Pergamon

Wat. Sci. Tech. Vol. 40, No. 4–5, pp. 321–329, 1999

0273–1223/99 $20.00 + 0.00

PII: S0273-1223(99)00514-4

BIOLOGICAL PHOSPHORUS REMOVAL USING A BIOFILM MEMBRANE REACTOR: OPERATION AT HIGH ORGANIC LOADING RATES

Pedro A. Castillo*, Simón González-Martínez** and Iñaki Tejero*

** University of Cantabria, Department of Water and Environment, School of Civil Engineering, Avda. de los Castros s/n, 39005 Santander, Spain*
*** Institute of Engineering, National University of Mexico, 04510 Mexico D.F., Mexico*

ABSTRACT

This research describes Biological Phosphorus Removal at Organic Loading Rates from 5 to 30 g $COD/m^2 \cdot d$ using a laboratory scale Sequencing Batch Biofilm Membrane Reactor. The reactor was fed with synthetic wastewater based on sodium acetate with a COD:N:P ratio of 20:5:1. An average PO_4-P removal of 72% was observed when the organic load was kept under 15 $gCOD/m^2 \cdot d$. Maximum PO_4-P removal of 85% was associated with a consumption rate of 700 $mgPO_4\text{-}P/m^2 \cdot d$. Increasing with the organic load, the PO_4-P released during the anaerobic phase averages 40% over the influent concentration, showing a maximum value of 107%. Throughout the experiments, overall COD removal rates were above 90%, and the COD uptake during the anaerobic phase ranged between 60 and 80% for organic loading rates under 15 $gCOD/m^2 \cdot d$. Simultaneous nitrification and denitrification took place during the transition from aerobic to anaerobic conditions at the beginning of every cycle. Average transformation rates between 0.6 to 2.0 $gNH_4\text{-}N/m^2 \cdot d$ and 0.3 to 1.2 $gNO_3\text{-}N/m^2 \cdot d$ were observed for organic loading rates under 15 $gCOD/m^2 \cdot d$, corresponding to average NH_4-N removal rates between 50 and 70%. Average effluent NO_3-N ranged between 1.5 and 10.6 mg/l. Phosphorus contents of the biofilm based on dry mass ranged between 4.2 and 5.2%. © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

KEYWORDS

Biofilm; membranes; biological phosphorus removal; nutrient removal; phosphate; sequencing batch reactor.

INTRODUCTION

Biological Phosphorus Removal (BPR) using biofilm reactors is a recent technique that requires the use of Sequencing Batch Reactors (SBR). After filling the reactor with wastewater, turning off and on the air/oxygen supply provides anaerobic and aerobic conditions. After the reaction time, the treated wastewater is drawn. BPR has been successfully achieved, for intermittent and continuous flow, using submerged biofilm reactors (SFBR), biofilters (BF), and fluidized fixed film reactor (FBR), in treating both synthetic and domestic wastewaters (González-Martínez and Wilderer, 1991; Gonçalves and Rogalla, 1992; Gonçalves *et al.*, 1994; Rovatti *et al.*, 1995; Garzón-Zúñiga and González-Martínez 1996; Muñoz-Colunga and González-Martínez, 1996). These authors report average PO_4-P removal rates from 50 to 90% with P-release during the anaerobic phase from 100-300% above the influent concentration and average PO_4-P contents on dry mass basis in the biofilm from 4.3 to 6.1%. They also report that successful BPR is limited to organic loading values under 5 $gCOD/m^2 \cdot d$ for submerged biofilms and to 5 $kgCOD/m^3 \cdot d$ for biofilters.

Tejero *et al.* (1997) showed that biofilm membrane reactors can remove up to 180 $gCOD/m^2 \cdot d$ using flat membranes and 138 $gCOD/m^2 \cdot d$ with tubular membranes. Nitrification rates of 47 $gNH_4/m^2 \cdot d$ were associated with biofilm densities from 80 to 105 kg/m^3. In previous work, using air or pure oxygen during the aerobic phase, membrane reactors were used to achieve phosphorus removal at OLR under 5 $gCOD/m^2 \cdot d$ with 12 hour cycles and anaerobic and aerobic phases of 5 and 7 hours, respectively (Castillo and Tejero, 1998). In this study, it has been established that P-uptake improves when working with pure oxygen during the aerobic phase and that the system performance can be upgraded by allowing shorter anaerobic times and longer aerobic phases within the global cycle duration. Thus, the objective of the present research was to evaluate the ability of the Sequencing Batch Biofilm Membrane Reactor (SBBMR) to accomplish BPR at organic loading rates higher than 5 $gCOD/m^2 \cdot d$ and shorter anaerobic duration.

MATERIALS AND METHODS

The reactor consisted of a plexiglass cylinder of 1.2 liter with biofilm grown on tubular membranes permeable to gases (Accurel™) that served as substratum to the biofilm and as aeration device (without bubble production) at the same time. The tubular membranes were connected with a gas distribution chamber allowing a total biofilm surface of 0.094 m^2 (figure 1). Purging the distribution chamber with N_2 or O_2 provided anaerobic or aerobic conditions. A recirculation pump was used to mix the liquid (17 l/h). In order to measure dissolved oxygen (DO) and temperature a port was provided in the recirculation line. Organic loading rates from 5 to 30 $gCOD/m^2 \cdot d$ were applied adjusting the COD in the influent to 200, 400 and 600 mg/l and combining cycle duration of 12, 8, and 6 hours. The anaerobic phase corresponds to 25% of the total cycle and the rest to aerobic conditions. The reactor was operated under the fill-and-draw procedure (batch) and was fed with synthetic wastewater based on sodium acetate, with a COD:N:P ratio of 20:5:1. During the whole experimentation the wastewater temperature and the pH ranged between 18-28°C and 6.3-7.7, respectively. The nitrogen source was urea and phosphorus was provided with potassium phosphate.

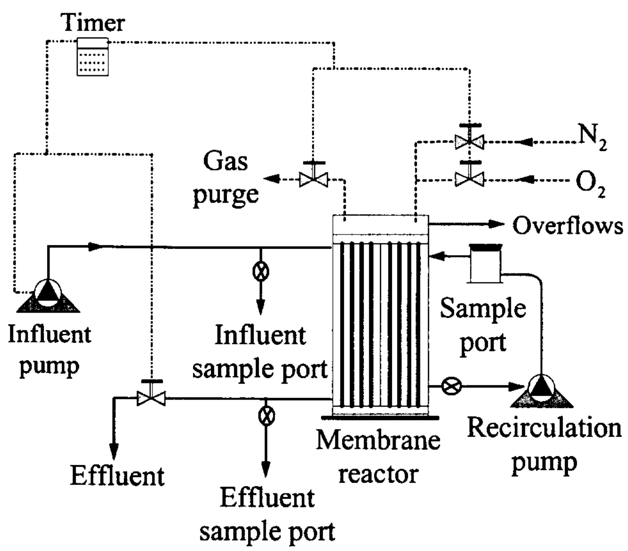

Figure 1. Biofilm membrane reactor.

RESULTS

Overall performance of the reactor. COD. In Table 1 it can be observed that the highest COD removal rates of 97% were achieved with the 12-hour cycles for the highest influent COD values. The runs with the lowest influent COD did not show a defined behaviour but good removal rates. Throughout the experimentation, the COD removal was over 90%. **PO_4-P**. Similarly to COD, the best PO_4-P-removal rates (from 80 to 85%) were achieved with the 12-hour cycles independently of the organic loading rates and of the influent PO_4-P concentration. Maximum PO_4-P removal of 85% is associated with a consumption rate of 700 mg PO_4-P/m^2·d. The highest amounts of PO_4-P released during the anaerobic phase correspond to the 12-hour cycle with the organic load of 12.8 gCOD/m^2·d. The PO_4-P released during the anaerobic phase averages between 8 and 76% over the influent concentration. **Nitrogen**. Average nitrification rates between 0.6-2.0 gNH_4-N/m^2.d and denitrification rates between 0.3-1.2 gNO_3-N were observed for organic loads under 15 gCOD/m^2·d, corresponding to average NH_4-N removal rates between 57 and 74%. Average effluent NO_3-N ranged between 1.5 and 10.6 mg/l. **Biomass-P**. Phosphorus contents on dry mass basis ranged between 4.2 and 5.2%.

Table 1. Summary of operation characteristics and results

Cycle duration h	Influent COD mg/l	Removed COD %	OLR gCOD/m^2·d	Influent PO_4-P mg/l	Released PO_4-P %	Removed PO_4-P %	Influent NH_4-N mg/l	Removed NH_4-N %	Effluent NO_3-N mg/l
12	196	95	4.9	9.8	16	82	51.2	26	1.4
8	195	97	7.3	9.5	42	60	34.3	69	4.0
6	209	96	10.4	9.5	34	67	38.2	74	4.7
12	439	97	10.9	20.1	46	85	96.7	57	8.4
8	400	91	14.9	20.1	22	67	83.2	57	3.4
6	345	90	17.2	19.5	20	13	81.2	28	2.3
12	515	97	12.8	29.0	76	80	117.0	70	3.9
8	607	94	22.7	29.6	08	10	119.8	19	1.6
6	602	91	30.0	29.8	09	4	119.8	9	0.6

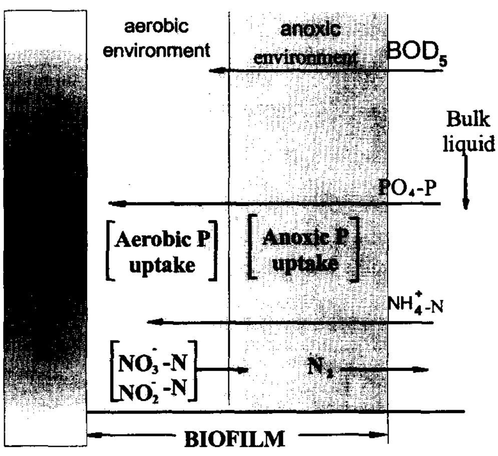

Figure 2. Behaviour of the biofilm at the beginning of anaerobic conditions.

Influence of oxygen in the system. At the beginning of every cycle the reactor was filled with fresh wastewater and, inside the membranes, oxygen was washed out with nitrogen in order to produce anaerobic conditions in the system. When the cycle begins, the biofilm is penetrated by oxygen from the previous cycle, thus, limited amounts of phosphate are consumed as long as oxygen and nitrates are present (see

Figure 2). The microorganisms require several minutes to consume the rest of the dissolved oxygen and to reduce nitrates to molecular nitrogen (denitrification). During this time phosphate was not released and aerobic COD-removal took place.

Figure 3 shows that during the first half-hour, due to aerobic/anoxic conditions phosphate was not released and, during the second half-hour, the microorganisms switched metabolism to anaerobic causing COD not to change significantly (USEPA, 1987; Wentzel *et al.*, 1985; Comeau *et al.*, 1986; Kerrn-Jespersen and Henze, 1993; Kerrn-Jespersen *et al.*, 1994).

At the beginning of the aerobic phase, P-uptake will not start until the biofilm is fully penetrated with oxygen. The oxygen requires time to diffuse through the membrane and to reach the microorganisms. The biofilm has to be penetrated in order to guarantee oxygenation of the bulk liquid. P-release continues until the oxygen reaches the biofilm.

Figure 3 shows a lag period of about half-hour after the oxygen replaces the nitrogen where P-release continues until oxygen rules again the bacterial metabolism.

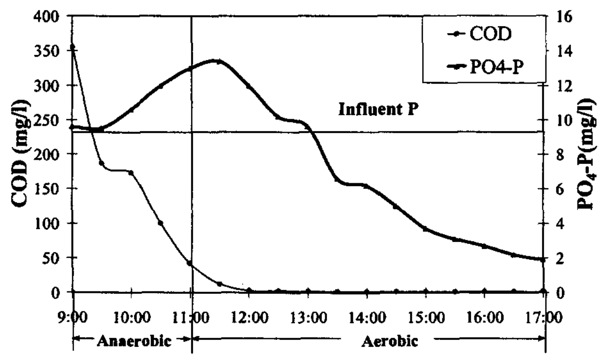

Figure 3. COD and PO_4-P profiles in one cycle.

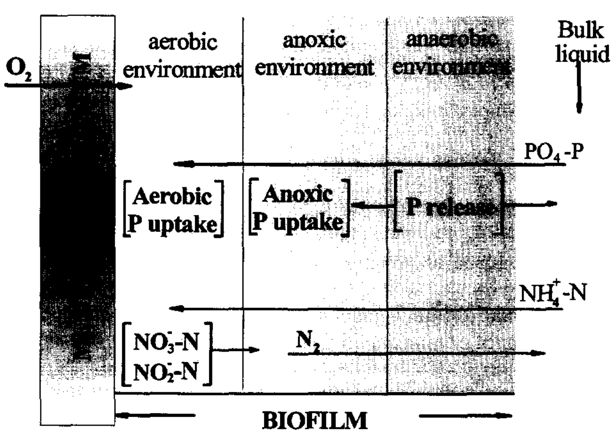

Figure 4. Conditions of the biofilm at the beginning of the aerobic phase.

Figure 4 shows the situation of the biofilm after washing-out the nitrogen and re-establishing aerobic conditions. Oxygen diffuses through the membrane to the biofilm. As oxygen penetrates the biofilm, nitrification in the inner part of the biofilm starts and the produced NO_3-N diffuses to the anaerobic region of the biofilm where it is denitrified (Figure 4). Increasing the organic load leads to thicker biofilms and the time necessary to penetrate the biofilm with oxygen increases (Figure 5). The amounts of P released during the anaerobic phase (8 to 76% over the influent concentration) are low according to the ones between 100 and 300% reported by González-Martínez and Wilderer (1991); Gonçalves and Rogalla (1992), and Rovatti *et al.* (1995).

As Castillo and Tejero (1998) have stated, there is the possibility that, when a dominant culture of *Acinetobacter lwoffi* develops, low P release is expected. Fuhs and Chen (1975) report the value of 24% when working with a pure culture of *Acinetobacter lwoffi*. Another possibility for low P-release is anoxic P-uptake simultaneously with COD removal at the beginning of every cycle (Figure 3). This situation prevents *Acinetobacter* from using an important fraction of the COD under anaerobic conditions at the beginning of the cycle.

Ammonia nitrogen. Average NH_4-N removal rates of 50, 41, and 22% were achieved during the "so called" anaerobic phase for different organic loads. Higher removal corresponds to lower organic loading rates. Considering the extreme situation that about 10% of the influent NH_4-N is used by the microorganisms, in the times shown in Figure 5, for anabolic functions, the difference correspond to nitrification. This lead to the conclusion that important amounts of NH_4-N are nitrified during the time the biofilm requires to consume the remnant oxygen (Table 2). The subsequent anoxic/anaerobic phase did denitrify and nitrates were not present at the beginning of the aerobic phase.

Nitrate concentration is a function of ammonium concentration and the capability of the system to denitrify at the beginning of every cycle. However, to denitrify, organic molecules are required as electron donors, provided by influent COD. In order to allow phosphates to be released during the anaerobic phase, higher amounts of readily biodegradable carbonaceous substances have to "survive" the aerobic/anoxic period at the beginning of every cycle. This can be achieved whether increasing the COD or decreasing ammonia nitrogen in the influent. This situation leads to the consideration that the reactor performance for phosphorus removal can be improved by increasing the influent COD:N ratio of the wastewater. As reported by Barnard (1976), nitrate reduction in the anaerobic zone utilises substrate that would otherwise be available for assimilation by the poly-P microorganisms. Also, nitrate has the effect of reducing the net influent BOD:P ratio for the system.

Figure 6 relates the overall NH_4-N removal rate with the organic load. At organic loading rates above 15 gCOD/m^2·d the ammonium removal rate decreases with the organic load. For organic loading rates under 15 gCOD/m^2·d, the ammonia removal is not predictable. The same behaviour can be observed for PO_4-P removal.

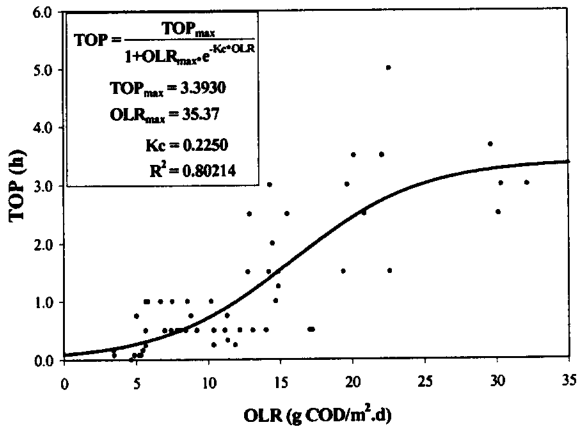

Figure 5. Time for Oxygen Penetration (TOP).

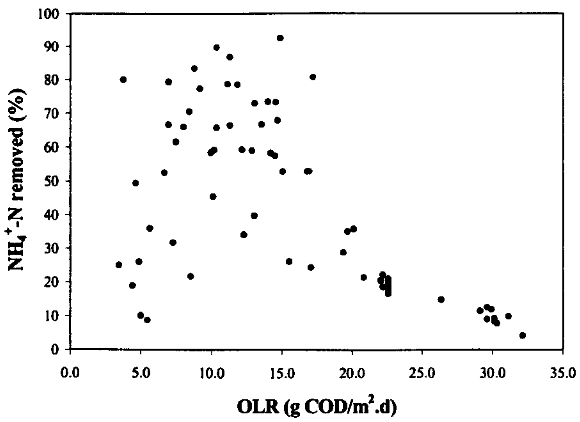

Figure 6. NH_4-N overall removal values.

Table 2. Ammonia and nitrate-nitrogen during the anaerobic phase

Organic Load gCOD/m²·d	Influent NH_4-N mg/l	End of anaerobic phase, NH_4-N mg/l	Removal NH_4-N mg/l	Removal NH_4-N percent
9.5	38.2	19.0	19.2	50
12.8	117.0	68.8	48.2	41
14.9	83.2	65.0	18.2	22

The highest NH_4-N removal rates (from Figure 6, 57 to 69%) were obtained for organic loads between 7.3 and 15 gCOD/m^2·d. However, it was not possible to reach the mean NH_4-N removal rates of 95-100% and 90-95% obtained by Garzón-Zúñiga and González-Martínez (1996) and Gonçalves and Rogalla (1992). A possible explanation for these low nitrogen removal rates could be the high nitrogen load applied during this research (between 1 and 3 g NH_4-N/m^2.d). At high organic loading rates the low mean cellular residence times do not allow nitrifying bacteria to grow in the biofilm.

Denitrification was estimated by subtracting the effluent NO_3-N from the NH_4-N removed. The obtained rates, under the consideration that all the NH_4-N removed was nitrified, are higher than the 0.6 gNH_4-N/m^2·d and 0.7 gNO_3-N/m^2·d obtained in a biofilm reactor by Garzón-Zúñiga and González-Martínez (1996). The values of 0.6 kgNH_4-N/m^3·d obtained by Gonçalves *et al.* (1994) are also lower than the ones estimated in this research.

COD removal. As expected, the removal of COD during the anoxic/anaerobic phase is inversely proportional to the organic load. Figure 7 shows that during the so-called "anaerobic phase" COD removal reaches values over 90% for organic loading rates between 5 and 15 gCOD/m^2·d. The removed COD to released P ratios were 72, 57 and 40 $mgCOD_{removed}/mgP_{released}$ for influent COD values of 200, 400, and 600 mg/l, respectively.

This demonstrates that the capacity of the system to release phosphate is proportional to the influent COD or the organic load (Arun *et al.*, 1988).

The values of the $COD_{removed}/P_{released}$ ratio indicate that the required energy for the C-uptake is less when low organic loading rates are applied or that the microorganisms, during the short aerobic/anoxic period previous to the anaerobic phase, use COD efficiently, shifting the values of the ratio to higher values. Rapid COD uptake is a well-known characteristic of low and very low organic loaded activated sludge systems.

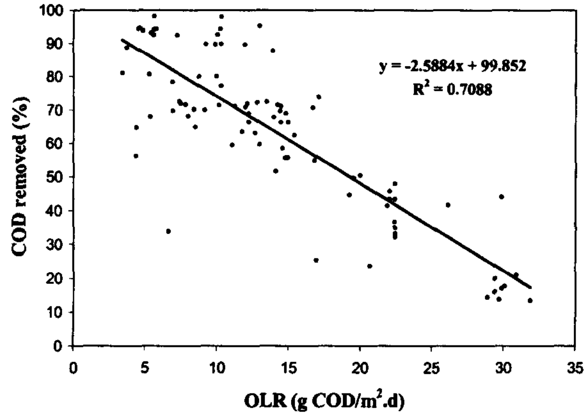

Figure 7. COD removal during the anoxic/anaerobic phase.

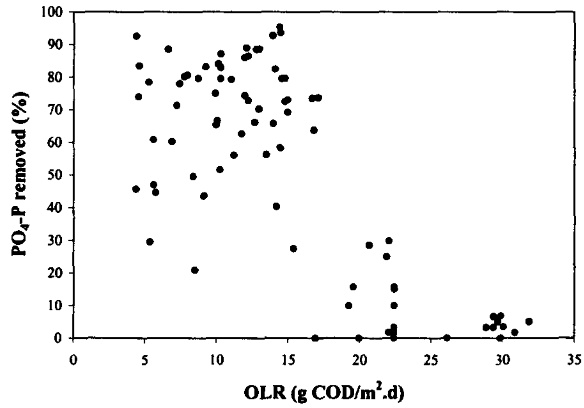

Figure 8. Influence of the organic load on P removal.

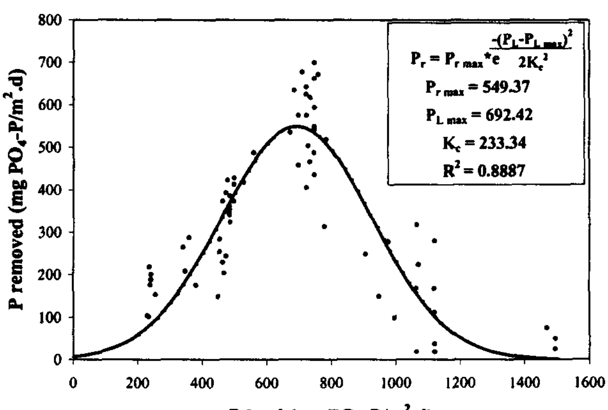

Figure 9. Phosphate removal rates and organic load.

Phosphate removal. These results (Figure 8) are comparable with the average 70 to 90% removal rates obtained by González-Martínez and Wilderer (1991), Garzón-Zúñiga and González-Martínez (1996), and Muñoz-Colunga and González-Martínez (1996). Gonçalves and Rogalla (1992) and Gonçalves *et al.* (1994)

obtain values between 70 and 80% with Biofilter (BF). Rovatti *et al.* (1995), using a Fluidized Bed Reactor (FBR) reached 60 to 70% removal rates. These authors report too that P uptake between 9.5 to 45.3 mg/l during the aerobic phase is commonly observed. Longer cycle duration results in a more stable system behaviour, allowing more time for P release and uptake. Contrary to longer cycle duration, the operation with 6-hour cycles does not guarantee enough time for P release and uptake.

The system showed an average P consumption rate of 200-580 $mgPO_4\text{-}P/m^2\cdot d$, with values that reach 700 $mgPO_4\text{-}P/m^2\cdot d$, doubling the 200 to 300 $mgPO_4\text{-}P/m^2\cdot d$ obtained with aerobic SFBR, and tripling the 100 to 145 $gPO_4\text{-}P\ /m^3\cdot d$ achieved with BF. The P consumption rate is influenced by the P load and its rate is directly proportional to the P load but, for P loads of over 800 $mgPO_4\text{-}P/m^2\cdot d$ a gradual fall of the P consumption rate is observed (see Figure 9).

CONCLUSIONS

1. According to the presence of oxygen, one cycle can be divided into several phases: a) aerobic until the microorganisms consume the rest oxygen from the previous aerobic phase, b) anoxic for the time required by the bacteria to reduce nitrates formed in the previous aerobic phase, c) anaerobic when no oxygen or nitrates are present, and d) aerobic when oxygen diffuses through the membrane to the biofilm after the anaerobic phase.
2. Nitrification takes place at the beginning of every cycle and during the aerobic period. Denitrification takes place shortly before the anaerobic phase is established.
3. Phosphate uptake takes place at the beginning of every cycle as long as aerobic and anoxic conditions prevail and during the formal aerobic phase. Phosphates are released during the anaerobic phase.
4. The time of oxygen penetration at the beginning of the aerobic phase increases with the increase of the organic load.
5. At the beginning of the aerobic phase simultaneous nitrification, aerobic P uptake, denitrification and anoxic P uptake are present.
6. The rate of P release increases with the organic load when the overall P removal is greater than 50%.
7. Phosphate accumulation processes improve when the COD:N ratio of the influent wastewater is increased.
8. The reactor configuration and operation allow the presence and activity of P-accumulating and nitrifying bacteria with organic loading rates 3 times higher than other conventional biofilm reactors.
9. Phosphate release during the anoxic/anaerobic phase is limited by the presence of nitrates.
10. Twelve-hour cycles allow better performance than shorter ones.

ACKNOWLEDGEMENT

This research was possible through the financial support of the Spanish Commission of Science and Technology (Comisión Interministerial de Ciencia y Tecnología (CICYT)). Project AMB 96-0549.

REFERENCES

Arun, V., Mino, T. and Matsuo, T. (1988). Biological mechanism of acetate uptake mediated by carbohydrate consumption in excess phosphorus removal system. *Wat. Res.*, **22**(5), 565-570.

Barnard, J.L. (1976). A review of biological phosphorus removal in the activated sludge process. *Water S.A.*, **2**, 136.

Castillo, P. A.and Tejero, I. (1998). Biological phosphorus removal using a biofilm membrane reactor. *IAWQ 19th Biennial International Conference: Water Quality International, Vancouver, Canada.* June, 21-26 (in press).

Comeau, Y., Lamarre, D., Roberge, F., Perrier, M., Desjardins, G., Hade, C. and Mayer, R. (1996). Biological nutrient removal from a phosphorus-rich pre-fermented industrial wastewater. *Wat.Sci.Tech.*, **34**(1/2), 169-177.

Fuhs, G. W. and Chen, M. (1975). Microbiological basis of phosphate removal in the activated sludge process for the treatment of wastewater. *Microbial Ecology*, **2**, 119-138.

Garzón-Zúñiga, M. A. and González-Martínez, S. (1996). Biological phosphate and nitrogen removal in a biofilm sequencing batch reactor. *Wat. Sci. Tech.* **34**(1-2), 293-301.

Gonçalves, F. R. and Rogalla, F. (1992). Biological phosphorus removal in fixed films reactors. *Wat. Sci. Tech.* **25**(12), 165-174.

Gonçalves, F. R., Nogueira, F. N., LeGrand, L. and Rogalla, F. (1994). Nitrogen and biological phosphorus removal in submerged biofilters. *Wat. Sci. Tech.* **30**(11), 1-12.

González-Martínez, S. and Wilderer, P. (1991). Phosphate removal in a biofilm reactor. *Wat. Sci. Tech.* **23**(7-9), 1405-1415.

Kerm-Jespersen, J. P. and Henze, M. (1993). Biological phosphorus uptake under anoxic and aerobic conditions. *Wat. Res.* **27**(4), 617-624.

Kerrn-Jespersen, J. P., Henze, M. and Strube, R. (1994). Biological phosphorus release and uptake under alternating anaerobic and anoxic fixed-film reactor. *Wat. Res.* **28**, 1253-1255.

Muñoz-Colunga, A. and González-Martínez, S. (1996). Effects of population displacements on biological phosphorus removal in a biofilm SBR. *Wat. Sci. Tech.* **34**(1-2), 303-313.

Rovatti, M., Nicolella, C., Converti, A., Chicliazza, R. and Di Felice, R. (1995). Phosphorus removal in fluidized bed biological reactor (FBBR). *Wat. Res.* **29**(12), 2627-2634.

Tejero, I., Eguía, E., Vidart, T., Jácome, A., Osa, J. J. and Lorda, I. (1997). Wastewater treatment with biofilm membrane reactors. Proceedings of the International Conference on Advanced Wastewater Treatment Processes. Leeds, United Kingdom, Sept. 8-11.

USEPA (1987) Design Manual. Phosphorus Removal. EPA/625/1-87/001.

Wentzel, M.C., Dold, P.L., Ekama, G.A. and Marais, G.v.G. (1985) Kinetics of biological phosphorus release. *Wat. Sci. Tech.*, **17**(11-12), 57-71.