



Treatment of dyeing wastewater by hollow fiber membrane biological reactor

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ABSTRACT

A submerged hollow fiber membrane bioreactor (MBR) with a capacity up to 400 L/d was used for treatment of dyeing wastewater from a printing and dyeing factory in Changzhou, China. The MBR device was operated continuously for 100 days. The removal ratio of COD reached 90% and the COD values of effluent from the reactor were 52–97 mg/L, when the COD values of inlet were 600–1200 mg/L, 10–20% of which were rejected by membranes. The removal ratios for NH₃-N and colour were 90–95% and 60–75%, respectively. The result of this work could be used as a reference for the application of MBR technology to dyeing wastewater treatment on an industrial scale.

Keywords: MBR; Hollow fiber membranes; Dyeing wastewater; Activated sludge

1. Introduction

The textile processing industry is characterized by its fairly high specific water consumption and its large amount of wastewater discharges [1]. In China, the discharged wastewater from printing and dyeing mills accounts for 650 million tons per year, which is 80% of the total discharged wastewater from the textile processing industry [2]. The technologies used for the treatment of dyeing wastewater in China are mainly based on biological methods, most of which are activated sludge methods with aeration tanks [3,4]. However, only 43% of the total treatment equipment are in operation, and 43% of the equipments in operation fail to meet the required national disposal standard with regard to COD, which hampers the development of Chinese enterprises. The COD of treated textile effluents need to be lower than 100 mg/L in order to be in compliance with the first class discharge standard and lower than 180 mg/L in order to be in compliance with the second class discharge standard required in GB4287-1992 "Discharge standard of water pollutants

for dyeing and finishing of textile industry". The major drawback of the conventional biochemical treatment is that it needs a large footprint, has low treatment efficiency and cannot reach the discharge standard of dyeing wastewater that has been increased gradually by the state [5,6].

Membrane bioreactor (MBR) technology is a relatively new technique for wastewater treatment and reuse, which emerged in the nineties [7–11]. It has gradually increased in the treatment of municipal and industrial wastewater in recent years. In MBR treatment technology the conventional secondary settlement tank is replaced by a membrane separation unit. The advantages of MBR technology include high efficiency in solid-liquid separation; high volume loading and low footprint, because the retention of membranes can keep high concentration of microorganisms in the bioreactor; low residual sludge by decreasing the sludge loading; and high quality of product water, which can be reused directly as non-potable water [12,13]. Since hollow fiber membranes were used in the activated sludge method in 1989 by Yamamoto et al. [14], the running cost was significantly decreased and the application prospect widened for this combined technology.

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Several publications demonstrated that MBR treatment can be an effective tool to treat dyeing and printing wastewater [15–17]. However, more practical experience through field trials in textile factories is needed. In this paper, a submerged hollow fiber MBR was combined with the traditional activated sludge method to treat the dyeing wastewater and the removal efficiency of COD, $\text{NH}_3\text{-N}$ and colour were studied, providing a new concept for reforming wastewater treatment in printing and dyeing mills.

2. Materials and methods

2.1. Equipment

A schematic of the experimental set-up is shown in Fig. 1. The aeration biochemical tank was made of PVC with a dimension of 0.5 m (length) \times 0.3 m (width) \times 0.7 m (height) and a working volume of 90 L. Two hollow fiber membrane modules were submerged opposite each other in the biochemical tank and two air bubble diffusers placed directly under the membrane modules. The membrane fouling was slowed by the turbulence produced by the aeration. The maximum and minimum water levels were controlled by the water level controller, and the product water suction period was set by the computer incorporated in the MBR. The vacuum pressure gauge was used to monitor the change in transmembrane pressure.

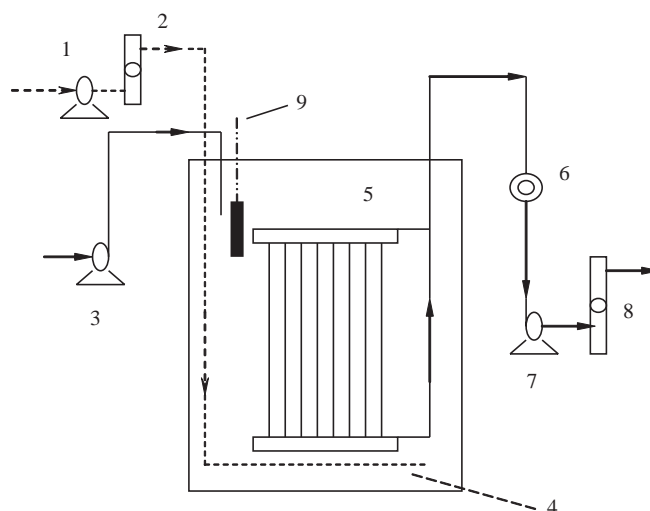
2.2. Hollow fiber membrane module

The hollow fiber membrane modules used in the submerged MBR, which are made of PVDF, were provided by Tianjing Motian Membrane Co. Ltd. Each of the two modules have an effective membrane area of 1 m² and a pore size of 0.2 μm . The length, inner diameter and outer diameter of the fibers are 400 mm, 0.65 mm and 1.0 mm, respectively.

2.3. Wastewater quality

The experiments were carried out in a printing and dyeing factory of Changzhou, China. The following treatment technology was used, based on the wastewater quality, the original wastewater treatment process and the equipment used in the factory, replacing the biochemical tank, secondary settlement tank and final settlement tank by the MBR system (see Fig. 2).

The quality of wastewater produced in this factory is shown in Table 1 and is determined by the methods specified in the national standard [18].



1. Air pump; 2. Gas flowmeter; 3. Feedwater pump; 4. Air bubble diffuser; 5. Membrane module; 6. Vacuum pressure gauge; 7. Product water pump; 8. Effluent flowmeter; 9. Water level controller.

Fig. 1. Schematic of the experimental set-up.

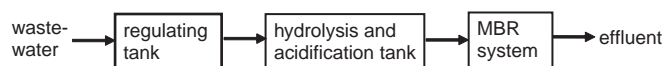


Fig. 2. Flow chart of the applied effluent treatment in the printing and dyeing factory.

Table 1
Water quality of dyeing wastewater.

COD, mg/L	BOD ₅ , mg/L	NH ₃ -N, mg/L	pH	Colour, m ⁻¹
600–1200	90–170	10–23	10–14	250–400

3. Results and discussion

3.1. COD removal effect

The sludge used in the MBR system was taken from the wastewater treatment workshop of the factory, and needed adaption before use because of the difference in aeration velocity and temperature of the MBR system compared with the traditional biochemical unit. The hydraulic retention time (HRT) of the MBR system reduced gradually from 22.5 h to 6 h during the operation cycle (HRT = 22.5 h at start; HRT = 15 h and 10 h, after 30 days and 45 days respectively; HRT = 6 h, after 60 days) because the sludge had not reached the optimum conditions and needed a long HRT to meet the drainage requirements in the early stage of operation. The respective permeate flux was between 2 and 8 L/(m²·h.) at a transmembrane pressure of 0.05–0.1 bar. This was close to the pure water flux of about 8–10 L/(m²·h.) at the same transmembrane pressure. The

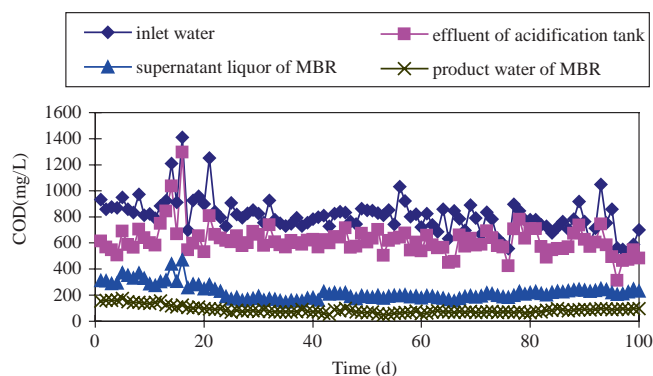


Fig. 3. COD values after biochemical and MBR treatment.

MBR was operated periodically with 15 minutes permeate drain and 3 minutes stop time. No chemical cleaning was needed during the pilot test period. The changes in COD values of water coming from different units of the MBR system are shown in Fig. 3. The COD values of the supernatant liquor showed a typical increase during the early stage of MBR operation, which was induced by the high retention of hollow fiber membranes with regard to organic macromolecules (including the soluble metabolite of microorganisms), and formed the accumulation of macromolecules except when induced by the fluctuation of COD values in inlet water. As the operation time extended, the COD concentration of supernatant liquor gradually decreased because the microorganism in the MBR system adapted to the environment of the MBR, and the organic macromolecules in wastewater can be decomposed by the microorganisms. After 20 days operation, the activated sludge reached maturation, and the MLSS could be kept at 9 to 11 g/L. Hence, it should be noted that despite the low ratio of BOD_5/COD

(~0.15, see Table 1), which indicates a difficult wastewater in terms of biodegradability, the overall COD elimination proves to be high since the microorganisms in the MBR adapted to the biochemical environment.

The COD values of the effluent from the MBR system remained lower than 100 mg/L, with a minimum value of 52 mg/L, though there was a large fluctuation of COD values in inlet water (from 710 to 1253 mg/L). This satisfied the first class discharge standard required in GB4287-1992 “Discharge standard of water pollutant for dyeing and finishing of textile industry” in China.

The COD removal ratios of water from different units of the MBR system are shown in Fig. 4. In Fig. 4 the total COD removal ratio of the MBR system is split up in the fraction of biochemical degradation (inlet/supernatant liquor removal ratio) and that of the membrane (supernatant liquor/outlet removal ratio). In the early stage, the activated sludge had not reached maturation and the COD removal ratio of biochemical treatment was relatively low, and sometimes lower than the removal ratio of the membranes; the COD removal ratio of the biochemical treatment reached a higher level after 20 days because the adaption of sludge was complete; the COD removal ratio of the biochemical treatment decreased slightly and had a similar level to that of the membrane when the HRT decreased from 22.5 h to 15 h (after 30 days) and reached stabilization in the following operation, in spite of the change of HRT values, which indicated that the system had reached a steady state and could ensure the quality of effluent. The COD removal ratio remained 85–92% after 10 days of operation and the COD concentration of effluent could be kept at lower than 100 mg/L.

The MBR system showed the following characteristics in COD removal, based on the results obtained from 100 days of operation:

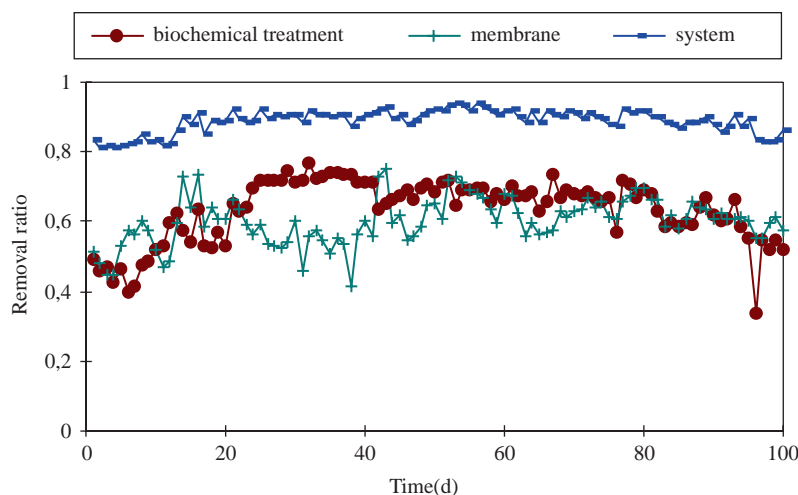


Fig. 4. COD removal ratio of biochemical unit, membrane and MBR systems.

(1) MBR treated effluent can meet the discharge standard in COD values at lower HRT and higher loading capacity.

Despite HRT values changing during the operation time (from 22.5 h to 6 h), the COD values of effluent could be kept at 50 to 90 mg/L and satisfied the first class of discharge standard after the sludge matured (after 20 days of operation), which indicates that the MBR system has a stronger resistance to the change of feedwater than the biochemical tank in that factory, in which the HRT is 30 h and the COD values of effluents range from 130–160 mg/L.

Although the loading capacity of the MBR system fluctuated from 0.5 kg COD/(m³·d) to 1.5 kg COD/(m³·d), the effluent quality remained stable. The respective sludge loading range was between 0.05 and 0.15 kg COD/(kg MLSS·d). The unit handling capacity of the MBR system was five times that of the conventional activated sludge technology currently used in this factory. It can also guarantee that the effluent quality meets the first class of the discharge standard, which can decrease the footprint of the equipment and provide a new concept for reforming wastewater treatment equipment in printing and dyeing enterprises.

(2) The activated sludge plays an important role in COD removal.

The activated sludge in the bioreactor still performed excellently although the COD values of the inlet water had fluctuation and loading capacity increase, because the sludge concentration in the MBR was high and the sludge loading decreased. The organic substances can be decomposed thoroughly at these conditions, and the influence of change in inlet water quality on the system and the loading of membranes were reduced.

(3) The retention of membranes plays a critical role in stabilizing the effluent quality.

The sludge retention time (SRT) in the MBR system was >30 days, hence it is largely greater than the HRT value because the sludge can be separated completely from water by membrane separation, which enriches the microorganisms that reproduce slowly (such as nitrobacteria). Hence the organic substances, which have difficult degradation, can decompose better. At the same time, the retention of membranes can ensure that the macromolecules and low degradable substances have enough retention time in the MBR and make the effluent quality stable. The COD values of effluent from the MBR system can be kept below 100 mg/L although the fluctuation of COD values in inlet water is great (from 710 to 1253 mg/L). This is mainly controlled by the high efficiency of membrane filtration.

3.2. NH₃-N removal effect

The content of nitrobacteria, which is the main microorganism for biological nitrification, and the influence of the nitrification rate is relatively low in traditional wastewater treatment systems, so increasing the content of nitrobacteria in the bioreactor becomes the primary problem in improving the denitrification ability [19,20]. In theory, the MBR system has the advantage of nitrification, because the whole retention of membranes to microorganisms provides a benefit for the reproduction of nitrobacteria. The nitrobacteria can grow freely in the MBR system and ensure the two necessary conditions for nitrification reaction: the quantity and quality of nitrobacteria.

The treatment effect of the MBR system on NH₃-N is shown in Fig. 5. The removal ratio of NH₃-N in the

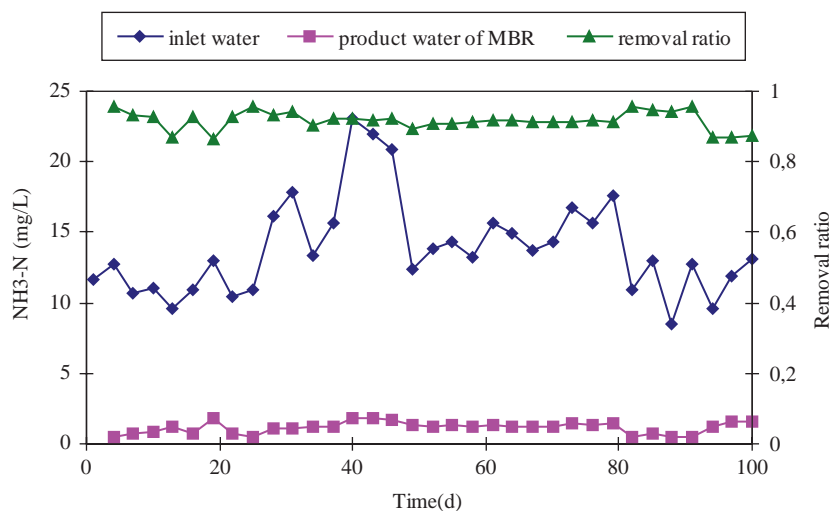


Fig. 5. Change of NH₃-N value and removal ratio with time.

MBR system could reach about 90%, and the $\text{NH}_3\text{-N}$ concentration in product water was lower than 2 mg/L which complies with the first class discharge standard of GB4287-1992 (15 mg/L). The retention of the membranes does not contribute to the removal of $\text{NH}_3\text{-N}$ because $\text{NH}_3\text{-N}$ exists in water as ions and can permeate through the micropores of the membrane. Therefore the concentration of $\text{NH}_3\text{-N}$ in the supernatant liquor was the same as that in the outlet water.

3.3. Colour removal effect

The membranes used in the MBR system have almost no retention of colour. The colour of the supernatant liquor was the same as that of the inlet water. The removal ratio of colour in the MBR system can reach 60 to 75% through the biochemical unit. The effluent colour level is between the first class (40 m^{-1}) and the second class discharge standard (80 m^{-1}) of GB4287-1992 because some chromophore groups are difficult in biodegradation and the membranes used in this system had almost no retention of dyes. This problem is now being studied by membrane distillation and the results will be published in following papers. However, it is already known that a complete dye rejection and recovery of pure water can be achieved using membrane distillation as reported in literature [21].

4. Conclusion

- (1) The COD removal ratio can be kept at 85–92% after 10 days of operation and the COD concentration of effluent remains lower than 100 mg/L at $\text{HRT} = 6 - 22.5$ h and $\text{MLSS} = 9 - 11$ g/L, which satisfied the first class discharge standard required in GB4287-1992 "Discharge standard of water pollutants for dyeing and finishing of textile industry" in China.
- (2) The MBR can maintain a higher SRT because the retention effect of membranes and the removal ratio of $\text{NH}_3\text{-N}$ in the MBR system could reach about 90%.
- (3) The effluent colour level is between the first class and the second class discharge standard and needs further study.
- (4) The retention of membranes plays a critical role in stabilizing the effluent quality.

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