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Degradation of formaldehyde in anaerobic sequencing batch biofilm reactor (ASBBR)

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ABSTRACT

The present study evaluated the degradation of formaldehyde in a bench-scale anaerobic sequencing batch reactor, which contained biomass immobilized in polyurethane foam matrices. The reactor was operated for 212 days at 35 °C with 8 h sequential cycles, under different affluent formaldehyde concentrations ranging from 31.6 to 1104.4 mg/L (formaldehyde loading rates from 0.08 to 2.78 kg/m^3 day). The results indicate excellent reactor stability and over 99% efficiency in formaldehyde removal, with average effluent formaldehyde concentration of 3.6 ± 1.7 mg/L. Formaldehyde degradation rates increased from 204.9 to 698.3 mg/L h as the initial concentration of formaldehyde was increased from around 100 to around 1100 mg/L. However, accumulation of organic matter was observed in the effluent (chemical oxygen demand (COD) values above 500 mg/L) due to the presence of non-degraded organic acids, especially acetic and propionic acids. This observation poses an important question regarding the anaerobic route of formaldehyde degradation, which might differ substantially from that reported in the literature. The anaerobic degradation pathway can be associated with the formation of long-chain oligomers from formaldehyde. Such long- or short-chain polymers are probably the precursors of organic acid formation by means of acidogenic anaerobic microorganisms.

1. Introduction

Formaldehyde is commonly used as a raw material in a great number of industrial processes. This compound is widely used due to its high reactivity, colorless nature, stability, purity in commercial form and low cost [1]. Relatively high formaldehyde concentrations can be present in wastewater, which contains 0.2–4.0 g/L of formaldehyde from industrial production of adhesives [2]. Other industrial wastewater can reach concentrations as high as 10 g/L [3]. Such formaldehyde-rich industrial wastewater may cause microbial activity inhibition in biological processes [4]. Formaldehyde can react directly with DNA, RNA and proteins, thereby damaging cells and causing the death of microorganisms [5]. Due to its mutagenic and carcinogenic effects [6,7], discharging formaldehyde into the aquatic environment without treatment can cause serious damage to the aquatic life. Moreover, formaldehyde discharges resulting from anatomy laboratories, where it is largely used as preservative of anatomic pieces, can cause serious disturbances to biological wastewater treatment plants [8].

The anaerobic treatment, presenting low energetic consumption and small sludge production, is an alternative method for degradation of toxic compounds such as formaldehyde. Although some industrial processes apply physico-chemical or aerobic processes for the treatment of wastewaters containing formaldehyde, the search for anaerobic technologies is growing, motivated especially from an economic point of view.

Some researches on treatment of formaldehyde pointed to the feasibility of its anaerobic degradation [3,9–11]. Nevertheless, the literature contains little definite information about the anaerobic degradation and toxicity of formaldehyde. Many studies were completed with different kinds of anaerobic reactors, using formaldehyde as the sole carbon source or with several co-substrates, and fed in as a slug or in a continuous manner. These studies do not point to any consensus about the concentrations that can inhibit microbial activity [5,12–14]. In addition, the pathways of anaerobic formaldehyde degradation and the microorganisms involved in this process are still discrepant [4,10,14].

Most research indicates that formaldehyde is successfully degraded by anaerobic consortia in continuously fed reactors operated under high cellular retention times [12,15,16]. However, in some cases, as in anatomy laboratories, the formaldehyde is dis-

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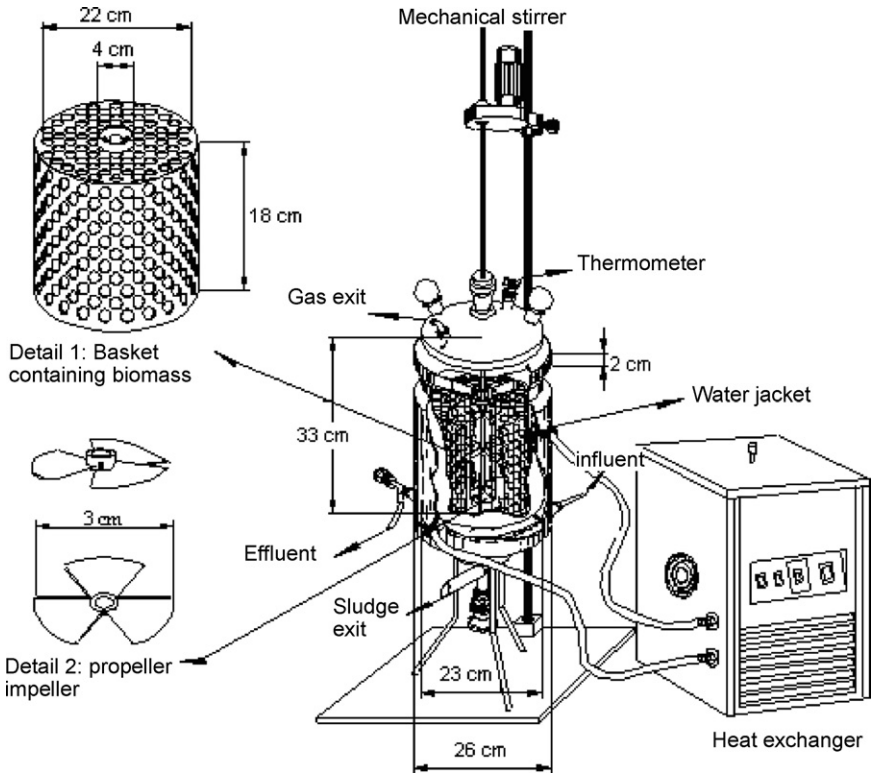

Fig. 1. Schematic of the ASBBR.

charged intermittently and the discontinuous regimen can be the best choice. Batch reactors have been studied for formaldehyde degradation, but the studies were performed in very small systems, with the primary goal of evaluating the degradation pathway or the toxicity limit [5,13–15]. Technological aspects of the operation of batch reactors have not been evaluated, hindering the possible application of such an alternative.

In this way, the aim of the present work was the evaluation of formaldehyde degradation in an anaerobic sequencing batch biofilm reactor (ASBBR), filled with polyurethane foam matrices for biomass immobilization.

2. Materials and methods

2.1. Anaerobic sequencing batch biofilm reactor

The anaerobic sequencing batch biofilm reactor (Fig. 1) consisted of a 23 cm diameter cylindrical glass flask with total capacity of 5 L. The biomass was immobilized in 1 cm cubic particles of polyurethane foam (apparent density of 23 kg/m^3) placed in a basket inside the cylindrical flask. Three 3 cm diameter propeller impellers provided mechanical mixing. The reactor was surrounded by a water jacket that allowed the operation to proceed at a constant temperature throughout the experiment.

2.2. Inoculum

For use as an inoculum, sludge was taken from a full-scale up-flow anaerobic sludge blanket (UASB) reactor treating poultry slaughterhouse wastewater. The sludge was thoroughly mixed with 70 g of cubic polyurethane particles, resulting in 22 g SSV-volatile suspended solids/L of biomass concentration at the beginning of the experiment.

2.3. Synthetic wastewater

The reactor was fed with synthetic wastewater prepared with formaldehyde, mineral medium [17] and vitamin solution [18] (Table 1). Formaldehyde was obtained from a formalin solution containing 38% formaldehyde and 10% methanol as a stabilizing agent. The substrate was refrigerated at 4 °C to maintain its characteristics throughout the experiment. Before entering the reactor, the liquid medium was heated to 35 °C in a heat exchanger.

2.4. Reactor operation

The experiments with formaldehyde-based substrates were performed with a progressive increment of formaldehyde concentration from 31.6 ± 8.7 to 1104.4 ± 130.8 mg/L. The reactor was operated under each influent formaldehyde concentration up to the stability of the system, after which temporal formaldehyde profiles in a cycle were recorded. The reactor was operated for 212 days (633 consecutive cycles) at 35 ± 1 °C with 8 h sequential cycles and constant agitation intensity of 300 rpm. In each cycle, the reactor was fed with 4.2 L of synthetic wastewater for 7 min and, after 465 min of reaction, discharged for 7 min. An idle time of 1 min was set between the feed and discharge operations.

2.5. Analytical methods

Formaldehyde concentrations were determined based on the colorimetric method proposed by Bailey and Rankin [19]. This method is based on the catalytic effect of formaldehyde on the hydrogen peroxide oxidation of *p*-phenylenediamine.

Analyses of chemical oxygen demand (COD), pH and solids were performed according to the standard methods for the examination of water and wastewater [20]. Formic acid was analyzed by high-pressure liquid chromatography (Shimadzu LC-10 AD

Table 1
Composition of the synthetic wastewater

Compound	Concentration (mg/L)
Formaldehyde	31.6–1104.4
Sodium bicarbonate (buffer agent)[a]	30.0–1100.0
Yeast extract	0.5
Mineral medium (adapted from Ref. [17])	
NH_4Cl	100.00
NaCl	100.00
$MgCl_2{\cdot}6H_2O$	50.00
$CaCl_2{\cdot}2H_2O$	100.00
$K_2HPO_4{\cdot}3H_2O$	400.00
$FeCl_2{\cdot}4H_2O$	2.00
H_3BO_3	0.05
$ZnCl_2$	0.05
$CuCl_2{\cdot}2H_2O$	0.038
$MnCl_2{\cdot}4H_2O$	0.05
$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	0.05
$AlCl_3$	0.05
$CoCl_2{\cdot}6H_2O$	0.05
$NiCl_2{\cdot}6H_2O$	0.092
EDTA	0.50
HCl	0.001 mL[b]
$Na_2SeO_3{\cdot}5H_2O$	0.10
Vitamin solution (adapted from Ref. [18])	
D-biotin	0.009
Folic acid	0.009
Riboflavin	0.0225
Tiamine hydrochloride	0.0225
Cianocobolamin	0.0225
Nicotinamide	0.0225
p-Aminobenzoic acid	0.0225
Pirodoxine hydrochloride	0.045

[a] Added in increasing concentrations as the formaldehyde concentration was increased.
[b] From a supersaturated solution.

VP with UV detector-210 nm and Aminex 874-300 mm × 7.8 mm column). The mobile phase was a H_2SO_4 solution of 0.005 mol/L (0.5 mL/min); the oven temperature was 35 °C. Methanol and volatile fatty acid concentrations were determined using a Hewlett Packard 6891 gas chromatograph equipped with a HP INNOWax column (30 m × 0.25 mm × 0.25 μm) and flame ionization detector. Hydrogen (2.0 mL/min) was used as a carrier gas. Oven, injector and detector temperatures were 50, 300 e and 250 °C, respectively, for methanol determination. For volatile acid determination, the injector temperature was 250 °C, with a split ratio of 1:20, and the detector temperature was 300 °C. The oven temperature was held at 100 °C for 3 min, changed at 5 °C/min to 180 °C, and then held for 5 min.

2.6. Microbiological observations

The amount of biomass attached to the polyurethane foam was determined after solid detachment from the supports in hand-agitated flasks containing glass beads. Microbiological observations of the biomass were conducted by phase-contrast microscopy using a Leica DM LB microscope and by scanning electron microscopy (SEM) with a Zeiss DSM-960 microscope. The biomass was examined before starting the experiments and after all experiments. Fluorescence was verified using a UV light source attached to the microscope.

Samples of polyurethane foam particles for optical microscopy examination were rinsed with distilled water and drops of the resulting liquid were immediately examined.

Samples for SEM analysis were fixed for 12 h at 4 °C in 0.1 M phosphate buffer (pH 7.3) containing 2.5% glutaraldehyde, after which they were rinsed three times in 0.1 M phosphate buffer (pH 7.3) and gradually dehydrated after successive immersions in increasingly concentrated ethanol solutions (50, 70, 80, 90 and 95%). Each rinsing and dehydrating cycle took 10 min. The samples were then washed three times in 100% ethanol (PA grade) and immersed for 30 s in hexamethyldisilazane. Drying was completed at 60 °C for 2 h. The particles were then coated with gold powder and attached to supports with silver glue.

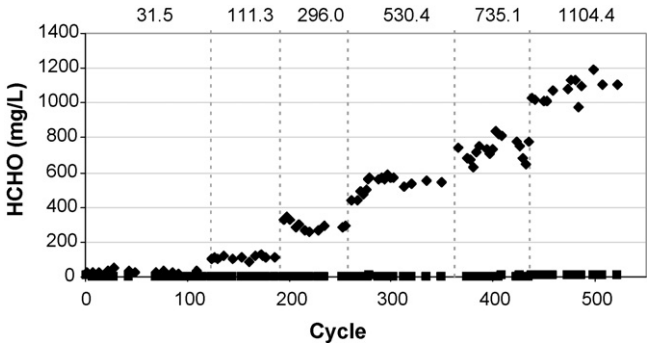

Fig. 2. Variation in influent (♦) and effluent (■) formaldehyde concentrations throughout the ASBBR operation.

2.7. Estimation of kinetic parameters

Apparent kinetic parameters of formaldehyde conversion were estimated through temporal profiles of formaldehyde taken for each operating condition, using the Levenberg–Marquardt method (Microcal Origin 5.0®). Initial formaldehyde conversion rates ($t = 0$) were obtained for each initial formaldehyde concentration using the same software.

3. Results and discussion

3.1. Formaldehyde degradation and COD removal

Fig. 2 presents the formaldehyde concentrations measured over 212 days of ASBBR operation. The reactor presented excellent stability in the removal of formaldehyde during all sequential batches monitored. The average effluent formaldehyde concentration was 3.6 ± 1.7 mg/L, for influent concentrations ranging from 31.6 ± 8.7 to 1104.4 ± 130.8 mg/L, and formaldehyde removal efficiencies higher than 99% were reached. The initial formaldehyde-loading rate ranged from 0.08 to 2.78 kg HCHO/m^3 day. Based on previous studies [4,14,15], the removal of formaldehyde by adsorption was considered negligible.

Influent and effluent COD variations throughout the reactor operation are presented in Fig. 3. Although formaldehyde was

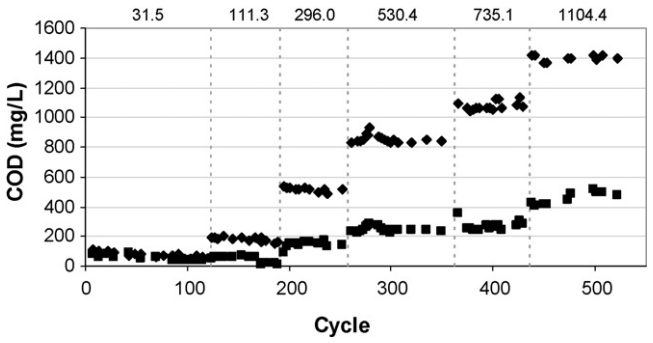

Fig. 3. Variation in influent (♦) and effluent (■) COD concentrations throughout the ASBBR operation.

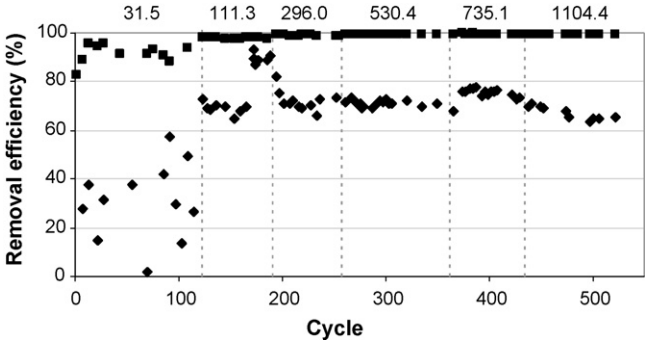

Fig. 4. Variation in removal efficiency of formaldehyde (■) and COD (♦) throughout the ASBBR operation.

almost completely removed from the system, a considerable residual concentration of organic matter was detected in the effluent and, consequently, an unsatisfactory COD removal was observed. The increase in influent formaldehyde concentration caused an increased accumulation of organic matter, which reached values above 500 mg/L. This behavior can be better observed in Fig. 4, which compares formaldehyde and COD removal efficiencies throughout the experiment. COD removal was around 70% when the reactor was fed with formaldehyde concentrations ranging from 111.3 to 1104.4 mg/L. In agreement with this work, Lu and Hegemann [5] observed inhibition in COD removal even with formaldehyde removal above 90%. Although conversion to organic acids had been observed, no drastic impact on the pH values could be observed. The mean effluent pH was 6.6 ± 0.1 throughout the operation for an average influent value of 7.6 ± 0.1. Effluent samples with low formaldehyde concentrations and some residual organic matter were similarly observed in other research works [10,21]. The instability observed during the first 115 days can be attributed to the initial operational phase of process startup and biomass acclimation.

3.2. Formaldehyde degradation pathway

A deep evaluation of the formaldehyde degradation pathway was only possible with temporal sampling along batch cycles for experimental conditions with different effluent formaldehyde concentrations. Fig. 5 depicts the typical temporal curves obtained for formaldehyde, COD and intermediates. This behavior, obtained for a formaldehyde influent concentration of 1104.4 mg/L, is representative for all the operating conditions. In this condition, formaldehyde degradation occurred in the first 5 h of operation and the COD remained constant over the last 3 h, suggesting the presence of persistent intermediate compounds or the inhibition of some type of biomass (Fig. 5A). The time for formaldehyde consumption was shorter for lower influent formaldehyde concentrations, but the behaviors of formaldehyde degradation and byproduct production and consumption were the same for all experimental conditions.

Analyses of formic acid and methanol were carried out to investigate the anaerobic pathway of formaldehyde degradation and to verify the accumulation of byproducts in the system. These compounds are reported to be the intermediates in the anaerobic degradation of formaldehyde [22], according to the following reactions:

$$HCHO + H_2O \rightarrow H_2 + HCOOH$$

$$HCHO + H_2 \rightarrow CH_3OH$$

$$2HCHO + H_2O \rightarrow CH_3OH + HCOOH(Total)$$

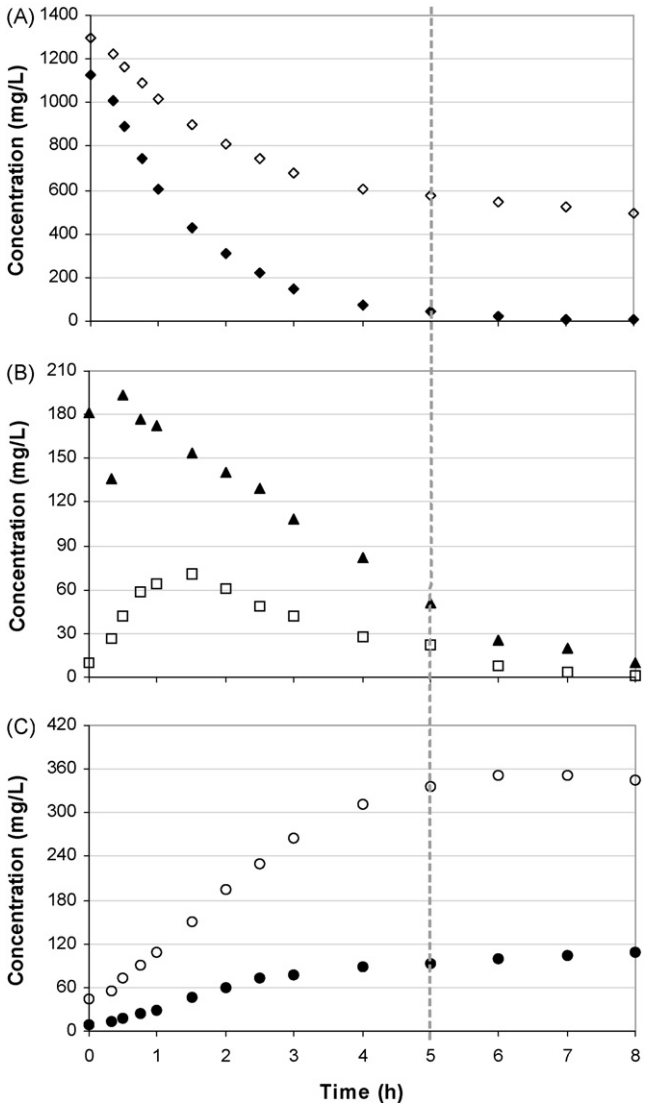

Fig. 5. Temporal variation in COD (◊), formaldehyde (♦), methanol (▲), formic acid (□), acetic acid (○) and propionic acid (●) concentrations related to a formaldehyde influent concentration of 1104.4 mg/L.

Formic acid was not detected in effluent samples in all the operations. Methanol was only detected in low concentrations, below 5.0 mg/L, when the reactor was operated with formaldehyde concentrations of 500 mg/L or higher. So, formic acid and methanol were not responsible for the high values of effluent COD observed as the formaldehyde was increased. Temporal profiles make clear the rapid conversion of formaldehyde into formic acid (Fig. 5B), confirming investigations carried out by Gonzalez Gil et al. [22]. However, Oliveira et al. [10] point out that this conversion could be chemical instead of biological, following a mechanism similar to the "Cannizzaro reaction", in which two aldehyde groups are transformed into the corresponding hydroxyl functions, existing separately or in combination as an ester.

In Fig. 5B, the formic acid is seen to rapidly form in the beginning of the cycle and undergo complete consumption within 5 h. The results obtained in the methanol profiles (Fig. 5B) were not very clear in relation to the production of this compound. The profiles indicated a progressive decrease in methanol concentration along the cycle, but methanol was present in the feeding medium and it was not possible to confirm the production of this compound and

its presence in the anaerobic formaldehyde degradation pathway. It is possible that the production and consumption of methanol were at equilibrium.

The detection of organic acids along the horizontal-flow anaerobic immobilized biomass (HAIB) reactor [10] motivated this study's search for the occurrence of these acids during the formaldehyde conversion in ASBBR. Chromatographic analyses indicated the presence of volatile fatty acids in the effluent when the reactor was subjected to formaldehyde concentrations higher than 296 mg/L. Low concentrations of isobutyric, butyric, isovaleric, valeric and caproic acids and high concentrations of acetic and propionic acids were detected. The presence of these acids confirms the results obtained by Oliveira et al. [10].

Fig. 5C shows that the production of acetic and propionic acids occurred in the first 5 h of the cycle, following the formaldehyde degradation. After this time, the acid concentrations remained stable, leading to the conclusion that the organic acids are associated with the residual effluent COD. As these acids are easily degradable compounds, some type of inhibition can explain their persistence in the reactor after formaldehyde consumption. In fact, Omil et al. [14], studying formaldehyde degradation using volatile acids as co-substrates, reported severe inhibition of organic acid conversion (mainly propionic and butyric) in the presence of formaldehyde.

Although the temporal profiles of formaldehyde and byproduct concentrations have elucidated the nature of the residual COD, the production of organic acids contradicts most of the work on anaerobic formaldehyde degradation, since methanol and formic acid are thought to be intermediates. This newly studied anaerobic degradation pathway can be associated with the formation of long-chain oligomers from formaldehyde. According to Grützner and Hasse [23], in solutions containing formaldehyde and methanol, the concentration of monomeric formaldehyde is low, even at moderate temperature. Formaldehyde reacts with water and methanol, forming poly(oxymethylene)glycols [$HO(CH_2O)_nH$] in aqueous solutions that, in turn, can be transferred to short-chain poly(oxymethylene)hemiformals. Such long- or short-chain polymers are probably the precursors of organic acid formation by means of acidogenic anaerobic microorganisms.

As mentioned previously, production of organic acids was also observed by Oliveira et al. [10] in an anaerobic packed-bed reactor operating with formaldehyde-loading rate ranging from 0.05 to 2.26 kg $HCHO/m^3$ day. However, in that work, the acids were completely consumed and no representative residual COD could be observed. This indicates that continuous immobilized-cell reactors are more suitable for complete formaldehyde degradation than ASBBR. In continuous-flow reactors with flow pattern close to plug-flow, specialized biomass can grow along the reactor's length so that, in each segment, a group of microorganisms can be adapted to specific compounds, thus optimizing the degradation of primary substrates and byproducts. In ASBBR, the entire microbial community is subjected to primary substrates, byproducts and end products, increasing the possibility of activity inhibition. However, the acids produced in ASBBR from formaldehyde degradation can be easily degraded in other anaerobic reactors used as post-treatment units. The reactor can be operated for formaldehyde degradation (less than 5 h for influent formaldehyde at 1104.4 mg/L) and discharged to another ASBBR whose biomass is acclimatized for organic acid consumption.

3.3. Microbiological observations

The microbiological observations indicated the presence of *Methanosarcina*-like cells in the ASBBR reactor. Such indication was based on the fluorescence that results from the presence of the coenzyme F_{420} and on the cubic disposition of the cocci forming sarcina [24,25]. Furthermore, *Methanosaeta*-like cells were rarely observed, in disagreement with the observations of the HAIB reactor studied by Oliveira et al. [10]. The absence of this microorganism, so common in the HAIB reactor, can justify the accumulation of volatile acids. The good performance of the HAIB reactor was attributed to the presence of this microorganism, which is capable of consuming organic acids. This difference in microorganism populations can be related to the different configuration of the reactors, supposing that *Methanosaeta* sp. is more susceptible to formaldehyde inhibition. In this way, as discussed previously, the HAIB reactor seemed to be more favorable for the development of segmented biomass along the reactor's length.

Table 2
Apparent first-order kinetics constants (k_1) and initial formaldehyde degradation rates (r_F and r'_F) at different initial formaldehyde concentrations (C_F), and correlation coefficient (R^2) for the adjustment

C_F (mg/L)	k_1 (h^{-1})	R^2	r_F (mg/L h)	r'_F (mg FA/mg SV h)
109	1.88	0.9976	204.92	0.009
248	1.11	0.9954	274.78	0.012
473	0.82	0.9938	385.50	0.017
694	0.61	0.9913	423.34	0.018
1130	0.62	0.9930	698.34	0.030

3.4. Estimation of kinetic parameters

Kinetic studies were performed and the formaldehyde degradation was found to obey first-order model for all the experimental conditions. The initial formaldehyde concentrations (C_F), first-order constants (k_1), correlation coefficients (R^2) and initial formaldehyde conversion rates (r_F and r'_F) are presented in Table 2. The apparent first-order kinetics constants decreased as initial formaldehyde concentrations were increased, indicating the occurrence of some type of inhibition. However, degradation rates increased as the initial concentration of formaldehyde as increased. Other studies also concluded that an increase in initial formaldehyde concentrations yield inhibition [26,27].

Reports on the kinetics of formaldehyde degradation are rarely observed in the literature. According to Qu and Bhattacharya [27] and Oliveira et al. [10] the formaldehyde degradation follows the Monod model, but the kinetic parameters found by these authors are quite different. According to Gonzalez-Gil et al. [22], the initial formaldehyde conversion rates followed a first-order kinetic model, and the conversion rates decrease with time, probably due to inactivation of enzymes.

4. Conclusions

The results of this study indicate that the anaerobic sequencing batch biofilm reactor was efficient for formaldehyde removal, presenting constant operational stability for concentrations ranging from 111.3 to 1104.4 mg/L. The average formaldehyde removal efficiency was 99.3%.

The reactor was inadequate for the removal of the byproducts generated from formaldehyde degradation presenting organic matter accumulation as volatile acids. The average COD removal efficiency was 70.8%. The production of organic acids indicates that part of the formaldehyde reacted with water and methanol, forming oligomers that were efficiently converted by the anaerobic consortium.

The microbiological observations presented a small diversity of biomass and prevalence of microorganisms similar to *Methanosarcina* sp., leading to the conclusion that the accumulation of organic acids was due the inhibition of organisms like

Methanosaeta sp., which could not tolerate high concentrations of formaldehyde in the reactor.

All formaldehyde conversion occurred during the first 5 h of the cycle, indicating that a shorter cycle could be used. Also, degradation of the generated products could occur in another reactor placed in series and containing biomass adapted for organic acid removal.

The formaldehyde conversion followed first-order kinetics for all initial formaldehyde concentrations studied in this work, and the first-order constants decreased with the increase of initial formaldehyde concentrations, suggesting some inhibitory effect due to the excess of formaldehyde.

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