Aerobic granules cultivated using industrial rubber wastewater: Effect of size distribution and Performance of granules.

N A Rashid¹*, A L Abdul Rani², M F Omar¹, and M A H Abdullah¹

¹Faculty of Engineering Technology, Department of Civil Engineering Technology, University Malaysia Perlis, Kampus UniCITI Alam Sungai Chuchuh, Padang Besar 02100 Perlis, Malaysia
²Faculty of Engineering Technology, Department of Chemical Engineering Technology, University Malaysia Perlis, Kampus UniCITI Alam Sungai Chuchuh, Padang Besar 02100 Perlis, Malaysia

Abstract. Sequential batch reactors (SBR) have been successfully developed granular sludge using industrial rubber wastewater on a cylindrical shaped SBR. SBR was introduced to industrial wastewater with varying chemical oxygen demand (COD) loadings from as low as 0.01 to 0.28 kgCOD/m³/d. First phase of experiment utilized 24 hours cycle time whilst second phase of experiment utilized 4 hours cycle time. Granules were successfully developed at the second phase (4 hours) of experiment. Fortunately, the overall performance for both cycles were excellent. COD removal efficiency throughout the experiment was kept at about 78 % to 98 %. Although higher COD removal was observed for both cycle, granulation did not occur in the first phase (24 hours). Decrement of cycling time to 4 hours promotes the growth of dense and structured sludge granules.

1. Introduction

Treating industrial rubber wastewater can be difficult due to varying contaminant level of rubber wastewater. Rubber processing poses higher
contamination due to chemicals added for concentrating process [1]. Rubber effluent contain high level of ammonia and various nutrients, creating conventional biological treatment seems irrelevant. Moreover, the production of rubber products generate large amount of water. Adding more demands in search of practical and viable technology suitable for treating varying pollution level in rubber wastewater. Particularly, treatment within industrial compound with limited area [2]. Chemical oxygen demand (COD) concentration of industrial wastewater particularly rubber wastewater in Malaysia was greatly varied from an extreme low to high COD concentration. Variation of low and high substrate level will influenced the granule formation. Such limitations can cause difficulty for extensive application specifically in Malaysia for rubber wastewater treatment.

Unfortunately, very few studies have been carried out for cultivation of aerobic granules using industrial rubber wastewater. Since most of the studies focussed on treatment of synthetic wastewater with constant COD level to control the granules progression in the reactor [3]. Therefore, this present work was carried out to evaluate the feasibility of a laboratory scale sequencing batch reactor (SBR) for the development of aerobic granules and to assess its performance and size distribution.

2. Materials and methods

2.1 Reactor design
Cylindrical shaped SBR was utilized to cultivate sludge granules with reactor configuration of 0.05 m in diameter. To attain aerobic condition in the reactor, the reactor was aerated through an air diffuser in order to produce fine air bubbles that was installed at the bottom of the reactor. SBR had a working volume of 1 L.

2.1.1 Setting up of bioreactor
Wastewater was fed to the reactors during “Fill” using dosing pumps, whereas diffuser controlled by aeration pump was installed at the bottom part of the bioreactor. To achieve a stable source of aeration, gas flow meter was fixed between aeration pump and diffuser. Fine bubbles were introduced by a porous stone and the sequential operation of the reactor was automatically controlled by timers. pH value throughout the investigation was not controlled and temperature of reactors were kept at a room temperature of 28±2°C. First phase of experiment were conducted within a complete cycling time of 24 hours. Second phase of experiment were conducted within a complete cycling time of 4 hours.
3. Results and discussion

3.1 Development of Aerobic Granules.
In order to establish a suitable cycle length, this section utilized cycle time of 24 hours in the first experimental phase and subsequently utilized shorter cycle time of 4 hours (second phase).

![Figure 1. Size distribution of granules in reactor.](image)

Selection of cycle time was first carried out by applying 24 hours and 4 hours cycle length. Cycle time of 4 hours were selected since 3 hours is considered to be unsuitable workable cycle length as supported by Cydzik-Kwiatkowska [4]. Granulation will not occurred at an extensive cycle time as the sludge only exists in the form of sludge flocs [4]. He further stated, utilization of shorter cycle time of 3 hours will destroy the process formation of granules due to leach out of nitrifying bacteria.

This section investigate the effect of cycle time on the development of granules by examining its size distribution throughout experimental investigation. Figure 1 showed volume fraction of granules from day 1 to 34. On day 1 till 17 seed sludge with fluffy, irregular shape and loose structured appeared. Seed sludge of 0.1 to 1 mm dominated the reactor after 17 days of operation. Therefore, during this period granulation did not achieved when cycle time of 24 hours were utilized. The full granulation was defined as when clear granular particles were observed [5]. Since cycle time of 24 hours failed to achieve granulation, cycle time of the reactor was altered to only 4 hours after day 17. The change in size distribution after 4
hours of cycle time was apparent, approximately 75% of 4.75 mm size granules remained dominant in the reactor. Granules cultivated in the reactor consist of dense structured granules that assist a rapid separation of effluent and granular sludge within shorter time compared to longer operational time of 24 hours.

### 3.2 Performance of Granular Biomass.
To establish a suitable cycle length, cycle time of 24 and 4 hours were compared for removal efficiency of organic and nitrogen compounds. As cycle time promotes microbial growth, consequently resulted in formation of dense and structured granules followed by efficient removal of both organic and nitrogen removal.

In order to establish a suitable cycle length, this section utilized cycle time of 24 and 4 hours for comparison of COD removal efficiency. Since cycle time promotes microbial growth, that will resulted in formation of dense and structured granules followed by efficient removal of COD. **Figure 2**, showed the reactor performance during the operational periods for cycle time of 24 and 4 hours.

![Figure 2. COD removal during granulation](image)
COD removal efficiency shows a significant increment when cycle time of 24 hours were utilized in the first phase of experiment. Cycle time was then reduced to 4 hours after day 18, intended to promote development of granules in reactor. Fortunately, COD removal efficiency was at sensible
range with removal percentage of 78 to 98 % from day 19 till day 34. Although the average COD removal efficiency of 24 hours cycle is slightly higher than cycle time of 4 hours, volume of clean water generated was 6 times higher than in 24 hours cycle time. COD removal at 4 hours cycle time were considered to be satisfactory with only 4 % difference than in 24 hours cycle time. Highest COD removal efficiency was observed on day 4 at a maximum influent COD level. This can be explained by the ability of microorganisms to easily degrade a simple form of organic substrates by observing the COD level that has been removed by various microorganisms exist in the granules. The larger and denser the granules the higher level of microorganisms exist in the granules [4]. However, towards the end of the experiment COD removal begin to reduce slightly. This is due to the growth of large granules as suggested by Li [6-7]. As granules size increases the degree of substrate diffusion reduces causes reduction of COD removal [8].

In order to investigate the removal of nitrogen compounds, conversion of ammonia nitrogen (NH$_4^+$-N) should be monitored (Figure 3). Since nitrification process indicate the presence of nitrifying bacteria in the reactor [9]. Complete degradation of NH$_4^+$-N resulted in formation of nitrite, followed with further oxidation of nitrite to nitrate [10].

**Figure 3.** Percentage of NH$_4^+$-N removal by aerobic granules

**Figure 3** showed the variation of NH$_4^+$-N removal efficiency with operating days. NH$_4^+$-N removal efficiency was fairly stable in the first phase of experiment (24 hours). This indicates that all the ammonium exist in the influent was degraded by nitrifying bacteria consequently converted it to
nitrite and nitrate [5]. Thereafter, the cycling time was reduced to 4 hours and the feeding was continued till day 34. Unfortunately, in the second phase of experiment NH$_4^+$-N removal was not constant. This is mainly due to loss of nitrifying bacteria in the second phase (4 hours) as explained by Cydzik-Kwiatkowska [4]. Nitrifying bacteria also known as slow growing nitrifiers favours a longer cycle time since it has to compete with heterotrophs [4]. Shorter cycle time together with high COD concentration resulted in a prominent heterotroph's growth that are able to surpasses the growth of nitrifying bacteria in the reactor. It has also been demonstrated in Figure 3, an average NH$_4^+$-N removal for 4 hours cycle time is 86 % whereas cycle time of 24 hours achieved average NH$_4^+$-N removal of 93 %. Ammonia uptake in cycle time of 4 hours are lower than cycle time of 24 hours, consequently resulted in lower NH$_4^+$-N removal in second phase (4 hours) [11]. Result depicted the growth of nitrifiers were abundant during the first phase (24 hours) compared to second phase (4 hours) due to application of longer cycling time.

Increment of COD value during the operational time can also be one of the reason for reduction NH$_4^+$-N removal in the second phase of experiment (4 hours). As COD level increases, nitrification was delay since nitrifiers do not compete well for oxygen compared to heterotrophs [12]. The growth rate of nitrifying was much slower than that of heterotrophic bacteria so the reaction rate of NH$_4^+$-N to NO$_2^-$-N and NO$_3^-$-N was slow resulting in reduction of removal efficiency [13]. These findings are possible explanation for reduction of NH$_4^+$-N removal in cycle time of 4 hours on day 22, 26, 33 and 34.

4. Conclusions

Industrial rubber wastewater was applied throughout this study for the development and performance of granules. Sudden fluctuation of influent characteristics (COD level) does not affect the granules development. Reaction rate by granules depend on the physical structure of granules. The bigger and denser granules resulted in slower reaction rate due to mass transfer limitation in granule, it has been proven by the slight decrease in COD removal rate. The result suggested that large size granules may not be considered as the main goal for granulation if effluent quality is considered. In conclusion, application of aerobic granules in SBR using industrial rubber wastewater (inconsistent COD level) is possible, however selection of cycle time proves to be more significant than the influent itself.
References

1. Iyagba, M.A., A. Adoki, and T.G. Sokari, Testing biological methods to treat rubber effluent. African Journal Agricultural Research, 2008. 3(6): p. 448-454.

2. Nhu Hien, N., et al., Application of Oxygen Limited Autotrophic Nitritation/Denitrification (OLAND) for anaerobic latex processing wastewater treatment. International Biodeterioration & Biodegradation, 2017. 124: p. 45-55.

3. Ghosh, S. and S. Chakraborty, Influence of inoculum variation on formation and stability of aerobic granules in oily wastewater treatment. Journal of Environmental Management, 2019. 248: p. 109239.

4. Cydzik-Kwiatkowska, A., et al., Treatment of high-ammonium anaerobic digester supernatant by aerobic granular sludge and ultrafiltration processes. Chemosphere, 2013. 90(8): p. 2208-2215.

5. Gao, D., et al., Comparison of four enhancement strategies for aerobic granulation in sequencing batch reactors. Journal of Hazardous Materials, 2011. 186(1): p. 320-327.

6. Li, A.-j., X.-y. Li, and H.-q. Yu, Effect of the food-to-microorganism (F/M) ratio on the formation and size of aerobic sludge granules. Process Biochemistry, 2011. 46(12): p. 2269-2276.

7. Rollemberg, S.L.d.S., et al., Effects of carbon source on the formation, stability, bioactivity and biodiversity of the aerobic granule sludge. Bioresource Technology, 2019. 278: p. 195-204.

8. Chen, F.-y., et al., Operational strategies for nitrogen removal in granular sequencing batch reactor. Journal of Hazardous Materials, 2011. 189(1–2): p. 342-348.

9. Guo, J., et al., Combination process of limited filamentous bulking and nitrogen removal via nitrite for enhancing nitrogen removal and reducing aeration requirements. Chemosphere, 2013. 91(1): p. 68-75.

10. Wang, Y., et al., Insight into the response of anammox granule rheological intensity and size evolution to decreasing temperature and influent substrate concentration. Water Research, 2019. 162: p. 258-268.

11. Chen, X., G. Sin, and B.-J. Ni, Impact of granule size distribution on nitrous oxide production in autotrophic nitrogen removal granular reactor. Science of The Total Environment, 2019. 689: p. 700-708.
12. Cassidy, D.P. and E. Belia, *Nitrogen and phosphorus removal from an abattoir wastewater in a SBR with aerobic granular sludge*. Water Research, 2005. **39**: p. 4817-4823.

13. Yuan, X. and D. Gao, *Effect of dissolved oxygen on nitrogen removal and process control in aerobic granular sludge reactor*. Journal of Hazardous Materials, 2010. **178**(1–3): p. 1041-1045.

Acknowledgement

This research was supported by the Malaysian Government under the Fundamental Research Grant Scheme (FRGS), Grant no.: FRGS/1/2018/TK02/UNIMAP/02/7.