Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25219

182 (2020) 109–117
April

Performance of a hybrid system for antibiotic wastewater treatment

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Received 30 May 2019; Accepted 20 November 2019

ABSTRACT

A hybrid anaerobic/aerobic moving bed biofilm reactor (A/O MBBR) system was established for wastewater treatment which contained tetracycline (TC) at the "μg/L" level. The pilot-scale system was contained an 11.87 L anaerobic unit, a 32.29 L aerobic unit and a 21.53 L secondary sedimentation tank. Results for the single-factor experiment showed that the optimal temperature for this A/O MBBR was 25°C with chemical oxygen demand (COD) and NH_4^+–N removal rate at 85.71% ± 0.94% and 90.46% ± 1.45%, respectively. Otherwise, the A/O MBBR system showed a high organic load that when the influent COD concentration was about 450 mg/L, the removal efficiency of COD and NH_4^+–N was 84.51% ± 1.23% and 81.24% ± 1.35% respectively, with effluent concentration of 71.94 ± 5.18 and 7.24 ± 0.63 mg/L respectively. The highest TC removal efficiency occurred at an influent concentration of 50 μg/L under 8 h of hydraulic retention time, and the average degradation rate during this phase was 50.03% ± 1.67%. In addition, the highest TC removal amount was 73.40 μg/L occurred at a fourth phase when the initial concentration of TC was 206.46 μg/L, showing the desired performance than many existed municipal sewage treatment plants. Moreover, this research provides a case study of a pilot-scale model for TC wastewater biodegradation and practical application.

Keywords: Antibiotic; Tetracycline; Anaerobic/aerobic; Moving bed biofilm reactor (MBBR)

1. Introduction

Currently, pharmaceutical effluents belong to a major kind of emerging organic contaminants in the aquatic environment which recognized as adverse impacts on both the ecosystems and the health of living beings [1,2]. Among these drugs, antibiotics attracted special attention due to their wide usage in human and livestock medicine at therapeutic levels, and to promote the growth of domestic animals at sub-therapeutic levels [3]. The presence of antibiotics and their corresponding transformation products could lead to antibiotic-resistant genes, further disrupting the microbial, crop and animal communities [4]. Tetracycline antibiotics (TCs), known as the broad-spectrum antibiotics in the worldwide for human, aquaculture and veterinary to prevent bacterial infections, which has been paid a great deal of concern attributed to their discharge and accumulation in an aqueous environment, even their biodegradation-resistance under traditional treatment [5–7]. As previously studied, TCs have a long half-life up to 180 d in its environmental conditions, and 25%–90% of TCs were excreted via feces and urine by active metabolites from living bodies [2,8]. Recently, TCs

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have been revealed in natural waters, according to Selvam et al. [9] that tetracycline, chlortetracycline, and oxytetracycline were about 30–497, 23–227, and 7–104 ng/L in the Yuen Long, Kam Tin, and Shing Mun Rivers of Hong Kong, respectively [9]. And the occurrence of TCs at ng/L or μg/L levels has also been detected in surface water, groundwater, even in drinking water which could cause genotoxic effects on microorganisms at such low value [10,11].

Various physical and chemical processes have been effectively researched to dispose of TCs wastewater, including adsorption by metal-doped biochars [12], magnetic microsphere [13], metal-organic framework [14,15], and graphene oxide nanosheets [16]. Electro-oxidation as a non-toxicity method was demonstrated to be effective to remove TCs from wastewater [17,18]. Another hotspot method was photocatalysis which used a series of highly efficient photocatalysts under illuminant [19–21]. However, the practice proved that the above processes had the disadvantages of the complicated preparation process and high cost of adsorbent or catalyst, as well as the relatively low capacity so that hardly be used in large-scale wastewater treatment projects.

Biological processes are usually considered to overcome the above shortcomings, being a more environmentally friendly and cost-effective alternative by sewage treatment plants. An anaerobic-anoxic-oxic (A^2/O) system coupled with UV disinfection which had an average capacity of more than $1.9 \times 10^5\ m^3/d$ has been employed in the largest wastewater treatment plant in Changsha, Hunan province to dispose of 37 pharmaceuticals including TCs [22]. Cetecioglu et al. [23] investigated that the majority fraction (more than 80%) of TC was biodegraded using an anaerobic sequencing batch with the organic substrate. Huang et al. [24] found that the biodegradation without ozonation of TC contributed 21.4% to the total removal, meanwhile the adsorption onto sludge contributed 28.8% under that modified AAO process. Besides, Taskan et al. [11] investigated the performance of hydrogen-based membrane biofilm reactor (H_2-MBfR) for simultaneous biodegradation of nitrate and TC, while the results showed that the removal efficiency of TC reached 80%–95% at hydrogen pressure of 0.41 atm and hydraulic retention time (HRT) of 10 h, respectively. Although activated sludge systems possess the ability to adsorb TC molecules, hardly be fully or partially degraded into harmless compounds. On the other hand, the biofilm reactors combine the superiority of activated sludge systems with membrane technologies, generally showed relatively higher biodegradation efficiency of TC.

Moving bed biofilm reactors (MBBRs) operate on a series of small plastic carriers to provide bacteria with an attachment and growth condition [25]. On the one hand, the carriers can effectively retard the membrane fouling caused by the suspended sludge to ensure the microorganism activity. On the other hand, MBBRs have shown great performance at high biomass amount, longish sludge age and even short HRT [26,27]. The MBBR technology was well established in municipal sewage plants including biological organic matter and nutrient removal [28,29], also demonstrated in the brewery, oilfield, and pharmaceutical industrial wastewater treatment including antibiotics degradation such as ciprofloxacin, azithromycin, and sulfamethizole [30–33]. The application of MBBRs to these organic compounds indicates the possibility that the processes can be practical for TC biodegradation. After all, there were few types of research about TC removal by MBBR under controlled conditions.

To understand the impact of TC on the biological wastewater treatment process, a quick start-up anaerobic/aerobic (A/O MBBR) system with the pilot-scale model was innovatively set up to evaluate whether it could be used to polish TC from wastewater. After monitoring the chemical oxygen demand (COD) and ammonia nitrogen (NH_4^+–N) removal efficiencies, the operating parameters such as temperature (15°C–35°C), influent COD and NH_4^+–N concentration (250–450 and 50–140 mg/L, respectively) were conducted respectively. Furthermore, the effect of different TC concentrations (50–200 μg/L) on A/O MBBR system performance and TC degradation efficiency was investigated. This research aimed to provide a new approach for the municipal wastewater treatment plants containing pharmaceutical compounds, even at the "μg/L" level, based on the A/O MBBR system.

2. Materials and methods

2.1. Reagents and testing method

The simulated municipal wastewater contained TC (molecular structure is shown in Fig. 1) was prepared by dissolving tetracycline hydrochloride (95%, purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD) into artificial synthetic wastewater. The HPLC (Agilent 1200, USA) was used for quantifying the TC removal efficiency in the reactor system which was equipped with the Agilent Eclipse XDB C18 column. The UV detector was used for TC testing with a wavelength of 268 nm. The injection volume and column temperature was 50 μL and 25°C respectively. The mobile phase was set as methanol-acetonitrile 0.01 mol/L oxalic acid solution (12:12:76, V/V) with a flow rate of 1.0 mL/min, all chemicals and solvents were HPLC-grade. The testing method of COD and NH_4^+–N concentration in influent and effluent was followed by Chinese National Standard GB 11914-89 (Dichromate method) and HJ 535-2009 (Nessler's reagent spectrophotometry). In addition, the biochemical oxygen demand, total nitrogen (TN) and total phosphorus (TP) measurement were followed by GB 7488-87 (Dilution and inoculation method), GB 11894-89 (Alkaline potassium persulfate digestion-UV spectrophotometric method) and GB 11893-89 (Ammonium molybdate spectrophotometric method).

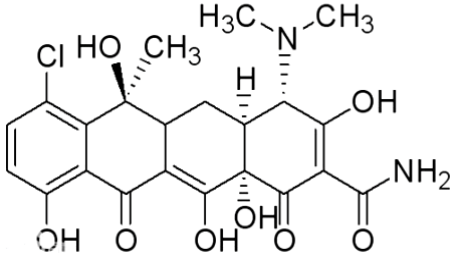

Fig. 1. Molecular structure of tetracycline.

2.2. A/O MBBR system configuration and operation

A designed A/O MBBR made of entire plexiglass with a rated wastewater treatment capacity of 150 L/d was constructed as shown in Fig. 2. The effective volumes of the anaerobic reaction unit, aerobic reaction unit, and secondary sedimentation tank were 11.87, 32.29, and 21.53 L respectively. The influent was drawn from the feed tank by a peristaltic pump (WT600-1F, Longer®, China) at 2,000 mL/min. The carriers were K1 suspension type made of PP and PE with a specific gravity of 0.95 g/cm^3, and a specific surface area was more than 500 m^2/m^3. Microporous aeration tubes were located at the bottom of the aerobic zone and aerated by an air pump (RESUN®, China) to maintain the dissolved oxygen (DO). During the aeration process, the sludge and water were evenly mixed, and the suspended carriers were kept in fluidized all the time. The temperature of the reactor during the operation was conducted by the heating rod and the temperature controller. The basic operating parameters in the batch experiment are listed in Table 1.

2.3. Activated sludge inoculation and biofilm culturing

Activated sludge for inoculation was sampled from an aeration tank of a sewage treatment plant in Hainan province and spontaneous inoculation of biofilm was chosen in this research. The activated sludge supernatant was removed and then mixed with artificial synthetic water to adjust the initially mixed liquor suspended solid of 4,000 mg/L. The medium of synthetic wastewater contained 245.25 mg/L sucrose, 285.6 mg/L CH_3COONa, 152.83–229.24 mg/L NH_4Cl (as the temperature increased in batch experiment), 40 mg/L KH_2PO_4, 354 mg/L $NaHCO_3$, 20 mg/L $CaCl_2$, 20 mg/L $MgCl_2$, 20 mg/L $AlCl_3$, and 1 mL/L trace elements. Thereinto, the trace elements contained 60 mg/L $CuSO_4{\cdot}5H_2O$, 130 mg/L $MnCl_2{\cdot}4H_2O$, 100 mg/L $ZnSO_4{\cdot}7H_2O$, 80 mg/L $CoCl_2{\cdot}6H_2O$, 550 mg/L $FeCl_3$ and 60 mg/L ammonium molybdate. As the running time extended, the microorganisms on the suspended carriers were gradually enriched, and the biofilm was thickened that led some of them aged and fell off. Therefore, the sludge in the reactor was discharged quantitatively to maintain the activated sludge concentration. In this paper, the steady removal efficiency of COD and NH_4^+–N was a sign of biofilm maturity.

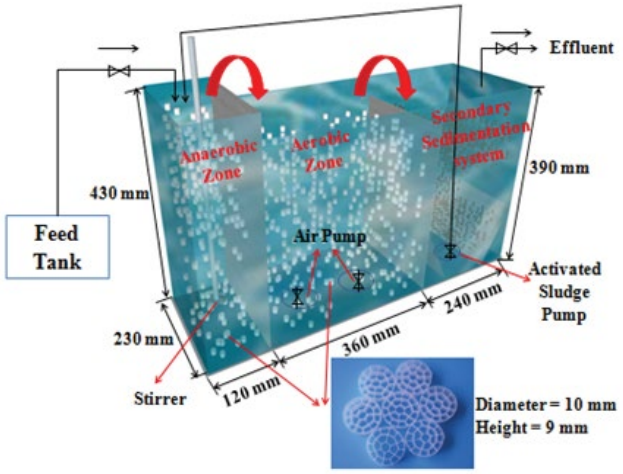

Fig. 2. Schematic structure of the A/O MBBR system.

2.4. Batch experiments

To evaluate the performance of A/O MBBR at different conditions, three temperature ranges were set as 15°C, 25°C, and 35°C. Based on the previous research, the concentrations of major pollutants in typical antibiotic wastewater were presented as follows: 200–300 mg/L COD [33], 200–2,055 mg/L TN, 100–620 mg/L TP, and 110–1,650 mg/L NH_4^+–N [34]. Taking the start-up stage activity of A/O MBBR system into consideration, three COD as well as NH_4^+–N concentration ranges were conducted as ~250 to ~450 mg/L, and ~50 to ~140 mg/L, respectively. Every round of the experiment lasted for 45 d, and simulated wastewater samples were tested every day. Furthermore, the effect of TC on A/O MBBR performance was investigated by setting four groups of TC concentration as 50, 100, 150 and 200 μg/L, respectively, with more than 160 h continuous operation time and testing every 2 h.

3. Results and discussion

3.1. Performance of A/O MBBR start-up stage

The start-up stage of biofilm reactors was usually ended up with a stable COD removal efficiency, as well as NO_3^-–N, NO_2^-–N [26,35]. In this study, the COD and NH_4^+–N removal performance of the A/O MBBR system during the natural inoculation process was investigated in regular intervals as

Table 1
General operating parameters of A/O MBBR

Anaerobic unit		Aerobic unit	
Parameters	Values	Parameters	Values
Dissolved oxygen (DO)	2.2–3.0 mg/L	Dissolved oxygen (DO)	3.4–4.0 mg/L
Mixed liquor suspended solids (MLSS)	4,000 mg/L	Mixed liquor suspended solids (MLSS)	4,000 mg/L
pH	6.5–7.8	pH	6.5–7.8
Hydraulic retention time (HRT)	8 h	Hydraulic retention time (HRT)	8 h
Carrier dosage	30%	Carrier dosage	15%
Sludge reflux ratio	100%	–	–

Figs. 3a and 3b shown. In the initial response, the removal efficiencies of COD and NH_4^+–N were relatively low until this stage reached 30 d, the removal rates were as high as 82.0% and 85.4%, respectively. From then on, the effluent concentration and removal efficiency of COD and NH_4^+–N was gradually stabilized as it also could be found in Fig. 3c. As calculation results showed that the mean values of COD effluent concentration and removal efficiency were 49.0 mg/L and 85.97% respectively from day 41 to 90, meanwhile for NH_4^+–N were 4.5 mg/L and 89.14% respectively when the influent concentration varied in a wide range from 35 to 50 mg/L, which both better than the Standard A of the 1st class of Chinese Standard "Discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002)" (8 mg/L), indicating that the A/O MBBR system possessed good nitrification capability and strong impact load capacity. Briefly, after 30 d of inoculation, the sludge settling ratio reached 10%–15%, and the biofilm on suspended carriers was mature and abundant which was a sign for stable biomes in the reactor and further experiment.

3.2. Effect of temperature on A/O MBBR performance

The temperature was found to be a significant parameter for MBBR performance due to the susceptibility of bacteria and a key factor affecting their metabolism [30]. On the other hand, the TCs are quite unstable due to their unique chemical structure, thereby undergoing the abiotic degradation under some surrounding conditions including temperature [3]. Considering its importance for this complex bioprocess, the effect on COD and NH_4^+–N removal efficiency of three different temperature intervals were investigated after the start-up phase (Fig. 4). When the influent temperature was in the range of 15°C–35°C, the removal efficiency of COD was maintained at 80% and above, whilst for NH_4^+–N was more than 75% throughout the whole phase. In the high-temperature range (35°C), the average removal efficiency of COD and NH_4^+–N was 83.94% ± 1.00% and 79.64% ± 1.34%, respectively. Nevertheless, in the low-temperature range (15°C), the removal rate of COD and NH_4^+–N was measured roughly the same at 83.13% ± 1.32% and 83.46% ± 1.61%, respectively. In the contrast, the moderate temperature (25°C) showed the best removal effect for both COD and NH_4^+–N namely 85.71% ± 0.94% and 90.46% ± 1.45% respectively, which particularly evident for NH_4^+–N. Similar impacts of temperature on the NH_4^+–N oxidation, even the NO_3^-–N accumulation has been demonstrated previously, that ammonia-oxidizing bacteria (AOB) seemed to have an obvious growth as temperature increased, however, when met the relatively high-temperature ranges, the heterotrophic bacteria in the system were more competitive for nutrient matrix and DO than AOB and anaerobic AOB (anammox), so that the

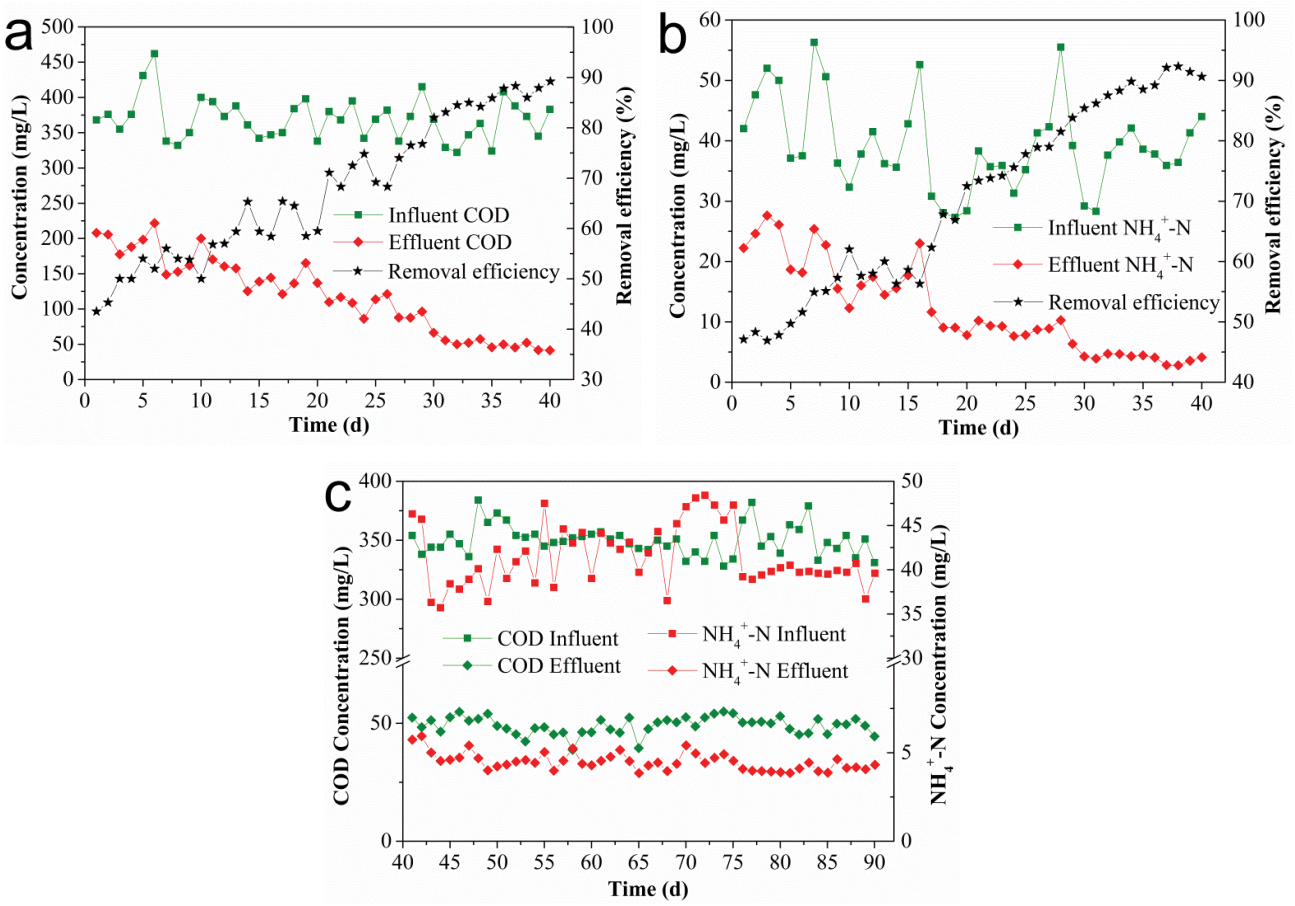

Fig. 3. COD and NH_4^+–N concentration of influent and effluent in start-up (a,b) and steady running stage (c).

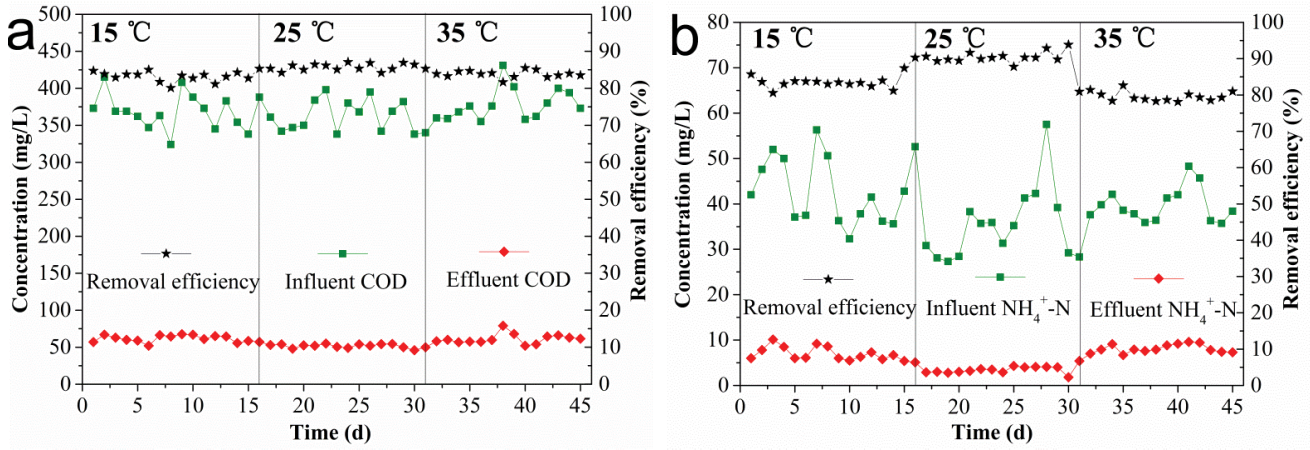

Fig. 4. Effect of temperature (15°C, 25°C, and 35°C, respectively) on COD (a) and NH_4^+–N (b) removal efficiency.

inhibition might occur at these bacteria which caused lower ammonium oxidation efficiency [36]. The setting of temperature condition was consistent with published pre-denitrifying MBBRs for pharmaceuticals elimination that operated under ambient temperature, however, the extreme temperature was rarely reported [35]. Therefore, the moderate temperature range was designated as the following experimental condition at which the effluent concentration was 52.12 ± 2.96 and 3.49 ± 0.81 mg/L for COD and NH_4^+–N respectively.

3.3. Effect of influent COD concentration on A/O MBBR performance

Organics in the influent are the basis of the metabolic activities and provide nutrients for the growth of microorganisms. Therefore, changing the concentration of organic matters in the influent might affected the microbial community, further impacting the system performance. As shown in Fig. 5, the COD removal rate changed little as increasing influent concentration, while the NH_4^+–N removal rate increased first, then decreased when influent COD rose to more than 450 mg/L. In the range of high organic loading (influent COD concentration of ~450 mg/L), the average COD removal rate was 84.51% ± 1.23% with an effluent concentration of 71.94 ± 5.18 mg/L. The larger surface area of the suspended carriers provided ample space for microbial growth then coupled with activated sludge that might ensure the higher organic load of the A/O MBBR system. But meanwhile, that neither low (~250 mg/L) nor high (~450 mg/L) organic loading was conducive to NH_4^+–N removal. When the average influent COD concentration was 365.47 ± 21.54 mg/L, the effluent NH_4^+–N was as low as 4.03 ± 0.77 mg/L which met the GB 18918-2002 requirement of the Standard-A 1st class (8 mg/L). This organic load range was higher than the pilot plant for real hospital wastewater treatment consisting of MBBRs in series (with influent COD of 274 mg/L) [32].

3.4. Effect of influent NH_4^+–N concentration on A/O MBBR performance

Ammonia in the influent not only provides nutrients necessary for microbial growth but also is one of the major pollutants to be removed in sewage. As the influent NH_4^+–N concentration changed, the COD removal efficiency remained at ~80%–85% with minor fluctuations (Fig. 6).

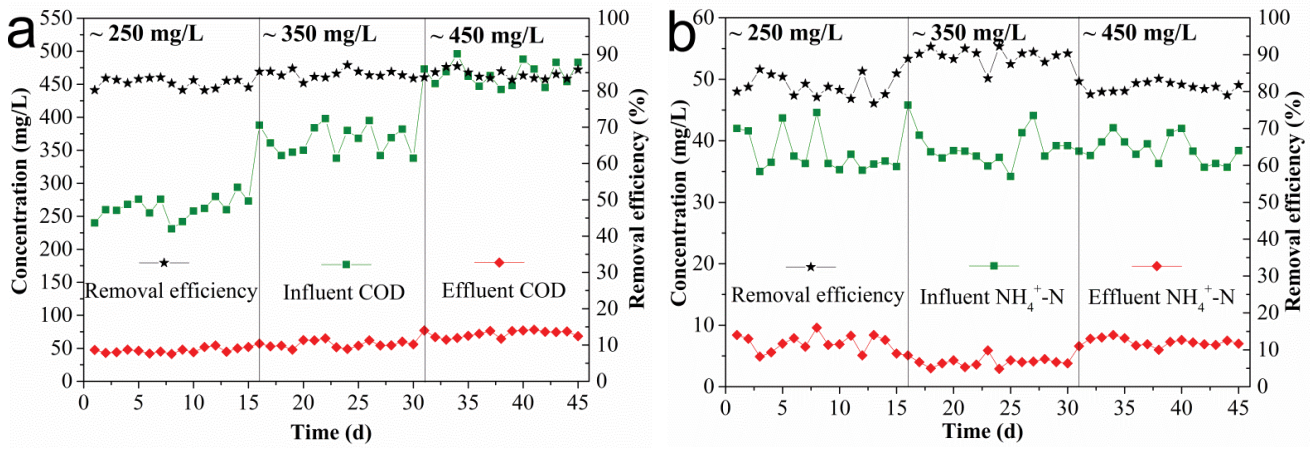

Fig. 5. Effect of influent COD concentration (~250, ~350, and ~450 mg/L, respectively) on COD (a) and NH_4^+–N (b) removal efficiency.

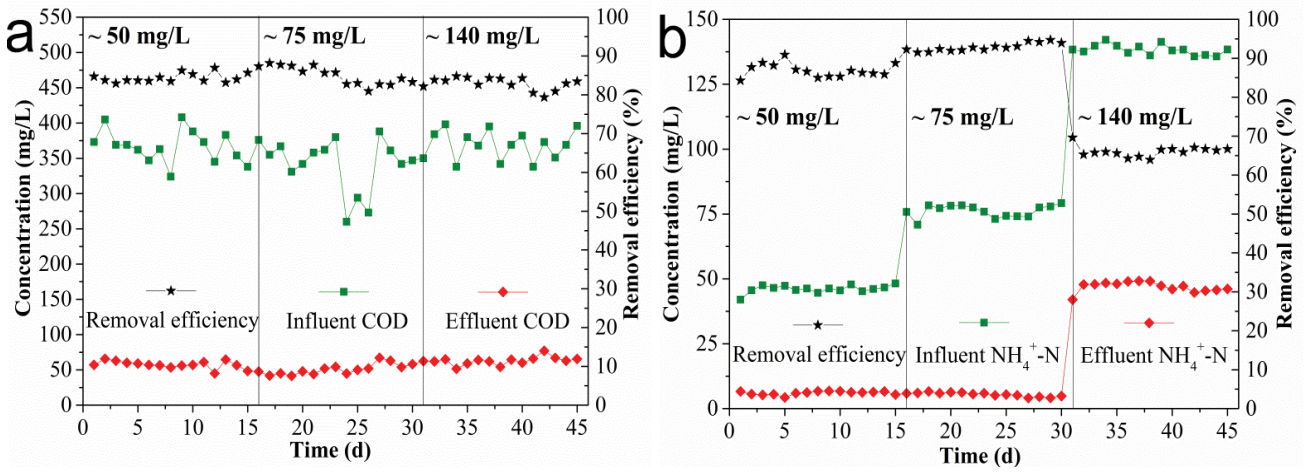

Fig. 6. Effect of influent NH_4^+–N concentration (~50, ~75, and ~140 mg/L, respectively) on COD (a) and NH_4^+–N (b) removal efficiency.

When the influent concentration was 80 mg/L, and the effluent COD concentration was 50.87 ± 7.51 mg/L with an average removal rate of 85.02% ± 2.37%, which showed a best disposal condition. Even at a high loading rate (~140 mg/L of influent NH_4^+–N), the A/O MBBR possessed a relatively stable COD degradation effect with the average effluent concentration and removal efficiency of 62.87 ± 5.80 mg/L and 82.93% ± 1.61% respectively. In contrast, with the increase of NH_4^+–N concentration in the influent, the removal rate of NH_4^+–N showed large variation that firstly increased and then decreased, with the best treatment effect occurred at the concentration of ~75 mg/L (average NH_4^+–N effluent concentration and removal efficiency were 5.44 ± 0.78 mg/L and 92.85% ± 1.03% respectively). But it was regrettable that when the influent NH_4^+–N was up to ~140 mg/L, the load-carrying capacity of the biosystem was exceeded, resulting in a removal rate of NH_4^+–N was only 66.06% ± 1.36%. The higher inlet NH_4^+–N might be led to the excessive free ammonia in the inoculums, which would inhibit the growth of AOB and anammox, further altering the composition and function of microbial communities and thus impairing the NH_4^+–N removal efficiency [37].

3.5. Effect of tetracycline concentration on A/O MBBR performance

The removal efficiency of high COD reflected the biodegradation potential of antibiotic organic wastewater. Followed by the detection of COD and ammonia load-carrying capacity of this A/O MBBR system, the tetracycline removal performance under the bioprocess was carried out in the influent concentration of COD and NH_4^+–N was 350–400 and 35–45 mg/L, respectively (Fig. 7). With the increase of the TC concentration in the feed tank, the removal efficiency of COD in the A/O MBBR process decreased gradually. When the feed water contained 50 μg/L TC, the removal rate of COD was 78.73% ± 5.35%, whilst the effluent quality (81.58 ± 22.87 mg/L) was slightly higher than the Standard B 1st of GB 18918-2002 requirement (60 mg/L), but within 2nd Standard (100 mg/L). When the influent TC concentration was 100 μg/L, the removal rate of COD was 64.82% ± 5.22%. When TC concentration increased from 150 to 200 μg/L, the COD removal rate decreased from 63.41% ± 2.85% to 59.50% ± 5.96%. Analogous, NH_4^+–N removal efficiency showed a more significant decrease trend with increased TC concentration. The removal efficiency was dropped from 69.45% ± 5.03% to 51.08% ± 2.91% with the increase TC concentration from 50 to 200 μg/L, even though the effluent NH_4^+–N was less than 19.54 ± 2.05 mg/L that within 2nd Standard of GB 18918-2002 (30 mg/L).

Under this operation condition, the TC biodegradation performance was shown as Fig. 7c. The removal efficiency of TC was tardily reduced as increase TC influent concentration, but still demonstrated relatively stable runability which indicated the resistance of microbial communities in this A/O MBBR system. As seen, the average removal efficiency of TC decreased from 50.03% ± 1.67% to 33.18% ± 1.50% within the variation range of inoculums. The input of low TC concentration at first 42 h might gradually induce microbial resistance and make them adapted to the changing environment. Nevertheless, the phenomenon occurred at the high TC range that as the concentration of TC increased, the activated sludge gradually turned darker from brown, and the accumulation of ammonia indicated the reduction in the microbial population. At this moment, the abiotic adsorption by deactivated sludge and biodegradation by activated sludge as well as biofilm might both involved in the TC treatment process. The degradation of TC was regarded as hydrolysis and oxidation in macro. As the molecular structure of tetracycline shown in Fig. 1, the hydroxyl and enol groups were easily hydrolyzed to be open-loop lipid which further hydrolyzing to provide macromolecular carbon for microbial metabolism and oxidizing to CO_2 and H_2O [38]. In contrary, no disturbance was observed in COD removal and nitrification process after the TC injection in a membrane bioreactor (MBR) for swine wastewater, even no toxicity occurred when the TC level was up to 20 mg TOC L^{-1}, as the results showed that the origin of cultured activated sludge made a significant difference on the pilot performance [39]. However, the inlet TC loading and corresponding elimination efficiency were preceded by published municipal sewage treatment plants [40].

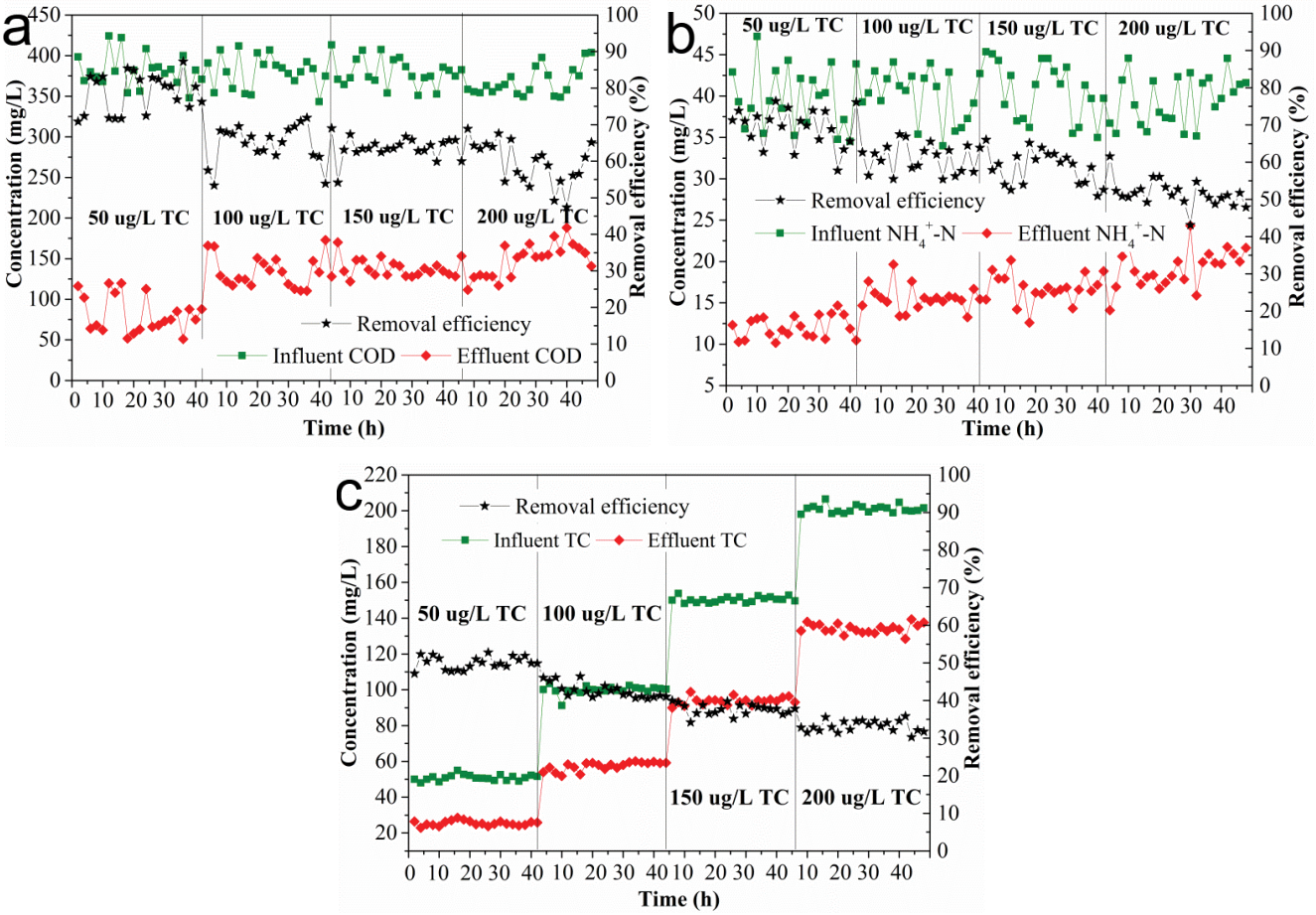

Fig. 7. Effect of tetracycline concentration (50, 100, 150, and 200 μg/L, respectively) on (a) COD, (b) NH_4^+–N, and (c) tetracycline removal efficiency.

4. Conclusion

In this research, a novel A/O MBBR system was constructed for tetracycline degradation, and some operation factors were investigated to achieve optimal performance. As a result, the optimal temperature for this system was 25°C with COD and NH_4^+–N removal rate at 85.71% ± 0.94% and 90.46% ± 1.45%, respectively. Otherwise, the A/O MBBR system showed a high organic load that when the influent COD concentration was 450–500 mg/L, the removal efficiency of COD and NH_4^+–N was 84.51% ± 1.23% and 81.24% ± 1.35% respectively, which indicated its potential ability for TC degradation. The TC removal efficiency achieved 50.03% ± 1.67% when influent TC was 50 μg/L with effluent concentration at 25.43 ± 1.40 μg/L. From then on, the removal rate declined gradually to 33.18% ± 1.50% when the influent TC was as high as 200 μg/L. Increasing the HRT or drug-resistant domestication time of the activated sludge to TC may have the ability to increase the treatment performance for TC wastewater. In addition, hydrolysis and oxidation were regarded as two main procedures for TC degradation combined with its molecular structure. From the above, this study provided a new method for the biodegradation application of wastewater contain tetracycline.

Acknowledgments

The authors gratefully acknowledge the Natural Science Foundation of Hainan province (Grant No: 419MS068), trial-production project of Sanya (Grant No: 2017KS07) and Open Research Fund of Hubei Key Laboratory of Mine Environmental Pollution Control & Remediation (Grant No: 2018105).

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