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OLIVE OIL MILL WASTEWATER AS CARBON SOURCE IN POST ANOXIC DENITRIFICATION

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ABSTRACT

A study was undertaken to evaluate the efficiency of applying olive oil mill wastewater as a non-nitrogenous external carbon source in the second anoxic stage of a five stage modified Bardenpho system for nutrients removal in order to assure consistently very low concentrations of total nitrogen (well below 3 mg/l) in the treated effluent. Addition of olive oil mill wastewater was found acceptable only up to 50 mg sCOD of mill waste/l of wastewater fed to the system because at higher additions color problems in the treated effluent were encountered. The required dosage of olive oil mill wastewater was found to be in the range 4.6-5.4 mg sCOD/mg N-NO_3 removed. Operation with olive oil mill wastewater effects at the same time higher removal of phosphorus. Addition of physicochemically pretreated olive oil mill wastewater with lime to the second anoxic tank at a rate of 22-45 mg sCOD/l of municipal type wastewater fed (ratio of volume of the mill waste added to the volume of the municipal type wastewater fed 1:1000-1:2000) resulted in a treated effluent with total nitrogen below 3 mg/l and soluble phosphorus well below 1 mg/l. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Denitrification; modified Bardenpho process; nitrogen and phosphorus removal; non-nitrogenous carbon sources; olive oil mill wastewater; post anoxic denitrification.

INTRODUCTION

Olive oil mills are small agro-industrial units which process olives for the extraction of olive oil. A flow diagram for classic and centrifugal olive oil mills is given in Figure 1. The mean total wastewater from classic mills is about 1.2 m^3/1000 kg of olives processed and its organic load is about 80 kg COD/1000 kg of olives processed. The same characteristics for the mean total wastewater from centrifugal mills are about 1.7 m^3/1000 kg olives and 120 kg COD/1000 kg olives respectively (Tsonis *et al.*, 1989). The majority of mills are of the centrifugal type. The main waste stream in centrifugal mills originates from the olives kernel separation step (1st centrifuge) and has the following mean characteristics: volume 0.95 m^3/Mg of olives processed, SS 28.5 g/l, COD 118 g/l, sCOD 67 g/l, BOD_5 52 g/l, $sBOD_5$ 33 g/l, TKN 1150 mg/l, sTKN 480 mg/l, Total-P 210 mg/l and sTotal-P 200 mg/l (Tsonis, 1988). The annual volume of the wastewater expected from very large size centrifugal mills is in the range 4000-8000 m^3/yr.

The organic content of the mill waste with high concentrations of soluble, colloidal and suspended matter makes conventional anaerobic digestion the first choice for biological treatment. Olive oil mill waste is well suited for low loading anaerobic treatment (Tsonis and Grigoropoulos, 1993) and could also be effectively treated in conventional aerobic systems after an appropriate high dilution (Tsonis and Grigoropoulos, 1989). Combined treatment of the mill waste with sewage is effective but as the organic load of the mill waste is very high only a correspondingly quite low ratio of waste volume is permissible in municipal wastewater treatment works without operational problems. The main problem of combined treatment of olive oil mill wastewater with sewage is the very low removal of color and the colored appearance of the treated effluent. In order to obtain permissible color values in the treated effluent, quite high ratios of the volume of the sewage to the volume of the mill wastewater fed to the aerobic treatment units must be secured (usually over 1000:1, depending on the strength of the mill waste).

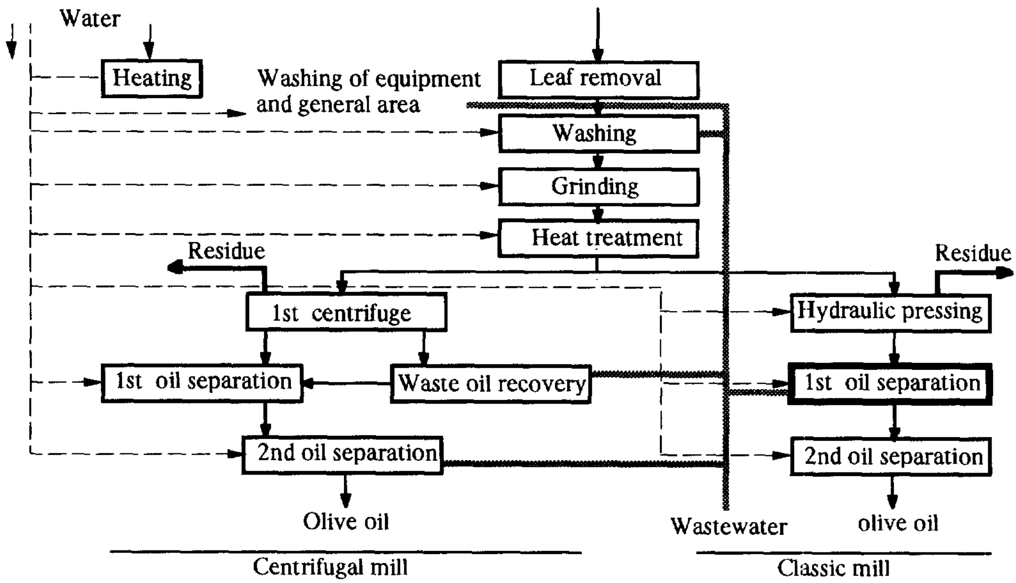


Figure 1. Flow diagram for classic and centrifugal olive oil mills.

Appropriate physicochemical pretreatment of olive oil mill wastewater with lime results in complete removal of SS and phosphorus and the mean COD/TKN ratio in the treated effluent is 100:0.8 (Tsonis *et al.*, 1989). The very low concentration of TKN and phosphorus and the very high organics content of physicochemically pretreated olive oil mill wastewater makes it attractive as a carbon source in denitrification processes. Denitrifying bacteria can utilize a wide spectrum of substances as energy sources. Among the organic materials, the interest is particularly linked to the organics in wastewater and sludge (internal energy sources). Among the external carbon and energy sources, methanol, acetic acid, wastewater from breweries and organic matter in wastewater have been extensively used in practice. Other reductants used in denitrification experiments are acetone, glucose, methane, cherry juice, molasses, olive oil, etc. (Henze *et al.*, 1995).

In the combined (or single) sludge type plants, designed for nitrogen removal the sludge which performs the nitrification in the aerobic stage recycles through the denitrification stages (pre-denitrification stage and/or post denitrification stage) where it participates in the conversion of the nitrate nitrogen to nitrogen gas. Combined (or single) sludge system means that each train contains only one secondary clarifier and settled biomass must recycle through all zones. The organic matter for the pre-denitrification stage is the organic matter contained in the sewage to be treated, whereas the organic matter for the post denitrification step comes from the degradation processes in the sludge, which means that this step is slow or less effective. The five stage modified Bardenpho process consists of a series of five tanks (anaerobic, 1st anoxic, 1st aerobic, 2nd anoxic and 2nd aerobic) (Randall *et al.*, 1992). In the anaerobic zone the influent organics create conditions for phosphorus release. The second anoxic zone provides additional denitrification, using nitrate produced in the first aerobic stage as the electron acceptor and endogenous organic carbon as the electron donor. The final aeration stage converts ammonia residual concentration to nitrate and minimizes phosphorus release in the final clarifier by increasing the dissolved oxygen concentration. Addition of an appropriate carbon source in the post denitrification stage (Fig. 2) may result in a faster and more effective conversion of nitrates to nitrogen gas. The nitrogen content of the carbon source to be added in the post denitrification zone must be quite low because otherwise elevated nitrogen concentrations will appear in the treated effluent.

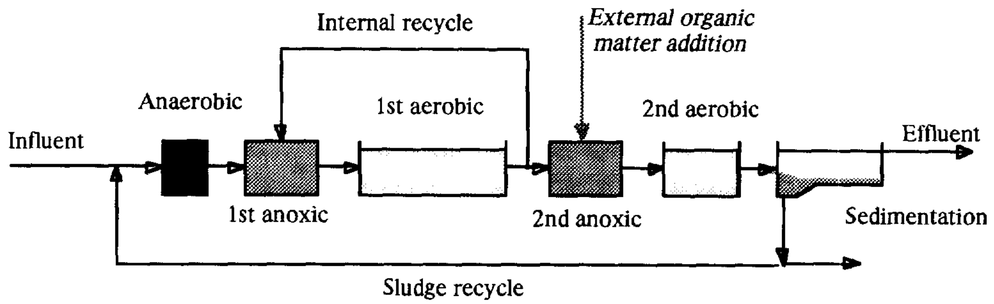


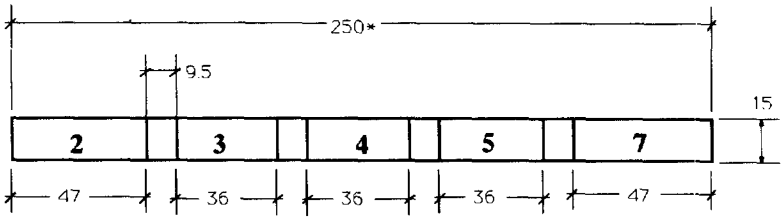
Figure 2. Five stage modified Bardenpho biological nutrients removal system with external organic matter addition in the 2nd anoxic stage.

In the literature pertaining to denitrification, the use of methanol, acetate and molasses as non-nitrogenous carbon sources is described. For large scale plants the use of such substrates incurs a heavy cost where no other nitrogen-free wastes or by-products happen to be available. The purpose of this paper is to examine the possibility of using olive oil mill wastewater in treatment plants where very low levels of nitrogen and phosphorus in the treated effluent are obligatory.

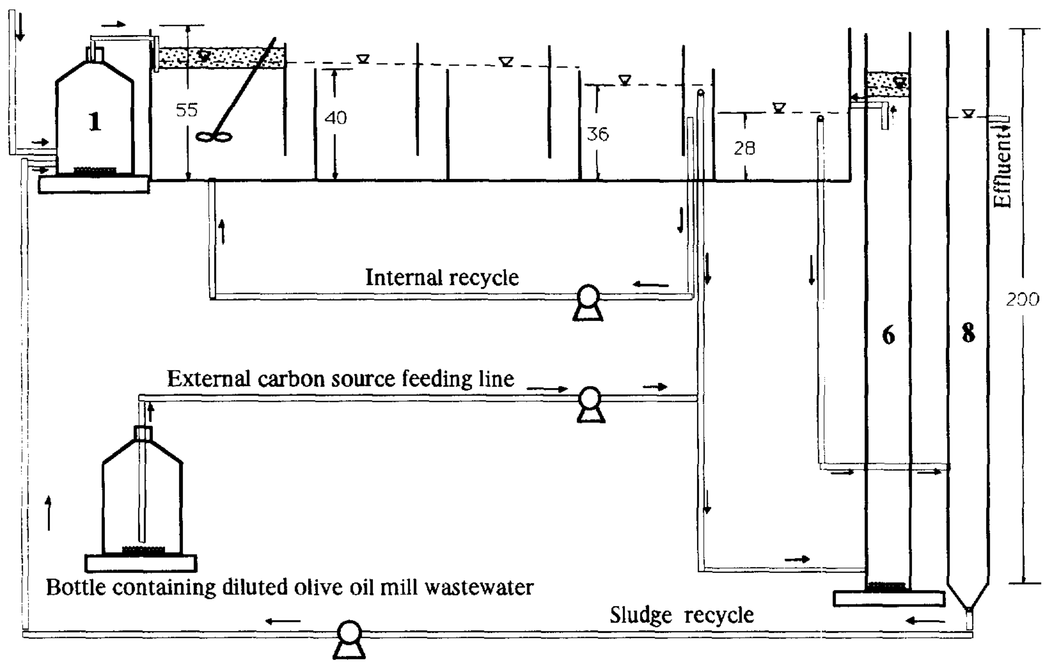
MATERIAL AND METHODS

A pilot scale five stage modified Bardenpho type system was used in this study (Fig. 3). The anaerobic tank was a 20 l glass bottle which was agitated with a variable speed heavy duty magnetic stirrer. The first anoxic tank was the first partition of a baffled Plexiglas tank and its effective volume was 33.5 l. The surface of this tank was covered with a multiple layer of hollow polypropylene balls (diameter of each ball 10 mm) in order to avoid entrainment of atmospheric oxygen. This anoxic tank was agitated with a variable speed bench type laboratory mixer. The 1st aerobic stage corresponded to the next three partitions of the baffled Plexiglas tank (zones 3, 4 and 5, Fig. 3). The volumes of these partitions were 26.2, 24.7 and 23.6 l correspondingly. The total effective volume of the first aerobic stage was 74.5 l. The second anoxic tank was a Plexiglas tube (ID 14.2 cm). The closed bottom end of this tube was supported on the top plate of a heavy duty variable speed magnetic stirrer and mixing of the anoxic tank content was effected via a magnetic bar (bar length 135 mm and diameter 27 mm). The effective volume of the second anoxic stage was 25.0 l and a multiple layer of floating hollow polypropylene balls (diameter of each ball 10 mm) was placed on the liquid surface in order to secure anoxic conditions. The second aerobic tank was the final section of the long narrow Plexiglas tank and its effective volume was 19.7 l. The sedimentation tank was a Plexiglas tube (ID 14.2 cm) and the working liquid volume in this tank was 25.3 l. The relative effective volumes of the anaerobic, 1st anoxic, 1st aerobic, 2nd anoxic and 2nd aerobic stages were 13.2%, 19.0%, 42.4%, 14.2% and 11.2% (total volume for all these stages 100%).

The municipal type wastewater fed, was prepared from the effluent of a long narrow anaerobic tank fed with raw sewage in the wastewater treatment plant of the Patras University Campus. The anaerobic tank achieved 25-35% organic matter removal in terms of sCOD. This anaerobic effluent was augmented with organic matter and nutrients by addition in each feeding barrel (205 l) of 25 g commercial sugar, 25 g wheat flour, 5g totally soluble monammonium phosphate crystalline (N 12%, P_2O_5 61%) and 5 g urea (N 46.3%). The characteristics of the wastewater fed to the experimental unit used in this study were the following: COD (mg/l) mean 407 and range 388-439, sCOD (mg/l) mean 248 and range 216-265, TKN (mg/l) mean 34.8 and range 32.2-37.5, sTKN (mg/l) mean 30.8 and range 29.1-33.0, Total-P (mg/l) mean 11.8 and range 9.8-14.1 and sTotal-P (mg/l) mean 10.1 and range 9.2-13.1.



a. View from the top of the baffled long narrow Plexiglas tank



b. Schematic flow diagram of the experimental unit

1. Anaerobic stage
2. 1st anoxic stage
3. 1st zone of the 1st aerobic stage
4. 2nd zone of the 1st aerobic stage
5. 3rd zone of the 1st aerobic stage
6. 2nd anoxic stage
7. 2nd aerobic stage
8. Sedimentation tank

* All dimensions are given in cm

Figure 3. The experimental setup used in this study.

The olive oil mill wastewater used, was taken from the 1st centrifugation waste stream of a centrifugal mill in the Patras area. The characteristics of this mill waste {raw (waste A), after physicochemical treatment with lime (waste B) and acidified physicochemically pretreated mill waste (over a period of 5 months) (waste C)} were the following:

Type of mill waste	Concentration, mg/l							
	COD	sCOD	TOC	sTOC	TKN	sTKN	total-P	s total-P
A (raw)	118000	83700	44800	37400	1100	790	240	135
B (pretreated)	68200	65800	24300	22600	720	640	42	31
C (acidified pretreated)	46000	44700	12700	12100	480	390	28	27

All analytical determinations were made according to the procedures outlined in the Standard Methods for the examination of water and wastewater (APHA, 1992). TOC was measured with a Rosenmount, Dohrmann DC-190 Total Organic Carbon Analyser, nitrate nitrogen was determined by the Cadmium Reduction Method and by the Nitrate Electrode Method {a Hach One Laboratory pH/ISE Meter was used with a nitrate electrode from Hach (Catalog Number 44430-21)}, ammonia nitrogen was determined by the Titrimetric Method on samples that have been carried through preliminary distillation, by the Phanate Method and by the Ammonia-Selective Electrode Method (an Orion ammonia electrode Model No. 95-12 was used).

EXPERIMENTAL STUDY AND RESULTS

The experimental unit was initially operated for a period of 5 months as a modified 5 stage Bardenpho system and the influence of various operational parameters on system performance was investigated. In this initial period the system operated without addition of external carbon source. After that the experimental setup was used to investigate the effectiveness of post anoxic denitrification by adding small proportions of olive oil mill wastewater directly to the second anoxic stage. The permissible volumes of olive oil mill wastewater added were selected to be less than 1 ml/l of municipal type wastewater fed (dilution over 1000) in order to avoid color problems in the treated effluent.

In the present paper the operation of the experimental setup in four different study periods is given. The duration of each study period was 15-20 d. In the first period the experimental setup was operated without addition of olive oil mill wastewater. In the second period 0.5 ml of acidified mill waste were added per liter of municipal type wastewater, in the third period the addition of the acidified mill waste was increased to 1 ml/l and finally in the fourth study period 0.5 ml of physicochemically pretreated mill wastewater (which has not undergone acidogenesis) were added per liter of municipal type wastewater. In all study periods the sludge recycle from the sedimentation tank to the anaerobic stage was kept in the range 7-8 l/h. Addition of mill waste to the second anoxic tank was made after appropriate dilution with tap water at a rate of 500-600 ml/h. Feeding of the influent as well as the internal nitrate recycle and the sludge recycle from the sedimentation tank were accomplished by appropriate variable speed peristaltic pumps.

The operational parameters for the experimental system in the four different study periods are given in Table 1. The values given for each study period are mean values. The mean values for sCOD, sTotal-P, nitrate nitrogen and ammonia nitrogen in the anaerobic , 1st anoxic, 1st aerobic (3rd zone) and 2nd anoxic stages and in the treated effluent, for each of the four different study periods, are given diagramatically in Fig. 4.

Table 1. Mean values of the operational parameters during each of the four experimental periods

Parameter	Waste line or position in flow diagram 1								
	Influent	1	2	3	4	5	6	7	Effluent
1st period of operation (without olive oil mill wastewater addition)									
Wastewater fed, l/h	11.2								
Internal recycle, l/h			22.6						
sCOD, mg/l	238	58.3	34.1	29.1	24.3	23.2	24.1	22.1	20.9
sTOC, mg/l	82.5	23.5	14.2	13.2	11.2	10.8	10.4	10.5	10.1
MLSS, g/l		2.12	4.82	4.65	4.28	5.12	4.32	3.35	
MLVSS, g/l		1.48	3.32	3.22	2.91	3.47	2.88	2.27	
sTotal-P, mg/l	10.7	13.6	4.2	1.9	1.8	1.6	1.6	1.4	1.4
sTKN, mg/l	32.6	20.2	10.1	8.4	4.6				1.2
Nitrate nitrogen, mg N/l			0.12	2.6	4.9	8.9	4.4	5.2	5.3
Ammonia nitrogen, mg N/l	28.0	18.2	8.8	7.1	3.6	0.94	1.2	0.16	0.38
2nd period of operation {addition of 0.5 ml acidified mill waste (waste C)/l of municipal type wastewater fed}									
Wastewater fed, l/h	10.9								
Internal recycle, l/h			21.8						
sCOD, mg/l	244	63.3	36.1	35.1	34.0	32.8	36.1	33.6	30.6
sTOC, mg/l	86	24.5	15.3	15.2	14.7	14.0	15.7	14.5	14.0
MLSS, g/l		1.93	4.67	4.97	4.13	4.96	4.02	3.96	
MLVSS, g/l		1.35	3.18	3.43	2.99	3.42	2.70	2.74	
sTotal-P, mg/l	11	15.7	4.7	2.3	1.6	0.92	2.4	0.38	0.23
sTKN, mg/l	33.2	24.4	10.8	7.1	2.8				1.1
Nitrate nitrogen, mg N/l			0.15	2.7	5.7	9.4	1.92	2.8	2.7
Ammonia nitrogen, mg N/l	28.6	19.8	9.6	5.8	1.9	0.23	0.76	0.16	0.22
3rd period of operation {addition of 1 ml acidified mill waste (waste C)/l of municipal type wastewater fed}									
Wastewater fed, l/h	11.4								
Internal recycle, l/h			22.5						
sCOD, mg/l	231.2	70.3	52.4	42.1	39.1	36.8	53.2	49.1	44.2
sTOC, mg/l	78.1	26.2	20.8	15.5	15.1	14.7	18.3	18.0	17.8
MLSS, g/l		2.02	5.12	4.53	3.98	5.34	4.48	3.65	
MLVSS, g/l		1.42	3.54	3.12	2.74	3.56	2.96	2.55	
sTotal-P, mg/l	10.1	17.1	5.2	1.1	0.54	0.32	3.1	0.54	0.36
sTKN, mg/l	31.8	21.7	10.4	7.9	3.5				1.0
Nitrate nitrogen, mg N/l			0.36	3.3	6.7	9.5	0.16	0.59	0.65
Ammonia nitrogen, mg N/l	29.3	19.6	8.7	6.1	2..3	0.38	0.57	0.24	0.32
4th period of operation {addition of 0.5 ml raw mill waste (waste B)/l of municipal type wastewater fed}									
Wastewater fed, l/h	10.8								
Internal recycle, l/h			21.3						
sCOD, mg/l	245.7	74.3	56.2	47.1	40.2	34.4	43.0	42.8	42.1
sTOC, mg/l	83.2	25.4	22.7	19.3	16.2	14.1	16.1	15.9	15.4
MLSS, g/l		1.82	4.94	4.59	4.62	4.88	4.15	4.20	
MLVSS, g/l		1.26	3.42	3.26	3.12	3.41	2.74	2.91	
sTotal-P, mg/l	12.1	19.1	5.6	0.65	0.54	0.32	2.5	0.21	0.15
sTKN, mg/l	34.7	22.4	10.8	6.9	3.7				1.2
Nitrate nitrogen, mg N/l			0.23	2.8	5.9	9.2	0.24	0.65	0.64
Ammonia nitrogen, mg N/l	29.4	19.1	9.1	5.3	2.4	0.17	0.60	0.32	0.37

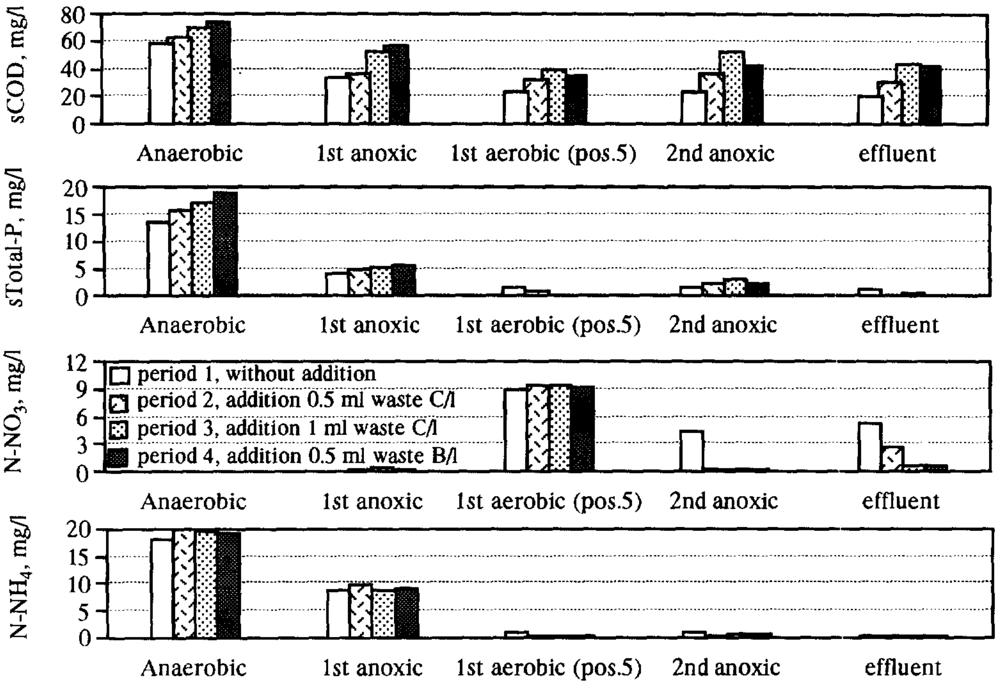


Figure 4. Organic matter and nutrients profiles in the four study periods.

DISCUSSION

The wastewater was fed to the experimental system in the four different periods with mean rates 10.8-11.4 l/h, the sludge recycle was 7-8 l/h (65-70%) and the mean internal recycle was 21.3-21.6 l/h (190-200%). The mean hydraulic retention time in the first aerobic stage was 6.5-6.8 h and the liquid temperature was in the range 24-26.5°C (the experimental setup was installed inside an air conditioned room). With the above set of experimental conditions the system effected complete nitrification in the final zone of the 1st aerobic stage (pos. 5), as shown by the mean concentrations for nitrate nitrogen (8.9-9.4 mg/l) and the quite low concentration of ammonia nitrogen (0.17-0.94 mg/l) (Table 1 and Fig. 4). Complete nitrification in the final zone of the 1st aerobic stage was very important in order to compare the denitrification effectiveness of the added organic matter with the olive oil mill wastewater in relation to the denitrification degree achieved by the biomass degradation products in the 2nd anoxic stage.

Mass balances around the second anoxic tank, with the data given in Table 1, for sCOD, sTOC and $N\text{-}NO_3$ concentrations result in approximate estimates for the organic matter of the mill wastewater used in the denitrification process. sCOD of the mill wastewater added was 4.7, 5.4 and 4.6 mg/mg $N\text{-}NO_3$ removed in the study periods 2, 3 and 4 respectively and the corresponding values for sTOC were 1.2, 1.4 and 1.7 mg/mg $N\text{-}NO_3$ removed. The $N\text{-}NO_3$ removal, when the system operated without olive oil mill wastewater addition, was considered due to endogenous biomass degradation in all the study periods. The mean sCOD value in the treated effluent without olive oil mill wastewater addition was 20.9 mg/l and was increased in the range 30.6-44.2 mg/l after the addition of the mill waste.

As it can be seen from the data given in Table 1 and Fig. 4 a limited phosphorus release was observed in the 2nd anoxic stage in the periods 2,3 and 4 when addition of olive oil mill wastewater was made. On the contrary the concentration of phosphorus in the treated effluent was below the value achieved without mill wastewater addition. Also the results for the concentration of soluble phosphorus in the anaerobic tank show that an elevated phosphorus release was obtained when mill waste was added. The above findings show that addition of olive oil mill wastewater had also beneficial effects on phosphorus removal.

It must be emphasized here that addition of olive oil mill wastewater in post denitrification processes must be kept as low as possible because of the color problems encountered in the treated effluent. Additions of olive oil mill wastewater greater than 1:1000 of the volume of the wastewater fed seem to be impractical when the color of the treated effluent is of high concern. That is why the most probable application of olive oil mill wastewater for denitrification may be in connection with the modified Bardenpho nutrients removal concept, in order to secure concentrations of total nitrogen in the treated effluent well below 3 mg/l.

CONCLUSIONS

Based on the findings of an experimental work for investigation of the effectiveness of olive oil mill wastewater addition as a non-nitrogenous carbon source in the second anoxic stage of a modified Bardenpho system for nutrients removal, the following conclusions may be drawn.

1. The required organic matter addition is in the range 4.6-5.4 mg/mg $N\text{-}NO_3$ removed in terms sCOD and 1.2-1.7 mg/mg $N\text{-}NO_3$ removed in terms of sTOC.

2. Additions of the olive oil mill wastewater corresponding to higher than 50 mg sCOD/l of wastewater fed, result in unacceptable color values in the treated effluent.

3. The addition of olive oil mill wastewater has beneficial effects on phosphorus removal

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