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Ammonia-Nitrogen (NH_3-N) and Ammonium-Nitrogen (NH_4^+-N) Equilibrium on The Process of Removing Nitrogen By Using Tubular Plastic Media

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Abstract

The biological process of nitrification-denitrification, involving a tubular plastic bio filter, reduces nitrogen in wastewater. During the process, ionised ammonia (NH_4^+) and unionised ammonia (NH_3) are formed simultaneously in the water. The presence of NH_4^+ causes the breakpoint of chlorination and the formation of disinfection by-products (DBPs) in the form of trihalomethana, while unionised ammonia (NH_3) is toxic to aquatic organisms. In this study, total ammonia nitrogen (TAN) removal efficiency using a tubular plastic bio filter was 14.31% with pH of 7.89 on the first day. TAN concentration in the bio filter reactor was 77.08 mg/l, and the NH3-N equilibrium reached 4.8 mg of NH_3-N/l while NH_4^+-N equilibrium went to 72.2 mg of NH_4^+-N/l. In the control reactor, TAN removal efficiency was 12.98%, where the NH_3-N equilibrium touched 1.94 mg of NH_3-N/l, and the NH_4^+ equilibrium reached 76.33 mg of NH_4^+-N/l with a pH of 7.56. With the rising of the pH, the equilibrium of the reaction tends to increase the concentration of the toxic NH_3-N.

1. Introduction

Wastewater derived from blackwater and greywater potentially contains nitrogen [1], which is a greater contributor to the decline in the quality of a body of water when compared to wastewater coming from industrial facilities [2]. Excessive nitrogen concentration in the environment can lead to changes in the natural nitrogen cycle between living beings, soil, water, and atmosphere [3]. Nitrogen contamination in water body can create serious problems, such as deterioration of water quality, eutrophication of dam, and potential hazard to animal and human health [4]. The nitrogen compound is a nutrient that can cause algal bloom, which reduces the amount of oxygen in the water, while the ammonia-nitrogen (NH_3-N) is toxic to aquatic life [5]. Nitrogen in domestic wastewater is in the form of organic nitrogen (± 40%) and ammonium nitrogen (± 60%) [6]. According to Gupta [5], the most widely used nitrogen-ion ammonium removal technology is ion exchange, adsorption, and biological technology. In general, nitrogen removal can be done by using biological processes like the nitrification-denitrification process[7,8]. Besides this particular process, there are several other removal processes, such as anaerobic ammonium oxidation (anammox), simultaneous nitrification and denitrification, and a combination of both [9]. In aerobic condition, a nitrification process occurs and consists of two stages of oxidation in sequence: ammonia is converted to nitrite by ammonia-oxidizing bacteria:

$$NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \qquad (1)$$

and nitrite is transformed to nitrate by nitrite-oxidizing bacteria:

$$NO_2^- + 0.5\ O_2 \longrightarrow NO_3^- \qquad (2)$$

The ionised ammonia (NH_4^+) and unionised ammonia (NH_3) exist simultaneously in the water, and can be measured as the total ammonia nitrogen (TAN). NH_3 is an unionised ammonia that can react with water to form ionised ammonia (NH_4^+) in a weak base; it is represented by the chemical equilibrium in equation 3.

$$NH_4^+ + OH^- \Leftrightarrow NH_3.H_2O \Leftrightarrow NH_3 + H_2O \qquad (3)$$

Ammonia, which is soluble, exists in equilibrium as both molecular ammonia (NH_3) and as ammonia in the form of the ammonium ion (NH_4^+). The relative concentration of each depends on the pH and temperature, with higher pH values and temperatures favouring the formation of a molecular ammonia that is toxic. The higher pH also leads to a higher ionised ammonia, thereby increasing toxicity [10]. The relative concentration of each depends on the pH and temperature, with higher pH values and temperatures favouring the formation of a molecular ammonia that is toxic. The higher pH also leads to a higher ionised ammonia, thereby increasing toxicity [11]. The effluent from the nitrogen removal process of blackwater and greywater biologically still contains pathogenic micro-organisms that could potentially contribute to human health problems. Therefore, a disinfection process must be performed [12]. Generally, this process is carried out at the stage of tertiary treatment. The chemical compound used most frequently in the disinfection process is chlorine [13]. However, chlorine is highly reactive with other compounds and can form new compounds that are toxic and may have carcinogenic effects to humans [5]. The presence of NH_4^+-N led to breakpoint chlorination (Cl_2 NH_4^+-N weight ratio=7.6÷15:1) and formation of trihalomethana as a by-product of disinfection [14,15].

The innovation of biological nitrogen removal is that it can be performed using a biofilm process, simultaneous nitrification/denitrification, shortcut nitrification/denitrification, and nitritation-anammox process [16]. Shortcut nitrification/denitrification process, in the form of sequencing batch reactor (SBR), can remove up to 95% of NH_4^+-N in domestic wastewater, with an initial concentration of 160-310 mg/l, while the total nitrogen removed is about 50% [17]. The Anaerobic/Oxic process is able to remove up to 93% of NH_4^+-N in wastewater, with an initial concentration of 65.4 to 105.7 mg/l [18]. The two-phase biotrickling filter (BTF) system is capable of removing ammonium nitrogen by 80% [19]. However, all these studies only discussed a decrease in nitrogen (NH_4^+-N and total nitrogen), and they did not mention the equilibrium between ionised ammonia (NH_4^+) and unionised ammonia (NH_3). In fact, the formation of NH_3 is undesirable thing due to its toxicity.

2. Materials and methods

2.1. Material

Domestic wastewater used in this study was obtained from the outlet of the communal wastewater treatment plant in Pedalangan, Banyumanik Subdistrict, Semarang City, Indonesia. The study was conducted in laboratory scale using a continuous reactor. Wastewater was collected in a 300-liter tank equipped with a pump to drain the sewage into the equalisation basin. Wastewater flowed into the reactors at the rate of 31 ml/sec.

2.2. Apparatus

This study was performed using two reactors. The first reactor was filled with a tubular shaped of plastic for the microorganism's growth medium and was equipped with a heater and an aerator, while the second one was only equipped with a heater and an aerator (Figure 1).

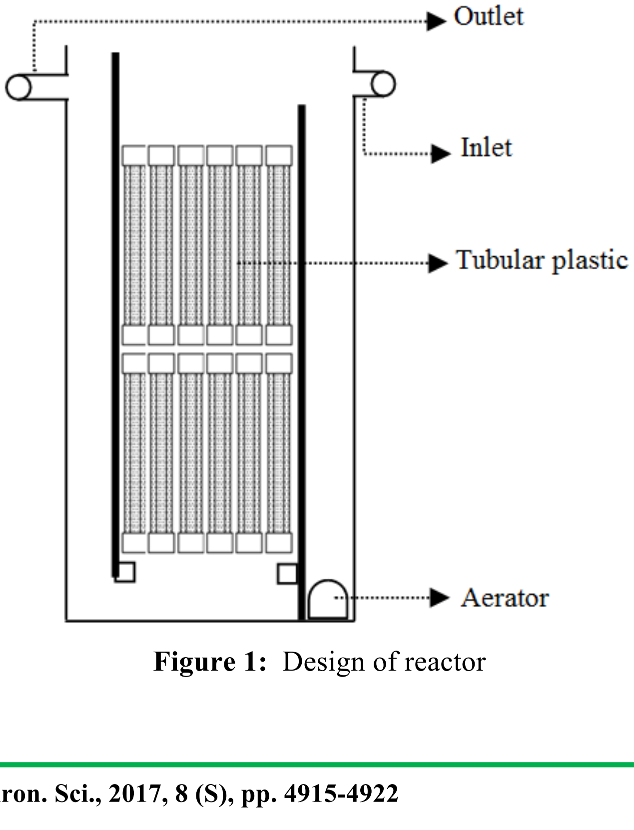

Figure 1: Design of reactor

The effective volume of the reactor was 45 litres that consisted of three baffles with different volumes: an aeration baffle with a capacity of 7.65 litres, a bio filter baffle with a capacity of 30 litres, and a settling baffle with a capacity of 7.35 litres. The hydraulic retention time (HRT) of wastewater was designated at 12 and 24 hours. Bio filter media were composed of tubular shaped plastic (Figure 2), 40 cm in height, 1 cm in diameter, and a total of 90 pieces. Every single tubular plastic was perforated randomly across its surface, giving a specific surface area of bio filter media of 200 m2/m3.

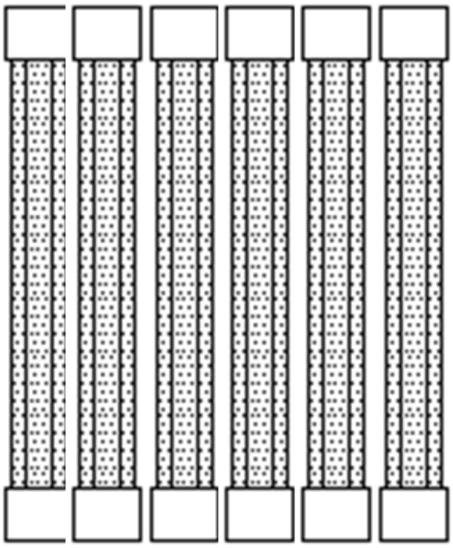

Figure 2: Illustration of Tubular plastic media

2.3. Procedures

Seeding and acclimatization are performed at the beginning of the experiment. Seeding was done by flowing the feedwater, containing a mixture of cow manure and domestic wastewater, into the reactor continuously until the water level reached 1 cm above the growth medium. To deal with fluctuation of bacterial populations in the stage of the stationary phase, the wastewater are batched for approximately 150 hours or 6.25 days from initial seeding [20]. Acclimatisation was performed by pumping the domestic wastewater from the wastewater collection tank to the equalisation basin, then gravitationally flowed to the reactor through a hose which is equipped with a flow regulator. Entry flow was set at 225 ml/min, the optimal flow for the growth of high biomass accumulation on the growth medium [21]. Air was also injected into the incoming wastewater in the reactor using an aerator for about two weeks or until the reduction efficiency of organic substances was stable (3-5 times reduction in Chemical Oxygen Demand /COD by the difference + 10%).

The pH parameter was measured using WalkLAB TL9000 pH meter, while dissolved oxygen (DO) was measured using WalkLAB DO meter. The concentration of COD (Chemical Oxygen Demand) was measured using the closed reflux method, the Total Ammonia Nitrogen (TAN) was measured using the Nessler method, and the N organic was measured by the Micro-Kjeldhal method. All reagent used was pure analysis (PA) by Merck Production, Germany. The NH_3-N concentration was calculated based on the TAN concentration [22] as follows:

$$NH_3\text{-}N = \frac{\text{TAN x } 10^{\text{pH}}}{e^{\left(\frac{6344}{273+℃}\right)}+10^{\text{pH}}} \qquad (4)$$

where:

NH3-N = ammonia concentration as nitrogen (mg NH_3-N/litre)

TAN = TAN concentration (mg/litre)

pH = pH value

^{o}C = temperature

Ammonium Calculation (NH4+-N) as Nitrogen:

$$NH_4^{+}\text{-}N = TAN – NH_3\text{-}N \qquad (5)$$

where:

NH4+-N = ammonium concentration as nitrogen (mg NH4+-N/litre)

Efficiency Calculation of Concentration Reduction

$$\text{Reduction efficiency} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\ \% \qquad (6)$$

where:

Reduction Efficiency = concentration reduction efficiency (%)

C_{in} = inlet sample concentration (mg/litre)

C_{out} = outlet sample concentration (mg/litre)

3. Results and discussion

3.1. Early state monitoring

Organoleptic observation of the acclimatisation process was performed for 7 days. The observation was conducted to determine the biofilm growth on the growth medium, since the biofilm growth was very slow and therefore difficult to be analyse quantitatively. This condition was in accordance with previous research by Gerardi [23] who stated that in the first few days, the bacterial growth in biofilm formation is not significant.

On the fourth day, the biofilm was already formed and on the ninth day, the biofilm became masses that thickened and spread onto most of the growth medium. On the tenth day, sampling was conducted at the inlet (equalisation basin) and outlet of each reactor to determine the quality of the effluent. On the fourteenth day, the efficiency of concentration reduction of COD (measured as total COD) in the wastewater was considered in a steady state, since the differences between three measurements were not greater than 10%. The maintenance process was conducted on the fifteenth day by washing the bio filter media using wastewater sprayed from above, manually cleaning the water stone, and also vacuuming the deposited mud.

On the nineteenth day, another wastewater quality measurement was conducted in order to determine whether the ability of COD concentration reduction efficiency had increased. The results showed that the efficiency of concentration reduction of COD had increased both in the bio filter reactor and the control reactor. According to Yong-you and Li-li [21], COD removal efficiency will decline after maintenance but will increase three to four days after maintenance.

3.2. Removal Efficiency of Total Ammonia Nitrogen (TAN)

The use of a tubular shaped plastic bio filter as a growth medium can improve the removal efficiency of TAN. The removal efficiency of the TAN pattern after four days has increased from 14.31% to 28.93%. Comparing this result with the control reactor (no growth medium), the removal efficiency was 12.98% on the first day,), 15.6% on the second day, 6.75% on the third day, and 12.31% on the fourth day, as shown in Figure 3.

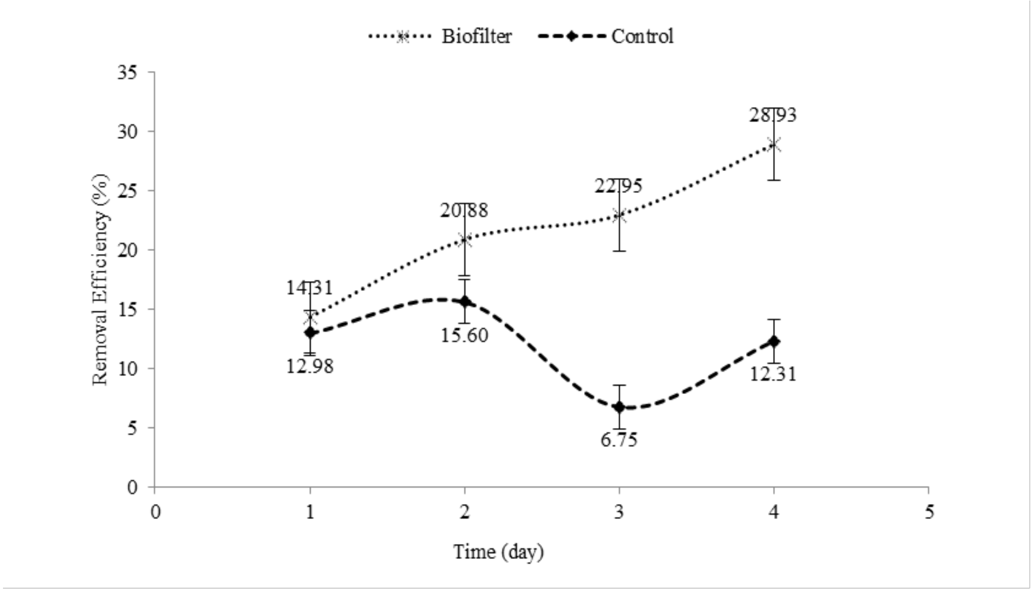

Figure 3: Removal Efficiency of TAN

According to the result, it was clear that the presence of a growth medium can increase the removal efficiency of TAN as a result of the nitrification process, the conversion of ammonia to nitrite and nitrite to nitrate. Ammonia was converted to nitrite by ammonia-oxidizing bacteria, while the conversion of nitrite to nitrate was performed by nitrite-oxidizing bacteria [9, 20, 24]. These processes took place sequentially in accordance with the reactions occurring as follows:

$$NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \quad (7)$$
$$NO_2^- + 0.5\ O_2 \longrightarrow NO_3^- \quad (8)$$

The surface of the tubular plastic growth medium allows the growth and colonisation of the bacteria, so creating a stronger bond among the bacteria [25, 26]. According to Graaff [27], TAN removal efficiency in black water using batch sequencing (SBR) reactor is 85% with 70 days of processing time with reactor's temperature of 35^{o}C. Li [28] used artificial waste with an initial ammonium concentration of 70 mg NH_4^+-N / l and be able to remove ammonium nitrogen by 81% with HRT of 32 hours. Li's study used aerobic aerobic biofilm (UMABR) reactor. Compared to previous studies, the TAN removal efficiency in this study is low. However, the use of Tubular plastic media has an advantage in field applications. The reactive surface area increases when the wastewater flow rises. This process also leads to an increase in the rate of biological reactions [29].

3.3. pH

According to Gaudy and Gaudy [30], low fluctuation of pH will accelerate the growth of bacteria that will improve the process' efficiency. It was found that the pH had increased due to the loss of carbon dioxide (CO2) in the water as a result of aeration that disrupted the following carbonate equilibrium reaction:

$$CO_3 + H_2O \Leftrightarrow CO_2 + 2\ OH- \quad (9)$$
$$HCO_3 \Leftrightarrow CO_2 + OH^- \quad (10)$$

The fluctuation of pH affects the equilibrium of ammonia (NH3) and ammonia in the form of ammonium ion (NH4+). The higher pH and temperature will allow the formation of ammonia (NH3), which is toxic [7]. During the experiment, pH fluctuated within the range of 7.1 to 8.1 as shown in Figure 4.

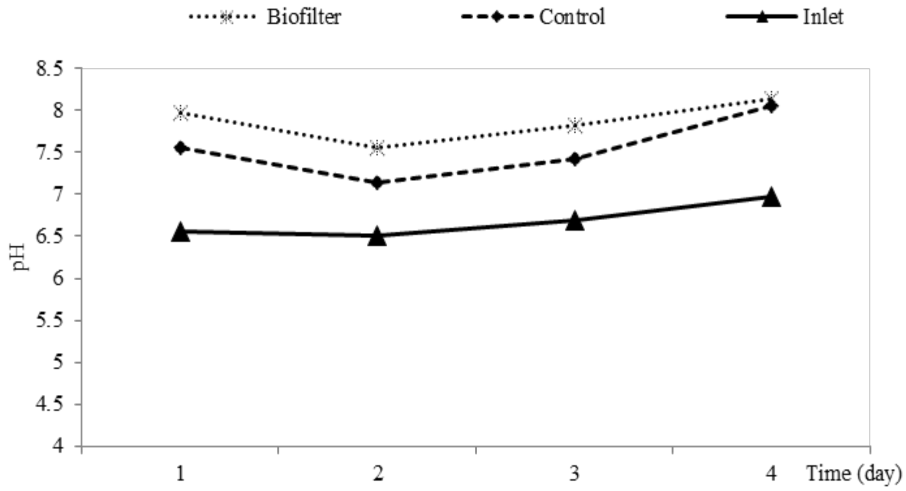

Figure 4: Fluctuation of pH in all reactors during TAN removal

The pH indicated that the wastewater tends to be in a neutral to alkaline state. At this pH, the denitrification process performs well and forms nitrate [8]. The pH will affect the equilibrium NH3 and NH4+. According to Gupta [5] and Adeva [31] when the pH of the solution is less than 9.3, the hydrogen ion reacts with ammonia to produce ammonium ions.

3.4. Dissolved Oxygen

Dissolved Oxygen (DO) is one of key parameters that affects nitrogen removal. DO plays a role in nitrification process and inhibits the denitrification process. Oxygen is functional as an electron acceptor to restrain the enzymes that are involved in the denitrification process [32]. Adequate DO concentration can improve the ability of heterotrophic and autotrophic bacteria to break up organic compounds and ammonia [33]. In this study, the DO concentration was in the range of 5.2 to 7.0 mg O_2/l (Figure 5). According to Metcalf [34], the optimal DO concentration to remove nitrogen is more than 1 mg O_2/l.

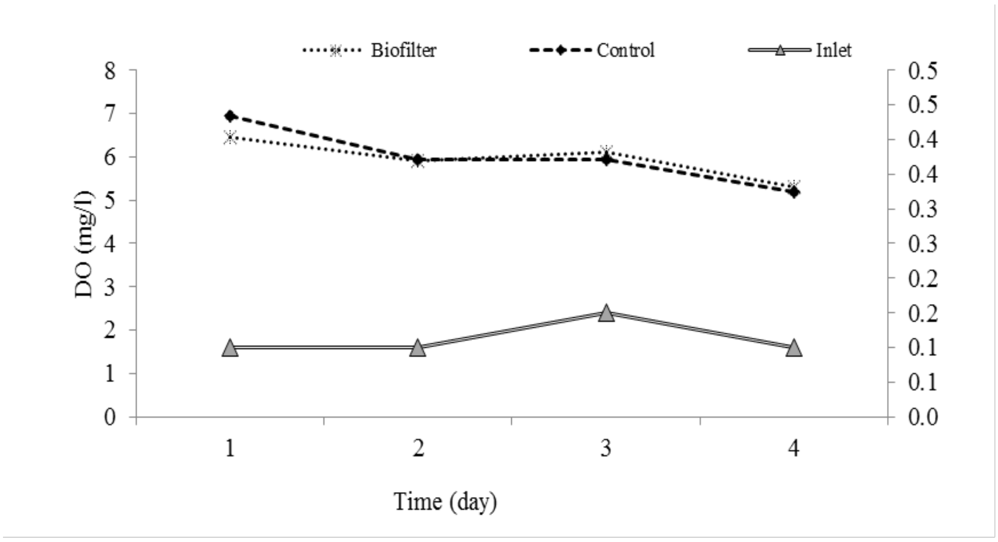

Figure 5: The concentration of DO during running stage

3.5. The equillibrium of Ammonia-nitrogen (NH3-N) and Ammonium-nitrogen (NH4+-N)

Figure 6 showed the equilibrium of NH3-N and NH4+-N in the wastewater at an early stage. The NH3-N concentration of initial wastewater varied on days 1, 2, 3, and 4 by 0.21 mg of NH3-N/l, 0.19 mg of NH3-N/l, 0.27 mg of NH3-N/l, and 0.5 mg of NH3-N/l, respectively. Meanwhile, the concentration of NH4+-N on days 1, 2, 3, and 4 were 89.75 mg of NH4+-N/l, 88.91 mg of NH4+-N/l, 94.07 mg of NH4+-N/l, and 81.67 mg of NH4+-N/l, respectively. Fluctuation in the concentration was an indication that the initial concentration of the wastewater used was varied.

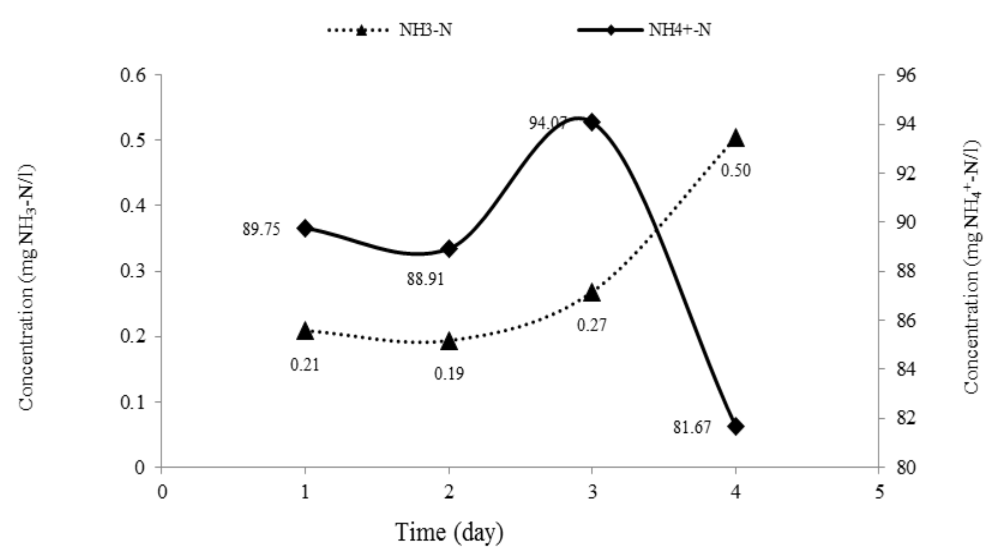

Figure 6: Equilibrium of NH_3-N and NH_4^+-N at early stage

The equilibrium of NH3-N and NH4+-N/l in the bio filter reactor outlet is shown in Figure 7. On the first day, TAN removal efficiency on the bio filter reactor reached 14.31%. TAN concentration in the plastic media bio filter reactor was 77.08 mg/l, with the equilibrium of NH3-N at 4.8 mg of NH3-N/l and NH4+-N at 72.2 mg of NH4+-N/l. Compared to the concentration of wastewater in the inlet, it appeared that NH4+-N had decreased from 89.75 mg of NH4+-N/l to 72.2 mg of NH4+-N/l. On the other hand, NH3-N level had increased from 0.21 mg of NH3-N/l to 4.8 mg of NH3-N/l. The pH on the first day was 7.98, which indicated base condition. The higher the pH, the more the equilibrium of the reaction tended to increase the concentration of NH3-N, which is toxic [7].

The NH3-N concentration in the bio filter reactor on the second day had decreased, but on the third and fourth days had increased to 5.2 mg of NH3-N/l when the pH reached 8.14, as shown in Figure 7. The TAN removal efficiency in the control reactor on the first day was 12.98%. The TAN concentration was 78.28 mg/l, with the NH3-N equilibrium at 1.947 mg of NH3-N/l and NH4+-N at 76.335 mg of NH4+-N/l, with a pH of 7.56. The

NH3-N concentration in the control reactor on the second day had decreased, but on the third and fourth days had increased to 5.61 mg of NH3-N/l when the pH reached 8.05, as shown in Figure 8.

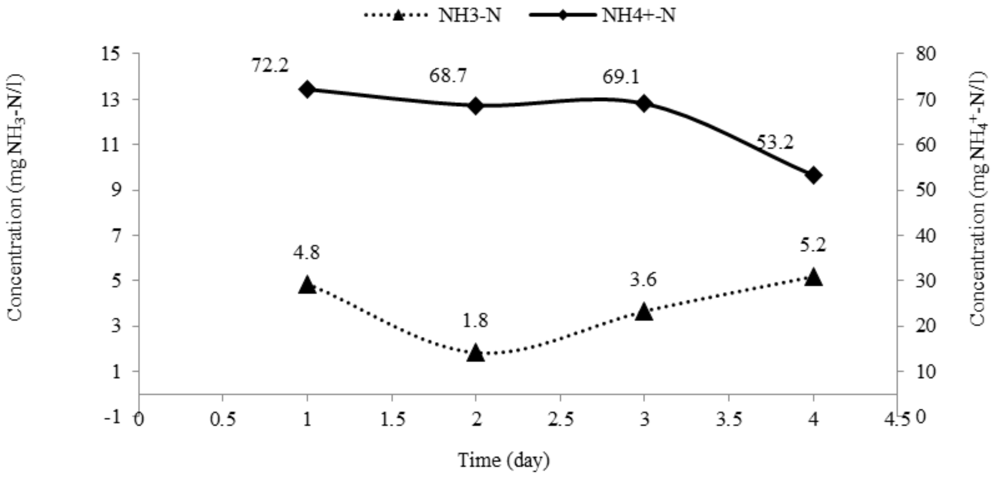

Figure 7: Concentration of NH3-N and NH4+-N of wastewater in bio filter reactor

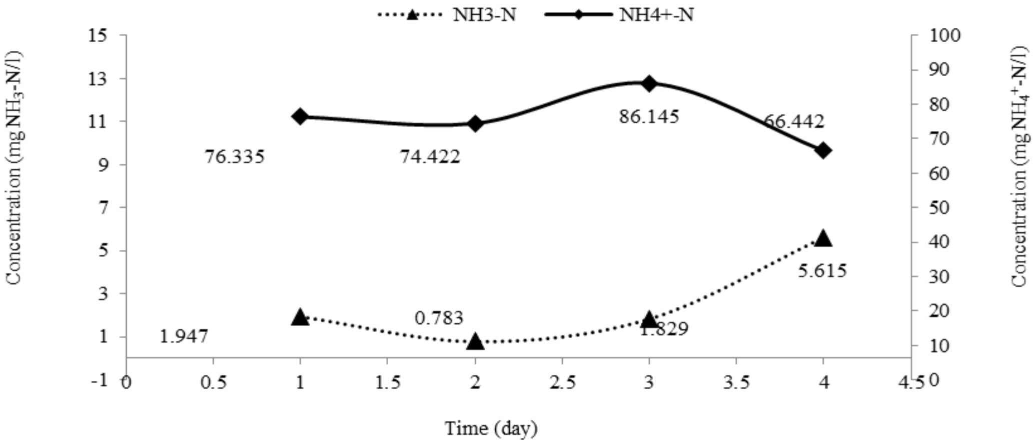

Figure 8: Concentration of NH_3-N and NH_4^+-N in control reactor

Based on the equilibrium on the biofilter reactor and the control tends to be influenced by the pH. The greater the pH value the reaction equilibrium tends to form NH3-N as the following equation.

$$NH_3 + H^+ \Leftrightarrow NH_4^+$$

Based on the equilibrium reaction, if the pH is large (H + small), then the reaction equilibrium will shift to the reactant to form NH_3-N which is toxic. This is in accordance with revelation [5,31] when the pH of the alkaline solution does not react with ammonia to produce ammonium ions.

Conclusion

This study discussed the equilibrium between ammonium-nitrogen (NH4+-N) and ammonia-nitrogen (NH3-N) in the Total Ammonia Nitrogen (TAN) removal process in domestic wastewater, using a biological process involving tubular plastic media. The results showed that the TAN removal efficiency using a tubular plastic bio filter on the first day reached 14.31% with a pH of 7.89. The TAN concentration in the plastic media bio filter reactor was at 77.08 mg/l, with an equilibrium of 4.8 mg of NH3-N/l and 72.2 mg of NH4+-N/l. The TAN removal efficiency in the control reactor on the first day was up to 12.98% with a pH of 7.56. The TAN concentration in the control reactor was 78.28 mg/l, with a NH3-N equilibrium of 1.94 mg of NH3-N/l and a NH4+-N equilibrium of 76.33 mg of NH4+-N/l. The TAN removal process in wastewater decreased the NH4+-N and generated NH3-N, but the NH3-N level could increase due to a rise in pH.

References

1. L.A. Ghunmi, G. Zeeman, M. Fayyad, and J. B.Van Lier.*Crit. Rev. Env. Sci. Technol,* 41 (2011) 657-698.
2. D. Nourmohammadi, M.B. Esmaeeli, H. Akbarian, M. Ghasemian. *J. Environ. Public Health,* 6 (2013).
3. D. Obaja, S. Macé, J. Costa, C. Sans, J. Mata-Alvarez, *Bioresour Technol,* 87 (2003) 103–111.
4. M. Khan, F. Mohammad. *Eutrophication: Challenges and Solutions. In: Ansari A., Gill S. (eds) Eutrophication: Causes, Consequences and Control*. Springer, Dordrecht. (2014).
5. V. K. Gupta, H. Sadegh, M. Yari, R. Ghoshekandi, B. Maazinejad, M. Chahardori. *Glob. J. Environ. Sci. Manag,*1 (2) (2015).
6. R.P. Schwarzenbach, T. Egli, T.B. Hofstetter, U.V. Gunten, B. Wehrli, *Annu. Rev. Env. Resour,* 35 (2010) 109-136.
7. Water Environment Federation. *Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants.* Water Environment Federation: Alexandria, Virginia (2005).
8. C. Grady, G. Daigger, N. Love, C. Filipe, *Biological wastewater treatment*, IWA Publishing, (2011).
9. Breisha, Gaber Z. *Nature and Science.* 8(12) (2010) 210-228.
10. S. I. Abou-Eleala, M. E. Fawzy, M. El-Khateeb, W. Abdel-Halim, *J. Appl. Sci. Res*, 8 (10) (2012) 5190-5197.
11. R. Erickson, *J. Water Res,* 19 (8) (1985) 1047-1058.
12. M. Jiawen, F. Yaoyu, H. Yue, N.V. Eric, X. Lihua, *J. Water and Health*, (2016).
13. X. Zhang, L, Weiguang, R. Ernest, Blatchley, W. Xiaoju, R. Pengfei, *Water Research,* 68 (2015) 804-811.
14. V. Patroescu, C. Jinescu, C.Cosma, I. Cristea, V. Badescu, C.S. Stefan, *Journal Metrics,* 66 (4) (2015) 537-541.
15. R. Liu, C.Tian, X.Liu, H.Jiang, H.Liu, J. Qu, W. Jefferson, *J. Chem. Eng,* 197 (2012) 116-122
16. X. Li, S. Sun, B. D. Badgley, S. Sung, H. Zhang, Z. He, *Water Res.* 94 (2016) 23–31.
17. P. Yongzhen, G.Shouyou, W. Shuying, B. Lu, *Chin. J. Chem. Eng*, 15 (1) (2007) 115-121.
18. X.Wang, Y. Ma, Y. Peng, S. Wang, *Bioprocess Biosyst. Eng,* 30 (2) (2007) 91-97
19. W.Li, C.Loyola-Licea, D.E.Crowley, Z.Ahmad, *Process Safety and Environmental Protection,* 102 (2016) 150–158.
20. L. D. Mackenzie, *Water and wastewater engineering. Design Principles and Practice*. New York: McGraw-Hill Professional (2010).
21. H.Yong-you, W. Li-li, *J. Environ. Sci,* 17 (2) (2005) 281-284.
22. A. Anthonisen, R.Loehr, T. Prakasam, E.Srinath, *J. Water Pollut. Control Fed,* (1976) 835-852.
23. M. H. Gerardi. *Wastewater bacteria (Vol. 5):* John Wiley & Sons (2006).
24. D. Dharumadurai, N. Thajuddin. *Microbial Biofilm: Important and application.* InTech: India (2016).
25. K.Kawai, M. Urano, S. Ebisu, *J. Prosthet. Dent,* 83 (6) (2000) 664-667.
26. H. Tang, T.Cao, A.Wang, X.Liang, S. O. Salley, J. P. McAllister, *J. Biomed. Mater. Res. A.* 80 (4) (2007) 885-894.
27. M. S. Graaff, H.De, G.Temmink, Zeeman, M.C.M.V. Loosdrecht, *Water Research,* 5 (2015).
28. X.Li, S.Sun, B.D.Badgley, S.Sung, H.Zhang, Z. He, *Water Res.* 94 (2016) 23–31.
29. N. Duong, Q. Chanh, L. Bing, T.V. Quang, M.Terashima, R. Goel, *Journal of Water and Environment Technology* 14 (5) (2016) 398–410.
30. A. F. Gaudy, E. T. Gaudy, *Microbiology for Environmental Scientists and Engineers.* New York: McGraw-Hill (1980).
31. M.M. Adeva, G. Souto, N. Blanco, C. Donapetry. *Metabolism* 61(11) (2012) 1495-1511.
32. W. G. Zumft. *Microbiol. Mol. Biol. Rev.* 61 (4) (1997) 533-616.
33. L. Hu, J.Wang, X.Wen, Y. Qian, *Process Biochem.* 40 (1) (2005) 293-296.
34. E. Metcalf, *Wastewater engineering: treatment and reuse*. New York: McGrawHill. (2003).

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