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Anaerobic Digestion of a Petrochemical Wastewater Using the UASB Process

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ABSTRACT

Anaerobic digestion of effluent from a petrochemical plant producing terephthalic acid has been tested using two Upflow Anaerobic Sludge Blanket (USAB) reactors. The reactors were seeded with two different inocula: one from an anaerobic stabilization pond receiving wasted sludge from the aerobic treatment plant of the petrochemical industry (reactor A); the other was an anaerobically adapted activated sludge from a municipal wastewater treatment plant (reactor B). At the beginning of the experiment, reactor A attained higher COD removal efficiencies and biogas production, but both reactors reached the same performances after 7 mo operation. The efficiencies in COD removal were low. At a 3 d hydraulic retention time (HRT), reactor A was loaded at 2.6 kg COD/m^3 d and reactor B at 2.2 kg COD/m^3 d. COD removals were 46.4 and 43.9% for reactor A and B, respectively. In view of these results, the UASB reactor does not appear as the most suitable treatment process for this kind of effluent.

Index Entries: UASB; anaerobic digestion; aromatic compounds; anaerobic inoculum; biogas.

INTRODUCTION

Despite evidence of microbial ability to degrade anaerobically recalcitrant compounds to methane, such as homocyclic and heterocyclic aromatic

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compounds (*1–4*), there are still few data in the literature about the use of anaerobic reactors for the treatment of chemical wastewater containing this kind of products. Biomethanation of phenolic compounds by anaerobic reactors has recently received more attention (*5–8*). However, the variety of aromatics found in industrial effluents make it difficult to predict the treatment efficiencies in anaerobic reactors. Furthermore, the different possible anaerobic designs must be tested for a specific chemical wastewater in order to assess which process is the most appropriate. Apart from the inoculum characteristics, the type of reactor used is of major importance for successful operation.

The USAB reactor and the anaerobic filter have been applied successfully for treatment of effluents from the food industry, as well as domestic sewage (*9,10*). The literature shows high and medium COD removal efficiencies for anaerobic treatment of chemical effluents containing aromatic compounds. Vogel and Winter (*6*) obtained a COD reduction of 55% at 10 d of HRT with a fixed film loop reactor for petrochemical wastewater mainly composed of phenol and cresol (COD: 1550 mg/L). Suidan et al. (*8*) found that an anaerobic filter had marginal COD removal efficiencies (10%) and no biogas production when treating coal gasification synthetic wastewater (COD: 1346 mg/L). They obtained much better results with a 24% expanded bed anaerobic granular activated carbon filter (GAC): 90% of COD removal at 1 d of HRT. These authors explained that the high efficiency of the GAC anaerobic filter was owing to the ability of the activated carbon to adsorb nondegradable or inhibitory compounds, protecting the anaerobic bacteria. The UASB process was tested by Borghans and van Driel (*5*) with a chemical wastewater containing mainly phenol, benzene, toluene, and acetic acid (COD: 30,500 mg/L). They obtained 95% COD removal efficiency at volumetric loads between 9–12 kg COD/m^3 d and HRt around 3 d. However, this excellent result may be explained by the high content of acetic acid (68% of influent COD). Under these conditions, a possible toxic or inhibitory effect of the aromatics may had been reduced or eliminated.

In this study, we tested the capability of a UASB reactor for anaerobic treatment of chemical plant wastewater containing terephthalic acid (1,4-benzenedicarboxylic acid) and other aromatic byproducts. The application of anaerobic processes may be an energy-saving alternative to the commonly applied aerobic process used to treat this kind of effluent (*11*).

METHODS

Two identical UASB reactors with working volumes of 3 L were used. They were built with a glass column of 45 cm height and a diameter of 9.6 cm. The wastewater was kept at 6°C and continuously fed using a peristaltic pump. The biogas production was measured with a gas meter column filled with an acidified brine. The reactors were maintained at 33°C.

Table 1
Characteristics of the Inocula
Used for Seeding the UASB Reactors

	Reactor A	Reactor B
TSS, g/L	42.3 (100%)	26.0 (100%)
FSS, g/L	16.1 (38%)	8.6 (33%)
VSS, g/L	26.2 (62%)	17.4 (67%)
SVI, mL/g	33.2	86.6
V_{max}, m/h	1.8	1.3
Bacterial counts[a]		
HM[b]	8.0×10^{10}	4.0×10^{8}
AM[b]	3.1×10^{9}	5.0×10^{6}
Propionate users	2.8×10^{9}	6.0×10^{6}
Butyrate users	1.5×10^{9}	nd

[a]Bacteria/g VSS.
[b]HM: hydrogenophilic methanogens; AM: acetoclastic methanogens.
[c]nd: not determined.

To determine whether there would be a limitation owing to the origin of the inoculum, two sludges sampled from different places were used as seed: reactor A was inoculated with a sludge from a stabilization pond receiving the wasted sludge of an aerobic plant treating the wastewater of the petrochemical industry; reactor B was inoculated with an anaerobically adapted activated sludge obtained from a conventional municipal wastewater treatment plant. The main characteristics of the inocula are presented in Table 1.

Each reactor received 1 L of sludge, 1 L wastewater, and 1 L tap water for start-up. One month later, continuous feeding began, and three different hydraulic retention times (HRT) were tested over a period of approximately 200 d: 7, 3, and 2 d.

Analysis of the raw effluent from the plant gave the following composition (mg/L): COD (9500), BOD (5500), and TSS (2200) with a pH of 4.5. The main aromatic compounds identified were: terephthalic acid (2671), p. toluic acid (480), benzoic acid (354), and 4-carboxy benzaldehyde (20). Acetic acid was present in concentrations below 500 mg/L. The raw wastewater had a high content of fast settling suspended solids, so it was decided to remove them before feeding. From an initial total chemical oxygen demand (COD) of 10,612 mg/L (SD = 1406, SD: standard deviation) in the raw effluent, nearly 37% of the total COD and 70% of the TSS were removed by sedimentation at 6°C. Owing to the density of terephthalic acid (1.5 kg/L) and its very low solubility (19 mg/L at 25°C), most of it should be in the settled solid. Some finely dispersed particules remained in suspension (708 mg/L) and the effluent presented better characteristics for

Table 2
Characteristics of the Settled Wastewater
Fed to the Reactors for Each HRT Applied

Parameters, mg/L	Hydraulic Retention Time (HRT) 7 d d 30 to 108	3 d d 109 to 134	2 d d 135 to 194
Total COD	6336	6977	6323
SD[a]	1160	1311	395
soluble COD	5896	6347	5752
SD	942	1666	373
ammonium	107.5	87.9	103.3
SD	51.5	0.5	24.5
TS	6965	7885	5900
SD	2047	445	234
TSS	722	713	677
SD	552	226	259

[a]SD: standard deviation.

feeding the UASB reactors. The pH of the effluent was adjusted to 6.15 (*SD* = 0.22) *with* $NaHCO_3$.

Total, Fixed, and Volatile Suspended Solids (TSS, FSS, VSS), Total Solids (TS), COD, ammonium, and alkalinity were measured according to Standard Methods (*12*). The Sludge Volume Index (SVI) was adapted (25 mL of sludge with 75 mL of settled effluent) from the usual technique (*12*). The maximum settling velocity (V_{max}) was calculated with the steepest slope of the settling curve obtained during SVI determination. The size of granules was measured with the method described by Mahoney et al. (*13*). Gas composition was determined by gas chromatography. Counts of anaerobic bacteria were performed using the msot probable number (MPN) technique with 5 tubes/dilution (*14*). Cultivation media and the inoculation techniques were used, as described by Hungate (*15*) and Balch et al. (*16*).

RESULTS AND DISCUSSION

The main characteristics of the influent are shown in Table 2 for each HRT applied. Reactors A and B were operated at 6.9 and 6.8 d of HRT over 108 d. This was done in order to know if a long adaptaton period might allow better efficiencies of COD removal, but no improvement was noticed (Fig. 1). According to the gas production (Fig. 2), it took nearly 1 mo to reach a steady state. Reactor A was more stable (Fig. 1) and presented a

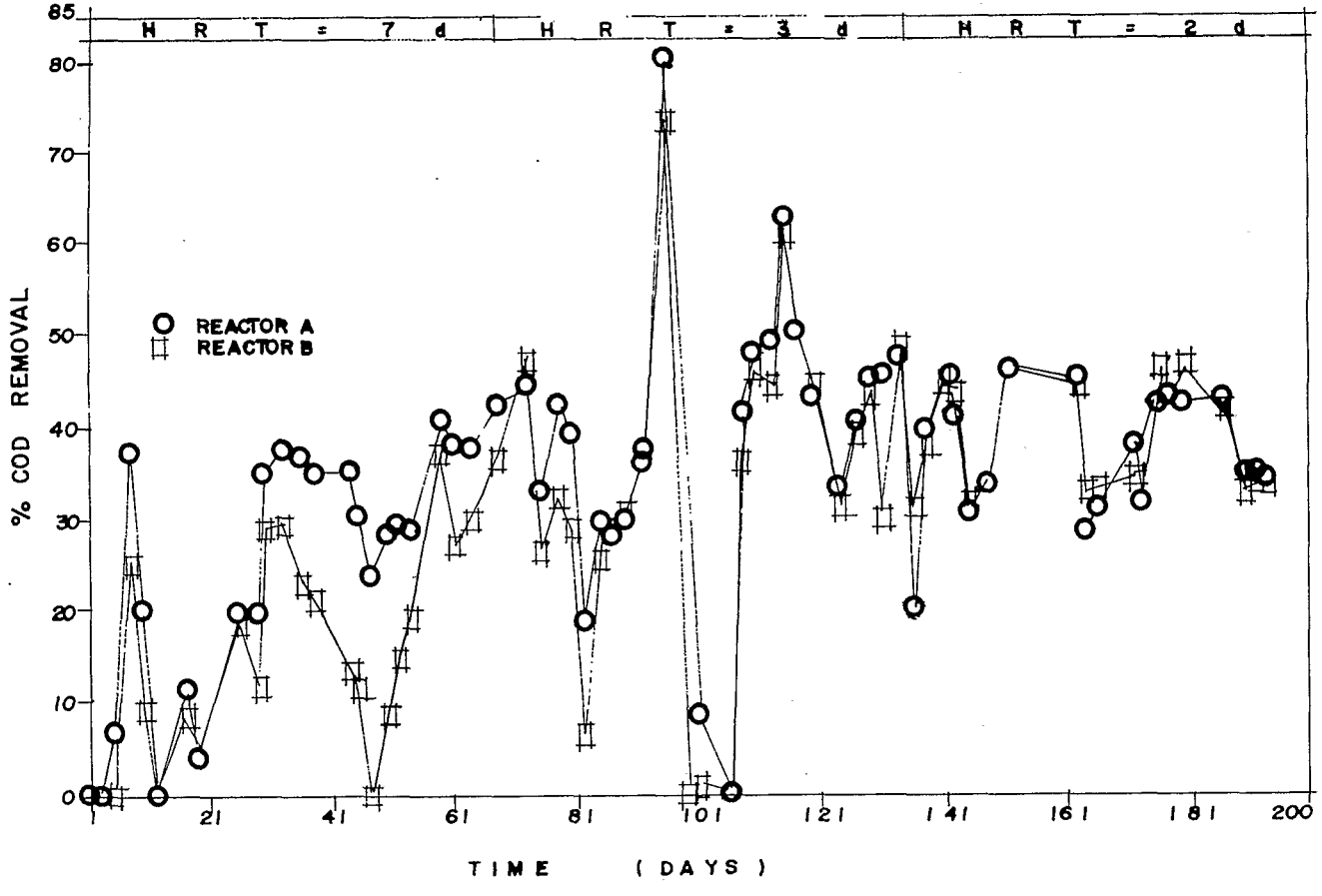

Fig. 1. Percentage of COD removal at different HRT.

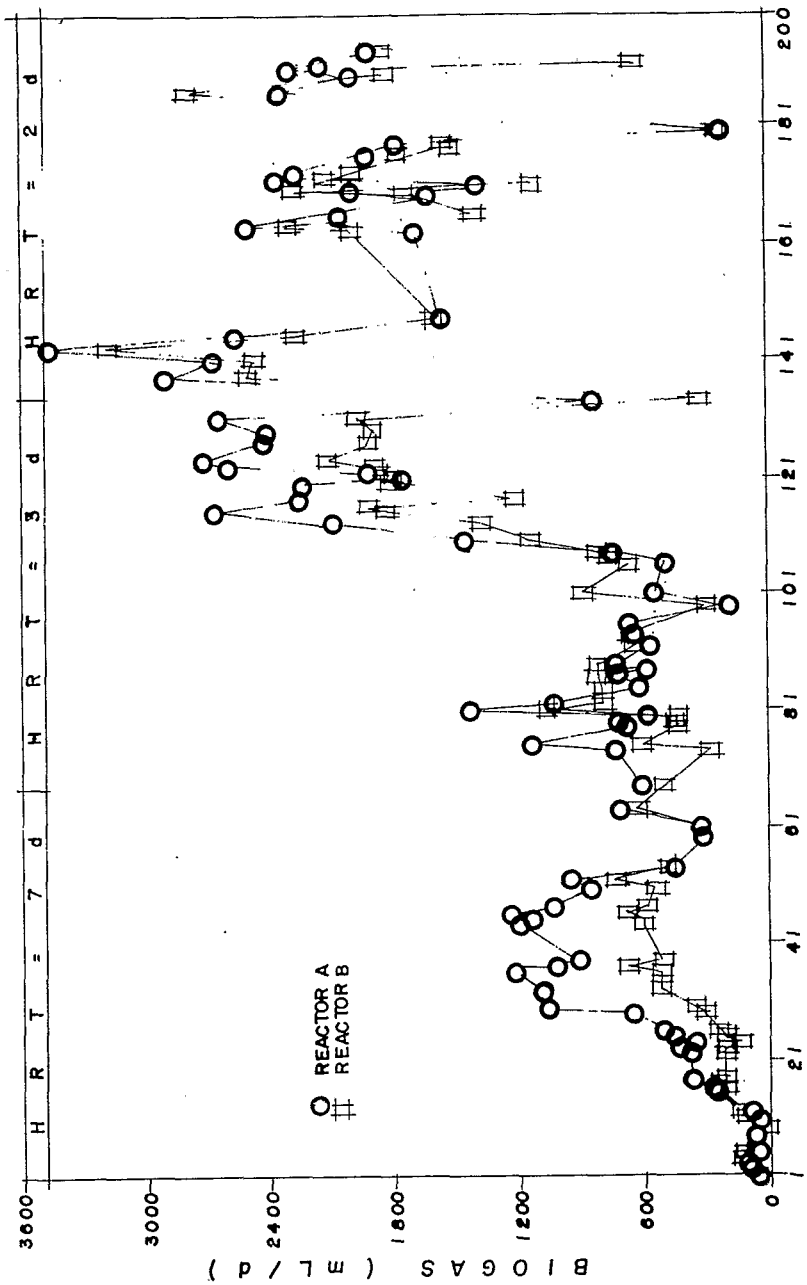

Fig. 2. Biogas production at different HRT, P=585 mm Hg, T=33°C.

Table 3
Results Obtained for Each Reactor at the Different HRT

	Reactors					
	A	B	A	B	A	B
TRH,	6.8	6.9	2.7	3.2	2.0	2.2
SD[a]	1.7	2.0	0.6	0.7	0.3	0.8
Volumetric load, kg COD/m^3 d	0.9	1.0	2.6	2.2	3.2	2.8
Organic load, kg COD/kg SSV d	0.10	0.16	0.29	0.38	0.36	0.49
% removal, total COD	33.8	23.3	46.4	43.9	37.0	38.3
SD	13.7	16.5	7.4	9.0	6.8	5.7
biogas (NPT)[b], L/L reactor d	0.17	0.13	0.47	0.35	0.45	0.40
SD	0.10	0.05	0.18	0.16	0.22	0.23
methane, %	59.6	57.7	60.6	63.1	50.2	52.9
SD	5.8	9.5	11.3	5.9	3.0	4.0
Specific activity,[c]	0.036	0.039	0.136	0.165	0.134	0.186

[a]SD: standard deviation.
[b]NPT: normal pressure and temperature.
[c]g COD/g VSS d.

higher efficiency in COD removal than reactor B: 33.8 and 23%, respectively, at an HRT of approximately 7 d (Table 2). However, it must be considered that reactor A was inoculated with more sludge than reactor B: 26.2 and 17.4 g of VSS, respectively (Table 1). If we examine the efficiencies at the other HRT, we can note they tend to equalize. In this particular case, it may be observed that a sludge sampled from a conventional municipal wastewater treatment plant, once it has been adapted to anaerobic conditions, has the same potentialities as sludge that, we might suppose, already adapted to the effluent. Furthermore, according to our calculations (Table 3), the sludge of reactor B presented a higher specific activity (kg COD removed/kg VSS d). Then, the use of an anerobically adapted activated sludge is recommended as an inoculum for a wide range of wastewaters, which is in agreement with the results of Wu et al. (*17*).

Another relevant point is the microbial composition of the sludges (Table 1). At the beginning of the experiment, the sludge of reactor A had a higher content of anaerobic bacteria per gram VSS than the sludge of reactor B. It seems that the seed of reactor A was in proper conditions in the sludge stabilization pond, where it was sampled, since a good anaerobic microbial consortium was allowed to develop. Nevertheless, when receiving the settled raw wastewater, which contains a higher concentra-

tion of organic matter, recalcitrant, and possible toxic or inhibitory compounds, the sludge certainly had to adapt to the new conditions. This stress might explain the reduction in the microbial activities of the sludge.

At the other HRT (3 and 2 d), the efficiencies of COD removal were better than at 7 d HRT (Table 3). This may be explained by the fact that, for HRT less than 7 d, there is a better hydraulic distribution of the effluent and a better mixing of the sludge owing to an increase in the biogas production (Fig. 2), that would improve substrate transfer. The best values of COD removal were obtained at 3 d of HRT: 46.4 and 43.9% for reactors A and B, respectively. Thus, it seems that the efficiency of the UASB process is limited for this kind of effluent.

Literature results previously cited suggest that the aromatic compounds may have inhibitory effects on anaerobic digestion. In our case, a similar response could be expected. Biodegradation tests in serum bottles showed that the settled wastewater (0.56 g COD/g VSS), as well as terephthalic acid, inhibited biogas production, at least during the tested period (2 mo). The low efficiencies obtained here may be partially explained by this fact.

Looking further into the results, we observe that the biogas production is inferior to 1 vol/vol of reactor/d (Table 3). As a consequence, the application of this process is not very attractive for energy production in this particular case.

The behavior of the reactors was tested under organic overload. At 7 d HRT, an effluent with a COD of 15,000 mg/L was applied to both reactors (d 95). Two days later, the usual conditions of organic load were reestablished. The sludge activities were completely inhibited, and it took 11 d for the reactors to restore normal conditions of COD reduction (Fig. 1). Apparently, although the sludges were very sensitive to organic overloads, they were not irreversibly inhibited and could recover their initial activities.

The overload did cause a sharp decrease to pH 6 (Fig. 3), which can partially account for the inhibition of the sludge methanogenic activities. The pH of the sludges was very stable during the entire operation period (Fig. 3), and both reactors presented similar pH values. The alkalinity in the reactors remained in the range of accepted values (1300–3200 mg $CaCO_3$/L), but the buffering capacity was not strong enough to prevent a pH drop when the reactors were overloaded (Fig. 3). The reactors by themselves produced only around 450 mg $CaCO_3$/L.

At the end of the experiment, the percentages of VSS at the lower and upper parts of the sludge beds were measured. For reactor A and B, it was found that these percentages were higher at the upper part: 56.3 and 48.2%, respectively, than the lower part: 36.4 and 39.1%, respectively. This might be explained by the precipitation of minerals of the influent toward the bottom of the reactor. An estimation, in the case of reactor A, calculated over the period of operation results in an accumulation of 30 g of minerals.

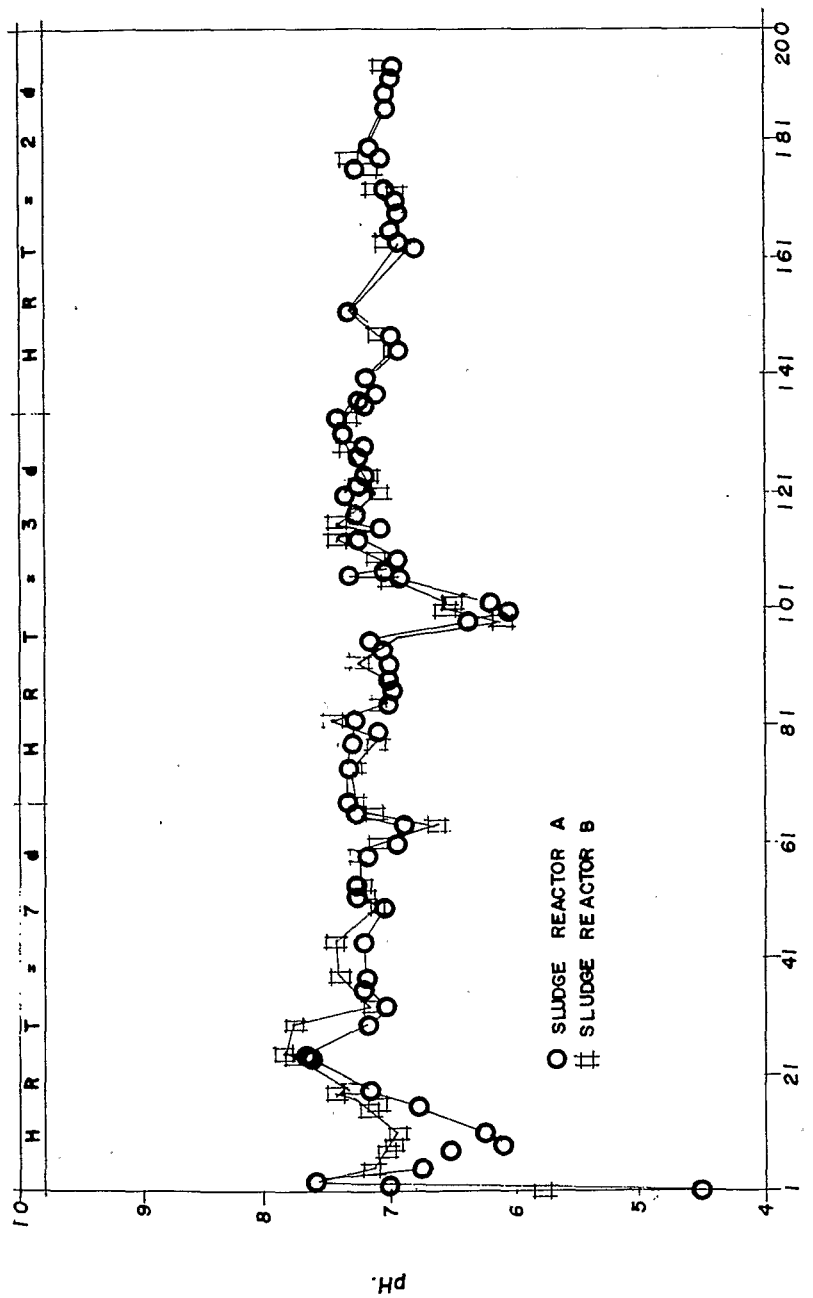

Fig. 3. Sludge pH during the operation of the reactors.

The SVI and the V_{max} were also measured for both reactors at the end of the study. In the case of reactor A, an SVI of 29.9 mL/g and a V_{max} of 2.6 m/h were obtained; for reactor B, the values were 26.2 mL/g and 3.15 m/h. Both sludges had very small mean granule diameters (A: 0.31 mm, SD=0.39; B: 0.22 mm, SD=0.23) and a brownish color, although reactor B was darker. Comparing the SVI and V_{max} with those reported in Table 1, it can be observed that the sludge of reactor B improved both parameters significantly, contrary to the sludge of reactor A, which only increased its V_{max}. Sludge A slightly changed in color, getting darker, whereas sludge B passed from black to a dark brownish color. The texture of both sludges, very different at the beginning, were practically the same at the end, resembling the aspect of the inoculum of reactor A. Apparently, the inoculum of reactor B improved its initial characteristics and evolved faster than sludge A, developing rather good physicochemical and microbiological properties.

As a final conclusion, we can say that application of the UASB reactor for COD removal and biogas production has given poor results. The efficiency of the reactors we used could have been limited by their low sludge content since the sludge of reactor B presented a fair COD removal specific activity. Another reason for the low COD removal may be the possible toxicity of some constituent of the wastewater and the poor substrate transfer owing to the very low upward velocities and gas production. The anaerobically adapted activated sludge had a good capacity to adapt to the influent, and it may be successfully employed for seeding UASB reactors in a variety of cases. Another anaerobic alternative (tubular fixed film reactor) is being investigated to establish whether this process can treat the same wastewater with better results.

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