Denitrification of High Nitrite and Nitrate Wastewater in Moderate Weather

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Abstract-- **This study includes two parts; in the first part, enrichment of heterotrophic denitrification organisms (HDEO) in anoxic sequencing batch reactor (ANSBR) in moderate weather and without temperature control , while in the second part; consideration of the influence of major operational parameters including; temperature, pH, oxidation reduction potential (ORP) to evaluate the denitrification process of high nitrite and nitrate performance in moderate weather without temperature control are investigated. Relatively higher nitrite and nitrate removal efficiencies up to 88.96% and 97.52% were obtained, respectively in anoxic sequencing batch reactor ANSBR fed with effluent of nitrification reactor after adding the required minerals for organisms growth and inoculate with mixed liquor activated reactor. The average denitrification rate with nitrite faster than average denitrification rate with nitrate by 2.6. Denitrification rate independent of electron donor concentration when it was added in excess concentration.**

Keywords denitrification, High, ANSBR, moderate, weather.

I. INTRODUCTION

High nitrite and nitrate wastewaters discharged by nitrification of high ammonium concentration in reject water in wastewater treatment plants WWTP need to be treated in anoxic biological process (denitrification). The treatment involves the addition of an external source of carbon, as electron donor for denitrification reactions because the reject water has not an organic component. Treatment of high nitrate wastewater were achieved in different types of bioreactors, such as anoxic activated sluge reactor [4], membrane bioreactors [12], and sequencing batch reactors [8]. Many types of organic carbon sources were used as electron donor for denitrification process [4] and [3].

II. METHODS

A. Experimental setup

The heterotrophic denitrifying organisms acclimation has been at natural laboratory temperature. The reactor has diameter of 14cm and total height of 20 cm. It was constructing of Perspex cylindrical with 2.0 liters work volume of and which able to adjust to operate at minimum volume of one liter (which is the residual volume at the end of each cycle of operation). As shown in Figure (1). During react phases, a submersible pump used to circulate the reactor contents to keep under homogenous condition at all times. Filling, purging and extraction events were achieved by three electrical valves. The biomass was not removed from reactor. Fill – react – settle – and draw mode following a predefining cycle and operated continuously as explain in Figure (2). During react phases, a submersible pump used to circulate the reactor contents to keep under homogenous condition at all times. Filling, purging and extraction events were achieved by three electrical valves. The biomass was not removed from reactor. Treated wastewater was discharge from the reactor until predefined minimum reactor water level was reached. The anoxic sequencing batch reactor ANSBR was operated by electrical board control supplied with timers which able to repeat over time previously defined cycle operation by controlling the switching on/off of filling. The inoculums for denitrifying organism acclimation process was taken from Rustamiya WWTP -Baghdad mixed liquor from aerobic reactor which mostly contain heterotrophic bacteria, that remove organic carbon aerobically due to fact that a large fraction of the bacterial mass that develops in an activated sludge process is facultative. The reactor fed with effluent of SBR for enrichment of ammonium oxidizing organism as the substrate after adding the minerals required for organism growth.

B. Analytical methods

Manually three time per day measurement of pH, ORP, EC. Manually acid and base (H_2SO_4 and 1M $NaHCO_3$) doses were added to keep the reactor with required pH. Two times per week nitrite nitrogen NO_2^--N, and nitrate nitrogen NO_3^--N was analyzed by spectrophotometric method.

1) Influent storage tank.
2) ANSBR reactor.
3) Effluent collection tank.
4) pH meter.
5) Submersible pump for mixing.
6) Electrical control panel.
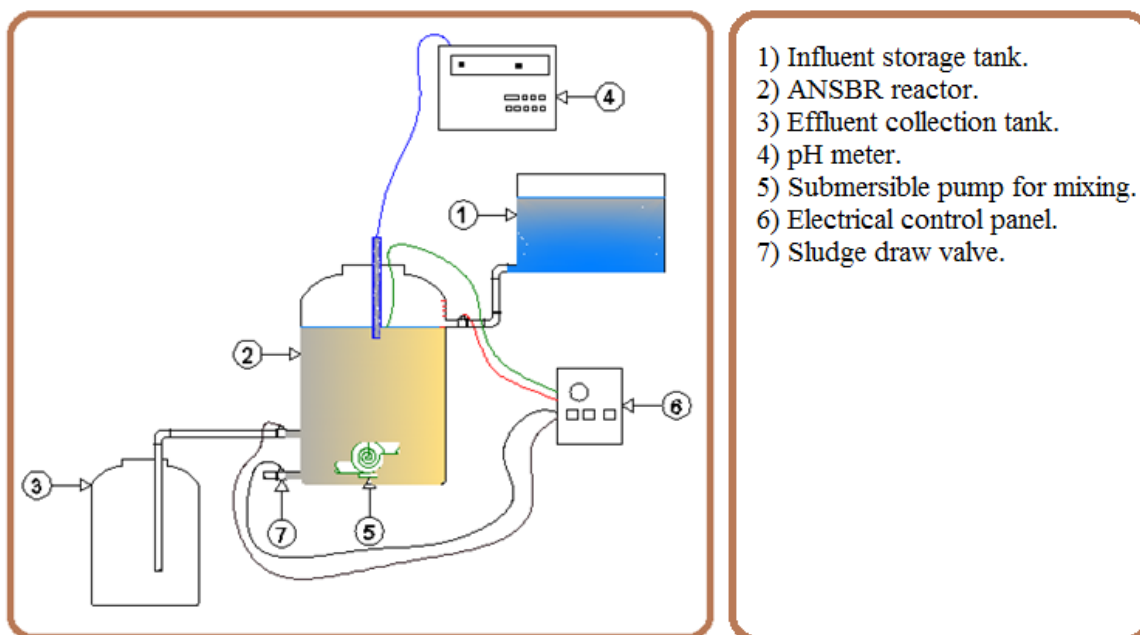7) Sludge draw valve.

Figure 1 Schematic diagram of enrichment of denitrification organism ANSBR experimental setup
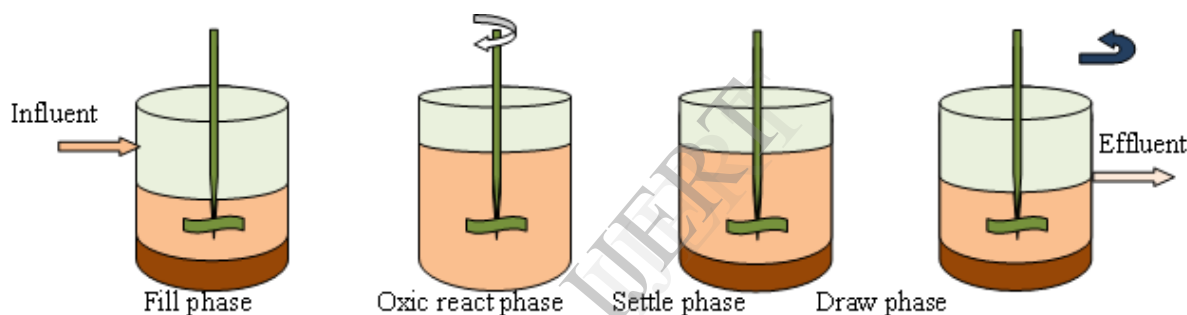

Figure 2 ANSBR sequence operation for enrichment of denitrifying organisms

III.   RESULTS

The performance of the enrichment phase of heterotrophic denitrification organism (HDEO) was evaluated mainly in terms of the ammonium oxidization to nitrite and nitrate as well as the volatile suspended solid (VSS).

A.   Physical parameters:

Temperature, pH, electrical conductivity (EC), and oxidation reduction potential ORP, during the enrichment of HDEO period are discussed below.

It can seen that the temperature in ANSBR for enrichment of HDEO was kept around 30.10∓ 1.12 ℃ which was natural temperature of laboratory without using additional heating therefore the fluctuation was appear during whole enrichment period as shown in Figure (3). The increase in temperature shown was due to increase in temperature of laboratory. So, the ANSBR temperature was one of the physical parameters that increase the denitrification rate [11] and encourage the best removal efficiency of nitrite and nitrate by HDEO which gave that

the best removal efficiency placed between 30-40 ℃ as given by {5], [10].

The pH is an index of acidity and alkalinity. The pH profile in Figure (4), that demonstrate the influent pH was stable with an average value of 6.02$\pm$0.18. Low value of influent pH attribute to high concentration of H^+ ion during nitrification process. The pH values inside ANSBR reactor were rise up to 8.01$\pm$0.98. The increment in pH was started after two days of enrichment because low concentration of HDEO in the beginning of process and due to adding acetic acid in excess as an electron donor to avoid substrate limitations.The increase of pH as a result of H^+ ion removal and due to alkalinity release during denitrification. The values of pH for ANSBR were with optimal range as limited by [13], [2]. The control of pH was help to obtaining a high yield of HDEO as given by [7]. During the denitrification process the increment in pH value of ANSBR controlled by acetic acid which was added as external carbon.

Electrical conductivity was used as a tool to monitoring the influent and effluent of ANSBR for enrichment of HDEO due to easy and quickly measuring. The enrichment of HDEO process was caused depletion in electrical conductivity due to removal of H^+, NO_2^- and NO_3^- ions by denitrfication process. During the operational period of ANSBR, electrical conductivity in the influent was on average 1.51 ± 0.39 mS/cm while the average values of electrical conductivity of effluent was 0.82 ∓ 0.09mS/cm as shown in Figure (5).

Oxidation reduction potential ORP was used as an operational method of ensuring that the denitrification is occurring. Figure 5.18 shows the variation of ORP of influent with average value of 58.0 ± 29.66 mV and the variation of effluent (at the end of reaction phase) with average value of -150.93 ± 46.38 mV for denitrification process at ANSBR . The ORP values depend on temperature, dissolved oxygen concentration and organic substrate activity of organisms. The change in ORP measurement was more important than the absolute value because, it was use as controlling tool for ANSBR. However, the observed ORP measurement were in a very good agreement with the previously reported ORP range for denitrification process [6]. From Figure (6), ORP values can be used as control parameters for denitrification [1]. So, the change in ORP in low dissolved oxygen was occurred due to activity of organisms [9].

B. Chemical analysis:

The chemical analyses was showed that influent nitrite and nitrate concentration were with an average 54.03 ∓ 38.47 mg/l and 20.62 ∓ 9.74 mg/l respectively while effluent nitrite and nitrate concentration were with an average 13.69 ∓ 4.93 mg/l and 7.25 ∓ 6.63 mg/l respectively. This result refers to growth of HDEO in ANSBR reactor as shown in Figure (7) and Figure (8).

Figure (9) shown the rate of reaction which is the change in concentration of $NO_x - N$ during HDEO enrichment period. The best fit was between the the concentration versus time with $R^2 = 0.847$ which mean that the rate of reaction was zero order. This means that denitrification was occurred at a rate independent of the $NO_x - N$ concentration as well as the electron donor concentration (acetic acid) due to excess adding. However, these findings are in a good agreement with the previously published results for denitrification process for high nitrite concentration as well as the available nitrate [4], [10], [11].
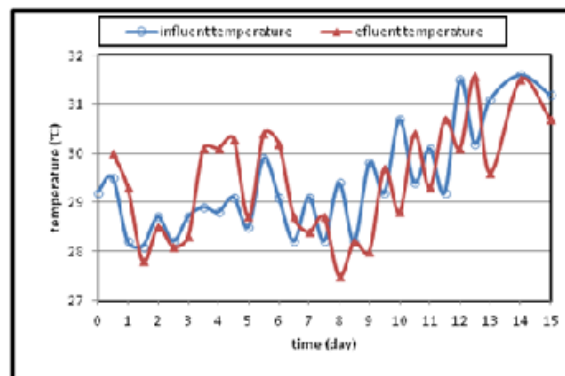

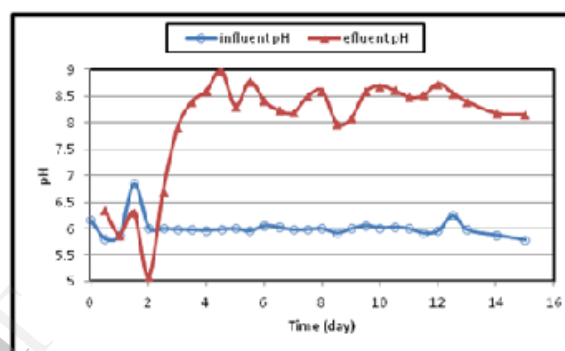Figure 3 variation of temperature during HDEO enrichment period.

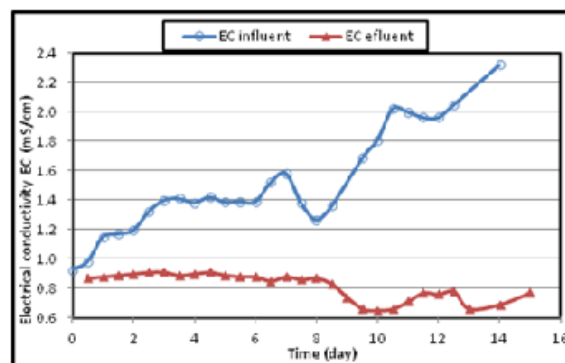Figure (4): variation of pH during HDEO enrichment period.

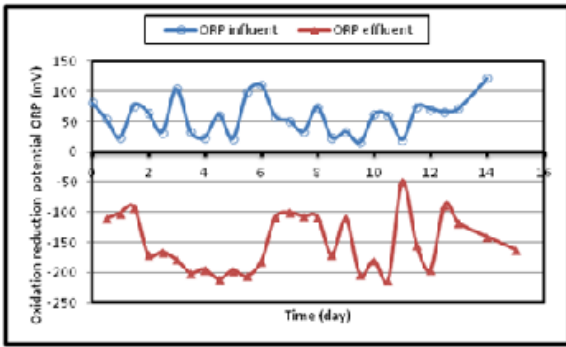Figure 5: variation of EC during HDEO enrichment period.

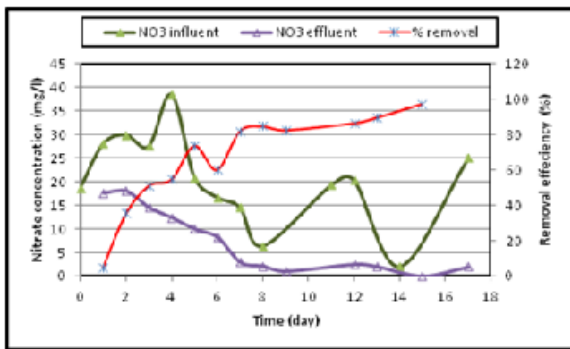Figure 6 variation of ORP during HDEO enrichment period.

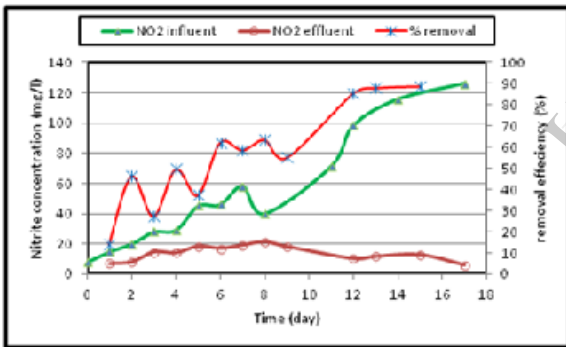Figure 7 Nitrate removal effeciency during HDEO enrichment period.

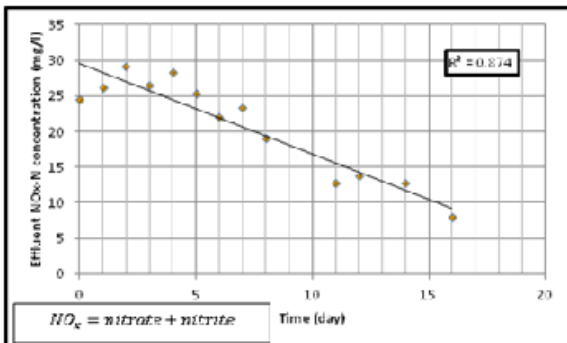Figure 8 Nitrite removal efficiency during HDEO enrichment period.

Figure 9 $NO_x - N$ variation during HDEO enrichment period.

C. Denitrification activity:

However the rate of denitrification depends primarily upon the nature and concentration of the organic matter present. But the adding of electron donor (acetic acid) in excess was made the denitrification process to be occurring at a rate independent of the electron donor concentration as given previously. To evaluate the denitrification activity in ANSBR, denitrification rates for nitrite and nitrate was calculated in same way given by Zafarzadeh[13];

$$R_{DN} = \frac{S_0 - S_1}{HRT}$$
….(1)

Where R_{DN} is denetrification rate in ($\frac{mg}{l.d}$), S_{in} and S_{out} are nitrite or nitrate influent and effluent concentration in (mg/l) and the HRT in (day).

As shown in Figures (10), (11) and (12), the highest observed denitrification rate for whole denitrification process $NO_x - N$ was 105.11 mg/l.d while the highest observed denitrification rate for $NO_2^- - N$ was 103.02 mg/l.d and the highest observed denitrification rate for $NO_3^- - N$ was 28.5 mg/l.d. However, these findings are in a good agreement with the previously reported results for denitrification rate by Dançer[2].

The results was observed demonstrate that the average denitrification rate with nitrite faster than average denitrification rate with nitrate by 2.6 which slightly higher than the reported value by Zafarzadeh et al.[13]. This increment attribute due to difference in reactor conditions and electron donor used. So, the nitrification via nitrite process such as SHARON being attractive due to this reason. The low correlation between denitrification rate and loading rate for nitrate was due to oscillation in influent nitrate concentration.
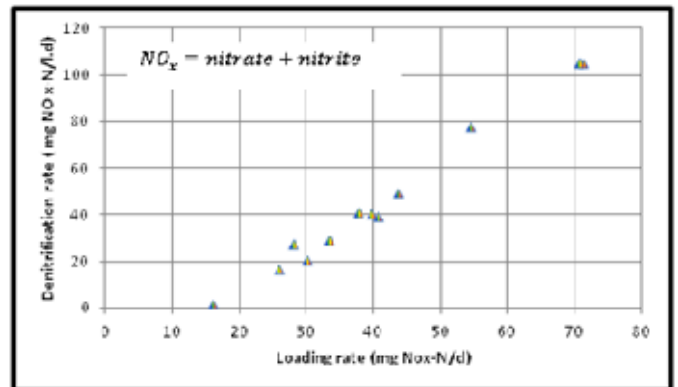

Figure 10 Denitrification rate of $NO_x - N$ as a function of loading rate during HDEO enrichment period.
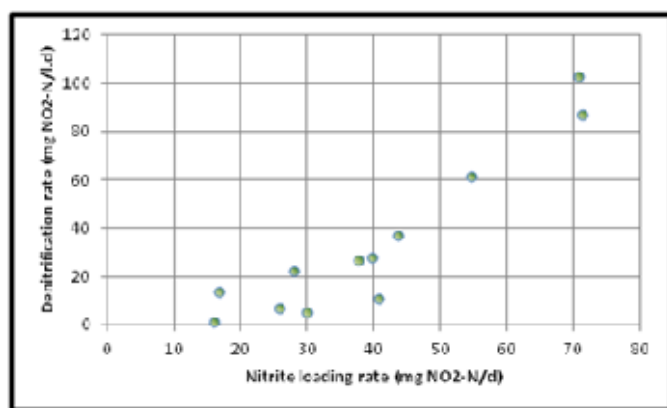
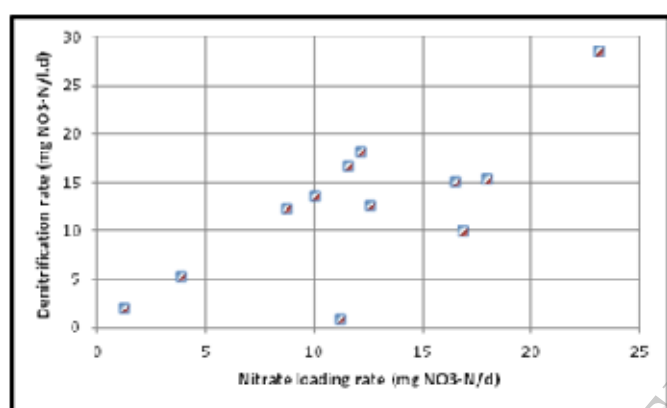Figure 11 Denitrification rate of nitrite as a function of loading rate during HDEO enrichment period.

Figure 12 Denitrification rate of nitrate as a function of lading rate during HDEO enrichment period.

IV.   CONCLUSIONS

1. The HDEO was enriched in ANSBR reactor successfully with moderate laboratory temperature of 31.1 ± 1.12℃. The nitrite and nitrate removal efficiency of ANSBR were 88.96% and 97.52% respectively. pH, EC and ORP were use as controlling tools. pH was rise up due to H^+ removal and release of al kalinity. EC was dropped from 1.51 ± 0.39 mS/cm to 0.82 ± 0.09 mS/cm was due to decrease the sum of absolute value of charges H^+, NO_2^- and NO_3^- as a result of HDEO activity during denitrification. So, electrical conductivity can be use as indicator of denitrification process as well as nitrification. The ORP was with average value of -150.93 ± 46.38 mV which is with range for denitrification process. Thus, ORP readings, coupled with DO and pH readings was an effective means of controlling denitrification process.

2. The rate of reaction for high nitrite concentration was zero order like that for low concentration with $R^2=0.847$.

3. Denitrification rate independent of electron donor (acetic acid) concentration when it was adding in excess concentration.

4. The average denitrification rate with nitrite faster than average denitrification rate with nitrate by 2.6.

ACKNOWLEGEMENT

REFERENCES

[1] Akın , B.S. and Ugurlu, A., 2005. Monitoring and control of biological nutrient removal in a Sequencing Batch Reactor. Process Biochemistry 40, 2873–2878.

[2] Dinçer, A., Kargi, F., 2000.   Kinetics of sequential nitrification and denitrification processes. Enzyme and Microbial Technology. 27, 37–42.

[3] Fernández-Nava Y., Maranón E., Soons J., Castrillón L., 2010, Denitrification of high nitrate concentration wastewater using alternative carbon sources, J. Haz. Mater. 173, 682–688.

[4] Filippis, P., Palma, L., Scarsella, M., Verdone, N., 2013. Biological Denitrification of High-Nitrate Wastewaters: a Comparison Between Three Electron Donors. Chemical Engineering Transactions. Vol. 32, 319-324.

[5] Gali, A., Dosta, J., van Loosdrecht, M. C. M., Mata-Alvarez, J., 2006. Biological Nitrogen Removal via Nitrite of Reject Water with a SBR and Chemostat SHARON/Denitrification Process. Ind. Eng. Chem. Res., 45, 7656-7660.

[6] Hamlin, H. J., Michaels, J. T., Beaulaton, C. M., Graham, W. F., Dutt, W, Steinbach, P., Losordo, T.M., Schrader, K. K., Main, K. L., 2008. Comparing denitrification rates and carbon sources in commercial scale upflow denitrification biological filters in aquaculture. Aquacultural Engineering . 38 ,79–92.

[7] Ishak, A. A., Hussain, M. A., 2003. Review of Critical Ranges in pH Control for Bioprocesses. 2nd Technical Postgraduate Symposium, TechPos'03.

[8] Mekonen A., Kumar P., Kumar A., 2001, Use of sequencing batch reactor for biological denitrification of high nitrate-containing water, J. Environ. Eng., ASCE, 127, 273-278.

[9] Myers, M., Myers, L., Okey, R., 2006. The use of Oxidation – Reduction Potential as a Mean of Controling Effluent Ammonia Concentration in an Extended eration Activated Sludge System. Proceeding of the water environment Federation. WEFTEC67:5901-5926.

[10]   Sabalowsky, A. R., 1999. An Investigation of Feasibility of Nitrification and Denitrification of a Complex Industerial Wastewater with High Seasonal Temperature. Master Thesis , Faculty of Virginia Polytechnic Institute and State University, Blacksburg.

[11]   Sedlak, R. l., 1991. Phosphorus and nitrogen removal from municipal wastewater: principles and Practice. The Soap and Detergent Association, New York, 2nd edition, pp.240 .

[12] Shen J., He R., Han W., Sun X., Li J., Wang L., 2009, Biological denitrification of high-nitrate wastewater in a modified anoxic/oxic-membrane bioreactor (A/O-MBR) Journal of Hazardous Materials 172, 595–600.

[13] Zafarzadeh, A., Bina, B., Nikaeen, M., Attar, H. M., Hajian nejad, M, 2010. Performance of Moving Bed Biofilter for Biological nitrogen Compounds Removal From wastewater by Partial Nitrification- Denitrification Process.   Iran. J. Environ. Health. Sci. Eng., 7, 4, 353-364.