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ORIGINAL PAPER

Removal of phenols and methane production with coffee processing wastewater supplemented with phosphorous

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Abstract This manuscript addresses the evaluation of the methane production and removal of organic matter and phenols from coffee fruits processing wastewater (CPW). The systems consisted of two serial upflow anaerobic sludge blankets (UASB1 and UASB2) and one sequential batch reactor (SBR). The organic loading rate (OLR) was increased from 3 to 6 g COD/L.d, and the hydraulic retention times (HRT) applied to UASB1, UASB2 and SBR were 60, 30 and 75 h, respectively. Similar OLRs were tested with raw CPW (tests 1 and 2) and CPW after the addition of Simple Super Phosphate (SSP) (tests 3 and 4). The COD removals in the two stages UASB + SBR were approximately 85 % in tests 1 and 3 and 88 % in tests 2 and 4. The total phenols (TF) removal ranged between 70 and 92 %. The highest bioenergy productivities were achieved in UASB1, i.e., approximately 0.33 and 0.70 L CH_4/L.d with OLR of approximately 3 and 6 g COD/L.d. Although, the addition of SSP did not induce a superior methane production or TF removal, it promoted enabled a faster biomass growth after acidification time. SBR was tested with two cycles—cycle 1 with anaerobic + aerobic reactions (tests 1 and 2) and cycle 2 with anaerobic + aerobic + anaerobic reactions and lower sedimentation time (tests 3 and 4). Cycle 2 obtained higher COD and TF removal. The addition of SSP enhanced the SBR performance and increased between 13 and 24 % the TF removal.

Keywords Acidified reactor recuperation · Organic loading rate increase · Removal of toxics · SBR post-treatment · Wet processing of coffee fruits

Introduction

Coffee is one of the most cultivated products worldwide, and approximately 80 countries are involved in its trade. Brazil, Vietnam and Colombia are responsible for more than half of the world production. Regarding marketing, quality is a key factor directly affected by the processing applied to the grains, which may be wet or dry. The wet processing is preferred in approximately 70–80 % times, as it enables the removal of the pulp and mucilage from the fruit and improves the quality of the product (Kulandaivelu and Bhat 2012).

1–15 L of water are required for a wet processing of 1 L of coffee grain and 10×10^5–31×10^5 m^3 of coffee processing wastewater (CPW) are produced annually, with chemical oxygen demand (COD) of up to 50,000 mg/L (Kulandaivelu and Bhat 2012; Beyene et al. 2014; Rattan et al. 2015). CPW is highly polluting; therefore, it has led to great concerns by the agricultural sector regarding its reuse, high volume of storage and negative effects on the environment, as eutrophication capacity and death of aquatic biota of water bodies, acidification and salinization of soils, and presence of toxic compounds, as polyphenols, which can reach concentrations of 105 mg/L (Kulandaivelu and Bhat 2012).

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Due to its high COD and energy demand for coffee drying, the production of methane by anaerobic digestion has appeared as an interesting alternative and motivated the study of various biological technologies. Some conditions evaluated are environmental parameters, inoculum source and operating strategies.

The CPW characteristics are highly variable and must be considered for the avoidance of an imbalance between the amount of organic matter and nutrients (Rossmann et al. 2013). An inadequate nutrient concentration in the biological reactors substrate can affect their ability to remove organic matter, generate biogas, and tolerate toxic compounds, as phenols. For example, phosphorous is necessary for the microorganisms growth and metabolism (Wang et al. 2008); therefore, the effect of its addition for the anaerobic and aerobic treatments of CPW is an important study object that has been little investigated (Chen et al. 2008; Lei et al. 2010). Sources commonly found in the agricultural sector, as single superphosphate (SSP), could be exploited, or cheaper solutions, as waste active sludge pretreated with free nitrous acid, might be technically and economically more appropriate (Zhao et al. 2015).

Likewise, the reactor configuration directly affects the efficiency of organic matter removal and methane production; therefore, the following anaerobic reactors have been tested for the treatment of CPW: horizontal anaerobic reactor (HAR), anaerobic fixed-bed reactors (FBR), upflow anaerobic sludge blanket (UASB) and hybrid UASB (Bruno and Oliveira 2013, Selvamurugan et al. 2010a, b; Fia et al. 2012; Guardia-Puebla et al. 2014).

HAR (Oliveira and Bruno 2013) and FBR (Fia et al. 2012) achieved COD removals of 97 and 52 % of total phenols (TF) with biomass brackets; hence, a bioenergy productivity between 1.4 and 1.7 L CH_4/L.d. HAR included three 1.2-L serial reactors filled with sludge blanket, bamboo and coconut fiber, respectively, which operated at 90 h hydraulic retention time (HRT) and organic load rate (OLR) between 8.9 and 25 g COD/L.d. The upflow FBR consisted of three types of brackets, namely blast furnace cinders, polyurethane foam and crushed stone. The HRT was 31 h, and the OLR ranged between 0.8 and 4.4 g COD/L.d.

The UASB system showed superior performance with CPW. The UASB reactors operated by Jung et al. (2012) reached maximal removals of 98 % for COD and high bioenergy productivity of 0.8 L CH_4/L.d with OLR of 3.5 g COD/L.d. The conditions applied were 48 h HRT and controlled temperature of 35 °C (Jung et al. 2012).

Such results have shown the UASB reactor is appropriate for the CPW treatment. CPW has variable COD and production volume, as a consequence of the type of pulping process applied, quantity of grains per pulping cycle, type and origin of the grains, fermentation step, water recirculation, mechanical or manual system and other parameters of coffee processing (Esquivel and Jiménez 2012). Therefore, the low HRT and high OLR commonly applied in the UASB reactor can provide adequate results, despite the variable affluent characteristics.

Similarly, the two-stage configuration of the UASB system can separate acidogenic and methanogenic phases for the enrichment of specific microorganisms in separate reactors, prevention of overload and inhibition of toxic elements, as phenols (Camarillo and Rincón 2012). The systems can also act on quickly acidified compounds present in the waste that can cause reactors to collapse in the CPW treatment (Guardia-Puebla et al. 2014).

The combination of anaerobic systems with a sequencing batch reactor (SBR) can improve the biological treatment for the removal of COD and nutrients that remained from anaerobic systems (Foresti et al. 2006). As the water quality increases, in some cases, the effluents are released into water sources or reused for a new coffee fruits pulping process or fertigation.

The configuration of the two-stage UASB reactor with SBR was tested by Bruno and Oliveira (2013). The authors achieved removals of 95 % for COD and 84 % for TF with HRT of 329.5 h (223.2 h for UASB reactors and 106.3 h for SBR) and OLRs between 2.3 and 4.3 g COD/L.d. However, studies for improvements in the reactors operation conditions, lower HRT and increase in the substrate volume in UASB systems must be conducted for the full-scale performance of the reactors, according to the actual conditions of the residue production.

This research evaluated the performance of two-stage UASB reactors and SBR for improvement in the CPW quality and methane production, under increasing OLR, decreasing HRT and phosphorus addition to the substrate.

Materials and methods

CPW preparation

Arabian coffee fruits used for the preparation of CPW were obtained from the Farm of Education, Research and Extension of the São Paulo State University, Jaboticabal (Brazil) at the end of the coffee harvests of 2013 and 2014 and transported in jute bags to the laboratory. They remained stored under room temperature and ventilation conditions.

The substrate was simulated by a manual pulping of the grains and subsequent screening (2-mm mesh size). 2 L of water per 1 L of coffee beans were reposed for 24 h, and the husk was removed for the obtaining of a highly concentrated liquid for which the pH was adjusted between 6.5 and 7.0 with hydrated lime ($Ca(OH)_2$). The non-pulped grain was reused for the preparation of a new CPW. Finally, the COD was adjusted to concentrations of approximately 7500 (tests 1 and 3) and 15,000 mg/L (tests 2 and 4).

Two-stage UASB reactors and SBR

The UASB system on a bench scale consisted of a first reactor of 20 L (UASB1) and a second of 10 L (UASB2) (Fig. 1), and both were constructed with PVC pipe in a Y shape and an 45° angle (Cavalcanti et al. 1999). An influent storage tank (20 L) fed UASB1 and subsequently UASB2 and SBR by gravity.

An SBR of 25 L was built in PVC with a mechanical agitator and consisted of three impellers, a shaft and a gear motor. An ALEAS aquarium pump with a rubber diffuser injected fine air bubbles at the bottom of the reactor. Both agitator and aquarium pump were controlled by timers (Fig. 1).

Inoculum

The aerobic and anaerobic sludges used for the reactors inoculation were obtained from UASB and SBR systems that treated swine wastewater with volatile solids (VS) of 27 and 24 g/L, respectively. The UASB reactors were inoculated with 30 % (6 L for UASB1 and 3 L for UASB2) and SBR with 68 % of their volumes (17 L), respectively.

Reactors start-up

The OLR gradually increased from 0.5 to 3 g COD/L.d (test 1) for 45 days.

Operational conditions

The treatment system with UASB and SBR reactors was operated under room temperature between August/2013 and January/2015. Tests 1 and 2 were conducted from August/2013 to March/2014 (spring/summer), and tests 3 and 4 were performed from November/2014 to January/2015 (summer).

SBR was operated with 75 h HRT. Two 24-h operational cycles were tested:

Cycle 1

For tests without phosphorus supplementation (tests 1 and 2), the cycle was divided into 9 h under anaerobic conditions without agitation, 9 h in continuous aeration, 5.5 h in sedimentation and 0.5 h for effluent disposal. The influent was continuously supplied by UASB2 at 8 L/d flow rate. 8 L of effluent were disposed once a day (batch mode).

Cycle 2

For tests with phosphorus supplementation (tests 3 and 4), the cycle was divided into 5 h under anaerobic conditions with agitation, 6 h in continuous aeration, 10 h in anaerobic reaction with agitation, 2.5 h in sedimentation and 0.5 for effluent disposal. The influent was continuously supplied by UASB2 at 8 L/d flow rate. 8 L of effluent were disposed once a day (batch mode).

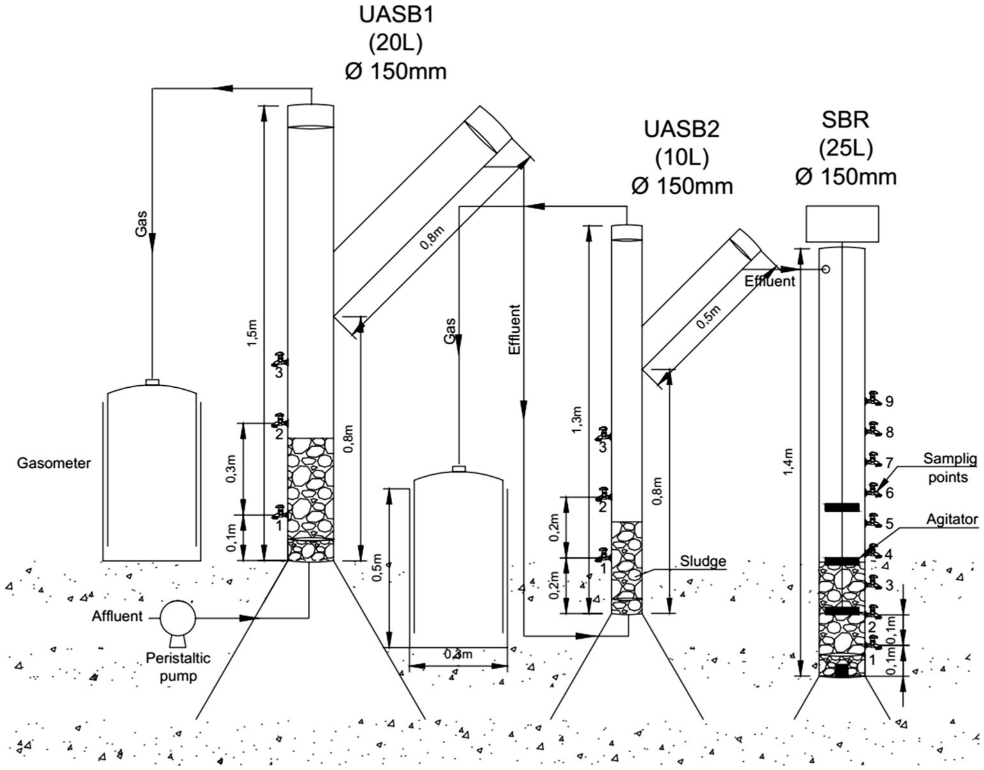


Fig. 1 Two-stage UASB reactors and SBR

Table 1 Operational conditions of the two-stage UASB reactors

Test	OLR (g COD/L.d)	SSP (g/L)	COD:N:P	Duration (d)	HRT (h)		COD (mg/L)
					UASB1	UASB2	
1	3.0	–	350:9.1:2.1	62	60	30	7613
2	6.0	–	350:8.7:0.7	57	60	30	14,939
3	2.8 + SSP	2	350:16.8:2.1	30	60	30	6974
4	6.0 + SSP	4	350:10.1:4.2	30	60	30	15,067

Effect of the organic loading rate increase

Water recirculation is a common practice in the coffee sector for reductions in the liquid waste generation. This research focused on two OLRs applied to UASB1 obtained through the adjustment of COD in the substrate (Table 1): OLR of 3 g COD/L.d substrate obtained with 4 L of water per 1 L processed coffee, with no water recirculation (tests 1 and 3); and OLR of 6 g COD/L.d substrate obtained with 4 L of water per 2 L processed coffee, with water recirculation (test 2 and 4).

After the evaluation of test 2, a test with 9 g COD/L.d of OLR was applied to the two-stage UASB reactors and SBR. The CPW was either simulated, or collected from "Da Lagoa" farm in the Pedregulho city, São Paulo state. The CPW was collected after mechanical pulping and degumming of coffee beans collected during the day. The CPW was diluted to values close to 25000 mg/L for the obtaining of the desired OLR and sieved and neutralized under the same conditions that simulated CPW.

Effect of phosphorus addition

Tests 3 and 4 were conducted with CODs similar to those of tests 1 and 2; however, phosphorus was added to the substrate (Table 1). Single superphosphate (SSP) ($Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 2H_2O$) was the phosphorous source for the obtaining of a COD:N:P relation of minimal 350:5:1 (Speece 1996). A minimal proportion of COD:SSP necessary was 350:4.6 with maximal deficiency of phosphorous in CPW between 60 and 70 % (Bruno and Oliveira 2013; Rossmann et al. 2013), 15–16 % SSP solubilization in water and a 18 % P_2O_5 content in the product (corresponding to 50.8 % of phosphorous). The SSP was manually macerated and mixed in excess with the CPW at concentrations of 2 g/L for test 3 and 4 g/L for test 4, respectively (Table 1).

Sampling and analytical methods

Influent and effluent

Composite samples of influents and effluents of the reactors were collected twice a week from 8:00 a.m. to 2:00 p.m., with intervals of 30 min between each single sampling. The physical and chemical tests applied were total alkalinity (TA), partial alkalinity (PA), intermediate alkalinity (IA), chemical oxygen demand (COD), total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), total phosphorous (TP) and total Kjeldahl nitrogen (TN), according to the Standard Methods methodology (APHA et al. 1995) and Ripley et al. (1986). Volatile fatty acids (VFA) were determined according to Dilallo and Albertson (1961), whereas total phenols (TF) were analyzed once a week following the Folin–Ciocalteu method described by Shahidi and Naczk (1995).

Sludge

Sludge samples were collected at intervals of 30 days from different sludge sampling points (Fig. 1). Points 1, 3, and 5 were analyzed for SBR at the end of the sedimentation cycle, so that any interference in the inoculum mass of the reactor would be avoided. TS and VS were determined from the samples (APHA et al. 1995).

Biogas

The biogas was collected and measured daily by gasometers constructed of fiberglass as described by Oliveira (1997) (Fig. 1). Its composition was determined fortnightly by a FININGAN 6C-9001 gas chromatograph with a thermal conductivity detector, "Poropac Q" (3 m 1/8″) columns and a molecular sieve, according to the methodology described by APHA et al. (1995). The volume was corrected to Standard Temperature and Pressure conditions (STP, 273 K and 1 atm) for the calculation of the methane production.

Statistical analysis

A completely randomized design with four treatments was considered for the statistical analysis: 3 g COD/L.d (test 1), 6 g COD/L.d (test 2), 2.8 g COD/L.d + SSP (test 3) and 6 g COD/L.d + SSP (test 4), with different numbers of repetitions for each attribute, according to the sampling frequency. The values were compared by *Student t* test with 5 % probability. Only positive values were considered for the calculation of the efficiency.

Results and discussion

CPW characteristics

The concentrations of VFA were higher than 1200 mg/L (Table 2), which demonstrated the CPW preacidification. CPW has a high sugar content that suffers rapid hydrolysis and acidification and leads to a high production of volatile acids (Selvamurugan et al. 2010a, b; Guardia-Puebla et al. 2014). Although this condition is desirable for anaerobic digestion, it requires greater attention to the operational process control for the avoidance of instability or failure in the process caused by VFA accumulation (Guardia-Puebla et al. 2014).

PA in the substrate of tests 1 and 2 ranged between 261 and 338 mg/L, as a result of the lime addition for neutralization. In tests 3 and 4, the SSP allowed PA higher than in the other tests ($\alpha = 0.05$).

TSS for tests 1 and 2 corresponded to over 50 % of total organic matter represented as COD, which can be considered particularly high in comparison with values of 12 % (Guardia-Puebla et al. 2014) or at most 25 % (Beyene et al. 2014) obtained in other studies with CPW. However, over 50 % of TSS were in the volatile form, whereas dissolved COD exceeded 60 % of the total COD. Tests 3 and 4 revealed a large amount of solid material with a minimum of 40 % of VS. All tests showed highly volatile solids and organic material available for the anaerobic degradation.

TF was variable and not proportional to COD, as it reached values above 500 mg/L. Such concentrations were approximately 4.5 times higher than those reported by Oliveira and Bruno (2013) (105 mg/L TF) through a CPW simulation process for COD of 16,000 mg/L.

The TN influent ranged between 201 and 446 mg/L and was variable and superior in tests 3 and 4 with the SSP addition. Such results are similar to those reported by Bruno and Oliveira (2013) with 332 mg/L of TN and 13891 mg/L of COD. Approximated values of TN between both substrates might be a consequence of the collection of the fruits on the same university farm in Jaboticabal, São Paulo.

During tests 1 and 2, the concentration of TP was approximately 40 mg/L and higher than the values for the CPW found in Beyene et al. (2014), Rossmann et al. (2013) and Guardia-Puebla et al. (2014).

Such differences regarding solids, TF, TN and TP are commonly observed among CPW from different sources, according to the post-harvest processing techniques and the characteristics of the fruits that influence the physical and chemical composition of the waste, such as cultivation conditions, coffee fruit maturation degree, harvest method, steps of coffee processing and mechanization (Esquivel and Jiménez 2012).

Table 2 CPW characteristics

Test	OLR (g COD/L.d)	pH	VFA (mg/L)	PA	COD	Dissolved COD	TSS	VSS	TF	TP	TN	COD:N:P
1	3.0	$6.8^{bc} \pm 0.1$	$1277^{b} \pm 188$	$261^{b} \pm 95$	$7613^{b} \pm 892$	$4524^{b} \pm 1150$	$4141^{\underline{b}} \pm 1093$	$2679^{\underline{b}} \pm 687$	$223^{c} \pm 97$	$49^{b} \pm 14$	$201^{b} \pm 49$	350:9.1:2.1
2	6.0	$6.6^{c} \pm 0.1$	$2438^{a} \pm 178$	$338^{b} \pm 90$	$14939^{a} \pm 869$	$8398^{a} \pm 2141$	$8763^{\underline{a}} \pm 1124$	$6363^{\underline{a}} \pm 707$	$583^{a} \pm 97$	$40^{b} \pm 14$	$382^{a} \pm 49$	350:8.7:0.7
		pH	VFA (mg/L)	PA	COD	–	TS	VS	TF	TP	TN	COD:N:P
3	2.8 + SSP	$7.1^{b} \pm 0.2$	$1276^{b} \pm 252$	$635^{a} \pm 128$	$6974^{b} \pm 1196$	–	$7648^{B} \pm 3144$	$3389^{B} \pm 281$	$513^{a} \pm 119$	$82^{ab} \pm 18$	$339^{a} \pm 59$	350:16.8:2.1
4	6.0 + SSP	$7.3^{a} \pm 0.2$	$1452^{b} \pm 271$	$796^{a} \pm 135$	$15067^{a} \pm 483$	–	$12248^{A} \pm 653$	$9281^{A} \pm 531$	$263^{bc} \pm 144$	$144^{a} \pm 24$	$446^{a} \pm 81$	350:10.1:4.2

Different letters (t test, $p < 0.05$) mean statistical difference. With the solids, the comparisons were performed between tests 1 and 2 (underline lowercase) or between tests 3 and 4 (uppercase), as a consequence of the different methodologies applied

According to requirements of nitrogen and phosphorous for anaerobic biological processes, a 350:5:1 COD:N:P in test 2 showed approximately 30 % TP deficiency for the same origin of substrate. The result showed the phosphorous content in CPW might be inadequate for the biological treatment. In tests 3 and 4, the addition of SSP increased the nutritional composition of the simulated CPW in relation to phosphorus; however, it does not justify the wastewater nutrients supplementation regarding their final excessive concentration and difficulty for removal in anaerobic systems.

Bruno and Oliveira (2013), Beyene et al. (2014) and Rossmann et al. (2013) obtained inferior phosphorous concentrations of 350:8.0:0.3, 350:15:0.7 and 350:4.7:0.4 for simulated CPW and collected CPW, which showed the variable nutritional characteristic of the wastewater. However, according to the authors, this was not a limiting factor for the continuity of the anaerobic process.

As information about the nutritional importance of phosphorus in biological treatments of CPW is contradictory, we evaluated the effect of SSP addition in the substrate over the performance of two-stage UASB reactors and SBR.

Removal of organic matter, solids and phenols by two-stage UASB reactors

The removal of COD, dissolved COD, solids and TF ranged between 71 and 95 % in tests without SSP addition, and between 70 and 94 % in tests with SSP addition (Table 3).

The major degradation of organic matter and TF was detected in UASB1, with removals between 48 and 92 % for both parameters (Table 3). The superior performance of UASB1 may have been influenced by the lime addition. Some authors have reported lime and high pH enable the sedimentation of particulate organic matter and phenols. Therefore, some intermediates, as maleic acid, oxalic acid, and high molecular weight products may react with calcium ions to form insoluble compounds that precipitate (Chen et al. 2008; Fia et al. 2013).

UASB1 + UASB2 obtained removal efficiencies of COD, solids and TF between 68 and 92 %. However, UASB2 showed inferior biodegradation efficiency, possibly because the influent (UASB1 effluent) showed compounds of difficult degradation and low organic matter concentration, which might cause toxicity for the microorganisms and reduction in the enzymatic activity (Murthy and Madhava Naidu 2012).

Two-stage UASB system achieved similar performance for an OLR of 3 and 6 g COD/L.d during tests 1 and 2, showing a stable response. The load in tests 2 and 4 was twice higher than that in tests 1 and 3, although the organic matter removal ranged between 70 and 90 %. This result may have been influenced by the microorganism adaptation to CPW and operational conditions. The start-up of the reactor enabled such an adaptation, because the gradual increase in the TF and COD concentrations was responsible for the growth of anaerobic biomass.

The phosphorus supplementation in tests 3 and 4 did not increase the COD removals; therefore, SSP is not required for improvements in the efficiencies of organic matter reductions in the anaerobic systems evaluated. However, it enabled a stable operation of the reactors with approximately 92 % COD removal after the application of OLR of 9 g COD/L.d and high VFA concentrations (Final section, Fig. 3).

The highest TF concentrations were found in tests 2 and 3 with values of approximately 500 mg/L, which are higher than the phenol inhibition constant (Ki) (363 mg/L) and might cause toxic effects on the microorganisms (Suidan et al. 1989). During tests 2 and 3, the two-stage UASB system showed TF removals of 79 and 92 %, respectively; therefore, the phenols concentrations exerted no toxic effect over the anaerobic biomass.

When SSP was added in tests 3 and 4, the removal efficiencies increased between 11 and 22 %. However, it cannot be concluded the phosphorous addition during the tests improved the phenols degradation, because the TF and COD concentrations were different in tests with and without SSP addition (583 mg/L TF during test 2 and 263 mg/L TF in test 4 for affluent COD of approximately 15,000 mg/L). Similarly, variable environmental temperatures observed during the reactor operation (Table 5) might have influenced the differences in the TF removal efficiencies.

The performance of two-stage UASB reactors + SBR was compared with that of other reactors configurations that treat CPW (Table 4). The system developed by Jung et al. (2012) showed higher COD removal efficiency (98 %) with a single UASB reactor and HRT of 48 h, which are the same operational conditions used in our approach. The results may have been a consequence of the controlled temperature above 35 °C and the preacidification of the reactors for the hydrogen production, because higher temperatures increase the biochemical reactions rate and lead to high acids concentrations directly available as a substrate for methanogenic archaea. In contrast, the energy investment required for the temperature control may increase the treatment costs, in comparison with the ambient conditions evaluated in this study.

Fia et al. (2010) combined constructed wetland systems with anaerobic filters. The substrate was supplemented with urea and SSP (source of nitrogen and phosphorous). The authors observed COD removals twice higher during the nutrients addition in constructed wetland and four times higher in wetland + anaerobic filters than in systems with no supplementation. The highest COD removal was 85 %, and HRT ranged between 111 and 126 h.

Phosphorus enhanced the COD removal in anaerobic filters (Fia et al. 2010). However, the advantages of the

Table 3 Removal of organic matter, solids and TF by two-stage UASB reactors and SBR and effluent characteristics

Tests	Reactor	COD		Dissolved COD		TSS		VSS		TF	
		Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)
1	UASB1	80 ± 3	1407 ± 348	77 ± 4	965 ± 305	75 ± 8	925 ± 400	82 ± 4	443 ± 170	71 ± 13	47 ± 12
	UASB1 + UASB2	86 ± 3	973 ± 338	78 ± 4	917 ± 305	77 ± 8	829 ± 400	88 ± 5	238 ± 170	74 ± 13	41 ± 4
	UASB1 + UASB2 + SBR	87^{ab} ± 4	915^{a} ± 384	81^{a} ± 4	793^{a} ± 346	$91^{\underline{a}}$ ± 9	$100^{\underline{a}}$ ± 454	$94^{\underline{a}}$ ± 5	$71^{\underline{a}}$ ± 201	70^{a} ± 12	49^{a} ± 26
2	UASB1	72 ± 3	4000 ± 839	70 ± 4	2558 ± 290	75 ± 8	1720 ± 380	79 ± 4	960 ± 162	48 ± 12	222 ± 115
	UASB1 + UASB2	81 ± 3	2623 ± 330	72 ± 4	2373 ± 297	84 ± 8	950 ± 380	92 ± 4	401 ± 166	79 ± 13	127 ± 98
	UASB1 + UASB2 + SBR	82^{b} ± 3	2492^{b} ± 329	76^{b} ± 4	1935^{b} ± 297	$93^{\underline{a}}$ ± 8	$260^{\underline{b}}$ ± 380	$95^{\underline{a}}$ ± 4	$190^{\underline{b}}$ ± 166	77^{a} ± 12	151^{a} ± 85
		COD		Dissolved COD		TS		VS		TF	
		Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)	Removal (%)	Effluent (mg/L)
3	UASB1	77 ± 4	1588 ± 429	–	–	69 ± 11	2496 ± 642	62 ± 7	1272 ± 326	92 ± 13	41 ± 26
	UASB1 + UASB2	81 ± 6	478 ± 167	–	–	74 ± 11	2025 ± 574	68 ± 7	1139 ± 305	92 ± 19	43 ± 21
	UASB1 + UASB2 + SBR	84^{b} ± 5	426^{a} ± 158	–	–	75^{A} ± 11	1984^{A} ± 574	70^{B} ± 7	989^{A} ± 305	94^{a} ± 13	30^{a} ± 22
4	UASB1	89 ± 5	1611 ± 757	–	–	49 ± 12	6391 ± 687	55 ± 7	3930 ± 326	73 ± 16	69 ± 9
	UASB1 + UASB2	92 ± 3	1226 ± 462	–	–	74 ± 11	3343 ± 642	77 ± 7	1890 ± 305	83 ± 16	44 ± 9
	UASB1 + UASB2 + SBR	94^{a} ± 3	898^{a} ± 445	–	–	84^{A} ± 11	1794^{A} ± 606	88^{A} ± 7	950^{A} ± 288	90^{a} ± 16	23^{a} ± 6

Different letters (t test, $p < 0.05$) mean statistical difference. Only with the solids the comparisons were between tests 1 and 2 (underline lowercase) or between tests 3 and 4 (uppercase), as consequence of applied different methodologies

Table 4 Anaerobic reactors and post-treatment systems operating with CPW

References	Reactor	OLR (g/L.d)	HRT (h)	Temp. (°C)	Bioenergy productivity (L CH$_4$/L.d)	CH$_4$ (%)	Removal efficiency (%)	
							COD	TF
Anaerobic reactors								
This research	Two-stage UASB reactors without phosphorous	3–6	90	24–25	0.41–0.75	66–79	81–86	74–79
	Two-stage UASB reactors with phosphorous	2.8–6	90	23–25	0.35–0.73	65–83	81–92	92–90
Guardia-Puebla et al. (2014)	UASB	3.6	21.5	35	0.10	58.3	77	–
	Hybrid two-stage UASB reactors	2.6	16	37	0.03	58	84	–
Bruno and Oliveira (2008, 2013)	Two-stage UASB reactors	3.0–3.6 and 2.3–4.5	187–223 and 223.2	22.1–23.7 and 20.0–21.0	0.45–0.48 and 0.27–0.32	69–89 and 75–80	96–98 and 91–95	86–90 and 47–66
Campos et al. (2013)	UASB	0.1–20.3	8–69.7	20–26	0.06–1.56	48.6–68.1	70–82	0–28
Jung et al. (2012)	UASB	3.5	48	35	0.80	73	98	–
Selvamurugan et al. (2010a, b)	Hybrid UASB	7.0–28.5	6–24	–	0.13–0.26	50–62	54–70	–
Post-treatment								
This research	Two-stage UASB reactors + SBR: cycle 1 without phosphorous	3–6	165	24–25	–	–	82–87	70–77
	Two-stage UASB reactors + SBR: cycle 2 with phosphorous	2.8–6	165	23–25	–	–	84–94	94–90
Bruno and Oliveira (2013)	Two-stage UASB reactors + SBR	2.3–4.5	329.5	20.0–21.0	–	–	95	84
Selvamurugan et al. (2010a)	Hybrid UASB + Continuous aeration	2.2	198–216	–	–	–	68.6	–
	Hybrid UASB + Intermittent aeration	2.2	198–216	–	–	–	46–59	–

UASB system proposed in this paper are it requires no nutrients addition for achieving satisfactory removal efficiencies and lower HRT in comparison with the integration of constructed wetlands (Fia et al. 2010).

Other treatment systems fed with CPW (Table 4), UASB reactor (Campos et al. 2013), hybrid UASB (Selvamurugan et al. 2010a; b) and two-stage UASB reactors, whose second stage was a hybrid reactor (Guardia-Puebla et al. 2014) showed maximum removal of 84 % of COD and 28 % of TF, which indicates the treatment system can potentially improve the CPW quality.

Despite such favorable results, the effluent from the two-stage UASB reactors reached COD concentrations between 973 and 2623 mg/L (Table 3); therefore, an SBR could be used as a post-treatment system for the achievement of superior effluents quality.

Removal of phenols and organic matter by SBR

The capacity of organic matter and TF removal through a post-treatment SBR designed for nitrogen and phosphorous removal was evaluated. SBR increased the removals of COD, dissolved COD and solids only between 1 and 14 % (Table 3).

The low organic matter removals in SBR were not justified by the deficiency in carbon or nutrients sources, because the COD:N:P relation for the tests was approximated or superior to those recommended for COD removal in SBR, i.e., 100:2:0.5 (100:8.6:2.1 in test 1, 100:6.7:0.6 in test 2, 100:15.7:1.1 in test 3 and 100:23.9:0.6 in test 4) (Kargi and Uygur 2003). Therefore, the affluent that fed the SBR might present recalcitrant composts of low degradability, as a consequence of the high removal occurred in the two-stage UASB system.

The SBR showed no TF removal in tests 1 and 2 (without SSP addition), as phenols can be resistant to biological decomposition and inhibit microorganism at low concentrations of 10 mg/L (Fia et al. 2007; 2013). Similarly, the aerobic phenol degradation is achieved only at high retention time, otherwise, the incomplete bio-oxidation can generate intermediary molecules that remain in the effluent (Moussavi et al. 2010), as observed during tests 1 and 2 in the SBR. Consequently, a continuous aeration is more adequate when the objective of the post-treatment process is the removal of phenols and polyphenols from CPW.

In tests 3 and 4 (with SSP addition), the SBR removed between 2 and 7 % of TF, as a consequence of the phosphorus addition, which is an essential macronutrient for the cells that promoted biomass growth, and consequently, increased the TF removal efficiency in tests 3 and 4. Similarly, aerobic microorganisms for the phenols degradation have a low specific growth rate (μ) (between 0.051/h for *P. putida ATCC 700007* and 0.618/h for *P. fluoroescens*) (Shetty et al. 2011), and phosphorous addition would provide adequate nutritional conditions for the achievement of the maximal velocity. Cycle 2 applied to

SBR in tests 3 and 4 led to higher TF bio-oxidation because it increased the time for biological phases (anaerobic–aerobic–anaerobic reactions) (Moussavi et al. 2010).

Aerobic phenol-degrading microorganisms have low Monod constants (Ks) (between 1.5 mg/L for *Acitenobacter* and 71.4 mg/L for *P. fluoroescens*) (Shetty et al. 2011), which might result in a superior substrates uptake for low concentrations. However, the TF degradation would be inferior in tests with higher TF concentrations (tests 2 and 3 with approximately 500 mg/L TF). The removal did not differ between tests, which showed the microbiota had adapted to high polyphenols concentrations. The SSP addition (tests 3 and 4) provided better nutritional conditions with higher microorganisms tolerance to concentrated substrates and superior degradation.

The system for the CPW treatment developed by Selvamurugan et al. (2010a) applied continuous and intermittent aeration, while Mahesh et al. (2014) used electrocoagulation and SBR and obtained COD removals of 69 and 85 %, respectively. Such results were below than or close to those obtained by the anaerobic–aerobic system evaluated here and show the ability of serial reactors to stabilize the organic matter with the advantage of biogas production.

Bruno and Oliveira (2013) studied the same UASB reactors and SBR and observed 95 % of COD removal with 106.3 h of post-treatment retention time and 12-h aeration. Rossmann et al. (2012, 2013) applied the combination of aeration + wetlands and obtained 91 % COD removal with 288 h of HRT. The systems showed superior results in comparison to tests without phosphorus addition (maximum 84 %), but close to those obtained in test 4 with phosphorus supplementation (94 %). Therefore, the SBR supplemented with SSP provided adequate COD removal efficiencies at lower HRT and inferior aeration requirements.

The SBR post-treatment did not improve the TF removal in CPW significantly under the operating conditions applied. According to the Brazilian regulation, the effluent phenol concentration did not reach the release patterns in water bodies of 0.5 mg/L (CONAMA Resolution No. 357, 2005). However, the SBR performance for the removal of phenols during tests with phosphorous addition was promising for future investigations with SBR.

Finally, the pH values were close to neutrality and the COD removal efficiency was higher than 80 % (Table 3), whereby the effluent showed potential characteristics for reuse in a new coffee pulping process, significantly reducing the water use and enabling plants fertigation.

Methane production from CPW

Proper conditions of temperature, VFA, alkalinity and pH were established for the methane production (Table 5). The average temperatures between 23.3 and 25.2 °C were maintained and corresponded to the mesophilic range. Despite the high temperature in test 4, no differences were observed in the methane production in comparison with the other tests ($\alpha = 0.05$).

The substrates showed high VFA concentrations between 1276 and 2438 mg/L (Table 2); however, they were consumed in the UASB system with increasing OLR (Table 5) due to the anaerobic process stability in response to a balanced relation between populations of acidogenic and methanogenic microorganisms.

Tests 2 and 3 showed a high TF influent concentration, which, according to Podeh et al. (1995), might decrease the VFA metabolism by methanogens, due to the toxic effect that reduced the substrate affinity. However, approximately 65 % of VFA were consumed in tests with no phosphorus and 80 % in tests with phosphorus (Table 5) for the biomass adaptation to high concentrations of acids and toxic compounds.

The buffering capacity (PA, Table 5) in the UASB reactors increased between 98 and 1300 mg/L in relation to the substrate. Alkalinity provided an IA/PA relation between 0.2 and 0.5 suitable for the stability of anaerobic digestion (Ripley et al. 1986) and adequate pH in the

Table 5 Methane production and operational control of the two-stage UASB reactors

Test	Temperature (°C)	Reactor	pH	VFA (mg/L)	PA (mg/L)	IA/PA	CH_4 (%)	Bioenergy productivity* (L CH4/L.d)	Methane yield* (L CH_4/g $COD_{removed}$)
1	$24.0^{bc} \pm 0.5$	UASB1	$7.9^{a} \pm 0.1$	$413^{b} \pm 188$	$1178^{b} \pm 92$	$0.33^{b} \pm 0.07$	$79^{a} \pm 2$	$0.38^{b} \pm 0.04$	$0.153^{a} \pm 0.01$
		UASB2	$7.8^{A} \pm 0.1$	$399^{B} \pm 188$	$1276^{C} \pm 92$	$0.30^{AB} \pm 0.07$	$78^{AB} \pm 7$	$0.03^{A} \pm 0.13$	$0.077^{CB} \pm 0.06$
2	$24.9^{ab} \pm 0.5$	UASB1	$7.9^{a} \pm 0.1$	$879^{a} \pm 178$	$1663^{a} \pm 88$	$0.48^{a} \pm 0.06$	$78^{a} \pm 2$	$0.74^{a} \pm 0.04$	$0.186^{a} \pm 0.01$
		UASB2	$7.8^{A} \pm 0.1$	$813^{A} \pm 183$	$1869^{A} \pm 90$	$0.42^{A} \pm 0.06$	$66^{B} \pm 8$	$0.01^{A} \pm 0.11$	$0.008^{C} \pm 0.05$
3	$23.3^{c} \pm 0.7$	UASB1	$8.1^{a} \pm 0.2$	$271^{b} \pm 252$	$1304^{b} \pm 124$	$0.21^{b} \pm 0.11$	$65^{b} \pm 3$	$0.29^{b} \pm 0.06$	$0.135^{a} \pm 0.03$
		UASB2	$7.8^{A} \pm 0.2$	$249^{B} \pm 252$	$1459^{BC} \pm 124$	$0.21^{B} \pm 0.11$	$83^{A} \pm 4$	$0.06^{A} \pm 0.08$	$0.273^{A} \pm 0.04$
4	$25.2^{a} \pm 0.7$	UASB1	$8.0^{a} \pm 0.2$	$439^{b} \pm 261$	$1443^{ab} \pm 142$	$0.23^{b} \pm 0.12$	$76^{a} \pm 3$	$0.66^{a} \pm 0.05$	$0.135^{a} \pm 0.02$
		UASB2	$7.8^{A} \pm 0.2$	$204^{B} \pm 261$	$1728^{AB} \pm 142$	$0.18^{B} \pm 0.12$	$71^{B} \pm 3$	$0.07^{A} \pm 0.07$	$0.121^{B} \pm 0.04$

Different letters (*t* test, $p < 0.05$) mean statistical difference. The comparisons were between UASB1 (lowercase) and UASB2 (uppercase).
*Standard Temperature and Pressure conditions (STP, 273 K and 1 atm)

reactors. Appropriate alkalinity was stimulated by the hydrated lime addition, which avoided high sodium concentrations in the effluent and enabled their reuse in fertigation in comparison with NaOH (Fia et al. 2010).

The VFA, PA and pH values provided adequate conditions for the methanogenic archaeas, with methane content in biogas between 65 and 83 %. During test 3, UASB1 showed 65 % methane in the biogas, possibly due to the acidification that occurred in the system prior to the tests (Final section, Fig. 3). The bioenergy productivity in UASB1 increased with the OLR ($\alpha = 0.5$), i.e., approximately 0.33 L CH_4/L.d in tests 1 and 3 and 0.7 L CH_4/L.d in tests 2 and 4 (Table 5; Fig. 2).

UASB2 showed a low methane production in all tests due to a substrate of less biodegradability and COD (maximum of 4000 mg/L). Therefore, UASB2 was not interesting for the bioenergy production under the conditions applied.

Superior results were expected in the bioenergy productivity with SSP supplementation, because the nutritional deficiency had been prevented. However, the phosphorus supplementation did not affect the methane production significantly ($\alpha = 0.05$) during test with and without SSP, consequently, the phosphorous addition is not necessary for the methane production with CPW in UASB systems (Tables 3, 5).

Likewise, over 50 % of the COD were converted to methane in UASB1, which showed higher methane yields of 0.153 L CH_4/g $COD_{removed}$. In UASB2, the maximum methane yield in tests without phosphorous was 0.077 L CH_4/g $COD_{removed}$, whereas in tests with phosphorus, it was 0.273 L CH_4/g $COD_{removed}$. Such values correspond to 22 and 78 % of the COD conversion to methane, respectively. Therefore, the nutritional supplementation with SSP resulted in no increase in the methane yield in UASB1, but improved UASB2.

In comparison with other studies (Table 4), the two-stage UASB reactors generated between 1.3 and 8 times more bioenergy productivity than other UASB systems (Campos et al. 2013; Guardia-Puebla et al. 2014). However, the UASB reactor for the co-production of hydrogen (Jung et al. 2012) showed 26.2 times more bioenergy productivity than system under study, which has proven the energy recovery from CPW can be maximized. For example, Jung et al. (2012) increased the methane yield to 0.33 L CH_4/g $COD_{removed}$ through the reactor conditioning for the production of metabolites, such as hydrogen, acetic acid and butyric acid, which are interesting for the methane production and operation at an optimum temperature for the anaerobic digestion at 35 °C.

Such a superior methane production in comparison to other systems (Table 4; Campos et al. 2013; Selvamurugan et al. 2010a; b; Guardia-Puebla et al. 2014) can be explained by the start-up period application and gradual OLR increase (Fig. 2). The strategy was important because the inoculum was obtained from reactors fed with swine wastewater, and the adaptation period enabled the microorganism growth and specific metabolisms for the adequate treatment of CPW.

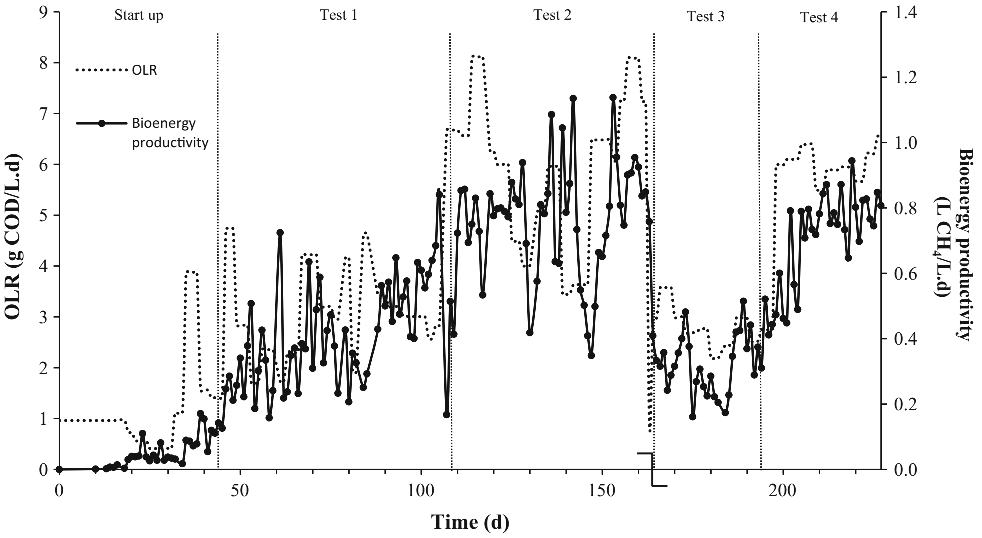
Sludge of two-stage UASB reactors and SBR

After the recovery of energy and effluents from CPW, TS and VS were measured in the sludges by sampling different points in the reactors (Table 6).

Initially, SV and ST were reduced from the bottom to the top layer of the UASB1 in all tests. The solids (according to TS) and microbial biomass (according to VS) in UASB1 accumulated in the lower layers, i.e., the region of higher mineralization and adequate microbial activity for anaerobic digestion (Caicedo et al. 2015).

TS and VS increased in test 2 for the microbial growth and solids sedimentation through time. However, VS diminished in test 3, due to the acidification of the reactors prior to the test. An OLR of 9 g COD/L.d applied after test 2 (test of

Fig. 2 Bioenergy productivity (UASB1 + UASB2) at different OLR in the two-stage UASB reactors



volumetric organic load increase, final section, Fig. 3) caused VFA to overload and lose inoculum (Rajeshwari et al. 2000).

UASB2 and SBR showed low concentrations of TS and VS in all sludge layers, characteristic of sludge of low graininess. Such characteristics of reactors UASB2 and SBR led to a low methane production and removal of organic matter and phenols, because the low biomass concentration produced no stable response to the organic load applied (Latif et al. 2011).

Biomass washing may be a consequence of the exchange of substrate, since the kinetics and metabolic pathways in the biomass were changed when CPW was applied. A substrate alteration can produce spontaneous washing in the granules, which explains the VS reduction from the inoculum (Saravanan and Sreekrishnan 2006). The biomass was gradually recovered, as VS increased in test 2; however, the biomass lost in UASB2 and SBR caused an insufficient degradation of TF in the test with no phosphorus addition (tests 1 and 2).

On the other hand, no considerable biomass growth was observed in tests 1 and 2 for SBR, which may be a consequence of the low specific growth rates (μ) characteristic of aerobic organisms that degrade phenol and high concentrations of TF in the substrates (Shetty et al. 2011).

For tests 3 and 4, after acidification and biomass washing, VS increased in most sludge sampling points, especially in UASB1, which indicates the SSP potentiated a faster growth of anaerobic microorganisms; hence, a shortest stabilization period and a best reactors answer to toxic compounds, as TF. Chemical phosphate sources, as SSP might be expensive, however, waste activated sludge pretreatment with free nitrous acid and other alternative sources might be used for improving the biological reactor performance during acidification and biomass losses (Zhao et al. 2015).

According to the Brazilian regulation, a maximum 0.70 of VS/TS is accepted for the sludge reuse as plants fertilizer (Resolution No. 375 of CONAMA, 2005), which avoids high organic matter concentrations in the soil and microbial activity. According to the parameter, all points of test 1, 8 points of test 2, 5 points in test 3 and 7 points in test 4 are appropriate for applications in the soil. Therefore, the reactor produced material of potential use in soils under all operational conditions studied.

Acidification and recovery of biological reactors

After test 2 (day 202 of reactors operation), a test with OLR of 9 g COD/L.d and COD of 25000 mg/L was conducted. The CPW collected from a farm was applied in the reactors. This CPW was obtained from mechanical production on the farms during the wet processing of coffee fruits in the harvest season (Pedregulho, São Paulo). The addition of unneutralized CPW increased the VFA and

Table 6 TS and VS in the sludge of the two-stage UASB reactors and SBR

Test	Point	UASB1			Point	UASB2			Point	SBR		
		TS (g/L)	VS	VS/TS		TS (g/L)	VS	VS/TS		TS (g/L)	VS	VS/TS
1	1	$47.0^{a} \pm 10.4$	$35.7^{a} \pm 9.1$	0.7 ± 0.2	1	$5.0^{b} \pm 10.4$	$2.8^{a} \pm 9.1$	0.5 ± 0.2	1	$2.1^{a} \pm 10.4$	$4.3^{a} \pm 9.1$	0.5 ± 0.2
	2	$16.0^{A} \pm 10.4$	$11.9^{A} \pm 9.1$	0.7 ± 0.2	2	$5.9^{A} \pm 10.4$	$3.9^{A} \pm 9.1$	0.7 ± 0.2	3	$2.2^{A} \pm 10.4$	$4.2^{A} \pm 9.1$	0.5 ± 0.2
	3	$8.5^{\underline{b}} \pm 10.4$	$5.7^{\underline{b}} \pm 9.1$	0.7 ± 0.2	3	$5.1^{\underline{a}} \pm 10.4$	$2.8^{\underline{a}} \pm 9.1$	0.6 ± 0.2	5	$1.4^{\underline{a}} \pm 10.4$	$2.4^{\underline{a}} \pm 9.1$	0.6 ± 0.2
2	1	$65.1^{a} \pm 10.4$	$51.7^{a} \pm 9.1$	0.8 ± 0.2	1	$8.9^{a} \pm 10.4$	$4.8^{a} \pm 9.1$	0.5 ± 0.2	1	$7.4^{a} \pm 10.4$	$3.4^{a} \pm 9.1$	0.5 ± 0.2
	2	$34.0^{A} \pm 10.4$	$19.6^{A} \pm 9.1$	0.6 ± 0.2	2	$10.0^{A} \pm 14.7$	$5.2^{A} \pm 13.0$	0.5 ± 0.3	3	$11.1^{A} \pm 10.4$	$5.6^{A} \pm 9.1$	0.5 ± 0.2
	3	$8.9^{\underline{b}} \pm 14.7$	$5.3^{\underline{b}} \pm 13.0$	0.7 ± 0.3	3	$8.5^{\underline{a}} \pm 10.4$	$4.6^{\underline{a}} \pm 9.1$	0.5 ± 0.2	5	$8.7^{\underline{a}} \pm 10.4$	$3.8^{\underline{a}} \pm 13.0$	0.4 ± 0.2
3	1	$46.2^{a} \pm 8.6$	$36.8^{a} \pm 8.0$	0.8 ± 0.4	1	$36.5^{a} \pm 8.6$	$30.5^{a} \pm 8.0$	0.8 ± 0.4	1	$8.1^{a} \pm 8.6$	$5.6^{a} \pm 8.0$	0.7 ± 0.4
	2	$46.1^{A} \pm 8.6$	$36.8^{A} \pm 8.0$	0.8 ± 0.4	2	$4.4^{A} \pm 8.6$	$2.8^{A} \pm 8.0$	0.6 ± 0.4	3	$3.4^{A} \pm 8.6$	$2.0^{A} \pm 8.0$	0.6 ± 0.4
	3	$39.2^{\underline{a}} \pm 8.6$	$31.^{\underline{a}} \pm 8.0$	0.8 ± 0.4	3	$4.4^{\underline{a}} \pm 8.6$	$2.7^{\underline{a}} \pm 8.0$	0.6 ± 0.4	5	$3.7^{\underline{a}} \pm 8.6$	$2.3^{\underline{a}} \pm 8.0$	0.6 ± 0.4
4	1	$45.8^{a} \pm 6.1$	$32.9^{a} \pm 5.7$	0.7 ± 0.2	1	$31.2^{a} \pm 6.1$	$25.3^{a} \pm 5.7$	0.8 ± 0.2	1	$6.2^{a} \pm 6.1$	$4.4^{a} \pm 5.7$	0.7 ± 0.2
	2	$45.9^{A} \pm 6.1$	$33.3^{A} \pm 5.7$	0.7 ± 0.2	2	$6.0^{A} \pm 6.1$	$3.5^{A} \pm 5.7$	0.6 ± 0.2	3	$3.1^{A} \pm 6.1$	$2.4^{A} \pm 5.7$	0.8 ± 0.2
	3	$44.6^{\underline{a}} \pm 6.1$	$31.1^{\underline{a}} \pm 5.7$	0.7 ± 0.2	3	$3.6^{\underline{a}} \pm 6.1$	$2.5^{\underline{a}} \pm 5.7$	0.7 ± 0.2	5	$3.3^{\underline{a}} \pm 6.1$	$1.6^{\underline{a}} \pm 5.7$	0.5 ± 0.2

Different letters (*t* test, $p < 0.05$) mean statistical difference. The comparisons were performed between reactor points 1 (lowercase), 2 (uppercase), and 3 (underline lowercase) for UASB1, UASB2 and SBR separately

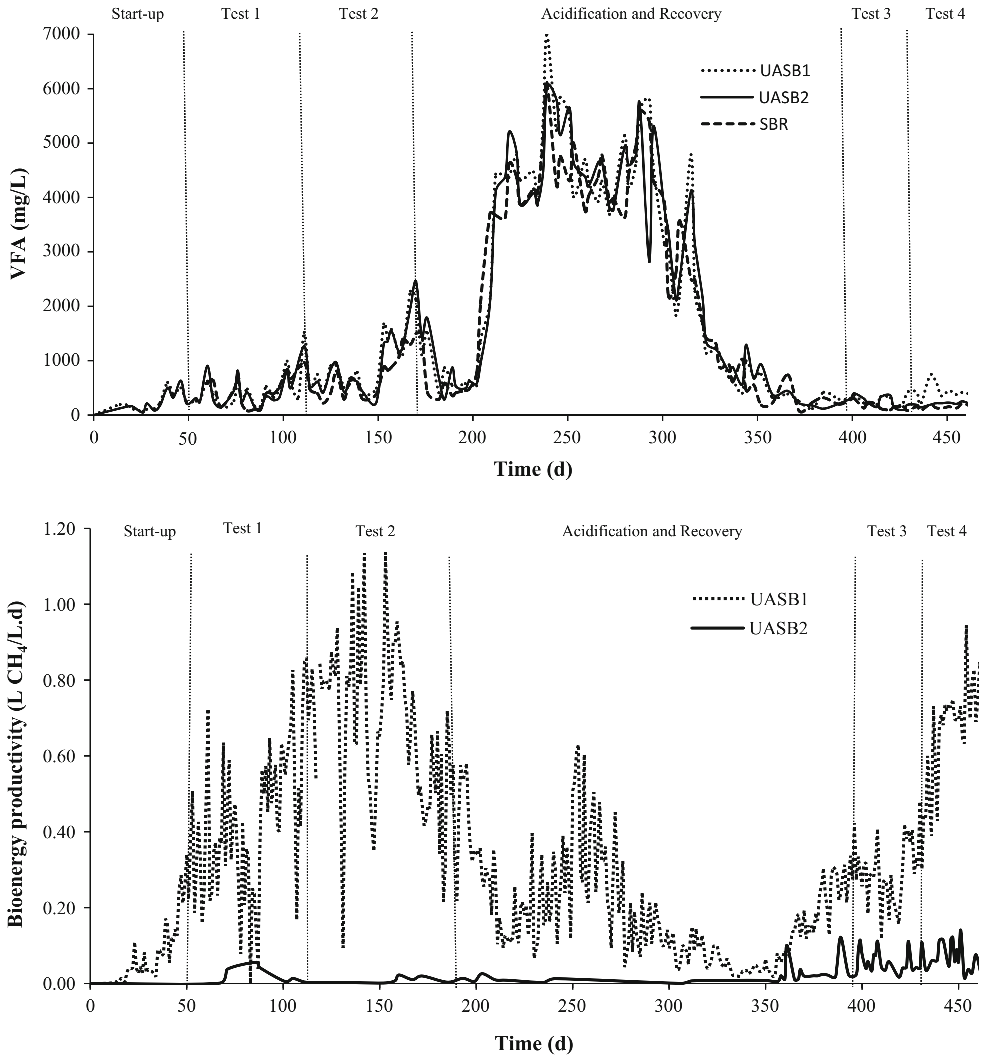


Fig. 3 VFA and bioenergy productivity in the two-stage UASB reactors

decreased the methane production (Fig. 3), which caused acid shock and instability in the reactors.

The OLR of 9 g COD/L.d applied was unfavorable because the VFA concentrations increased to 6998 mg/L and caused reactor acidification. CPW has a high content of soluble compounds, which causes rapid hydrolysis and uncontrolled formation of acids (Harper and Pohland 1986).

Subsequently, the high acid concentrations induced acetoclastic methanogens inhibition, hence, the interruption of the methane production in the reactors at day 340 (Fig. 3; Speece 1996). Similarly, high VFA concentrations in the two-stage UASB stimulated the acetogenic bacteria growth and methanogenic biomass losses as a consequence of differences in the specific growth rates.

The CPW collected on the farm showed variable characteristics, with TF concentrations of up to 1528 mg/L. Similarly, alterations in the microbial community and a new metabolic adaptation may result in the partial or complete breakage of the granule when a substrate is changed (Liu et al. 2003; Saravanan and Sreekrishnan 2006).

Several strategies were applied for decreasing the acids concentrations and recovering the methane production (Fig. 4), so that the adverse conditions in the biological reactors could be overcome.

Initially, the pH in the substrate was adjusted to values between 7.6 and 7.8 for a higher neutralizing capacity in the reactors (Recovery 1). As such a strategy enabled no reactors recovery, the influent concentration was decreased to 1020 mg/L COD (Recovery 2) and the VFA accumulated in the reactors started to be consumed. As the VFA concentration remained high (approximately 2000 mg/L), 50 % of the substrate were mixed with 50 % of effluent of the reactor treating swine manure wastewater (SMW).

The SMW application enabled the reactor recovery because PA increased to approximately 2031 mg/L. The mixture was decreased to 40 % SMW:60 % CPW at day 351, 30 % SMW:70 % CPW at day 366 and 10 % SMW:90 % CPW at day 371. The feeding with 100 % of CPW started at day 374 after the reactors operation. The application of the collected CPW was interrupted at day

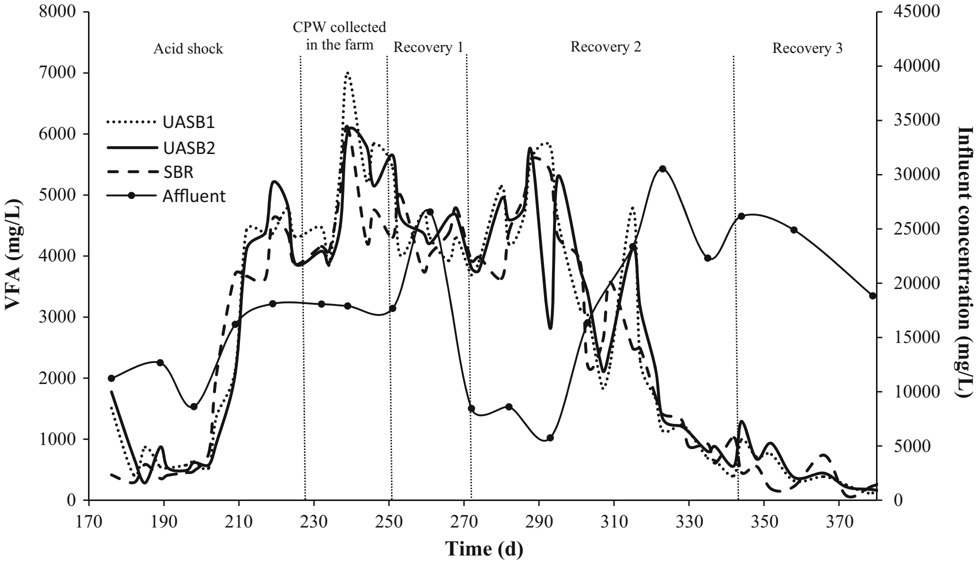


Fig. 4 VFA and influent concentration during acidification and recovery periods of two-stage UASB reactors and SBR

368, as it was the end of the coffee harvest season. Later, simulated CPW was used as substrate.

When 90 % of CPW were applied, the VFA decreased from 1200 to 73 mg/L and the methane synthesis was recovered (361 operation days) after a long period of zero production. The reactors recovery showed the methanogenic biomass remained viable during the acidifying period and the strategies applied enabled microbial growth, hence, methane production.

After the reactors recovery, test 3 was started with lower VFA concentrations, but after an important loss of aerobic and anaerobic biomass. The recovery restored the active biomass adapted to toxic compounds common in CPW, as polyphenols. The results of acidification and recovery phases were not considered, because they were obtained under uncontrolled conditions; however, the recovery strategies evaluated can be applied to real systems with problems of acids accumulation.

Conclusion

The two-stage UASB reactors and SBR improved the CPW quality by reducing over 80 % of the organic load represented as solids and COD and 70 % of TF and provided 50 % conversion of organic matter to methane. HRT of 90 h for the UASB system and 75 h for SBR were enough for the dual purpose of organic matter stabilization and bioenergy production. They represent a technological breakthrough in comparison to other systems operating with CPW, as they enable the treatment of higher volumes of waste daily.

The addition of phosphorus to CPW did not improve the methane production and removals of TF and COD in the two-stage UASB reactors; however, it promoted microbial growth and TF removal in SBR.

UASB and SBR reactors could be recovered after acidification conditions through the mixture of CPW with swine manure wastewater treated in anaerobic reactor and supplementation of the substrate with phosphorous sources.

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