Fermentation of a low VFA wastewater in an activated primary tank

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Abstract

A low volatile fatty acid wastewater from a Barcelona residential area was prefermented in a laboratory-scale primary clarifier operated as a prefermenter -an activated primary tank. Total suspended solids (TSS), oxidation-reduction potential (ORP) and temperature were measured in the prefermenter. Influent and effluent were characterised through chemical oxygen demand (COD), soluble COD, volatile fatty acids (VFA), VFA potential, soluble PO_4-P, NH_4-N, pH and alkalinity. Solids retention times (SRT) of 5 d and 10 d were tested. Best results were obtained for the 5 d SRT with the prefermenter covered for better temperature and ORP control. For these conditions, COD solubilisation was measured as 22 mg COD/ℓ, 66 mg COD/g influent particulate COD, or 91 mg COD/g influent VSS. VFA-formation was measured as 34 mg VFA-COD/ℓ, 142 mg VFA-COD/g influent VSS, or 77 mg VFA-COD/g influent COD. These values indicate remarkable solubilisation and fermentation in the prefermenter. The VFA/PO_4-P ratio was improved from 0.9 to 5.5 mg VFA-COD/mg PO_4-P, but did not approach the recommended value for biological P removal (20 mg/mg). VFA production could not reach the influent VFA-potential either (110 mg VFA-COD/ℓ) and VFA-potential was lower in effluent than in influent. With a 5 d SRT and the prefermenter uncovered, a small VFA formation and no solubilisation were observed. This was interpreted as the VFA being formed from the influent soluble COD. With a 10 d SRT, a very low ORP was measured. Neither solubilisation nor VFA production were detected in the prefermenter. Concurrent acidogenic fermentation and methanogenesis are compatible with these results. P and N solubilisation was low or moderate in the prefermenter over all periods, and increased with increasing SRT and TSS, and decreasing ORP, and pH and alkalinity were quite stable, due to the high influent alkalinity and the moderate VFA formation and N solubilisation.

Introduction

Soluble organic compounds are required for biological nutrient removal (BNR) in wastewater treatment plants. Denitrification requires readily-biodegradable COD as a carbon source, while volatile fatty acids (a fraction of soluble COD) are required by P-accumulating organisms (PAO) for enhanced biological P removal (Abu-Ghararah and Randall, 1991; Henze et al., 1995a; Maurer et al., 1997). In full-scale BNR plants, soluble COD (including VFA) should be present in the influent, in order to avoid costly external source addition. About 20 mg VFA-COD are required for removing 1 mg P (Abu-ghararah and Randall, 1991). These amounts of VFA are not always available in wastewater, particularly when COD is low. Hydrolysis and fermentation in the anaerobic stage of a BNR plant provide an additional supply of soluble COD, including VFA. However, a substantial fraction of particulate COD is retained in primary clarification, thus reducing the wastewater potential for hydrolysis and fermentation in the BNR process. Fermentation of primary sludge has been used as a means of increasing soluble COD, including VFA, in the BNR plant influent (Pitman et al., 1992; Skalsky and Daigger, 1995; Christensson, 1997).

Fermentation of primary sludge can be carried out in either primary clarifiers or separate prefermenters receiving primary sludge. Primary clarifiers can be operated as prefermenters by increasing SRT and recycling sludge to the clarifier influent, in order to elutriate soluble fermentation products from sludge. These prefermenters are known as primary activated tanks. Separate prefermenters have been classified in completely mixed, static and two-stage prefermenters (Münch and Koch, 1999). The primary activated tank is one of the simplest ways of producing VFA (Randall et al., 1992), because it does not require additional tanks when applied to continuous BNR plants.

In this study, a laboratory-scale primary activated tank was built and operated, in order to study COD solubilisation and fermentation in the wastewater from a residential area in Barcelona (Catalonia, Spain). Design and performance of the prefermenter are presented in this paper. Typical prefermenter parameters are presented (TSS, HRT, SRT, temperature and oxidation-reduction potential). Solubilisation and fermentation are studied by analysing different parameters in influent and effluent, namely TSS, COD, soluble COD, VFA, VFA-potential, soluble PO_4-P, NH_4-N, pH and alkalinity.

Experimental

Raw wastewater was taken daily from a street sewer in the residential area around the university laboratory in Barcelona, and was pumped to a stirred 200 ℓ tank, from where it was fed to the prefermenter. Influent and effluent parameters were determined by analysing 8 h daytime composite samples.

Prefermenter features

Figure 1 shows a scheme of the activated primary tank, including inner mechanisms and feed, waste, and recycle streams. Table 1 displays the main prefermenter features and operational parameters.

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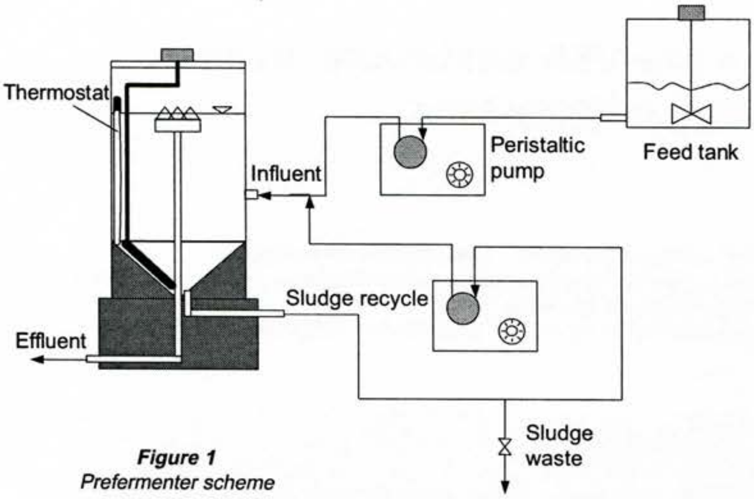

Figure 1
Prefermenter scheme

TABLE 1
Main prefermenter features and operational parameters

Prefermenter type	Activated primary tank
Material	PMMA
Volume	3.3 l
Influent flow rate	2.5 ℓ/h
Scraper speed	0.5 r/min
Flow regime	Continuous
Recycle ratio	52%
Recycle flow rate	1.3 ℓ/h
SRT	5 and 10 d
HRT	1.3 h

The basic prefermenter design is based on a scheme described by Sedlak (1991). Operational parameters and process control were set according to recommendations from different references (Pitman, 1991; Pitman et al., 1992; Randall et al., 1992; Skalsky and Daigger 1995; Christensson, 1997). The prefermenter was a primary clarifier operated at a higher SRT. Besides, primary sludge was recycled and mixed with influent wastewater, in order to allow for sludge elutriation.

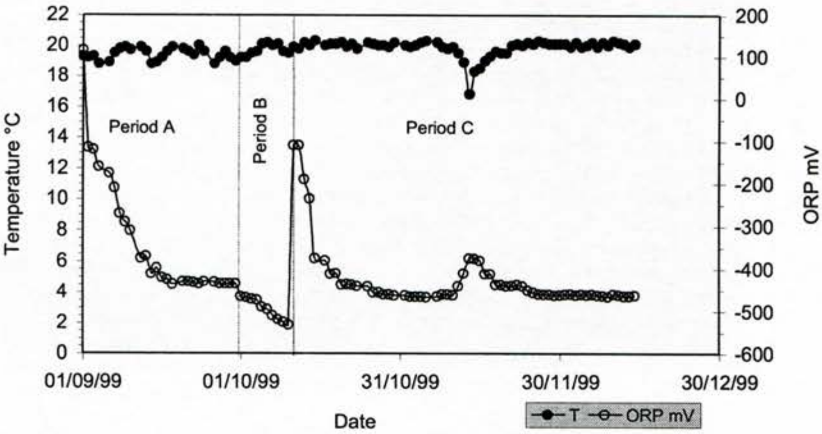

Figure 2
Temperature and ORP evolution throughout the three operational periods

The prefermenter was built of polymethylmethacrylate (PMMA) and had a 3.3 ℓ capacity. The cylindrical side of the prefermenter was 210 mm high, with 150 mm ID, and a wall thickness of 3.5 mm. The conic bottom was 70 mm high, with a 45° slope. The prefermenter was side-fed and had a central weir of 40 mm ID. The prefermenter was equipped with a rotary scraper, driven by a 0.5 r/min electric motor. A 50 W thermostatic device was used for controlling temperature at 20°C at the bottom of the prefermenter. Temperature at this point was monitored with a portable electronic thermometer.

Wastewater flowrate was 2.5 ℓ/h for the whole study. Recycle flow was 1.3 ℓ/h (52% recycle). Hydraulic retention time (HRT) was 1.3 h. Solids retention time of 5 and 10 d were tested.

Prefermenter operation

The prefermenter performance was studied over three operational periods, namely A, B and C. Period A lasted 30 d, from 1 to 30 September 1999, and had a 5 d SRT. In Period B, a 10 d SRT was set. Period B was studied for 10 d (1 to 10 October 1999), since it clearly showed poor conditions for acidogenic fermentation. The prefermenter was not covered during Periods A and B. In Period C, SRT was set to 5 d again, but non-hermetic covers were added to the prefermenter in order to improve temperature and ORP control. Period C extended for 65 d (11 October to 14 December 1999).

In order to evaluate acidogenic fermentation in the studied periods, routine analysis of several parameters was carried out. TSS, ORP and temperature were determined in primary sludge. Parameters determined in influent and effluent were TSS, COD, soluble COD, VFA, soluble PO_4-P, NH_4-N, pH and alkalinity. *Standard Methods* (1995) were applied, except for VFA determination. For VFA determination, samples were filtered through 0.45-µm membrane filters and analysed by solid-phase micro-extraction (Ábalos et al., 2000). VFA concentrations were converted to COD by using conversion factors: 1.066 for acetic acid, 1.514 for propionic acid, 1.818 for butyric acid, and 2.039 for valeric and isovaleric acid. VFA-potential was determined by a modification (Barajas et al., 2000) of the Lie and Welander (1997) method.

Statistical analysis of results was carried out through t-tests for mean comparison. F-tests were required for variance comparison in order to select the kind of t-test to be applied (equal or different variances). Box and whisker plots have been used when required in order to show differences in both mean values and dispersion. Montgomery and Runger (1994) statistical analysis techniques were used.

Results and discussion

Prefermenter parameters

Temperature and ORP

Figure 2 displays temperature and ORP evolution throughout the three operational periods. During most of the time, the temperature at the prefermenter bottom was controlled between 18.9 and

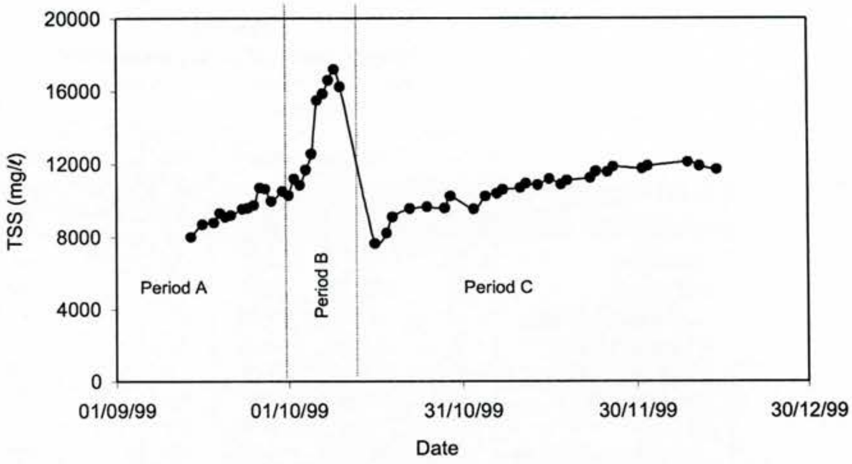

Figure 3
Evolution of TSS in primary sludge

20.3°C. During Periods A and B, temperature oscillations were higher than normal oscillations in Period C -probably due to the absence of prefermenter covers. Better temperature control was achieved for the most of Period C by covering the prefermenter. However, rain and cold conditions prevailed in mid-November, with influent temperatures of 5°C. This fact, along with stratification inside the prefermenter, caused the temperature at the prefermenter bottom to fall below 18.9°C for 3 d. This affected the prefermenter performance for some days.

Very low ORP prevailed for most of the study period (Fig. 2). During Period A, ORP gradually decreased from +116 to -425 mV and kept below this value for the rest of the period. During Period B, ORP fell to -465 mV in one day and kept decreasing to -532 mV, when conditions were changed for starting Period C. The strong sludge wasting at the beginning of Period C (1.64 l) caused the ORP to rise to -110 mV. From then on, ORP decreased again, and was below -460 mV for most of the time. As with temperature, ORP was affected by the cold influent conditions in mid-November, rising to -375 mV.

Acidogenic fermentation takes place even above -300 mV, while methanogenic fermentation occurs below -550 mV (Randall et al., 1992). Therefore, ORP values measured in Periods A and C fell well within the acidogenic fermentation range, while the ORP measured in Period B approached values which were typical of methanogenic fermentation. Probably, the 10 d SRT set in Period B caused these excessively reducing conditions, thus allowing methanogenic conditions to prevail, which should be avoided in a prefermenter (Pitman et al., 1992). Therefore, SRT was set to 5 d again.

TSS in primary sludge

Figure 3 shows the evolution of TSS throughout the three operational periods. Mean TSS in primary sludge was 9 530, 13 800 and 10 600 mg/ℓ respectively, for Periods A, B and C. Population means were found to be different in 95% confidence t-tests. During Period B, TSS was clearly higher than in the other periods, due to lower sludge wasting. The sharp decrease in TSS at the beginning of Period C is due to the strong sludge wasting carried out at the beginning of the period in order to rapidly remove methanogenic bacteria from the system.

Influent and effluent parameters

Table 2 shows the values of influent and effluent parameters measured throughout the three investigation periods. These results are presented and discussed below.

TSS and COD removal

Mean influent TSS values were 305, 280 and 284 mg/ℓ, for Periods A, B and C respectively. Population means were found equal, at a 95% confidence level. The common mean was estimated as 290 mg/ℓ. Mean effluent TSS values were 120, 138 and 114 mg/ℓ respectively, for Periods A, B and C. TSS removal efficiencies were 60%, 50% and 60% for the same periods. These removal efficiencies fall within the typical range for primary clarifiers, 50 to 70% (Metcalf-Eddy, 1991). However, operating at 10 d SRT caused a decrease in TSS removal efficiency in the prefermenter. This can be attributed to the higher TSS concentration inside the prefermenter, since high TSS concentration has been documented as a cause for lower solids settleability during acidogenic fermentation (Skalsky and Daigger, 1995).

Influent COD mean values for Periods A, B and C were 399, 424 and 468 mg/ℓ respectively. Population means were found equal, at a 95% confidence interval. The common mean was estimated as 439 mg/ℓ. Effluent COD mean values for Periods A, B and C were 299, 318 and 355 mg/ℓ respectively. Mean COD removal efficiency was 24% in each period, ranging between 7 and 35%, 10 and 33% and 11 and 37%, respectively. In conclusion, mean influent COD and COD removal efficiencies were the same over the three periods.

Soluble COD and COD solubilisation

Mean values for influent soluble COD in Periods A, B and C were 126, 136 and 135 mg/ℓ respectively. Population means were found to be equal at a 95% confidence interval, with a common mean of 133 mg/ℓ. Influent soluble COD represented 31% of influent COD. On the other hand, mean soluble COD values in effluent were 114, 128 and 154 mg/ℓ respectively for Periods A, B and C. Mean soluble COD gradually increased through Periods A, B and C. Soluble to total COD ratios were 0.38, 0.40 and 0.42. These values are higher than the influent ratio (0.31), due to partial TSS removal and, for Period C, solubilisation, as shown below.

Figure 4 displays soluble COD production in Periods A, B and C. No soluble COD production was observed in Periods A and B. Furthermore, soluble COD showed a decrease in these periods (12 mg/ℓ in Period A, and 8 mg/ℓ in Period B). These results are comparable to Christensson (1997) data. In a 4-week sampling in a full-scale prefermenter, no solubilisation between prefermenter influent and effluent was observed in this study.

In Period C, COD solubilisation was observed in 19 of the 23 samples analysed. One of the samples not showing solubilisation belonged to the beginning of the period. Two others belonged to the mid-November cold influent conditions, which inhibited

TABLE 2
Influent and effluent parameters

	Influent				Effluent			
	n	**Range**	**Mean**	**STD**	**n**	**Range**	**Mean**	**STD**
Period A								
TSS (mg/ℓ)	20	173-780	305	136	20	69-300	120	52
COD (mg/ℓ)	13	267-577	399	99	13	190-398	299	60
COD soluble (mg/ℓ)	13	96-158	126	22	13	67-158	114	30
VFA (mg COD/ℓ)	9	1.2-7.6	5.1	2.4	9	5.3 - 28	14	7.8
PO_4-P (mg P /ℓ)	13	3.3-9.5	6.3	1.8	13	3.7-9.7	6.7	1.8
NH_4-N (mg N /ℓ)	13	22-45	34	6.5	13	23-45	35	6.4
pH	23	7.79-8.52	8.11	0.2	23	7.71-8.40	8.05	0.2
Alkalinity (mg CO_3/ℓ)	17	296-431	377	38	17	302-450	392	39
Period B								
TSS (mg/ℓ)	10	176-468	280	96	10	77-206	138	45
COD (mg/ℓ)	10	285-600	424	122	10	191-418	318	80
COD soluble (mg/ℓ)	10	88-215	136	42	10	75-189	128	40
VFA (mg COD/ℓ)	6	1.3-7.6	4.2	3.0	6	0.0-6.1	2.7	2.5
PO_4-P (mg P /ℓ)	10	3.9-7.0	5.9	0.9	10	6.4-9.2	8.0	0.7
NH_4-N (mg N /ℓ)	10	17-45	32	9.9	10	19-47	35	9.8
pH	10	7.92-8.26	8.13	0.1	10	8.0-8.31	8.17	0.1
Alkalinity (mg CO_3/ℓ)	10	312-410	354	34	10	350-490	413	45
Period C								
TSS (mg/ℓ)	46	125-500	284	101	46	44-190	114	40
COD (mg/ℓ)	23	331-749	468	130	23	246-596	355	99
COD soluble (mg/ℓ)	23	96-210	135	27	23	80-235	154	37
VFA (mg COD/ℓ)	9	1.2-13	6.6	4.6	9	17-68	39	17
PO_4-P (mg P /ℓ)	23	3.1-9.6	6.2	1.8	23	3.7-10.2	7.1	1.8
NH_4-N (mg N /ℓ)	23	14-48	28	9.3	23	14-49	30	9.6
pH	54	7.90-8.25	8.06	0.10	54	7.48-8.12	7.87	0.2
Alkalinity (mg CO_3/ℓ)	23	315-414	370	29	23	345-450	398	31

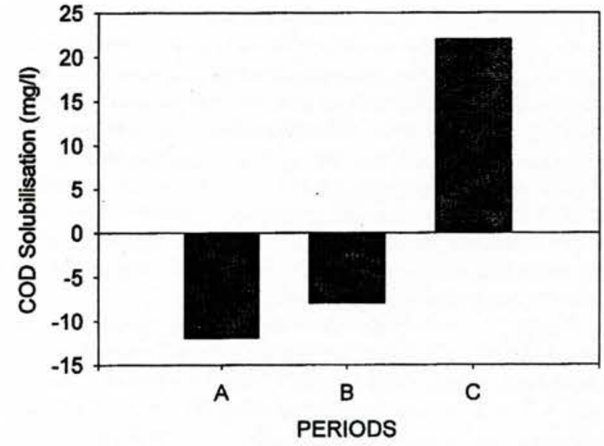

Figure 4
Mean COD solubilisation in the studied periods

TABLE 3
Degree of solubilisation in Period C

Degree of solubilisation	Soluble COD production
mg COD/ℓ	22
mg soluble COD/g influent VSS	91
mg soluble COD/g influent particulate COD	66

fermentation. For the 21 samples not affected by the cold influent conditions, the mean increase in effluent soluble COD was 22 mg/ℓ (16 to 28 mg/ℓ, 95% confidence interval). This value is lower than the value obtained by Gonçalves et al. (1994). In batch studies, these authors found a maximum soluble COD production of 30 mg/ℓ, with HRT of 2.1 to 2.8 h. On the other hand, Christensson (1997) found a 10 mg/ℓ solubilisation in a prefermenter, when comparing the effluents of two parallel primary clarifiers, one of them operated as a prefermenter.

TABLE 4
Typical VFA-COD concentration in urban wastewater

References	VFA concentration (mg COD/ℓ)
Narkis et al. (1980)	91.6[a] and 33.2[b]
Rabinowitz et al. (1987)	9.1
Gonçalves et al. (1994)	41.3
Abu-Ghararah and Randall (1991)	0.0
De Haas and Adam (1995)	36.6
Lie and Welander (1997)	45.0
Christensson (1997)	22.3
Münch and Greenfield (1998)	37.5

[a] Mean value of Neveh Shaanan residential wastewater
[b] Mean value of Haifa municipal treatment plant influent

TABLE 5
VFA potential and related parameters in influent

Parameters	Barajas et al. (2000)	Barajas et al. (2000)	This work, Period C	Mean
VFA, mg COD/ℓ	2.6	16	8.6	9.1
Influent VFA potential, mg COD/ℓ	86	150	93	110
Influent VFA/VFA potential ratio	0.030	0.11	0.092	0.076
Influent COD, mg/ℓ	396	616	438	483
VFA potential/COD ratio	0.22	0.24	0.21	0.22
Soluble PO_4-P, mg PO_4-P/ℓ	5.9	6.8	6.2	6.3
VFA potential/soluble PO_4-P ratio	15	22	15	17

The degree of solubilisation (DS) can also be expressed as the ratio of soluble COD production to influent VSS (mg soluble COD/g VSS), or as the ratio of soluble COD production to influent particulate COD (mg soluble COD/g particulate COD). Table 3 displays the degree of solubilisation obtained in Period C.

A COD solubilisation of 66 (mg soluble COD)/(g influent particulate COD) was observed in Period C. It was similar to the 60 mg/g reported by Gonçalves et al. (1994). An approximate DS of 32 mg/g can be derived from Christensson (1997) data. Higher degrees of solubilisation have been reported from studies, where completely mixed reactors or solids pre-precipitation have been applied, reported in a review by Gonçalves et al. (1994).

VFA in influent

Influent VFA concentrations for the three periods were 5.1, 4.2 and 6.6 mg/ℓ respectively, as COD. Population means were found to be equal in t-tests for the three periods, at a 95% confidence interval. The common mean was 5.6 mg/ℓ. Influent VFA concentration showed a high variability, with a common standard deviation of 3.8 mg/ℓ. The influent VFA concentrations determined in this study are much lower than the values reported in most other studies, summarised in Table 4. The only similar values found were reported by Rabinowitz et al. (1987) and Abu-ghararah and Randall (1991). VFA concentration in influent represented 1.2% of influent COD. This value is much lower than the 5 to 10% value suggested by Henze et al. (1995b) for raw wastewater. VFA concentration in the influent was low, both in absolute and relative terms.

Though VFA concentration in influent was low, it was found that the wastewater was able to produce VFA by fermentation. The VFA-potential test (Lie and Welander, 1997) can measure the maximum concentration of VFA that can be obtained by fermentation of a wastewater. VFA potential in influent was determined in daytime composite samples in a previous study (Barajas et al., 2000) and in Period C (Table 5). VFA potential in influent showed a considerable variability (86 to 150 mg VFA-COD/ℓ), but the VFA-potential/COD ratio was quite constant (0.21 to 0.24 mg VFA-COD/mg COD). The VFA/VFA-potential ratio was low in all samples (0.03 to 0.11), thus indicating the potential for fermentation not being developed in the influent.

Mean VFA/soluble PO_4-P ratio in the prefermenter influent was 0.9 mg VFA-COD/(mg P). For biological P-removal, 20 mg VFA-COD/mg P are required (Abu-Ghararah and Randall, 1991). The influent ratio was clearly very low for P-removal purposes. The VFA-potential/soluble PO_4-P ratio is a better indicator for the P-removal suitability of a wastewater. Table 5 shows the influent VFA-potential/soluble PO_4-P ratio. The mean value was 17 mg VFA-COD/mg P (15-22 mg/g). This value is much higher than the VFA/soluble PO_4-P ratio, and approaches the 20 mg/g required ratio.

VFA in effluent and VFA production

Differences were observed in effluent VFA concentrations. Effluent VFA concentrations for the three periods were 14, 2.7 and 39 mg/ℓ respectively, as COD. Population means were found to vary in 95% confidence t-tests. Mean effluent VFA-COD was 25 mg/ℓ higher in Period C than in Period A (10 to 39 mg/ℓ, 95% confidence interval) and 36 mg/ℓ higher than in Period B (23 to 49 mg/ℓ, 95% confidence interval).

Periods A and C (5 d SRT) showed VFA production, while no VFA production was detected in Period B (10 d SRT). Fig. 5 displays mean VFA production in the studied periods. Mean VFA production in Period A was 9.1 mg/ℓ, as COD. In this case, weak VFA production was observed with no COD solubilisation. In the mentioned 4-week sampling, Christensson (1997) observed a 17 mg/ℓ VFA production, with no COD solubilisation either. This can be interpreted as the VFA being produced from soluble rather than particulate COD (Christensson, 1997). Consequently, solids hydrolysis was not significant in Period A.

In Period C, mean VFA-COD generation in the prefermenter was 32 mg/ℓ. Only one of the samples showed no COD solubilisation, belonging to the low temperature influent period. Analysing the set of samples not affected by the cold influent conditions, VFA production averaged 34 mg/ℓ (22 to 46 mg/ℓ, 95 % confidence interval), as COD. Fig. 6 displays VFA production vs. COD solubilisation in Period C. A clear correlation between these variables can be observed.

According to Fig. 6, 1.4 mg of VFA-COD were produced for each unit increase in soluble COD. Extrapolation of the regression line indicates that no VFA production would be observed for COD solubilisations below 7 mg/ℓ. The slope and the determination coefficient are very similar to those obtained by Gonçalves et al. (1994). Assuming that 90% of COD solubilisation yields VFA

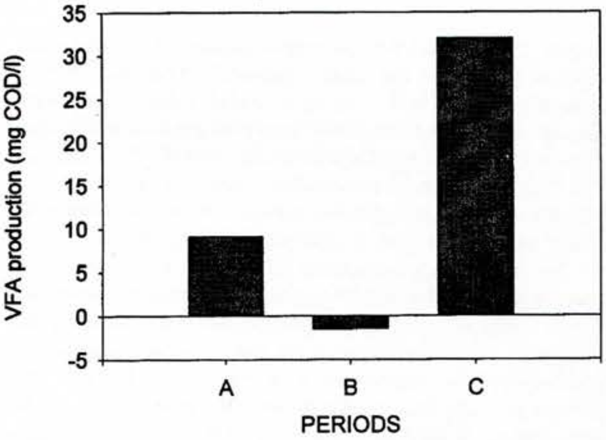

Figure 5
Mean VFA production in the studied periods

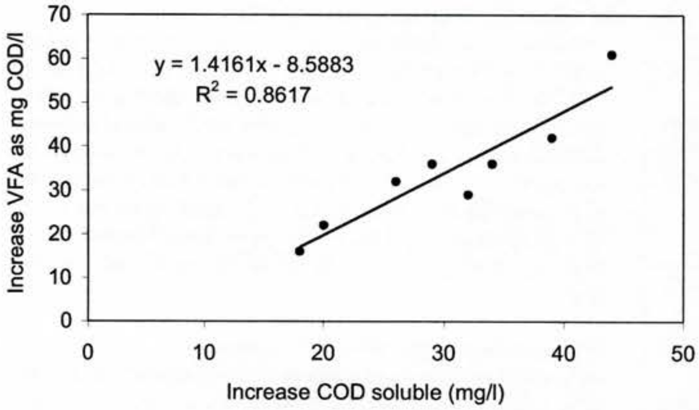

Figure 6
Correlation between VFA production and COD solubilisation, in Period C

TABLE 6
Degree of acidogenic fermentation in Period C

Units	VFA production
mg VFA-COD/ℓ	34
mg VFA-COD/g influent VSS	142
mg VFA-COD/g influent COD	77

(Eastman and Ferguson, 1981), 20 mg/ℓ of solubilised COD (out of 22 mg/ℓ) would contribute to VFA. The difference to 34 mg/ℓ of VFA-COD generated (14 mg/ℓ) would be produced by fermentation of influent readily fermentable COD. So, it can be concluded that VFA were produced by hydrolysis and fermentation of solids, and by fermentation of influent readily fermentable COD.

VFA production can also be expressed through the ratio (mg VFA-COD produced)/(mg influent VSS), and the ratio (mg VFA-COD produced)/(mg influent COD). These ratios have been compiled for Period C, in Table 6.

VFA production per unit influent VSS in Period C was 142 mg COD/g VSS. This value is much lower than the ratio reported by Skalsky and Daigger (1995) for a 5 d SRT (244 mg VFA-COD/g VSS). These authors worked with a mixed primary sludge fermenter. VFA-COD production per unit COD in influent was 77 mg VFA-COD/g COD in Period C. This value is much lower than the value reported by Gonçalves et al. (1994) (117 mg VFA-COD/g COD) with a 2.3 h HRT. However, it is comparable to VFA production reported by other authors in a review by Gonçalves et al. (1994): Rabinowitz et al. (1987), 83 to 99 mg VFA-COD/g COD, and T'Seyen (1986), 90 mg VFA-COD/g COD. On the other hand, it is higher than the VFA production computed from Christensson (1997), 32 mg VFA-COD/g COD.

VFA production could not approach the influent VFA-potential. Since VFA production was 34 mg VFA-COD/ℓ in Period C, only 31% of influent VFA-potential was reached in the prefermenter. VFA production (Christensson, 1997) could not approach the VFA potential either, since VFA production accounted for only 51% of the VFA potential. It should be taken into account that most of influent readily fermentable COD and a fraction of solids are not in contact for long periods of time with fermenting sludge in activated primary tanks. This is not the case for upflow anaerobic sludge blanket (UASB) or completely mixed reactors, where all influent wastewater is mixed with or passes through the fermenting sludge.

In the VFA potential test applied in Period C, VFA potential was determined in effluent, too. While influent VFA potential was 93 mg VFA-COD/ℓ, effluent VFA potential was 67 mg/ℓ. These results show a decrease in VFA potential in the prefermenter. It should be taken into account that 60% of solids were trapped in the prefermenter and could not contribute to the effluent VFA potential. Besides, these solids were only partially fermented as it can be derived from the solubilisation and VFA production data. Christensson (1997) also obtained a decrease in VFA potential in a full-scale primary clarifier operated as a prefermenter. The VFA potential/soluble PO_4-P ratios also decreased in the prefermenter. Influent and effluent ratios were 15 and 9.3 mg COD/mg P respectively.

The VFA/soluble PO_4-P ratio in effluent was 5.5 mg VFA-COD/mg PO_4-P while it was 0.9 mg VFA-COD/mg PO_4-P influent. The ratio clearly improved but still remained well below the recommended 20 mg/mg value.

In conclusion, in Period A, with a 5 d SRT and the prefermenter uncovered, VFA was produced without overall COD solubilisation. This has been interpreted as VFA being formed from soluble COD only. In Period B, the 10 d SRT induced strong anaerobic conditions that could reach methanogenesis. Though methanogenesis has not been confirmed, concurrent acidogenic fermentation and methanogenesis could explain the behaviour of soluble COD and VFA in Period B: both solubilisation and VFA production were negative. In Period C, with a 5 d SRT, the non-hermetic prefermenter cover favoured temperature regulation and appropriate ORP for hydrolysis and acidogenic fermentation of solids. A remarkable VFA production was achieved. The 5 d SRT was found to be optimum, when better control of operational parameters was achieved. Skalsky and Daigger (1995) also found the 5 d SRT to be optimum for VFA production. Although solubilisation and fermentation were remarkable in Period C, the VFA/soluble PO_4-P ratio was far from reaching the 20 mg/mg recommended value. Besides, VFA potential was lower in effluent than in influent.

TABLE 7
PO_4-P solubilisation observed in the prefermenter

Period	%TSS	PO_4-P (mg PO_4-P/ℓ)	mg PO_4-P/ (g influent COD)	mg PO_4-P/ (g VFA produced as COD)
A	0.95	0.4	0.9	44
B	1.38	2.0	5	-
C	1.06	0.9	2.1	26

P solubilisation

Mean concentrations of soluble PO_4-P in influent for Periods A, B and C were 6.3, 5.9 and 6.2 mg/ℓ respectively. Population means were found to be equal, in 95% confidence t-tests. Mean concentrations of soluble PO_4-P in effluent were 6.7, 8.0 and 7.1 mg/ℓ respectively. When effluent population means were compared in 95% confidence t-tests, differences could be found between Period A and B only. On the other hand, an increase of PO_4-P in the prefermenter effluent was observed during the three studied periods. According to Christensson (1997), PO_4-P release in a prefermenter is caused by the reduction of ferric phosphate (insoluble) to ferrous phosphate, which is soluble. This reduction is favoured by the low ORP conditions present inside the prefermenter. Table 7 compiles the PO_4-P solubilisation values observed in each period.

Phosphate solubilisation figures (as PO_4-P) for the three periods were 0.4, 2.0 and 0.9 mg/ℓ respectively. Figure 7 displays the PO_4-P solubilisations in each period, in a box and whisker plot. It can be observed that solubilisation in Period B was clearly higher than in Periods A and C. The lowest solubilisation was observed in Period C. The highest dispersion was found in Period C, as well as a higher number of outliers. Comparing evolution of ORP with solubilisation in the studied periods, it was found that lower ORP potentials yield higher PO_4-P solubilisation, as could be expected from the iron (III) reduction mechanism for PO_4-P solubilisation in a prefermenter.

PO_4-P solubilisation can also be measured as the ratio of PO_4-P released to influent COD or, to VFA production. Mean solubilisations of 0.9, 5.0 and 2.1 mg P/g influent COD were observed for Periods A, B and C respectively. Mean TSS concentrations were 0.95%, 1.38% and 1.06%. The highest solubilisation value was obtained, again, for Period B, with the highest SRT, and the lowest ORP. The ratio of P release to VFA production was 44 mg P/g VFA-COD for period A, and 26 mg/g for Period C. No VFA production was observed in Period B, so the ratio could not be computed.

Banister et al. (1998) ran batch fermentation tests to evaluate the fermentation of primary sludges from BNR plants in Johannesburg. With 6 d SRT sludges, 18 to 20°C, and 0.47 to 5.6% TSS, they obtained mean solubilisations of 3.5 mg P/g influent COD, and 34 mg P/g VFA-COD. Ratios derived from Christensson (1997) are 0.96 mg P/g influent COD and 29 mg P/g VFA-COD produced. The results obtained in Periods A and C of this study are of the same order but lower than those of Banister et al. (1998), and very similar to Christensson's (1997) results.

In conclusion, PO_4-P solubilisation fell within the ranges reported in the literature, although it was somewhat lower. Maximum solubilisation was observed with highest SRT and TSS, and lowest ORP. P solubilisation can negatively affect the VFA/P ratio, and some authors have proposed PO_4 precipitation after prefermentation (Banister et al., 1998). However, solubilised PO_4-P should not affect BNR, since it will re-precipitate when ferrous iron is re-oxidised during the aerobic stage of the BNR plant (Christensson, 1997).

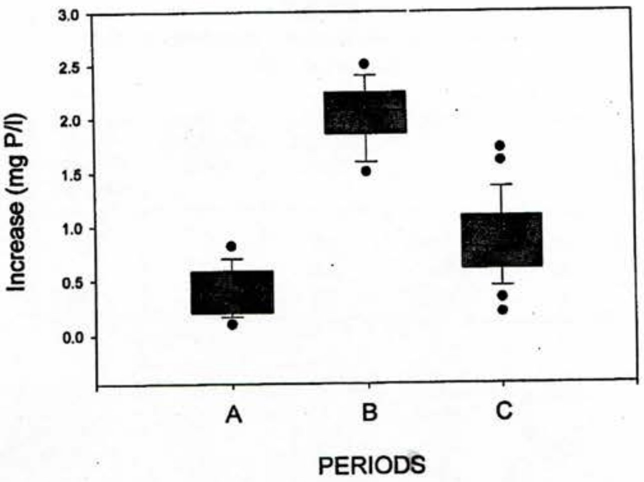

Figure 7
Box and whisker plots for PO_4-P solubilisation

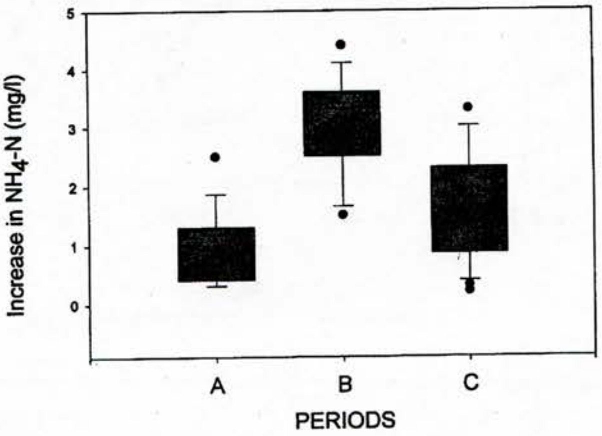

Figure 8
Box and whisker plots for N solubilisation

N solubilisation

Mean concentrations of NH_4-N in the influent were 34, 32 and 28 mg NH_4-N/ℓ for Periods A, B and C respectively. Population means were found equal, with a 95% confidence interval. The common mean was 31 mg NH_4-N/ℓ. Mean concentrations of NH_4-N in effluent were 35, 35 and 30 mg NH_4-N/ℓ. Population means of effluent NH_4-N were found to be equal, with a 95% confidence interval. The common mean was 32.5 mg/ℓ.

Some N solubilisation was measured in the three periods. Mean solubilisations for Periods A, B and C were 1.0, 3.0 and 1.7 mg NH_4-N/ℓ respectively. These values represent only small increases in NH_4-N. The greatest increase was that of Period B, when anaerobic conditions were strongest. Figure 8 displays the three solubilisations in box and whisker plots.

Table 8 displays the degrees of N solubilisation, expressed as mg NH_4-N/g influent COD, and mg NH_4-N/mg VFA-COD produced. TSS concentrations are given too. The NH_4-N to

TABLE 8
Nitrogen solubilisation observed in the prefermenter

Period	% TSS	Increase of NH_4-N (mg/ℓ)	mg NH_4-N/ (g influent COD)	mg NH_4-N/ (g VFA produced as COD)
A	0.95	1.0	2	112
B	1.38	3.0	7	-
C	1.06	1.7	4	48

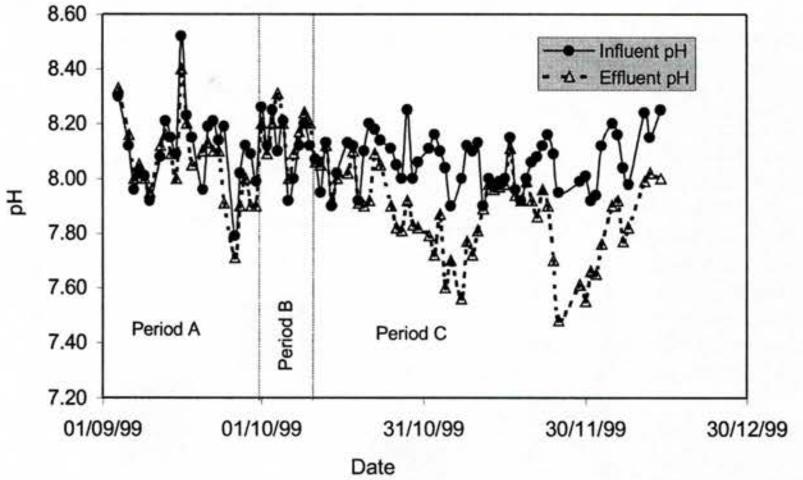

Figure 9
pH evolution throughout Periods A, B and C

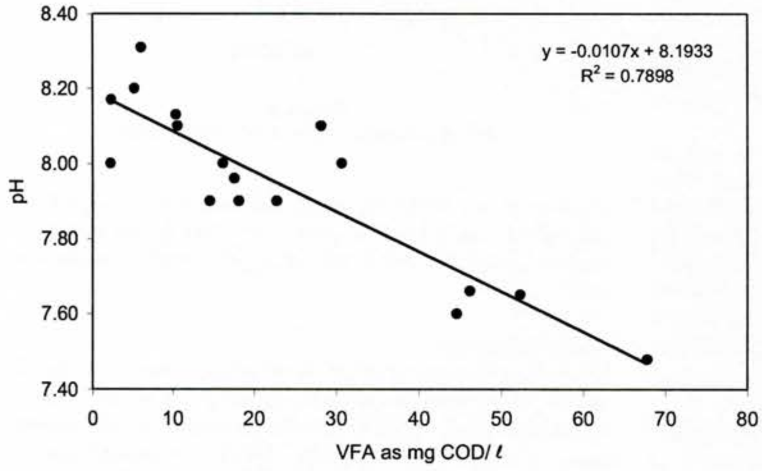

Figure 10
Effluent pH and VFA correlation

influent COD ratios for Periods A, B and C were 2, 7 and 4 mg/g respectively. Degree of solubilisation increased with TSS. For the N to VFA ratio, only data for Periods A and C are given, since no VFA production was observed in Period B. The ratios were 112 mg NH_4-N/g VFA-COD for Period A, and 48 mg/g for Period C.

Banister et al. (1998) measured higher mean DS in primary sludge, with 9 mg NH_4-N/g influent COD. They also observed similar N production to VFA production ratios, with a mean of 80 mg NH_4-N/g VFA-COD. These values were observed with TSS in the range of 0.47 to 5.6%.

When comparing PO_4-P and N solubilisation, it has been found that N solubilisation was higher than P solubilisation. This has been reported in other investigations, and is attributed to the fact that nitrogenated COD is easily biodegradable in the acidogenic phase of anaerobic fermentation (Banister et al., 1998). In conclusion, N solubilisation was weak and values were lower or similar to previously reported values. N solubilisation increased with increasing SRT and TSS, and decreasing ORP.

pH

Mean pH values for Periods A, B and C were 8.11, 8.13 and 8.06 respectively. Population means were found to be equal in 95% confidence t tests, with a common mean of 8.01. Mean pH values in effluent were 8.05, 8.17 and 7.87 respectively. Effluent population means were all found to be different in 95% confidence tests. Fig. 9 displays the evolution of influent and effluent pH throughout Periods A, B and C. Period C had the lower effluent pH, followed by Periods A and B. The decrease observed in pH was correlated to VFA production: the higher the VFA generation, the lower effluent pH. This had been reported before (Christensson, 1997; Lie and Welander, 1997; Münch and Greenfield, 1998). Figure 10 displays the correlation between effluent pH and VFA concentrations obtained in this work.

The wastewater showed a remarkable buffering capacity for the levels of VFA generation observed, and pH remained within the range of 7.5 to 8.5. This can be attributed to the moderate VFA concentrations reached, and the high alkalinity in influent (367 mg/ℓ). The cold influent conditions in mid-November affected VFA generation and pH rose for some days, as displayed in Fig. 9.

Alkalinity

Mean influent alkalinity values for Periods A, B and C were 377, 354, 370 mg $CaCO_3$/ℓ respectively. Influent population means were found to be equal in 95% confidence t-tests, with a common mean of 367 mg/ℓ. Mean effluent alkalinity values for Periods A, B and C were 392, 413 and 398 mg $CaCO_3$/ℓ respectively. Effluent population means were found to be equal in 95% confidence t-tests, with a common mean of 399 mg/ℓ. It can be concluded that the release of species affecting alkalinity (VFA, PO_4-P and NH_4-N) in the studied periods did not lead to statistically different effluent alkalinities.

A small increase in alkalinity was detected when comparing effluent to influent (Fig. 11). This can be attributed to ammonification, which causes alkalinity production at a ratio of 3.57 mg $CaCO_3$/mg N (Araújo et al., 1998). Another mechanism for alkalinity increase can be the production of bicarbonate from evolved CO_2 reacting with calcium carbonate (Wetzel, 1983). Alkalinity was determined on filtered samples in influent and effluent, so $CaCO_3$ solubilisation would have contributed to measured alkalinity production. However, $CaCO_3$ content of wastewater was not determined and this mechanism could not be confirmed.

Mean alkalinity production in Periods A, B and C was 15, 59 and 28 mg/ℓ respectively. Fig. 12 displays a box and whisker plot of alkalinity production in Periods A, B and C. Alkalinity production in Period B was clearly higher than in the other periods, due to negative VFA production and highest N and PO_4-P solubilisation.

In conclusion, small or moderate alkalinity increases (4.0 to 17%) were observed in the three fermentation periods. The greatest alkalinity production occurred in Period B, with negative VFA production, and maximum N and P solubilisation.

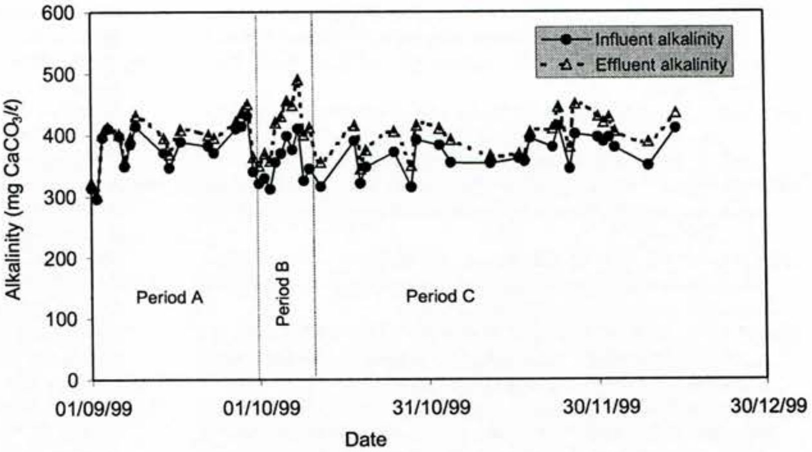

Figure 11
Alkalinity in influent and effluent throughout Periods A, B and C

Conclusions

A low-VFA wastewater from a residential area in Barcelona was prefermented in a laboratory-scale primary clarifier operated as a prefermenter. For the best conditions tested, solubilisation and fermentation were remarkable. VFA to PO_4-P ratios were improved but still kept well below the required ratio for biological P removal.

The best results were obtained in a covered prefermenter with a 5 d SRT. Cover was added in order to optimise temperature and ORP control (Period C). Under these conditions, both COD solubilisation (22 mg/ℓ) and VFA production (34 mg VFA-COD/ℓ) were observed. VFA production was attributed to both particulate COD solubilisation and fermentation, and influent soluble COD fermentation. The degree of solubilisation (66 mg COD/g influent particulate COD) was similar or higher than data found in the literature, though higher values were found in completely-mixed reactors or reactors with pre-precipitation. Specific fermentation ratios were in the mid-range, when compared with literature data. Though fermentation was remarkable, VFA production (34 mgVFA-COD/ℓ) accounted for only 35% of the influent VFA potential. This fact has been attributed to the intrisic non-completely mixed flow in the prefermenter: in an activated primary tank, most of influent soluble COD, and a fraction of the particulate COD, is not in contact with the fermenting sludge for long enough. In addition to the moderate VFA formation, wastewater VFA potential decreased in the prefermenter. This means that the wastewater potential for VFA formation in a BNR was reduced in the prefermenter.

When a 5 d SRT was applied without covering the prefermenter (Period A), some fermentation was observed with no solubilisation. This was interpreted as the VFA being produced from influent soluble COD rather than from solids fermentation. Though the ORP fell within the range for acidogenic fermentation, hydrolysis and fermentation were poor under these conditions. This was attributed to poor temperature and ORP control in the prefermenter.

When a 10 d SRT was applied (Period B), ORP fell to the lowest values. Both solubilisation and VFA production were negative. These could be explained as concurrent acidogenic fermentation and methanogenesis. TSS removal efficiency decreased, and N and P solubilisation were higher under these conditions.

Alkalinity and pH were not strongly affected by fermentation in any period. This has been attributed to the high influent alkalinity and the moderate hydrolysis and fermentation observed. Also, the lower solids concentration in primary activated tank led to lower VFA concentrations and a higher pH.

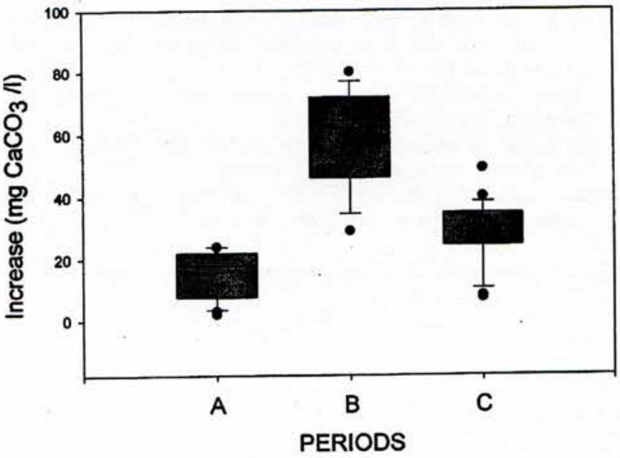

Figure 12
Box and whisker plots for alkalinity production

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