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ANAEROBIC TREATMENT OF WASTEWATER FROM THE HOUSEHOLD AND PERSONAL PRODUCTS INDUSTRY IN A HYBRID BIOREACTOR

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Abstract - The anaerobic treatment of wastewater from the household and personal products industry was studied using a 16.3 L hybrid reactor (UASB and biofilter). The top of the UASB reactor was filled with coconut shells to act as the support material for the biofilter. The wastewater was characterized in terms of pH (1.0 – 12.0), COD (1,000 – 5,000 mg/L), BOD_5 (700 – 1,500 mg/L), chloride (55 – 850 mg/L), ammonia nitrogen (0.4 – 0.9 mg/L), total Kjeldahl nitrogen (22.1 – 34.0 mg/L), phosphorus (2.0 – 2.5 mg/L), anionic surfactants (100 – 600 mg/L), turbidity (115 – 300 NTU) and total suspended solids (450 – 1,440 mg/L). The bioreactor was operated continuously for 120 days at room temperature (26 ± 5^{o}C) with hydraulic retention times of 50, 40 and 60 h. COD and BOD removals and biogas production were evaluated in order to analyze process efficiency. The average removal efficiencies for COD (77%, 72% and 80%) and BOD_5 (approximately 90%) were obtained with HRTs of 50, 40 and 60 h, respectively. The average specific biogas production was 0.32 L/g COD (at standard temperature and pressure) for the three experimental runs. These data indicate good reactor efficiency and suggest the possibility of using this system to treat wastewater generated by the household and personal products industry.

Keywords: Anaerobic treatment; Household and personal products industry; UASB; Biofilter; Hybrid bioreactor.

INTRODUCTION

Household detergents and cosmetic products contain anionic, cationic, nonionic and amphoteric surfactants and complexing agents, preservatives, bleaching agents, acids and bases, solvents and fragrances. Linear alkylbenzene sulfonates (LAS) are, by volume, the main constituent of detergents and cleaning agents.

Among the feasible treatment alternatives for wastewater from the household and personal products industry, anaerobic processes stand out as potentially effective choices. They offer a number of advantages over traditional aerobic processes, namely 1) low energy demand, 2) transformation of most organic substances present in the waste into methane, a source of energy, 3) minimum sludge formation and 4) low nutrient demands (Speece 1996).

Because anaerobic microorganisms tend to have a low growth rate, various techniques have been developed to immobilize them within bioreactors in order to avoid loss of microorganisms in the effluent stream, which may reduce the process rates. Among

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the bioreactors most commonly used for this purpose are hybrid reactors, such as the combination of a UASB and biofilter, where the granular sludge bed is associated with bacterial colonies on particles of support material.

The biofilter section of the hybrid reactor increases the surface available for bacterial growth and the contact time between microorganisms and recalcitrant constituents in wastewater. These bioreactors may also have the largest volume, which makes them suitable for the treatment of wastewater with high organic loads (Speece 1996; Büyükkamaci and Filibeli 2002; Najafpour et al. 2006).

The treatment performance of an anaerobic hybrid reactor was studied for different types of concentrated wastewaters. Synthetic wastewater was fed into the reactor at different hydraulic retention times (0.5, 1 and 2 d) and organic load rates (1–10 kg COD/m^3 d) over two years. COD removal efficiencies ranging from 77 to 90% were achieved. The treatment of Baker's yeast and meat processing industry wastewaters with hydraulic retention times of 2 d and organic load rates of 9.0 and 1.0 kg COD/m^3 d resulted in about 78 and 75% COD removal efficiencies, respectively. The biogas produced had methane contents of 58, 58, and 70% for synthetic, yeast industry and meat processing wastewaters, respectively. The organic matter removal efficiency of the reactor indicated that this type of reactor is suitable for the treatment of high-strength effluents (Büyükkamaci and Filibeli 2002).

Najafpour et al. (2006) evaluated the treatment of palm oil mill effluent in an upflow anaerobic sludge-fixed film reactor (a hybrid reactor with a part of upflow fixed film on an upflow anaerobic sludge blanket section). The authors claim that the major problem associated with UASB reactors is the long start-up period (2 – 4 months) and a hybrid bioreactor with tubular flow behavior was developed in order to shorten the start-up period at low hydraulic retention times. The reactor was operated at 38°C and organic loads from 2.63 to 23.15 g COD/L d. High COD removals of 89 and 97% at HRT of 1.5 and 3 days were achieved, respectively. A methane yield of 0.346 LCH_4/g $COD_{removed}$ at the highest organic load rate was obtained.

The treatment of synthetic coal wastewater at 27 ± 5°C was studied in hybrid reactors. Synthetic wastewater consisted of a mixture of phenolics (752 mg/L) and volatile fatty acids and had an average COD of 2,240 mg/L. After granulation, the hybrid reactor performed steadily with phenolic and COD removal efficiencies of 93% and 88%, respectively, at a volumetric load rate of 2.24 g COD/L d and a hydraulic retention time of 24 h (Ramakrishnan and Gupta 2006).

The objective of this study was to evaluate the anaerobic treatment of wastewater from the household and personal products industry in a hybrid bioreactor containing immobilized microorganisms as granular sludge and biofilm and to determine the feasibility of applying this process on a commercially successful basis.

MATERIALS AND METHODS

Wastewater Collection and Characterization

The wastewater employed in this study came from a household and personal products industrial facility (Uberlândia, MG, Brazil) containing residues of products deposited in the reactors employed on the industry production line, water from the washing of these reactors and spills that occurred during the packaging of the products. Since the industry uses linear alkylbenzene sulfonic acid, ethanol, butyl glycol, formol, nonylphenol ethoxylate, quaternarium ammonium compounds, sodium hydroxide, chlorine, ammonia, pine oil and fluorhydric and chloridric acids as raw materials (data supplied by industry personnel), one estimates that all these materials are constituents of the wastewater. The wastewater was collected daily in the equalization tank during periods of maximum flow. At the end of each week, aliquots were sampled for physicochemical analyses and the wastewater was stored at 8°C before being introduced into the reactor with a peristaltic pump.

All aliquots were properly preserved according to the analyses to be performed. Storage at a low temperature was necessary to reduce microbial activity and to retain the characteristics of the wastewater, since the room temperature (around 30°C most of the time) was high and the time between collection and usage was long (one week). Characterization of the wastewater generated weekly included pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), turbidity, total (TSS) and volatile suspended solids (VSS), ammonia nitrogen, total Kjeldahl nitrogen (TKN), total phosphorus, anionic surfactants and chloride. Since products from the industrial processes varied considerably because of fluctuations in market demand, the composition of the wastewater also varied. The main wastewater characteristics are given in Table 1.

Table 1: Overall composition of the household and personal products industry wastewater.

Parameter	Range*
pH	1.0 - 12.0
BOD_5	700 - 1500
COD	1000 - 5000
Turbidity	115 - 300
Total suspended solids	450 - 1440
Volatile suspended solids	250 - 1000
Total Kjeldahl nitrogen	22.1 - 34.0
Ammonia nitrogen	0.4 - 0.9
Total phosphorus	2.0 - 2.5
Anionic surfactants	100 - 600
Chloride	55 - 850

*Results were obtained for 12 samples and each parameter was analyzed in triplicate. All parameters are expressed as mg/L, except for pH and turbidity (NTU).

Equipment

A hybrid bioreactor (a combination of upflow anaerobic sludge blanket reactor – UASB – and biofilter), made of Plexiglas (total height = 0.8 m, diameter = 0.19 m) with a working volume of 16.3 L, was employed. The reactor had three sections: the first section, located from the bottom of the reactor up to 0.3 m, was formed by the sludge blanket; the second, with a height of 0.4 m, was filled with a support material; and the last section consisted of a bell-shaped solid-liquid-gas separation system to separate gas bubbles and to send them to the biogas outlet canalization in the upper part of the reactor. Six sampling points were established at 0.1, 0.22, 0.37, 0.49, 0.61 and 0.7 m from the bottom of the reactor. Temperature was not controlled, but it was monitored by two thermometers fastened to the side of the bioreactor in order to give a temperature reading at the central point of the sludge blanket and biofilter. During the operational period, the temperature in the sludge blanket and biofilter remained in the range of 29 ± 2°C and 30 ± 2°C, respectively. The bioreactor was continuously fed at different flow rates in order to obtain different hydraulic retention times. The gas was continuously evacuated and its volume was measured with a gasometer.

The support material used to immobilize the bacterial biomass and to avoid loss of solids was coconut shells prepared in the form of an equilateral triangle with each side measuring 0.025 m. Coconut water is widely consumed in Brazil generating large amounts of shells, a residue that can be recycled as raw material for different purposes. The widespread availability and low cost of this residue in addition to other characteristics (its durability is high and it causes no clogging in the biofilter bed) make it good material to be used as support in bioreactors. The coconut shell bed had 60% porosity and a density of 0.95 – 1.1 g/mL. A schematic representation of the reactor used in the experiments is shown in Figure 1.

Sludge Acclimatization

The reactor was inoculated with granular sludge from an anaerobic reactor used in a tobacco industry after acclimatization to the industrial wastewater. After the acclimatization period, the sludge had the following characteristics: intense black and homogeneous color and mineral and volatile suspended solids of 84,000 and 45,000 mg/L, respectively. The sludge was acclimatized in a 40 L reactor, operated in a 24 h batch mode at a temperature of 35°C for approximately three months. During this period, the proportion of wastewater derived from the industrial facility was gradually increased until it comprised 100% of the feed material. Acclimatization was followed by biogas production, changes in pH and COD removal. The pH was adjusted to 7.0 with the addition of sodium bicarbonate at the beginning of each batch. The pH changed during the batch process and the variation was monitored in order to control the progress of the anaerobic degradation process.

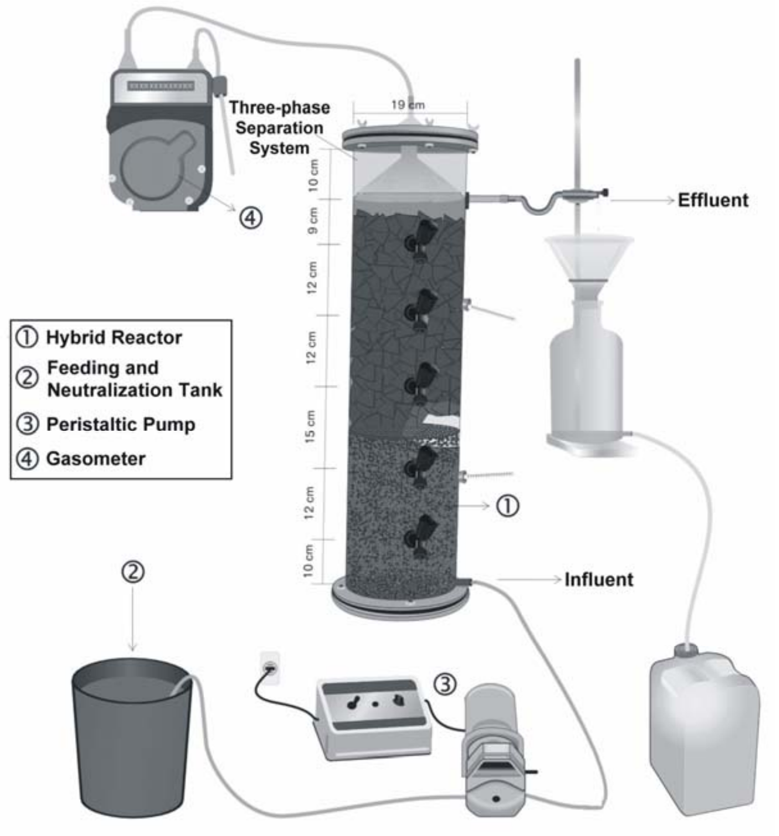


Figure 1: Schematic drawing of the experimental hybrid (UASB + biofilter) reactor.

Start-up and Operation of the Hybrid Bioreactor

Seven liters of adapted sludge were added to the reactor (corresponding to one third of its volume). After a rest period of 24 h, 8.2 L of wastewater were added to the reactor (50% of its volume) and it was allowed to rest for an additional 72 h. Supernatant samples were collected and the analysis indicated 70% COD removal. Shortly thereafter, the entire volume of the reactor was filled with wastewater (16.3 L) which was allowed to rest for 148 h. Once again, supernatant samples were analyzed and continuous feeding began only after 80% COD removal had been achieved. The bioreactor operated for 120 d with hydraulic retention times (HRTs) of 50, 40 and 60 h during 37, 42 and 41 days, respectively, with average organic loads ranging from 0.6 to 2.0 kg COD/m^3 d. The industrial wastewater was supplemented with nitrogen and phosphorus in order to correct the low nutrient levels. A COD:N:P ratio of 150:5:1 was used as a basis for this correction.

Analytical Methods

Reactor influent and effluent samples were periodically collected for analyses performed in accordance with the guidelines of the Standard Methods for the Examination of Water and Wastewater (APHA 1998). Reactor effluent samples for BOD and COD analyses were left to rest for 10 minutes before analysis to avoid interference of small sludge particles occasionally drawn in by the upflow. Biogas production, temperature, pH and COD were determined daily. Volatile acids and bicarbonate alkalinity were determined three times a week. Ammonia nitrogen, TKN and total phosphorus were determined once a week. Turbidity, anionic surfactants (MBAS), TSS, VSS and BOD were determined only once at the end of each regimen studied.

The cellular retention time (CRT) was calculated using the profile of solids in the reactor. This was obtained by analyzing the VSS of samples collected at the sampling points on the side of the reactor. This measure did not consider the biomass adhering to the surface of the packaging material (coconut shells), but rather only the biomass retained in the sludge blanket and within the voids of the biofilter bed. At any rate, the amount of adhering biomass was far smaller than the biomass in granular form. The VSS level of each sampling point was multiplied by the corresponding section volume, giving the mass of solids in each section. The sum of all individual masses resulted in the total volatile solids mass inside the reactor. The CRT was obtained dividing by the total mass of solids in the reactor by the concentration of solids removed per unit of time, i.e.,

$M_r = \sum C_i V_i$

$CRT = M_r / (Q_e X_e)$

where

M_r = total mass of volatile solids in the reactor

C_i = VSS at the sampling points along the height of the reactor

V_i = volume of each sampling section

Q_e = reactor feed rate

X_e = VSS in reactor effluent

RESULTS AND DISCUSSION

The wastewater characteristics were highly variable over time (Table 1). This variability is due to alterations in the batch characteristics that are associated with market demands. In other words, different compounds and wastewaters are produced each day. In general, wastewaters contain high concentrations of surfactants and chlorides, substances employed in the formulation of detergents and disinfectants. These substances act as bactericides and microbial activity inhibitors, usually impairing the wastewater biological treatment, without a preliminary treatment step.

The progress of COD removal during the acclimatization period is shown in Figure 2. On the twentieth day of operation, a decline in COD removal as a result of substantial modifications in the wastewater characteristics was observed. These modifications may be attributed to the synthesis of new products and some operational problems in the facility, such as an acid spill during its transfer from storage tanks, resulting in a substantial decrease in wastewater pH (from 6.5 to 2.5). Fluctuations in wastewater characteristics occurred throughout the experimental period, delaying the biomass acclimatization.

After the acclimatization period, experiments to monitor the decrease in COD over time were conducted in order to estimate the minimum HRT for continuous operation of the reactor (Figure 3). It was observed that the COD values decreased over time, indicating progressive degradation of organic matter. After 50 h, the COD reduction decreased very little up to the last hour of the experiment. Based on these results, three HRTs were studied: 40, 50 and 60 h. Results from these studies indicated that the nonbiodegradable fraction of the substrate was approximately 17%; this information was used for subsequent calculations of specific biogas production.

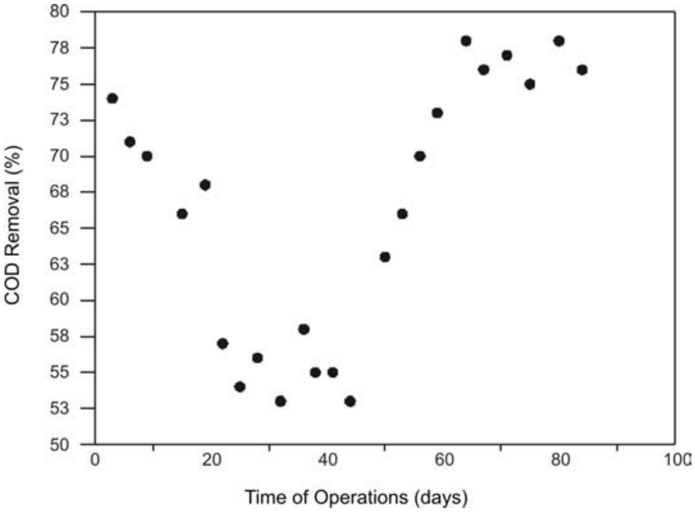


Figure 2: COD removal during the biomass acclimatization period of wastewater in the batch reactor.

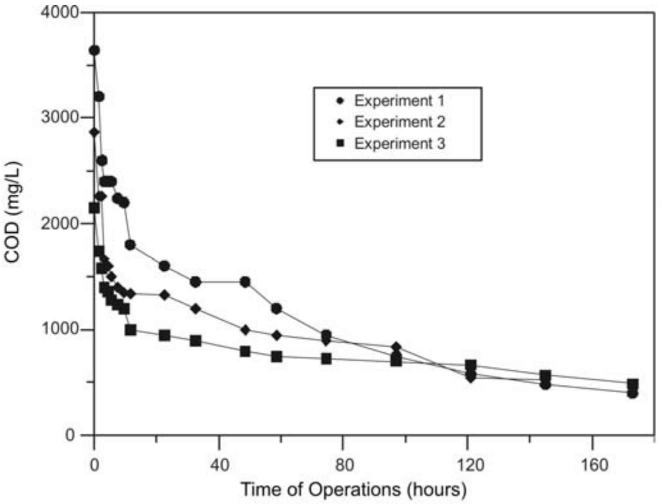
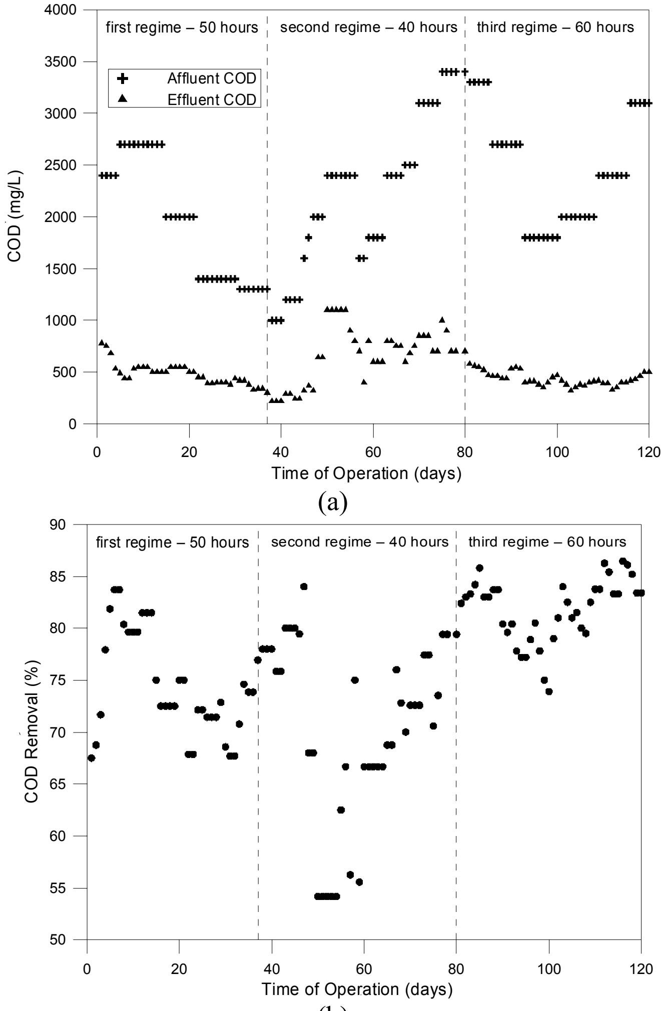


Figure 3: Kinetics of COD removal from the household and personal products industry wastewater after biomass acclimatization.



(a)

(b)

Figure 4: Temporal variations in influent (+) and effluent (▲) COD (a) and COD removal efficiency (b) in the hybrid reactor at different HRTs.

Data on influent and effluent COD obtained during continuous operation of the hybrid reactor are shown in Figure 4a. In the first regimen, despite the variability in COD in the feed material, the effluent COD decreased only slightly, stabilizing at around 340 mg/L. This result indicates that the reactor was efficient in absorbing variations in organic load. However, when the HRT was reduced to 40 h, the effluent COD increased to as much as 1,100 mg/L. COD decreased again when the HRT was increased to 60 h. Figure 4b illustrates the COD removal efficiencies obtained during the three experimental runs. The average COD removal efficiencies were 77, 72 and 80% for HRTs of 50, 40 and 60 h, respectively. In the HRT range studied (40 to 60 h), it had little effect on reactor performance (COD removal), as shown in Figure 3. It was observed that throughout the operational time, a greater stability and the maintenance of the average COD removal values with smaller standard deviations occurred (Figure 4a). During operation of the reactor, the sludge load rate ranged from 0.02 to 0.16 g COD/g VSS d, a value in accordance with those recommended for UASB reactor start-up (0.05 – 0.15 g COD/g VSS d). Since the decrease in HRT (from 50 h to 40 h) was not successful, it was not possible to operate the reactor at higher sludge load rates. This result is in part due to the acclimatization process still in progress and in part due to the characteristics of the wastewater, which had low biodegradability (as exemplified by the BOD/COD ratio of on average 0.37).

During the operational period, the influent pH was maintained at around 6.5 to 7.0 by adding sodium bicarbonate. The effluent pH ranged from 5.8 to 8.0, with an average value of 6.7. Adequate monitoring and control of the anaerobic process are necessary to avoid disturbances in the system that could lead to serious problems, including the total loss of microbial activity. An indicative parameter of the anaerobic process is the excess of volatile fatty acids (Speece 1996). A volatile acidity/bicarbonate alkalinity ratio (VA/BA) higher than 0.3 indicates a disturbance in the anaerobic process (Ripley et al. 1986). During half of the operational period in the first regimen, VA/BA ratios above 0.3 were obtained, suggesting system instability and volatile acid accumulation in the bioreactor. After the twentieth day of operation, VA/BA ratios were lower than 0.3, indicating a stable process through the third regimen (Figure 5).

Considering that the volume of gas produced, V_G (L, measured under standard conditions of temperature and pressure – STP) is proportional to the amount of substrate consumed, then

$$V_G = Y_{P/S} (S_o – S) q$$

where $Y_{P/S}$ is the yield coefficient (L /g COD), S_o and S are the substrate concentrations (g COD/L) and q is the volumetric feeding flow rate (L/d). By plotting this equation in the form (V_G/t) vs $[(S_o-S)q]$ over the range of all test conditions, an average value of 0.32 L biogas STP/g COD for the yield coefficient is obtained (Figure 6). The percentage of methane gas in the biogas produced was about 60%, resulting in a yield coefficient of 0.19 L CH_4 STP/g COD. This value is lower than the maximum theoretical methane production (0.35 L CH_4 STP/g COD) and lower than those reported in the literature. An average value of 0.32 L CH_4/g COD was obtained using synthetic wastewater, baker´s yeast and meat processing industry wastewater (Büyükkamaci and Filibeli 2002). A methane yield of 0.346 L CH_4/g COD from a hybrid reactor treating palm oil mill effluent was reported (Najafpour et al. 2006). Low specific biogas production might be due to the accumulation of organic matter inside the filter (upper section of the bioreactor), which is caused by imperfect mixing resulting in the consumption of organic matter for maintenance instead of cell growth, and thus a reduction in process stability (Berardino et al. 2000). The effect of various surfactant concentrations (loads of 21.7 – 217 g/kg cell dry weight) on starch anaerobic digestion was studied (Feitkenhauer and Meyer 2002). Starch hydrolysis was inhibited at loads above 65 g/kg, and acidogenesis demonstrated the greatest resistance to surfactant inhibitory effects, whereas methanogenesis proved to be the most sensitive. The authors reported a biogas production rate of 0.2 L/d for dodecylsulfate concentrations from 150 to 500 mg/L over a 40-day process period. This value is lower than the production rate found in the current study (Figure 6).

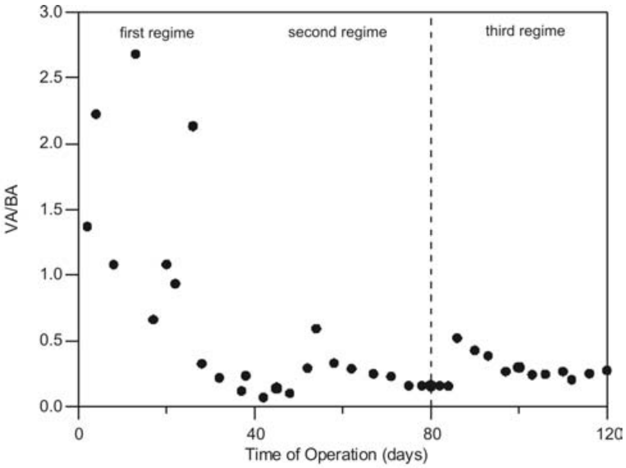


Figure 5: Evolution of the volatile acidity/bicarbonate alkalinity ratio (VA/BA) during the operational period.

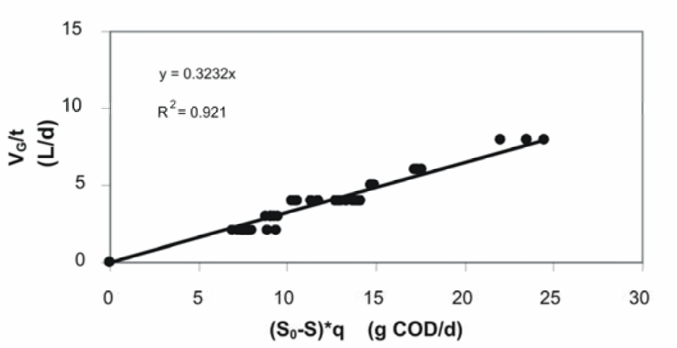


Figure 6: Specific biogas production during the operational period under different conditions.

Using VSS concentration *vs* reactor height, it was possible to calculate the biomass concentration in the reactor and sludge bed zone, with values from 29 to 31 and from 76 to 80 g VSS/L, respectively. These concentrations are similar to those reported in the literature: 20 – 40 and 40 – 70 g VSS/L in the reactor and sludge bed zone, respectively (Stronach et al. 1986). The cellular retention times were 878, 347 and 987 d for runs operated at HRTs of 50, 40 and 60 h, respectively. These high cellular retention times are probably due to a combination of various biomass retention mechanisms: sludge granulation, retention in support matrix and biofilm formation. The lower value of 347 d for the 40 h run compared with those of the other two runs may be explained by the intense loss of biomass during the first days of this regimen, even though values corresponding to effluent TSS, VSS and turbidity reported in Table 2 were not demonstrated because they are values of samples collected at the end of the regimen. The lower COD removal values in this regimen are probably related to a lower biomass concentration in the reactor.

Data corresponding to other parameters analyzed immediately after steady state was established in the reactor are shown in Table 2. Turbidity, anionic surfactants and BOD_5 removals of approximately 73, 75 and 90%, respectively, were observed in the third regimen. Analyzing the average surfactant and BOD removals, a relation between these values is observed. BOD removal increases with surfactant removal, proving the inhibitory effect of the former on the BOD removal. The removal of organic N corresponded to increased ammonia N concentration, which also contributed to maintaining alkalinity in the reactor. Turbidity values were 90, 100 and 80 NTU for HRTs of 50, 40 and 60 h, respectively. These turbidity values in the reactor effluent were so low that it could essentially be considered clear.

Table 2: General characterization of the reactor influent and effluent for the three hydraulic retention times (HRTs) studied.

Parameter	1st Regimen (HRT = 50 h)		2nd Regimen (HRT = 40 h)		3rd Regimen (HRT = 60 h)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Total suspended solids	400	50	600	40	600	30
Volatile suspended solids	240	< 20	400	< 20	370	< 20
Turbidity	260	90	300	100	300	80
Total nitrogen	20	7	81	51	50	12.5
Ammonia nitrogen	1.7	3.7	7	21	5	12
Total phosphorus	2.5	4.4	16.5	39.0	5.5	10.5
Anionic surfactants	316	100	343	112	350	87
BOD_5	1100	200	1100	270	1200	120

All concentrations are expressed as mg/L, except for turbidity (NTU). Data are from samples collected after steady state had been achieved during each run studied.

CONCLUSIONS

The hybrid bioreactor (upflow anaerobic sludge blanket reactor plus biofilter) proved to be efficient in the treatment of wastewaters from the household and personal products industry when operated with organic loads ranging from 0.6 to 2.0 kg COD/m^3 d. Average COD removal efficiencies of 77%, 72% and 80% were obtained with HRTs of 50, 40 and 60 h, respectively. BOD_5 removal of approximately 90% was obtained at all HRTs. Effluent produced by the reactor came out clear, with a turbidity below 100 NTU. The average specific biogas production oscillated around 0.32 L/g COD, regardless of the organic load applied. The sludge retention in the reactor yielded very good values, with cellular retention times above 300 days. The hybrid bioreactor proved to be efficient in the removal of TSS and VSS, yielding average removals of 92%.

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