Combination of chemical coagulation, photo-Fenton oxidation and biodegradation for the treatment of vinasse from sugar cane ethanol distillery

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ABSTRACT

The post-treatment of biodigested sugarcane vinasse was envisaged in the present study following three different approaches: i) coagulation/flocculation — Approach 1; ii) combination of coagulation/flocculation with photo-Fenton reaction — Approach 2; iii) coagulation/flocculation followed by biological degradation and photo-Fenton reaction — Approach 3.

The coagulation/flocculation per se provided a slight increase in effluent's biodegradability, a decrease in toxicity and turbidity, and provided moderate removals of total organic carbon (TOC), biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD). The operating costs associated with chemicals consumption are low (5.7 R\$/m^3 ≈ 1.4 €/m^3).

The second and third treatment approaches allowed to reach a nontoxic effluent, improved the biodegradability and led to similar high global organics removal efficiencies. The combined treatment consisting of coagulation/flocculation plus photo-Fenton oxidation (Approach 2) revealed to be a promising solution for treating this wastewater, in order to be recirculated into the high rate anaerobic reactor. Additionally, this solution provides smaller costs (84.9 R\$/m^3 ≈ 20.2 €/m^3) associated with chemicals and energy consumption, which are however very high. Nonetheless, this cost can be reduced by about 40% if solar radiation is used in the photo-Fenton process.

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1. Introduction

With the increasing shortage of fossil fuels, strategies have been implemented worldwide stimulating the production of biofuels, namely ethanol. In this scenario, since 1975 Brazil has encouraged the production of ethanol from sugarcane under the Brazilian Alcohol Program "Proálcool" (Moraes et al., 2015; Christofoletti et al., 2013), being the country with the highest production worldwide, approximately 26 billion litres in 2012/2013 (Júnior et al., 2014).

The distillation of sugarcane juice and molasses to produce ethanol generates large quantities of vinasse: about 10–14 L per litre of ethanol produced (Júnior et al., 2015; Ortegón et al., 2016). This effluent is characterized by strong brown colour, acidic pH, high turbidity, high content of organic compounds (acids, alcohols, aldehydes, ketones, esters and sugars) that contribute for its chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5), and high concentration of ions (K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Cl^- and SO_4^{2-}) (Barrera et al., 2013; Christofoletti et al., 2013; Marinho et al., 2014; Ortegón et al., 2016).
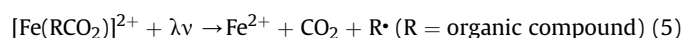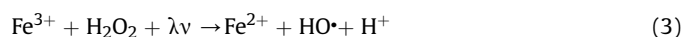
As vinasse presents high organic matter and nutrient contents, it has been common practice to use it as fertilizer in sugarcane fields (Júnior et al., 2014; Moraes et al., 2015). The benefits should not be

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used as the sole justification for the indiscriminate disposal of vinasse into agricultural fields, so that this practice might be a palliative alternative providing a false impression of solving efficiently the management of vinasse (Fuess and Garcia, 2014). In fact, when used in large quantities, the soils become saturated and there is a risk of contamination of surface water and groundwater nearby the fields (Christofoletti et al., 2013; Marinho et al., 2014), causing serious environmental problems. Due to its strong organic matter content (high values of BOD_5 and COD), vinasse causes depletion of dissolved oxygen in surface water, lowers the pH, causes the death of aquatic fauna and flora, and introduces contaminants that hinder the use of water for human routines; further, it provides unpleasant odours (Christofoletti et al., 2013). In order to minimize the environmental impacts of vinasse it is necessary to apply a treatment process prior to discharge into a water body or disposal on land. In general, anaerobic digestion is the process usually adopted (Syaichurrozi et al., 2013; Júnior et al., 2014, 2015; Barrera et al., 2015; Moraes et al., 2015) because this effluent presents high carbon:nitrogen ratio, leading to methane production, which represents an economic advantage (Wilkie et al., 2000). Anaerobic digestion presents high efficiencies with regards to organic compounds removal, however the treated wastewater still contains recalcitrant compounds that are not biodegradable, and are even inhibitory to biological activity. This is a very critical issue because part of the biodigested vinasse is recirculated back into the anaerobic reactor. The advantage of recirculating the treated vinasse is to reduce the consumption of chemicals for neutralization of the stream fed to the anaerobic digester, taking advantage of the alkalinity of the biodigested vinasse (Barros et al., 2016; Guerreiro et al., 2016).

In this context, it is crucial to partially oxidize the recalcitrant compounds present in biodigested vinasse using an efficient process able to improve its biodegradability and generate a nontoxic effluent. In this perspective, the advanced oxidation processes, and particular the photo-Fenton oxidation, seems to be a good option for that purpose. This process is based on principles that are common to the dark Fenton one, namely the generation of extremely reactive hydroxyl radicals (that will unselectively attack the organic compounds), making use of hydrogen peroxide and a catalyst like ferrous ion in acidic medium (Eq. (1)) (Walling, 1975), but with simultaneous use of ultra-violet/visible radiation that allows the decomposition of hydrogen peroxide into hydroxyl radicals (Eq. (2)) (Sun and Pignatello, 1993). Additionally, there is the production of further HO• (and others) radicals upon Fe^{2+} regeneration either by Eq. (3), by photolysis of iron (III) hydroxide (Eq. (4)), or by photolysis of complexes formed between the organic compounds or their intermediates with Fe^{3+} (Eq. (5)) (Sun and Pignatello, 1993; Huang et al., 2008).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO• + OH^- \tag{1}$$

$$H_2O_2 + \lambda \nu \rightarrow 2HO• \tag{2}$$

$$Fe^{3+} + H_2O_2 + \lambda \nu \rightarrow Fe^{2+} + HO• + H^+ \tag{3}$$

$$Fe(OH)^{2+} + \lambda \nu \rightarrow Fe^{2+} + HO• \tag{4}$$

$$[Fe(RCO_2)]^{2+} + \lambda \nu \rightarrow Fe^{2+} + CO_2 + R• \text{ (R = organic compound)} \tag{5}$$

As vinasses are characterized by high turbidity that will filter the radiation, a pre-treatment to reduce turbidity is required. One possibility is to use coagulation/flocculation, because this process is easily applied and requires low capital and operating costs, being usually employed as a pre-treatment stage (Zayas et al., 2007). Coagulation/flocculation promotes the destabilization of the colloids by adding coagulants (usually iron or aluminium salts) and their further aggregation with addition of flocculants (polymers). The removal of the particles formed is achieved through filtration or sedimentation (Pang and Abdullah, 2013). Use of iron salt as coagulant might be particularly advantageous as the remaining dissolved metal might be employed as catalyst in a downstream Fenton/photo-Fenton process, thus reducing costs with chemicals.

Following the strategy just described, the organic compounds not removed by coagulation/flocculation are then subjected to an advanced oxidation process to be partially oxidized. The subsequent biological treatment, if required, can be carried out for instance in a sequential batch reactor (SBR) operating in 5 stages per cycle (feeding, reaction, sedimentation, discharge of the clarified effluent, sludge purge and idle) (Metcalf and Eddy, 2003). Such configuration presents some advantages comparatively to the conventional biological treatment, namely flexibility and simplicity, low cost and increased resistance to fluctuations in the feeding (Suresh et al., 2011). Additionally, equalization, reaction and clarification occur in the same reactor (EPA, 1999).

In the open scientific literature, only one study was found dealing with the treatment of sugarcane vinasse by Fenton or photo-Fenton processes (Hadavifar et al., 2009) and another one about the use of chemical coagulation/flocculation (Zayas et al., 2007) per se. In both cases the processes were tested as standalone technologies and no costs data are provided. More recently it was shown that integration of dark Fenton with coagulation/flocculation could be a promising solution, but costs are high (Guerreiro et al., 2016). The photo-Fenton process allows reaching similar or even better performances, with lower consumptions of chemicals as compared with the dark one. Moreover, if solar radiation is used, sustainability (economic and environmental) can be further enhanced. So, the main goal of this work is to reach the best treatment strategy considering different possibilities: coagulation/flocculation alone − Approach 1, coagulation/flocculation plus photo-Fenton oxidation − Approach 2, and coagulation/flocculation combined with biological degradation and photo-Fenton oxidation − Approach 3, in order to improve the biodegradability and decrease the toxicity of the biodigested sugarcane vinasse for its recirculation into high rate anaerobic reactors, associated with the maximum mineralization of organic compounds, at the lowest treatment cost. Other combinations of these technologies have been discarded as discussed along the manuscript.

2. Materials and methods

2.1. Wastewater

The vinasse used in this study was collected in a sugar cane ethanol distillery located in Ribeirão Preto, São Paulo, Brazil. Firstly, this wastewater is fed to two upflow anaerobic sludge blanket (UASB) reactors in series operating at thermophilic temperature (55 °C) for organic matter degradation and methane production. The UASB reactors have a total volume of 12.1 L and of 5.6 L for first and second, respectively, and operated with hydraulic detention time (HDT) of 24.0 h and 11.1 h, respectively. The resulting effluent, used in this study, was characterized as described in Section 2.3.

2.2. Experimental procedure

2.2.1. Coagulation/flocculation

The coagulation/flocculation runs were performed in a Jar Test apparatus (Velp Scientifica, model JLT6) at room temperature (24−28 °C). In each beaker, the coagulant (ferric chloride hexahydrate - $FeCl_3.6H_2O$ from LABCHEM) was added to 600 mL of vinasse and then the pH was adjusted to the desired value using 10 M NaOH

and/or 1 M H_2SO_4. Subsequently, the mixture was subjected to rapid stirring (150 rpm) for 3 min and finally to slow stirring (20 rpm) for 15 min; the operating conditions concerning the stirring speed and time were fixed in accordance with studies reported in the literature (Eckenfelder, 2000; Satterfield, 2004; Bose, 2010; Poland and Pagano, 2010; Rodrigues et al., 2013a). No flocculant was added because it was observed in a preliminary study that it did not improve the organic matter removal during the slow stirring stage (Rodrigues et al., 2013a). This way the operating costs are reduced.

After coagulation/flocculation the effluent was decanted for 24 h for sedimentation of the flocs formed and separation of the liquid phase. The supernatant was collected and several parameters were measured, namely turbidity, BOD_5, COD, TOC, toxicity and dissolved iron (when necessary) as detailed below.

2.2.2. Photo-Fenton's oxidation

The photo-Fenton oxidation runs were performed in a 500-mL capacity glass cylindrical batch reactor equipped with a UV/visible lamp (150 W high mercury vapour pressure lamp from Heraeus, model TQ 150), emitting 500 W/m^2 at wavelengths from 200 to 600 nm. The lamp was located axially within an immersion quartz tube connected to a water thermostatic bath (Huber, polystat cc1) for temperature control.

For each run, 250 mL of biodigested vinasse was used. After reaching the pre-defined temperature (in the range 20–55 °C), the pH was adjusted using 1 M H_2SO_4 or 1 M NaOH. Then, the required amount of iron (as $FeCl_3.6H_2O$ from Labchem), when necessary, and H_2O_2 (30% w/v, from Chem-Lab®), was added. Finally, after the radiation source was switched on, the reaction was left to extend up to 3 h. In the case of Approach 2 there was no need to add $FeCl_3.6H_2O$ because the dissolved iron resulting from the coagulation/flocculation stage (258.3 mg/L) was used as catalyst. Normally the catalyst for Fenton's process is Fe(II), added as ferrous sulphate; however, in this study ferric chloride was used to avoid odour and toxicity problems resulting from sulphate reduction to hydrogen sulphide by anaerobic bacteria present in the vinasse.

The oxidation reaction proceeded under constant stirring, using a magnetic bar and a magnetic stirrer (Falc). Periodically, samples were taken from the reactor for measuring the total organic carbon (TOC); the reaction in the sampling vials was stopped by adding excess of sodium sulphite (that reacts instantaneously with remaining hydrogen peroxide). As regards to other parameters measured at the end of reaction (3 h), namely COD, BOD_5 and toxicity (through inhibition of *Vibrio fischeri*), the reaction was stopped by eliminating the residual H_2O_2 and precipitating the iron in solution. For that, the pH was initially raised to 12.0 by the addition of 10 M NaOH, and then the sample was neutralized to pH ~7.0 using conc. H_2SO_4. The samples for toxicity assessment were neutralized with HCl 1 M as proposed by the analytical method.

2.2.3. Biological degradation

The SBR consists of a cylindrical reactor with 2.0 L of capacity, operating for 19 cycles (i.e. up to a pseudo-steady state was reached), each with a duration of 24 h divided as follows: 1 h for feeding, 14 h for reaction, 8 h for sedimentation, 0.8 h and 0.2 h for discharge and idle, respectively. For the first cycle, 0.5 L of activated sludge from the aeration tank of Parada Wastewater Treatment Plant (WWTP) - located in Águas Santas, Portugal - with volatile suspended solids (VSS) of ~5 g/L was fed to the reactor. Then, the reactor was fed with 0.5 L of pre-treated effluent after addition of the amount of nitrogen and phosphorous usually required for biological treatment (BOD_5:N:P of 100:5:1). In subsequent cycles,

the reactor was fed with 0.4 L of vinasse pre-treated by coagulation/flocculation. During the reaction stage, the mixed liquor was stirred at 300 rpm using a magnetic bar and a stirrer (Falc). The dissolved oxygen (OD) was maintained at ~3.0 mg O_2/L by using a diffused air aeration system coupled to an air pump (Aquamedic Mistral 2000). The biological reactor operated at ambient temperature (average value ~27 °C). COATI timers were used to turn on/off the peristaltic pumps (Gilson M312), the magnetic stirrer and the air pump.

The duration of each cycle and each cycle stage as well as the concentration of dissolved oxygen were established in accordance with studies reported in the literature (Sirianuntapiboon and Sansak, 2008; Al-Amrani et al., 2014; Sathian et al., 2014; Rodrigues et al., 2014a, 2014b; Esteves et al., 2015).

2.3. Analytical methods

The inhibition of *Vibrio fischeri* test was performed according to standard DIN/EN/ISO 11348-3 (International Organization for Standardization, 2005). The bacteria were put in contact with the sample for incubation at 15 °C. After contact times of 5, 15 and 30 min the bioluminescence was measured in a Microtox Analyzer (model 500).

The hydrogen peroxide was measured following the method developed by Sellers (1980). It quantifies the yellow-orange colour of the complex formed from the reaction of hydrogen peroxide with titanium oxalate. For that, the absorbance at 400 nm was measured in a Thermo Electron Corporation model Helios γ spectrophotometer.

The dissolved iron was measured by flame atomic absorption spectrometry (Method 3111 B (APHA, 1998)) using an AAS UNICAM spectrophotometer, model 939/959. The samples were firstly filtered through 0.45 μm pore size cellulose nitrate membranes (Filter-Lab). Other parameters were measured according to methods described in Standard Methods (APHA, 1998): the turbidity was evaluated by method 2130 B using a turbidimeter HI88703 from Hanna Instruments; the biological oxygen demand after 5 days (BOD_5) was measured according to method D 5210, using an OxiTOP (Velp Scientifica) apparatus; the chemical oxygen demand (COD) was assessed by the closed reflux method (Method 5220 D); the TOC was determined by catalytic combustion at about 680 °C - method 5310 D, using a TC/TOC analyzer (Shimadzu 5000 A apparatus); the total phosphorus was quantified by colorimetry by the ascorbic acid method (Method 4500P − E), after digestion with ammonium persulfate; the total suspended solids (TSS) and volatile suspended solids (VSS) were quantified by gravimetric analysis − Method 2540 B and Method 2540 E, respectively; the total nitrogen was determined by colorimetry (Method D992-71 of ASTM Standards (ASTM, 1973)) after previous digestion (Method 4500 - N C).

All analytical determinations were performed in duplicate, and the coefficients of variation were less than 2% for TOC, 6% for BOD_5, 4% for COD and inhibition of *Vibrio fischeri*, and 3% for the other parameters.

3. Results and discussion

The biodigested vinasse used in this study shows high levels of organic matter (quantified in terms of COD, TOC and BOD_5), turbidity and TSS, low biodegradability (BOD_5/COD ratio < 0.4) and some toxicity to *Vibrio fischeri* (see Table 1), reinforcing the importance of an appropriate post-treatment, for recirculation into anaerobic reactors and/or discharge into water bodies/land disposal.

Table 1
Characteristics of the raw biodigested sugarcane vinasse effluent, after coagulation/flocculation (Approach 1) and after photo-Fenton oxidation previously treated by coagulation/flocculation (Approach 2), and respective global treatment efficiency (partial removal efficiencies are shown between brackets), for optimized operatory conditions, along with respective operating costs.

Parameter	Biodigested vinasse	After coagulation/flocculation (Approach 1)	After Photo-Fenton oxidation (Approach 2)	Global treatment efficiency (%)
pH	6.2	7.1[b]	7.0[b]	–
COD (mg O_2/L)	12,550	7079.3 (43.6)	1153.2 (83.7)	91.0
BOD$_5$ (mg O_2/L)	4114	3074.0 (25.3)	795 (74.1)	81.0
TOC (mg C/L)	4202	2460.7 (41.4)	229.4 (90.4)	95.0
BOD$_5$:COD ratio	0.33	0.43 (–)	0.69 (–)	–
P$_t$ (mg P/L)	15.4	13.7 (11.0)	n.d. (–)	–
N$_t$ (mg N/L)	4.0	2.0 (50.0)	n.d. (–)	–
Turbidity (NTU)	900	6.5 (–)	n.d. (–)	–
TSS (mg/L)	1500	10 (–)	n.d. (–)	–
Vibrio fischeri Inhibition 5 min (%)	45.1	5.6 (–)	0.0 (–)	–
Vibrio fischeri Inhibition 15 min (%)	46.7	6.3 (–)	0.0 (–)	–
Vibrio fischeri Inhibition 30 min (%)	47.1	7.7 (–)	0.0 (–)	–
Operating cost of each step (R\$/m^3/€/m^3) [a]	–	5.7/1.4	79.2/18.9	–

nd. – not determined.

[a] Operating costs are related to the consumption of chemicals (the costs of treatment/processing of the sludge generated were not considered). The costs of reagents were those given by OCC Química and Solvay - Peróxidos do Brasil (Brazil): H_2O_2 (50.0% (w/v), density at 25 °C = 1.2 g/cm^3) – 2.0 R\$/kg; FeCl$_3$ (38% (w/w)) – 1.5 R\$/kg. Energy cost for Brazilian companies = 0.4 R\$/kWh. For converting from Brazilian Real to Euro, it was used the exchange rate of 4.2 R\$/€ - European Central Bank and Portugal Bank, 07 April 2016 (www.bportugal.pt).

[b] Upon neutralization of the effluent.

3.1. Coagulation/flocculation (Approach 1)

3.1.1. Effect of pH

For optimization during coagulation/flocculation, the pH was adjusted in the range 2.0–6.2 (the highest value corresponding to the pH of the biodigested vinasse). Fig. 1 shows that the maximum TOC (41.4%), BOD$_5$ (25.3%) and COD (43.6%) removals occurred at pH 3, originating an effluent with low turbidity (6.5 NTU) – see Fig. 1b - and increased biodegradability, i.e., BOD$_5$:COD ratio increased from 0.33 in biodigested vinasse to 0.43 after coagulation/flocculation. The toxicity decreased at pH 3 but the effluent still presents 5.6–7.7% inhibition of *Vibrio fischeri* (see Fig. 1b).

These results allow establishing the pH of 3.0 as the best one for operating the coagulation/flocculation process. This pH value was the same reached by Guerreiro et al. (2016) for biodigested vinasse with a much lower amount of organic compounds (COD = 6836 mg/L, TOC = 1790 mg/L and BOD$_5$ = 2096 mg/L) comparatively to the one used in this study. At pH 3.0, the iron species present in solution are Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$, so the coagulation/flocculation occurs probably by the charge neutralization mechanism (Duan and Gregory, 2003).

3.1.2. Effect of coagulant dose

Once the optimum pH (3.0) was established, the effect of the concentration of Fe^{3+} (between 125 mg/L and 1000 mg/L) was assessed. It was found that removals of TOC, COD, BOD$_5$ and turbidity increased with the coagulant dose until 500 mg Fe^{3+}/L, and higher doses did not provide any efficiency improvement (see Fig. 2). The appearance of an optimum coagulant dose can be explained by the charge neutralization theory. When coagulant was added to vinasse, Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ interacted with negative colloids and neutralized their charges, which promoted the colloids destabilization. However, when coagulant was in excess, colloids can absorb the cations and become positively charged, so, the colloids were stable again as a result of electrical repulsion [Verma et al., 2010]. For $[Fe^{3+}]$ = 500 mg/L the removals of TOC, COD and BOD$_5$ were 41.4, 43.6 and 25.3%, respectively, the BOD$_5$:COD ratio reached 0.43, turbidity was 6.5 NTU and the percent inhibition of *Vibrio fischeri* decreased to 5.6–7.7%.

The coagulant dose (corresponding to 1.45 g FeCl$_3$/L) was

previously reported by Guerreiro et al. (2016) as the optimal dose for the treatment of vinasse from sugar cane ethanol distillery after treatment by anaerobic digestion with less quantity of organic matter, and also by Günes (2014) for the treatment of a landfill leachate with high organic matter content, similar to the biodigested vinasse used in this study. However, Zayas et al. (2007) reported an optimum dose of 20 g FeCl$_3$/L for treating a biodigested vinasse (although with a slightly smaller COD of 8525 mg/L).

Operating at pH = 3 and $[Fe^{3+}]$ = 500 mg/L, coagulation/flocculation reduced the turbidity and the toxicity of effluent and led to a considerable organic matter reduction, but the biodegradability improvement (BOD$_5$:COD ratio increased from 0.33 to 0.43) was very low. For this reason, it becomes important to subject the vinasse to a subsequent treatment. The coagulation is an important preliminary process, with low operating cost (5.7 R\$/m^3 ≈ 1.4 €/m^3) – see Table 1 – mainly associated with iron chloride consumption, because the costs of acid and base for pH adjustment are negligible.

3.2. Coagulation/flocculation followed by photo-Fenton reaction (Approach 2)

Firstly, the biodigested vinasse was treated by photo-Fenton per se, at temperatures in the range 20–55 °C. Temperatures below 20 °C were not tested because this is the average ambient temperature in the region of São Paulo – Brazil at the time of vinasse production (April till November). On the other hand, temperatures higher than 55 °C were also not tested because this is the temperature of the vinasse at the outlet of the anaerobic reactor. In addition, the use of higher temperatures would mean a higher treatment cost. Moreover, for temperatures above 60–70 °C the thermal decomposition of H_2O_2 is intensified, impairing the formation of hydroxyl radicals, thereby affecting the oxidation of the organic matter.

The experimental results (not shown for brevity reasons) evidenced that the photo-Fenton process by itself is inefficient, providing very low removals of TOC (9.1%), COD (2.5%) and BOD$_5$ (1.3%) after 3 h. Such low efficiency of the process is associated with the high turbidity of vinasse that impairs the penetration of
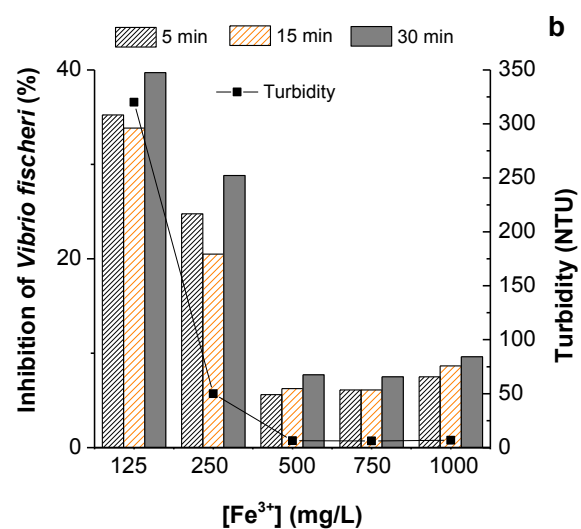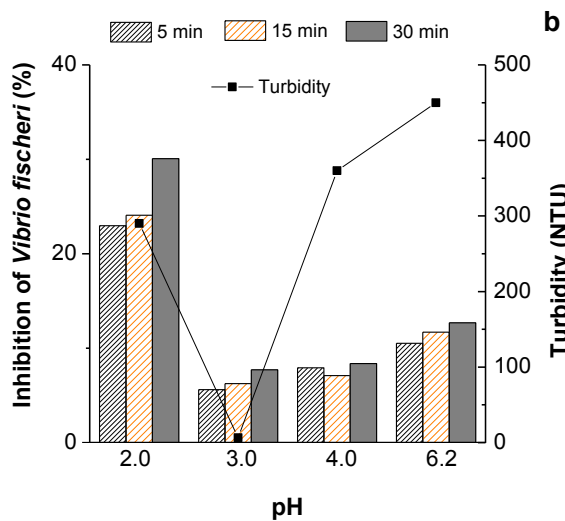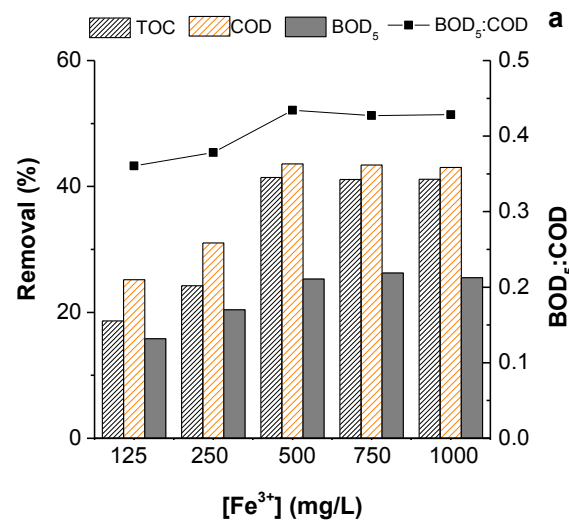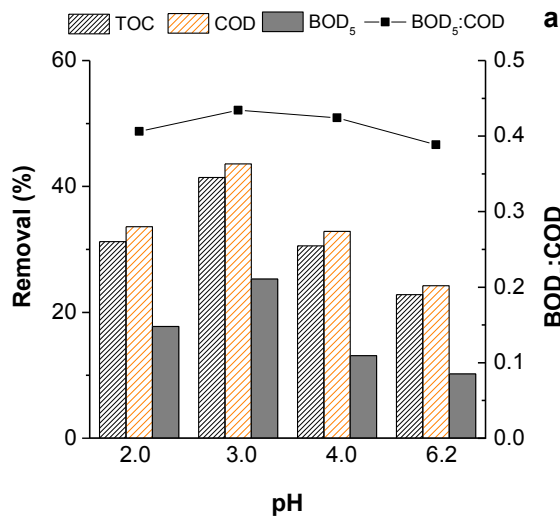
Fig. 1. Removals of TOC, COD and BOD$_5$ and biodegradability (a), turbidity and toxicity of the effluent (b) for different pH values in the coagulation/flocculation process - Approach 1 ($v_{coagulation}$ = 150 rpm, $t_{coagulation}$ = 3 min, [Fe^{3+}] = 500 mg/L, $v_{flocculation}$ = 20 rpm, $t_{flocculation}$ = 15 min).

Fig. 2. Effect of Fe^{3+} dose in the removal of TOC COD, BOD$_5$ and BOD$_5$:COD ratio (a), turbidity and toxicity of the effluent (b) in the coagulation/flocculation process - Approach 1 ($v_{coagulation}$ = 150 rpm, $t_{coagulation}$ = 3 min, pH = 3.0, $v_{flocculation}$ = 20 rpm, $t_{flocculation}$ = 15 min).

radiation in solution. Thus, the coagulation/flocculation as pre-treatment step has an important role in the treatment, because this process reduces the turbidity of the effluent (as shown in Section 3.1). Therefore, the photo-Fenton process was optimized for effluent previously treated by coagulation/flocculation under the best operating conditions found (pH = 3 and [Fe^{3+}] = 500 mg/L). To improve the biodegradability and generate a non-toxic effluent the photo-Fenton reaction seems to be a good alternative, employing as catalyst the dissolved iron resulting from the previous coagulation/flocculation stage (258.3 mg Fe/L). Therefore, a parametric study was carried out aiming to find the best dose of H_2O_2, temperature, pH and irradiance required to maximize the organic compounds removal, reduce the toxicity and improve the effluent biodegradability. This will be dealt with in the following sections.

3.2.1. Influence of temperature

The influence of temperature on the process efficiency was evaluated by performing some runs where this parameter was varied in the range 20–55 °C. Fig. 3a shows the histories of mineralization at different temperatures, with best results being reached at the highest temperature tested of 55 °C. The final COD and BOD$_5$ removals, the BOD$_5$:COD ratio, as well as the efficiency of hydrogen peroxide use (determined as the ratio between the TOC conversion and H_2O_2 consumption – X_{TOC}:X_{H2O2}) follow the same tendency of TOC reduction; the best results were achieved at 55 °C (see Fig. 3b and Table 2) with 88, 80, and 70% for TOC, COD and BOD$_5$ removals, respectively, 0.64 for the BOD$_5$:COD ratio and 0.88 for H_2O_2 efficiency.

Regarding the toxicity of the effluent, quantified by the inhibition of *Vibrio fischeri*, it should be noted that at 20 °C there was an increased toxicity compared to the effluent after coagulation/flocculation (from 5.6-7.7% to 12.5–19.5% - see Table 2), which can be due to the formation of some oxidation by-products, more toxic than those coming from coagulation/flocculation. For the other
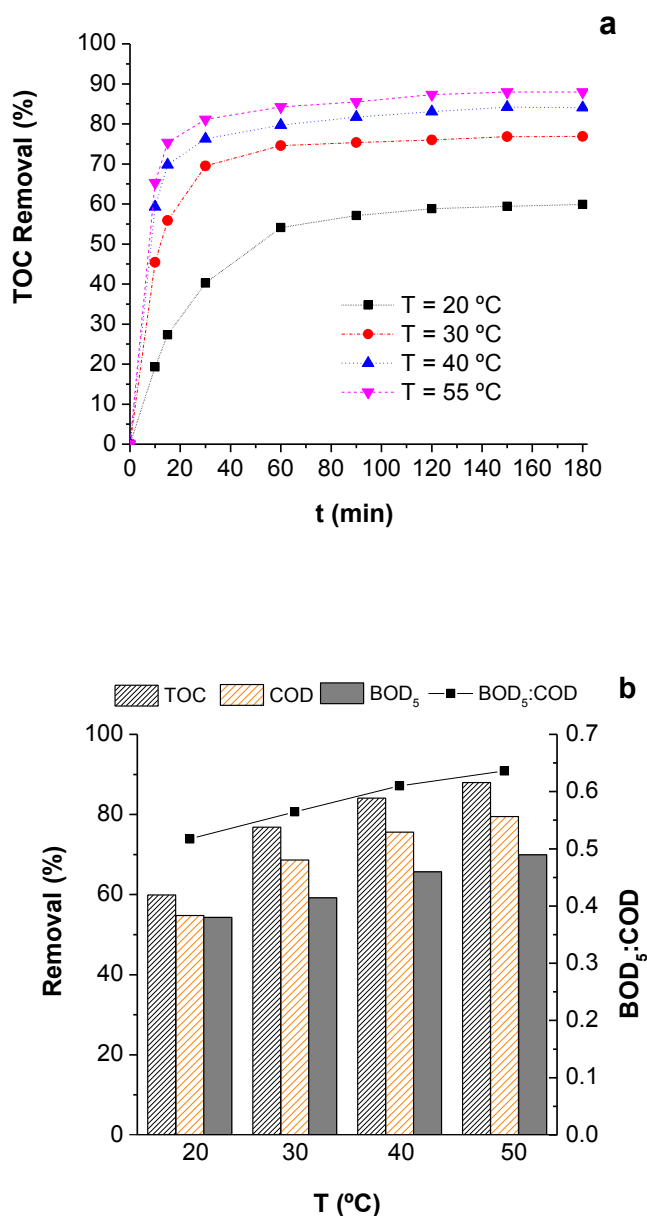
Fig. 3. Influence of temperature on TOC removal along the reaction (a) and removal of TOC, COD and BOD$_5$ and BOD$_5$:COD ratio after 180 min of photo-Fenton reaction (b) after the coagulation/flocculation step - Approach 2 ([H$_2$O$_2$] = 14.5 g/L, pH$_{initial}$ = 3.0, [Fe^{3+}] = 258.3 mg/L, I = 500 W/m^2).

temperatures tested, the effluent showed no toxicity – Table 2. The optimum value of temperature (55 °C) is the same as reported by Guerreiro et al. (2016) when treating a similar effluent by dark Fenton oxidation.

The total operating costs related to the consumption of chemicals (hydrogen peroxide and iron chloride used in the coagulation/flocculation step) and energy (associated to the lamp used) are presented in Table 2. The energy costs associated with the effluent heating were considered to be null (because the natural effluent temperature ranges from 20 to 55 °C), whereby the total cost is the same for all temperatures tested as the other operating parameters remain constant. It must be emphasized that the energy cost considerably contributes (36.0 R\$/m^3 ≈ 8.6 €/m^3) to the overall process cost. The H$_2$O$_2$ consumption is the second variable that most influences the treatment cost. Using 14.5 g/L of H$_2$O$_2$, the

residual iron concentration from the coagulation step, and an irradiance of 500 W/m^2, the total cost amounts to 105.6 R\$/m^3 (25.1 €/m^3).

3.2.2. Effect of pH

To evaluate the effect of pH four experiments were performed, varying this parameter in the range 1.5–4.0. All the other variables were fixed: [H$_2$O$_2$] = 14.5 g/L, T = 55 °C and irradiance = 500 W/m^2 (corresponding to a lamp power of 150 W). Fig. 4a presents the results of the TOC removal along the reaction time. It is possible to observe, for all pH values tested, that the TOC reduction is fast in the first 60 min of reaction, then the oxidation rate slightly decreases till 120 min of reaction and finally TOC remains nearly constant. The maximum mineralization (and also COD and BOD$_5$ removals), as well as BOD$_5$:COD and X$_{TOC}$: X$_{H2O2}$ ratios, were reached at pH 3 with 70, 80 and 88% removals for BOD$_5$, COD and TOC, respectively, 0.64 for BOD$_5$:COD ratio and 0.88 for X$_{TOC}$:X$_{H2O2}$ ratio – see Fig. 4b and Table 2. Thus, pH 3 can be considered as the optimal value; the optimum pH for a photo-Fenton system usually lies in the range 2–3, regardless of the type of effluent to be treated (Wu et al., 1999). As a matter of fact, the pH affects the amount of Fe^{3+} present in solution. On one hand, for pH values higher than 4 the formation of insoluble iron oxides occurs reducing the fraction of Fe^{3+} dissolved (Kwon et al., 1999). On the other hand, in very acidic pH values the complex Fe(OH)$^{2+}$ is present in a reduced amount, and the two more photo reactive compounds (Fe(OH)(H$_2$O)$_5^{2+}$ and Fe(OH)$_2$(H$_2$O)$_4^+$) are also present in smaller quantities to generate the radicals and regenerate the catalyst. However, the Fe(H$_2$O)$_6^{3+}$ species is present in a greater amount but it has lower absorptivity, which limits the absorption of radiation (Safarzadeh-Amiri et al., 1996). Moreover, pH < 2.5 allows to occur the scavenging reaction between the hydroxyl radical and H$^+$ (HO$^•$ + H$^+$ + e$^-$ → H$_2$O) (Spinks and Woods, 1990).

Regarding toxicity data, evaluated by the percentage of *Vibrio fischeri* inhibition, these are shown in Table 2. There was an increase from 5.6 to 7.7% (biodigested vinasse toxicity recorded after coagulation/flocculation) to 12.0–21.3% after photo-Fenton reaction at pH 1.5 and 6.6–9.5% at pH 2 (see Table 2). For the other pH values tested - 3 and 4 - the effluent showed no toxicity. The increase of toxicity for pH 1.5 and 2 may be again due to the formation of by-products, more toxic than those present in the biodigested vinasse after coagulation/flocculation.

3.2.3. Effect of the initial H$_2$O$_2$ dose

To evaluate the influence of the initial dose of hydrogen peroxide, five runs were carried out using the following H$_2$O$_2$ concentrations: 0, 4.5, 7.0, 9.0 and 14.5 g/L. In the first experiment the photo-Fenton process was applied to biodigested vinasse after coagulation/flocculation without addition of H$_2$O$_2$ to highlight the importance of its application to improve process efficiency.

The effect of the amount of oxidant in TOC removal along the reaction time and in the BOD$_5$:COD ratio, TOC, COD and BOD$_5$ removals at the end of the run are presented in Fig. 5 a and b, respectively. It is possible to observe that the reaction without addition of oxidant ([H$_2$O$_2$] = 0 g/L) achieved minor removal efficiencies (9, 3 and 1% for TOC, COD and BOD$_5$, respectively) and a BOD$_5$:COD ratio of 0.44. The resulting effluent showed toxicity, quantified in terms of percent inhibition of *Vibrio fischeri* (4.6% after 5 min of contact with the bacteria; 6.7% after 15 min and 8.1% after 30 min – see Table 2). These values are similar to those achieved in biodigested vinasse after coagulation/flocculation (5.6–7.7% - see Table 1).

The presence of H$_2$O$_2$ led to an improvement of the process efficiency up to a H$_2$O$_2$ dose of 9 g/L. Such concentration allowed obtaining final removals of 74, 84 and 90% for BOD$_5$, COD and TOC,

Table 2
Conditions employed in the photo-Fenton oxidation runs (Approach 2), hydrogen peroxide consumption and efficiency of use, toxicity of the final effluent and operating costs for the photo-Fenton step. In bold are highlighted optimum conditions in each set of the parametric study.

Run	T (°C)	pH	Fe^{3+} (mg/L)	H$_2$O$_2$ (g/L)	I (W/m^2)	H$_{2}$O$_{2consumed}$ (g/L)	X$_{H2O2}$ (%)	X$_{TOC}$:X$_{H2O2}$	Inhibition of *Vibrio fischeri* @5min/15 min/30 min (%)	Cost (R\$/m^3/€/m^3)
T (°C)	20	3.0	258.3	14.5	500	14.5	100	0.60	12.5/17.3/19.5	**105.6/25.1**
	30					14.5	100	0.77	0.0/0.0/0.0	
	40					14.5	100	0.84	0.0/0.0/0.0	
	55					14.5	100	**0.88**	**0.0/0.0/0.0**	
pH	55	1.5	258.3	14.5	500	14.5	100	0.60	12.0/16.6/21.3	**105.6/25.1**
		2.0				14.5	100	0.81	6.6/8.5/9.5	
		3.0				**14.5**	**100**	**0.88**	**0.0/0.0**	
		4.0				14.5	100	0.76	0.0/0.0	
[H$_2$O$_2$] (g/L)	55	3.0	258.3	0	500	—	—	—	4.6/6.7/8.1	36.0/8.6
				4.5		4.5	14.5	0.40	0.0/0.0	57.6/13.7
				7.0		7.0	14.5	0.69	0.0/0.0	69.6/16.6
				9.0		**9.0**	**14.5**	**0.90**	**0.0/0.0**	**79.2/18.9**
				14.5		14.5	100	0.88	0.0/0.0	105.6/25.1
I (W/m^2)	55	3.0	258.3	9.0	27.3	8.8	98.7	0.41	0.0/0.0	45.2/10.8
					220	8.9	99.8	0.66	0.0/0.0	59.0/14.1
					500	**9.0**	**100**	**0.90**	**0.0/0.0**	**79.2/18.9**

respectively, and improving considerably the biodegradability (BOD$_5$:COD ratio increased from 0.43, after coagulation/flocculation, to 0.69, after photo-Fenton). The optimal oxidant dose (9 g/L) also proved to be more efficient as regards the oxidant use, i.e. led to a higher value of X$_{TOC}$:X$_{H2O2}$ (0.90) − Table 2. Such optimal dose is similar to what was reached by Primo et al. (2008) (10 g/L) for treating a landfill leachate by the photo-Fenton process with less organic matter (TOC = 2120.3 mg/L, COD = 3828.8 mg O$_2$/L and BOD$_5$ = 680 mgO$_2$/L).

The existence of an optimal concentration of hydrogen peroxide has been reported in other photo-Fenton studies (Primo et al., 2008; Barndõk et al., 2016; Rodríguez-Chueca et al., 2016), and is explained by parallel reactions between H$_2$O$_2$ in excess and the hydroxyl species (HO• + H$_2$O$_2$→ H$_2$O + HO$_2$• (Walling, 1975)), whereby a less amount of radicals is present in solution to oxidize the organic compounds. Regarding toxicity (% inhibition of *Vibrio fischeri*), for all oxidant concentrations tested it was null − see Table 2.

The costs associated with this process increased with the oxidant dose (see Table 2), as expected. The cost for the optimal concentration of H$_2$O$_2$ was 79.2 R\$/m^3 (corresponding to ≈18.9 €/m^3).

3.2.4. Influence of irradiance

For evaluating the effect of irradiance three runs were performed varying this parameter in the range 27.3−500 W/m^2. This range was established taking into account the incidence of solar radiation (13.1−204 W/m^2) in the State of São Paulo and the average value in Brazil (277 W/m^2). It was also decided to test the irradiance of 500 W/m^2, which is the maximum value given by the mercury lamp used, in order to extrapolate the results to other sites exposed to higher solar radiation, where wastewater with organic loads similar to the biodigested vinasse used in this study needs an adequate treatment. The other parameters were fixed at: [H$_2$O$_2$] = 9.0 g/L, pH = 3.0 and T = 55 °C.

The experimental results shown in Fig. 6 demonstrated that the organic matter removal, biodegradability (BOD$_5$:COD ratio) and efficiency of oxidant use (X$_{TOC}$:X$_{H2O2}$) − in Table 2 − increased with irradiance. This fact is explained by favouring the radicals formation and regeneration of the ferrous ion when increasing the intensity of the incident radiation (Rodrigues et al., 2013b; Vaishnave et al., 2014). The toxicity of the final effluent was null for all irradiances tested (Table 2).

The global cost of the photo-Fenton process increases with the irradiance. For the maximum value of irradiance used - 500 W/m^2 - the total cost amounts to 79.2 R\$/m^3 (≈18.9 €/m^3), as reported in the previous section.

3.3. Coagulation/flocculation plus SBR and photo-Fenton process (Approach 3)

In order to reduce the effluent treatment cost, after coagulation (conducted at the best operating conditions found in Approach 1) the biodigested vinasse was subjected to aerobic biological degradation, since coagulation increased the biodegradability from 0.33 to 0.43 and reduced the toxicity from 45.1-47.1% to 5.6−7.7% (see Table 1). Moreover, by decreasing the organic matter content by biodegradation less amount of oxidant is needed to the photo-Fenton process (last step in this approach).

3.3.1. Biological degradation

The biological treatment was carried out in a SBR operated in accordance with the description provided in Section 2.2.3. The aerobic biological degradation was not applied to treat the vinasse, because it had been subjected to an anaerobic treatment, and then all biodegradable organic compounds have been removed.

During the treatment of vinasse by the SBR (after coagulation/flocculation), the pH, temperature and DO were measured in each cycle, and average values of 8.8, 27.2 °C and 3.0 mgO$_2$/L, respectively, were obtained. During SBR operation, it was found that the removal of organics and nutrients increased along the first 9 cycles (see Fig. 7a) due to the biomass acclimatization to the effluent that is being fed to the reactor, and then remained almost constant. The average removal values, after reaching the pseudo-steady state (19 cycles), were as follows: 37% - COD, 40% - BOD$_5$, 46% - TOC, 34% - total nitrogen and 18% - total phosphorus. The TSS content in the effluent discharged from the biological reactor declined along the first seven cycles (see Fig. 7b) and then remained practically constant with an average value of 1021 mg/L, which means that after 7 cycles a better sedimentation of the sludge occurred. The VSS content, inside the reactor (which gives idea of the growth/death biomass), had a very accentuated decay in the first four cycles, continuing to decay more slowly in the four subsequent cycles, thus indicating that there is lysis and mineralization of biomass. After 8 cycles the VSS content remained nearly constant (average value of 3633 mg/L), indicating that biomass death is compensated by biomass growth.

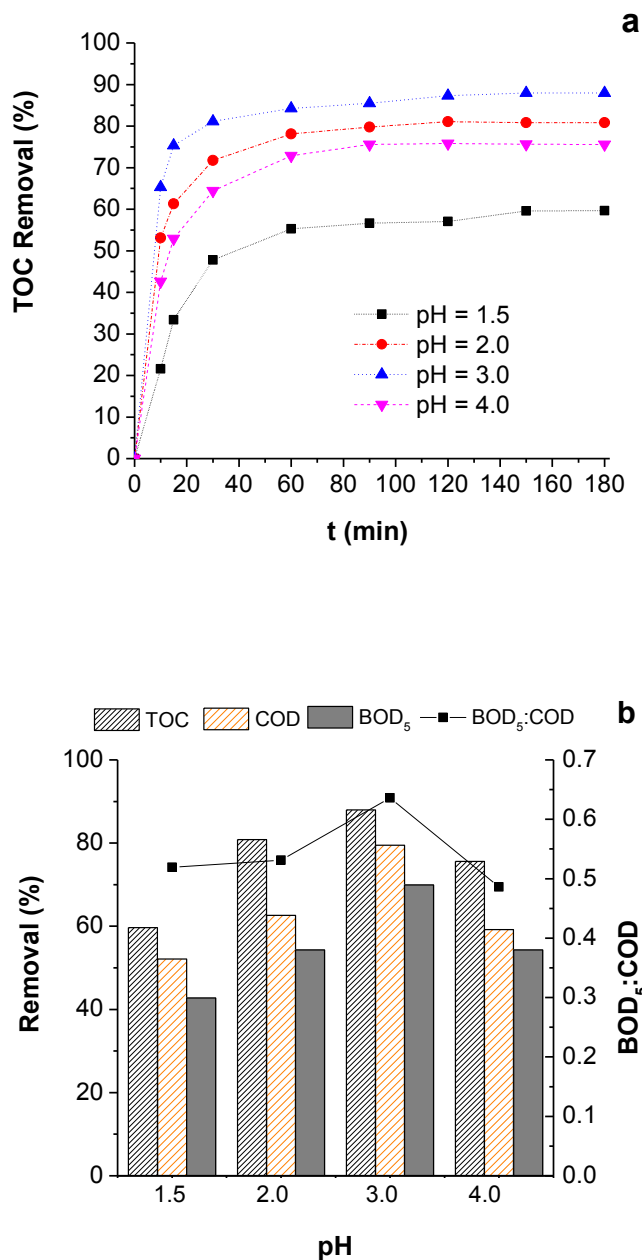The operating cost of the SBR was considered to be only

Fig. 4. Effect of pH on TOC removal along the reaction (a) and removal of TOC, COD and BOD$_5$ and BOD$_5$:COD ratio after 180 min of photo-Fenton reaction (b) after the coagulation/flocculation step - Approach 2 ([H$_2$O$_2$] = 14.5 g/L, T = 55 °C, [Fe^{3+}] = 258.3 mg/L, I = 500 W/m^2).

associated with energy consumption for agitation (power required = 0.26 W) and air insufflation (power required = 4.5 W). Assuming an average energy cost of 0.4 R\$/kWh ($\approx$0.10 €/kWh), the cost associated with the biological reactor operation was 10.7 R\$/m^3 ($\approx$2.5 €/m^3) – see Table 3.

3.3.2. Photo-Fenton oxidation

In view of the high amount of organic compounds still present in the effluent from the biological degradation (SBR), it was further treated by photo-Fenton oxidation. Parameters like iron and hydrogen peroxide concentration and irradiance were optimized. The temperature and pH were fixed at optimum values (55 °C and 3, respectively) found for this process in Approach 2.
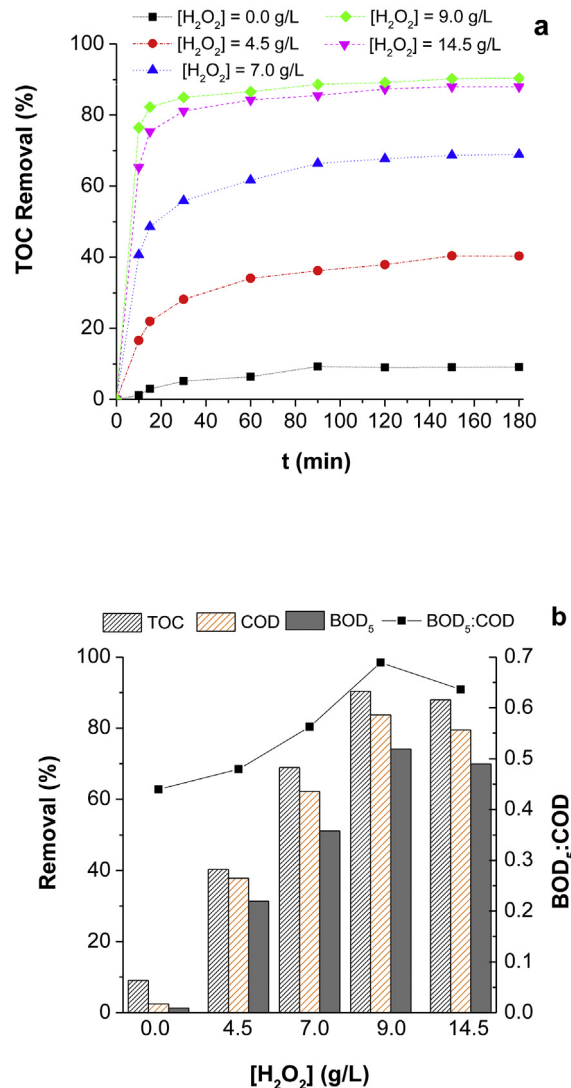
Fig. 5. Effect of oxidant concentration on TOC removal along the reaction (a) and removal of TOC, COD and BOD$_5$ and BOD$_5$:COD ratio after 180 min of reaction (b) after the coagulation/flocculation step - Approach 2 (T = 55 °C, pH$_{initial}$ = 3.0, [Fe^{3+}] = 258.3 mg/L, I = 500 W/m^2).

3.3.2.1. Influence of hydrogen peroxide concentration.
The hydrogen peroxide concentration to be used in the photo-Fenton process was optimized by varying it in the range 2.5–9.0 g/L. In Figure S1a is shown the TOC removal history data, evidencing that performance increased up to the oxidant dose of 7.0 g/L. The same trend is observed for overall COD and BOD$_5$ removal and final BOD$_5$:COD ratio (see Figure S1b and Table 4). As explained in Approach 1, this optimal concentration of oxidant exists due to the fact that the excess of hydrogen peroxide reacts with hydroxyl radicals (scavenging effect). The hydrogen peroxide dose of 7.0 g/L provided an effluent with BOD$_5$:COD = 0.69 and X$_{TOC}$:X$_{H2O2}$ = 0.78; the toxicity of the effluent is null for all concentrations tested – see Table 4. Again, as expected, the operating costs for this process increased with the hydrogen peroxide dose (see Table 4). For the optimal dose (7.0 g/L) the cost amounts 72.6 R\$/m^3 ($\approx$ 17.3 €/m^3).

3.3.2.2. Effect of iron dose.
Given that the effluent is neutralized before being fed to the SBR, and consequently precipitation of iron occurs, it was needed to add and optimize the amount of catalyst in
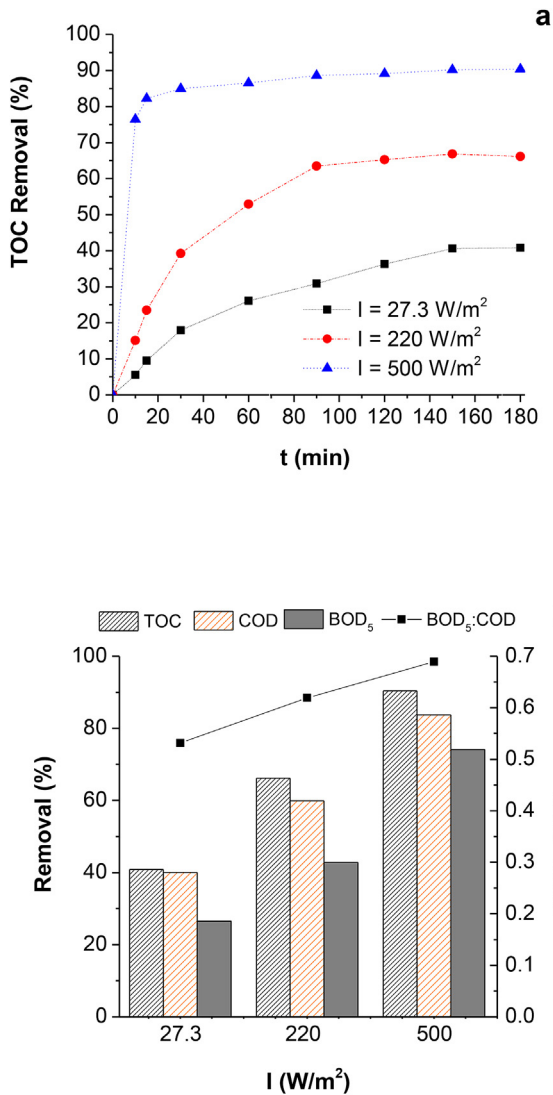
Fig. 6. Influence of irradiance on TOC removal along the reaction (a) and removal of TOC, COD and BOD$_5$ and BOD$_5$:COD ratio after 180 min of photo-Fenton reaction (b) after the coagulation/flocculation step - Approach 2 (T = 55 °C, pH$_{initial}$ = 3.0, [H$_2$O$_2$] = 9.0 g/L, [Fe^{3+}] = 258.3 mg/L).

the photo-Fenton process. So, its effect was evaluated by carrying out four experiments where this parameter was varied in the range 129–517 mg/L. The results presented in Figure S2 and Table 4 show that TOC, COD and BOD$_5$ removals, as well as biodegradability and efficiency of the oxidant use, increased with the iron concentration up to 258.3 mg/L. For higher catalyst doses the process efficiency decreased. The existence of an optimal iron dose is explained by the occurrence of radical scavenging reactions with the excess iron (Fe^{2+} + HO$^\bullet$ → Fe^{3+} + OH$^-$). The toxicity of the treated vinasse was null for all iron concentrations tested, as presented in Table 4. As regards operating costs, there is only a slight increase derived from the iron used in the process (see Table 4). For the iron concentration of 258.3 mg/L the cost was 72.6 R\$/m^3 (≈17.3 €/m^3).

3.3.2.3. Influence of irradiation. As in Approach 1, the effect of irradiance was evaluated from the results obtained in three runs carried out under irradiances varying in the range 27.3–500 W/m^2. The organic matter reduction, biodegradability and efficiency of H$_2$O$_2$ use increased with irradiance (see Figure S3 and Table 4) as expected, since the formation of hydroxyl radicals and catalyst
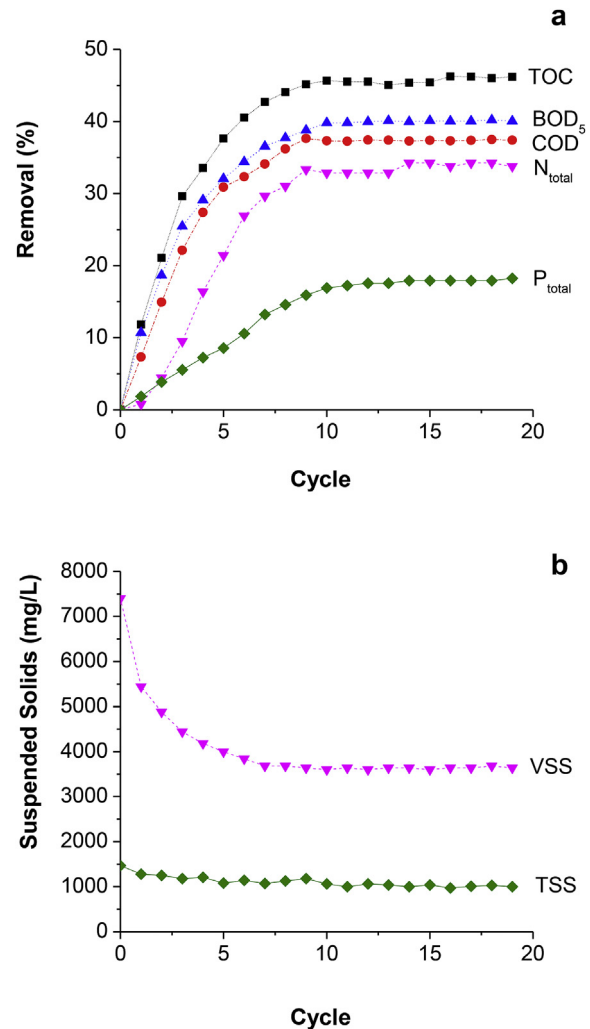

Fig. 7. Variation of TOC, COD, BOD$_5$, total nitrogen and phosphorus removal (a) and TSS and VSS (b) during 19 cycles of SBR operation, after effluent treatment by coagulation/flocculation - Approach 3 (T ~ 27 °C, D.O. ~3.0 mg O$_2$/L and v$_{agitation}$ = 300 rpm).

regeneration are favoured by the increase of the irradiance. Regarding the inhibition of *Vibrio fischeri*, it was 0.0% for all tested irradiations. For the maximum irradiance (500 W/m^2) removals of 78.0% for TOC and COD, and 64.0% for BOD$_5$, BOD$_5$:COD = 0.69 and X$_{TOC}$:X$_{H2O2}$ = 0.78 were achieved. The cost associated with energy consumption increased with irradiance (see Table 4), being very high as compared to hydrogen peroxide and particularly iron costs. For the maximum irradiance (500 W/m^2) the total operating cost was 72.6 R\$/m^3 (≈17.3 €/m^3).

The global removal efficiency of the treatment process (coagulation followed by aerobic biological degradation and photo-Fenton oxidation) was 92.0, 98.0 and 84.0% for COD, TOC and BOD$_5$, respectively (see Table 3) with an associated operating cost of 89.0 R\$/m^3 (≈21.2 €/m^3). However, the treatment cost can be reduced to 52.9 R\$/m^3 (≈12.6 €/m^3), i.e. by about 40%, if solar radiation is used in the photo-Fenton process.

4. Conclusions

Given the high organic load and the presence of refractory and toxic compounds in the sugar cane vinasse after anaerobic digestion, a treatment is needed before recirculation to the anaerobic reactors. Thus, this study evaluated the treatability of biodigested

Table 3
Characteristics of the biodigested sugarcane vinasse effluent after each treatment step of Approach 3 and respective global efficiency (partial removal efficiencies are shown between brackets), for optimized operatory conditions, along with respective operating costs.

Parameter	After coagulation/flocculation	After SBR	After Photo-Fenton	Global efficiency (%)
pH	7.1[b]	8.8	7.1[b]	—
COD (mg O_2/L)	7079.3 (43.6)	4468.9 (37.4)	983.1 (78.0)	92.0
BOD_5 (mg O_2/L)	3074.0 (25.3)	1879.8 (40.0)	678.0 (64.0)	84.0
TOC (mg C/L)	2460.7 (41.4)	1345.1 (45.7)	296.6 (78.0)	98.0
BOD_5:COD ratio	0.43 (−)	0.42 (−)	0.69 (−)	—
P_t (mg P/L)	13.7 (11.0)	105.4 (33.6[a])	n.d. (−)	—
N_t (mg N/L)	2.0 (50.0)	25.8 (17.7[a])	n.d. (−)	—
Turbidity (NTU)	6.5 (−)	n.d. (−)	n.d. (−)	—
TSS (mg/L)	10 (−)	1021 (−)	n.d. (−)	—
Vibrio fischeri Inhibition 5 min (%)	5.6 (−)	n.d.	0.0 (−)	
Vibrio fischeri Inhibition 15 min (%)	6.3 (−)	n.d.	0.0 (−)	—
Vibrio fischeri Inhibition 30 min (%)	7.7 (−)	n.d.	0.0 (−)	—
Operating cost of each step (R\$/m^3/€/m^3) [c]	5.7/1.4	10.7/2.5	72.6/17.3	—

nd. − not determined.

[a] Calculated from total phosphorus and nitrogen in effluent after coagulation/flocculation and after adding phosphate buffer and urea (17.6 mg P/L and 154.7 mgN/L).

[b] Upon neutralization of the effluent.

[c] Operating costs are related with consumption of chemicals (it was not considered the costs of treatment/processing of sludge generated). The costs of reagents were those given by OCC Química and Solvay - Peróxidos do Brasil (Brazil): H_2O_2 (50.0% (w/v), density at 25 °C = 1.2 g/cm^3) − 2.0 R\$/kg; $FeCl_3$ (38% (w/w)) − 1.5 R\$/kg. Energy cost for Brazilian companies = 0.4 R\$/kWh. For converting from Brazilian Real to Euro, it was used the exchange rate of 4.2 R\$/€ - European Central Bank and Portugal Bank, 07 April 2016 (www.bportugal.pt).

Table 4
Conditions employed in the photo-Fenton oxidation runs (Approach 3), hydrogen peroxide consumption and efficiency of use, toxicity of the final effluent and total operating costs. In bold are highlighted optimum conditions in each set of the parametric study.

Run	T (°C)	pH	Fe^{3+} (mg/L)	H_2O_2 (g/L)	I (W/m^2)	$H_2O_{2consumed}$ (g/L)	X_{H2O2} (%)	X_{TOC}:X_{H2O2}	Inhibition of *Vibrio fischeri* @ 5min/15 min/30 min (%)	Cost (R\$/m^3/€/m^3)
[H_2O_2] (g/L)	55	3.0	258.3	2.5	500	2.5	100	0.47	0.0/0.0/0.0	51.0/12.1
				4.5		4.5	100	0.60	0.0/0.0/0.0	60.6/14.4
				7.0		**7.0**	**100**	**0.78**	**0.0/0.0/0.0**	**72.6/17.3**
				9.0		9.0	100	0.63	0.0/0.0/0.0	82.2/19.6
[Fe^{3+}] (mg/L)	55	3.0	129.0	7.0	500	7.0	100	0.44	0.0/0.0/0.0	71.1/16.9
			193.0			7.0	100	0.63	0.0/0.0/0.0	71.8/17.1
			258.3			**7.0**	**100**	**0.78**	**0.0/0.0/0.0**	**72.6/17.3**
			517.0			7.0	100	0.65	0.0/0.0/0.0	75.5/18.0
I (W/m^2)	55	3.0	258.3	7.0	27.5	7.0	100	0.44	0.0/0.0/0.0	38.5/9.2
					220	7.0	100	0.62	0.0/0.0/0.0	52.4/12.5
					500	**7.0**	**100**	**0.78**	**0.0/0.0/0.0**	**72.6/17.3**

sugar cane vinasse by three different strategies: i) chemical coagulation/flocculation per se (Approach 1), ii) coagulation/flocculation followed by photo-Fenton reaction (Approach 2) and iii) coagulation/flocculation, aerobic biological degradation in a SBR and photo-Fenton reaction (Approach 3). Approach 1 led to low organic matter removal efficiency; however the efficiency increased when vinasse was treated by combined processes (Approaches 2 and 3). Removals higher than 80% for BOD_5 and higher than 90% for the COD and TOC, a nontoxic effluent with increased biodegradability (BOD_5:COD ratio = 0.69) were achieved in Approach 2 and 3. However, the operating cost of treatment in Approach 3 (89.0 R\$/m^3 − ≈21.2 €/m^3) is slightly higher than in Approach 2 (84.9 R\$/m^3 − ≈20.2 €/m^3). Both costs are high, but can reduced by a factor of around 40% if solar photo-Fenton oxidation is employed.

The combination of coagulation/flocculation with photo-Fenton oxidation (Approach 2) or biological degradation and photo-Fenton oxidation (Approach 3) increased the biodegradability and eliminated the toxicity of the wastewater, which allows to recirculate it into the anaerobic reactor, but the effect of the recirculation on the biogas production has to be evaluated.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2016.10.104.

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