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Anaerobic treatment of low-strength wastewater with a high fraction of particulate matter in an unconventional two-phase ASBRs system

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ABSTRACT

The results of a two-phase anaerobic system using anaerobic sequencing batch reactors (ASBRs), treating low-strength wastewater (COD ~ 500 mg/L) with a high fraction of particulate organic matter (70%, COD basis), are presented. Two reactors in series were used; the first one was hydrolytic–acidogenic, while the second one was methanogenic. This configuration was proposed to promote high efficiency solids removal. During the experiment, 69% and 50% efficiencies of total COD removal were obtained for OLRs of 0.63 and 1.22 kgCOD/(m³ d), respectively. Values of the solubilized organic fraction (SOF) achieved in the hydrolytic–acidogenic reactor were within the range of 0.3–0.6 gCOD_{solubilized}/gCOD_{removed}, and the average acidified organic fraction (AOF) was 0.6 gCOD_{VFA-produced}/gCOD_{fed}. The methanogenic reactor had a VFA removal fraction (VFARF) between 0.4 and 0.6 gCOD_{VFA-removed}/gCOD_{VFA-fed} for the OLR of 0.63 and 1.22. The two-phase ASBR system is suitable, and can be implemented, for the anaerobic treatment of this kind of wastewater.

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1. Introduction

The anaerobic treatment of low-strength wastewater, such as domestic wastewater, has not been extensively implemented because the process has a lower performance under these conditions. This is because the concentration of organic matter (substrate) is in the same range or near the value of the saturation constant of the anaerobic biomass (K_s). Hence, biomass is not growing at the maximum specific growth rate and, at the same time, is consuming the substrate at a low-degradation rate (with respect to the Monod kinetics). Moreover, if a high fraction of particulate or suspended organic matter is present ($\geq 0.45 \mu\text{m}$), the overall reaction slows down even further since hydrolysis of the complex composite particulates must first occur [1], which can become the limiting step of the whole process.

The application of a two-phase anaerobic system to treat this type of effluent may present significant advantages over a one-phase system. The separation of the main reactions of anaerobic digestion, acidogenesis and methanogenesis, allows the selection and enhancement of microbial populations in each reactor in terms of temperature and pH as well as control of the intermediate products [2]. Pohland and Ghosh [3] proposed the separation of acid-producers and acid-consumers in two reactors in order to opti-

mize the activity of each population, improving their particular environmental and operational conditions.

The implementation of these systems has focused on the treatment of high-strength waste and wastewater using continuous anaerobic reactors. Different configurations have been evaluated: CSTR + UASB [4,5], CSTR + CSTR [6–10], and CSTR + UAF [11].

The anaerobic sequencing batch reactors (ASBRs), developed by Sung and Dague [12], is an anaerobic digestion system that works through consecutive cycles of operation, each of which has the following stages: feeding, reaction, settling, discharge and idle time. At the beginning of the reaction stage, the concentration of organic matter is at its maximum level, which in turn maximizes the degradation rate since the substrate is greater than the K_s . This situation presents an important kinetic advantage over continuous systems, where the concentration of substrate in the reactor is equal to the effluent, which is lower than the K_s [13]. Thus, the application of a two-phase ASBR system, besides enriching the development of both populations, can increase their growth rate and hence their degradation ability, improving the acidogenesis and hydrolysis rates in the first reactor and methanogenesis rate in the second one, and the overall performance of the system.

Few studies have evaluated or tested a two-phase system with ASBRs. Dugba and Zhang [14] worked with two ASBR in series, but in this case the objective was to study the effect of temperature (thermophilic/mesophilic, thermophilic/thermophilic) using an industrial effluent. Bouallagui et al. [15] reported a study with two-phase ASBR system (acidogenic and methanogenic), in which fruit and

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Nomenclature

ASBBR	anaerobic sequencing batch biofilm reactor
ASBR	anaerobic sequencing batch reactor
COD_{VFAi}	COD of VFA of the ASBR1 influent
COD_{VFA1}	COD of VFA of the ASBR1 effluent
COD_{VFA2}	COD of VFA of the ASBR2 effluent
k_H	hydrolysis catalytic constant
K_{S1}	saturation constant of acidogenic biomass
K_{S2}	saturation constant of methanogenic biomass
OLR	organic load rate
pCOD	particulate COD
pCODi	particulate COD of the ASBR1 influent
pCOD1	particulate COD of the ASBR1 effluent
sCOD	soluble COD
sCODi	soluble COD of the influent
sCOD1	soluble COD of the ASBR1 effluent
tCOD	total COD
VFA	volatile fatty acids

Greek letters

μ_{M1}	maximum specific growth rate of acidogenic biomass
μ_{M2}	maximum specific growth rate of methanogenic biomass

vegetable wastes were treated. The focus was to optimize each of the reactions, which resulted in over 80% hydrolysis in the first reactor and high percentages of biogas production (320 L/kgCOD_{effluent}) in the second reactor. Both studies were carried out with high-strength substrates.

The objective of this study was to implement and evaluate the performance of a two-phase ASBR system in the treatment of low-strength wastewater with a high fraction of particulate organic matter, simulating domestic wastewater.

2. Materials and methods

2.1. Experimental setup

Two laboratory scale reactors of acrylic, both with a total volume of 6 L and effective volume of 5 L were used (ASBR1, hydrolytic–acidogenic and ASBR2, methanogenic). Both reactors were jacketed and the temperature kept at approximately 35 °C. The

reactor was mixed by liquid recirculation during the reaction step. Peristaltic pumps were used for feedings, effluent discharge and mixing. The automated operation of the system (pumps, valves and mixer) was programmed using timers and counters in Microwin STEP7 using a PLC Siemens S7200. Fig. 1 shows a diagram of the system used in this study. The time distribution for the stages in each reactor was as follows: feeding 15 min, settling 30 min, discharge 20 min, and idle time 5 min. The reaction times were 410 and 180 min for OLR1 and OLR2, respectively.

The ASBR1 was fed with synthetic wastewater that simulated domestic wastewater with the following composition: Potato solution 2.0 g/L, ovalbumin 0.12 g/L, vegetable oil 0.025 g/L, urea 0.033 g/L. In addition to the macronutrients NH₄Cl 0.074 g/L and KH₂PO₄ 0.01 g/L, the following micronutrients were added: FeCl₃·4H₂O 4.0 mg/L, ZnCl₂ 0.1 mg/L, MnCl₂·4H₂O 1.0 mg/L, CoCl₂·6H₂O 4.0 mg/L, CuCl₂·2H₂O 0.06 mg/L, NiCl₂·6H₂O 0.1 mg/L, H₃BO₃ 0.1 mg/L, Na₂SeO₃·2H₂O 0.2 mg/L and (NH₄)₆MoO₇·4H₂O 0.18 mg/L. To maintain the alkalinity of the system, 0.5 g/L NaHCO₃ was added. The ASBR1 was seeded with acidogenic sludge, with negligible methanogenic activity. The ASBR2 was fed with the effluent of the ASBR1 and it was seeded with an anaerobic granular sludge, with a methanogenic activity of 0.62 gCOD_{CH₄}/(gVSS d). Each of the reactors was inoculated in order to obtain an initial biomass concentration of 5 gVSS/L.

2.2. Start-up and operation of the two-phase system

The start-up was carried out with the operation of ASBR1 at an OLR of 1.21 ± 0.12 kgCOD/(m³ d) (3 cycles/day) and a pCODi/tCODi ratio of 0.66 ± 0.04 . Once start-up of the ASBR1 was complete, the ASBR2 was connected to the system and fed with the discharge of ASBR1. A system OLR of 0.63 ± 0.064 kgCOD/(m³ d) with a pCODi/tCODi ratio of 0.67 ± 0.04 was applied, as well as a second system OLR of 1.22 ± 0.16 kgCOD/(m³ d) (6 cycles/day) with a pCODi/tCODi ratio of 0.70 ± 0.04 . The dynamic behavior of the reactor was analyzed by follow-up procedures, which were done by taking consecutive samples during the reaction stage in both reactors. The first samples were taken from the ASBR1. Samples were then taken from ASBR2 when the effluent was fed from the ASBR1.

2.3. Analytical methods

During the operation of the system, the influent to the system, the ASBR1 and the ASBR2 effluents were sampled for the following analysis: total COD (tCOD) and soluble COD (sCOD) were measured by the Closed Reflux-Titrimetric Method [16]; samples for sCOD

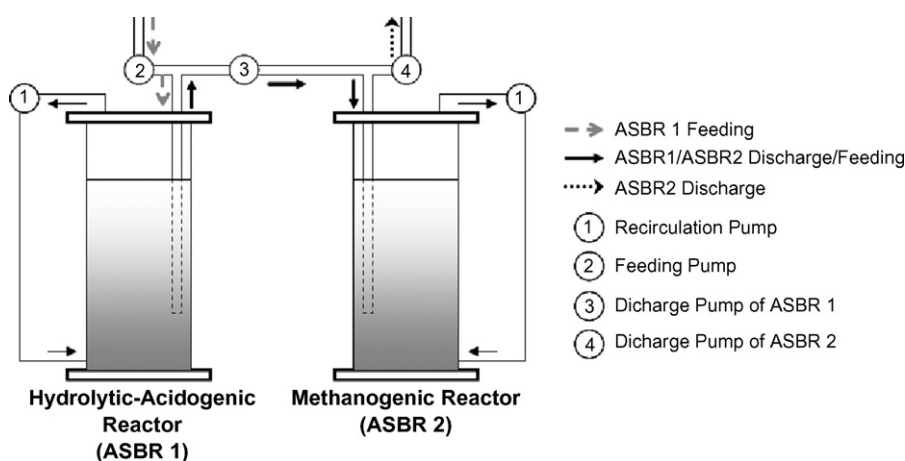


Fig. 1. Schematic diagram of the two-phase system implemented for the anaerobic treatment of low-strength wastewater with a high fraction of particulate organic matter.

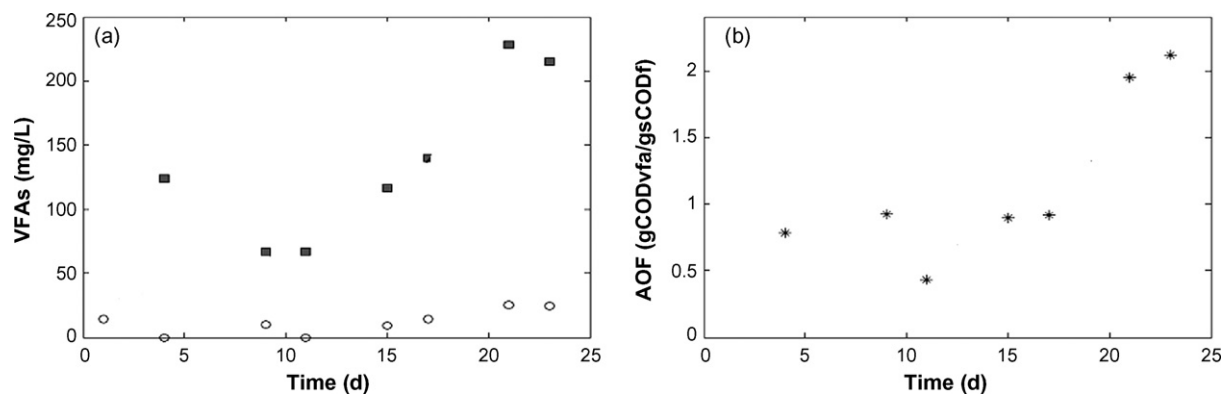


Fig. 2. VFA Concentration (a) and AOF performance (b) during the start-up of ASBR1: (■) acetic acid; (○) propionic acid; (*) AOF.

and volatile fatty acids (VFA) were filtered through glass-fiber filter paper (Whatman GF/C), and the VFAs were determined by gas chromatography [16]; total alkalinity (TA) and intermediate (IA) alkalinity were measured by Titration Method [16]; total suspended solids (TSS), total volatile suspended solids (TVSS) and pH were analyzed according to Standard Methods [16]; the methane produced in the ASBR2 was measured by the indirect method, for the displacement of a NaOH 3 M solution connected to the reactor head space.

2.4. Performance parameters

To determine and evaluate the solubilization (hydrolysis process), acidification and VFA removal activity, several performance parameters were defined.

The solubilized organic fraction (SOF) is the ratio between the solubilized COD and the particulate COD removed in the ASBR1 (Eq. (1)). The solubilized COD is the difference between the soluble COD of the ASBR1 effluent and the soluble COD of the ASBR1 influent. Thus, if the removal of pCOD was done by settling and not by hydrolysis, an important change will not occur in the sCOD, and hence the SOF will be less. The maximum value of 1 corresponds to a solubilization of 100%:

$$\text{SOF} = \frac{\text{sCOD}_1 - \text{sCOD}_i}{\text{pCOD}_i - \text{pCOD}_1} \quad (1)$$

The acidified organic fraction (AOF) is the ratio between the COD of the VFAs produced during the acidification process and the soluble COD of the ASBR1 influent (Eq. (2)). To determine the COD of the VFAs, the concentration of each VFA was multiplied by the conversion factor (1.07, 1.51 and 1.82 gCOD/gVFA for acetic, propionic and

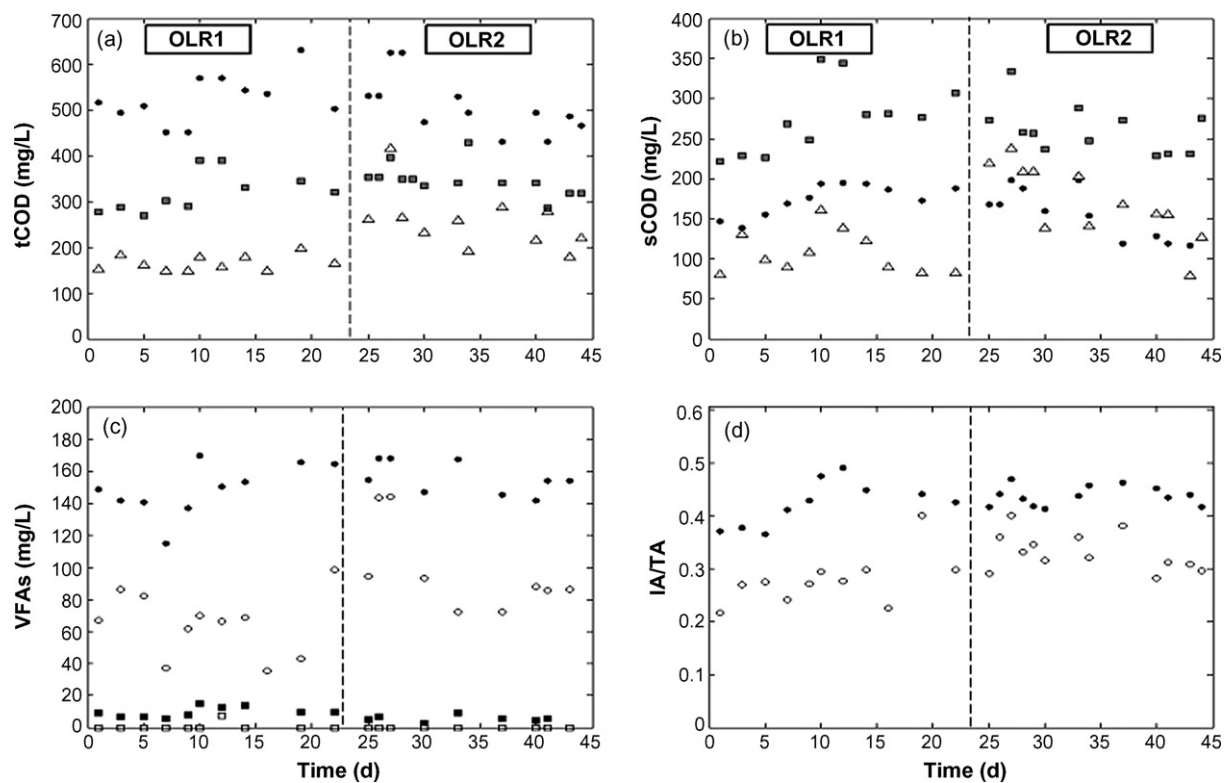


Fig. 3. Operation of the two-phase system during phase II: (a) and (b) tCOD and sCOD of the system, respectively: (■) influent; (■) ASBR effluent; (△) ASBR2 effluent. (c) VFA concentration of the system: (●) acetic acid of ASBR1 effluent; (○) acetic acid of ASBR2 effluent; (■) propionic acid of ASBR1 effluent; (□) propionic acid of ASBR2 effluent. (d) (●) Alkalinity ratio of ASBR1 effluent; (○) alkalinity ratio of ASBR2 effluent.

butyric acid, respectively). Finally, the values obtained were added:

$$\text{AOF} = \frac{\text{COD}_{\text{VFA}1} - \text{COD}_{\text{VFA}2}}{\text{sCOD}_i} \quad (2)$$

The VFA removal fraction (VFARF) for the ASBR2 correspond to the ratio between the COD of the VFAs degraded in the ASBR2 and the COD of the VFAs fed to the ASBR2 (Eq. (3)):

$$\text{VFARF} = \frac{\text{COD}_{\text{VFA}1} - \text{COD}_{\text{VFA}2}}{\text{COD}_{\text{VFA}1}} \quad (3)$$

3. Results and discussion

3.1. Start-up

The start-up of ASBR1 lasted 23 days and finished when it was producing about 220 mg/L of acetic acid at the end of the cycle, which is equivalent to $0.47 \text{ gCOD}_{\text{VFA}}/(\text{Ld})$, on average, indicating that the acidogenic process was being achieved. Fig. 2(a) shows the VFA concentration at the end of each cycle during the start-up. Significant increase in the production of VFA was observed throughout the start-up period (mainly acetic acid was produced). Fig. 2(b) shows the evolution of AOF during this period, which obviously shows a similar behavior. From then, the methanogenic reactor (ASBR2) was incorporated to the system.

3.2. Operation

Fig. 3 shows the behavior of the main variables of the system during the whole operation of the two-phase reactor. During OLR1, ASBR1 and ASBR2 had removal efficiencies of tCOD of $38.8 \pm 6.0\%$, and $47.2 \pm 6.8\%$, while the overall system reached a $68.4 \pm 2.7\%$ of removal efficiency. It can be noted that the sCOD of the ASBR1 effluent was greater than the influent, indicating a high-rate solubilization process (Fig. 3(b)). As expected, a higher concentration of acetic acid than propionic acid was found (between 15- and 20-fold), which mostly occurs in the presence of high protein and lipid containing substrates or in high-strength substrates like solid waste [17]. The values of the alkalinity ratios were maintained around 0.42 and 0.3 for ASBR1 and ASBR2, respectively, indicating a stable process, especially for ASBR2.

During OLR2, ASBR1, ASBR2 and the overall system had tCOD removal efficiencies of $31.4 \pm 8.2\%$, $36.7 \pm 13.9\%$ and $49.6 \pm 10.8\%$, respectively. After the OLR increase, the system showed a short unstable period, and ASBR2 decreased its efficiency in VFA degradation; however, after 6 days, stable conditions of removal were reached again. Despite, the OLR increase, the system maintained tCOD removal efficiencies close to 50%. At the beginning, the alkalinity ratio was mostly affected in the ASBR2 due to the increase of the OLR, which reached values near 0.4, showing a slight VFA accumulation (which does not produce inhibition of the methanogenic biomass activity, due to the low strength of the wastewater). As will be discussed later, 4 days after the alkalinity ratio reached a value of 0.3, it remained constant. The volumetric productivity rate of VFAs was maintained during the whole operation between 0.40 and $0.42 \text{ gCOD}_{\text{VFA}}/(\text{Ld})$, lower than the reported value of $1.20 \text{ gCOD}_{\text{VFA}}/(\text{Ld})$, in the solid waste treatment [15].

Bodik et al. [18] studied the performance of an ASBR treating diluted wastewater, obtaining an 88% removal efficiency for tCOD; this result was obtained at a similar HRT used in this study. The wastewater used by Bodik et al. [18] consisted mainly of soluble COD (mixture of raw domestic wastewater plus glucose and acetate), which made up more than 60% of the solution. Furthermore, after the supplementation, the tCOD in the feeding was close to 650 mg/L throughout the study; therefore, the treatment conditions were more advantageous for anaerobic digestion, which

could explain their results. Sarti et al. [19] studied two different mixing systems in an ASBR treating domestic wastewater, over the same OLR range applied in this study. The reactor with liquid recirculation showed a poor efficiency, obtaining a 40% tCOD removal efficiency, reasonably lower than the removal efficiency obtained in the present study. A better performance was obtained with another ASBR operated under mechanical mixing, reaching 60% tCOD removal. A periodic washout of biomass occurs with both mixing systems. Ratusznei et al. [20], using an ASBR with immobilized biomass (ASBBR) and a mechanical stirrer, treated synthetic domestic wastewater and obtained an 86% removal efficiency for tCOD. This result was attained with a high speed of rotation (750 rpm), thus, part of the solubilization could have been carried out by mechanical stirring and not by biochemical reactions, with an OLR of $0.3 \text{ kgDQO}/(\text{m}^3 \text{ d})$, which lower than that used in the present study.

The pH values of the effluents during the study for ASBR1 were 6.86 ± 0.11 for OLR1 and 6.88 ± 0.09 for OLR2, and for ASBR2, they

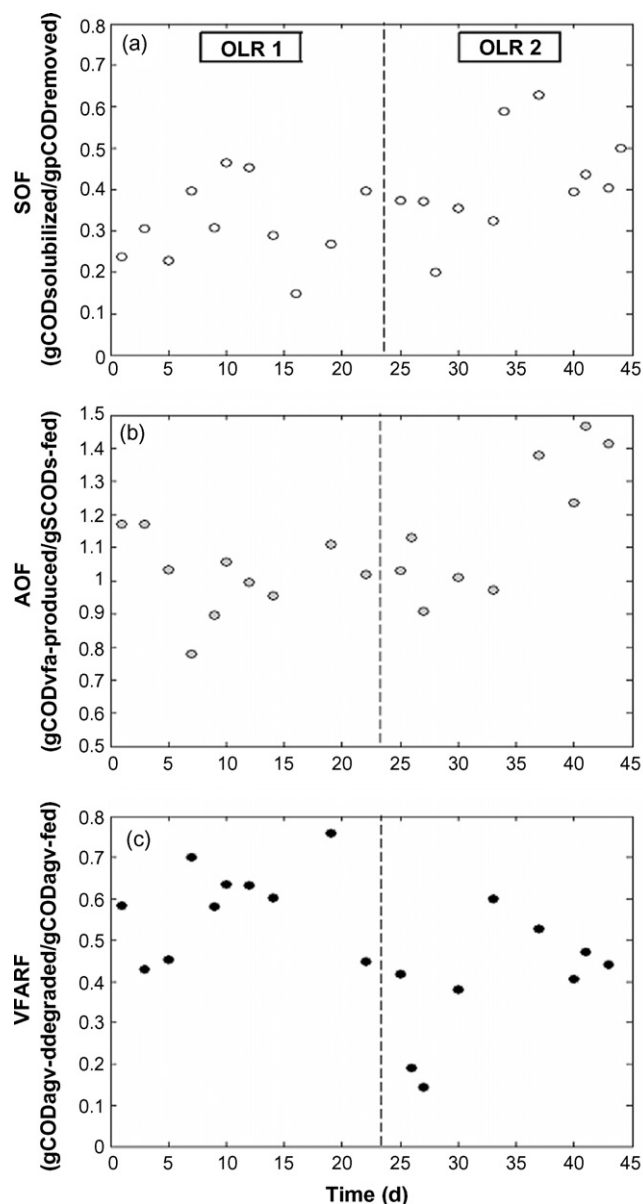


Fig. 4. Behavior of the performance parameters during the two-phase system operation (a) SOF (b) AOF and (c) VFARF.

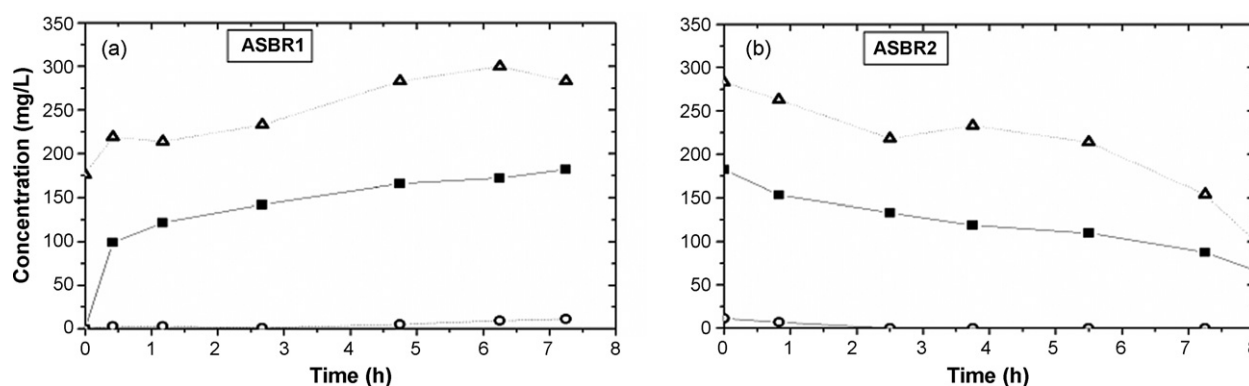


Fig. 5. Follow-ups carried out during a complete cycle of the system operation: (a) ASBR1 and (b) ASBR2: (Δ) sCOD; ($\blacksquare$) acetic acid; ($\circ$) propionic acid.

were 7.07 ± 0.16 and 7.00 ± 0.10 for each OLR, respectively. This increase in the pH in ASBR2 can be explained by the conversion of VFAs into CH_4 and CO_2 , increasing the reactors' alkalinity. This situation was not, apparently, a determining factor in the behavior of the acidogenic process as the good performance of the reactor; Demirer and Chen [8] obtained similar results operating with a pH of around 7.

Due to the low strength of the synthetic wastewaters used in this study, unreliable results of biogas production were obtained (data not shown). This was also reported previously [21,22].

Fig. 4 shows the behavior of the performance parameters of the two-phase system operation. Throughout the study, the SOF was between 0.3 and 0.6 $\text{gCOD}_{\text{solubilized}}/\text{gPCOD}_{\text{removed}}$ (to be equivalent to 30–60% of solubilization). An 81% hydrolysis yield was obtained by Bouallagui et al. [15] in the two-phase anaerobic treatment vegetable waste. In this case, the hydrolysis performance was defined as the difference between the pCOD of the effluent and the influent. This definition is probably not completely reliable for the estimation of this parameter, due to the fact that there is a fraction of the particulate matter that is continuously settling down inside the reactor (during the settling step) and is not removed. This situation is more critical in ASBR where settling steps occur in the same tank as the treatment. A similar value of solubilization yield was reported by Penaud et al. [23], who studied the optimal conditions for the pharmaceutical microbial biomass treatment in CSTR. As in the present study, a high fraction (over 85%) of the tCOD was particulate.

The solubilization was not greatly affected by the increase of OLR, showing a good acclimation of the sludge at these conditions and an adequate solubilization performance of the particulate matter. This was also observed by Pavan et al. [7], who studied the effect of HRT on the performance of a two-phase system treating the organic fraction of municipal solid waste.

The AOF had a value around 1.0 (100%) at OLR1, and it reached a maximum value of 1.3 during the OLR2, which indicates that part of the particulate matter settled in the previous cycle and was also being acidified. This result is significantly higher than those reported by Yeoh [6], who obtained a 15.6% of acidification in a two-phase anaerobic system treating cane-molasses alcohol stillage (which had a VS content of 80 g/L). As in the case of SOF, there were no important changes in the AOF with the increase of OLR.

At the beginning, a sharp increase in VFARF was observed, stabilizing in values between 0.4 and 0.6 during the OLR1. After the increase of the OLR, there was a significant decrease of the VFARF during a short unstable period, which then stabilized at values close to 0.4. This behavior agreed with the alkalinity ratio, confirming that the unstable period was successfully overcome after 6 days.

Fig. 5 shows the dynamic behavior of one cycle at day 22. Clear acidogenic and methanogenic processes and a high concentration of acetic acid were obtained, while propionic acid was negligible. According to these profiles and considering a first-order reaction for hydrolysis, as well as Monod kinetics for acidogenesis and methanogenesis, it was possible to calculate the kinetic parameters of both populations: first-order hydrolytic constant $k_H = 0.99 \text{ d}^{-1}$, $\mu_{M1} = 1.22 \text{ d}^{-1}$, $\mu_{M2} = 0.74 \text{ d}^{-1}$, $K_{S1} = 0.50 \text{ g/L}$ and $K_{S2} = 0.2 \text{ g/L}$.

It should be pointed out, that these results were obtained in two reactors with the same HRT, which is rarely reported because it is assumed that the methanogenesis process is the limiting step. Generally, the methanogenic reactor operates with HRT two or four times higher than the acidogenic reactor.

4. Conclusions

A two-phase anaerobic system with two ASBRs connected in series – hydrolytic–acidogenic and methanogenic reactors – was evaluated for the treatment of a low-strength synthetic wastewater ($\sim 500 \text{ mg/L}$) with a high fraction of particulate organic matter (66–68%). A quick start-up period of the hydrolytic/acidogenic reactor (ASBR1) was obtained, showing a good acclimation of biomass at these treatment conditions. After the connection of the methanogenic reactor (ASBR2), the tCOD removal efficiency was 68% for an OLR of $0.6 \text{ kgCOD}/(\text{m}^3 \text{ d})$, and 50% for an OLR of $1.2 \text{ kgCOD}/(\text{m}^3 \text{ d})$. According with the results and those ones obtained in previous studies the separation of the two groups of microorganisms involved in anaerobic digestion is necessary to improve the performance of the overall process.

Acknowledgement

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