A Study on Total Nitrogen Balance and Alkalinity Balance in a PVA Gel-Based Bioreactor

Ghazal Srivastava and Absar Ahmad Kazmi

Abstract PVA gel beads are proven out to be an effective structure for enrichment of large number of bacteria, providing high nitrification rates at lesser filling percentages. The treatment configuration (oxic–anoxic–oxic along with a settler) has shown a characteristic balance of nitrogen and alkalinity through the nitrification and denitrification phenomenon in the tanks. Ammonia removal rates were >90%, organic matter removal (COD) was 87–96%, and TSS removal was 96–99% at variable HRTs (6, 5, and 4.4 h) and temperatures. Total nitrogen balance was figured out as, average TN was 4.507 g/d in inlet, out of which 0.121–0.526 g/d (2.69–11.67%) get into the waste sludge, 0.191–0.947 g/d (4.25–21.01%) remained in the outlet, and the rest 3.077–4.151 g/d (68.27–92.11%) was removed. Accordingly, alkalinity balance showed that 25% of the inlet alkalinity was consumed in overall nitrification and denitrification process.

Keywords Chemical Oxygen Demand (COD) · Hydraulic Retention Times (HRTs) · Polyvinyl Alcohol (PVA) gel · Total Nitrogen (TN) · Total Suspended Solids (TSS)

1 Introduction

As we know, domestic sewage commonly contains organic contaminants, high suspended solids and numerous pathogens and insects which give rise to eutrophication of lakes, etc., if released to water bodies or groundwater without any treatment. But through appropriate analysis and gaining control over the environment, effective biological treatment of nearly all wastewaters having biodegradable components can be accomplished using proper elementary knowledge of microorganisms [1]. Biological wastewater treatment technology has proceeded

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stupendously since its origin toward the end of 1800s and Conventional Activated Sludge (CAS) systems came into picture in the early 1900s for treating both municipal wastewaters and the effluents discharged from industries. Although CAS process played a very good role in removing these pollutants it still had some issues like disposal of too much sludge produced, low treatment efficiency, i.e., presence of lesser number of microorganisms in each unit volume and a larger area requirement. Eventually the prolonged use of fixed-growth concepts came forth by the introduction of synthetic media into treatment processes during 1950s. Integrated Fixed-Film Activated Sludge (IFAS) is a comparatively advanced technology that delineates any suspended growth system as it integrates an attached growth media inside the suspended growth reactor [2]. It has gained the benefits of both conventional activated sludge and biofilm systems by merging these two technologies together as it allowed two separate biological populations to act in harmony, with the Mixed Liquor Suspended Solids (MLSS) depleting the bulk of organic load (BOD), and the biofilm helping in the oxidation of the nitrogenous load (NH_4^+) by cultivating a dynamic nitrifying community. Recently, Polyvinyl Alcohol (PVA) gel beads are observed as excellent immobilization media, have been proven effective in growth and enrichment of bacteria [3]. The 4 mm spherical shaped PVA gel bead possesses a mesh of 10–20 micron pores crossing through it, which enables growth of bacteria in a shielded mode and minimizes sloughing of biomass. Due to its better fluidity, minimum energy is consumed for mixing and the larger porosity of gel beads favors better supply of oxygen and carbon residing bacteria, resulting in stable treatment under variable loading. Volumetric packing ratios of the beads are typically 5–15%, which is much less compared with other carriers (50–70% usually) [4].

PVA gel displayed better performance as an immobilization medium by providing higher nitrification rates, with less bulk, thereby occupying little space in the reactor [5]. Consequently, even a lesser filling ratio of PVA gel beads in a reactor provides a high treatment potential. PVA gel treatment produces much less surplus sludge in contrast to conventional biological treatment methods; therefore, it requires lesser area to construct their tanks. A certain experiment carried out on MBBR process model provided an outcome that the effective specific surface area for PVA gel beads is around 2500 m^2/m^3 which is about 2.5 times larger in comparison to when only outer specific surface area of beads is taken into account and which is literally responsible for residing large number of bacteria in its pores with a protected atmosphere [4].

The aim of the study was the performance evaluation of this IFAS system containing only 4% PVA gel beads being a biomass carrier targeting the Total Nitrogen (TN) as well as Ammonical Nitrogen (NH_4–N) removal and to draw out TN balance in the entire system and also total alkalinity consumption linked with that removal during nitrification and denitrification processes occurring within the tanks. As worldwide, a multitude of people are feeling an extreme agony due to improper sanitation, dissatisfactory wastewater treatment, and unavailability of utilizable water. The situation is seriously worsened in smaller towns and rustic regions of developing countries [6]. So, this study actually drives our attention toward the decentralized sewage treatment systems especially for the nitrogen removal in rural areas, not much focused in India in past but now India needs their successful implementations for the better future of water bodies.

2 Materials and Methods

2.1 Reactor Configuration and Operational Parameters

Throughout the study, although as per variable conditions prevailing in the reactor regarding changes in Hydraulic Retention Times (6, 5, and 4.4 h), and in temperature (20–33 °C), this Integrated Fixed-film Activated Sludge system has been found capable to provide consistently effective ammonia removal rates >90%. Each of the reaction tanks (oxic–anoxic–oxic) was found to work satisfactorily at optimum maintenance of D.O, ORP, and pH. The three reaction tanks were: (1) media tank (consisting of 4% beads in the 10 L of tank) with aeration (for nitrification) (2) an anoxic tank (denitrification tank) of 10 L, (3) an oxic tank (i.e., secondary aerobic tank), whose reaction volume was 10 L first but was decreased to 5 L and then to 2 L which resulted in changes in HRT from 6 h to 5 h and then to 4.4 h, respectively, and also a 5 L settling tank with rotating scraper was installed at the end of treatment process (Fig. 1). The media used in the first tank was Polyvinyl Alcohol (PVA) gel beads occupying 4% or 0.4 L of reactor volume. Aeration in media tank and oxic tank was provided with diffusers placed at bottom. Continuous mixing was carried out in anoxic tank with the help of rotating shaft. Thus, an effective nitrogen mass balance was figured out using the tank-wise data analysis, nitrification as well as denitrification rate experiments were also conducted during this period and the results were found appreciable. The raw sewage on which the study was performed had COD/TN ratio of about 11.1:1 and Solids Retention Time (SRT) of 8.5 days on average. Performance evaluation showed that organic matter removal (COD) was 87–96% and suspended solids removal was 96–99%.

All the operational parameters were measured timely in which physicochemical parameters were pH, temperature, D.O., and ORP and sludge parameters were MLSS, MLVSS, SVI, and Solids Retention Time (SRT).

Physicochemical Parameters. In each of the three tanks, these parameters were maintained in PVA gel tank (media tank) D.O. values were kept on an average 6.76 mg/l with pH approximately 8.17 and ORP as +42 ± 74 mV; in anoxic tank (denitrification tank), D.O. value was 0.19 mg/l, pH was 7.68, and ORP was −138 mV on an average and in the oxic tank 4.01 mg/l, 7.81 and +66.7 mV, respectively (Figs. 2 and 3). pH of the inlet tank was 7.52 ± 0.3 and of the outlet was 7.9 ± 0.5. Maximum and minimum ambient temperatures at the study location were 33 °C and 20 °C, respectively, as the period of study of the pilot plant was from May 2, 2017 to October 31, 2017.

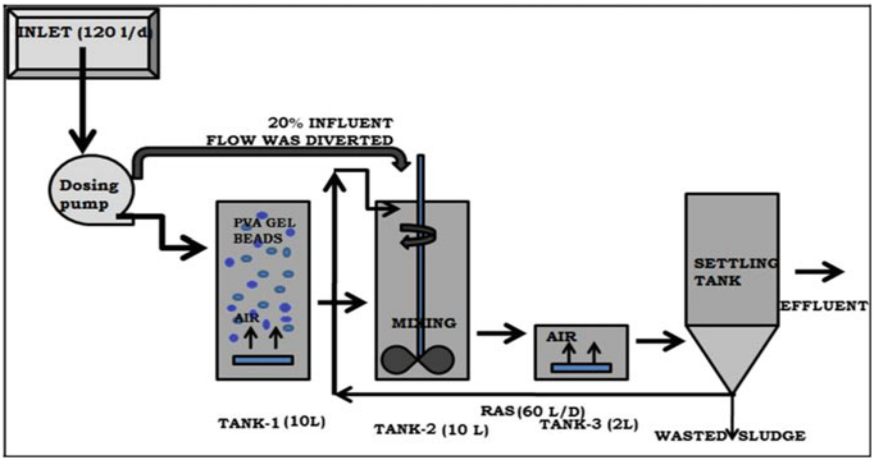

Fig. 1 Current schematic diagram of the pilot plant used in the study

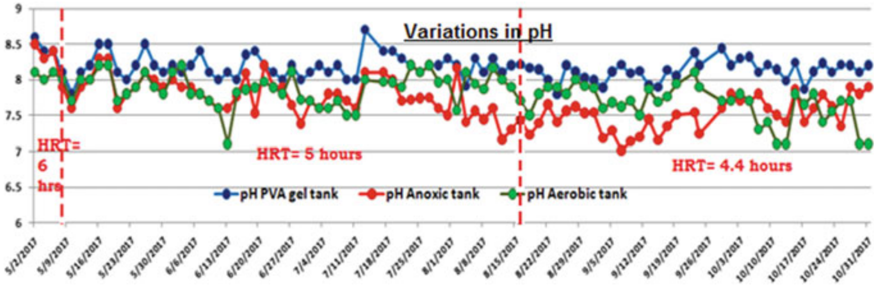

Fig. 2 Graph showing pH values in all the three tanks

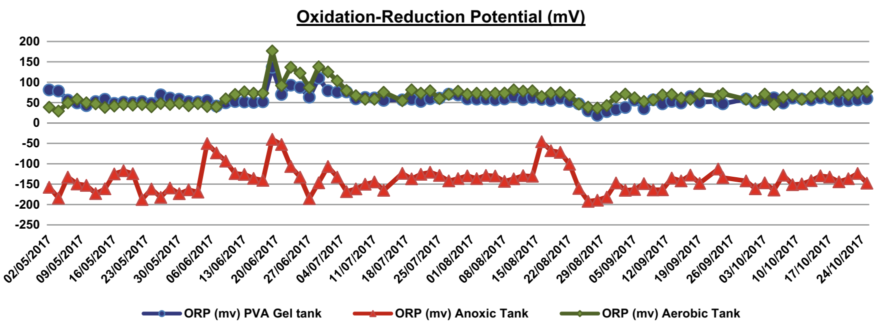

Fig. 3 Variations in ORP in all the three tanks

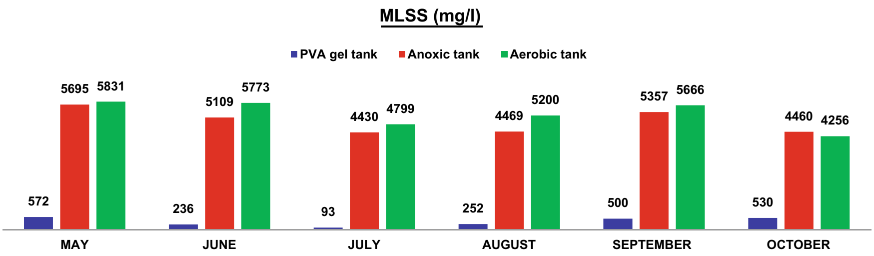

Fig. 4 Month-wise variations of MLSS (only suspended biomass) in all the three tanks

Sludge Parameters. Since May, average MLSS (mg/l) of the PVA Gel tank (except attached biomass) was maintained as 358 ± 247 mg/l, of the anoxic tank was 4942 ± 1001 mg/l and of the aerobic tank was 5336 ± 1074 mg/l and in the same way MLVSS (mg/l) was 179 ± 131 mg/l, 2291 ± 760 mg/l and 2449 ± 584 mg/l, respectively (Fig. 4). And thus, their ratio was approximately maintained as 0.494 ± 0.13 on an average generally in all the tanks with good settling characteristics having SVI 67 ± 16 ml/g and SV30 around 330 ± 60 (ml/l). The average attached biomass (inside the beads) was found to be as 436 mg/l.

The laboratory-scale plant was operating at an average Solids Retention Time (SRT) of 8.5 days. SRT was calculated using the MLSS (suspended) in all the three tanks, the sludge concentration (attached) in the beads (0.4 L of beads in 10 L of first oxic tank), and the daily sludge wasted in g/d.

2.2 *Method and Analysis*

The influent flow rate was maintained as 120 L/d in the inlet (80% in the PVA gel tank and 20% diversion to the anoxic tank just for external BOD loading for denitrification) and it was maintained as 60 L/d for RAS. It was measured regularly by visual measurement with measuring cylinder and timer. A portable DO meter (Hach 110Q multimeter, Hach, USA) was used to measure DO and temperature in the reaction tanks. The pH was measured by a portable pH meter (HQ11d pH Meter, Hach) and ORP by the portable ORP meter. Grab samples of 0.5 L were taken on every alternate day from the raw sewage tank, the three reaction tanks and from the outlet of the sedimentation tank for the analysis of Chemical Oxygen Demand (COD), Bio-chemical Oxygen Demand (BOD), Total and Volatile Suspended Solids (TSS and VSS), Total Nitrogen (TN), ammonia, nitrate, and alkalinity was done in accordance with *Standard Methods* [7].

Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS) of the wasted sludge, and reaction tanks were investigated as stated in *Standard Methods* [7].

3 Results and Discussions

3.1 Reactor Performance

COD and BOD Removal. This pilot plant was found very effective in the removal of organic matter and suspended solids. During the study of 6 months it was found that the COD removal was on an average 92.3 ± 4.2% (where COD in the influent was 398 ± 162 mg/l and in the effluent was 26 ± 9 mg/l). And in the same way, BOD removal was 96.4 ± 2.15% (having influent BOD as 194 ± 76 mg/l and effluent as 6 ± 2 mg/l) thus, the plant was showing good results in organic matter removal (as according to new effluent standards) (Fig. 5 and Fig.6).

TSS and VSS Removal. This plant was consistently very effective in removing suspended solids as well. The influent and effluent TSS and VSS were found to be as 279, 4, and 169, 2 respectively on average. Thus, the VSS: TSS ratio was maintained as 0.59 and 0.42 of influent and effluent, respectively. And the average removal percentages were 98.39% and 98.89% of TSS and VSS, respectively (Fig. 7 and Fig. 8).

Total Nitrogen (TN) and Ammonical Nitrogen (NH4–N) Removal. As described earlier, nitrification was undergoing in the PVA gel tank and secondary

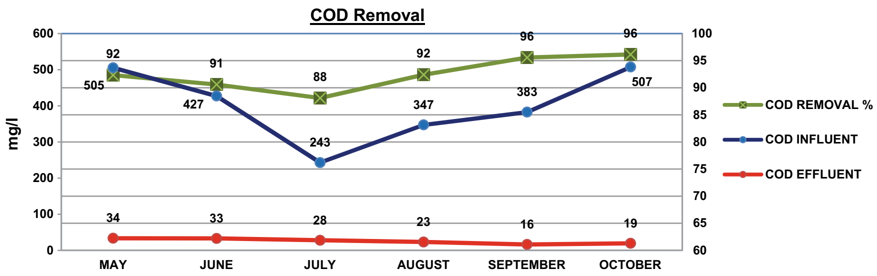

Fig. 5 COD month-wise graph of the pilot plant (values were taken as an average during a full month)

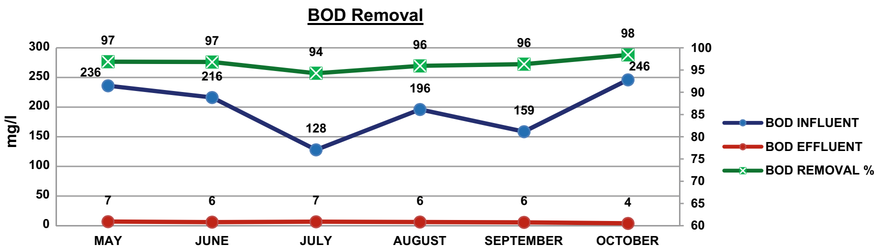

Fig. 6 BOD month-wise graphs of the pilot plant (values were taken as an average during a full month)

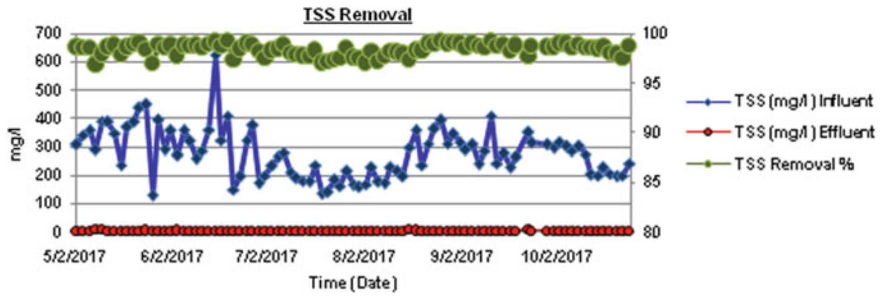

Fig. 7 TSS removal in the pilot-scale plant

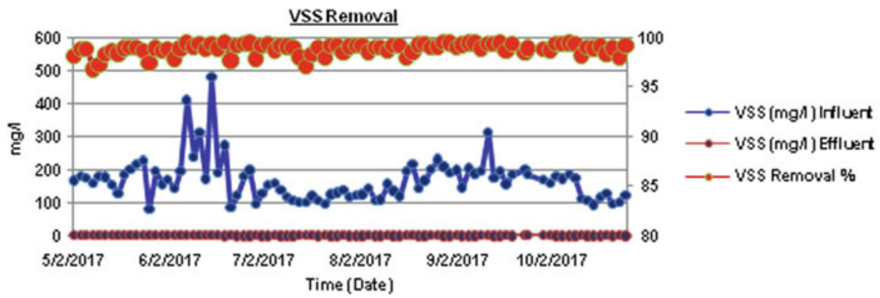

Fig. 8 VSS removal in the pilot scale plant

aerobic tank and denitrification process were being carried out in anoxic tank which brought out the objective of removing TN.

Significance of nitrification in wastewater treatment

1. Hazardous role played by ammonia on water bodies with respect to lowering of DO concentrations and increasing fish toxicity compels us to remove ammonia,
2. Issues related to eutrophication direct us for nitrogen removal and
3. For reusability of water covering groundwater recharge applications, etc., there's an ultimate need for effective nitrogen removal (Metcalf & eddy, Inc.) [1].

Nitrifiers are the dominant bacteria when organic food supplies have been consumed and polyvinyl alcohol gel beads (having diameter of 3–4 mm) are an excellent immobilization media having a network of minute pores about 10–20 microns-meter for enrichment of large number of bacteria in their protective cores [8]. Having advantages of both suspended as well as attached growth processes within a single system leads to simultaneous removal of organic matter (BOD) and nitrogen (Total Nitrogen and Ammonia).

These bars (Fig. 9) show that how deammonification and nitrification is taking place in the PVA gel tank and how at last >90% is getting removed in the effluent (Fig. 10).

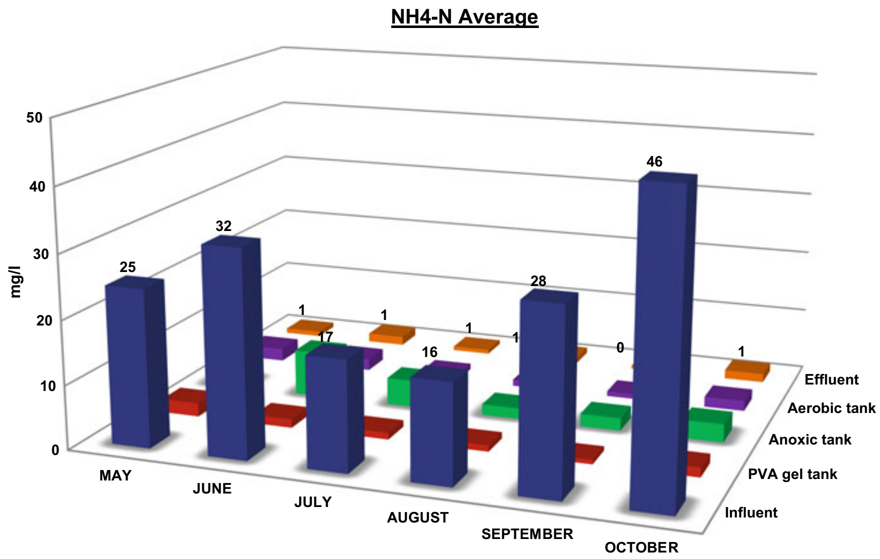

Fig. 9 Bar graph of ammonical nitrogen values in each of the tanks, in influent and in effluent taken an average value for a month

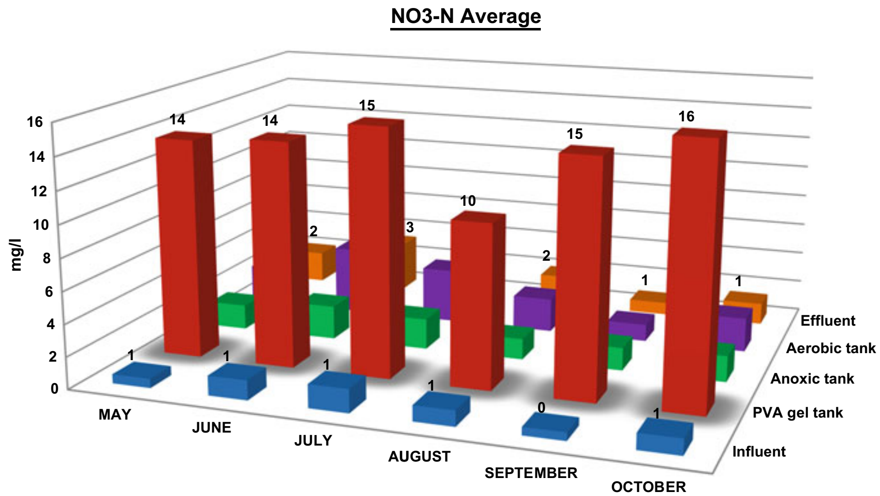

Fig. 10 Bar graph of nitrate values in each of the tanks, in influent and in effluent taken an average value for a month

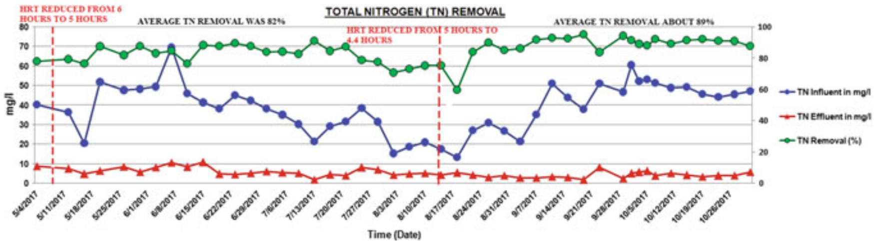

Fig. 11 Total Nitrogen (TN) removal in the pilot scale plant

These bar graphs show that most of the ammonia removal occurred in the PVA gel tank by simultaneous nitrification and denitrification inside the beads. The anoxic tank performed denitrification, i.e., reducing nitrate to nitrogen gas in a very satisfactory manner. Then the oxic tank (i.e., aerobic tank) did further nitrification of the 20% diverted inflow (containing about 2–4 mg/l ammonia) from the anoxic tank. Then, removal of nitrate which was formed in the oxic tank due to 60 L/d Return Activated Sludge (from the sedimentation tank to the anoxic tank) took place. Through this journey, only 0.2–3 mg/l of nitrate remained in the effluent. Total Nitrogen removal is shown in Fig. 11.

3.2 Total Nitrogen Balance

PVA gel tank with combination of anoxic and secondary aerobic tanks, i.e., IFAS configuration (oxic–anoxic–oxic) has shown a characteristic balance of nitrogen through nitrification and denitrification phenomenon in the tanks. Thus, an effective Total Nitrogen Mass Balance was figured out by doing tank-wise total nitrogen content analysis.

This balance used the following equations for the calculation of each part of TN distribution:

$$\text{Mass (Influent TN)} = \text{Q} * \text{TN inf.} \tag{1}$$

Mass of nitrogen in the influent per day (Mass (Influent TN)) was calculated by a product of the influent flow rate (Q) and content of total nitrogen in influent in mg/l (TN inf.) which constitutes each form of nitrogen organic nitrogen, ammonical nitrogen (NH_4–N), and nitrate (NO_3–N) [9, 10].

$$\text{TN (Mass (Influent TN))} = \text{Mass}_{\text{DEN}}\text{TN} + \text{Mass waste TN} + \text{Mass (Effluent TN)} \tag{2}$$

This Eq. (2) is showing balance of TN in the reactor. The influent nitrogen present in the form of ammonia was nitrified in the PVA gel tank. The portion of ammonia which was not nitrified came out of the system in effluent. This nitrate from nitrified ammonia, nitrate already present in influent, and nitrate coming from secondary oxic tank (aerobic tank) to anoxic tank through RAS or due to 20% diversion were denitrified in the anoxic tank denoted here as Mass $_{DEN}$TN. The remaining amount of nitrate, which was not denitrified came out of the system with the effluent and in wasted sludge.

$$\begin{aligned}\text{Mass waste TN} &= \text{q waste (l/d)} * \text{MLSS (wasted sludge) (g/l)} \\ &\quad * \text{x \% TN in sludge}/100\end{aligned} \tag{3}$$

This mass of TN in the wasted sludge in g/d was calculated by multiplying daily sludge wasted in l/d (q waste) and MLSS of the sludge wasted in g/l to the fraction "x", where "x" generally found to be in the range of 1.9–2.4% in the sludge.

$$\text{Mass (Effluent TN)} = \text{Q} * \text{TN eff.} \tag{4}$$

Mass of nitrogen in effluent per day (Mass (Effluent TN)) was calculated in the same way as a product of the flow rate (Q) and content of total nitrogen in effluent in mg/l (TN eff.). So, to calculate denitrified content of TN, an indirect approach was used through subtracting Mass waste TN and Mass (Effluent TN) from the Mass (Influent TN).

"Q" is influent flow rate, i.e., 120L/d, whereas "q waste" is wastage flow rate generally about 1.2 l/d. All masses in g/d and MLSS concentration in g/l. Mass DEN corresponds to the mass of denitrified portion of Total Nitrogen in g/d. In the nutshell, fate of the influent TN is discussed here. Influent TN showed its destination after its overall tank-wise journey in three ways; some part of it went to the wasted sludge, some part remained in the outlet (effluent), and the rest got liberated as Nitrogen gas through denitrification [10]. The results can be expressed through this bar chart (Fig. 12).

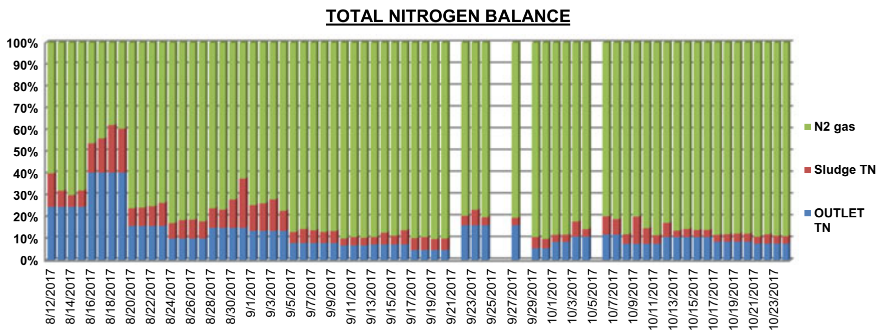

Fig. 12 Comprising the percentage distribution of all the three parts of the Total Nitrogen as described above

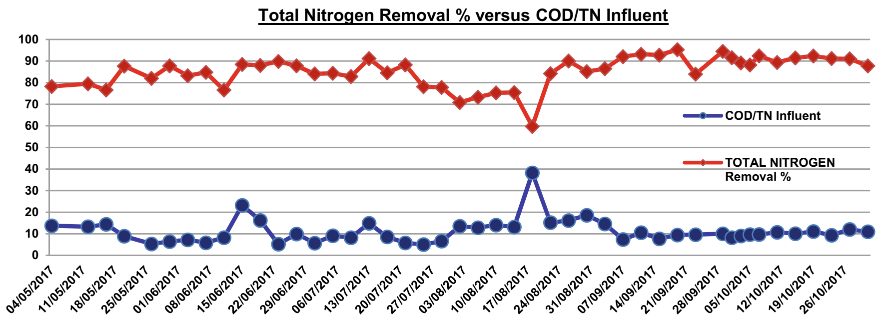

Fig. 13 TN removal % at varying COD/TN influent values

Average Total Nitrogen (TN) was 4.507 g/d in inlet, out of which 7.18 ± 4.5%, i.e., on an average 0.324 g/d got into the waste sludge, 0.569 g/d (12.63 ± 8.4%) remained in the outlet and the rest 3.610 g/d (80.1 ± 11.9%) was removed as N_2 gas. Based on primary effluent, the percent nitrogen removal by assimilation in the treatment of domestic wastewater may range from 8 to 20% and appreciable results were found here. The sludge was of better quality and was exhibiting good settling characteristics with SVI < 70. The COD: TN ratio of the raw sewage was approximately 11:1 (as shown in Fig. 13).

3.3 Alkalinity Balance

The alkalinity of water is a measure of its capacity to neutralize acids. For wastewater operations, alkalinity is measured and reported in terms of equivalent calcium carbonate. We know that 7.14 mg of alkalinity as $CaCO_3$ is consumed during nitrification (oxidation of every "mg of ammonium ion") [11]. Lack of carbonate alkalinity will stop nitrification as, $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$.

So, one mole of NH_4–N liberates two moles of H + ions which corresponds to $2HCO_3$ ions. And thus, after calculations, it was found that 7.14 mg was consumed at 1 mg oxidation of ammonia. In the same way during denitrification, 3.57 mg of alkalinity was released. Inlet alkalinity during this study was about 330 ± 33 mg/l and of outlet about 240 ± 30 mg/l of $CaCO_3$. Here, a balance is obtained between calculated values and observed values (alkalinity of inlet and outlet experimentally obtained) of total alkalinity consumed within the reactor by nitrification and denitrification phenomenon (Fig. 14 and Fig. 15).

This was achieved through the calculations as shown in the Table 1.

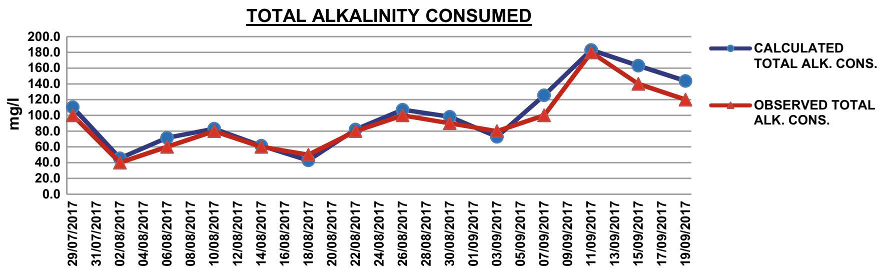

Fig. 14 Graph showing a balance in calculated and observed total alkalinity consumed

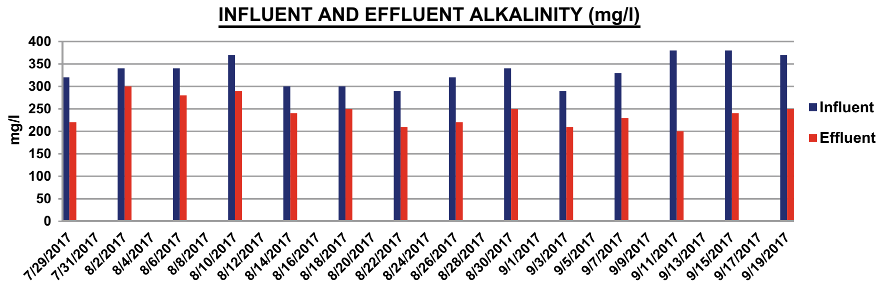

Fig. 15 Influent and effluent alkalinity observed after doing lab experiments

Table 1 Calculated versus observed values of the total alkalinity consumed

(NH_4–Ninf + Org N inf)-(NH_4–Neff-Org N eff)	Alkalinity consumed	TN inf (except TN in wasted sludge)-TN eff	Alkalinity released	Dates	Calculated	Observed
	(NH_4–Ninf + Org N inf-NH_4–Neff-Org N eff) * 7.14		(TN in (except sludge)-TN eff) * 3.57		Total alk. cons.	Total alk. cons.
26.6	189.9	22.30	79.6	7/29/2017	110.3	100
11.3	80.3	9.74	34.8	8/2/2017	45.5	40
16.2	115.7	12.39	44.2	8/6/2017	71.5	60
18.8	134.2	14.33	51.2	8/10/2017	83.1	80
14.6	104.2	11.98	42.8	8/14/2017	61.5	60
9.5	68.0	7.06	25.2	8/18/2017	42.8	50
22.0	157.0	21.00	75.0	8/22/2017	82.1	80
27.9	199.1	25.73	91.9	8/26/2017	107.2	100
24.2	173.0	20.93	74.7	8/30/2017	98.3	90
18.7	133.5	17.00	60.7	9/3/2017	72.8	80
32.5	232.3	29.94	106.9	9/7/2017	125.5	100
47.6	339.9	43.93	156.8	9/11/2017	183.0	180
41.7	297.7	37.72	134.7	9/15/2017	163.1	140
36.9	263.5	33.54	119.7	9/19/2017	143.7	120

4 Conclusion

The outcomes of the study revealed that good TN (Total Nitrogen) balance and alkalinity balance were exhibited by this IFAS system. The nitrification and denitrification processes in the tanks were going on satisfactorily at optimum maintenance of ORP, D.O., and pH and even at variable HRTs and temperature differences and PVA gel beads have come out to be an effective structure for residing numerous of bacteria in its protective cores with good oxygen permeability and thus higher nitrification rates at just 4% filling percentages were obtained. This system was also showing a very good response (according to new effluent standards) in suspended solids removal and organic matter removal. This detailed study during its operation can be helpful in laying out a better performance evaluation of the system and in figuring out many operational problems in future too and maybe implementation of these types of reactors, a considerable and a significant step toward decentralized sewage treatment approaches.

References

1. Metcalf and Eddy: Wastewater Engineering Treatment, Disposal and Reuse, 4th edn. McGraw-Hill, Indian Edition (2003)
2. U.S. EPA: Nutrient control design manual. United States Environmental Protection Agency, Washington, DC (2010)
3. Wang, Y., Liu, Y., Feng, M., and Wang, L.: Study of the treatment of domestic sewage using PVA gel beads as a biomass carrier. J. Water Reuse Desalination **8**(3), 1–10 (2017)
4. Levstek, M., Plazl, I., Rouse, J.D.: Estimation of the specific surface area for a porous carrier. Acta Chimica Slovenica, 45–51 (March 2010)
5. Rostron, W.M., Stuckey, D.C., Young, A.A.: Nitrification of high strength ammonia wastewaters: comparative study of immobilisation media. Water Res. **35**(5), 1169–1178 (2001)
6. Singh, N.K., Kazmi, A.A., Starkl, M.: A review on full-scale decentralized wastewater treatment systems: techno-economical approach. Water Sci. Technol. **71**(4), 468–478 (2015)
7. APHA, AWWA, WPCF: Standard Methods for the Examination of Water and Wastewater, 22nd edn. American Public Health Association, Washington, DC (2005)
8. Onnis-Hayden, A., Dair, D., Johnson, C., Schramm, A., Gu, A.Z.: Kinetics and nitrifying populations in nitrogen removal processes at a full-scale integrated fixed-film activated sludge (IFAS) plant. Water Environ. Fed. 3099–3119 (2007)
9. Gani, K.M., Singh, J., Singh, N.K., Ali, M., Rose, V., Kazmi, A.A.: Nitrogen and carbon removal efficiency of a polyvinyl alcohol gel based moving bed biofilm reactor system. Water Sci. Technol. **73**(7), 1511–1519 (2015)
10. Barker, P.S., Dold, P.L.: COD and nitrogen mass balances in activated sludge systems. Wat. Res. **29**(2), 633–643 (1995)
11. Benninger, R.W., Sherrard J.H.: Nitrification and alkalinity relationships in activated sludge. Water Pollut. Control Fed. **50**(9), Annual Conference Issue, 2132–2142 (September 1978)