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Bio-electrochemical treatment of wastewater with high ammonium concentration

Seyyed Alireza Mousavi[a,b,*], Shaliza Ibrahim[c], Mohamed Kheireddine Aroua[d,e], Arezoo Mahmoudi[a], Parastoo Darvishi[a]

[a]*Department of Environmental Health Engineering, School of Public Health, and Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran, emails: seyyedarm@yahoo.com/ sar.mousavi@kums.ac.ir (S.A. Mousavi), aam.740428@gmail.com (A. Mahmoudi), Pd.740531@gmail.com (P. Darvishi)*
[b]*Social Development and Health Promotion Research Center, Kermanshah University of Medical Sciences, Kermanshah, Iran*
[c]*Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia, email: shaliza@um.edu.my*
[d]*Research Centre for Carbon Dioxide Capture and Utilisation (CCDCU), School of Science and Technology, Sunway University, Jalan Universiti, Bandar Sunway, 47500 Selangor Darul Ehsan, Malaysia, email: kheireddinea@sunway.edu.my*
[e]*Department of Engineering, Lancaster University, Lancaster, LA1 4YW, UK*

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ABSTRACT

In this study, a multi-storey bio-electrochemical reactor equipped with a pump-around system has been developed to adjust pH at desired value during treatment of synthetic ammonium-rich wastewater. The efficiency of the reactor to remove a high concentration of ammonium has been evaluated at various C/N ratios. The results demonstrated that a multi-storey reactor had high potential to remove ammonium within the function of an extensive operational range of C/N ratio (0.5–4), which is three times higher than the twin-chamber up-flow bio-electrochemical reactor. The accumulation of nitrite in the anode at the highest C/N ratio of 4 was less than other applied ratios, with 64% ammonium removal.

Keywords: Wastewater; Nitrification; Denitrification; Electrolysis; Pump-around system

1. Introduction

The release of a high amount of ammonium from sewage sludge digester into the water body causes some environmental problems (e.g., eutrophication) and human diseases (e.g., blue baby syndrome) [1]. The effluent of sludge dewatering namely reject water as an ammonium-rich wastewater is about 1.5%–3.0% of the influent wastewater treatment plants in volume [2], which creates about 15% to 25% of the influent nitrogen loading for the activated sludge process [3]. Furthermore, the special characteristic of reject water such as low COD/N makes treatment of this wastewater difficult due to lack of organic carbon for denitrification through conventional denitrification [4]. Thus researchers carried out different reject water treatment methods, including fully autotrophic nitrification and denitrification via nitrite. The autotrophic process has attracted the attention of researchers because of several advantages such as 25% lower oxygen requirement and 40% less organic carbon demand for denitrification, no residual carbon sources, less clogging in reactors, faster kinetics of the process, less effluent turbidity because of lower growth rate [4,5]. Many studies have been developed to applied BER that has been inoculated by autotrophic bacteria, using CO_2 and $NaHCO_3$ as carbon

* Corresponding author.

source and molecular hydrogen as energy source [6–8]. The autohydrogenotrophic bacteria as denitrifiers use hydrogen as an energy source that can be produced through water electrolysis by using a bio-electrochemical reactor (BER) [9].

The BER allows sequential nitrification and denitrification (SND) due to the generation of suitable electron donors (H_2) and electron acceptors (O_2) as expressed in Eqs. (1) and (2) [10].

$$5H_2O \rightarrow 2.5O_2(g) + 10H^+ + 10e^- \quad (1)$$

$$10H_2O + 10e^- \rightarrow 5H_2(g) + 10OH^- \quad (2)$$

Important controlling factors in BER include pH, dissolved oxygen concentration, carbon source, energy source, temperature, electric current, as well as hydraulic retention time (HRT) [9]. To increase the rate of nitrification and denitrification and to overcome certain drawbacks such as accumulation of nitrite, high cost, low efficiency of process optimization of controlling factors are necessary [9,11,12]. Among the various factors influencing the nitrogen removal rate, substrate concentration plays a key role, such as carbon, which is the main object of this research.

The control of pH in a suitable range is critical in a BER. The alteration of pH in BER due to the nature of nitrification and denitrification process as well as the electrolysis of wastewater, may create unfavorable impact towards the performance of nitrifying and denitrifying bacteria when the current intensity is high [10,13]. On the other hand, the provision of a required electron acceptor and electron donor is very important to guarantee the performance of nitrification and denitrification process, respectively. Therefore, to overcome this shortcoming and to provide a stable microbial activity, in our previous work, a pump-around system is designed to adjust pH at desired values [10]. Bio-electrochemical systems demonstrated a promising potential for treating ammonium-rich wastewaters; recently, Kondaveeti et al. (2019) operated a bio-electrochemical denitrification system for treating leachate wastewater with high ammonium concentration. The results showed that by increasing voltage (0.7 to 2 V) the efficiency of system enhanced for nitrate removal form 81% to 97% [14]. Wu et al. [15] investigated the treatment of coking wastewater rich in ammonia nitrogen using an integrated three-dimensional electrochemical system. The rector showed a high ability to remove total nitrogen (70.7%) and COD (55.8%).

Several studies investigated the possibility of simultaneous nitrification and denitrification applying BERs for treatment of wastewater with low concentration of nitrogen components [16,17]. Mousavi et al. [4] have attempted to overcome shortcomings of previous studies by developing a new twin-chamber up-flow BER for treating ammonium-rich wastewater. Result of this study demonstrated that the optimum condition for ammonium removal was 90% at initial concentration of 200 mg L^{-1}. At higher concentration of 600 and 1,000 NH_4^+–N/L, the efficiency of system decreased to 39% and 19%, respectively. Therefore, the design and fabricate of a new reactor namely multi-storey BER equipped with a pump-around system was the aim of this research work to overcome on the shortcomings of the previous twin-chamber up-flow BER that has been developed by Mousavi et al. [4]. To the best of our knowledge, no multi-story BER with a pump-around system has been developed. Furthermore, the effect of the C/N ratio on the system has been investigated at the high concentration of ammonium.

2. Materials and methods

2.1. Medium composition

All chemicals in this study as analytical reagents were purchased from Merck Company, (Germany) and used without further purification. Artificial medium containing 1,000 mg L^{-1} NH_4^+–N; 1,000 mg L^{-1} NO_3^-–N; $NaHCO_3$ (C/N = 0.5,1, 2, 4), KH_2PO_4, K_2HPO_4, and 1 mL L^{-1} of stock solution according to Table 1 was prepared.

2.2. Activated sludge and bacteria acclimatization

The raw sludge was obtained from the Pantai Dalam wastewater treatment plant, Kuala Lumpur, Malaysia. The raw sludge has been filtered and was washed several times for removing debris and internal nitrogen components. The raw sludge has been used for a short-term enrichment of nitrifying and autohydrogenotrophic bacteria. The enrichment phase performed using laboratory-scale sequential batch reactors with a working volume of 5 L. Sludge with an initial mixed liquor suspended solid concentration of 2 g L^{-1} was inoculated in SBRs to acclimatize bacteria with high ammonium (1,000 mg L^{-1} NH_4^+–N), and nitrate (1,000 mg L^{-1} NO_3^-–N) concentration. The reactors were fed separately with the aforementioned synthetic wastewater.

2.3. Electrode and Nafion preparation

The pretreatment of electrodes was carried out at several phases; to remove impurities, all electrodes have been soaked in ethanol (100%) for 30 min, then were immersed in HCl solution (1 M) for 1 h. The cleaning of electrodes before each run was carried out by immersing in an acid chloride solution (1 M) for 1 h, soaking in 1.0 M NaOH for 1 h, and washing several times with deionized water.

The cation permeable membrane (CPM) was also pretreated before and after being installed in the BER by boiling

Table 1
Composition of trace element solution

Constituent	Value (mg L^{-1})
EDTA	10
$ZnSO_4{\cdot}7H_2O$	2.2
$CoCL_2{\cdot}6H_2O$	3.2
$MnCl_2{\cdot}4H_2O$	10.2
$CuSO_4{\cdot}5H_2O$	0.22
$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	2.2
$CaCl_2{\cdot}2H_2O$	1.1
$FeSO_4{\cdot}7H_2O$	10
H_3BO_3	0.3
$NiSO_4{\cdot}6H_2O$	1

in 30% v/v H_2O_2 and deionized water for 1 h, immersing in H_2SO_4 (0.5 M) for 1 h, and then soaking in deionized water until be installed in the reactor [18].

2.4. Bio-electrochemical reactor setup

According to Fig. 1, a multi-storey bio-electrochemical reactor (MS-BER) consists of four Plexiglass chambers (length: 42 cm, ID: 10 cm) with a total volume of 3.5 L for each compartment has been developed. Stainless steel plates (mesh: hole size 1 mm × 1 mm and 0.1 cm thickness) that have been screwed with 12 rods (D: 5 mm and H: 40 mm) were used as the cathode and anode electrodes at the bottom of all chambers. A programmable DC power supply (IPS-3202, RS Components, UK) was connected to the electrodes by the copper wire. The chambers have been filled by palm shell granular activated carbon (PSGAC) as biocarrier and third electrode in the range of 2–4 mm (600 g, height of 22 cm). Therefore, the effective volume as anode and cathode zones for each cell was 2 L. The anode and cathode chambers were joined together by a connection (length: 8 cm, and ID: 6 cm) located 4 cm from the bottom of each chamber. The CPM (Nafion 117, Dupont Wilmington, DE) has separated the anode and cathode chambers. A number of sampling ports (SP) were installed along the opposite side of each column to control pH. The entire system was equipped with two pump-around systems (anode and cathode, which comprises of four "multi-head peristaltic pumps" working at the same speed to recirculate wastewater from the anode and cathode chambers to maintain the pH level to approximately 7.5 ± 0.2 at the same flow rate (20 mL min^{-1}). Furthermore, the undesirable effect of pH was limited by considering the recirculation of flow from the last sampling port of each cathode zone to each anode zone. This step was done to transfer the produced alkalinity from the cathode chambers into the anode chambers for a more cost-effective operation that uses fewer chemicals to maintain desirable pH values. Four pH meters (pH/pH-MV/ORP portable meters, model HI 991002, Hanna Instruments, Romania) and four DO meters (model HI 9146, Italy) were located on opposite sides at a height of 25 cm from the bottom of each chambers. To limit the temperature interference, all experiments were conducted at 29°C ± 1°C.

2.5. Biomass growth and reactor operation

All compartments of the reactor have been filled with 600 g of GAC with the sticky surface (saturating in 1% agar solution (Bacto™ Agar) at boiling temperature). The enriched biomasses consist of nitrifying bacteria and autohydrogenotrophic denitrifying bacteria have been inoculated on the surface of GAC as biocarrier through sampling ports into anode and cathode zones, respectively.

The results of field emission scanning electron microscopy (FESEM), according to Fig. 2a, indicates the microporous activated carbon with the irregular shapes on it. Fig. 2b shows that bacteria successfully adhered to the PSGAC surface with different shapes such as straight rod, curved rod, and Vibrio at different sizes.

The system after 30 d of biomass acclimatization with synthetic wastewater has been operated at a constant

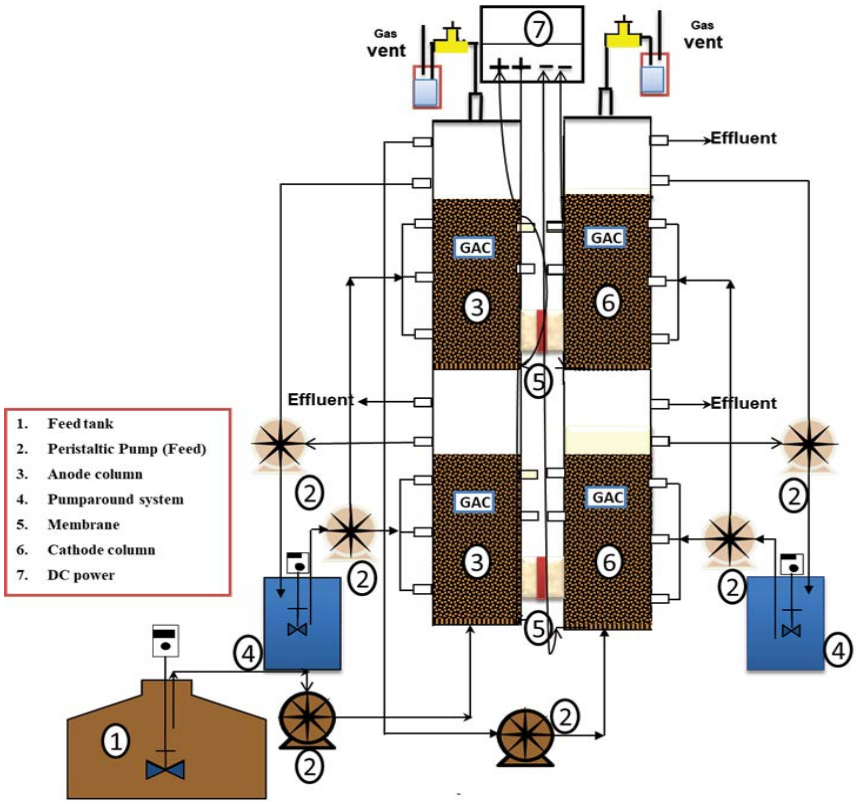

Fig. 1. Schematic of the laboratory-scale multi-storey bio-electrochemical reactor (MS-BER).

influent of flow 20 mL min^{-1} for 50 d. The main variable was the C/N ratio of 0.5, 1, 2 and 4 when all operational and environmental parameters were constant (I = 50 mA, T = 29°C ± 1°C and HRT = 24 h). All samples at the steady-state condition have been collected and after filtering by 0.2 μm syringe filters were analyzed for nitrogen components removal based on standard methods for water and wastewater experimental works [19]. During the operational phase after each run, the structure of electrodes has been investigated using FESEM. The results indicate that corroded electrodes have irregular surface texture due to bio-electrochemical reaction (Figs. 3a and b).

2.6. Analytical methods

The concentrations of NH_4^+–N, NO_3^-–N and NO_2^-–N have been determined by an advanced compact ion chromatograph (Metrohm® Ltd., Herisau, Switzerland). Temperature, pH and DO were continuously monitored. For errors higher than 5% in the samples, the analysis was repeated. The structure of biocarrier, bacterial adhesion on the surface of GAC and electrode corrosion have been investigated by an FESEM system (AURIGA® the new CrossBeam® Workstation (FIB-SEM) from Carl Zeiss NTS) with a computer system at a magnification capacity ranging from 5 to 30 kV folds.

3. Results and discussion

A developed twin-chamber up-flow bio-electrochemical reactor (TCUBER) by Mousavi et al. [4] indicated the SND with significantly adequate removal of nitrogen components at 200 mg L^{-1} ammonium. However, the performance of TCUBER resulted in very low efficiency for ammonium concentrations higher than 200 mg L^{-1} (Fig. 4) when the current intensity and HRT were 50 mA and 24 h, respectively. This finding may be due to the absence of pH control at the optimum level for nitrification compartment, nitrogen shock loading, no acclimatization of biomass with a high concentration of nitrogen components, the insufficient concentration of carbon source, and lack of carbon during SND in a BER [7, 9,10,17]. To tackle these shortcomings, three major courses of action were taken. First, to achieve bacteria with a high ability to eliminate high concentrations of nitrogen components, re-acclimatization of biomass for both compartments (nitrification and denitrification) was conducted for 30 d

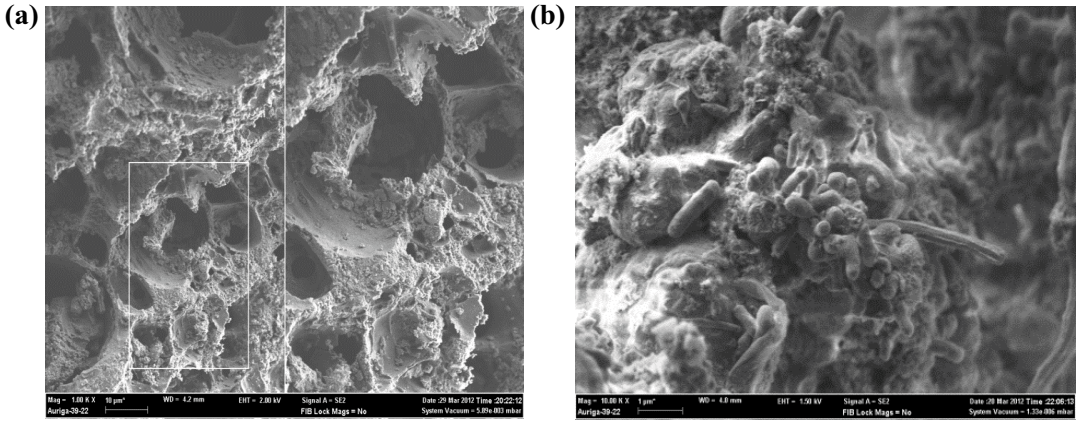

Fig. 2. Field emission scanning electron microscopy of the PSGAC structure ((a) Mag. = 1 kX), bacterial adhesion on GAC particles ((b) Mag. = 10 kX).

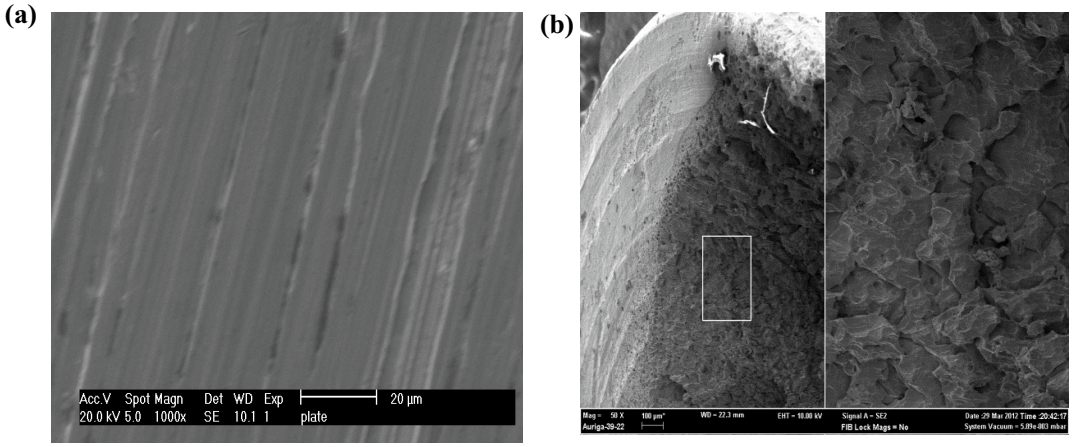

Fig. 3. Field emission scanning electron microscopy of electrode structure (Mag. = 50×).

when ammonium was 1,000 mg L^{-1}. Second, to maintain the pH constant at a favorable range (7.5 ± 0.2), the pump-around system and pH controller for anode and cathode compartments were employed. Third, to achieve high percentage removal, the BER was modified into a multi-storey configuration. The ability of a new reactor configuration to treat high ammonium concentration (1,000 mg L^{-1}) was investigated. The results obtained were reasonably far better (64% removal of ammonium) than those achieved for TCUBER (about 19%) under the same conditions.

3.1. Effect of C/N ratio

A series of experiments was conducted to investigate the effect of C/N ratios as important and critical parameters in biological processes, particularly in the nitrification and denitrification process. As shown in Fig. 5, the ammonium consumption decreased as the C/N ratio dropped from 4 to 0.5. This result confirmed that high C/N ratios could accelerate the growth of nitrifying and denitrifying bacteria in biofilms and thus promote total nitrification and denitrification rates. Furthermore, the MS-BER showed a high nitrification rate in a wider C/N ratio range. The results are in agreement with the findings of other researchers, who applied different ratios of C/N; Ghafari et al. [8] confirmed that the best optimum of the C/N ratio is about 7.8, and lower concentration of C/N ratio lead system to accumulate nitrite. Visvanathan et al. [20] applied C/N = 2 [20] and Karanasios et al. [21] achieved denitrification at C/N ratio = 0.5.

As seen in Fig. 6, the accumulation of nitrite in the anode under the highest C/N ratio of 4 was less than those of under the other applied ratios, removing 64% ammonium. By contrast, the accumulation of nitrite under the lowest C/N ratio of 0.5 increased. Besides, due to the carbon source limitation, partial nitrification was achieved. During first stage (I), because of the high ammonium-loading rate, partial nitrification was carried out with nitrite accumulation at a high C/N ratio of 4. In addition to the consumption of carbon by the nitrifying and denitrifying bacteria, the anode electrochemical oxidation could also produce carbon dioxide from the carbon electrode according to Eq. (3) [22], which can act as an inorganic carbon source for bacterial growth.

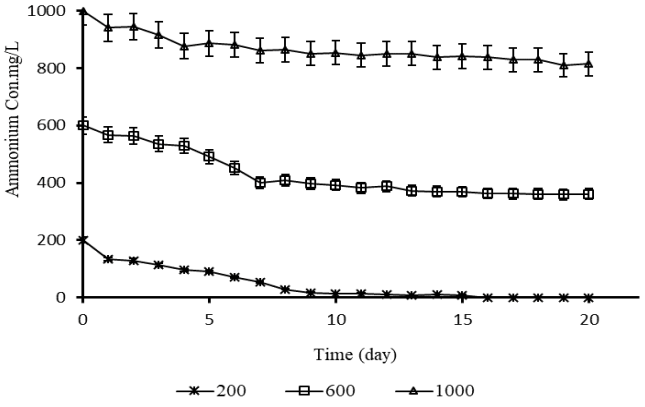

Fig. 4. Efficiency of ammonium removal at different concentrations (200, 600 and 1,000 mg NH_4^+–N/L) by TCUBER.

$$2H_2O + C \rightarrow 4H^+ + CO_2 + e^- \quad (3)$$

During the first stage (I), a significant impact was observed because of the high oxidation of ammonium, high availability of alkalinity and buffer capacity of the bicarbonate to maintain a constant pH as well as a high carbon concentration, which enhanced the efficiency of the system. The loading of the denitrification compartment depended on the efficiency of the nitrification compartment. Thus, at the highest C/N ratio of 4, higher nitrate and nitrite concentrations were generated than the other stages (0.5, 1 and 2). A decrease in carbon source results in weaker ability to oxidize ammonia, which leads to the decrease in nitrate and nitrite concentrations in the influent of the cathode compartment. The nitrite concentration was high at all runs, which can be due to the high concentration of ammonium in the system, the low concentration of DO and short HRT. Furthermore, incomplete denitrification could be another reason for the inhibition of the system when the initial nitrite and nitrate concentrations were high in the final effluent. The multi-storey reactor showed high nitrification and denitrification rates compared with previous research by a BER [4] but could not attain discharge standards for nitrogen components in a wider C/N ratio range. This finding could be attributed to low O_2 and H_2 generation as a function of low current and short HRT.

4. Conclusions

This study developed a novel reactor namely MS-BER with the ability to overcome the shortcomings of the

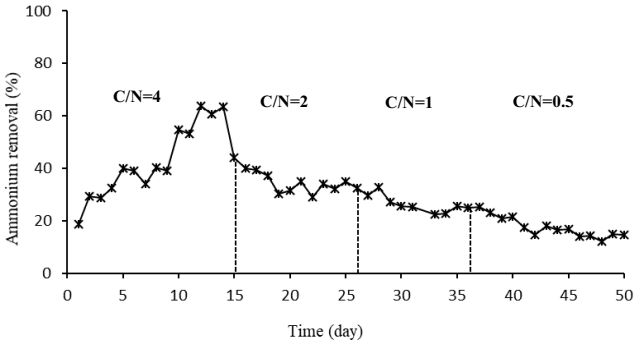

Fig. 5. Effect of C/N ratio on the removal efficiency of NH_4^+–N.

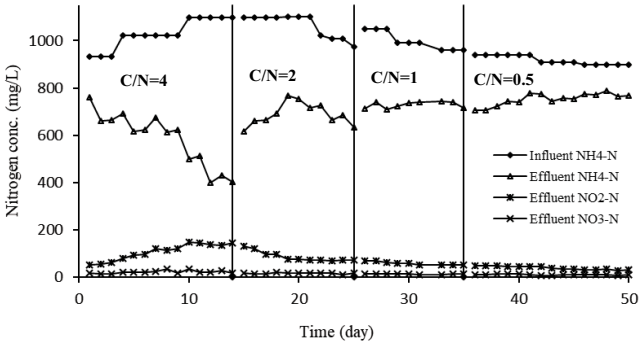

Fig. 6. Alteration of nitrogen components at different C/N ratio.

previous BER_S such as pH alteration and nitrite accumulation as well as inability to treat high concentration of nitrogen. MS-BER overcame the pH alteration by adjusting it around neutrality and made possible the high percentage removal of nitrogen that was not achievable by BERs in previous research. The results indicated that the efficiency of the system was influenced by the C/N ratio, and was greatly improved to 64% ammonium removal at high C/N of 4.

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