IranJOC
Iranian Journal of
Organic Chemistry

The effect of reducing the air basin on concentration phosphate (orto, total), nitrate and nitrite ions waste water treatment

Shamsi Esmaeilzadeh*

Department of Chemistry, Science and Research Branch, Islamic Azad University, Kerman, Iran

Abstract: In this study, the amounts of phosphate, nitrate and nitrite ions in a domestic wastewater treatment plant were evaluated. The six-month study period, from winter to summer and twice per month, sampling from both influent and effluent was performed following analysis of samples using simple, valid and developed spectrophotometric method. The effective parameters on the amounts of nitrate, nitrite and phosphate ions such as pH, MLSS, MLVSS, DO, BOD_5, COD, F/M, and T were investigated.Under the optimum conditions, the calibration curve was linear in the range of 0.1-1.0 mg L^{-1} (R^2 =0.999). The results wereshown that, in the timeframe of this study, the efficiency of treatment process was much better before stopping because of appropriate food to microorganism ratio (F/M). In other words, at this stage, nitrification was performed properly and phosphates were removed from the system to a large extent.The percentage of elimination of COD and BODs was acceptable while analyzing.

Introduction

Nitrates in various water supplies, including wastewater, has raised concerns due to its severe impact on human and animal health. Diverse methods are reported to remove nitrate from water streams which almost fail to entirely treat nitrate, except biological denitrification which is capable of reducing inorganic nitrate compounds to harmless nitrogen gas.

A review of numerous studies in biological denitrification of nitrate containing water resources, aquaculture wastewaters, and industrial wastewater confirmed the potential of this method and its flexibility towards the remediation of different concentrations of nitrate [1].

Up to the present time, researchwas conducted on the removal of nitratefrom water resources, aquaculture ponds or aquaria, and industrial wastewater [2]. The removal of nitrate from rinse wastewater generated by the stainless steel manufacturing process was studied by denitrification in a sequential batch reactor (SBR) [3] . A modified anoxic/oxic- membrane bioreactor has been applied to the denitrification of a high strength nitrate waste (about 3600 mgL^{-1} nitrate) generated from an initiating explosive factory [4]. In many sources of water, nitrate contamination is a widespread environmental problem [5,6],primarily in areas of intensive agriculture. Nitrate is believed to be a contributing factorof certain major health conditions in humans such as blue baby syndrome' in infants, as well as liver damage and cancer [7,8].

*Corresponding author. Tel.: +983432810948; E-mail: esmaeelzadeh137@yahoo.com.

For the nitrate removal methods, biological denitrificationrequiresthe continuous monitoring of pH control, the addition of a carbon source, and temperature maintenance [1,9,10].Extractive methodssuch as reverse osmosis and ion exchange resins [11-12] produce a large amount of effluentcontaining a high concentration of nitrate which results ina secondary pollution. Thus,it must be subsequently treated,increasing the overall cost of the process. Electrochemical denitrificationhas had been the focusof many researchers recently [13-17]. Phosphorus is an essential nutrient for biomass growth; however, excessive intake in water bodies such as rivers, lakes or lagoons causes an abnormal growth of algae and aquatic plants resulting in the degradation of the water quality. Therefore, legislation on phosphate disposal into the surrounding environment is becoming more stringent worldwide, and those strict regulations extend to smaller wastewater treatment plants (WWTPS). One appropriate technology for proving phosphate removal is filtration through materials with high affinities for phosphate binding. Since common filler substrates (such as sand gravel) have limited phosphate removal capacities, research on alternative materials have become a priority. In the last two decades, a large number of potential substrates, including natural materials (rocks, soils and sediments), industrial by products (steel slag, burnt oil shale and fly ash) and man-made products (light-weight aggregates specifically produced for phosphate removal) have been tested [18].

Results and discussion

Calibration curves:

The standard solutions with concentrations of 0.1, 0.2, 0.5, and 1 mgL^{-1}of nitrate ions, 0.1, 0.2, 0.4 and 0.8 mg L^{-1}of nitrite and 0.1, 0.2, 0.3, and 0.4 mg L^{-1} of phosphate ions werepreparedand their absorbance at 410 and 880 nm were measured by spectrometer. Finally, the calibration curves were obtained and presented in Fig.**S1**.

Method evaluation:

To measure accuracy, mean of concentrations was applied.The percentage of relative error related to each concentration was obtained. The relative standard variation was used for evaluating precision of method. The percentage of relative error (RE) and relative standard variation (RSD) for NO_3^-, NO_2^- and PO_4^{3-} were calculated according to equations (1,2) and demonstrated in Table **2**.

$$RE\ (\%) = \frac{\frac{x-\mu}{\mu} \times 100}{} \qquad (1)$$

$$RSD\ (\%) = \frac{SD}{\bar{x}} \times 100 \qquad (2)$$

Where x, μ and $\bar{X}$ are calculated concentration,real concentration and mean.

Biological removal percent of phosphorus:

The sampling of treatment plant was conducted 12 times. The percentage of biological removal of phosphorus and total phosphorus was obtained according Eq. 3. Percentage of removal: initial concentration-final concentration/initial concentration×100 (3). The results are displayed in table **3** and **4**.

Removal percent of BOD$_5$ and COD:

According to initial and final BOD and COD densities in wastewater and equation 3, the percent of removal of COD and BOD$_5$ was obtained and shownin Table **5.**

Concentration of Effluent nitrate and nitrite ions:

The input and output concentrations of each ion was obtained. The results are shown in Table **6**.

Diagrams of concentration variation of phosphate, nitrate, and nitrite ions:

The variation of concentration underlying orthophosphate, total phosphate, nitrate, and nitrite were drawn and shown in Fig (**1-7**) according to Table **1**.

It should be noted that one parameter may not determine the concentrationvariation of all ions. It is the reason that theincrease or reduction of one ion concentration is not in conformity with the variation of one parameter. Other parameters could intervene in concentrationvariation of ion in active sludge method due to biological purification of wastewater.

Table 1: Control parameters of sampling

F/M	$T^0_{(C)}$	DO mg/1	MLVSS mg/1	MLSS mg/1	TSS mg/1 output	TSS mg/1 input	COD mg/l output	COD mg/l input	BOD_5 mg/l output	BOD_5 mg/l input	pH output	pH input	Sample
0.04	19	2.8	2905	4150	30	510	30	300	17.10	173	7.60	7.50	1
0.04	19	2.9	3024	4320	30	300	37	250	19.50	157	7.70	7.60	2
0.03	20	2.8	2954	4220	27	275	45	320	16.50	159	7.65	7.55	3
0.03	20	2.8	2814	4020	30	260	35	250	20.50	170	7.77	7.60	4
0.05	22	2.7	4074	5820	40	390	21	300	11.40	125	7.70	7.90	5
0.09	23	2.0	2688	3840	40	300	35	430	47.10	171	7.42	7.36	6
0.25	25	1.55	3024	4320	20	860	30	540	54.20	242	7.57	7.47	7
0.25	27	1.50	5019	7020	10	340	25	310	11.50	124	7.60	7.50	8
0.40	33	1.50	2975	4250	50	450	42	410	29.00	165	7.60	7.50	9
0.40	34	1.50	2674	3820	60	600	50	435	35.00	195	7.65	7.55	10
0.30	32	1.50	2121	3030	55	450	40	400	25.00	162	7.77	7.56	11
0.50	29	1.60	2350	3500	15	450	45	450	29.00	168	7.70	7.65	12

Table 2: Relative error and standard variation of NO_3^-, NO_2^-, and PO_4^{3-} ions

Ion	Real Concentration (mg L^{-1})	Calculated concentration 1	Calculated concentration 2	Calculated concentration 3	Concentration mean	Relative error (%)	SD (mg L^{-1})	RSD (%)
NO_3^-	0.1	0.09	0.10	0.09	0.09	-3	0.097	2.58
	0.2	0.20	0.19	0.19	0.19	-0.53	0.198	3.35
	0.5	0.52	0.45	0.50	0.49	-1.26	0.493	5.53
	1.0	0.99	0.99	0.99	0.99	-0.50	0.995	0.36
NO_2^-	0.1	0.09	0.10	0.09	0.09	-1.48	0.001	1.55
	0.2	0.20	0.19	0.19	0.19	-0.49	0.002	1.02
	0.4	0.40	0.39	0.39	0.39	-0.75	0.003	0.75
	0.8	0.79	0.79	0.78	0.79	-1.08	0.005	0.63
PO_4^{3-}	0.1	0.09	0.09	0.10	0.09	-3.35	0.003	3.33
	0.2	0.19	0.19	0.20	0.19	-0.30	0.002	1.01
	0.3	0.29	0.29	0.29	0.29	-0.71	0.002	0.70
	0.4	0.29	0.40	0.39	0.39	-0.90	0.004	1.16

Table 3: percentage of biological removal of phosphorus (Orto)

Sample	Influent concentration 1	Influent concentration 2	Influent concentration 3	Influent concentration mean	Effluent concentration 1	Effluent concentration 2	Effluent concentration 3	Effluent concentration mean	Biological removal (%)
1	37.73	37.79	37.69	37.73	25.45	25.51	25.69	25.54	32.31
2	40.52	40.49	40.92	40.64	26.41	26.49	8.58	26.41	35.02
3	39.57	39.63	39.48	39.54	17.44	17.35	5.73	17.44	55.89
4	40.52	40.55	40.01	40.67	25.45	25.51	8.28	25.45	73.43
5	40.83	40.77	41.17	40.92	25.91	25.84	8.61	26.06	36.31
6	36.75	36.81	36.78	36.78	8.11	8.23	8.04	8.11	77.95
7	28.95	28.98	29.19	29.04	8.01	8.04	8.38	8.13	71.99
8	53.33	35.43	35.89	35.55	17.59	17.74	17.56	17.63	50.43
9	33.92	33.86	34.29	34.01	20.41	20.35	20.81	20.51	39.71

10	29.22	29.91	29.19	29.44	22.62	22.74	22.59	22.65	23.05
11	39.17	40.41	38.22	39.17	25.45	25.39	25.54	25.45	35.03
12	18.25	18.21	18.36	18.27	14.12	14.73	14.73	14.52	20.51

Table 4: percentage of biological removal of phosphorus (Total)

Sample	Influent concentration			Influent concentration mean	Effluent concentration			Effluent concentration mean	Biological removal (%)
	1	2	3		1	2	3		
1	39.57	39.82	39.54	39.64	27.57	27.01	27.66	27.41	31.53
2	47.12	47.03	48.14	47.43	31.41	31.28	31.71	31.47	33.64
3	56.55	57.19	56.61	56.76	39.57	39.29	39.94	39.61	30.23
4	45.56	45.51	45.99	54.68	29.84	30.12	29.75	29.91	34.52
5	47.12	48.01	47.18	47.43	28.43	28.61	28.49	28.49	39.93
6	50.25	50.28	50.84	50.44	12.95	12.86	13.38	13.05	74.13
7	47.12	47.92	47.15	47.41	12.95	13.54	12.89	13.11	72.34
8	57.77	57.75	58.27	54.93	18.84	18.79	19.55	19.06	65.31
9	50.25	50.45	50.99	50.51	37.94	37.88	38.41	38.07	24.62
10	47.25	47.77	47.31	47.43	29.84	29.91	30.51	30.08	36.58
11	45.16	45.23	45.99	45.43	35.33	36.41	35.39	35.71	21.39
12	43.59	44.67	43.65	43.96	36.41	27.71	24.09	23.73	46.02

Table 5: percentage of COD and BOD_5 removal

sample	COD removal (%)	BOD_5 removal (%)
1	90.0	90.1
2	85.2	87.5
3	85.9	89.5
4	86.0	87.9
5	93.0	90.88
6	91.86	72.45
7	94.4	77.6
8	91.93	90.72
9	89.75	82.42
10	88.50	82.05
11	90.0	84.56
12	90.0	82.73

Table 6: Effluent concentration of NO_3^- and NO_2^-

Sample	concentration NO_3^-			concentration mean NO_3^-	concentration NO_2^-			concentration mean NO_2^-
	1	2	3		1	2	3	
1	32.47	32.78	32.14	32.46	0.32	0.29	0.30	0.30
2	64.24	64.13	64.66	64.34	0.20	0.18	0.29	0.27
3	28.80	92.25	28.64	28.89	0.66	0.62	0.68	0.65
4	56.48	56.31	56.74	56.51	3.93	3.86	4.01	3.93
5	25.47	25.93	25.38	25.59	1.94	2.03	1.84	1.94
6	9.97	9.86	10.18	10.01	8.50	8.12	8.99	8.50
7	-	-	-	-	4.27	4.24	4.28	4.27
8	-	-	-	-	5.76	6.01	5.61	5.76
9	3.10	3.38	3.14	3.21	17.67	17.91	17.54	17.67
10	-	-	-	-	8.01	8.13	8.01	8.01
11	-	-	-	-	12.82	13.01	12.71	12.82
12	-	-	-	-	5.91	6.02	5.98	5.91

CHARTS
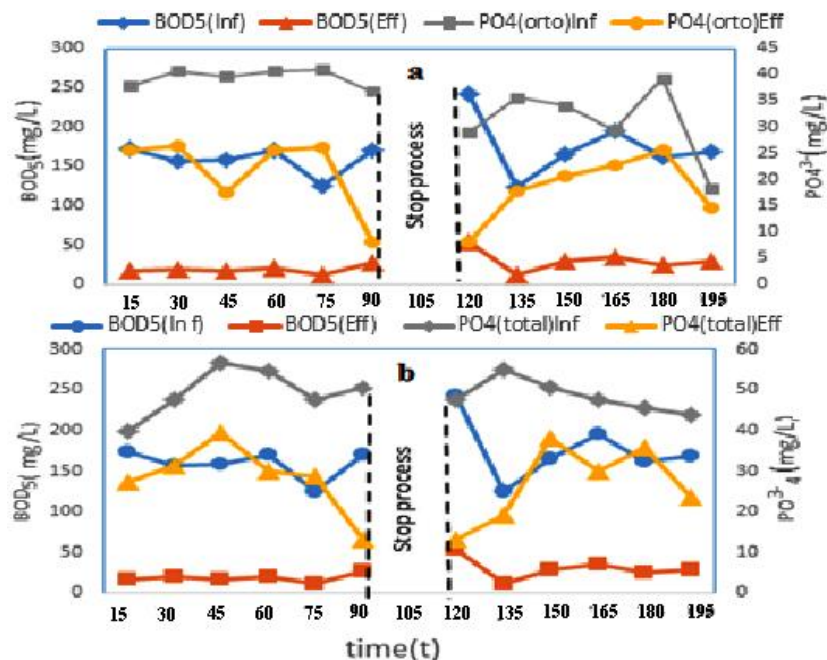
Figure 1: Variation of a) orthophosphate and b) total phosphate ions to variation of BOD_5 during the study
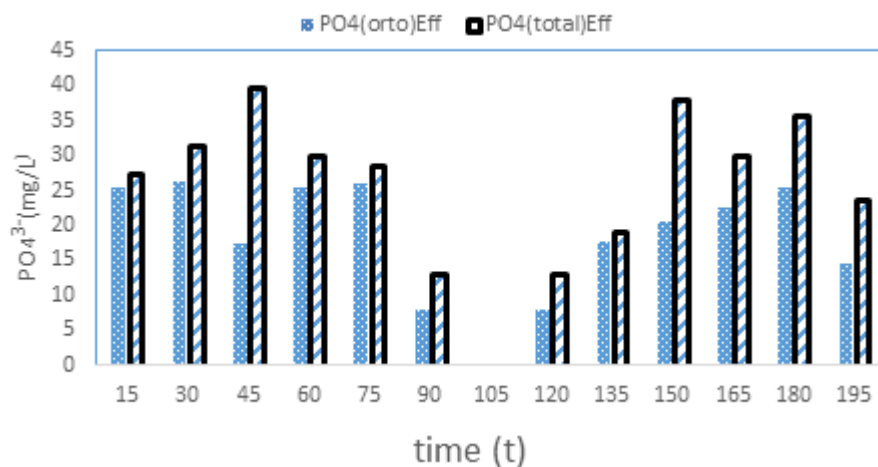
Figure 2: deviation of phosphate ion density
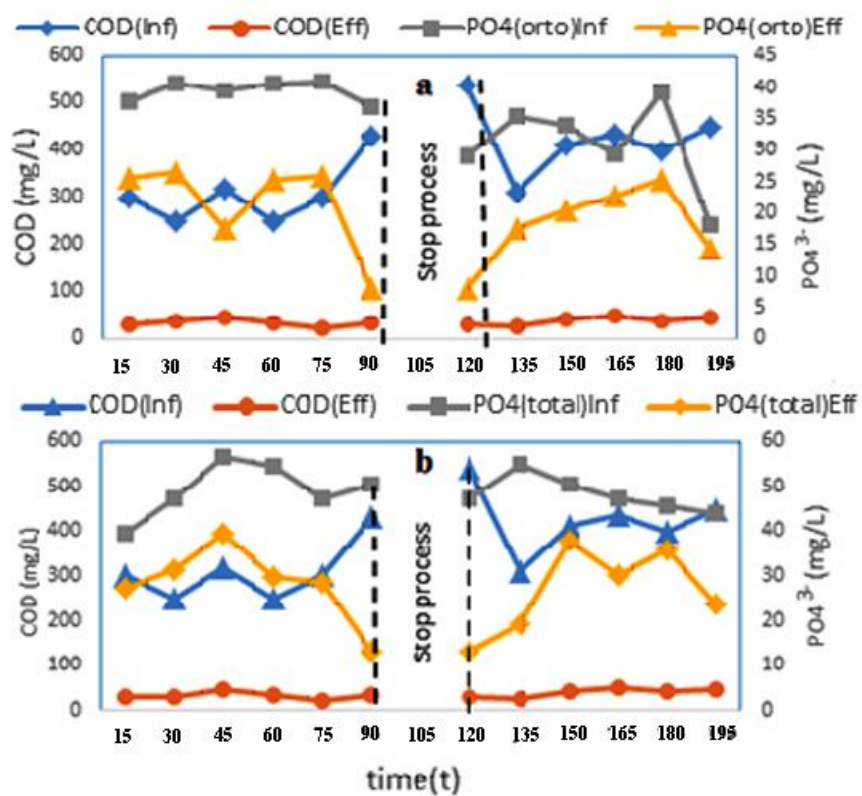
Figure 3: Variation of a) orto and b) total phosphate ions to variation of COD during the study
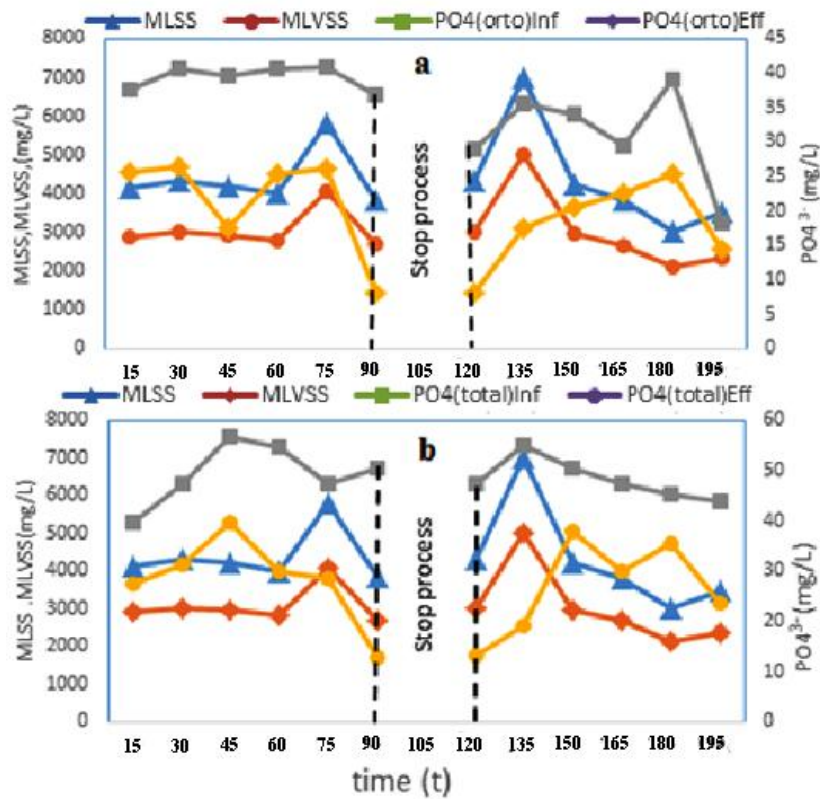
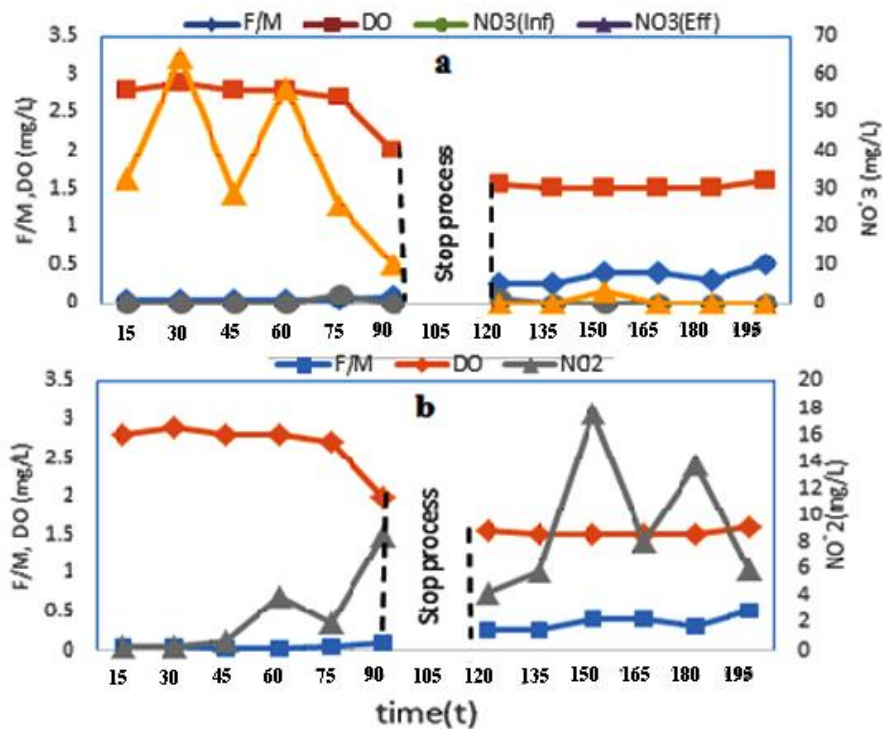**Figure 4:** Variation of a) orto and b) total phosphate ions to variation of MLVSS and MLSS during the study

Figure 5: Variation of a) nitrate and b) nitrite ions to variation of F/M and DO during the study
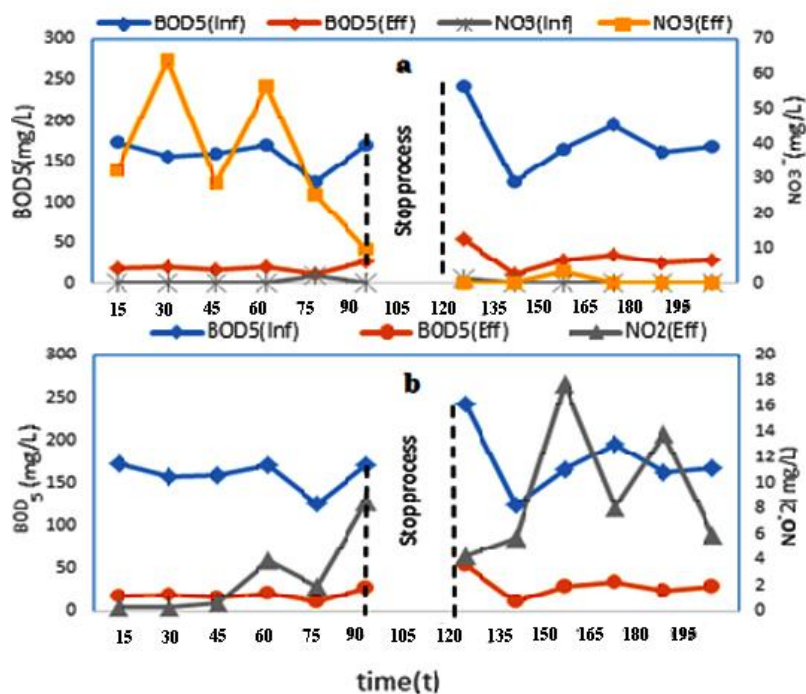

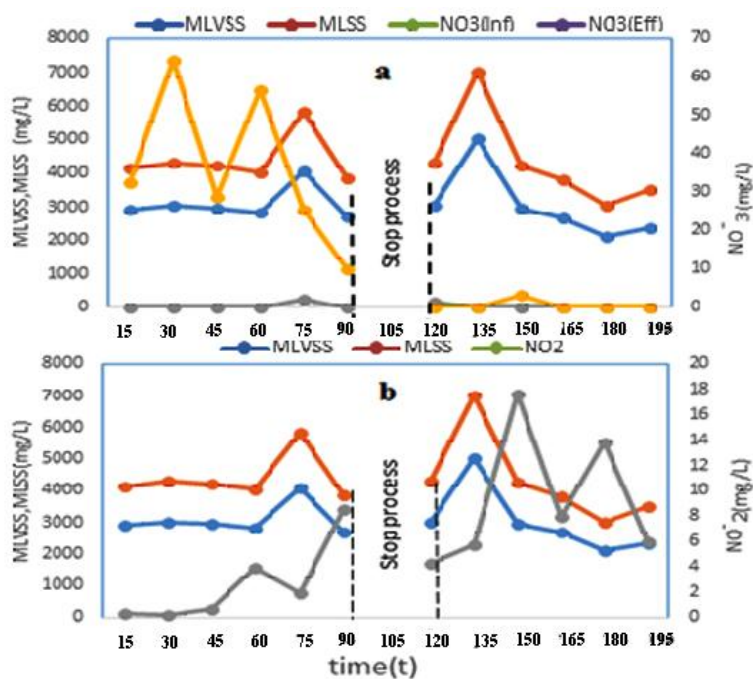**Figure 6:** Variation of a) nitrate and b) nitrite ions to variation of BOD$_5$ during the study

Figure 7: Variation of a) nitrate and b) nitrite ions to variation of MLVSS and MLSS during the study

Since domestic sewage treated wastewater of Kerman is applied for pistachio irrigation and no standard has been ratified for phosphate, nitrate, and nitrite, usage of sewage treated wastewater for pistachio irrigation does not cause any problems. Generally, concentration of total phosphate including orthophosphate, polyphosphate, and organic phosphate depends on the amount of BOD_5 and COD. Variation of BOD_5 and COD is an indicator of organic material of influent and effluent on different days. The amount of elimination of organic phosphate in wastewater relies upon the amount of the efficiency of purification. According to Fig. 1a, it can be noted that the amount of variation of effluent orthophosphate is in harmony with the amount of variation of effluent BOD5. However, the amount of variation of concentration of effluent orthophosphate declinedon day 90 and day 120. The related reason to this issue is the growth of amount of effluent BOD_5as well as the reduction of efficiency of biological treatment of wastewater which leads to the reduction of elimination of orthophosphate as illustrated in Fig. 1. Moreover, the Fig. 1b demonstrated that the variation of effluent BOD_5 was consistent with the variation of effluent total phosphate after the time that the process stopped. During this time, the concentration of total phosphate dramatically reduced which was an indication of low efficiency of purification as presented in Fig. 2.

As indicated in Fig. 3a, the variation of effluent orthophosphate is in harmony with the variation of COD, which is the required oxygen level for chemical oxidation of organic materials in wastewater. It occurred prior to the time the processceased when, with growth of effluent COD, the concentration of effluent orthophosphate ion dramatically reduced. The variation of total phosphate in Fig. 3b is consistent with the variation of influent COD and phosphate prior to the time process discontinued and concentration of total phosphate increased after this time. However, reduction of effluent COD as well as dramatic reduction of influent total phosphate led up to the reduction of concentration of effluent phosphate on the 195 day.

According to Fig. 4a, the amount of MLSS that involves living and non-living microbial population and Non-biodegradable organic materials and the amount of MLVSS that is the organic part of MLSS containing Non-biological organic materials, including live and dead organisms and cellular waste products,increased on day 75 and day 135. This indicates that the high amount of organic materials

found in the wastewater system led to an increase in the output of orthophosphate. In the 90 and 120 day the concentration reduction of MLSS and MLVSS was ensued by reduction of output orthophosphate.Furthermore, the concentration of input orthophosphate had a significant effect on variation of amount of MLSS MLVSS prior and after the time that process stopped. It should be noted that the variation of MLSS MLVSS did not have any relationship with concentrationvariation of output orthophosphate. The variation of output total phosphate is not in harmony with the reduction of MSLL MSLVSS (Fig. 4b) and the reason for this increasing change is the increase in the concentration of influent total phosphate. Reduction of MLSS MLVSS led up to the drastic reduction of the amount of effluent total phosphate (the lowest level) on day 90 and day 120. However, the suddenincrease in MSLL MSLVSS caused anincrease in the amount of total phosphate on day 135.

In Fig. 5 the changes of food to microorganismsoccurred from 0.04 to 0.09 prior to stop time. Nevertheless, after the time process discontinued, this ratio (F/M) increased due to the reduced size of aerated ponds. Consequently, thisincrease played anessential role in reducing the sludge age. Conversely, after the process stopped, the amount of DO declinedin comparisonto the earlier results, before the stop process occurred, leading to the creation of the anaerobic system and a sharp rise in nitrite concentration.

As shown in Fig.5a, the denitrification process performed wellas a result of the high amount of DO prior to the time of stop process. Additionally,the changes of nitrate concentration were consistent with DO changes. On day 90, reduction of nitrate concentration followed the reduction of DO. After stop time process, itwas observed that with the reduction of DO and the rising of F/M, the amount of nitrate concentration diminished considerably,except on day 150, when the amount of nitrate was zero.On other days,this occurrence was an indication of stop process of denitrification. This operation occurred due to the high concentration of denitrification bacteria. Moreover, the curve of changes of nitrate to changes of BOD_5 (Fig. 6a) demonstrated that the amount of BOD_5 output, that is, the amount of the elimination of organic materials of wastewater or efficiency of biological purification, prior to stop process, wassuperior than it was subsequent to stop process. As a result of this phenomenon, the denitrification procedure performed outstandingly well, prior to the time of stop process.

Given the concentrationvariation of nitrate to MLSS and MLVSS (Fig. 7a), the amount of MLVSS changes, which was an indication of the activities of microorganism in purification system, was in harmony with denitrification or concentration of nitrate prior to time of stop process. After this time, due to reduction of DO, increasing F/M and consequently reduction of sludge age, and reduction in amount of MLSS MLVSS could be observedleading up to the halting of the denitrification process.

Fig. 6b and S2 presented the changes of nitrite to changes of BOD_5 and COD. It can be said that that variation of nitrite ion was inconsistent with the changes of effluent BOD_5. That is, the sharp rise of BOD_5 and COD was representative ofthe poor performance of the biological purification system.

The low amount of MLVSS and DO caused growth of denitrification bacteria in anaerobic conditionswhich increased nitrite concentration. In the period after stop process, due to reduction of MLVSS and DO, the increasing amount of COD and effluent BOD_5, that is reduction of efficiency of biological purification was observed. During this anaerobic condition, due to denitrification, nitrite concentration rise sharplyin comparisonto the prior results of stop process. In the period before the process stopped, the temperature varied from 19 to 23 centigrade. However, after the process stopped, with seasonal changes and the onset ofwarm weather, the temperature changed from 23 to 34. The best pH for growth of microorganisms was 6-8. Therefore, it was selected between 7.30 and 7.90 for the present study.

According to Fig. S3 in supplementary content, the percentage of elimination of phosphate had an acceptable average because wastewater treatement system of Kerman had active sludge and elimination of phosphate was 30%. Since the elimination of phosphate was above 30% in sampling time, biological elimination of this component performed well in Kerman. Due to drastic reduction of orthophosphate and effluent total phosphate, the percentage of elimination of phosphate increased substantially due to the installation of valves in aerated ponds.

As illustrated in Fig. S4 in supplementary content, the percentage of elimination of COD and BODs was acceptable while analyzing.

Experimental

Apparatus:

A Metrohm 827 pH/Ion Meter was used for pH measurements[19]. An IEC-model HN-S centrifuge [20] was used to accelerate phase separation.

Reagents and solutions:

Potassium dihydrogen phosphate, potassium hydroxide,potassium nitrate, antimony potassium tartrate and ammonium hydroxide were purchased from Sigma-Aldrich.Ammonium molybdate sulfanilamide, Nitric acid, Ethylenediaminetetraacetic acid (EDTA), Na$_2$EDTA, N-(1-naphthyl)1-naphthylethylenediaminediacetichydrochloride, sodium nitrite, sulfuric acid, ascorbic acid and phenoldisulphonic acid were purchased from Merck (Darmstadt, Germany).

Sampling and stop in sampling:

The sampling was carried out twice in month for 6 months from winter to summer. Due to installation of valves in the aeration pools, aeration wasconducted inthe duration of two weeksin an effort to decrease the size of pools. Given the design of the wastewater treatment plant that was appropriate for a debit of 180 liter per second, one aeration pool was required due to the low input debit of 100 liters per second. In light of input debit, activated sludge age was increased (10 days) as a result of the reduction of food to microorganism in that organisms did not have sufficient food for growth and proliferation. The installation of this valve contributed to thereduction of sludge age and efficiency of refinery.

The effective parameters on the amounts of nitrate, nitrite and phosphate ions were investigated and brought in Table 1.

NO_3^- measurement method:

About 5 mL of thesample solution was poured into a beaker, and then pH was adjusted to 7. If the chloride ions were above the standard level, they were separated in the form of chloride silver from the solution through centrifuging or percolating. 2 mL phenoldisulphonic acid was poured into a dried sample, and then it was mixed until it could be dissolved. 20 mL distilled water was added for further dilution. 5 mL of potassium hydroxide was added for maximum color.Ifthere were any suspense particles in the solution, it was solved through adding EDTA or potassium hydroxide; then the sample was percolated and watered in a 500 mLflask. If the intensity of yellow color was not within the range of standard, the 100 mL flaskwould be applied. The nitrate

concentration was measured by UV-Vis spectrophotometer at 410 nm.

NO_2^- *measurement method:*

Diazotization method was employed to measure nitrite. In this method, sulfanilamide and N-(1-naphtyle)-ethylene diamine dioxide hydrochloride was applied. In acidic condition, nitrate ions was transformed into

nitroacid and interacted with amine in sulfanilamide and produced diazonium salt that interacted with N-(1-naphtyle)-ethylene diamine dioxide hydrochloride whichresulted in areddish solution, demonstrating a direct relationship with the amount of nitrate. For the reduction of transformation of NO_2^- to NO_3^- or NH_3, solutionwas stored at 4°C. The nitrate concentration was measured by UV-Vis spectrophotometer.

PO_4^{3-} *measurement method:*

20 mL the percolated sample was poured into beaker. The solution pH was adjusted to 7. The sample was transferred into 500 mL volumetric flask, and then 4 mL reagent was added and delivered the volume of solution. The blue color was an indication of the existence of phosphorous. Moreover, 4 mL reagent was added to standard and blank solutions. After 15 minutes, the phosphate concentration was measured by UV-Vis spectrophotometer at 410 nm.

Total phosphor measurement method:

To measure the total phosphor, all the phosphates in the sample was altered to orthophosphate through digestion method. For digestion, 1 mL sulfuric acid and 5 mL nitric acid were added to 20 mL sample solution. The sample was heated until the volume decreased to 2 mL. After cooling the solution, 20 mL distilled water and phenolphthalein was added to residue solution and pH was adjusted to 7. The sample was transferred to a 100 mL volumetric flask and delivered the solution volume. At last, phosphor was determined by orthophosphate measured.

References

[1]Chafari, S.; Hassau, M.; Aroua, M. K. *Bioresour. Technol.* **2008** , *99*, 3965-3474

[2] Feleke, Z.; Sakakibara, Y. A. *Water Res.* **2002**, *36*, 3092-3102

[3] Fernandez, N. Y,; Maranon, E.; Sonns, J.; castrillon, L.; *Bio. Res. Technol.* **2008**, *99*, 7976-7981.

[4] Shen, J.: He, R.: Han, w.; Sun, X.; Li. J.; wang, L. *J. Hazard. Mater.* **2009**, *17*, 2545-600

[5] Showers, J. W.; Genna, B.; McDade, T.; Bolich, R.; Fountain, J.C. *Environ. Sci. Technol.* **2008**, *42*, 4683-4688.

[6]Gray, N. F.; Drinking water Quality: problems and solutions. John Wiley and sons, Inc., chichester, **1994**

[7] Shrimali, M.; Singh, K, P. *Environ. Pollut.* **2001**, *11*, 2351-359.

[8]Gupta, S. K.; Gupta, A. B.; Gupta, R. C.; Seth , A.K.; Bassain, J. K.; Gupta, A. *Environ. Health perspect.* **2000**,*10*, 8363-365

[9] Nair, R. R.; Dhamole, P. B.; Lele, S. S.; Souza, S. F. D. *Chemosphere* **2007**, *67*, 1612

[10] Jia, Y. H.; Tran, H. T.; Kim, D. H.; Oh, S,J.: Park, D. H.; Zhang, R. H.; Ahn, D. H. *fule. cells. Biol. Bios. Eng.* **2008**, *31*, 315-321

[11]Park, J.; Byun, H.; Choi, w.; Kang, W.; *waste watger. Chemosphere*. **2008**, *70*, 1429-1437.

[12] Choi, J.; Batchelor, B.; *Chemophere*, **2008**, *70*, 1108-1116

[13] Feng, M.; Li, C.; Zhang, Z.; Shen, Z.; Sagiura, N.; *Electrochem. Commun.* **2009**, *11*, 1853-1856

[14] Reyter, D,; Belanger, D.; Roue, L. *water Res,* **2010**,*44*, 1918-1926

[15] Badea, G. E. *Electrochim. Acta.* **2009**, *54*, 996-1001

[16] Feng, M.; Li, C.; Zhang, Z.; Yang, S. *Bioresour. Technol.* **2010**, *101*, 6553-6557

[17] Katsounarso, I.; Ipsakis, D.; Polatides, C.; Kyriacou, G. *Electrochim. Acta.* **2006**, *52*, 1324-1338

[18] Bowden, L. I.; Jarvis, A. P.; Younger, P.L.; Johnson, K. T. *Environ. Sci. Technol*, **2009**, *43(7)*, 2476-2481.