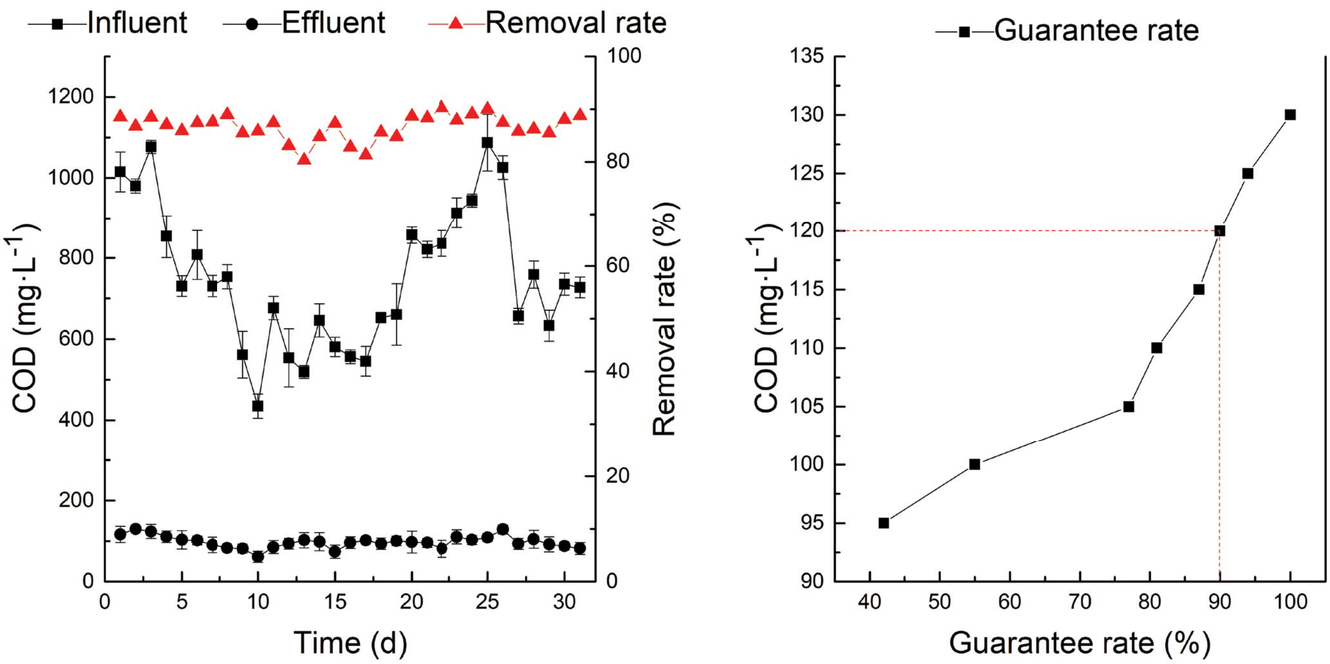

Fig. 9. Effluent COD.

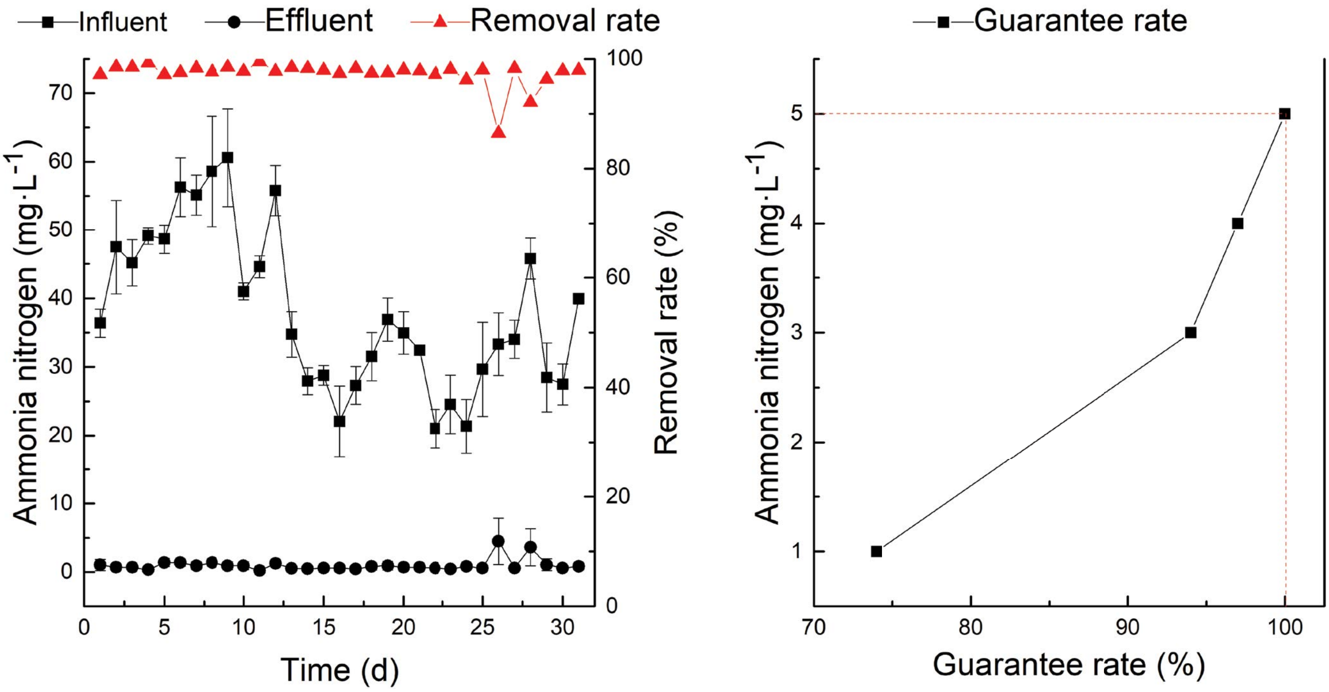

Fig. 10. Effluent NH_3–N.

emission standard. Compared with the values obtained without the MBR, through the MBR treatment, the effluent COD concentration can be reduced by approximately 50%, and NH_3–N can be reduced by approximately 70%.

Symbols

S_0	—	Concentration of substrate in the reactor influent, mg L^{-1}
S_e	—	Concentration of substrate in the reactor effluent, mg L^{-1}
HRT	—	Hydraulic retention time, d
X	—	Mixed liquor suspended solids, mg L^{-1}
K_s	—	Half saturation constant, mg L^{-1}
V	—	Specific growth rate, d^{-1}
V_{max}	—	Maximum specific growth rate, d^{-1}

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