

Ammonia-Nitrogen Reduction in Low Strength Domestic Wastewater by Polyvinyl Alcohol (PVA) Gel Beads

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ABSTRACT

This study aimed to evaluate the efficacy of polyvinyl alcohol (PVA) gel beads as an immobilized biofilm carrier to enhance the reduction rate of Ammonia-Nitrogen ($\text{NH}_3\text{-N}$) and Chemical Oxygen Demand (COD) in domestic wastewater. Laboratory scale reactors were developed to assess the reduction levels of ammonia-nitrogen and COD with and without PVA gel beads using optimal and non-optimal treatment mode settings based on operation procedures from the sewage treatment plant in Taman Kajang Utama, Selangor. The treatment method used is an activated sludge sequencing batch reactor with a treatment cycle duration of 288 minutes. The findings showed the ammonia-nitrogen reduction by non-optimal treatment mode is more effective, with a reduced rate of 62.96% to 65.71% compared to optimal treatment mode with a reduced rate of 30.94% and treatment without PVA gel beads (optimal and non-optimal) with a reduced rate of 32.41% to 47.85%. The ammonia-nitrogen reduction rate using PVA gel beads for non-optimal treatment mode was significantly increased from 17.86% to 18.82% and complied with ammonia-nitrogen reduction parameter 10mg/L, Standard A of Environmental Quality (Sewage) Regulations 2009 (EQSR 2009). The rate of COD reduction using the non-optimal treatment mode was also more stable, with a reduced rate of 70.68%. It was also found that the COD reduction

rate using PVA gel beads for the non-optimal mode was better than the optimal mode, which was 70.68% compared to 42.0%, and both treatment modes complied with COD reduction parameters 120mg/L, Standard A of EQSR 2009.

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INTRODUCTION

According to Malaysian Sewerage Industry Guideline (MSIG) Volume IV, 2009, all domestic sewage treatment plants (STP) in Malaysia are designed to treat the incoming biodegradable organic loading Biochemical Oxygen Demand (BOD) of 250mg/L and Chemical Oxygen Demand (COD) of 500mg/L of influent values (Services, 2016). Nonetheless, preliminary studies and previous data records show that Malaysia's biodegradable organic loading of sewage is low and fluctuating, which the influent measured COD concentration can reach as low as 50–150mg/L and the BOD reading can reach as low as 40–70 mg/L (Hanafiah et al., 2019). The ammonia-nitrogen reduction can be accomplished through the nitrification and denitrification processes, for which most STPs in Malaysia are either designed or upgraded. The efficiency of ammonia-nitrogen reduction is determined by several variables, including the amount of biodegradable organic material loaded into the STP. This low concentration is most likely the result of dilution or infiltration through the sewerage conveyance system. Infiltration occurs due to poor pipe jointing, cracks, aging pipe, and other factors (Suruhanjaya Perkhidmatan Air Negara, 2016). When the organic matter content of the wastewater influent is low, especially the carbon source, the denitrification process by denitrification bacteria is hampered. The process of converting nitrite ions (NO_2^-) and nitrate ions (NO_3^-) into harmless nitrogen gas (N_2) is inhibited, which impedes the ammonia-nitrogen reduction process. The high concentration of NO_3^- and NO_2^- ions released into the receiving water body does not meet the ammonia-nitrogen reduction parameter 10mg/L, Standard A of Environmental Quality (Sewage) Regulations 2009 (EQSR 2009) and it would disrupt the receiving water quality and aquatic ecosystem (Rahimi et al., 2020). To address water quality degradation by improving water quality, the Government spent approximately RM26.3 billion from the 8th Malaysia Plan to the 11th Malaysia Plan (2001–2020) to modernize sewerage facilities and infrastructure. Therefore, this study is relevant and essential for further analysis and proposing suitable and practical solutions for optimizing and removing ammonia-nitrogen from low-strength domestic wastewater.

MATERIALS AND METHODS

Biological Treatment Process by Sequencing Batch Reactor Without Polyvinyl Alcohol (PVA) Gel Beads

For this study, optimum and non-optimum treatment mode settings were adopted from the actual operation of the sewage treatment plant (STP) in Taman Kajang Utama, Selangor, as shown in Table 1. Taman Kajang Utama STP is operated by using sequencing batch reactor (SBR) process in continuous feed configuration targeting pollutants removal as specified under Standard A, EQSR 2009 (EQA 1974), and it received the same influent as the lab-scale reactor (though in continuous feed vs semi-batch feed) with similar operating

conditions. Originally, the Taman Kajang Utama STP was designed to operate in non-optimal treatment settings. However, for energy-saving measures, the plant operator has optimized the operation of the current sewage treatment system by minimizing the use of blowers during the aeration phase while at the same time maintaining the effluent quality that meets the Standard A effluent discharge.

Table 1

Summary of the biological wastewater treatment process in Taman Kajang Utama, Selangor

Treatment mode (Optimum)	Treatment duration (minutes)	Treatment mode (Non-optimum)	Treatment duration (minutes)
Aeration	72	Aeration	120
Denitrification - idling	48	Denitrification - idling	0
Denitrification - stir	48	Denitrification - stir	48
Settling	48	Settling	48
Discharged	72	Discharged	72
Total Treatment Time	288	Total Treatment Time	288

One lab-scale reactor with 5L capacity (4L raw sewage taken from the secondary screen chamber of Taman Kajang Utama STP and 1L of seed sludge (MLSS) taken from SBR tank No. 2 of Taman Kajang Utama STP was fed into the reactor) was developed to run an ammonia-nitrogen and COD reduction simulation using an activated sludge sequencing batch reactor. The simulation of the sequencing batch reactor was conducted based on two scenarios as per Table 2.

Table 2

Experiment set-up by a sequencing batch reactor

Scenario	Treatment Setting	Remarks
1st Scenario	Optimum	The total simulation time is 288 minutes. Raw sewage (low concentration) was taken from Taman Kajang Utama STP to run the simulation
Low COD and NH ₃ -N concentration at the beginning of the treatment process	Non-optimum	
2nd Scenario	Optimum	<ul style="list-style-type: none"> The total simulation time is 288 minutes, and raw sewage (low concentration) was taken from Taman Kajang Utama STP to run the simulation 1.2 g glucose (C₆H₁₂O₆) was added to the raw sewage at the beginning of the treatment process.
High COD and low NH ₃ -N concentration at the beginning of the treatment process	Non-optimum	

The low concentration of incoming raw sewage (consists of Biochemical Oxygen Demand (BOD), COD, Ammonia-Nitrogen, oil & grease, total organic carbon, and alkalinity, among others) and activated sludge were collected from the same sewage

treatment plant for this experiment. In this experiment, 1.2g glucose ($C_6H_{12}O_6$) was added to the raw sewage collected from Taman Kajang Utama, Selangor, at the beginning of the treatment process to increase the concentration of COD to play a vital role as a carbon source, especially in the denitrification process. Ventilation and stirring were used in the treatment process depending on the mode of treatment to be performed. The NH_3-N and COD parameter were observed

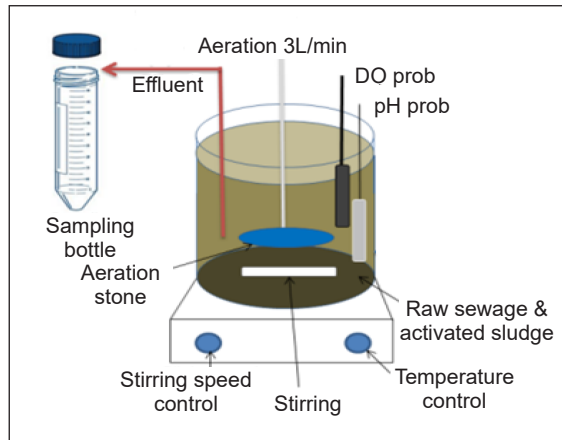


Figure 1. Schematic of a laboratory-scale reactor

and tested by American Public Health Association (APHA) standard method. Dissolved oxygen (DO), pH, and temperature were also measured during the operation of the lab-scale reactor. The setup of a lab-scale reactor is shown in Figure 1. The experiment observed that the pH range was between 6.0–7.5, and the temperature range was kept at 25–28°C with no alteration to the parameters. DO content was maintained at 4.71–7.10 mg/L

The COD and NH_3-N reduction efficiency (%) was determined by using the following Equation 1 (Kim et al., 2021):

$$\text{COD and } NH_3-N \text{ reduction efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where C_o : initial COD and NH_3-N concentration, mg/L; C_e : final equilibrium COD and NH_3-N concentration, mg/L

Biological Treatment Process by Sequencing Batch Reactor with Polyvinyl Alcohol (PVA) Gel Beads-Preparation of Synthetic Wastewater

This experiment developed two different size reactor tanks with 5L and 4L capacity. A 3L and 2.4L synthetic wastewater (60% of reactor capacity) with various compounds and compositions were prepared, contained (per lit): $C_6H_{12}O_6$ 500mg, NH_4Cl 122mg, K_2HPO_4 22mg, $MgSO_4$ 50mg, $FeSO_4 \cdot 7H_2O$ 40mg, $NaCl$ 15mg, $CaCO_3$ 100mg, EDTA 6mg and Na_2HPO_4 15mg (Tuyen et al., 2018). This experiment used $C_6H_{12}O_6$ and NH_4Cl chemical reagents as COD and ammonia sources. In addition, a 1L and 0.8L activated sludge (20% of reactor capacity) was collected from SBR Tank No. 2 at Taman Kajang Utama, Selangor sewage treatment plant, and 1L and 0.8L of PVA gel beads (16%–20% of total reactor volume) were added to the reactor tank and mixed with synthetic wastewater (Wang et al., 2018). PVA gel beads with 3–4mm diameter in a spherical shape with a

density of 1.025g/cm^3 , a surface area of $2,500\text{--}3,000\text{ m}^2/\text{m}^3$ and network $10\text{--}20\text{-micron}$ pores were purchased from Kuraray Co. Ltd., Japan. The experiment with PVA gel beads was performed for low COD and $\text{NH}_3\text{-N}$ concentrations at the beginning of the treatment process. The low concentration of raw sewage represents the actual state of domestic wastewater characteristics in Malaysia.

Experiment Start-Up Process with Polyvinyl Alcohol (PVA)-Gel Beads

All substances were mixed and continuously aerated (24 hours) in a 5L and 4L single reactor to promote microbial growth in highly porous PVA gel beads and to adapt bacteria to organic matter. The startup phase for microbial growth in synthetic wastewater took about 28 days (acclimatization phase). During this phase, $1.2\text{L--}1.5\text{L}$ synthetic wastewater in the reactor was replaced with new synthetic wastewater at certain interval days until the startup phase stabilized with a consistent reduction rate of COD and $\text{NH}_3\text{-N}$. On day 29, the synthetic wastewater was replaced with $1.6\text{L--}2.0\text{L}$ raw sewage collected from Taman Kajang Utama, Selangor, to acclimate the microbial growth in PVA gel beads with actual domestic sewage. This startup process continued until day 34, when the bacteria had reached the stationary phase and were ready to be used for the study until the reduction rate of COD and $\text{NH}_3\text{-N}$ became consistent and stable at $60\text{--}70\%$ at the end of the acclimatization period. The $\text{NH}_3\text{-N}$ and COD parameter were observed for 34 days startup phase and tested by American Public Health Association (APHA) standard method. Similarly, pH, dissolved oxygen (DO), and temperature were also measured for 34 days startup phase using digital portable devices, namely, Eutech Instruments Cyberscan pH 300 and Hanna multiparameter DO meter-HI2040. The overall timeline of the startup phase is shown in Figure 2.

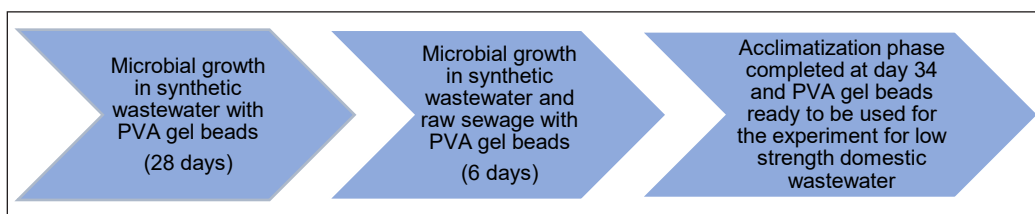


Figure 2. Overall timeline for the startup phase of microbes with PVA gel beads

RESULTS AND DISCUSSION

Biological Treatment Process by Sequencing Batch Reactor Without Polyvinyl Alcohol (PVA) Gel Beads

The summary of COD and $\text{NH}_3\text{-N}$ reduction performance without PVA gel beads is shown in Table 3. The graph of ammonia-nitrogen and COD reduction performance without PVA gel beads for low COD and $\text{NH}_3\text{-N}$ concentration at the beginning of the treatment process (optimum and non-optimum treatment setting) is shown in Figures 3 and 4.

Table 3
COD and NH₃-N reduction efficiency without PVA gel beads

Scenario	Treatment Setting	Temp (°C)	pH	COD Reduction Rate	NH ₃ -N Reduction Rate	C/N ratio
1st Scenario Low COD and NH ₃ -N concentration at the beginning of the treatment process	Optimum	25.0 to 27.7	6.52 to 7.50	55.95% to 86.14%	32.41% to 44.30%	2.62 to 2.89
	Non-Optimum	25.8 to 27.8	6.87 to 7.59	58.65% to 84.30%	44.14% to 47.85%	6.37 to 10.05
2nd Scenario High COD and low NH ₃ -N concentration at the beginning of the treatment process (1.2 g glucose (C ₆ H ₁₂ O ₆) was added)	Optimum	25.8 to 27.5	6.85 to 7.65	33.48% to 59.46%	11.68% to 26.20%	20.34 to 24.92
	Non-optimum	25.0 to 27.5	6.87 to 7.67	64.52% to 65.32%	53.03% to 55.50%	21.6 to 22.77

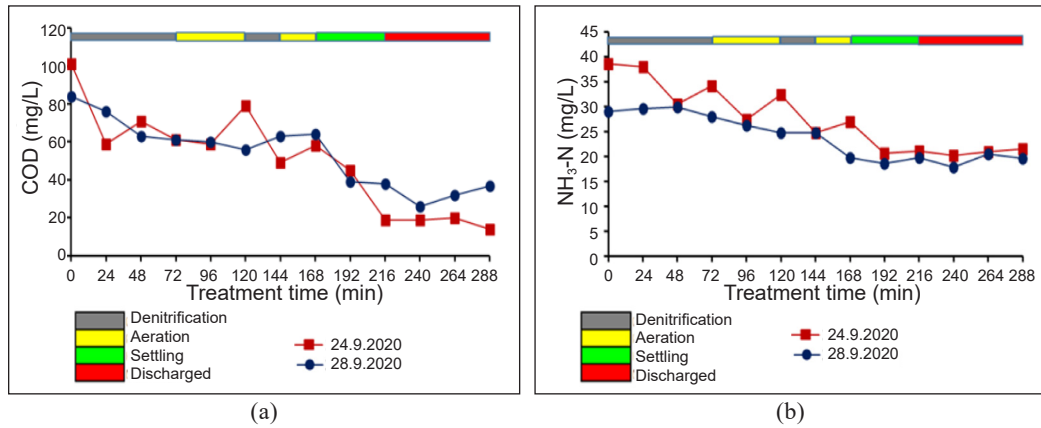


Figure 3. Graph of (a) COD analysis and (b) NH₃-N analysis for optimum mode treatment

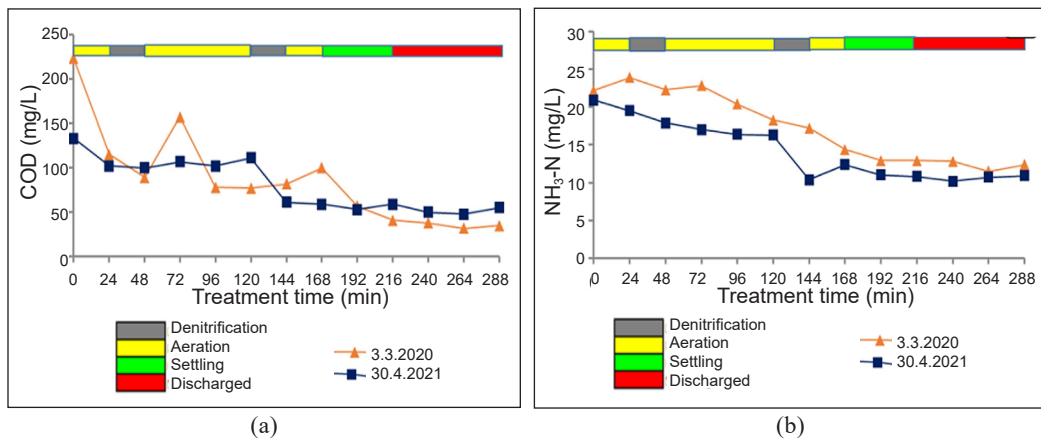


Figure 4. Graph of (a) COD analysis and (b) NH₃-N analysis for non-optimum mode treatment

The graph of ammonia-nitrogen and COD reduction performance without PVA gel beads for high COD and NH₃-N concentration at the beginning of the treatment process (optimum and non-optimum treatment setting) is shown in Figures 5 and 6.

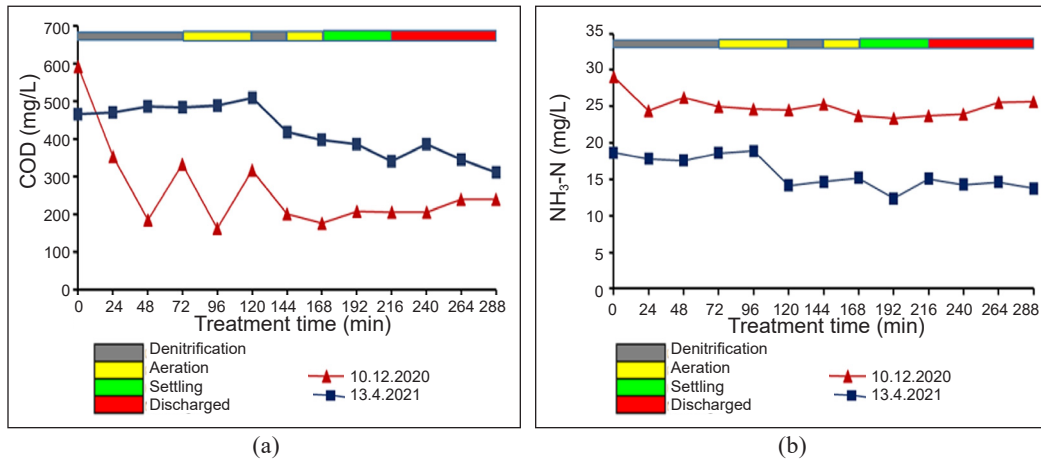


Figure 5. Graph of (a) COD analysis and (b) NH₃-N analysis for optimum mode treatment

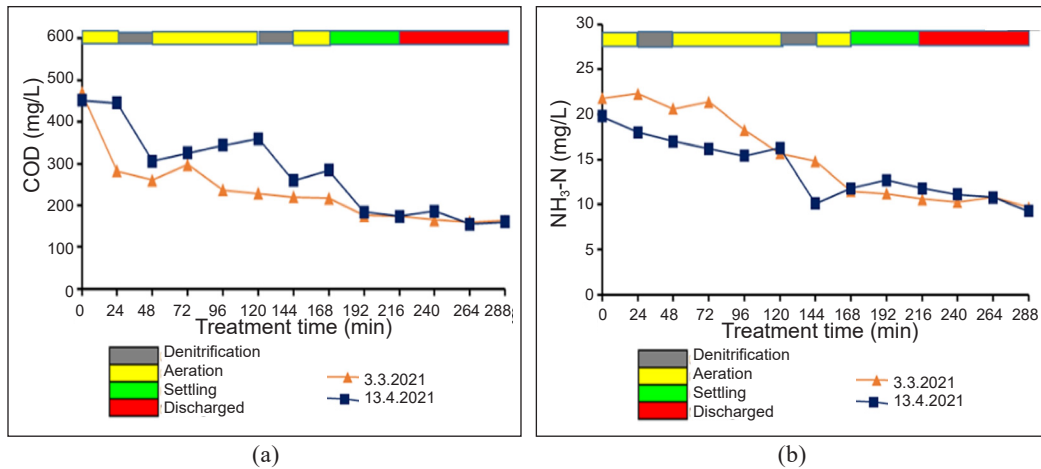


Figure 6. Graph of A) COD analysis and B) NH₃-N analysis for non-optimum mode treatment

Reduction Efficiency of Ammonia-Nitrogen Without PVA Gel-Beads

The experiments showed that nitrification and denitrification were the primary biological nitrogen reduction processes. The C/N ratio, variation of carbon sources, DO concentrations, and the number of intermittent aeration sequences affect the ammonia-nitrogen reduction in these experiments. However, other factors, such as temperature and pH, will also be discussed in this section.

As shown in Table 3, under the first scenario of the optimum mode setting, the ratio of carbon to ammonia-nitrogen nitrogen (C/N) is between 2.62 to 2.89 with a 32.41% to 44.30% reduction, while for the non-optimum mode setting, the C/N ratio is between 6.37 to 10.05 with 44.14% to 47.85% reduction, respectively. The influent for both treatment settings presented a low organic matter (COD) concentration of 84 to 223mg/L. Even though the experiment failed to achieve the required effluent discharge standard of 10mg/L, the non-optimum mode has shown better performance than the optimum mode setting. In the second scenario, it was observed that the C/N ratio for the optimum mode setting is between 20.34 to 24.92 with an 11.68% to 26.20% reduction, and for the non-optimum mode, the setting is between 21.6 to 22.77 with 53.03% to 55.50% reduction. The COD/N ratios were pretty high due to the addition of glucose to the fed wastewater. The influent for both treatment settings presented a high organic matter (COD) concentration of 451 to 592mg/L. The non-optimum mode setting has shown better performance than the optimum mode setting and met the required effluent discharge standard of 10mg/L.

In contrast, the optimum mode setting failed to achieve the desired effluent discharge limit. Therefore, it can be summarized that the low C/N ratio in the first scenario represents low organic matter (COD) in the substrate, and the high C/N ratio in the second scenario represents high organic matter (COD) in the substrate. In the denitrification process, heterotrophic bacteria perform biological denitrification and require a biodegradable organic carbon source as an electron donor.

Thus, the availability of organic carbon as an electron donor (typically written as biodegradable chemical oxygen demand (bCOD)) determines the denitrification potential of wastewater. According to Sun et al. (2010), in simultaneous nitrification and denitrification (SND), the optimal C/N ratio, in which the nitrification and denitrification reactions are balanced, was found to be 11.1. Water Environment Federation (2007) highlighted that 8.6 mg of COD is required to eliminate 1 mg of nitrate-nitrogen from wastewater. Moreover, it was found in the previous study that COD (readily biodegradable COD) (rbCOD) in tropical countries like Malaysia has low soluble COD content and high slowly biodegradable COD (sbCOD) content. Thus, the low rbCOD content was insufficient to reach the complete denitrification process (How et al., 2020). In the first scenario, it can be seen that the average C/N ratios are all below 11.1. Thus, the denitrification process is not in the best condition due to the lack of carbon sources for the denitrification process in the deep biofilm. In the second scenario, 1.2g glucose was added to increase the COD concentrations in the existing domestic sewage to investigate the effect of external carbon sources on nitrogen reduction performance. It was observed that the reduction rate of $\text{NH}_3\text{-N}$ has increased and improved in non-optimum mode as compared with the optimum mode and the first scenario experiment. Therefore, it can be concluded that the nitrogen reduction in the second scenario under non-optimum mode is supported by adding an external carbon source from

glucose in deep biofilm to facilitate denitrification. In addition, the average C/N ratio is above 11.1, thus improving the nitrogen reduction in this experiment.

In the SND process, due to diffusional limitations, the dissolved oxygen (DO) concentration gradients within the microbial biofilms (typical floc size: 100 to 150 μ m diameter, optimum floc size: 80 to 100 μ m diameter) form different populations throughout the biofilm: the nitrifying regions are located in high DO concentration zones, while the denitrifying regions are located in lower concentration zones (Bueno et al., 2018; Sun et al., 2010). Khanitchaidecha et al. (2015) reported that the rate of nitrification could be accelerated by increasing the DO concentration in the reactor tank. As a result, in this study, the reactor tank was aerated at a higher air flow rate of 3L/min with a DO of 5–7mg/L intermittently. However, it impacts the denitrification process since the increased air flow rate and DO concentration resulted in increased oxygen retention in the anaerobic stage, lowering denitrification activity and nitrogen reduction efficiency.

According to Jimenez et al. (2011), previous studies have found that DO concentrations for nitrification in SND should be higher than 1.0 mg/L, and the most recommended value is 2.0 mg/L or less to produce higher nitrification rates. Low DO concentrations may result in a low nitrification rate, affecting TN removal. When DO concentrations are high, it may lead to low denitrification rates due to the reduction of anoxic zones. How et al. (2018) reported low COD concentration in sewage may have contributed to active nitrification in low DO conditions by minimizing oxygen competition between heterotrophs and nitrifiers. At low DO concentrations, the microbial community structure of the nitrifying sludge is expected to be different from a standard high DO nitrifying community. Active nitrification in low DO settings has been associated with increased oxygen affinity in both ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB).

Therefore, the SND process's effectiveness depends on the proper DO concentrations range for both kinetic reactions, nitrification, and denitrification in the same reactor (Li et al., 2007). On the other hand, the higher ammonia-nitrogen reduction rate in non-optimal mode was attributed to a longer aeration process of 120 minutes (5 cycles of intermittent aeration) compared to 72 minutes (3 cycles of intermittent aeration) in optimum mode. The ample time taken and the optimum intermittent aeration sequences to supply DO concentration during the nitrification process have increased the conversion rate of NH_4^+ to $\text{NO}_3\text{-N}$, lowering the $\text{NH}_3\text{-N}$ concentrations in the reactor. Despite having an optimal C/N ratio of 11.1 in the denitrification process, sufficient aeration time also plays an important role in nitrogen reduction in these experiments. The DO concentration and the effective time taken to supply DO concentration during nitrification are crucial for the growth of nitrifying bacteria in the nitrification process. It is probably due to the nitrifiers requiring enough time to react with the ammonia, and they (autotrophic bacteria) grow slower in the nitrification process compared with denitrifiers (heterotrophic bacteria) in the denitrification process (Curtin et al., 2011; Rusalleda Beylier et al., 2011).

As discussed earlier, other factors influencing biological nitrogen reduction are temperature and pH reading. In these experiments, temperature and pH readings were measured at 6.52–7.59 and 25.0 to 27.8°C for the first scenario. While in the second scenario, temperature and pH readings were measured at 6.85–7.67 and 25.0 to 27.5°C, respectively. Alkalinity in the form of calcium carbonate (CaCO_3) in raw wastewater serves as a carbon source for nitrifiers to perform well in the nitrification process. Typically, 0.454kg of ammonia requires 3.239kg of alkalinity (CaCO_3) to oxidize to nitrate. Nitrification is a chemical reaction that results in the formation of acids. This acid production, together with the consumption of calcium carbonate during nitrification, can lower the pH of the nitrifiers, causing nitrifying bacteria to develop at a slower rate (Trygar, 2009). In nitrification, the optimum pH range is 6.8 to 8.0 (Curtin et al., 2011); for denitrification, the pH range is 6.5 to 7.5. Based on both scenarios, the pH reading is within the optimum range and has not significantly affected the nitrogen reduction process. According to Curtin et al. (2011), to maintain a stable population of nitrifiers, the temperature must be higher than 7°C. At liquid temperatures between 25–28°C (Rodziewicz et al., 2019), nitrification reaches its maximum rate. For denitrification, the optimal temperature is between 20–35°C (Ni et al., 2017). Hence, the experiments' temperatures of nitrification and denitrification were within an optimal range.

Reduction Efficiency of COD Without PVA Gel-Beads

The study was conducted to analyze the reduction efficiency of organic matter (COD). In the first scenario, COD concentrations decreased at a higher reduction rate of 55.95% to 86.14%. They met the required discharge limit of 120mg/L, whereas, in the second scenario, COD concentrations decreased at a lower reduction rate of 33.48% to 65.32%. However, under the non-optimum mode, the COD concentration was reduced in the second scenario more than in the optimal mode. In the suspended growth process, microorganisms are thoroughly mixed with organic matter (COD), stimulating their growth by allowing them to consume the organic matter as food. Individual bacteria clump together (floculate) to form an active mass of microbes (biologic floc) termed activated sludge as they proliferate and are mixed by air agitation. Air is introduced to mix the activated sludge with the wastewater, and oxygen is provided for the microorganisms to break down the organic matter.

Mixed liquor is the mixture of activated sludge and wastewater in the reactor tank. From the first scenario, it was envisaged that sufficient food (organic matter) and oxygen supplied to suspended microbes facilitated the reduction of organic matter in the wastewater. The concentration of MLSS/MLVSS in the mixture is also found to be in the appropriate quantity for effective treatment. Hence, there is no significant difference in performance for both optimal and non-optimal modes under the first scenario. In the second scenario, due to the addition of 1.2g glucose, the poor performance of organic matter reduction was observed, especially under the optimal setting. It is most likely due to the high loading of

organic matter (COD) into the system, low MLSS/MLVSS concentrations to consume the organic matter as food, and inadequate aeration period to supply oxygen to break down the organic matter. In addition, the adaptation of microorganisms with the additional organic matter has also led to ineffective treatment, affecting the microbes' ability to degrade the organic matter (Herlina et al., 2019). However, in non-optimal settings, reduction effectiveness is higher than in optimal settings, and this could be due to a longer aeration process of 120 minutes (5 cycles of intermittent aeration) compared to 72 minutes (3 cycles of intermittent aeration) in the optimal setting, which facilitated organic matter reduction.

Biological Treatment Process by Sequencing Batch Reactor with Polyvinyl Alcohol (PVA) Gel Beads

The summary of COD and NH₃-N reduction performance with PVA gel beads is shown in Table 4.

Table 4
COD and NH₃-N reduction efficiency with PVA gel beads

Scenario	Treatment Setting	Temp (°C)	pH	COD Reduction Rate	NH ₃ -N Reduction Rate	C/N ratio
1st Scenario	Optimum	24.0 to 26.1	7.00 to 7.59	42.02%	30.94%	8.56
Treatment with PVA gel-beads	Non - Optimum	25.0 to 27.0	6.78 to 7.69	70.68%	62.96% to 65.71%	8.8 to 11.26
Low COD and NH ₃ -N concentration at the beginning of the treatment process						

The graph of ammonia-nitrogen and COD reduction performance with PVA gel beads for low COD and NH₃-N concentration at the beginning of the treatment process (optimum treatment and non-optimum setting) is shown in Figures 7 and 8. Figure 9 depicts the color of new PVA gel beads (white) and used PVA gel beads (yellowish), and Figure 10 depicts the lab-scale reactor with PVA gel beads.

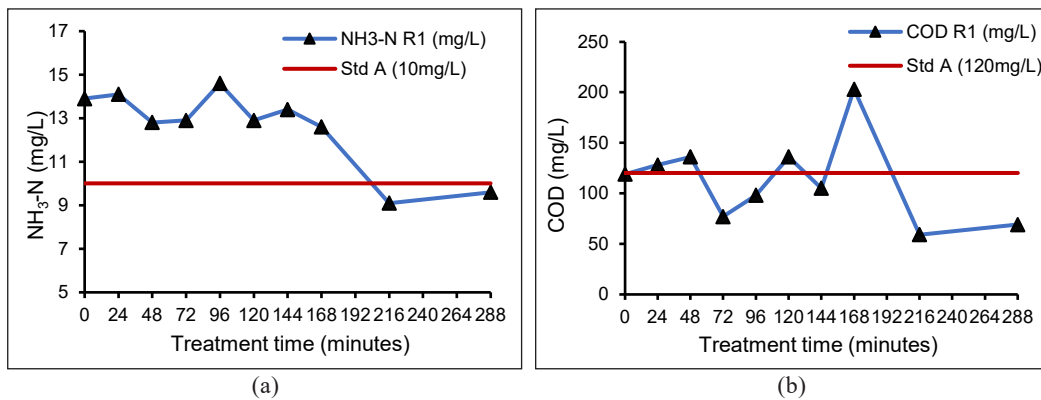


Figure 7. Graph of (a) NH₃-N analysis and (b) COD analysis for optimum mode treatment

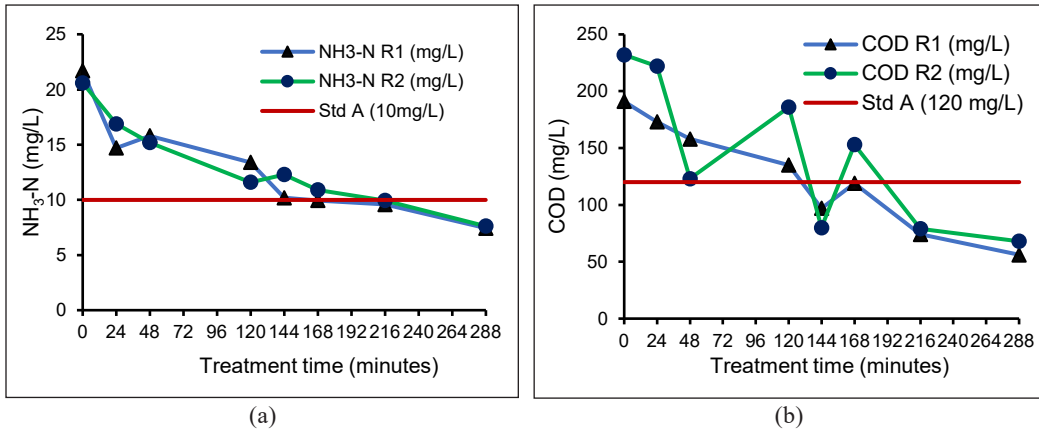


Figure 8. Graph of (a) $\text{NH}_3\text{-N}$ analysis and (b) COD analysis for non-optimum mode treatment



Figure 9. A) Unused PVA gel beads (white color) and B) used PVA gel beads (yellowish color) after a lab-scale experiment



Figure 10. Lab scale-reactor with PVA gel beads

Reduction Efficiency of Ammonia-Nitrogen Nitrogen with PVA Gel Beads

According to the experiment's results, under optimal setting, the C/N ratio is at 8.56, while under a non-optimal setting, the C/N ratio ranges from 8.8 to 11.26. Thus, the C/N ratio is within the optimal condition of 11.1 for nitrification and denitrification to perform well in SND as the reactions were balanced. Furthermore, an analysis of a lab-scale reactor under non-optimal conditions revealed that the nitrogen reduction efficiency significantly improved when PVA gel beads were added to the reactor. The $\text{NH}_3\text{-N}$ reduction performance, on average, was increased by 17.86% to 18.82% under the same treatment setting. The improvement of ammonia-nitrogen nitrogen reduction with PVA gel beads indicated that the active core and highly porous immobilized biofilm carriers developed an efficient denitrification microreactor. Each PVA gel bead with high specific surface areas provided an anoxic microenvironment when placed in an aerobic reactor (Li et al., 2021). On the

other hand, the microbes (living cells) are contained in a porous polymeric matrix that allows substrate molecules to diffuse in and product molecules to diffuse out (Pham & Tho Bach, 2014).

However, it is contrary to the optimal setting in which the reduction rate is not in the best performance. As discussed in the previous section, the ineffective treatment was most likely associated with high DO concentrations throughout the treatment process and less intermittent aeration sequences during the nitrification process. Zhang et al. (2021) highlighted that different DO concentrations significantly affect the activity of various functional microorganisms in the reactor, making it one of the most significant elements. As DO rises, the population of ammonium-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) rises, affecting nitrifying and denitrifying activities. DO can significantly affect the proportions of aerobic and anaerobic zones within the biofilm and the microbial community structure, thus making it the most critical parameter for improving the SND rate. It is suggested that DO concentration should be controlled at an optimal range, within 2.0 to 5.0mg/L in the aerobic phase, as reported by Jimenez et al. (2011), to maintain a suitable operational condition. Another factor that promotes effective nitrogen reduction is the concentration of organic loading (COD) in the raw sewage as a carbon source during the denitrification process. The best results of nitrogen reduction were found in a non-optimal setting as the influent COD level was relatively higher than the COD level in the optimal setting. The concentration of ammonia entering the treatment system, which will affect the growth of bacteria in the nitrification process (Rodríguez-Gómez et al., 2021), also affects the nitrogen reduction process.

As shown in Figure 9, the color of the new PVA gel beads was white and turned yellowish after 1 month of acclimatization. According to Jin et al. (2016), the color of PVA was yellowish after 1 month cultivation period, and after 5 months of treatment, the color of matured PVA gel beads was black. It is supported by another study by Khanh et al. (2011), where the matured black color of PVA gel beads was used in wastewater treatment. Another study found a similar finding in which the color of PVA gel beads turned from white to yellowish after 1 month of operation and became red-brown after 3 months. During the 3 months of operation, the reduction rate of $\text{NH}_3\text{-N}$ and COD were 70-80%, respectively. The change of color represents that microbial growth increased with the proportionality of time (Wang et al., 2018). Hence, the color changes in PVA gel beads in this study were still in the culture process, and the ammonia-nitrogen reduction rate increased with increasing acclimatization time. These findings are supported by the reduction levels of $\text{NH}_3\text{-N}$ and COD of 60–70% during the startup phase. Therefore, it is suggested that the acclimatization period with the domestic wastewater should be extended until the reduction efficiency of $\text{NH}_3\text{-N}$ and COD reaches a minimum of 70-80% and becomes stable prior to undertaking the sequencing operation based on the optimum and non-optimum setting.

As discussed previously, temperature and pH readings influenced the nitrogen reduction process. In these experiments, temperature and pH readings were measured at 7.14–7.59 and 24.0 to 26.3°C in an optimal setting, while temperature and pH measurements in the non-optimal configuration were 6.78–7.69°C and 25.0–27.0°C, respectively. Thus, as observed in both treatment settings, the pH value and temperature are within the ideal ranges of 6.8 to 8.0 in nitrification and 6.5 to 7.5 in denitrification and 25–28°C, respectively. Moreover, the total volumetric capacity of PVA gel beads in the range of 5 to 15% allows hydraulic capacity to enter the system more than 50 to 70% volumetric capacity for other carriers (Singh et al., 2016).

Reduction Efficiency of COD with PVA Gel Beads

Similar to ammonia-nitrogen nitrogen, the reduction rate of COD in a non-optimal setting has shown a high effect than in the optimal setting. During the experiment, the COD influent ranged from 119 to 232 mg/L. The COD reduction rate under the optimal setting was only 42.0%, while the COD reduction rate under the non-optimal setting was measured at 70.68%. In addition, an analysis of a lab-scale reactor with PVA gel beads under non-optimal conditions revealed that the COD reduction efficiency was stable and consistent. The gap in COD reduction efficiency without PVA gel beads is between 25–30%. This condition demonstrated that the treatment efficiency was inconsistent even though the reduction rate could achieve higher than 80%. The consistent and stable COD reduction rate with PVA gel beads is likely due to the microbes being preserved in their native form by encapsulation within a membrane, inhibiting leakage and protecting the microbes from adverse conditions.

Thus, PVA gel beads allow microbes to grow quickly and steadily on the media and in the inner part of the media resulting in non-flocculent biomass with fewer self-oxidizing protozoans and metazoans (Rajpal et al., 2021). In addition, these results show that the system can handle variable organic loading, thus delivering consistent results of organic matter removal (Singh et al., 2016). When microbes are confined or curbed within a semi-permeable membrane, tiny substrate molecules can diffuse while product molecules can diffuse out (Bouabidi et al., 2019; Krishnamoorthi et al., 2015). At the same time, this treatment has both biofilms in the carrier and freely suspended biomass in the same reactor. Unlike treatment without the carrier, the gap in COD reduction efficiency is likely due to microbes growing freely in suspended conditions and not being protected from the adverse environmental situation and easily washout from the reactor (El-Naas et al., 2013). However, more experiments need to be performed for this study to establish the findings. Other factors that affect microbes' proliferation are pH and temperature. According to Herlina et al. (2019), the anaerobic process is most effective in the pH range of 6.5–7.5, while the aerobic process is most effective in the pH range of 6.5–8.5. Furthermore, the

microbes can proliferate at the best temperature of 25–35°C. These experiments' average pH readings and temperature were 7.23 and 25.69°C, respectively. Thus, from the observation, the pH and temperature were in the optimal range and facilitated microbial growth in the reactor.

In addition, it was observed in non-optimal settings that reduction effectiveness is higher than in optimal settings. It is likely due to more intermittent aeration sequences with a total aeration period of 120 minutes vs. 72 minutes in an optimal setting, facilitating organic matter degradation. The trend of COD reduction performance with PVA gel beads at optimal configuration is similar to the COD reduction without PVA gel beads. Based on these trends, it can be concluded that the COD reduction with more intermittent aerobic sequences significantly improved the reduction of organic compounds.

CONCLUSION

Based on the study performed, it is proven that PVA gel beads as an immobilized carrier are able to treat low-medium concentrations of domestic wastewater in Malaysia. Wastewater treatment using this carrier can increase the reduction level of nitrogen and organic matter. In addition, it can be used as an alternative option to enhance existing biological wastewater treatment systems without involving major construction works, thus reducing the capital cost of building a new sewage treatment plant or upgrading the existing sewage treatment plant. It can be concluded that the reduction efficiency of ammonia-nitrogen and COD with PVA gel beads under a non-optimal setting is better than with PVA gel beads under the optimal setting and meets the required effluent discharge, Standard A of Environmental Quality (Sewage) Regulations 2009. The nitrogen reduction improved significantly, and organic matter reduction showed a more stable performance than wastewater treatment without PVA gel beads. The results showed that the combination of attached and suspended biomass was superior to the freely suspended biomass for nitrification and denitrification of wastewater. The color change of PVA gel beads from white to yellowish after one month of operation indicates that a colony of microbes was growing in the highly inner porous carriers.

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REFERENCES

- Bouabidi, Z. B., El-Naas, M. H., & Zhang, Z. (2019). Immobilization of microbial cells for the biotreatment of wastewater: A review. *Environmental Chemistry Letters*, 17, 241-257. <https://doi.org/10.1007/s10311-018-0795-7>

- Bueno, R. F., Piveli, R. P., Campos, F., & Sobrinho, P. A. (2018). Simultaneous nitrification and denitrification in the activated sludge systems of continuous flow. *Environmental Technology*, 39(20), 2641-2652. <https://doi.org/10.1080/09593330.2017.1363820>
- Curtin, K., Duerre, S., Fitzpatrick, B., Meyer, P., & Ellefson, N. (2011). *Biological nutrient removal*. Minnesota Pollution Control Agency. <https://www.pca.state.mn.us/sites/default/files/wq-wwtp8-21.pdf>
- El-Naas, M. H., Mourad, A. H. I., & Surkatti, R. (2013). Evaluation of the characteristics of polyvinyl alcohol (PVA) as matrices for the immobilization of *Pseudomonas putida*. *International Biodeterioration and Biodegradation*, 85, 413-420. <https://doi.org/10.1016/j.ibiod.2013.09.006>
- Hanafiah, Z. M., Mohtar, W. H. M. W., Hasan, H. A., Jensen, H. S., Abdullah, M. Z., & Husain, H. (2019). Diversification of temporal sewage loading concentration in tropical climates. *IOP Conference Series: Earth and Environmental Science*, 264, Article 012026. <https://doi.org/10.1088/1755-1315/264/1/012026>
- Herlina, N., Turmuzi Lubis, M., Husin, A., & Putri, I. (2019). Studies on decreasing chemical oxygen demand (COD) on artificial laundry wastewater using anaerobic-aerobic biofilter dipped with bio ball media. *MATEC Web of Conferences*, 276, Article 06015. <https://doi.org/10.1051/mateconf/201927606015>
- How, S. W., Lim, S. Y., Lim, P. B., Aris, A. M., Ngoh, G. C., Curtis, T. P., & Chua, A. S. M. (2018). Low-dissolved-oxygen nitrification in tropical sewage: An investigation on potential, performance and functional microbial community. *Water Science and Technology*, 77(9), 2274-2283. <https://doi.org/10.2166/wst.2018.143>
- How, S. W., Sin, J. H., Wong, S. Y. Y., Lim, P. B., Aris, A. M., Ngoh, G. C., Shoji, T., Curtis, T. P., & Chua, A. S. M. (2020). Characterization of slowly-biodegradable organic compounds and hydrolysis kinetics in tropical wastewater for biological nitrogen removal. *Water Science and Technology*, 81(1), 71-80. <https://doi.org/10.2166/wst.2020.077>
- Jimenez, J., Dursun, D., Dold, P., Bratby, J., Keller, J., & Parker, D. (2011). Simultaneous nitrification-denitrification to meet low effluent nitrogen limits: Modeling, performance and reliability. *Proceedings of the Water Environment Federation*, 2010(15), 2404-2421. <https://doi.org/10.2175/193864710798158968>
- Jin, Y., Wang, D., & Zhang, W. (2016). Treatment of high-strength ethylene glycol wastewater in an expanded granular sludge blanket reactor: Use of PVA-gel beads as a biocarrier. *SpringerPlus*, 5, Article 856. <https://doi.org/10.1186/s40064-016-2409-9>
- Khanh, D., Quan, L., Zhang, W., Hira, D., & Furukawa, K. (2011). Effect of temperature on low-strength wastewater treatment by UASB reactor using poly (vinyl alcohol)-gel carrier. *Bioresource Technology*, 102(24), 11147-11154. <https://doi.org/10.1016/j.biortech.2011.09.108>
- Khanitchaidecha, W., Nakaruk, A., Koshy, P., & Futaba, K. (2015). Comparison of simultaneous nitrification and denitrification for three different reactors. *BioMed Research International*, 2015, Article 901508. <https://doi.org/10.1155/2015/901508>
- Kim, E. J., Kim, H., & Lee, E. (2021). Influence of ammonia stripping parameters on the efficiency and mass transfer rate of ammonia removal. *Applied Sciences*, 11(1), Article 441. <https://doi.org/10.3390/app11010441>
- Krishnamoorthi, S., Banerjee, A., & Roychoudhury, A. (2015). Immobilized enzyme technology: Potentiality and Prospects Review. *Enzymology and Metabolism*, 1(1), 1-11.

- Li, H., Liu, Q., Yang, P., Duan, Y., Zhang, J., & Li, C. (2021). Encapsulation of microorganisms for simultaneous nitrification and denitrification in aerobic reactors. *Journal of Environmental Chemical Engineering*, 9(4), Article 105616. <https://doi.org/10.1016/j.jece.2021.105616>
- Li, J., Peng, Y., Gu, G., & Wei, S. (2007). Factors affecting simultaneous nitrification and denitrification in an SBBR treating domestic wastewater. *Frontiers of Environmental Science and Engineering in China*, 1, 246-250. <https://doi.org/10.1007/s11783-007-0042-0>
- Ni, B. J., Pan, Y., Guo, J., Viridis, B., Hu, S., Chen, X., & Yuan, Z. (2017). Denitrification processes for wastewater treatment. In I. Moura, J. J. G. Moura, S. R. Pauleta & L. B. Maia (Eds.), *Metalloenzymes in Denitrification: Applications and Environmental Impacts* (pp. 368-418). The Royal Society of Chemistry. <https://doi.org/10.1039/9781782623762-00368>
- Pham, D. V., & Bach, L. T. (2014). Immobilized bacteria by using PVA (Polyvinyl alcohol) crosslinked with Sodium sulfate. *International Journal of Science and Engineering*, 7(1), 41-47. <https://doi.org/10.12777/ijse.7.1.41-47>
- Rahimi, S., Modin, O., & Mijakovic, I. (2020). Technologies for biological removal and recovery of nitrogen from wastewater. *Biotechnology Advances*, 43, Article 107570. <https://doi.org/10.1016/j.biotechadv.2020.107570>
- Rajpal, A., Srivastava, G., Bhatia, A., Singh, J., Ukai, Y., & Kazmi, A. A. (2021). Optimization to maximize nitrogen removal and microbial diversity in PVA-gel based process for treatment of municipal wastewater. *Environmental Technology and Innovation*, 21, Article 101314. <https://doi.org/10.1016/j.eti.2020.101314>
- Rodríguez-Gómez, L. E., Rodríguez-Sevilla, J., Hernández, A., & Álvarez, M. (2021). Factors affecting nitrification with nitrite accumulation in treated wastewater by oxygen injection. *Environmental Technology*, 42(5), 813-825. <https://doi.org/10.1080/09593330.2019.1645742>
- Rodziewicz, J., Ostrowska, K., Janczukowicz, W., & Mielcarek, A. (2019). Effectiveness of nitrification and denitrification processes in biofilters treating wastewater from de-icing airport runways. *Water (Switzerland)*, 11(3), Article 630. <https://doi.org/10.3390/w11030630>
- Ruscalleda Beylier, M., Balaguer, M. D., Colprim, J., Pellicer-Nàcher, C., Ni, B. J., Smets, B. F., Sun, S. P., & Wang, R. C. (2011). Biological nitrogen removal from domestic wastewater. *Comprehensive Biotechnology*, 6, 329-340. <https://doi.org/10.1016/B978-0-08-088504-9.00533-X>
- Services, N. W. C. (2016). Section 3 sewage characteristics and effluent discharge requirements. *Malaysian Sewage Industry Guidelines*, 4, 27-34.
- Singh, N. K., Singh, J., Bhatia, A., & Kazmi, A. A. (2016). A pilot-scale study on PVA gel beads based integrated fixed film activated sludge (IFAS) plant for municipal wastewater treatment. *Water Science and Technology*, 73(1), 113-123. <https://doi.org/10.2166/wst.2015.466>
- Sun, S. P., Nàcher, C. P. I., Merkey, B., Zhou, Q., Xia, S. Q., Yang, D. H., Sun, J. H., & Smets, B. F. (2010). Effective biological nitrogen removal treatment processes for domestic wastewaters with low C/N ratios: A review. *Environmental Engineering Science*, 27(2), 111-126. <https://doi.org/10.1089/ees.2009.0100>
- Suruhanjaya Perkhidmatan Air Negara. (2016). *Section 2 Planning, Material and Design*. <https://www.span.gov.my/article/view/malaysian-sewerage-industry-guidelines-msig>

- Trygar, R. (2009). *Nitrogen Control in Wastewater Treatment Plants* (2nd Ed.). TREECo Center.
- Tuyen, N. V., Ryu, J. H., Yae, J. B., Kim, H. G., Hong, S. W., & Ahn, D. H. (2018). Nitrogen removal performance of anammox process with PVA-SA gel bead crosslinked with sodium sulfate as a biomass carrier. *Journal of Industrial and Engineering Chemistry*, 67, 326-332. <https://doi.org/10.1016/j.jiec.2018.07.004>
- Water Environment Federation. (2007). *Chapter 22: Biological nutrient removal processes*. <https://enviro2.doe.gov.my/ekmc/wp-content/plugins/download-attachments/includes/download.php?id=200697>
- Wang, Y., Liu, Y., Feng, M., & Wang, L. (2018). Study of the treatment of domestic sewage using PVA gel beads as a biomass carrier. *Journal of Water Reuse and Desalination*, 8(3), 340-349. <https://doi.org/10.2166/wrd.2017.181>
- Zhang, S., Chen, J., Yuan, J., & Wang, G. (2021). Response of simultaneous nitrification-denitrification to do increments in continuously aerated biofilm reactors for aquaculture wastewater treatment. *Water Practice and Technology*, 16(4), 1067-1077. <https://doi.org/10.2166/wpt.2021.062>