

AnSBBR Applied to the Treatment of Metalworking Fluid Wastewater: Effect of Organic and Shock Load

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Abstract An investigation was performed regarding the application of a mechanically stirred anaerobic sequencing batch biofilm reactor containing immobilized biomass on inert polyurethane foam (AnSBBR) to the treatment of soluble metalworking fluids to remove organic matter and produce methane. The effect of increasing organic matter and reactor fill time, as well as shock load, on reactor stability and efficiency have been analyzed. The 5-L AnSBBR was operated at 30°C in 8-h cycles, agitation of 400 rpm, and treated 2.0 L effluent per cycle. Organic matter was increased by increasing the influent concentration (500, 1,000, 2,000, and 3,000 mg chemical oxygen demand (COD)/L). Fill times investigated were in the batch mode (fill time 10 min) and fed-batch followed by batch (fill time 4 h). In the batch mode, organic matter removal efficiencies were 87%, 86%, and 80% for influent concentrations of 500, 1,000, and 2,000 mgCOD/L (1.50, 3.12, and 6.08 gCOD/L.d), respectively. At 3,000 mgCOD/L (9.38 gCOD/L.d), operational stability could not be achieved. The reactor managed to maintain stability when a shock load twice as high the feed concentration was applied, evidencing the robustness of the reactor to potential concentration variations in the wastewater being treated. Increasing the fill time to 4 h did not improve removal efficiency, which was 72% for 2,000 mgCOD/L. Thus, gradual feeding did not improve organic matter removal. The concentration of methane formed at 6.08 gCOD/L was 5.20 mmolCH₄, which corresponded to 78% of the biogas composition. The behavior of the reactor during batch and fed-batch feeding could be explained by a kinetic model that considers organic matter consumption, production, and consumption of total volatile acids and methane production.

Keywords AnSBBR · Metalworking fluid wastewater · Organic load · Fill time · Shock load

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Nomenclature

AVOL	applied volumetric organic load for non-filtered samples, mgCOD/L.d
BA	bicarbonate alkalinity concentration, mgCaCO ₃ /L
C _{CH4}	methane concentration in gaseous phase, mmol/L
C _I	non-filtered substrate concentration in the influent, mgCOD/L
C _M	methane concentration, mg/L
C _S	filtered substrate concentration in the reactor, mgCOD/L
C _{SF}	filtered substrate concentration in the effluent, mgCOD/L
C _{So}	organic matter concentration in the reactor feed, mgCOD/L
C _{SR}	filtered residual substrate concentration in the reactor, mgCOD/L
C _{ST}	non-filtered substrate concentration in the effluent, mgCOD/L
C _{TVAo}	total volatile acids concentration in the reactor feed, mgHAc/L
C _{TVAR}	residual total volatile acids concentration in the reactor, mgHAc/L
C _{X-TVS}	biomass concentration in total volatile solids in the reactor, g-TVS/L
IVA	intermediate volatile acids concentration via chromatography, mg/L
k _{1S}	apparent first-order kinetic parameter for the conversion of soluble substrate to total volatile acids, g-S/g-S.h
k _{1TVA}	apparent first-order kinetic parameter for the conversion of soluble substrate to total volatile acids, g-TVA/g-S.h
k _{2M}	apparent first-order kinetic parameter for the conversion of total volatile acids to methane, g-CH ₄ /g-TVA.h
k _{2TVA}	apparent first-order kinetic parameter for the conversion of total volatile acids to methane, g-TVA/g-TVA.h
<i>n</i>	number of cycles per day
R-NaHCO ₃ /COD	bicarbonate to organic matter ratio in the influent
R _M	methane formation reaction rate, mgCH ₄ /L.h
R _S	substrate removal reaction rate, mgCOD/L.h
R _{TVA}	total volatile acids reaction rate, mgHAc/L.h
RVOL _{SF}	removed volumetric organic load for filtered samples, mgCOD/L.d
SAOL	specific applied organic load for non-filtered samples, mgCOD/gTVS.d
SROL _{SF}	specific removed organic load for filtered samples, mgCOD/gTVS.d
<i>t</i>	cycle time, h
<i>t_C</i>	total cycle time, h
<i>t_F</i>	filling stage time, h
TS	total solids concentration, mg/L
TSS	total suspended solids concentration, mg/L
TVA	total volatile acids concentration via titration, mgHAc/L
<i>V</i>	volume of liquid medium in the reactor (5 L), L
<i>V_f</i>	volume fed (and discharged) per cycle, L
VSS	volatile suspended solids concentration, mg/L
X _{TVS}	biomass amount regarding total volatile solids, g-tvs
ε _{SF}	substrate removal efficiency for filtered substrate concentration, %
ε _{ST}	substrate removal efficiency for total substrate concentration, %

Introduction

Metalworking fluid wastewater poses a potentially high risk to the environment when disposed of without previous treatment due to the high organic load and bactericides

present. These bactericides include hydrazine, aldehydes, triazine, and isotiazolines. Due to the polluting potential of this type of wastewater, research and development of oils (from soy, sunflower, palm, and animal fat), which increase biodegradability of the emulsion and hence reduce its environmental impact, have become of great importance. In addition, longer utilization times of these fluids are required to render the production processes more efficient [1]. Previous assessment of the treatment and final disposal systems for the used emulsion are required by performing critical analysis of the costs and efficiencies of the treatment options.

Biological treatment of metal-cutting fluid wastewater has been studied by several researches (Table 1). In general, all these treatment schemes have shown to efficiently remove biodegradable organics but leave a substantial amount of residual organics in treated effluents. These residual organics appeared to be either nonbiodegradable or difficult to degrade organics. Approximately 35% of chemical oxygen demand (COD) in the wastewater appeared to be anaerobically nonbiodegradable. Because the anaerobically nonbiodegradable portion was considerable, additional treatment may be needed [2]. Kim et al. [3] preferred the anaerobic/aerobic treatment scheme (anaerobic followed by aerobic) over the straight aerobic scheme because of the lower sludge production, less oxygen supply requirement, and the potential for recovering energy through the production of methane.

Table 1 Metalworking fluid waste treatment (adapted from [4]).

System	Source of waste metalworking fluids	Influent COD (mg/L)	COD removal (%)	References
Aerobic fluidized bed process with sand as carrier	Metallurgical process	2,101~2,306	66~81	[11]
Activated sludge suspended-growth process	Metallurgical process	560~1,500	70~84	[12]
Anoxic/Aerobic process	Metallurgical process	14,000	87	[13]
Aerobic fluidized bed process with sand as carrier	Metallurgical process	N/A	N/A	[14]
Anaerobic fluidized bed process with GAC (granular activated carbon) as carrier	Simulated waste metalworking fluids	3,300	60	[15]
Packed bed reactor with peat as the packing	Metallurgical process	145.9~715.2	64	[16]
Anaerobic fluidized bed process with GAC (granular activated carbon) as carrier	Simulated waste metalworking fluids	1,029~5,324	68	[2]
Aerobic suspended growth	Simulated waste metalworking fluids	3,200~3,600	88	[3]
Aerobic, anaerobic, and aerobic/anaerobic with fluidized bed reactor and suspended growth	Simulated waste metalworking fluids	1,029~5,324	72~100	[17]
Aeration-suspended growth	Metallurgical process	560	26~78	[18]
Aerobic fluidized bed bioreactor with sand as carrier	Metallurgical process	3,000	>90	[19]

Fluidized bed reactors were the only type of attached growth-active sludge system used with sand and granular activated carbon as carriers. The selection of carriers directly affects the overall performance of wastewater treatment and recent developments in carriers have provided other alternatives, such as polypropylene beads, polyurethane foam, and ceramic particles. In the biological treatment, the influent COD concentration varied from 1,000 to 1,337,000 mg/L, which corresponded to organics loadings from approximately 2,400 to 16,800 mgCOD/day. The treatment efficiency in terms of COD removal ranged 60–99%. Most of the influent was simulated wastewater and most of the studies were operated in batch mode [4].

A more recent version of anaerobic reactors separating sludge retention time (SRT) from hydraulic retention time (HRT) is the anaerobic sequencing batch reactor (ASBR). The ASBR popularity stems largely from (1) elimination of a secondary clarifier tank, (2) good biomass retention, and (3) simple operation. The operating principle of the ASBR comprises four stages: feed, react, settle, and decant in a cyclic mode. A sequencing batch reactor, therefore, separates the SRT and HRT in the same reaction chamber so that the solids have a longer retention time while the easily degradable liquid spend a much shorter time in the reactor [5]. Within this context, the ASBR may be a potential alternative for the biological treatment of effluents containing vegetable and mineral oils, such as metalworking fluid wastewaters.

The goal of this investigation was to evaluate the application of a mechanically stirred anaerobic sequencing batch reactor containing immobilized biomass on polyurethane foam in the treatment of metalworking fluid wastewaters, specifically those containing soluble metal-cutting cooling oils, for the removal of organic matter and production of methane. Reactor stability and efficiency were assessed when increasing organic load was applied to the system, by varying the influent concentration, reactor fill time and occurrence of shock load.

Materials and Methods

Experimental Set-Up

The anaerobic sequencing batch reactor containing immobilized biomass (AnSBBR) consisted of a 20-cm high cylindrical acrylic flask with diameter of 20 cm and useful volume of 5 L, as shown in Fig. 1. Stirring frequency was 400 rpm provided by a variable speed motor coupled to a three-blade impeller with 6-cm outer diameter [6]. The impeller was installed inside a draft tube. The function of this draft tube was to optimize the flow direction inside the reactor by providing axial mixing and/or flowing features. Feed and discharge were performed by diaphragm pumps. Pumps and stirrer were turned on and off by an automatic timer system so as to implement the sequencing batch operation stages: feed, react, and discharge. To reach constant temperature at 30 °C, the reactor was placed inside a thermostatic chamber.

Inoculum and Inert Support

The inoculum came from a UASB reactor treating wastewater from a poultry slaughterhouse. The sludge had an initial concentration of total solids (TS) and total volatile solids (TVS) of 62 gTS/L and 51 gTVS/L, respectively.

As support for immobilization of the biomass 5-mm polyurethane foam cubes with an apparent density of 23 kg m⁻³ and porosity near 95% were used. Inoculation was performed

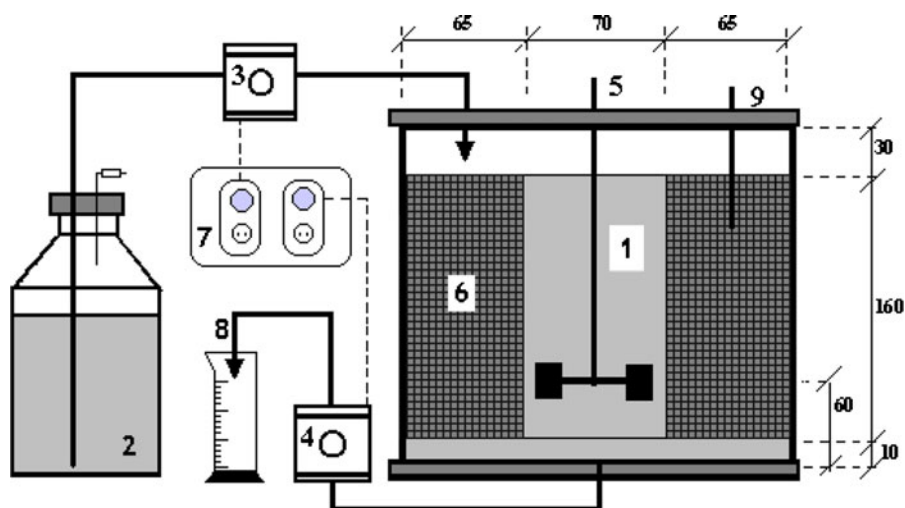


Fig. 1 Scheme of the mechanically stirred anaerobic sequencing batch biofilm reactor containing immobilized biomass and draft tube. (Note (dimensions in millimeters): 1 reaction tank with draft tube, 2 wastewater, 3 feed pump, 4 discharge pump, 5 mechanical agitator, 6 basket containing the immobilized biomass, 7 timers, 8 treated effluent, and 9 thermometer)

according to the method proposed by [7] using sludge from a UASB reactor treating wastewater from a poultry slaughterhouse. The sludge was crushed through a 0.5-mm mesh nylon sieve resulting in a suspension in which the foam was completely immersed. Intense homogenization followed after which 2-h rest was allowed. Poorly adhered solids were washed off and the medium was drained. After this period, the foam with the immobilized biomass was placed in the reactor. Next, to wash out the weakly attached cells, the reactor was fed with the same wastewater used during the experiments. The wastewater was discharged and the inoculum was ready for use in the reactor.

Industrial Wastewater

A synthetic wastewater simulating metalworking fluid wastewater containing soluble metal-cutting cooling oils contaminated with hydraulic mineral oil was produced in laboratory. A mixture of 6 wt% Ecocool Durant 27 (soluble oil) and 1 wt% Renolin B20 (hydraulic oil) was used to prepare this synthetic effluent. This composition is usually found in metalworking fluid wastewaters, in which hydraulic oil is considered as the only contaminant resulting from contact with soluble oil in industrial equipment. This oil mixture was diluted in tap water, forming an emulsion of soluble oil in water contaminated with hydraulic oil. Both oils were supplied by Fuchs do Brasil S/A.

The synthetic wastewater presented an approximate concentration in terms of COD of 100,000 mg/L, according to experimental measurements.

Wastewater concentrations fed to the AnSBBR were 500, 1,000, 2,000, and 3,000 mgCOD/L. All investigated concentrations were supplemented with 200 mgNaHCO₃/L. After preparation and supplementation of alkalinity, the wastewater was characterized in terms of organic matter concentration (as chemical oxygen demand COD for non-filtered samples), total concentration of volatile acids, alkalinity (intermedi-

ate, partial, total, and bicarbonate), pH, and solids concentration (total, total volatile, total suspended and volatile suspended), and then fed to the AnSBBR.

Analytical Methods

During reactor operation, influent and effluent samples were taken for the following analyses: organic matter concentration of the filtered and non-filtered effluent as COD (C_{SF} and C_{ST} , respectively), organic matter concentration of the non-filtered influent as COD (C_I) (spectrophotometric), total volatile acids (TVA—potentiometric) and intermediate volatile acids (IVA—chromatographic), bicarbonate alkalinity (BA—potentiometric), TS and TVS, total suspended solids (TSS) and volatile suspended solids (VSS; gravimetric), pH, and volume fed per cycle (measured in a measuring cylinder). Methods employed were according to [8].

IVA samples were analyzed by gas chromatography, using a gas chromatograph HP6890 with flame ionization detector at 300°C and an HP-INNOWAX column (30 m×0.25 mm×0.25 mm). The injector temperature was kept at 250°C; the oven was held at 100°C for 3 min, after which it was heated at a rate of 5°C min⁻¹ to 180°C and held at that temperature for 5 min.

Composition of the biogas generated by anaerobic degradation was analyzed by gas chromatography using a Hewlett Packard® 6890 gas chromatograph equipped with thermal conductivity detector. The sample volume was 1 mL, drag gas was hydrogen at a flow rate of 50.0 mL/h; the column, injector, and detector temperatures were 35, 60, and 160°C, respectively.

At the end of operation, condition biomass samples were withdrawn from the reactor for microbiological identification, which was performed by means of common optical and phase contrast microscopy employing an Olympus BH2® microscope.

Experimental Procedure

First, an assessment was made of the effect of organic load increase and shock load application, during one cycle, on AnSBBR efficiency and stability. The batch operation cycle was 8 h (480 min), totaling three cycles per day. At the beginning of an operation cycle, the reactor was fed with an approximate wastewater volume of 2.0 l during 10 min. The reaction phase lasted 459 min. At the end of the cycle, the effluent was also discharged in 10 min.

After reaching operation stability, that is, when the monitored effluent variables did not exhibit significant changes from one cycle to the other, a shock load was applied during one cycle. This shock load meant submitting the AnSBBR to a concentration of organic matter twice as high as that of the operation load, maintaining alkalinity supplementation at 200 mgNaHCO₃/L. After applying the shock load, the AnSBBR was operated until stability was regained. The purpose of this stage was to check system robustness to changes that may occur in industrial application. Afterwards, a new operation condition was implemented in the AnSBBR.

Reactor monitoring was performed by measuring the following parameters of influent and effluent samples: organic matter (for non-filtered influent samples, C_I , non-filtered samples, C_{ST} , and effluent filtered samples, C_{SF}), BA, TVA, TS, TVS, TSS, and VSS, in addition to pH and discharged volume. These parameters were monitored at least three times a week.

In a second stage, feeding mode was changed, maintaining the feed volume per cycle (2 L), total cycle time (8 h), and discharge time (10 min), as well as temperature (30°C) and stirring (400 rpm). The same volume was fed per cycle as in the previous tests (i.e., 2 L),

however in two steps. In the first step, 1 L influent was fed during 10 min, thus characterizing batch operation, and in the second step 1 L of influent was fed during 4 h, thus characterizing fed-batch operation. The purpose of this stage was to check the influence of fill time on reactor stability and efficiency as well as system robustness to changes that may occur in industrial application. This operation also used influent concentrations of 2,000 mgCOD/L and 200 mgNaHCO₃/L. System response was assessed when submitted to shock load of 4,000 mgCOD/L during one cycle.

Profiles were run along the operation cycle for a number of monitored variables under all implemented operation conditions and after reaching operational stability, before and after shock loads. These profiles were obtained by collecting samples along 8-h cycle. The relevant variables were concentration of filtered organic matter, total volatile acids, bicarbonate alkalinity, in addition to methane and pH. In this way, it was possible to achieve better comprehension on the degradation routes along a cycle, as well as to estimate the kinetic degradation parameters of organic matter.

Kinetic Model Formulation and Fitting

After reaching stability, verified by the attainment of approximately constant values of the monitored parameters of the effluent at final cycle condition, profiles were taken of filtered organic matter concentrations (C_S), bicarbonate alkalinity, total volatiles (C_{TVA}), intermediate acid, pH and methane (C_M), and carbonic gas concentrations and molar fractions. These profiles allowed better understanding of the organic matter degradation routes during an AnSBBR operation cycle, as well as estimation of kinetic parameters by fitting kinetic model to these profiles. Samples were taken at different time intervals during a cycle and the volume collected did not exceed 300 mL, being always 10% below total volume of wastewater in the reactor. After accomplishment of the profiles, the condition was modified and a new operation phase was started.

The kinetic model used in this work was developed by [9], based on the model of [10]. The latter is an adaptation of another model considered by the International Water Association (IWA) and applied to treatment systems with activated sludge. In the adopted kinetic model, developed for the anaerobic sequencing batch reactor, the anaerobic process of organic matter degradation was simplified in two consecutive steps. In the first one, the substrate (S) is converted into TVA, and in the second, these same acids are transformed into methane (M). Moreover, in the two stages the conversion reactions were considered as being first order. The model also admits the existence of a residual substrate concentration and total volatile acids in which the respective reaction rates were zero. Eqs. 1–4 present the organic matter degradation route and the reaction rate equations of substrate consumption, formation of total volatile acids, and methane formation, respectively.

$$a \cdot S \xrightarrow{k_1} b \cdot TVA \xrightarrow{k_2} c \cdot M \quad (1)$$

$$R_S = k_{1,S} \cdot (C_S - C_{SR}) \quad (2)$$

$$R_{TVA} = k_{1,TVA} \cdot (C_S - C_{SR}) - k_{2,TVA} \cdot (C_{TVA} - C_{TVAR}) \quad (3)$$

$$R_M = k_{2,M} \cdot (C_{TVA} - C_{TVAR}) \quad (4)$$

In Eq. 1, letters a, b and c stand for stoichiometric coefficients, and k_1 and k_2 stand for apparent kinetic parameters of the adopted model. In Eqs. 2, 3, and 4 k_{1S} , k_{1TVA} , k_{2TVA} , and k_{2M} are the same apparent kinetic parameters, but associated with the substrate consumption, total volatile acids formation and methane formation, respectively. C_S and C_{TVA} are the substrate concentration and total volatile acids concentration; and C_{SR} and C_{TVAR} , the residual values of these matters where the reaction rate is zero.

The reactor mass balance must consider two distinct operation conditions being the first one in batch mode and the second in fed-batch mode. Eqs. 5, 6, and 7 present the mass balance of each matter concerning the kinetic model (substrate, total volatile acids and methane), considering the operation in batch mode, whereas Eqs. 8, 9, and 10 refer to the same matters for the operation in fed-batch mode.

$$\frac{dC_S}{dt} = -R_S \quad (5)$$

$$\frac{dC_{TVA}}{dt} = +R_{AVT} \quad (6)$$

$$\frac{dC_M}{dt} = +R_M \quad (7)$$

$$\frac{dC_S}{dt} = \frac{F}{V} \cdot (C_{S0} - C_S) - r_S \quad (8)$$

$$\frac{dC_{TVA}}{dt} = \frac{F}{V} \cdot (C_{TVA0} - C_{TVA}) + r_{TVA} \quad (9)$$

$$\frac{dC_M}{dt} = -\frac{F}{V} \cdot C_M + r_M \quad (10)$$

In Eqs. 5–10, C_S , C_{TVA} , and C_M correspond to the concentrations of substrate, total volatile acid, and methane, respectively, and C_{S0} and C_{TVA0} , the respective feed values; F is the volumetric flow rate and V the reaction volume. These equations were used to determine the kinetic parameters k_{1S} , k_{1TVA} , k_{2TVA} , k_{2M} , C_{SR} , and C_{TVAR} of the model. To deal with the differential equations, Euler numerical integration method was used (constant integration step) implemented in Excel® software. Furthermore, these parameters were calculated using as objective function in the optimization procedure (function *Solver* of the Excel® software) the minimum square error between experimental and kinetic model data.

Results and Discussion

Effect of Organic Load in the Operation with Batch and Fed-Batch Feeding

Tables 2, 3, 4, and 5 contain the mean values of monitored variables for all the investigated conditions. The AnSBBR was submitted to five different experimental conditions in terms

Table 2 Mean values of monitored variables.

Condition	t_f/t_c	C_i (mgCOD/L)	C_s (mgCOD/L)		ε_s (%)		V (L)
			C_{ST}	C_{SF}	ε_{ST} (%)	ε_{SF} (%)	
B-500	0.02	500±37	80±7	67±8	84±1	87±2	2.03±0.05
B-1,000	0.02	1,039±121	173±61	151±60	84±6	86±6	2.03±0.09
B-2,000	0.02	2,026±163	456±77	397±66	77±4	80±3	2.17±0.09
B-3,000	0.02	3,125±210	1,234±222	1,099±216	61±7	65±7	2.14±0.07
FB-4-2,000	0.50	2,052±89	632±135	577±134	69±7	72±7	2.01±0.05

B batch feeding; *FB* fed-batch feeding (4–4 h)

of influent concentration (500, 1,000, 2,000, and 3,000 mgCOD/L), shock load (twice the operating concentration) and fill times (10-min batch and 4-h fed-batch).

In the first condition, the AnSBBR was operated for 30 days (90 cycles) and treated MWF wastewater with concentration of 500±37 mgCOD/L, resulting in an applied volumetric organic load of 1.50 gCOD/L.d. The influent was also supplemented with 200 mgNaHCO₃/L.

The system showed stable concentration values for organic matter in the effluent in a short period of time, as can be seen in Fig. 2a, reaching 87% removal at a volumetric organic load of 1.31 gCOD/L.d in terms of filtered samples. The concentration of total volatile acids was low, both in the influent (27±7 mgHAc/L) and in the effluent (28±8 mgHAc/L). Bicarbonate alkalinity was generated and the influent presented mean values of 214±17 mgCaCO₃/L, whereas the mean effluent values were 227±40 mgCaCO₃/L. Methane concentration in the reactor head space was 0.55 mmol/L, corresponding to a methane-carbon dioxide ratio of 42%.

On day28, a shock load with concentration of 1,020.8 mgCOD/L (twice the operation load) was applied during one cycle (8 h). After application of this shock load, the reactor was operated for 2 days (six cycles) and exhibited virtually the same values of organic matter concentration and removal efficiency for non-filtered and filtered samples as those of the period previous to the shock application.

In the second condition, the AnSBBR was operated for 53 days (159 cycles; Fig. 2b) and treated MWF wastewater with concentration of 1,039±121 mgCOD/L, resulting in an

Table 3 Mean values of monitored variables.

Condition	R NaHCO ₃ /COD	FB (mgCaCO ₃ /L)		TVA (mgHAc/L)		$C_{CH_4}^a$ (mmol/L)
		Influent	Effluent	Influent	Effluent	
B-500	200/500	214±17	227±40	27±7	28±8	0.55 (42%)
B-1,000	200/1,000	250±22	268±28	31±11	31±11	1.65 (61%)
B-2,000	200/2,000	321±13	340±25	27±6	25±6	5.20 (78%)
B-3,000	200/3,000	384±33	399±30	33±5	33±7	–
FB-4-2,000	200/2,000	314±25	368±18	26±3	30±4	4.10 (77%)

B batch feeding, *FB* fed-batch feeding (4-4 h)

^a Methane proportion in the CH₄/CO₂ mixture is shown enclosed in parentheses

Table 4 Mean values of monitored variables.

Condition	TS (mg/L)		TVS (mg/L)		TSS (mg/L)		VSS (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
B-500	510±65	494±15	285±93	223±40	42±14	63±16	25±8	46±12
B-1,000	609±66	581±52	361±53	352±15	54±19	80±15	36±12	54±13
B-2,000	791±79	626±66	519±78	367±73	49±15	73±7	39±17	67±6
FB-4-2,000	805±46	663±97	537±89	408±59	55±11	77±10	43±12	72±9

^a B batch feeding, FB fed-batch feeding (4–4 h)

applied volumetric organic load of 3.12 gCOD/L.d. The influent was also supplemented with 200 mgNaHCO₃/L.

A removal efficiency of 86% was achieved for a removed volumetric organic load of 2.68 gCOD/L.d in terms of filtered samples. Concentration of total volatile acids was low, both in the influent (31±11 mgHAc/L) and in the effluent (31±11 mgHAc/L). The influent exhibited mean bicarbonate alkalinity values of 250±22 mgCaCO₃/L, whereas the mean effluent values were 268±28 mgCaCO₃/L. Comparison of these bicarbonate alkalinity values with those of the previous condition (214±17 mgCaCO₃/L) shows increase in alkalinity, despite the fact that supplementation was maintained at 200 mgNaHCO₃/L. This increase is justified by the increase in influent concentration, since the influent contained alkaline compounds. Methane concentration in the reactor head-space was 1.61 mmol/L, corresponding to a methane-carbon dioxide ratio of 61%.

On day50, a shock load was applied with concentration of 1,874.9 mgCOD/L during one cycle (8 h). After application of this shock load, the reactor was operated for 3 days (nine cycles) and exhibited virtually the same organic matter concentration and removal efficiency values for non-filtered and filtered samples, as those of the period previous to shock load application, as can be seen in Fig. 2b.

Table 5 Mean values of monitored variables.

Condition	AVOL (gCOD/L.d)	SAOL (mgCOD/ gTVS.d)	RVOL _{SF} (gCOD/L.d)	SROL _{SF} ^a (mgCOD/gTVS.d)
B-500	1.50	27.8	1.31	24.3
B-1,000	3.12	57.8	2.68	49.6
B-2,000	6.08	112.6	4.86	90.0
FB-4-2,000	6.16	114.1	4.43	82.0

C'_{X-TS} 1.26 gTS/g-clean foam, X_{TS} 124 gTS, C'_{X-TVS} 1.10 gTVS/g-clean foam, X_{TVS} 108 gTVS ($R_{TVS/TS}$ = 87%),

2,000 mL volume of liquid medium treated by cycle; $2,000 + (2,626 - 98.2 - 124) = 4,404$ mL total volume of liquid medium in the reactor; $C_{X-TS} = 28.2$ gTS/L considering the total volume of liquid medium of 4.404 L; $C_{X-TVS} = 24.5$ gTVS/L considering the total volume of liquid medium of 4.404 L; $C_{X-TS} = 62$ gTS/L considering the total volume of liquid medium of 2.0 L; $C_{X-TVS} = 54$ gTVS/L considering the total volume of liquid medium of 2.0 L

$AVOL = \frac{(V_f \cdot n) \cdot C_L}{V}$; $SAOL = \frac{(V_f \cdot n) \cdot C_L}{X_{TVS}}$; $RVOL_{SF} = \frac{(C_L - C_{SF}) \cdot V_f}{V_{IC}}$; $SROL_{SF} = \frac{(V_f \cdot n) \cdot (C_L - C_{SF})}{X_{TVS}}$

B batch feeding; FB fed-batch feeding (4–4 h)

^a 98.4 g of clean foam and 2,626 g of inoculated foam ($R_{\text{inoculated-foam/clean-foam}} = 26.7$)

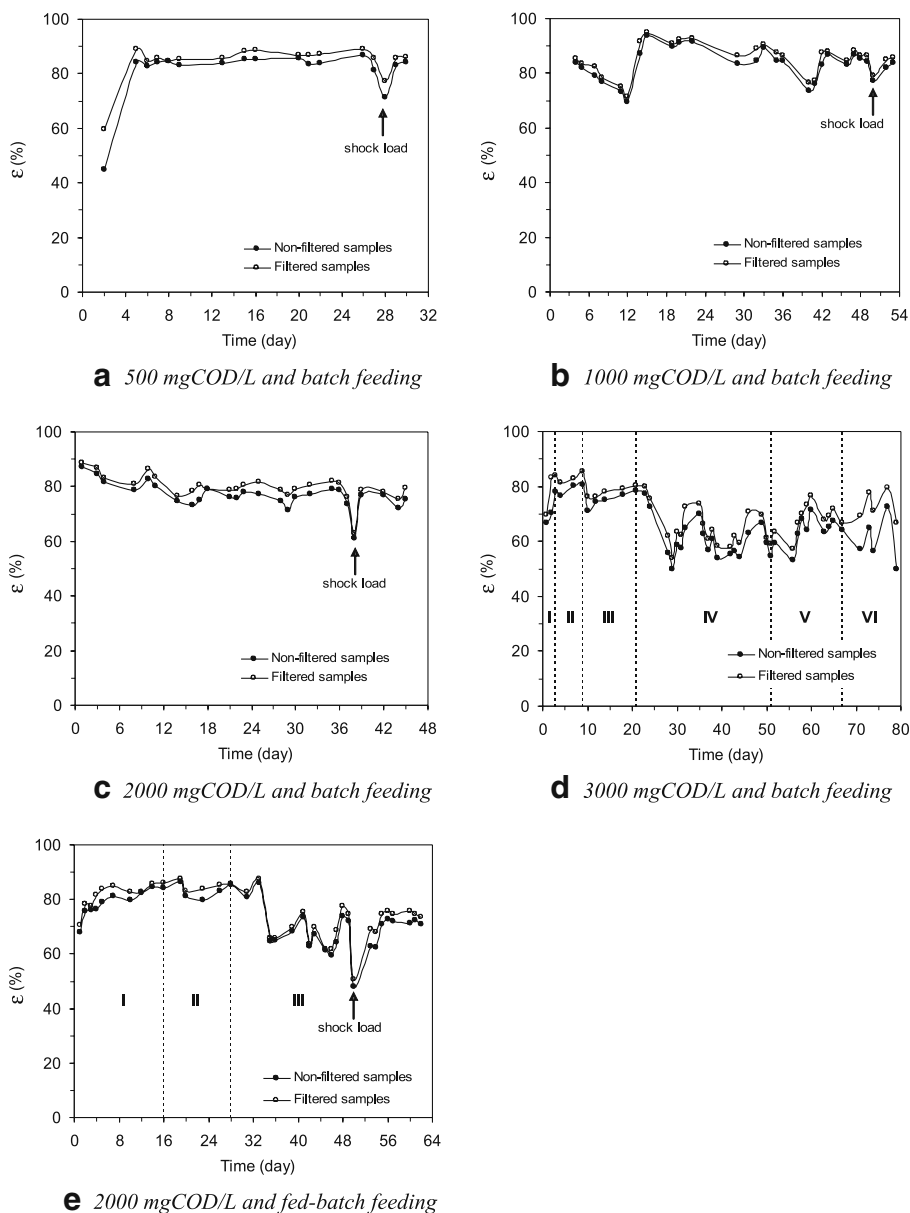


Fig. 2 Removal efficiency for filtered and non-filtered samples; **a** 500 mgCOD/L and batch feeding, **b** 1,000 mgCOD/L and batch feeding, **c** 2,000 mgCOD/L and batch feeding, **d** 3,000 mgCOD/L and batch feeding, and **e** 2,000 mgCOD/L and fed-batch feeding

In the third condition, the AnSBBR was operated for 45 days (135 cycles) and treated MWF wastewater with concentration of $2,026 \pm 163$ mgCOD/L, resulting in an applied volumetric organic load of 6.08 gCOD/L.d. The influent was also supplemented with 200 mgNaHCO₃/L.

The system showed stable concentration values for organic matter in the effluent, in a short period of time, as can be seen in Fig. 2c, reaching 80% removal at a volumetric organic load of 4.86 gCOD/L.d in terms of filtered samples. Total volatile acid concentration was low both in the influent (37 ± 6 mgHAc/L) and in the effluent (25 ± 6 mgHAc/L). The influent exhibited mean bicarbonate alkalinity values of 321 ± 13 mgCaCO₃/L, whereas the mean values of the effluent were 340 ± 25 mgCaCO₃/L. Comparison of the bicarbonate alkalinity values with those of the values in the previous conditions showed an increase in alkalinity despite the fact that supplementation was maintained at 200 mgNaHCO₃/L. As justified in the previous condition, this increase occurred due to the increase in the influent concentration, which contains alkaline compounds. Methane concentration in the reactor head-space was 5.20 mmol/L corresponding to methane-carbon dioxide ratio of 78%.

On day 38 a shock load was applied with concentration of 4,398.6 mgCOD/L during one cycle (8 h). After application of this shock load, the reactor was operated for 7 days (21 cycles) and exhibited virtually the same mean values of organic matter concentration for non-filtered and filtered samples as those of the period previous to the shock load application as can be seen in Fig. 2c.

In the fourth condition, the AnSBBR was operated in six stages (stages I–VI), as shown in Fig. 2d. Alkalinity supplementation was 200 mgNaHCO₃/L in all the stages.

It should be mentioned that after finishing the operation with concentration of 2,000 mgCOD/L, the assays with the AnSBBR was interrupted to repair the agitation motor. To maintain the same procedure of the previous assays (500, 1,000, and 2,000 mgCOD/L), the AnSBBR operation was restarted and influent concentration was gradually increased to allow adaptation of the biomass to higher influent concentration at which it would be submitted to under the next condition, i.e., 3,000 mgCOD/L. This decision was always motivated by the efficiency reduction that occurred between the last two conditions, which indicated that the reactor would be reaching the operation threshold, in terms of organic load applied, at influent concentration of 2,000 mgCOD/L.

Based on the premises above, stage I included AnSBBR operation for 3 days (nine cycles), and MWF wastewater with concentration of 528 ± 41 mgCOD/L. The removal efficiency achieved in this period, in terms of filtered samples, was $83 \pm 1\%$. Next, in stage II, the influent concentration was increased to 964 ± 45 mgCOD/L, and the system was operated for 6 days (18 cycles). The removal efficiency achieved was $83 \pm 2\%$. In stage III, the influent concentration was increased to $2,079 \pm 122$ mgCOD/L, and the system was operated for 12 days (36 cycles). Since the same removal efficiency ($79 \pm 1\%$) as that of the operation before interruption of AnSBBR operation was achieved, it was assumed that the biomass was ready to be submitted to influent with 3,000 mgCOD/L. Thus in stage IV, the AnSBBR was fed with MWF wastewater with concentration of $3,125 \pm 210$ mgCOD/L for 30 days (90 cycles). In this operation period, low removal efficiency ($65 \pm 7\%$) and high values of residual organic matter concentration were achieved in terms of filtered samples ($1,099 \pm 216$ mgCOD/L), and operational stability was not reached. No accumulation of volatile acids occurred, and effluent concentration was very close to that in the influent (33 ± 6 mgHAc/L).

In stage V, the influent concentration was reduced to $2,107 \pm 136$ mgCOD/L to check whether the values of the monitored variables would return to the values prior to the operation with concentration of 3,000 mgCOD/L. This strategy was unsuccessful because after operation for 16 days (48 cycles), the efficiency increased to $68 \pm 5\%$, i.e., less than that expected (80%). Stage VI included further reduction in influent concentration to 483 ± 62 mgCOD/L. Once again, the strategy showed to be unsuccessful because after operation for 12 days (36 cycles) the desired removal efficiency was not achieved, i.e., close to $87 \pm$

1.5%, when AnSBBR was operated with 500 ± 37 mgCOD/L but before the operation with $3,125 \pm 210$ mgCOD/L.

It can thus be concluded that the AnSBBR did not exhibit satisfactory results in terms of treating MWF wastewater with concentration of $3,125 \pm 210$ mgCOD/L and the concentration value of 2,000 mgCOD/L seems to be the threshold value for this configuration.

Based on the above, it was decided to reduce the concentration of wastewater fed to the AnSBBR to 2,000 mgCOD/L and to assess the effect of changing feed strategy. The strategy change was to keep the same influent volume, but to increase fill time, altering batch feeding (10 min) to 4-h fed-batch feeding.

In the fifth condition, the AnSBBR was reinoculated because of the results achieved in the previous condition. Thus, after washing the polyurethane foam and inoculation, it was decided to gradually increase the influent concentration to readapt the biomass to the MWF wastewater. Hence, under this condition, the AnSBBR was operated in three stages (stages I–III), as shown in Fig. 2e.

Stage I included operation of AnSBBR with concentration of 546 ± 36 mgCOD/L for 16 days (48 cycles). In this period, the removal efficiency achieved was $84 \pm 2\%$ in terms of filtered samples. In stage II, the influent concentration was increased to $1,028 \pm 78$ mgCOD/L and the system was operated for 12 days (36 cycles), achieving removal efficiency of $85 \pm 2\%$. Thus, the biomass in the AnSBBR was ready to be submitted to 2,000 mgCOD/L influent.

In stage III, influent concentration was increased to $2,052 \pm 89$ mgCOD/L. In addition, the influent feed strategy was changed. The strategy was to keep the same influent volume (2.0 L) as the previous conditions, but half of this volume (1.0 L) was fed in 10 min and the other half was fed in fed-batch mode in 4 h. The system was operated for 34 days (102 cycles); and at day 22 (day 50 when considering total operation time), it was submitted to a shock load with concentration of 4290.7 mgCOD/L, during one cycle. After application of the referred shock load, the system was operated for 12 days (36 cycles). In this period, the organic matter concentration values for non-filtered (627.3 mgCOD/L) and filtered (550.6 mgCOD/L) samples, and removal efficiency for non-filtered ($69.4 \pm 4\%$) and filtered ($73.2 \pm 3\%$) samples were superior to those in the period before application of the shock load ($69.1 \pm 8\%$ and $71.1 \pm 8\%$, respectively) as shown in Fig. 2e. In addition, the concentration values for volatile acids were low, approximately 30 mgHAc/L.

Thus, the AnSBBR showed to be robust when submitted to an organic shock load in the treatment of MWF wastewater with 2,000 mgCOD/L and 4-h fed-batch feeding. The removal efficiency achieved was $72 \pm 7\%$ in terms of filtered samples for an applied volumetric organic load of 6.16 gCOD/L.d and removed volumetric organic load of 4.43 gCOD/L.d. Total volatile acid concentration was low both in the influent (26 ± 3 mgHAc/L) and effluent (30 ± 4 mgHAc/L). The influent presented mean bicarbonate alkalinity values of 314 ± 25 mgCaCO₃/L, whereas the mean effluent values were 368 ± 18 mgCaCO₃/L.

This removal efficiency value ($72 \pm 7\%$) was lower than that achieved for the batch feeding condition ($80 \pm 3\%$). A justification for this behavior may be based on the contact between wastewater and biomass because when using a reactor with immobilized biomass, contact with the entire biomass occurs only when the reactor is full, that is, when the total volume of 2 L has already been fed. Thus, when only 1 L has been fed in 10 min and the remaining volume (1 L) is fed in 4 h, part of the biomass does not come in contact with the wastewater, but only gradually after 4 h. In addition, gradual feeding reduces the maximum concentration value of organic matter from approximately 1,500 mgCOD/L when the cycle starts at batch feeding (Fig. 3c), to 1,200 mgCOD/L in 1-h cycle time at fed-batch feeding (Fig. 3d). Regarding total volatile acids, the maximum value of approximately 40 mgHAc/L

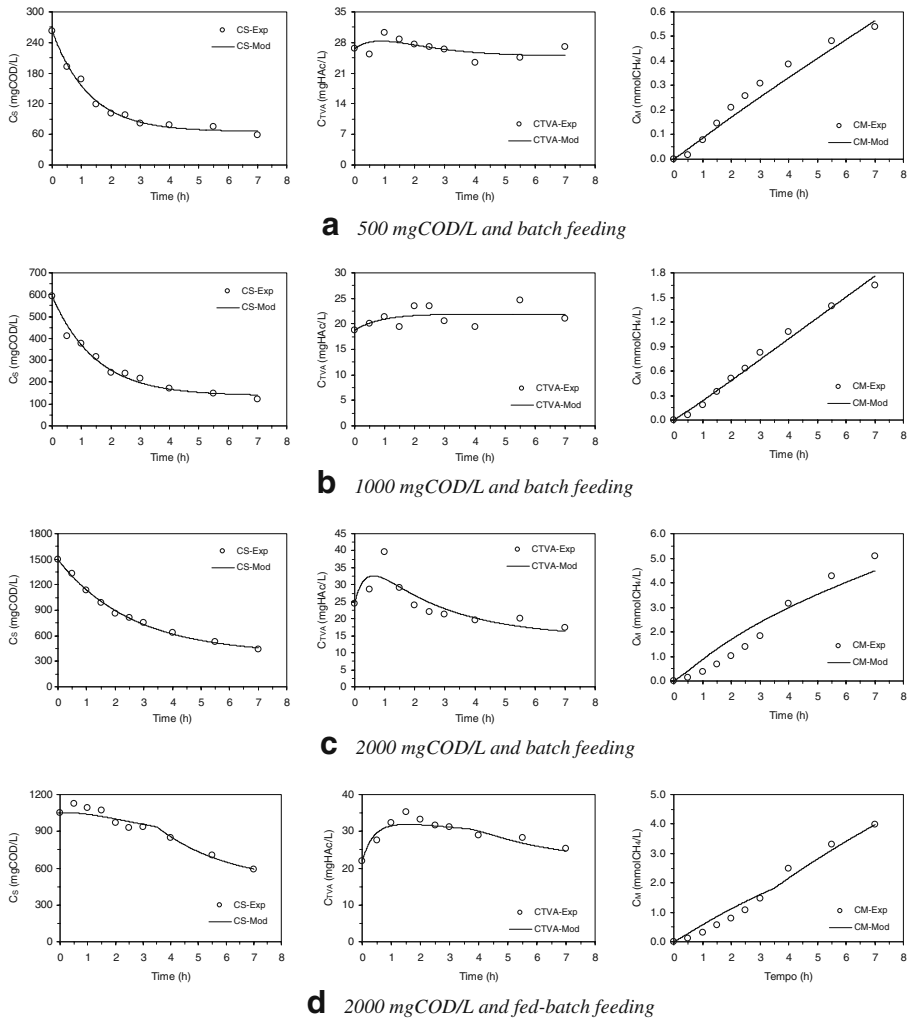


Fig. 3 C_S , C_{TVA} , and C_M profiles in batch and fed-batch feeding; **a** 500 mgCOD/L and batch feeding, **b** 1,000 mgCOD/L and batch feeding, **c** 2,000 mgCOD/L and batch feeding, and **d** 2,000 mgCOD/L and fed-batch feeding

in 1-h cycle time at batch feeding (Fig. 3c), was close to the 35 mgHAc/L obtained in 2-h cycle time at fed-batch feeding (Fig. 3d). Thus, this reduction in the maximum values found along the cycle may be an advantage when potentially toxic compounds are treated, but the reaction rate for organic matter and volatile acid consumption decreases, since this parameter is proportional to concentration.

Table 4 permits to observe that TS and TVS were removed by the treatment and that the inert support retained the biomass inside the reactor, since effluent values were lower than influent ones. However, TSS and VSS presented low values in both influent and effluent with no significant difference when the standard deviations are considered. Microbiological analyses performed on the polyurethane foam showed the presence of *Methanosaeta*-like and *Methanosarcina*-like morphologies, as well as hydrogenotrophic bacilli and nonfluo-

rescent cocobacilli, indicating a diversified community, essential for anaerobic metabolism. Moreover, it should be mentioned that solids analysis of the foam before and after the assays did not detect any difference that might indicate microbiological modification during the experiment.

These results are very important, especially when considering that generation of industrial effluents depends on the process involved and may exhibit considerable fluctuations in terms of volume. Thus, under conditions at which the effluent volume is sufficient to feed the reactor for a short period, i.e., with high feed flow rate, the system may be operated in batch mode. In case of reduced volume generation, feeding may be fed-batch wise with no great losses in the system.

Profiles along Operation Cycle

A first-order kinetic model was fitted to the duplicated experimental values, considering filtered samples, along the operation cycle, for batch and fed-batch feeding at 500–2,000 mgCOD/L. Figure 3a–d, contains the concentration profiles for C_S , C_{TVA} , and C_M and Table 6 contains the values of C_{SR} , C_{TVAR} , and kinetic parameters (k_{1S} , k_{1TVA} , k_{2TVA} , and k_{2M}), as well as the respective value of the square correlation coefficient (R^2).

Comparison of the first-order kinetic values showed that the behavior was similar for all the applied volumetric organic loads studied, i.e., the kinetic parameter decreases as applied volumetric organic load increases. With regard to the residual concentrations of organic matter, the increase in value and the decrease of the stability period at the end of cycle, as applied volumetric organic load increases indicates that the threshold value is close to 6 gCOD/L.d.

Comparison of the operation with applied volumetric organic load of 6.08 gCOD/L.d to that of 6.16 gCOD/L.d, i.e., when applied volumetric organic load applied to the AnSBBR was maintained and feed strategy was changed from batch to 4-h fed-batch, shows similar kinetic parameter (k_{1S}), from 0.39 to 0.38 h^{-1} despite an increase in the fitted residual organic matter concentration (from 385.0 mgCOD/L to 467.6 mgCOD/L), as well as in the experimental residual organic matter concentration (from 440.6 mgCOD/L to 591.4 mgCOD/L). These results are coherent with the decrease in removal efficiency, in terms of filtered samples, for the 4-h fed-batch feeding (from $80 \pm 3\%$ to $72 \pm 7\%$). TVA concentration was higher, during the cycle, for the fed-batch strategy, and the residual TVA concentration was 17.4 mgHAc/L for batch feeding and 25.4 mgHAc/L for the 4-h fed-batch feeding.

Therefore, the change in feed strategy, from batch to fed-batch (maintaining the organic load applied to the AnSBBR), which resulted in a decrease in residual organic matter concentration in terms of filtered and non-filtered samples, and consequent increase in removal efficiency is justified by the model since there was a decrease in the kinetic parameter quantifying substrate consumption (k_{1S}) as well as in the kinetic parameter

Table 6 Summary of the kinetic fit for batch and fed-batch feeding.

Condition*	k_{1S} (h^{-1})	k_{1TVA} (h^{-1})	k_{2TVA} (h^{-1})	k_{2M} (h^{-1})	C_{SR} (mgCOD/L)	C_{TVAR} (mgHAc/L)	R^2
B-500	0.79	0.03	0.98	0.003	65.6	24.9	0.866
B-1,000	0.68	0.01	1.12	0.012	138.0	21.9	0.836
B-2,000	0.39	0.06	2.72	0.028	385.0	14.5	0.943
FB-4-2,000	0.38	0.04	2.32	0.022	467.6	21.9	0.965

quantifying total volatile acid consumption (k_{1TVA}). This behavior agrees with the justification presented above, which states that gradual feeding reduces organic matter concentration and total volatile acids, which might be an advantage, but occasionally decreases system efficiency.

Conclusion

In the first phase of the study, in which AnSBBR feeding was batchwise (feed time 10 min, i.e., with fill time to total cycle time ratio of 0.02), the organic matter removal efficiencies were 87%, 86%, and 80% for influent concentrations of 500, 1,000, and 2,000 mgCOD/L, in which the applied volumetric organic loads were 1.50, 3.12, and 6.08 gCOD/L.d, respectively. Under these conditions, it was necessary to supplement the influent with 200 mgNaHCO₃. Total volatile acid concentrations in the effluent were 28, 31, and 25 mgHAc/L, and the removed volumetric organic loads were 1.31, 2.68, and 4.86 mgCOD/L.d. It was not possible to achieve operational stability at a concentration of 3,000 mgCOD/L, i.e., the organic load of 9.38 gCOD/L.d when alkalinity supplementation of the influent was maintained at 200 mgNaHCO₃, achieving total volatile acid concentration of 33 mgHAc/L, i.e., lack of stability was not related to accumulation of volatile acids but to the difficulty in metabolizing the compounds of this wastewater. For the applied volumetric organic load of 6.08 gCOD/L.d, concentration of formed methane was 5.20 mmolCH₄/L, and the average composition of biogas in terms of methane was 78%, assuming only methane and carbon dioxide are present in the biogas.

In the second phase, fill time was changed from batch to fed-batch and part of the volume treated per cycle (1 L) was fed in 10 min and the other part (1 L) was fed in 4 h, i.e., for a fill time to total cycle time ratio of 0.5, the organic matter removal efficiency was 72%, for influent concentration of 2,000 mgCOD/L, with applied organic volumetric load of 6.16 gCOD/L.d, and alkalinity supplementation of the influent of 200 mgNaHCO₃. Total volatile acid concentration of the effluent was 30 mgHAc/L and the removed volumetric organic load was 4.43 mgCOD/L.d. Thus, removal efficiency did not improve as fill time increased, i.e., gradual feeding did not improve removal efficiency, but smoothened the organic matter and total volatile acid profiles along the cycle.

The kinetic analysis for batch feeding was able to explain the behavior between the increase in applied volumetric organic load and reactor efficiency showing the decrease in the kinetic parameter related to substrate consumption. Regarding the residual organic matter concentrations, the model was also able to explain the decrease in the stability period occurring at the end of the assays, and hence to predict the treatment threshold value, in this case, around 6 gCOD/L.d. Regarding the fed-batch feeding strategy, the model reproduced the decrease in the kinetic parameters of substrate and volatile acid consumption, which led to the decrease in reactor efficiency, justified by the gradual contact between biomass and wastewater as the reactor was filled, and by the smoothening of the maximum values of organic matter and total volatile acids. This may be advantageous in the treatment of compounds with inhibiting features (which have not been studied in this investigation), but with the disadvantage of reducing the reaction rate as this is proportional to the concentration.

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