

# Influence of nitrogenous compound concentration in simulated coal processing wastewater on nitrogenous pollutant removal in moving bed biofilm reactors under different dissolved oxygen concentrations

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# ABSTRACT

Two lab-scale moving bed biofilm reactors (MBBRs) were used to treat simulated coal processing wastewater (CPW). The dissolved oxygen (DO) concentration of the two MBBRs was controlled at  $5.0 \pm 0.5$  mg/L (high dissolved oxygen concentration moving bed biofilm reactor, HDMBBR) and  $1.5 \pm 0.2$  mg/L (low dissolved oxygen concentration moving bed biofilm reactor, LDMBBR), respectively. The aim of the study was to investigate the effect of influent nitrogenous pollutant concentration on pollutant removal performance in the two reactors. The HDMBBR had a better resistance to the pollutant shock load than LDMBBR throughout the experiments. Variation of influent thiocyanate (SCN<sup>¬</sup>) and organic nitrogen (ON) concentrations had little effect on total nitrogen (TN) removal rate for the HDMBBR and the LDMBBR. TN removal rate of the LDMBBR dropped approximately 10% at feed NH<sub>4</sub><sup>+</sup>-N concentration of 300 mg/L, and elevated 5% at feed NH<sub>4</sub><sup>+</sup>-N concentration of 300 mg/L and 450 mg/L in the HDMBBR, respectively. The results obtained in the study indicated that organic nitrogenous compound in the CPW affected nitrogenous pollutant removal performance of the MBBR obviously, and to increase DO concentration in the reactor was a feasible method to resist the shock load.

*Keywords:* Moving bed biofilm reactor; Simulated coal processing wastewater; Ammonium; Thiocyanate; Organic nitrogen

# 1. Introduction

One of the most emerging challenge for the sustainable development of Chinese coal chemical industry is the wastewater generated during coal processing [1]. Numerous environmental problems made by coal processing wastewater (CPW) in many countries have been reported [2]. The factors, such as gasifier physical configuration, operating conditions, and coal type, can cause different qualities of the CPW [3]. The CPW contains high concentrations of organic (phenols, poly-nuclear aromatic hydrocarbons, etc.) and inorganic (cyanide, thiocyanate, ammonium, etc.) toxic pollutants generated mainly from the gas washing, condensation and fractionation processes [4]. For the sustainable development of coal chemical industry, a suitable CPW treatment technology is urgently needed [5].

After the pretreatment of ammonia stripping and phenols solvent extraction, the CPW is usually handled by biological treatment processes [6]. Biological processes have higher energy efficiency and better environmental performance compared with physical and chemical methods for CPW treatment [1]. Biological processes are mainly divided into suspended growth system and attached growth system. The suspended growth system, such as activated sludge processes, is used to treat the CPW achieving good phenols removal performance, but the nitrification performance is susceptible. The attached growth system, such as the bio-

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film processes, has been proved to be reliable for organic carbon and nitrogen removal [7]. The moving bed biofilm reactor (MBBR) is the combination of traditional activated sludge process and fluidized bed process [8]. The MBBR process incorporates free-floating carriers providing a large surface area for colonization with no need for biomass recycling [9,10], which is more steady and effective due to the cooperative effects of attached and suspended growth biomass [11]. The MBBR process is widely used to remove toxic compounds, such as phenols, ammonium and thiocyanate from different kinds of waste waters [12,13]. However, there are still few studies of nitrogenous pollutant load, organic or inorganic pollutants, on nitrogenous pollutant removal performance in the MBBR process, which is not sufficient for the development of coal gasification industry.

Biological nitrogen removal processes usually transform nitrogenous pollutants to nitrate through ammonification and nitrification, subsequently, further being transferred into nitrogen through denitrification. Nitrification is achieved by ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) [14], which can be divided into full and short-cut nitrification. Biological nitrogen removal processes adopting short-cut nitrification consume less oxygen and organic carbon resource demand comparing with full nitrification [15,16]. Many factors are used to control short-cut nitrification, such as pH value, temperature and hydraulic retention time (HRT), and dissolved oxygen (DO) concentration is adopted to facilitate nitrite accumulation usually because the DO concentration is easy to handle in the biological nitrogen removal processes. Moreover, the nitrification performance is affected usually by the variation of influent wastewater quality, such as organic or inorganic pollutant load. To the best of our knowledge, there has been few studies on the effect of influent nitrogenous pollutant load on TN removal performance of the MBBR process in treating the CPW, especially being operated under different DO levels.

Therefore, this study intended to study the effect of influent nitrogenous pollutant load, including ammonium (NH<sub>4</sub><sup>+</sup>-N), thiocyanate (SCN<sup>¬</sup>) and organic nitrogen (ON), on nitrogenous pollutant removal performance of the MBBR in treating simulated CPW. Moreover, the study were done in two parallel reactors. DO concentration of the reactor was controlled under  $5.0 \pm 0.5$  mg/L (high dissolved oxygen concentration MBBR, HDMBBR) and  $1.5 \pm 0.2$  mg/L (low dissolved oxygen concentration MBBR, HDMBBR) throughout the experiments, which was in conducive to study the influence of influent nitrogenous pollutant load on performance of the reactors being controlled under relative stable full and short-cut nitrification.

# 2. Materials and methods

#### 2.1. Experimental wastewater

Due to great fluctuation of pollutant concentrations in real CPW, the test was conducted using simulated CPW. The simulated wastewater was used in this research because the influent of the MBBR can be handled stably to study the influence of influent nitrogenous pollutant load on pollutant removal performance in the reactor. The main components of the simulated wastewater were ammonium  $(NH_4^+-N)$ , thiocyanate (SCN<sup>-</sup>) and organic nitrogen (in the

form of aniline, pyridine and quinolone), with the addition of nutrients and trace elements in the tap water. The quality of the simulated CPW is shown in Table 1.

### 2.2. Set-up of the MBBR

Two Plexiglas reactors with a cylindrical shape were used as the HDMBBR and LDMBBR. The schematic diagrams of the HDMBBR and LDMBBR are shown in Fig. 1. The working volume of the two reactors was around 6 L with an internal radius of 7.5 cm. Carriers adopted in the experiment were cylindrical shape (cross inside and 10 mm in diameter) being made of polyethylene with a density of about 0.97 g/cm<sup>3</sup>. The carrier filling ratio of the two reactors was around 40%. A sieve (with 5 mm opening) was placed at the outlet of the reactors to keep the carriers in the reactor. The simulated wastewater was supplied at the bottom of the reactor by a peristaltic pump, and effluent wastewater overflowed on the upper side of the reactor. Air was introduced to the reactor through porous diffusers, which placed at the bottom of the reactor with flow meters to keep the carriers continuous flowing. Moreover, a mixer was set in the LDMBBR to promote carriers flowing under relative low air flow rate. DO concentration was controlled by regulating inlet airflow rates using the flow meters.

Table 1

The quality of the simulated coal processing wastewater

Indicator	Concentration (mg/L)	Indicator	Concentration (mg/L)	
Phenol	200 (150-400) <sup>a</sup>	o-cresol	100 (50–200)	
Pyridine	25 (10-50)	quinoline	25 (10-50)	
Aniline	25 (10-50)	$NH_4^+-N$	150 (100–350)	
SCN <sup>-</sup>	100 (50–150)	NaHCO <sub>3</sub>	2000	
$\mathrm{KH}_{2}\mathrm{PO}_{4}$	150	$MgSO_4$	20	
$ZnSO_4$	10	CaCl <sub>2</sub>	20	
CuSO <sub>4</sub>	15	FeCl <sub>3</sub>	5	

<sup>a</sup>The range of possible pollutant concentration in real CPW shown in brackets.



Fig. 1. The schematic diagrams of the HDMBBR and LDMBBR

#### 2.3. Start up and operation of the MBBRs

The acclimated activated sludge used in the experiment was collected from a biological wastewater treatment facility in a full-scale coke plant located in the east of China. The two reactors were operated in a batch manner for more than one month to promote biofilm growth, and then were changed to a continuous flow mode and operated for more than half a year using the simulated wastewater. Hydraulic retention time (HRT) of the two reactors was kept at around 40 h to ensure nitrification performance of the two reactors with the existence of toxic compounds, including phenols, pyridine, quinolone, aniline, etc. DO concentration was controlled at  $5.0 \pm 0.5$ mg/L and  $1.5 \pm 0.2$  mg/L in the HDMBBR and LDMBBR, respectively. The temperature was maintained at  $30 \pm 2^{\circ}C$ by a constant temperature controller and pH was not handled in both reactors.

Nitrogenous pollutant removal performance of the two MBBRs were divided into three parts, which was the enhancement of influent  $NH_4^{+}-N$  concentration, influent SCN<sup>-</sup> concentration and influent ON concentration, respectively. ON shock load on the MBBRs was applied by adjusting the influent aniline, pyridine and quinoline concentrations in the simulated CPW, and the addition of the three organic nitrogenous compounds in the influent wastewater was averaged according to the nitrogen content in each compound. Detail operation conditions are shown in Table 2.

#### 2.4. Analytical methods

Samples were taken from effluent of the HDMBBR and LDMBBR every other day and were analyzed immediately after filtered through 0.45-µm filter paper.  $NH_4^{+-}N$ ,  $NO_2^{-}N$ ,  $NO_3^{-}-N$  and TN were measured in accordance with Standard Methods for Water and Wastewater Examination [17]. ON concentration was the difference between TN concentration and the sum of  $NH_4^{+-}N$ ,  $NO_2^{--}N$  and  $NO_3^{--}N$  concentration in the wastewater. SCN<sup>-</sup> was measured by ferric colorimetric method. DO concentration was measured using YSI  $O_2$ -electrode.

#### 3. Results and discussion

## 3.1. Increase of influent NH<sub>4</sub>+-N concentration

During the experiment, the NH<sub>4</sub><sup>+</sup>-N concentration in the influent gradually increased, which was controlled around

Table 2 Operation conditions during the experiments

150, 300 and 450 mg/L, respectively, and finally turned to 150 mg/L. Fig. 2 shows the evolutions of  $NH_4^+$ -N, SCN<sup>-</sup>, ON and TN concentration in the effluent of the HDMBBR and LDMBBR with the raising of influent  $NH_4^+$ -N concentration, along with the variation of nitrification performance.

Difference of effluent nitrogenous pollutant concentration between the two reactors could be observed after being operated more than two months. As shown in Figs. 2a and b, more than 90% of NH<sub>4</sub>+-N and SCN<sup>-</sup> removal efficiencies were obtained in the HDMBBR, but 84% of NH<sub>4</sub><sup>+</sup>-N removal efficiency was observed in the LDMBBR with influent  $\rm NH_4^{+}\text{-}N$  concentration of 150 mg/L. Li et al. [18] reported that until the influent NH4+-N concentration achieved 232 mg/L in the MBBR, effect of influent NH<sub>4</sub>+N concentration enhancement on SCN<sup>-</sup> removal was not apparent. Obvious increase of effluent NH4+-N concentration was observed when influent NH<sub>4</sub><sup>+</sup>-N concentration increased to 300 mg/L, and decreased below 50 mg/L in the HDMBBR and below 75 mg/L in the LDMBBR within several days. The effluent SCN<sup>-</sup> concentration in the HDMBBR was independent of the feed NH<sub>4</sub>+-N concentration, and average SCN<sup>-</sup> removal efficiency fell from 92% to 83% in the LDMBBR. However, the effluent  $NH_4^+$ -N and  $SCN^-$  concentrations of the two reactors significantly increased without obvious decline at the feed NH<sub>4</sub><sup>+</sup>-N concentration of 450 mg/L. The SCN<sup>-</sup> and NH<sub>4</sub><sup>+</sup>-N removal efficiencies could be weakened by the increase of influent NH4+-N concentration at varying degree. The high influent NH<sub>4</sub><sup>+</sup>-N concentration was the reason for the low removal efficiency of SCN<sup>-</sup> [19]. SCN<sup>-</sup> removal efficiency of the LDMBBR was affected seriously when the influent NH4+-N concentration increased, but caused a smaller influence in the HDMBBR. The results indicated that the HDMBBR had a faster NH<sub>4</sub><sup>+</sup>-N degradation rate compared with the LDMBBR, which reduced the inhibition of influent  $NH_4^+$ -N concentration on SCN<sup>-</sup> removal.

Nitrogenous compounds in the CPW usually existed in the form of ON, SCN<sup>-</sup> and NH<sub>4</sub><sup>+-</sup>N, containing little NO<sub>2</sub><sup>-</sup>-N and NO<sub>3</sub><sup>-</sup>-N. To be treated by the biological processes, most of the ON converted to NH<sub>4</sub><sup>+-</sup>N and other forms of inorganic nitrogen. The evolution of effluent ON concentration with the increase of influent NH<sub>4</sub><sup>+-</sup>N concentration was similar to the variation of effluent NH<sub>4</sub><sup>+-</sup>N concentration which could be obtained in Fig. 2c. ON removal efficiency fell from 78% to 67% when the feed NH<sub>4</sub><sup>+-</sup>N concentration ascended from 150 to 300 mg/L, and descended to 42% when the influent NH<sub>4</sub><sup>+-</sup>N concentration further rose to 450 mg/L. In the LDMBBR, average ON removal efficiency dropped to 21% at the influent NH<sub>4</sub><sup>+-</sup>N concentration of 450 mg/L. The results confirmed that the presence of high concentration of

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Stage	Ι	II	III	IV	V	VI	VII	VIII	IX	Х
Days	1–18	19–36	37–54	55–72	73–88	89–104	105–120	121–136	137–154	155–172
NH4+-N	150	300	450	150	150	150	150	150	150	150
SCN-	100	100	100	100	200	300	100	100	100	100
ON	25	25	25	25	25	25	25	50	75	25
TN	200	350	500	200	225	250	200	225	250	200

The units in the table are mg/L



Fig. 2. Pollutant evolution with the increase of influent  $NH_4^+$ -N concentration, along with nitrification performance of the HDMBBR and LDMBBR, (a)  $NH_4^+$ -N, (b) SCN<sup>-</sup>, (c) ON, (d) nitrification performance and (e) TN.

 $\rm NH_4^{+}\text{-}N$  in the two reactors had strong inhibitory effect over ON biodegradation.

Variations of NO<sub>2</sub><sup>--</sup>N and NO<sub>3</sub><sup>--</sup>N in the two reactors are shown in Fig. 2d. The HDMBBR and LDMBBR had different nitrification performance with the increase of influent NH<sub>4</sub><sup>+-</sup>N concentration. The HDMBBR showed a better nitrifying rate comparing with the LDMBBR. Effluent NO<sub>3</sub><sup>--</sup>N concentration reached about 150 mg/L, and effluent NO<sub>2</sub><sup>--</sup>N concentration was less than 1.0 mg/L. The ratio of NO<sub>3</sub><sup>--</sup>N/NO<sub>x</sub><sup>--</sup>N reached about 99.5%. The accumulation of NO<sub>2</sub><sup>--</sup>N in the LDMBBR maintained around 80 mg/L, and the effluent NO<sub>3</sub><sup>--</sup>N concentration was around 10 mg/L. The enhancement of influent NH<sub>4</sub><sup>+-</sup>N concentration would cause significantly increase of the free ammonia concentration in the reactor, which would affect nitrification performance of the reactor obviously [20]. At stage II, NO<sub>2</sub><sup>--</sup>N accumulation in the HDMBBR appeared with

the increase of influent NH<sup>+</sup>-N concentration, which disappeared in a few days. Turk et al. [21] also reported the adaptability of nitrification bacteria for free ammonia, and NO<sub>3</sub><sup>-</sup>-N concentration rose to 231 mg/L. For the LDMBBR, NO<sup>2</sup>-N concentration accumulation achieved 178 mg/L and  $NO_3^{-}$ -N concentration decreased to less than 1.0 mg/L. The toxic compounds and free ammonia (FA) had inhibitory effects on NOB which caused the high proportion of  $NO_2^{-}N$  accumulation [22,23]. When the influent  $NH_4^{+}-N$ concentration increased to 450 mg/L, NO<sub>3</sub>-N concentration in the HDMBBR fell to 165 mg/L fast, and gradually increased to 233 mg/L. NO2-N concentration in the HDMBBR heightened from 4.5 to 43.7 mg/L. The shock of NH<sub>4</sub><sup>+</sup>-N load on nitrification efficiency of the LDMBBR was much greater, and the effluent NO2-N concentration declined. Although ammonia was used as an electron source by the AOB for energy, it would inhibit the activity of the AOB at high concentration [24]. Therefore, the further improvement of influent  $NH_4^+$ -N concentration would affect the performance of the MBBR system, which led to the deterioration of the effluent wastewater quality of the two reactors.

TN removal efficiency with the increase of influent NH<sub>4</sub><sup>+</sup>-N concentration is shown in Fig. 2e. TN removal efficiency ascended from 15.1% to 25.1% gradually in the HDMBBR with the augment of influent NH<sub>4</sub>+N concentration. While in the LDMBBR, TN removal efficiency fell from 37.2% to 26.1% when the feed  $NH_4^+$ -N concentration increased to 300 mg/L. When the influent NH4+-N concentration further improved to 450 mg/L, TN removal efficiency was similar as in stage II. There was an obvious increase of TN removal efficiency during the beginning of stages II and III and TN removal efficiency decreased fast within several days. The results would be due to the relative long HRT in the two reactor. When the influent TN concentration increased with the enhancement of influent NH4+-N concentration, effluent NH4+-N concentration was not affected totally. Therefore, the calculation TN removal efficiency increased obvious at the beginning of stages II and III, and decreased quickly with the rise of effluent NH<sub>4</sub><sup>+</sup>-N concentration. TN removal efficiency in the LDMBBR was always higher than in the HDMBBR. The reason for this result might be due to that the LDMBBR had thicker biofilm on the carriers comparing with the HDMBBR because of the lower aeration rate in the LDMBBR. The relative thick biofilm in the LDMBBR would establish anoxic conditions in the inner zones of the biofilm, which was conducive to denitrification. The results also displayed that with the increase of influent NH<sup>+</sup>-N concentration, the gap between HDMBBR and LDMBBR for the effluent TN concentration diminished gradually, which was due to the improvement of aeration rate for the LDMBBR by the enhancement of influent NH4+-N concentration.

#### 3.2. Enhancement of influent SCN<sup>-</sup> concentration

SCN<sup>-</sup> was one of the main nitrogenous pollutants in the CPW besides ammonium. The feed SCN<sup>-</sup> concentration ascended from 100 to 300 mg/L and finally returned to 100 mg/L in stage VII. The influent concentration of NH<sub>4</sub><sup>+</sup>-N and ON was controlled at 150 mg/L and 25 mg/L, respectively. Evolutions of NH<sub>4</sub><sup>+</sup>-N, SCN<sup>-</sup> and ON concentration in the effluent and corresponding removal efficiency obtained with the variation of the feed SCN<sup>-</sup> concentration are illustrated in Fig. 3.

SCN<sup>-</sup> had inhibitory effect on the biodegradation of ammonia [25]. When the influent SCN<sup>-</sup> concentration increased from 100 mg/L to 200 mg/L, effluent NH<sub>4</sub><sup>+</sup>-N concentration of the HDMBBR increased from 14.2 mg/L to 23.4 mg/L, and then decreased to 15.7 mg/L gradually, which might be due to the enhancement of the adaptability to the SCN<sup>-</sup> shock load. Effluent NH<sub>4</sub><sup>+</sup>-N concentration of the LDMBBR increased from 23.2 mg/L to 36.3 mg/L without further decline. Degradation of SCN<sup>-</sup> produced a certain amount of NH<sub>4</sub><sup>+</sup>-N and 132 mg-N/L of ammonia was equivalent to 548 mg/L SCN<sup>-</sup> theoretically [24], which led to the increase of effluent NH<sub>4</sub><sup>+</sup>-N concentration in both reactors. The HDMBBR had better NH<sub>4</sub><sup>+</sup>-N removal efficiency under SCN<sup>-</sup> shock compared with LDMBBR.

It was proved that SCN<sup>-</sup> removal was complete and independent of influent SCN<sup>-</sup> concentration [26]. At HRT of 48 h, the MBBR could overcome the negative effect of toxic compounds and maintained high removal efficiency of SCN<sup>-</sup>, although biodegradation of SCN<sup>-</sup> might be affected by the rise of influent SCN<sup>-</sup> concentration. As shown in Fig. 3b, the removal efficiency of SCN<sup>-</sup> in the HDMBBR was more than 90%. In the LDMBBR, the concentration of effluent SCN<sup>-</sup> concentration increased gradually, particularly when the influent SCN<sup>-</sup> concentration increased to 300 mg/L. These results indicated that the HDMBBR, which was one of the reason that with the augment of influent SCN<sup>-</sup> concentration, effluent NH<sub>4</sub><sup>+</sup>-N concentration of the LDMBBR was higher than the HDMBBR.

The concentration of effluent ON gradually increased in both reactors with the increase of influent SCN<sup>-</sup> concentration. The degradation of ON in the HDMBBR was higher than in the LDMBBR. With the increase of the feed SCN<sup>-</sup> concentration, the difference of ON removal efficiency between the two reactors increased, which was mainly due to the lower SCN<sup>-</sup> degradation rate in the LDMBBR than in the HDMBBR.

Kim et al. [25] reported that the inhibitory effect of SCN<sup>-</sup> on nitrification took place in treating coking wastewater when the concentration of influent SCN- reached 200 mg/L. NH<sub>4</sub><sup>+</sup>-N produced by the degradation of SCN<sup>-</sup> caused nitrification inhibition as well. Nitrification performance of the HDMBBR and the LDMBBR with the increase of influent SCN<sup>-</sup> concentration is illustrated in Fig. 3d. In the HDMBBR, the effluent NO<sub>3</sub><sup>-</sup>-N concentration increased from 145 mg/L to 170 mg/L with the augment of influent SCN<sup>-</sup> concentration, and effluent NO<sub>2</sub><sup>-</sup>-N concentration was still less than 1 mg/L. Accumulation of NO<sub>2</sub><sup>-</sup>-N in the effluent of the LDMBBR was relative stable and ranged between 83.4 mg/L and 102 mg/L with the augment of feed SCN<sup>-</sup> concentration, and the maximum NO<sub>2</sub><sup>-</sup>-N accumulation concentration was 102 mg/L with the influent SCN<sup>-</sup> concentration of 300 mg/L.

TN removal efficiency with the increase of influent SCN<sup>-</sup> concentration is shown in Fig. 3e. Effluent TN concentration of the HDMBBR and the LDMBBR appeared a little enhancement with the increase of influent SCN<sup>-</sup> concentration and soon returned to the previous level in stages V and VI. Therefore, the increase of influent SCN<sup>-</sup> concentration did not have apparent effect on TN removal in the HDMBBR and LDMBBR. Nevertheless, TN removal efficiency in the LDMBBR was about two times higher than in the HDMBBR.

# 3.3. Variation of influent ON (aniline, pyridine and quinoline) concentration

Organic and inorganic nitrogenous pollutants were the main nitrogenous pollutants in the CPW [27]. ON was an important form in biologically treated wastewater effluents [28]. The influence of organic nitrogenous pollutant (aniline, pyridine and quinoline) on performance of the system would be investigated below. Influent ON concentration increased from 25 mg/L to 50 mg/L in stage VIII and further to 75 mg/L in stage IX, and finally returned to 25 mg/L in stage X. Evolutions of NH<sub>4</sub>+-N, SCN<sup>-</sup> and ON concentration increased from 25 mg/L in stage X.



Fig. 3. Pollutant evolution in the effluent and removal efficiency obtained with the increase of influent SCN<sup>-</sup> concentration, (a)  $NH_4^+$ -N, (b) SCN<sup>-</sup>, (c) ON, (d) nitrification performance and (e) TN.

tion in the effluent and corresponding removal efficiency obtained with the variation of the feed ON are illustrated in Fig. 4.

Bacteria converted dissolved ON to  $NH_4^+-N$  or  $NO_3^--N$ through hydrolysis and mineralization [29]. Aniline, pyridine and quinoline added in the influent wastewater were typical nitrogenous organic pollutants containing in the CPW, which had different degrees of  $NH_4^+-N$  biotransformation inhibition. Figs. 4a and b show that the removal efficiencies of SCN<sup>-</sup> and  $NH_4^+-N$  in the HDMBBR were higher than in the LDMBBR, although the biodegradability for SCN<sup>-</sup> and  $NH_4^+-N$  was affected with the increase of influent ON concentration in the two reactors.  $NH_4^+-N$ and SCN<sup>-</sup> removal efficiencies of the HDMBBR declined slightly with the augment of feed ON concentration, which were still more than 80%. However, SCN<sup>-</sup> removal efficiency dropped from 92.4% to 78.3% gradually with the augment of feed ON concentration in the LDMBBR, which was similar to the evolution of effluent  $NH_4^{+}-N$  concentration. Fig. 4c shows a slight increase of effluent ON concentration for the two reactors with the enhancement of feed ON concentration. Effluent ON concentration of the HDMBBR ascended from 6.8 to 12.5 mg/L when the feed ON concentration increased from 25 to 50 mg/L, and further increased to 23.5 mg/L when the feed ON concentration was 75 mg/L, and the corresponding effluent ON concentration for the LDMBBR increased from 7.8 to 16.5 mg/L, and further rose to 32.5 mg/L.

Aniline, pyridine and quinoline were typical nitrification inhibitors which caused insufficient nitrification [30]. In Fig. 4d, the shock of influent ON concentration affected LDMBBR more obvious than HDMBBR on nitrification performance. Effluent NO<sub>3</sub><sup>-</sup>-N concentration of the HDMBBR was maintained at around 150 mg/L with the feed ON concentration of 50 mg/L, and NO<sub>2</sub><sup>-</sup>-N accumulation in the LDMBBR decreased from 91.5 mg/L to 82.7 mg/L. When



Fig. 4. Pollutant evolution in the effluent and removal efficiency obtained with the increase of influent ON concentration, (a)  $NH_4^+-N$ , (b)  $SCN^-$ , (c) ON, (d) nitrification performance and (e) TN.

the influent ON concentration further increased to 75 mg/L, effluent NO<sub>3</sub><sup>-</sup>-N concentration of the HDMBBR decreased to 135 mg/L and 8 mg/L of NO<sub>2</sub><sup>-</sup>-N was detected. Effluent NO<sub>2</sub><sup>-</sup>-N concentration of the LDMBBR dropped further to 66.3 mg/L, which would further affect TN removal performance of the LDMBBR.

Effluent TN concentration of both reactors increased gradually with the increase of influent ON concentration, but TN removal rate was affected slightly with feed ON concentration of 50 mg/L after the system was stable. When the influent ON concentration further increased to 75 mg/L, TN removal rate of the LDMBBR was affected slightly and descended from 38.8% to 33.8%. The decrease of TN removal rate in the LDMBBR contributed to the influence of feed ON concentration on nitrification performance in the LDMBBR, which caused the reduction of TN removal efficiency. The HDMBBR maintained better nitrification performance comparing with the LDMBBR. Therefore, with the augment of feed ON concentration, the removal efficiency of TN by full nitrification and denitrification was more stable than short-cut nitrification and denitrification, although the LDMBBR had higher TN removal rate than HDMBBR throughout the experiments.

Finally, comparisons of nitrogenous pollutant removal efficiency between current research and other studies under the similar influent wastewater quality are shown in Table 3. According to the results from Table 3,  $NH_4^+$ -N removal efficiency was high under different processes for CPW treatment except for the LDMBBR, which would be due to the insufficiency of DO. Similar to  $NH_4^+$ -N removal efficiency, SCN<sup>-</sup> removal efficiency was high with different processes except for the HDMBBR. The maximum TN removal rate was 19% and 38% for the HDMBBR and the LDMBBR, which was much less than other CPW treatment processes. The insufficient TN removal performance of the two reactor in current study was because the anoxic environment

Table 3

Comparison of nitrogenous pollutant removal efficiency between current research and other studies under the similar in fluent wastewater quality

Pollutants	NH4+-N	SCN-	ON	TN	
A-A-O biofilm	98%	-	89%	-	[31]
MBBR	93%	94%	-	-	[18]
A <sup>2</sup> O-MBR	92.8%	-	-	79%	[32]
Fluidized biofilm process	99%	99%	_	93%	[33]
Pre-denitrification					
Anoxic-aerobic reactor	97%	100%	-	83%	[34]
HDMBBR	91%	97%	78%	19%	Current
LDMBBR	85%	92%	69%	38%	

was not enough for denitrification. Moreover, some interfering factors affecting the nitrogenous pollutant removal performance of the two reactors should be investigated in the following researches, such as the extension of HRT, the variations of DO concentration and the pH values of the influent wastewater.

# 4. Conclusion

Two MBBRs were operated to remove nitrogenous pollutants from simulated CPW. The increase of influent SCN and ON concentrations had little effect on TN removal rate for the HDMBBR (16-18%) and the LDMBBR (34-38%). Biodegradation rate of ON was the slowest comparing with NH,<sup>+</sup>-N and SCN<sup>-</sup> in the two reactors, followed by NH,<sup>+</sup>-N.  $\text{SC}\ensuremath{\vec{N}}\xspace^-$  removal rate of the HDMBBR was not affected with the influent SCN<sup>-</sup> concentration increasing from 100 mg/L to 300 mg/L, which decreased from 92% to 88% when the influent SCN<sup>-</sup> concentration was enhanced from 200 mg/L to 300 mg/L. The HDMBBR had better adaptability to the enhancement of nitrogenous pollutant shock load than the LDMBBR throughout the experiments besides TN removal rate. Nitrogenous pollutant removal performance of the two reactors would be recovered after the influent nitrogenous pollutant load turned to normal level.

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