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Treatment of micro-polluted water resource loaded with 2,4,6-trichlorophenol by a membrane bioreactor (MBR)

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ABSTRACT

A laboratory-scale flat-sheet membrane bioreactor (MBR) was employed to treat real micro-polluted surface water loaded with 2,4,6-trichlorophenol (2,4,6-TCP). MBR treatment performances were evaluated in terms of dissolved organic matters (DOM) degradation, target trace organic (2,4,6-TCP) removal, and effluent bio-stability improvement. The experimental results showed that the removal efficiency of DOM related closely with the biomass content in MBR. With continuous growth and accumulation of biomass under a long sludge retention time (SRT), stable DOM removal efficiency above 50% could be obtained, resulted in an effluent DOM kept below 2.0 mg TOC/L. Upon the steady state of MBR, more than 90% 2,4,6-TCP was removed by synergistic function of aeration volatilization, biological degradation, and activated sludge adsorption. The removal pathways of 2,4,6-TCP were specified by series of batch-scale trials, and corresponding contributions were estimated. It was revealed that fresh ultrafiltration rejection took a major responsible for 2,4,6-TCP removal in the start-up phase, which rejected about 15% 2,4,6-TCP. In comparison, for a steady state where had a high biomass content around 450 mg/L, biodegradation was the main pathway for 2,4,6-TCP removal, reflected by that above 300 μg/L 2,4,6-TCP was eliminated by microorganism degradation within no more than 1.2 h. The results herein claimed that MBR is a feasible way to treat micro-polluted water resource, and its removal pathway specification gave reliable guidance for MBR application.

Keywords: Membrane bioreactor (MBR); 2,4,6-Trichlorophenol (2,4,6-TCP); Biodegradation; Micro-polluted water resource

1. Introduction

Water resource is subject to a potential pollution from irregular discharge of domestic and industrial wastewaters in numerous of developing countries. For instance in some areas of China, surface water around urban agglomeration is being polluted and contains organic pollutants and refractory chemicals, leading to a serious risk for water supply. These organic matters, especially some chlorinated organic matters that are

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typically refractory and high toxicity to human beings [1], are important concerns in drinking water treatment [2]. For example, as one of potential water pollutants with pungent smell, trichlorophenol (2,4,6-TCP) has been widely used in the preparation of biocides and flame retardant and therewith is now found in natural water in many areas of southern China [3]. Since that it is of high chemical stability and easy to deposit in natural environment, 2,4,6-TCP is a member of the blacklist of hackneyed organic contaminant [4], whose standard in drinking water enacted in China is below 200 μg/L. However, it was reported that traditional drinking water treatment process has rather limited 2,4,6-TCP removal capability, makes the drinking water quality at risk [5].

Membrane bioreactor (MBR) is an attractive technology for wastewater and water treatment [6]. By combining biological degradation process with membrane filtration for direct solid–liquid separation [7,8], MBR has its own merits, such as a high biomass content, an excellent effluent quality independent on sludge solids properties, and an easy-manipulation [9,10]. MBR has been employed in the field of advanced treatment of drinking water [9, 11]. Notwithstanding, its treatment performance may be affected by the low biomass content accompanied with limited organic substances concentration in water resource [12]. Accordingly, many efforts have been made to enrich biomass concentration in MBR, including biomass augment and additional activated carbon dosage, to achieve a stable organic contaminants removal efficient by an individual MBR [13].

However, the removal pathways of specific organic contaminant in MBR should be clarified to get more evidenced guideline for its removal stability and enhancement. Chen and his coworkers found that biodegradation was the major way for bisphenol A (BPA) removal in MBR system, while activated sludge could also adsorb a certain amount of BPA [14]. Fallah found that a long-term operation of submerged MBR was able to remove styrene effectively, and up to 99% styrene was removed by biodegradation [15]. MBR also displayed a better removal efficiency in persistent organic pollutants (POPs) in contrast with the conventional activated sludge process, due mainly to its retention of biomass [16, 17]. As for 2,4-dichlorophenol and 2,4,6-TCP removal, Wang et al. found that a high removal efficiency above 95% could be stably achieved in a sequencing batch reactor (SBR), which mainly attribute to biodegradation [18, 19]. However, there were a few reports on 2,4,6-TCP removal in an individual MBR system, and accordingly to specify its removal pathway, to the best known of author's.

Therefore, the objective of this study was to evaluate the treatment performance of MBR treating micro-polluted water resource containing 2,4,6-TCP, and to specify its removal pathway under different sludge discharge interval. Total organic contaminants removal efficiency was investigated when there was limited extra sludge discharge. The results herein claimed that MBR is a feasible way for treatment of micro-polluted water resource, and its removal pathway specification gave reliable guidance for MBR application.

2. Materials and methods

2.1. Laboratory-scale flat-sheet MBR setup and experimental operation

A laboratory-scale submerged MBR with a working volume of 2.4 L was operated in a room temperature (~25°C) to treat micro-polluted water resource (Fig. 1). Flat-sheet polyvinylidene fluoride ultrafiltration (UF) membranes (surface area = 0.08 m^2, Peier, China) with an average pore size of 0.08 μm was immersed for sludge–liquid separation. A suction pump (BT100–2 J, Longer, China) was used to withdraw the effluent through the membrane at a filtration-to-idle cleaning ratio of 8 min: 2 min. Aeration was provided at the bottom of the reactor for dissolved oxygen (DO) supplement and continuous membrane cleaning, and the aeration intensity was kept consistently at 1.2 $m^3/(m^2 \cdot h)$. The MBR was operated in a constant-flux mode that was ranged from 25 to 30 $L/(m^2 \cdot h)$, resulted in a HRT ranged from 1 to 1.2 h. The trans-membrane pressure (TMP) was monitored by a manometer in mmHg to indicate membrane

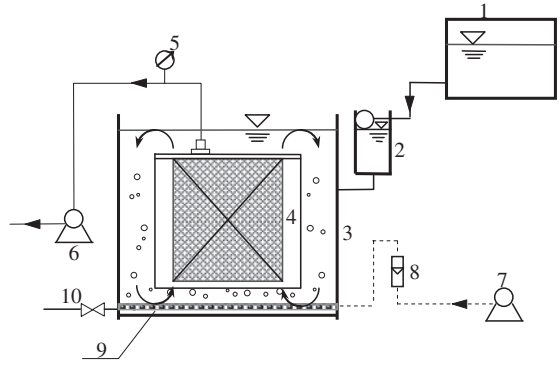

Fig. 1. Schematic diagram of the experimental setup (1) High level raw water tank; (2) constant level water tank; (3) bioreactor; (4) flat ultrafiltration module; (5) manometer; (6) suction pump; (7) aeration pump; (8) air flow meter; (9) air diffuser; (10) discharge valve.

fouling development. After a severe membrane fouling, membrane module was taken out from the reactor and gently washed by tap water for membrane flux recovery. According to the variation of sludge discharge interval, two operational phases were assigned. Phase I lasted for more than 60 d where sludge discharge was performed every day. Afterward, sludge was not discharged from day 60, which was termed as Phase II. Thus, the SRT in Phase I and Phase II was about 2 and 20 d, respectively.

Real raw water resource collected from a local reservoir (Xili reservoir, Shenzhen, China) was used to prepare micro-polluted water resource containing DOM and 2,4,6-TCP. Analytical reagent 2,4,6-TCP (Aladdin, China) was dissolved in raw water in a predetermined concentration. On average, MBR influent contained the total organic carbon (TOC) and ammonia-N content of 2.0 and 1.3 mg/L, respectively.

2.2. Biodegradation kinetics of 2,4,6-TCP

The maximum specific 2,4,6-TCP removal rate (q_{max}) was determined following the procedure developed in the previous report [20]. In brief, a glass beaker with a working volume of 4 L was used as a batch reactor. An air diffuser was fixed at the beaker bottom to provide DO. Upon the steady state of MBR, activated sludge was collected from MBR for substrate utilization rate measurement. More than 50 mL suspended solution was collected every 30 min to analyze its 2,4,6-TCP concentration, which was then plotted against reaction time to calculate 2,4,6-TCP biodegradation kinetic. The mass balance equation of 2,4,6-TCP in the reactor could be described by Eq. (1).

$$\frac{dS}{dt} = \frac{S_i \times Q}{V} - qX \quad (1)$$

where: S = 2,4,6-TCP concentration in the reactor, mg/L; t = hydraulic retention time, d; S_i = 2,4,6-TCP concentration in influent, mg/L; Q = influent flow rate; L/d; V = mixed liquor volume in reactor, L; q = specific substrate removal rate, d^{-1}; X = biomass concentration in batch reactor, mg/L.

During the substrate utilization measurement test, more than 3 L raw water resource and centrifuged mixed sludge solid from MBR was re-suspended to form a mixed solution contained a biomass content of 540 mg SS/L. A peristaltic pump with a constant flux of 1.5 mL/min was used to pump 200 mg/L 2,4,6-TCP into the reactor. Continuous aeration provided the same DO concentration in the batch reactor with that in MBR. Accordingly, Eq. (1) was converted to Eq. (2), where $v = dS/dt$, $v_i = S_i \cdot Q/V$.

$$q_{max} = \frac{v_i - v}{X} \quad (2)$$

2.3. Analytical methods

MBR influent, bulk solution and effluent were sampled twice a week for their pollutants analysis. MBR treatment performance was evaluated in terms of TOC, ammonia-N and 2,4,6-TCP removal efficiencies. TOC was measured by the TOC analyzer (TOC-L CPN, Shimadzu, Japan) using the high-temperature combustion method. The concentration of activated sludge in MBR tank was measured as mixed liquor suspended solids (DR850, Hach, USA). 2,4,6-TCP concentration was determined following US EPA Method 609 by gas chromatography (7890A, Agilent, USA).

3. Results and discussion

3.1. Organic pollutants removal

In micro-polluted water resource, organic contaminants mainly comprised of natural organic matters, which are hardly removed iwas observed that adsorption quantitin conventional drinking water treatment process. During the experimental phases, MBR influent had an average DOM of 4.09 ± 0.80 mgTOC/L. In Phase I, around 24.7% organic matters could be removed in MBR (Fig. 2(a)). However, the DOM concentration of MBR bulk was rather close to those in its influent. Considering that there was limited biomass content within MBR bulk in this phase, it was thought that organic matters were mainly retained by UF membrane in a short SRT, rather than biodegradation.

In comparison, in the beginning of phase II, organic contaminants were gradually accumulated in MBR bulk where DOM concentration increased from 3.5 to 5.5 mgTOC/L on day 70, which was relatively higher than those in its influent. Notwithstanding, the DOM content in MBR effluent was kept stable that was independent with the MBR bulk accumulation and variation of raw water.

During Phase II, a long SRT resulted in a relative high biomass content that helps to form a cake layer on the UF membrane surface, which could effectively reject organic matters from MBR bulk. It was estimated that cake layer could retained more than 3 mg TOC/L DOM on average to result in a stable low DOM content in MBR effluent. With a short HRT around 1.2 h,

activated sludge was not enriched in the first several days of Phase II. Thus, it was reasonable to deem that sludge adsorption and therewith biodegradation was the dominant way for DOM removal in MBR.

Fig. 2(b) illustrated the 2,4,6-TCP removal profile in MBR during Phase I and II. In the very beginning of Phase I, with a 2,4,6-TCP concentration in MBR influent averaged at 390 μg/L, the 2,4,6-TCP content in its effluent ranged from 220 to 260 μg/L, which related closely with the fluctuation of influent. This limited 2,4,6-TCP removal efficiency attributed to insufficient biomass available for organic degradation. With continuous membrane filtration and biomass accumulation, the bulk 2,4,6-TCP concentration decreased gradually to 100 μg/L. As for Phase II, the 2,4,6-TCP removal efficiency was consistently higher than those in Phase I. An adequate air supplement and a long sludge discharge interval resulted in great enrichment of biomass that could be acclimated to biodegrade 2,4,6-TCP. Therefore, after an accumulation of biomass, activated sludge ought to remove more than 250 μg/L 2,4,6-TCP from micro-polluted water resource by adsorption and biodegradation, resulting to a much lower 2,4,6-TCP concentration in the MBR bulk than those in its influent. When the 2,4,6-TCP concentration in MBR influent kept at 400 μg/L, the 2,4,6-TCP concentration in its bulk averaged at 89 μg/L. The difference of 2,4,6-TCP removal performance in these two phases confirmed MBR system could effectively remove micro-polluted water resource when it contained sufficient biomass content. With the combination of activated sludge degradation and membrane filtration, 2,4,6-TCP concentration in MBR effluent declined below 100 μg/L, which stably satisfied the national drinking water standards.

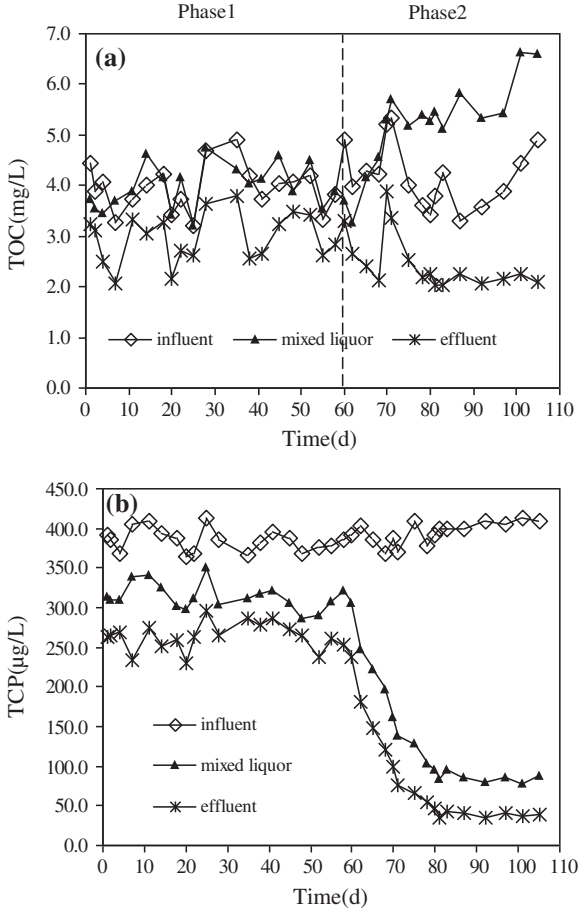

Fig. 2. TOC and 2,4,6-TCP removal performance in Phase I and II, (a): TOC concentration in MBR influent, mixed liquor and effluent; and (b) TCP concentration and variation in MBR influent, mixed liquor and effluent.

3.2. Biomass growth and accumulation in the MBR

In Phase I where aeration intensity was kept about 1.25 $m^3/(m^2 \cdot h)$ and daily sludge discharge was

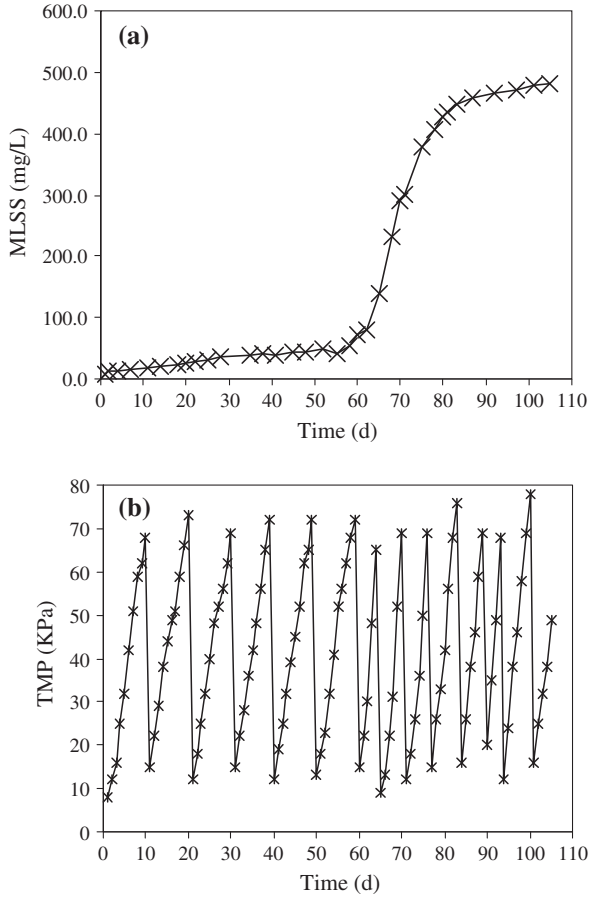

Fig. 3. Growth of MLSS (a) and development of TMP (b).

performed, no biomass accumulation was observed in the MBR bulk (Fig. 3(a)). It was estimated that the biomass content indicated as MLSS was less than 50 mg/L. Owing to insufficient aeration intensity for suspension mixing, sludge solids preferentially settled in the MBR bottom, which might constrain their effective substrate utilization.

During Phase II, by increasing the aeration intensity for stirring strengthen, and extending sludge discharge interval, biomass content increased up to 450 mgMLSS/L on day 80. The average MLSS growth rate was estimated to be 20 mg/(L·d) in the beginning of Phase II and then reduced to about 2 mg/(L·d) until a stable biomass reached to 480 mg/L.

TMP was monitored regularly to indicate membrane fouling evolution. Due to the deposition and continuous accumulation of suspended sludge onto membrane surface, a cake sludge layer formed and then led to a rapid increase of TMP. However, the cake layer had a rather loose structure that could be detached or removed by simple tap water washing and then reduced TMP to below 15 kPa. In contrast to Phase I, higher biomass content in Phase II could accelerate membrane fouling, and the average TMP evolution rate increased from 5 to 7 kPa/d. Throughout the experimental phases, there was very slight irreversible fouling occurred, as that physical method could recover more than 95% of membrane permeability (Fig. 3(b)).

3.3. TCP removal pathway analysis

3.3.1. Adsorption

Sufficient biomass content was essential for removal of organic substances, especially refractory organics. It is generally believed that biological adsorption and thereafter biodegradation are major processes for organic matters removal in activated sludge system. Nguyen found that sorption was the dominant way for removal micro-pollutants including 2,4,6-TCP, which was independent with biological activities [21]. In contrast to activated sludge process, co-existence of suspended solid in MBR bulk and attached solids on membrane surface would take major responsible for 2,4,6-TCP removal. In order to quantify the contribution of different solids, series of oscillation adsorption tests were carried out to estimate their adsorption capacity. The relationship between equilibrium adsorption capability and equilibrium concentrations by suspended solids was showed in Fig. 4. It was observed that adsorption quantities of 2,4,6-TCP by sludge solids increased with the increasing of equilibrium concentration. By regression, Freundlich's adsorption equation had the best

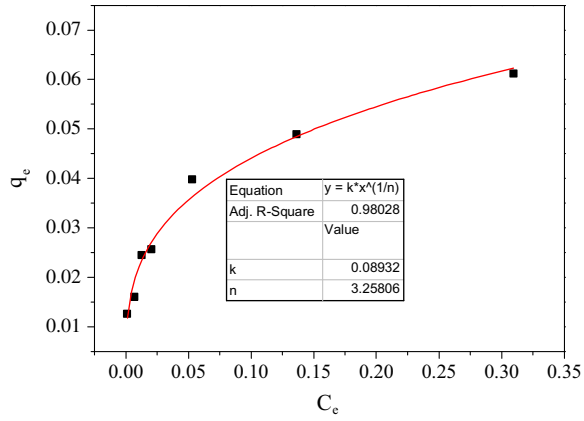

Fig. 4. 2,4,6-TCP adsorptive capacity of activated sludge.

fitting degree with the experimental results, and the adsorption capacity q_e could be obtained by Eq. (3).

$$q_e = 0.089 \times C_e^{\frac{1}{3.258}} \tag{3}$$

Considering the variation of activated sludge content with MBR operation and experimental progression, Eq. (3) could be modified into Eq. (4).

$$C_{\text{ad-bulk}} = q_e \times \Delta\text{MLSS} = 0.089 \times C_{\text{mix}}^{\frac{1}{3.258}} \times \Delta\text{MLSS} \tag{4}$$

where C_{mix} was 2,4,6-TCP concentration in mixed liquor, $C_{\text{ad-bulk}}$ was reduction of 2,4,6-TCP concentration caused by sludge adsorption in MBR bulk solution, and ΔMLSS was the change of biomass content during one HRT.

Cake sludge on the membrane surface was gently collected and tested to quantify the 2,4,6-TCP adsorption by attached solids, and its contribution for 2,4,6-TCP removal could be estimated by Eq. (5).

$$C_{\text{ad-m}} = \frac{M_{\text{de}}}{T \times 2.4 \times 24/\text{HRT}} \tag{5}$$

where $C_{\text{ad-m}}$ was reduction of 2,4,6-TCP concentration caused by adsorption of attached sludge, M_{de} was the mass of 2,4,6-TCP adsorbed by membrane sludge cake that was measured in the desorption test, and T was the cycle of membrane cleaning.

3.3.2. Biodegradation

Suspended solids collected from Phase I and II were used to test their degradation activities in a simulate reactor by measuring the concentration of

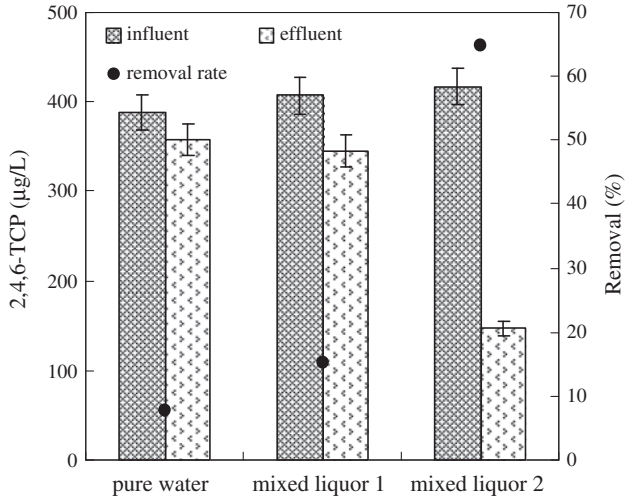

Fig. 5. 2,4,6-TCP removal by mixed liquor from MBR in activated sludge process.

2,4,6-TCP in mixed liquor after 2 h operation. As showed in Fig. 5, aeration volatilization could remove less than 7.7% 2,4,6-TCP from pure water (decreased from 388 to 358 μg/L) and remove up to 15% 2,4,6-TCP from MBR suspended solution (from 407 to 345 μg/L). The discrepancy of 2,4,6-TCP removal between mixed liquor and pure water was mainly caused by the involvement of activated sludge adsorption and biodegradation, and it was estimated that more than 32 and 40 μg/L 2,4,6-TCP was eliminated by sludge from Phase I and II, respectively. Thus, the 2,4,6-TCP removal capability by biodegradation could be calculated by Eq. (6).

$$E_{bio} = \frac{C_0 - C_e - C_{vol}}{MLSS} \quad (6)$$

where E_{bio} was the biodegradation capability of activated sludge (mg-2,4,6-TCP/g-MLSS). C_0 and C_e was 2,4,6-TCP concentration in the suspended solution in the beginning and at the end of the test, respectively. C_{vol} was the 2,4,6-TCP concentration removal by aeration volatilization.

Accordingly, E_{bio} for the suspended solids in Phase I and II was 0.8 and 0.6 mg 2,4,6-TCP /g-MLSS, respectively, and the 2,4,6-TCP biodegradation capability of MBR system could be calculated by Eqs. (7) and (8).

$$C_{bio\text{-}1} = 0.8 \times MLSS \quad (7)$$

$$C_{bio\text{-}2} = 0.6 \times MLSS \quad (8)$$

where $C_{bio\text{-}1}$ and $C_{bio\text{-}2}$ was 2,4,6-TCP biodegradation capability in phase 1 and phase 2, respectively.

The kinetic parameter of 2,4,6-TCP biodegradation in MBR was estimated, and the results were showed in Fig. 6. In the beginning of operation, there was very limited biological activity in MBR for 2,4,6-TCP removal (Fig. 6(a)). After several weeks, microorganisms gradually acclimated for degradation of 2,4,6-TCP. It could be calculated that 2,4,6-TCP cumulative rate (v) was 0.0086 mg/(L·min) when its feeding rate (v_i) was 0.0238 mg/(L·min), in the Phase I steady state period (Fig. 6(b)). After the biomass increased to about 450 mg/L in Phase II, q_{max} reached to 0.002 h^{-1}, and then the maximum 2,4,6-TCP removal capacity by biodegradation was up to 2 mg 2,4,6-TCP/g·MLSS·h.

3.3.3. Rejection

UF had a good rejection capability in water treatment, and it was able to intercept suspended solids,

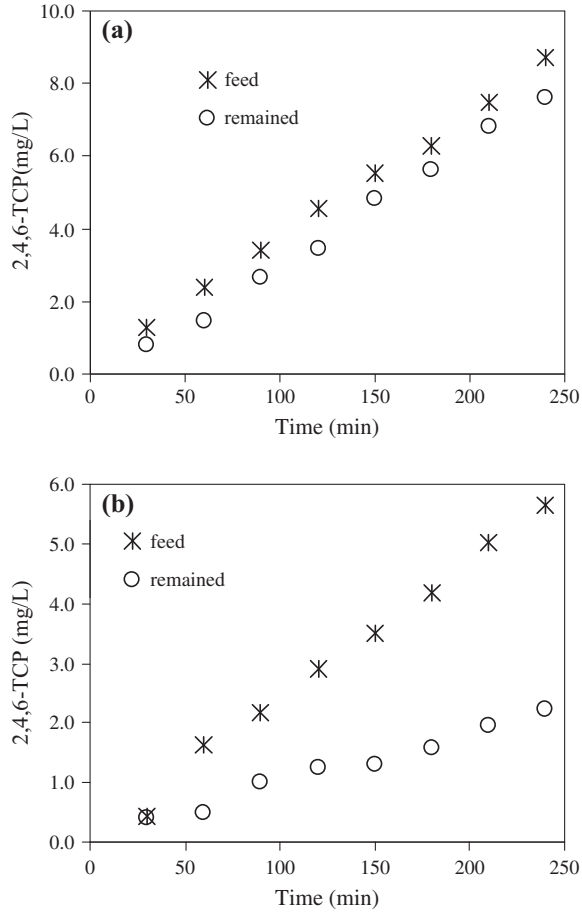

Fig. 6. Biodegradation kinetics for 2,4,6-TCP in the first (a) and second phases (b).

micrometer size particles, and microorganisms from raw water resource [22]. In MBR system, UF substituted conventional sedimentation tank to retain pollutants and suspended biomass, resulted to a high biomass concentration in bulk solution that was beneficial for the pollutants removal and treatment [23]. By comparison of 2,4,6-TCP concentration in MBR mixed liquor and its permeate, the rejection capability of membrane could be evaluated. As showed in Fig. 7(a), UF could retain more than 17% 2,4,6-TCP in Phase I, which was thought to be mainly caused by intrinsic membrane rejection. In comparison, during Phase II, the 2,4,6-TCP rejection efficiency increased gradually from 17 to 50%. This membrane rejection improvement attributed to continuous enrichment of biomass and attachment or formation of cake layer on membrane surface. Moreover, increased biomass content would also enhance biodegradation capability and then reduce 2,4,6-TCP content in MBR bulk. Notwithstanding, the relative lower 2,4,6-TCP concentration compared to DOM made the extent of membrane rejection improvement rather limited.

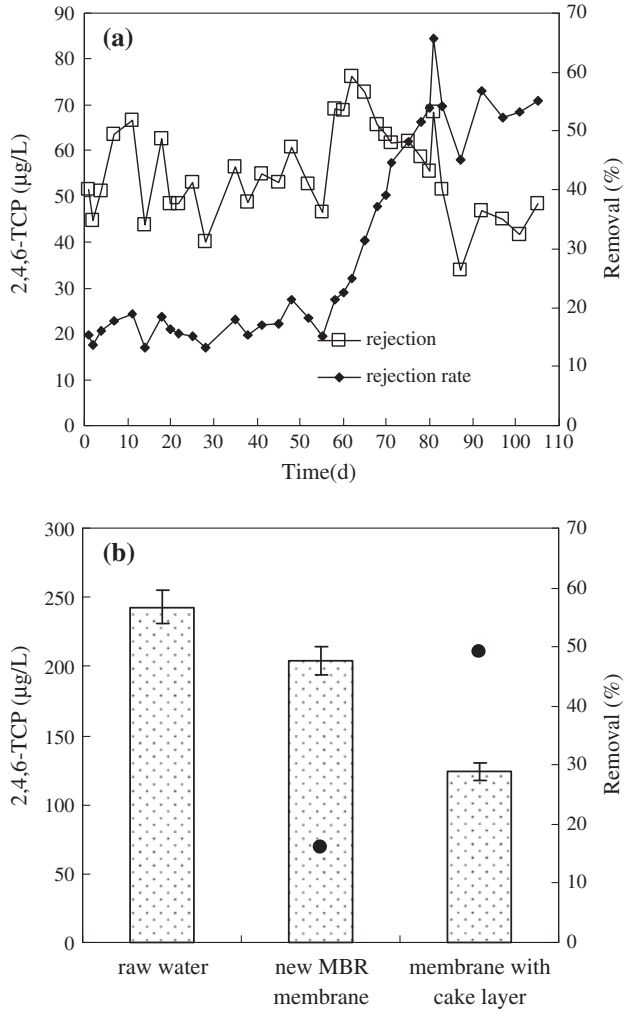

Fig. 7. Performances of UF membranes on 2,4,6-TCP rejection in MBR operation (a) and text (b).

To specify rejection efficiencies of fresh UF membrane and cake-covered membrane, an experimental trial was conducted using the membranes with and without sludge layer to filtrate raw water containing 2,4,6-TCP. As showed in Fig. 7(b), fresh UF membrane had a relative low rejection efficiency of 2,4,6-TCP of only about 19% from water. However, with a biomass cover rate of 1,320 mg SS/m^2 on the membrane surface, more than 51% 2,4,6-TCP could be rejected. It was recognized that cake layer adhered to membrane surface could significantly enhance membrane rejection efficiency. As small size particles would clog UF pore, while large size particles could build up a retention layer to adsorb or intercept pollutants, the rejection efficiency in removing small molecular weight organic matters was improved significantly [24].

3.4. Importance of suspended and attached solids to 2,4,6-TCP removal

Biomass accumulation and therewith cake layer formation on the membrane surface in MBR took major responsible for the enhancement of 2,4,6-TCP removal in Phase II. With sufficient biomass in MBR bulk, 2,4,6-TCP removal by means of solids adsorption, biological degradation and cake-enhanced membrane rejection would be improved. As the descriptions displayed in Eqs. (4), (7), and (8) for relationship of MLSS and 2,4,6-TCP adsorption, MLSS and biodegradation processes in phase 1 and 2, respectively, 2,4,6-TCP concentration in MBR effluent could be calculated by Eqs. (9) and (10).

$$C_{e\text{-}1} = C_0 - C_{vol} - C_{ad} - C_{bio-1} - C_{fil} = C_0 - 30 - 0.089 \times C_{mix}^{\frac{1}{3.258}} \times \Delta MLSS - 0.8 \times MLSS - C_{fil} \quad (9)$$

$$C_{e\text{-}2} = C_0 - C_{vol} - C_{ad} - C_{bio-2} - C_{fil} = C_0 - 30 - 0.089 \times C_{mix}^{\frac{1}{3.258}} \times \Delta MLSS - 0.6 \times MLSS - C_{fil} \quad (10)$$

where $C_{e\text{-}1}$ and $C_{e\text{-}2}$ were 2,4,6-TCP concentration in effluent in phases 1 and 2, respectively, C_{fil} was the contribution of membrane filtration in 2,4,6-TCP removal.

Fig. 8(a) illustrated the contributions of adsorption, biodegradation, and filtration processes for 2,4,6-TCP removal in MBR. It was observed that the amount of 2,4,6-TCP adsorption by biomass related closely with the MLSS enrichment profile, i.e., MLSS growth rate. In Phase I when MLSS in MBR bulk was kept less than 100 mg/L, and its growth rate was about 0.7 mg SS/d, only less than 0.1 μg/L 2,4,6-TCP could be removed by adsorption. In comparison, when MLSS growth rate increased from day 60 to day 80 in Phase II, 2,4,6-TCP removal by sludge adsorption increased gradually up to 0.4 μg/L. Notwithstanding, during the whole operational period, the biomass adsorption was relative lower compared with other two removal pathway, and its contribution for overall 2,4,6-TCP removal was averaged less than 10 μg/d.

2,4,6-TCP adsorption by cake sludge attached on the membrane surface was influenced by the cake sludge formation process. As shown in Fig. 8(a), cake sludge had a greater capability in 2,4,6-TCP adsorption compared with the suspended sludge did. Thanks to the membrane rejection for 2,4,6-TCP near membrane surface, a concentration polarization layer with a high 2,4,6-TCP content would be formed that was beneficial for an effective 2,4,6-TCP adsorption by cake sludge. On average, 0.45 and 0.61 μg/L of 2,4,6-TCP could be stably removed by cake sludge adsorption in phase I and II, respectively.

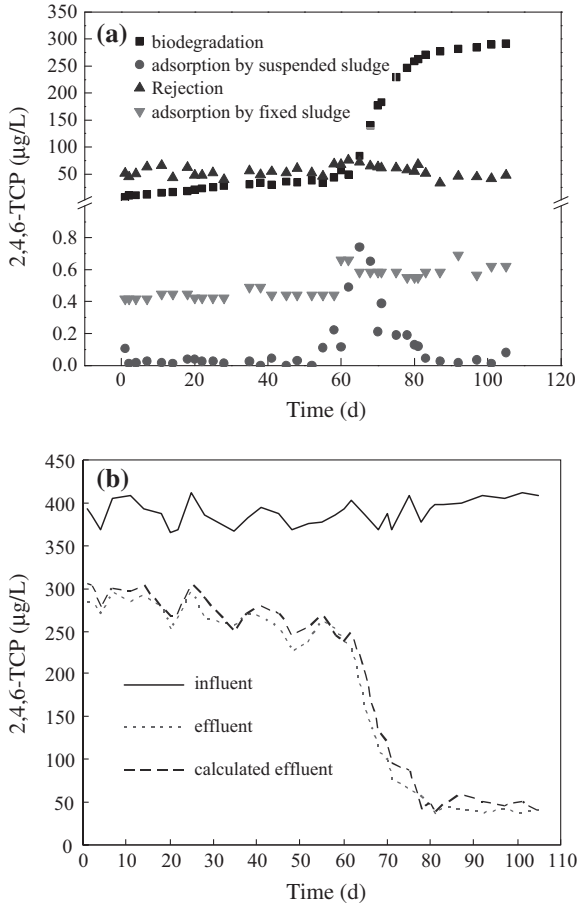

Fig. 8. 2,4,6-TCP removal in different pathways (a) and calculation of 2,4,6-TCP effluent (b).

Membrane rejection made a stable contribution for 2,4,6-TCP removal during the whole experimental operation, which seemed to be independent with the bulk biomass content. 2,4,6-TCP concentration in bulk solution related closely with the cake sludge on the membrane surface. It was estimated that the average 2,4,6-TCP retained by membrane filtration was about 52 μg/L in Phase I and then increased slightly to 56 μg/L in Phase II. Membrane filtration could enrich 2,4,6-TCP concentration around membrane surface and then to increase the biodegradation rate by increasing initial concentration. An enriched 2,4,6-TCP content would also cultivate functional microorganisms that utilize 2,4,6-TCP exclusively. Hence, an effective 2,4,6-TCP removal was mutual interaction between membrane rejection and cake sludge degradation, by the former one to accumulate 2,4,6-TCP concentration, and then by the later one to degrade 2,4,6-TCP biologically to produce a low effluent concentration.

Biodegradation capability of 2,4,6-TCP was enhanced by a long-term acclimation with assistant of membrane retention. During Phase I, owing to the low biomass content and fresh membrane filtration, biodegradation removal of 2,4,6-TCP was rather limited as low as 15 μg/L. In Phase II, the contribution of biodegradation for 2,4,6-TCP removal was improved from 50 to 300 μg/L, which was much higher than adsorption and filtration. The biodegradation removal capacity showed an obviously dependency with the MLSS enrichment profile (Fig. 8(a)). Hence, it is deduced that biodegradation process was the main removal pathway for 2,4,6-TCP in an individual MBR. However, a long-term acclimation process is necessary to enrich biomass and to cultivate microorganisms. As a result, 2,4,6-TCP concentration in the MBR effluent could be specified and calculated by Eqs. (9) and (10), which were illustrated in Fig. 8(b). The average relative deviation was 10.6% that indicated good fit with the experimental data for description of 2,4,6-TCP removal profile.

4. Conclusions

MBR is an effective process to remove DOM and 2,4,6-TCP, from micro-polluted water resource. With a

sufficient biomass above 400 mg/L in MBR bulk, the removal efficiency of DOM and 2,4,6-TCP was 56 and 90%, respectively. Membrane filtration could retain and enrich biomass to result in a significant improvement of organic contaminants removal. The pathways for 2,4,6-TCP removal in MBR, including bio-adsorption, membrane retention, and biodegradation, were analyzed experimentally and mathematically. It was revealed that the contribution of adsorption for 2,4,6-TCP removal was lower than 1 μg/L, which was rather lower compared with membrane retention and biodegradation. After a long-term biomass enrichment and acclimation, biodegradation could effectively remove 300 μg/L 2,4,6-TCP within 1.2 h, which took major responsible for refractory organic removal. Membrane filtration and cake-enhanced organic retention by fouled membrane were also important for 2,4,6-TCP removal, which could concentrate 2,4,6-TCP near membrane surface to acclimate microbes and to increase organic degradation rate. However, the sludge layer on membrane surface also accelerated membrane fouling to some extent. The experimental results in the present work claimed that MBR is a feasible way for treatment of micro-polluted water resource, and its removal pathway specification gave reliable guidance for MBR application.

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