New process for alleviation of membrane fouling of modified hybrid MBR system for advanced domestic wastewater treatment
Liu Shuo, Wang Baozhen, Han Hongjun and Liu Yanping

ABSTRACT
A pilot-scale hybrid membrane bioreactor using a submerged flat panel membrane was designed and applied for advanced treatment of domestic wastewater. The new process adapted to the hybrid membrane bioreactor exhibits substantial decrease in membrane fouling and much easier cleaning. In this study, the new process configurations including the addition of anoxic/anaerobic zones, the package of synthetic fibrous fabric carrier for biofilm attached growth, activated sludge recycling and modified dosage of polished diatomite with high activity and multi-functions were investigated to select the optimal operational parameters for the hybrid membrane bioreactor system. The carrier package in the aerobic zone contributed 3.65 g/L (maximum) of fixed biomass to the system, thus reducing the suspended biomass, and has decreased the membrane cleaning cycle remarkably. The operation performance at the sludge recycle rate 0, 100%, 200% and 300% showed that, the trans-membrane pressure of flat panel membrane declined sharply with the increase of sludge recycling rate within a certain range, and 200% was decided to be optimal for in the membrane bioreactor system. EPS concentration in each sludge recycling rate was 135 mg/L, 92 mg/L, 68 mg/L and 55 mg/L respectively. The addition of anoxic and anaerobic zones degraded some large molecular organic compounds, which facilitated the biodegradation and removal of organic substances in aerobic zone. The modified dosage of polished diatomite has played a major important role for both preventing of membrane from fouling and its much easier cleaning when it formed.

Key words | flat panel membrane, membrane fouling control, modified hybrid MBR, polished diatomite with high activity and multi-functions, synthetic fibrous fabric carrier

INTRODUCTION
The membrane bioreactor (MBR) is an innovative technology in which gravity settling of the activated sludge system is replaced by a membrane separation process. In recent years, submerged MBRs have become increasingly popular for domestic and industrial wastewater treatment. The utilization of MBR offers many advantages over the conventional activated sludge process, being compact, stable and providing a very high quality of effluent that is increasingly desirable where discharges go to recreational water, or to be reused for green belts watering, toilet flushing, recharge into underground water, etc., where is space constraint on the plant, or where upgrading of an existing installation is required (Howell et al. 2004). However, MBR processes have some serious problems, particularly membrane fouling and concentration polarization. When this occurs, a thick gel layer that usually consists of biological or abiotic substances is formed on and into the membrane causing the permeate flux to decline very fast. Many attempts have been made to reduce fouling by a large number of experiments and researches. Therefore, membrane fouling
control has become major issues for an economically feasible MBR system (Choi et al. 2002; Lee et al. 2002; Bae & Tak 2005).

Membrane fouling in MBR is influenced by membrane properties and filtration conditions such as trans-membrane pressure, cross-flow velocity, and module geometry, as well as sludge characteristics such as biomass concentration, floc size, and sludge rheology (Artiga et al. 2005; Drews et al. 2006). Recently, extracellular polymeric substances (EPS) have been identified as the major cause of fouling. To solve the membrane fouling problem, some optimal design and operational parameters have been chosen in MBR process, such as the optimal configuration of MBR, biomass concentration, aeration intensity, sludge recycling rate and so on.

In this study, a hybrid MBR system was initially designed to enhance nitrogen and phosphorus removal for domestic wastewater treatment. After 100 days’ operation, it was found that the modified hybrid MBR system is characterized by dividing anoxic, anaerobic and aerobic zones in configuration, packing synthetic fibrous fabric carrier for biofilm attached growth, aerobic sludge recirculation and adding polished diatomite, by means of which the modified hybrid MBR not only exhibited high removal rates of various main pollutants, but also alleviated the formation of membrane fouling and facilitated its cleaning when formed substantially.

Thus some experiments were conducted to study the influence of the packed synthetic fibrous fabric carrier, aerobic sludge recycling and polished diatomite addition on the operation performance, with the emphasis on membrane fouling alleviation and the improvement of its cleaning in the modified hybrid MBR system.

MATERIALS AND METHODS

Experimental equipment

A schematic design diagram of the pilot-scale modified hybrid MBR is shown in Figure 1, which consists of wastewater feed system, hybrid membrane bioreactor, effluent suction system, air supply system, sludge recycling system and control system.

The modified hybrid MBR with an effective volume of 190 L was divided into anoxic zone, anaerobic zone and aerobic zone. Six MF flat panel membrane modules from Shanghai Institute of Applied Physics, Chinese Academy of Sciences were packed and submerged in the aerobic zone, and its design parameters are shown in Table 1. A domestic product of novel synthetic fibrous fabric carrier was packed in aerobic zone, along with the membrane module. The domestic wastewater was fed to anoxic zone by influent pump, and then it was well mixed with recycling sludge, and then it was well mixed with recycling sludge from the aerobic zone.

![Figure 1](https://iwaponline.com/wst/article-pdf/58/10/2059/435905/2059.pdf)
Three mixers were equipped in anoxic zone and anaerobic zone to maintain sludge in suspension. The mixed liquid level in the modified hybrid MBR was controlled by a float level switch. The pH in aerobic zone was on-line detected by pH probe and maintained between 7, 8 by pH adjusting system. When the trans-membrane pressure was up to 40 kPa, the effluent pump was shuttled by the pressure gauge with electrical contact and then the membrane modules were started cleaning. To minimize membrane fouling, filtration was performed in intermittent fashion by alternating 13 min suction and 2 min pause and the treatment capacity of the modified hybrid MBR system was 0.5 ~ 0.6 m³/d.

**Experiment modes**

The experiment was divided into 7 phases and each phase operated 10 days. During the experiment periods, the flux for the membrane modules were maintained at 21.9 L/m²·h by suction pump with stable flux. At the end of each phase, the membrane modules were cleaned with chemical reagent. The operational conditions of membrane fouling lessening experiment are shown in Table 2.

**Raw wastewater and seed sludge**

The influent used in this study was domestic wastewater taken from a septic tank in the 2nd Campus of HIT. The seed sludge was obtained from Harbin 1st Municipal Wastewater Treatment Plant where a biological nutrient removal process has been adopted.

**Analytical methods**

Conventional analysis

The MLSS of the activated sludge were determined by standard methods. Molecular mass distribution in the modified hybrid MBR was measured by HPLC (Shimadzu, LC-10A, Japan), and chromatographic column applied gel column. Sludge particle size distribution was measured by a particle size analyzer (HIAC 9703, USA).

Measurement of EPS (extracellular polymeric substances)

The EPS solution from activated sludge was extracted using the CER extraction procedure (Frolund et al. 1996) and the

<table>
<thead>
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<th>Table 1</th>
<th>Membrane characteristics</th>
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<td>Parameter</td>
<td>Unit</td>
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<tr>
<td>Type</td>
<td>–</td>
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<tr>
<td>Dimension</td>
<td>Length × Width × Thickness (mm)</td>
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<tr>
<td>Area</td>
<td>m²</td>
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<tr>
<td>Mean pore size</td>
<td>μm</td>
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<tr>
<td>Flux</td>
<td>L/m²·h</td>
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<tr>
<td>Material</td>
<td>Modified polyethersulfone, PES</td>
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<td>Frame Material</td>
<td>ABS</td>
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<th>Table 2</th>
<th>Experimental operation conditions</th>
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<td>Phase</td>
<td>Days</td>
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<td>1</td>
<td>1–10</td>
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<td>2</td>
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<td>7</td>
<td>70–80</td>
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<td>8</td>
<td>80–90</td>
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*MLSS of suspended biomass.
†MLSS of total biomass including suspended biomass of 5 ~ 6 g/L and fixed biomass of 3 ~ 3.65 g/L.
amount of polysaccharides and protein in the EPS solution was referred to as “EPS concentration”.

The mixed liquid of activated sludge was collected from the aerated zones of the modified hybrid MBR and settled for 1.5h at 4, then the supernatant was decanted. Thickened sludge was centrifuged at 2,000 g for 15 min; after discharging the supernatant, the remaining pellet was resuspended to their original volume using a buffer consisting of 2 mM Na3PO4, 4 mM NaH2PO4, 9 mM NaCl and 1 mM KCl at pH 7, and then 60 g/gVSS CER(Cation Exchange Resin) was added. The suspension was stirred at 600 rpm for 2h and then was centrifuged again under the same conditions as above, and then the EPS in the supernatant was obtained in this manner. The protein in the EPS was measured by spectrophotometer methods; the Lowry method was used to quantify the protein using BSA (bovine serum albumin) as a standard; the anthrone-H2SO4 method was used for quantitative analysis of polysaccharides with glucose as a standard.

Morphological observation of membrane surface

Changes in the cake layer of flat panel surface were evaluated by scanning electron microscopy (SEM), using a S-4700 Hitachi apparatus.

RESULTS AND DISCUSSION

Package of synthetic fibrous fabric biofilm carrier

A MBR system can maintain higher MLSS concentration compared to a conventional activated sludge system through membrane separation technology. Many MBR researchers have operated their systems with higher biomass concentration, which could give rise to higher treatment efficiency. However, higher MLSS concentration could accelerate membrane fouling via rapid deposition of sludge particles on the membrane surface. In the modified hybrid MBR system, synthetic fibrous fabric carrier was packed in aerobic zone, which was intended to improve nitrification efficiency initially. However, the operational performance showed that the packed synthetic fibrous fabric carrier also alleviated membrane fouling effectively.

The influence of biofilm carrier on membrane fouling alleviation was observed, and the variations of suction pressure in the modified hybrid MBR with or without biofilm carrier package in aerobic zone are shown in Figure 2.

As shown in the Figure 2, the effects of synthetic fibrous fabric biofilm carrier package on the suction pressure appear to be significant within the tested range. After the package of biofilm carrier, the trans-membrane pressure was declined from 35 kPa to 22.5 kPa with the same operational time, from which it was found that suspended biomass contributed to the membrane fouling more than that of fixed biomass (biofilm). The biofilm carrier package in aerobic zone contributed 3.65 g/L (maximum) fixed biomass to the system. As a result, the suspended biomass was reduced, thus improving the membrane cleaning cycle remarkably. Although it maintained the similar total biomass concentration, the package of synthetic fibrous fabric biofilm carrier made the curve of suction pressure increase slower than that without biofilm carrier package. Therefore, the operational time of the modified hybrid MBR was extended with the increase of biofilm or fixed biomass.

Activated sludge recycling

The variation of trans-membrane pressure was measured in the operation of the modified hybrid MBR at the recycling rates ranging from 0 to 300%, and the result is illustrated in Figure 3.

When the sludge in aerobic zone was recycled to anoxic zone, as expected, the increased rate of trans-membrane pressure was decreased, while the trans-membrane pressure at sludge recycling rate of 0, 100%, 200% and 300%

Figure 2 | Variation of trans-membrane in the modified hybrid MBR with or without carrier packing.
was decreased to 22.5 kPa, 18.5 kPa, 14.5 kPa and 12.5 kPa respectively. It was observed that the trans-membrane pressure of flat panel membrane modules declined sharply with the increase of activated sludge recycling rate, which indicated that sludge recycling could extend operation time of membrane modules in the modified hybrid MBR.

To further investigate the effect of sludge recycling on the alleviation of membrane fouling, the EPS, which had been proved to cause membrane fouling dominantly, was analyzed at various recycling rates. Since EPS matrix is widely heterogeneous, in which a variety of polymeric materials have been found: carbohydrates, proteins, lipids and nucleic acids. In this study, however, the sum of total carbohydrates and proteins was considered to represent the total amount of EPS, because both of them are the dominant components typically found in extracted EPS.

The concentrations of carbohydrate, protein and EPS in mixed liquid at various sludge recycle rates are shown in Figure 4. During 40 day operation of the modified hybrid MBR system, at the end of each phase, the EPS concentration of mixed liquid in aerobic zone was measured. Under the sludge recycling rate of 0, 100%, 200% and 300%, the EPS concentration was 135 mg/L, 92 mg/L, 68 mg/L and 55 mg/L respectively. In contrast to EPS content of mixed liquid at sludge recycle rate 100%, 200% and 300%, no sludge recycling had a relatively high carbohydrate and protein concentration as well as high trans-membrane pressure. Although, the EPS concentration decreased with the increase of sludge recycling rate, in each hybrid MBR system, it had an economic recycle rate and in this study, it was 200%.

**Addition of anoxic and anaerobic zones**

The modified hybrid MBR system was divided into anoxic, anaerobic and aerobic zones. The addition of anoxic and anaerobic zones contributed to the degradation of large molecular substances with partial removal of organic substances in form of final liquid or gaseous products, such as CO2, H2O, CH4, N2 and H2 that left from the system.

During the operation of modified hybrid MBR system with sludge recycling rate of 200%, the molecular weight distribution of SMP in different zones of the modified hybrid MBR was analyzed, and the result proved that the sludge recycling promoted the degradation of EPS from large molecules into small ones in anoxic and anaerobic zones of the modified hybrid MBR. The molecular weight distribution of SMP in different zones of the modified hybrid MBR system is shown in Figure 5, from which it is evident that large molecular and small molecular...
substances coexisted in aerobic zone, however, only small molecular substances existed in anaerobic zone. The large molecular pollutants appearing in aerobic zone were the EPS released by air bubbling, which were not degraded or hardly degraded by aerobic bacteria, while in the anaerobic zone the large molecular substances were degraded into small ones, which means that the sludge recycling between the aerobic and anaerobic/anoxic zones promoted the realization of this phenomenon.

Application of polished diatomite to improve membrane filtration

Diatomite, also referred to diatomaceous earth, is durable, extremely lightweight and highly porous. It has a large surface area of 50–200 m$^2$/g (Yang et al. 1996) and mainly consists of the fossilized skeletons of diatoms, which were once marine planktons and algae. There were isolated and H bonded hydroxyl groups detected on the surface of diatomite. Due to its unique physical and chemical properties, diatomite has been put into industrial application as filtration media for various beverages.

In this study the polished diatomite with purity of 90% or greater was used to improve the anti-fouling performance of flat panel membrane modules in the modified hybrid MBR system. The modified diatomite powder was provided by Yunnan Qingzhong Environmental Co. Ltd., China. According to manufacturer’s information (Aytas et al. 1999; Qingzhong Environmental Co. Ltd 2004) diatomite was produced by milling diatomaceous sedimentary rock, and then refined and purified using a low-cost physical method instead of conventional expensive technique (i.e. acid washing). The refined diatomite contains 98% diatoms, which have honeycomb structure and particle size ranging from 40 to 200 $\mu$m.

The effect of diatomite addition on suction pressure increase, i.e., membrane fouling is shown in Figure 6, which indicates that the suction pressure was dropped by means of diatomite addition due to the improved filtration characteristics through membrane resulted from huge surface and multi-porous structure of diatomite. It should be noted that, excess diatomite addition for the alleviation of membrane fouling can result in high mass concentration in the modified hybrid MBR system, thus causing an increase of power consumption. In the modified hybrid MBR system for domestic wastewater treatment, the optimal dosage of polished diatomite is 5 g/L.

To investigate the floc size variation in the modified hybrid MBR system with diatomite addition, the sludge floc size distribution with different dose of polished diatomite is shown in Figure 7, which showed that the microbial floc size in aerobic zone was investigated in the range of 2–270 $\mu$m. With the increase of polished diatomite dose, the percentage of sludge floc size less than 10 $\mu$m were declined, however, the percentage of sludge floc size between 10–30 $\mu$m were increased correspondingly. The results showed that due to the polished diatomite dose, the small size of sludge floc was absorbed into inner pore of diatomite which caused the percentage of small size floc to decrease.

In Figure 8, the SEM images show the cake layer structure of flat panel membrane surfaces with 5 g/L and
0 g/L polished diatomite adding. With 5 g/L polished diatomite added, the membrane surface is observed to be porous and free of particles (Figure 8a). With no polished diatomite adding, the cake layer of membrane surface is observed to be dense and non-porous (Figure 8b).

It can be seen that the fouling cake, formed with 5 g/L polished diatomite adding, had a much higher porosity than with 0 g/L polished diatomite adding. The screening, blocking and adsorption functions of polished diatomite resulted in the formation and maintenance of a relatively higher porous cake layer which keep slow increase of suction pressure and membrane resistance.

CONCLUSIONS

The study demonstrated that the membrane fouling can be alleviated by the addition of anoxic and anaerobic zones, the package of synthetic fibrous fabric biofilm carrier, the recirculation of activated sludge and the application of polished diatomite with high purity and activity in the modified hybrid MBR system for domestic wastewater treatment. All the methods mentioned above have improved the removal efficiency for organic pollutants, nitrogen and phosphorus along with the alleviation of membrane fouling. Therefore, the new type of modified hybrid MBR system developed by the authors can be applied to municipal and domestic wastewater treatment projects, with the optimal operational parameter as follows: the total biomass should be controlled within the range of 8–10 g/L, of which the carrier package in aerobic zone contributed 3.65 g/L fixed biomass to the system and the suspended biomass maintain 5–6 g/L. With the biofilm carrier package, the optimal sludge recycle rate is 200%. The low EPS concentration will promote operational cycle of MBR system. The large molecular substance generated in aerobic zone can be degraded in anoxic and anaerobic zones. The polished diatomite application with the optimal dose of 5 g/L alleviated flat panel membrane fouling and improved the operational performance with the advantages of energy saving, cost effectiveness, high removal efficiency for various main pollutants and longer operation time with stable flux.

It should be noted that as the synthetic fibrous fabric carrier packed in the modified hybrid MBR was limited with much less package density as designed, with the package volume rate of only 5% vs 20% as normal. As a result, the fixed biomass (biofilm) was only 3.65 g/L, compared to 10–15 mg/L at package rate of 20%, and the typical ratio of suspended biomass to fixed biomass is 3:7, at which the performance of the modified hybrid MBR will further improved both in the alleviation of membrane fouling and the improvement of pollutant removal.

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REFERENCES


