Research article

Treatment of sugarcane vinasse by combination of coagulation/flocculation and Fenton's oxidation

Lígia F. Guerreiro [a], Carmen S.D. Rodrigues [a], Rose M. Duda [b], Roberto A. de Oliveira [c], Rui A.R. Boaventura [d], Luis M. Madeira [a, *]

[a] LEPABE — Laboratório de Engenharia de Processos, Ambiente, Biotecnologia e Energia, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Faculdade de Tecnologia de Jaboticabal, "Nilo Stéfani", Av. Eduardo Zambianchi, 31, 14883-130, Vila Industrial, Jaboticabal, SP, Brazil
[c] Laboratório de Saneamento Ambiental, Departamento de Engenharia Rural, Faculdade de Ciências Agrárias e Veterinárias, UNESP, Universidade Estadual Paulista, Av. Prof. Paulo Donato Castallene, km 5, 14884-900 Jaboticabal, SP, Brazil
[d] LSRE — Laboratório de Processos de Separação e Reação, Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

ABSTRACT

The efficiency of individual and integrated processes applied to organic matter reduction and biodegradability improvement of a biodigested sugarcane vinasse wastewater was assessed. Strategies considered were Fenton's oxidation (Strategy 1), coagulation/flocculation (Strategy 2) and the combination of both processes (coagulation/flocculation followed by Fenton's reaction) — Strategy 3.

It was found that Fenton's oxidation per se allowed reducing the organic matter, increasing the wastewater biodegradability and a non-toxic effluent was generated; however the cost of treatment was very high (86.6 R$/m^3 — 21.2 €/m^3). Under optimized conditions, coagulation/flocculation provided a slight increase in effluent's biodegradability, toxicity towards *Vibrio fischeri* was also eliminated and moderate removals of total organic carbon — TOC — (30.5%), biological oxygen demand — BOD$_5$ — (27.9%) and chemical oxygen demand — COD — (43.6%) were achieved; however, the operating costs are much smaller. The use of dissolved iron resulting from coagulation/flocculation (270 mg/L) as catalyst in the second stage — Fenton's oxidation — was shown to be an innovative and economically attractive strategy. Under optimal conditions overall removals of 51.6% for TOC, 45.7% for BOD$_5$ and 69.2% for COD were achieved, and a biodegradable (BOD$_5$:COD ratio = 0.54) and non-toxic effluent was obtained. In order to increase the efficiency of the process but using less hydrogen peroxide, the Fenton's oxidation was performed by gradually adding the oxidant. This procedure allowed to obtain the highest organic matter removal efficiency (as compared with the addition of all hydrogen peroxide at the beginning of the reaction). This way it was possible to minimize the reagent consumption and, consequently, reduce the treatment cost.

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1. Introduction

Sugarcane vinasse produced by the ethanol industry in large amount is becoming a matter of great concern, because it can cause negative environmental impacts when discharged directly into the aquatic environment. Besides containing mineral constituents, vinasse is very rich in organic matter, has low pH, is highly corrosive and presents recalcitrant compounds and inhibitors that hinder its biodegradation (Ferreira et al., 2011; Christofoletti et al., 2013). To minimize those impacts to the environment, efficient and economically viable processes for its treatment are required.

In general, anaerobic digestion (AD) is the technique commonly adopted for sugarcane vinasse treatment (Harada et al., 1996; Wilkie et al., 2000; España-Gamboa et al., 2012; Mota et al., 2013; Nogueira et al., 2015) because the high organic content of vinasse permits to generate energy from methane produced. Moreover, AD yields low amounts of sludge, making the process economically and environmentally advantageous (Wilkie et al., 2000). However, despite the high reduction of COD and BOD, the final effluent

* Corresponding author.
E-mail address: mmadeira@fe.up.pt (L.M. Madeira).

resulting from this process still contains recalcitrant compounds and inhibitors of the biological activity (Santos et al., 2005), which is very undesirable because part of the biodigested vinasse is recirculated back into the anaerobic reactor. The main goal of such strategy is to take advantage of the alkalinity of recirculated vinasse, therefore reducing the consumption of chemicals (NaOH) for neutralisation (Barros et al., 2016), as schematised in Fig. 1.

In the open scientific literature, only two studies, apart from AD, were found that applied Fenton and photo-Fenton oxidation (Hadavifar et al., 2009) and coagulation/flocculation (Zayas et al., 2007) to treat this type of effluents. Such processes are particularly interesting if they are capable of improving the effluent biodegradability and decrease its toxicity after treatment by AD.

The Fenton process consists in decomposing hydrogen peroxide in the presence of a catalyst, particularly Fe^{2+} (Eq. (1)), at pH values between 2 and 5 (Pignatello, 1992). Such reagents, when added to a system containing an organic substrate (RH) in acid conditions, promote its oxidation according to Eq. (2) (Walling, 1975):

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

$$HO^\bullet + RH \rightarrow H_2O + intermediates \tag{2}$$

In this process the key species are the highly oxidative and non-selective hydroxyl radicals, which oxidize either organics present in the initial effluent or the generated intermediary compounds; oxidation proceeds up to carbon dioxide and water (complete mineralization) or until formation of refractory by-products.

It is also possible to use physical-chemical processes such as coagulation/flocculation, alone or coupled to Fenton's oxidation. The coagulation/flocculation is easily applied and requires low capital and operating costs, being usually employed as pre-treatment (Zayas et al., 2007). The coagulation promotes the formation of large particles by the addition of chemicals (coagulant) that are agglomerated in the flocculation stage, which promotes their agglomeration by the addition of flocculants that permit the easy removal of the flocs formed by decantation or filtration (Cañizares et al., 2009).

The objective of this study was to determine the best operating conditions for coagulation/flocculation and Fenton's oxidation, applied either alone or combined to sugarcane vinasse treatment, in order to: i) improve the biodegradability and decrease the toxicity of the biodigested sugarcane vinasse for recirculation into high rate anaerobic reactors to increase the biogas production, and ii) maximize the mineralization of organic compounds and obtain a wastewater that meets the legislation values for subsequent discharge into water bodies, at the lowest treatment cost.

2. Materials and methods

2.1. Wastewater

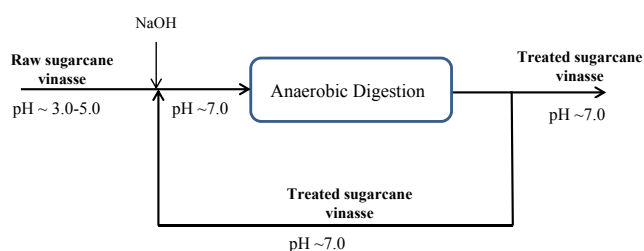The vinasse used in this study was collected in a sugarcane

distillery located in Ribeirão Preto, São Paulo, Brazil. It was submitted to thermophilic anaerobic digestion (55 °C) in two UASB reactors in series, the first with total volume of 12.1 L and the second of 5.6 L operated with hydraulic detention time (HDT) of 16.0 and 7.5 h, respectively.

2.2. Experimental procedure

2.2.1. Chemical coagulation/flocculation

All coagulation/flocculation experiments were performed in a jar test apparatus at room temperature (22–25 °C). In each beaker, the coagulant (ferric chloride − $FeCl_3 \cdot 6H_2O_2$, from Labchem®) was added to 200 mL of vinasse, and then the pH adjusted to the desired value with 10 M NaOH or 1 M H_2SO_4. Afterwards, it was performed a rapid stirring (150 rpm) stage for 3 min and, finally, a slow agitation (20 rpm) during 15 min; the operating conditions were established according to the literature (Eckenfelder, 2000; Satterfield, 2004; Bose, 2010; Poland and Pagano, 2010; Rodrigues et al., 2013). No flocculant was added because it does not improve organic compounds removal (Rodrigues et al., 2013) and so the costs are reduced. After coagulation/flocculation, the effluent was submitted to clarification during 20 h for sedimentation of the flocs and separation of the liquid phase. A portion of the supernatant was taken to measure turbidity, BOD_5, COD, TOC and dissolved iron, as detailed below.

2.2.2. Fenton's reaction

A 250 mL capacity glass batch reactor, connected to a water thermostatic bath (Huber, polystat cc1) to maintain constant the temperature inside the reactor, was used for the Fenton's oxidation studies. Immediately after the volume of effluent (150 mL) has reached the chosen temperature, pH was adjusted to the desired value with 1 M H_2SO_4 or 1 M NaOH. Subsequently, the required amount of iron (as $FeCl_3 \cdot 6H_2O$ from Labchem®) and H_2O_2 (30% w/v, from Chem-Lab®) was added. Although ferrous sulphate is widely reported in the literature as the iron salt in Fenton's oxidation, it has been replaced by ferric chloride in this work because sulphate can be reduced to hydrogen sulphide by anaerobic bacteria in the case of subsequently applying an anaerobic digestion, leading to odour and toxicity problems. Moreover, sulphuric acid may be formed downstream in the presence of oxygen, inducing possible corrosion complications. In some runs (Strategy 3, as detailed below) no iron salt was added, because only the dissolved iron resulting from the previous coagulation/flocculation stage was used as catalyst.

The reaction time started by the addition of hydrogen peroxide and was extended to 3 h. Constant stirring (at 200 rpm) was ensured by means of a bar and a magnetic plate (Falc®). The temperature and pH values of the medium were recorded over time. At 30 min time intervals, samples were taken to evaluate TOC; the reaction was stopped by addition of excess sodium sulfite (that reacts instantaneously with the remaining hydrogen peroxide). The hydrogen peroxide concentration as well as the BOD_5, COD and inhibition towards *Vibrio fischeri* (after eliminating the residual H_2O_2 and precipitating the iron by increasing the pH until ~12 and further neutralizing to pH ~7.0) were measured at the end of reaction; the samples for toxicity assessment were neutralized with 1 N HCl, as proposed by the analytical methodology.

For the Fenton tests performed with gradual addition of oxidant, a fractional amount of H_2O_2 was added every 5 min until 150 min of reaction.

2.3. Analytical methods

The biodegradability was evaluated by the BOD_5:COD ratio. The effluent acute toxicity was assessed by the *Vibrio fischeri* inhibition

Fig. 1. Scheme of sugarcane vinasse treatment by digestion anaerobic.

Table 1
Characteristics of the biodigested sugarcane vinasse effluent and after each treatment strategy (removal efficiencies are shown between brackets) along with respective operating costs.

Parameter	Biodigested vinasse	After Fenton (Strategy 1)	After coagulation/flocculation (Strategy 2)	After coagulation/flocculation plus Fenton[a] (Strategy 3)
Chemical oxygen demand (mg O_2/L)	6836	2516 (63.2%)	3856 (43.6%)	2107 (69.2%)
Biochemical oxygen demand (mg O_2/L)	2096	1323 (36.9%)	1511 (27.9%)	866 (45.7%)
Total organic carbon (mg C/L)	1790	1133 (53.7%)	1406 (30.5%)	1776 (51.6%)
BOD_5:COD ratio	0.31	0.53	0.39	0.54
Total phosphate (mg P/L)	11.6	<0.02 (100%)	<0.02 (100%)	<0.02 (100%)
Total nitrogen (mg N/L)	4.0	4.1 (−)	4.2 (−)	4.0 (−)
Ammonium (mg N/L)	<0.4	<0.4 (−)	2.0 (−)	0.6 (−)
Nitrate (mg N/L)	<0.05	<0.05 (−)	<0.05 (−)	<0.05 (−)
Nitrite (mg N/L)	<0.06	<0.06 (−)	<0.06 (−)	<0.06 (−)
Sulphate (mg SO_4^{2-}/L)	635	1241 (−)	2482 (−)	2432 (−)
Magnesium (mg/L)	137.5	128.6 (6.5%)	127.9 (7.0%)	124.6 (9.4%)
Calcium (mg/L)	7.2	7.0 (2.8%)	7.3 (−)	7.1 (1.4%)
pH	8.2	2.3	7.05[c]	7.02[c]
Turbidity (NTU)	1500	6.6	85	1.3
Vibrio fischeri inhibition 15 min. (%)	27.9	0.0	0.0	0.0
Vibrio fischeri inhibition 30 min. (%)	28.5	0.0	0.0	0.0
Operating cost (R\$/m³/€/m³)[b]	−	86.6/21.2	5.7/1.4	75.3/18.4

[a] Total addition of H_2O_2.

[b] 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/cm³) − 2.0 R\$/kg; $FeCl_3$ (38% (w/w)) − 1.5 R\$/kg. For converting from Brazilian Real to Euro, it was used the exchange rate of 4.0935 R\$/€ by 24/08/2015 of the European Central Bank and Portugal Bank (www.bportugal.pt).

[c] Upon neutralization of the effluent.

test, according to ISO 11348-3 (International Organization for Standardization, 2007). In short, the initial luminescence intensity emitted by the organisms before they contact with the sample is registered, followed by reading the luminescence just after exposure to the sample at 15 °C for 15 and 30 min, using a Microtox® model 500 analyzer. According to some researchers (Munkittrick et al., 1991) bioluminescence inhibition tests are not as sensitive as other acute lethality tests as regards effluents or leachates with a high component of insecticides, herbicides, inorganics, pharmaceuticals or textiles, or highly lipophilic contaminants. Nevertheless, they have been applied as a sensitive and rapid screening tool for determining the whole toxicity of various industrial effluents, such as wastewater from textile dyeing industry (Parvez et al., 2006).

The concentration of hydrogen peroxide was determined by molecular absorption spectrophotometry of the complex yellow-orange color formed from the reaction of hydrogen peroxide with titanium oxalate (Sellers, 1980). Measurements were done in a Thermo Electron Corporation model Helios γ® apparatus.

The determination of the chemical oxygen demand (COD) was performed according to method D 5220 in closed reflux (APHA, 1998). The biological oxygen demand (BOD_5) was measured according to method D 5210 (APHA, 1998), using an OxiTOP (Velp Scientifica) apparatus. The total organic carbon (TOC) analysis was performed in a Shimadzu® TOC analyzer (TOC-5000 CE model), by catalytic combustion of aqueous samples at temperatures near 680 °C − method D 5310 (APHA, 1998).

The total phosphorus was measured by the ascorbic acid method after digestion with ammonium persulphate (Method 4500P − E) (APHA, 1998) and the total nitrogen was determined by colorimetry according to Method D992-71 (Annual Book of ASTM Standards, 1973) after previous digestion (Method 4500 − N C). The magnesium, calcium and iron were measured by flame atomic absorption spectrometry (Method 3111 B), using an AAS GBC spectrophotometer (model 932 AB Plus). The sulphate, nitrate and nitrite were measured by ion chromatography (Dionex ICS-2100) using a Dionex Ionpac column (AS 11-HC 4 × 250 mm) and a suppressor ASRS 300 4 mm. Elution was performed in isocratic

mode with 30 mM NaOH at a flow rate of 1.5 mL/min. The ammonium was measured by ion chromatography too, but using a Dionex Ionpac column CS12A 4 × 250 mm and the flow rate of eluent (methanesulfonic acid) was set at 1.0 mL/min. The turbidity was measured according to Method 2130 B (APHA, 1998), using a turbidimeter HI88703 from Hanna Instruments.

3. Results and discussion

The main characteristics of the previously biodigested vinasse wastewater used in this work are summarized in Table 1. It is worth mentioning the high levels of organic matter (COD and TOC), sulphate and magnesium, the low amounts of ammonium, nitrate and nitrite, the low biodegradability (BOD_5:COD ratio <0.4), and the evidence for some toxicity towards Vibrio fischeri, reinforcing the importance of an appropriate treatment before its recirculation back into the anaerobic reactors and/or before discharge in the environment. Similar levels of organic matter were found in sugarcane vinasse by Hadavifar et al. (2009).

3.1. Fenton's reaction (Strategy 1)

The Fenton's oxidation was directly applied to the raw effluent aiming at (i) producing an effluent that meets legal discharge limits or (ii) improving its biodegradability and reducing its toxicity, allowing the recirculation into the high rate anaerobic reactor. A parametric study was performed to better understand the effect of each variable (Fe^{3+} concentration, initial H_2O_2 dose, pH and temperature) on the process efficiency, while also aiming at the process optimization.

3.1.1. Effect of initial H_2O_2 dose

The range of H_2O_2 concentration varied from 14.5 g/L to 25.0 g/L (corresponding to 1.0–1.7 times the stoichiometric dose based on the COD value). The iron concentration, initial pH and temperature were kept constant at 1.45 g/L, 3.0 and 30 °C, respectively. The results of TOC removal and pH over time are shown in Fig. 2a) and b), respectively; in these runs the temperature was kept constant at
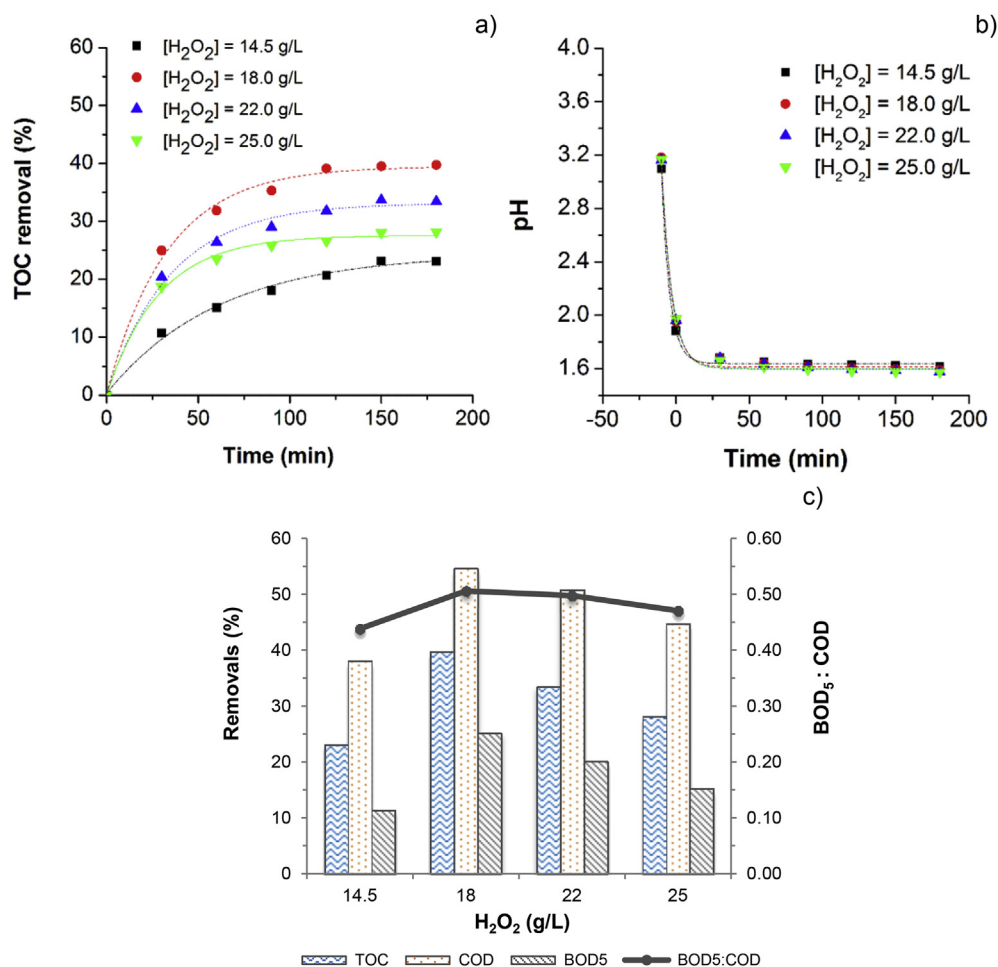
Fig. 2. Effect of H_2O_2 dose in the removal of TOC (a) and pH (b) during reaction and removals of TOC, BOD_5 and COD and BOD_5:COD ratio after 180 min of reaction (c) ($pH_{initial} = 3.0$, T = 30 °C; $Fe^{3+} = 1.45$ g/L).

30 ± 2 °C. It can be seen that for all H_2O_2 concentrations, TOC removal is faster in the first 30–60 min; afterwards it continues to rise, but more slowly and up to 120–150 min; from this time on, a plateau is observed. A similar temporal evolution is observed for the pH, which considerably decreases from t = 0 (that coincides with the H_2O_2 addition) up to 30–60 min, and then the variation is attenuated. The sharp decrease in pH for t < 0 is due to the addition

of the iron salt. The acidification of the medium along the reaction time is generally attributed to intermediates and oxidation products formed, namely short chain organic acids.

Regarding the removal of TOC, it should be noted that it increases with the dose of H_2O_2 from 14.5 to 18.0 g/L, reaching 39.7% of mineralization (after 3 h of oxidation). At higher doses, however, the final removals decrease (Fig. 2c). As regards the removal of

Table 2
Conditions employed in the Fenton's oxidation runs (Strategy 1), hydrogen peroxide consumption and its efficiency of use, along with toxicity of the final effluent and total operating costs. In bold are highlighted optimum conditions of each run along the parametric study.

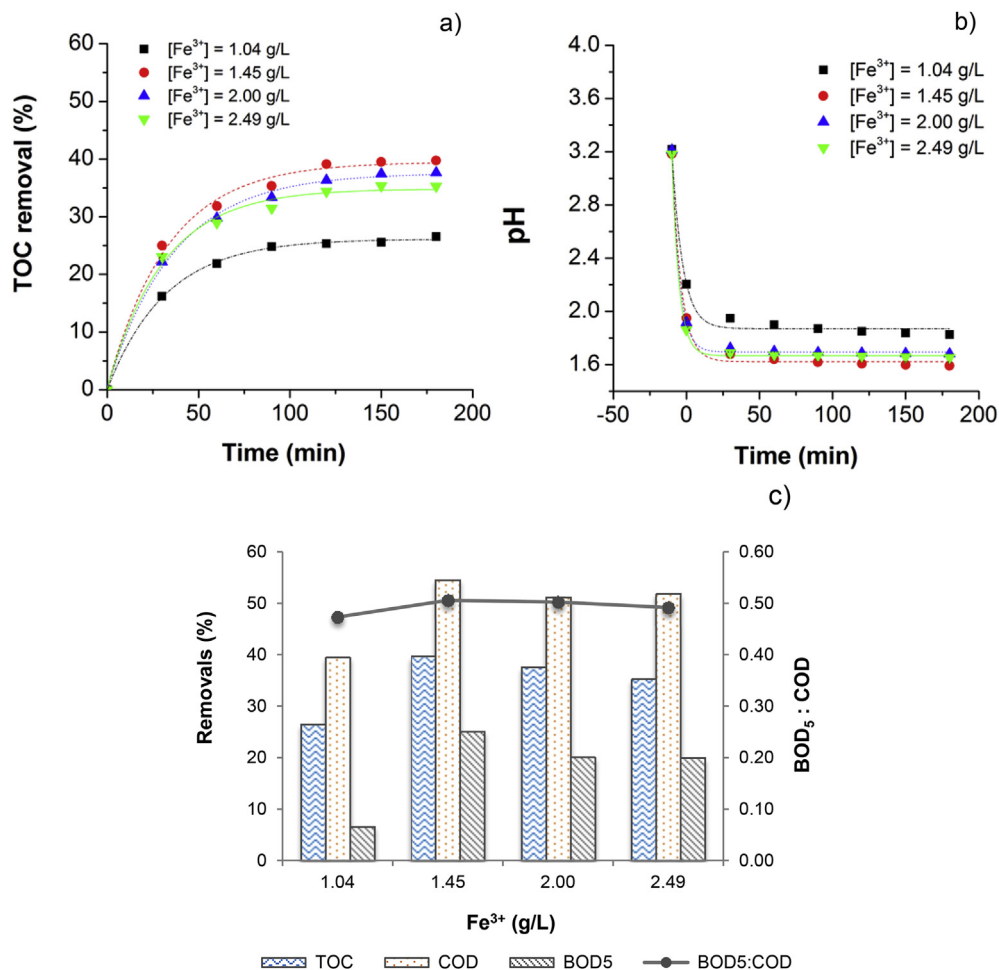| Run	H_2O_2 (g/L)	Fe^{3+} (g/L)	pH	T (°C)	$H_2O_{2consumed}$ (g/L)	$X_{H_2O_2}$ (%)	$X_{TOC}:X_{H_2O_2}$	Inhibition of *Vibrio fischeri* @15 min/30 min (%)	Cost (R\$/m³/€/m³)
H_2O_2 (g/L)	14.5	1.45	3.0	30	13.7	94.4	0.24	8.3/11.8	69.8/17.1
	18.0				**16.9**	**93.8**	**0.42**	**0.0/0.0**	**86.6/21.2**
	22.0				20.2	91.8	0.36	0.0/0.0	105.8/25.8
	25.0				21.8	87.3	0.32	0.0/0.0	120.2/29.4
Fe^{3+} (g/L)	18.0	1.04	3.0	30	14.8	82.0	0.32	10.0/14.2	86.5/21.1
	1.45				**16.9**	**93.8**	**0.42**	**0.0/0.0**	**86.6/21.2**
	2.00				17.7	98.4	0.38	0.0/0.0	86.6/21.2
	2.49				17.8	99.0	0.35	0.0/0.0	86.7/21.2
pH	18.0	1.45	3.0	30	16.9	93.8	0.42	0.0/0.0	**86.6/21.2**
			5.0		17.6	**97.7**	**0.44**	**0.0/0.0**	
			6.0		17.4	96.5	0.41	0.0/0.0	
			7.0		13.1	72.5	0.32	0.0/0.0	
T (°C)	18.0	1.45	5.0	20	16.9	93.8	0.38	5.7/8.6	
				30	17.6	97.7	0.44	0.0/0.0	86.6/21.2
				55	**17.2**	**95.4**	**0.56**	**0.0/0.0**	

Fig. 3. Effect of Fe^{3+} dose in the removal of TOC (a) and pH (b) during reaction and removal of TOC, COD and BOD_5 and BOD_5:COD ratio after 180 min of reaction (c) ($pH_{initial}$ = 3.0, T = 30 °C; H_2O_2 = 18.0 g/L).

BOD_5 and COD and the BOD_5:COD ratio, the optimal dose still occurs for 18.0 g H_2O_2/L (removals of 25.1%, 54.6% and 0.51, respectively). This dose corresponds to the better efficiency of oxidant use (as calculated by the ratio between TOC and H_2O_2 conversions − X_{TOC}:$X_{H_2O_2}$) of 0.42 (cf. Table 2).

The existence of an optimum H_2O_2 concentration was also observed by other authors (Ramirez et al., 2005; Rodrigues et al., 2010) and is explained by the fact that a parallel reaction between H_2O_2, in excess, and the hydroxyl radicals occurs, generating $HO_2^•$ species with a lower oxidation potential ($HO^• + H_2O_2 \rightarrow H_2O + HO_2^•$) (Walling, 1975); this is proved by the higher consumption of H_2O_2 for the doses of 22.0 and 25.0 g/L (see Table 2).

It is also worth noting that there was a reduction of toxicity as inferred by the inhibition of *Vibrio fischeri* from 27.9 to 28.5% (Table 1) to 8.3−11.8% (see Table 2), for the dose of 14.5 g H_2O_2/L. For higher oxidant doses, the final effluent presents no toxicity to such bacteria.

As expected, the cost of the process increased with the hydrogen peroxide concentration (see Table 2). For the optimum dose (18 g/L) the cost of chemicals represents 86.6 R\$/m³ (21.2 €/m³).

3.1.2. Effect of initial Fe^{3+} concentration

The oxidation efficiency was tested by varying the dose of iron in the Fe^{3+}:H_2O_2 range of 1:17 to 1:7 by weight (corresponding to the lowest and highest Fe^{3+} tested doses, respectively). The remaining variables were fixed at the following values: H_2O_2 concentration = 18.0 g/L, initial pH = 3.0 and T = 30 °C.

According to Fig. 3a), a rapid increase in TOC removal is again observed in the first 30−60 min. After this period and up to 120 min the increase is slowed down and almost no rise is detected later. The maximum removal (39.7%) was observed when using 1.45 g Fe^{3+}/L. In Fig. 3b), concerning the progress of pH, a somehow similar temporal profile as compared with that of TOC is depicted, significantly decreasing until 30−60 min, then slowing down and becoming nearly stable after 120 min. The smaller pH decrease corresponds to the smaller amount of catalyst, possibly because less organic acids are formed. Oppositely the dose of iron of 1.45 g/L provided the greatest mineralization and the highest acidification of the reaction medium.

The existence of an optimum dose of Fe (Fig. 3) is explained by the reaction of excess iron ions with the hydroxyl radicals ($HO^• + Fe^{2+} \rightarrow HO^- + Fe^{3+}$) (Walling, 1975), thereby decreasing by such scavenging effect the concentration of radicals available and limiting the oxidation of the organic compounds. It fact it is notorious that the consumption of hydrogen peroxide increased with the dose of Fe^{3+} (Table 2), but not provided better removals of organic matter.

The existence of an optimum amount of iron salt is also observed from the data of COD and BOD_5 removal (Fig. 3c)), which reached 54.6% and 25.1%, respectively, for 1.45 g/L of Fe^{3+} and after 3 h of reaction; moreover, the best BOD_5:COD ratio (0.51) occurred
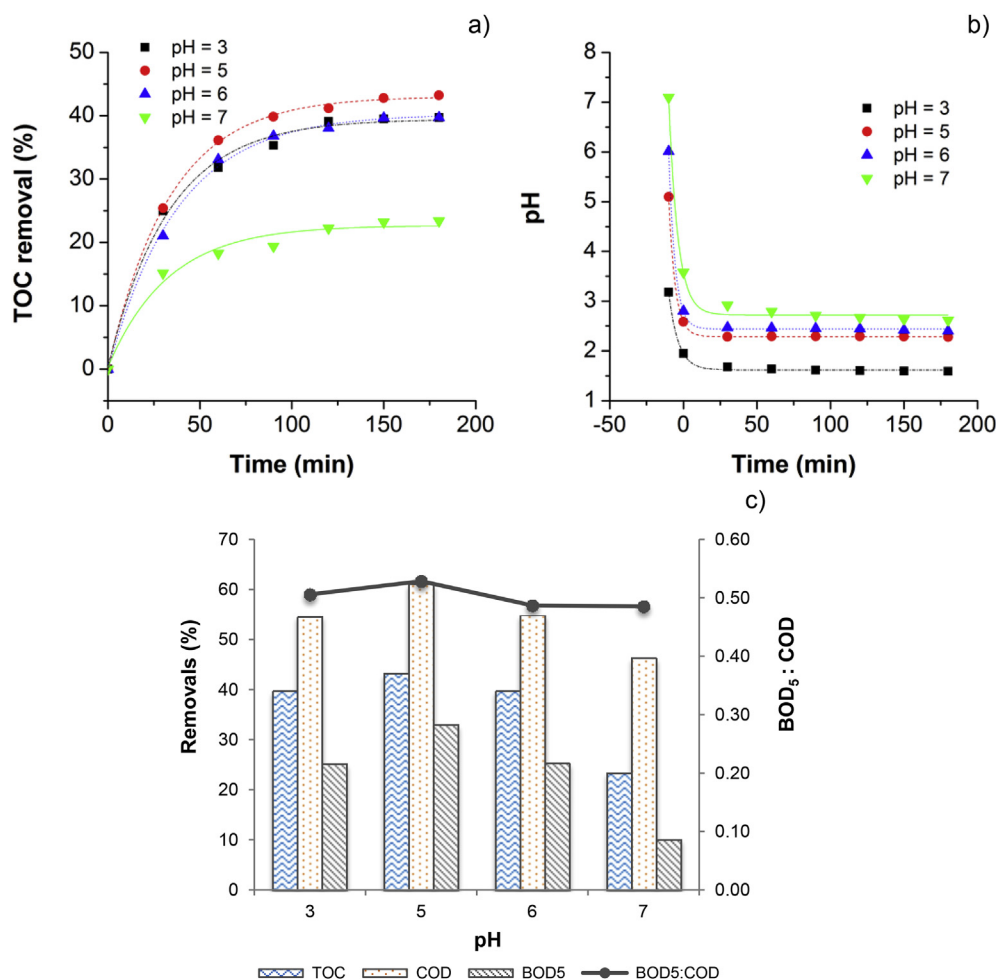
Fig. 4. Influence of pH in the removal of TOC (a) and pH (b) during reaction and removal of TOC, COD and BOD_5 and BOD_5:COD ratio after 180 min of reaction (c) ($H_2O_2 = 18.0$ g/L T = 30 °C; $Fe^{3+} = 1.45$ g/L).

for the same dose of iron. As experienced with the different oxidant doses tested, the optimum dose of Fe^{3+} provided also a more efficient use of hydrogen peroxide in the degradation of organic compounds ($X_{TOC}:X_{H_2O_2} = 0.42$ − Table 2).

Regarding the toxicity of the final effluent, the dose of iron of 1.04 g/L led to inhibition values of 10.0−14.2%; for the other doses the effluent is not toxic (0.0% of inhibition of *Vibrio fischeri*) − see Table 2.

The total operating cost for treating the effluent increased a little bit with the dose of iron (see Table 2); for the optimum Fe^{3+} concentration of 1.45 g/L was 86.6 R$/m^3 − 21.2 €/m^3.

Amat et al. (2014) obtained COD removals of 59.3% (very close to the value found in this study), using 5.6 g of Fe^{2+}/L for treating a raw vinasse sugarcane effluent. The dose of catalyst obtained by these authors is much higher than that found as optimal (1.45 g/L) in this work, probably due to the much higher organic content of their effluent (initial COD of 53,000−59,000 mg/L).

3.1.3. Effect of pH

The effect of pH was tested in the range 3−7 (iron dose = 1.45 g/L, H_2O_2 dose = 18.0 g/L and T = 30 °C). Fig. 4a) shows that the maximum TOC removal (43.3%) was achieved for the initial pH value of 5.0, possibly due to the fact that by adding the catalyst ($FeCl_3$ salt) a strong decrease in the pH of the vinasse to values close to 2.5 was observed (Fig. 4b)), which is very similar to the optimum pH values reported in the literature to treat effluents with organic

loads similar to this vinasse by the Fenton's process (Dantas et al., 2003; Zhang et al., 2005). For the initial pH of 6.0 and particularly 7.0, the pH of the effluent was considerably higher upon addition of the catalyst ($t = 0$), so that the oxidation process becomes less efficient, possibly as a result of the decreased solubilization of iron, making it unavailable for effectively catalyzing the reaction (cf. Fig. 4a)). For the run at an initial pH of 3, when the catalyst was added the pH of solution decreased to values < 2. At pH below 2 the generation of hydroxyl radicals decreases, because the hydrogen peroxide forms $H_3O_2^+$, reducing the reactivity with Fe^{3+}.

It was also observed that at the initial pH of 5 higher removals of BOD_5 and COD occurred and the BOD_5:COD ratio showed the greatest increase, with values of 33.0%, 61.1% and 0.53, respectively (Fig. 4c)); better usage of oxidant in the oxidation of organics was also reached at the same pH ($X_{TOC}:X_{H_2O_2} = 0.44$ − Table 2). Regarding the toxicity of the effluent, is should be noted that for all pH values tested the final effluent showed no toxicity. This finding, together with the results of BOD_5:COD ratio, demonstrates that the effluent may be subsequently subjected to a biological treatment.

An important aspect to note is that this treatment strategy allows to use vinasse with a pH not very acidic (typically the Fenton process requires acidification to pH 2.5−3.0). In fact, the addition of the oxidant and particularly the catalyst, iron chloride, considerably lowers the pH of the effluent; this way it is reduced the consumption of acid for acidification.

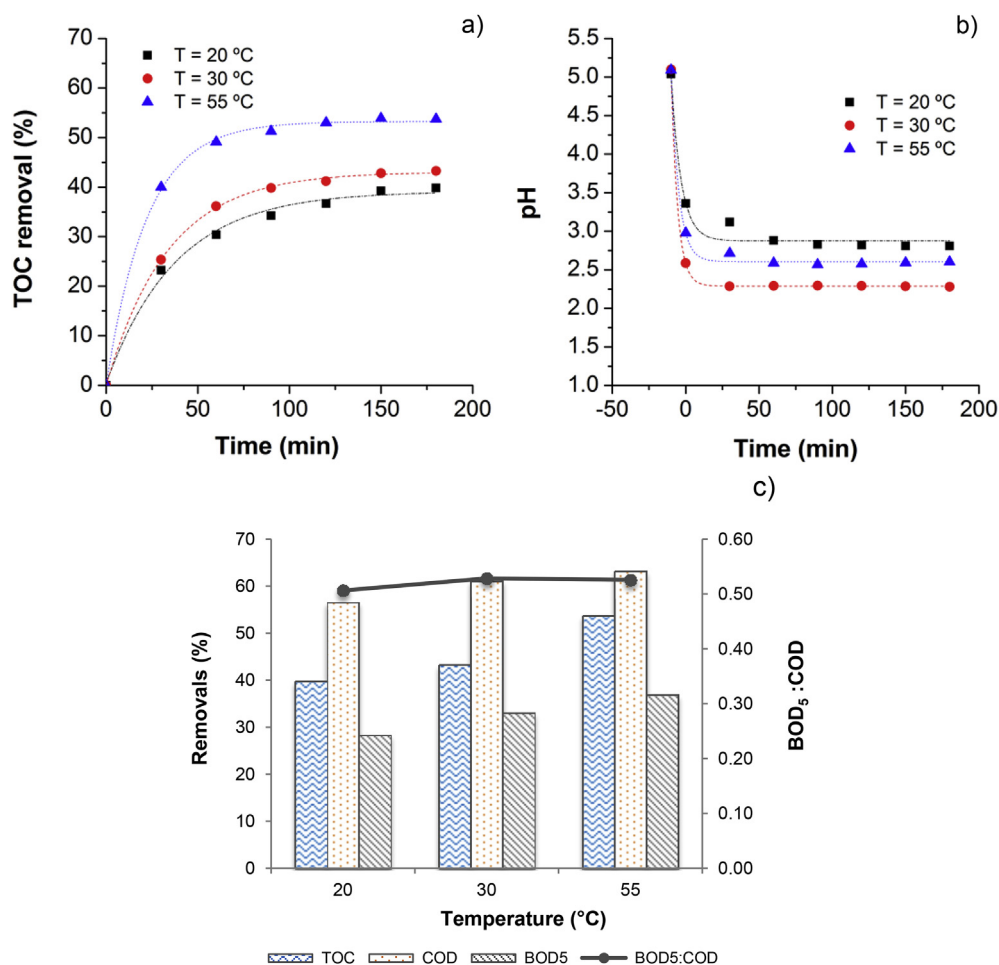It is also important to mention that the costs related to the use of

Fig. 5. Influence of temperature in the removal of TOC (a) and pH (b) during reaction and removal of TOC, COD and BOD_5 and BOD_5:COD ratio after 180 min of reaction (c) ($H_2O_2 = 18.0$ g/L; $pH_{initial} = 5.0$; $Fe^{3+} = 1.45$ g/L).

acid (H_2SO_4) and base (NaOH) for pH adjustment are almost negligible as compared to that of the other chemicals. Therefore, we considered only the values for the Fe^{3+} (0.2 R\$/m³ — 0.05 €/m³) and H_2O_2 (86.4 R\$/m³ — 21.1 €/m³) consumption, meaning an overall cost of 86.6 R\$/m³ — 21.2 €/m³ (see Table 2).

3.1.4. Effect of temperature

The tests were performed at 20, 30 and 55 °C. This range of temperatures takes into account the weather conditions in Brazil at harvest time, at which the production of vinasse is greater; in these months (April to November) temperatures generally are not below 20 °C in São Paulo state. On the other hand, taking into account the possibility of application of Fenton's process to biodigested vinasse (and that is to be recirculated to the digester), we have taken into account that such biological reactors operate at temperatures close to 55 °C. Furthermore, it is known that higher temperatures, usually above 60–70 °C, can enhance the thermal decomposition of H_2O_2 into O_2 and H_2O, hindering the formation of hydroxyl radicals and affecting the oxidation of organic matter. Moreover, higher temperatures require more energy for heating the effluent to be treated, making the treatment more costly.

In Fig. 5 it is possible to observe that the removal of organic matter increases with increasing temperature and the greater removal of organic matter was reached at 55 °C after 3 h reaction time (removals of TOC = 53.7%; BOD_5 = 36.9%; COD = 63.2% and BOD_5:COD ratio = 0.53). This trend is justified by the Arrhenius law

(which is reflected by the effect of temperature either on the radicals generation rate constant, or on the degradation of organic molecules by the same radicals). As shown in Table 2, at 55 °C it was also obtained the better utilization of oxidant for mineralization of the organic matter (X_{TOC}:$X_{H_2O_2}$ = 0.56). This temperature value is very close to the optimal 50 °C reported by Torrades et al. (2003) in the treatment of paper industry effluent, by Rodrigues et al. (2012, 2013, 2014) for textile dyeing effluents and by Ramirez et al. (2005) for degradation of Orange II dye.

The toxicity of the effluent, as quantified by the inhibition of *Vibrio fischeri*, was found to decrease from 27.9 to 28.5% (initial value of the vinasse — Table 1) to 5.7–8.6% (Table 2) after the Fenton reaction at 20 °C. For the other tested temperatures, the effluent is not toxic. The costs of energy were considered to be negligible for the above reasons (use of the own enthalpy of the effluent to be treated). Therefore, the costs are only linked to the consumption of reagents (Fe^{3+} and H_2O_2); the total operating cost is 86.6 R\$/m³ (21.2 €/m³) — see Table 2.

Under the optimum conditions found (18 g/L of H_2O_2, 1.45 g/L of Fe^{3+}, initial pH of 5 and 55 °C), the characteristics of the treated vinasse upon 3 h of Fenton's oxidation are reported in Table 1. It is worth noting the following results: the sulphate content increased with the treatment (because H_2SO_4 was used to adjust the pH), all phosphate was removed, a small removal of magnesium and calcium was reached, a considerable reduction of turbidity was observed (from 1500 to 6.6 NTU), as well as a significant increase of
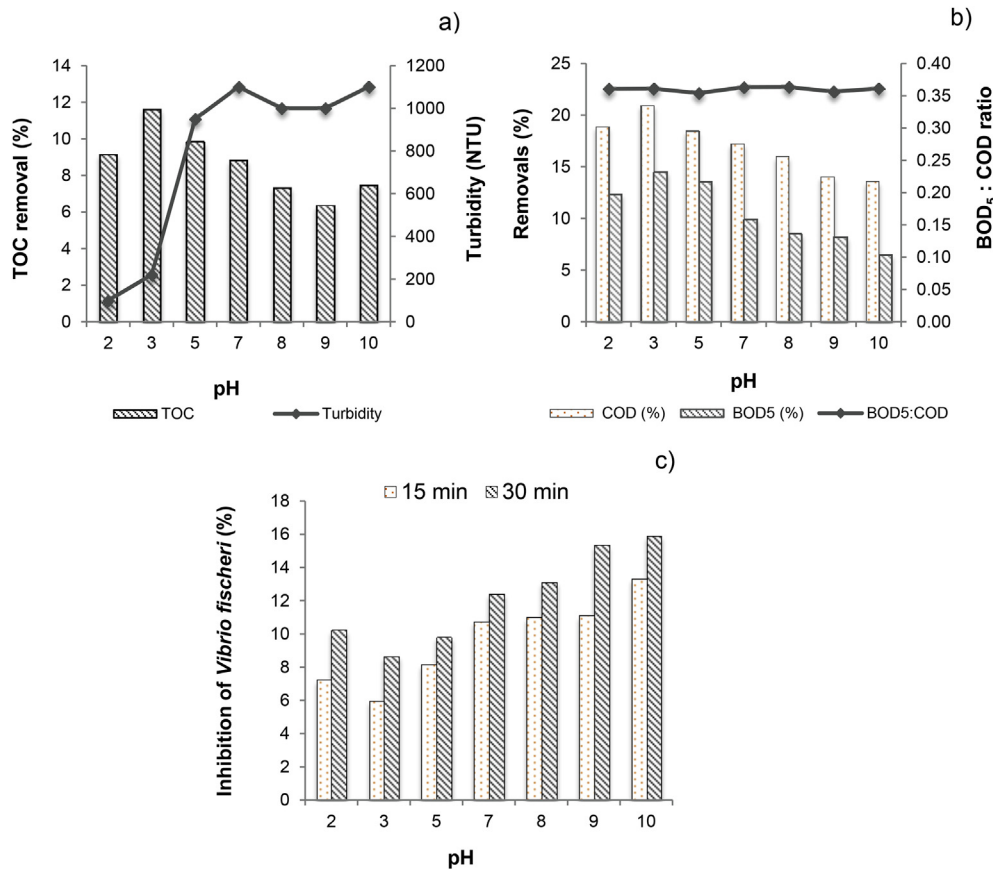
Fig. 6. Removal of TOC and turbidity of the effluent (a), removals of COD, BOD$_5$ and BOD$_5$:COD ratio value (b) and inhibition of *Vibrio fischeri* (c) as a function of the pH used in the coagulation/flocculation process (v$_{coagulation}$ = 150 rpm, t$_{coagulation}$ = 3 min, [Fe^{3+}] = 100 mg/L, T = 25 °C, v$_{flocculation}$ = 20 rpm, t$_{flocculation}$ = 15 min).

biodegradability (BOD$_5$:COD raised from 0.31 to 0.53) and decrease of toxicity, which is good for vinasse recirculation back to the anaerobic digester; however, the treatment cost is considerable. Therefore, another strategy was pursued, starting with the more conventional coagulation/flocculation stage, aiming also to reach better reductions of the organic load.

3.2. Chemical coagulation/flocculation (Strategy 2)

3.2.1. Effect of pH

Initially, it was decided to search for the optimum pH of the coagulation/flocculation process, fixing the concentration of Fe^{3+} at 100 mg/L; the pH variation range was from 2.0 to 10.0. The results for TOC removal and turbidity are shown in Fig. 6a). It was observed that the most significant TOC removal (11.6%) occurred at pH 3.0, with lower turbidity at pH 2 and 3 (100–220 NTU).

The COD and BOD$_5$ removals and BOD$_5$:COD ratio are shown in Fig. 6b). Again, the best removals of COD (21.0%) and BOD$_5$ (14.6%) and smaller inhibition of *Vibrio fischeri* (6.0–8.7%) were achieved at pH 3.0 – see also Fig. 6c); the ratio BOD$_5$:COD remained nearly unchanged in the pH range studied (ca. 0.36 vs. 0.31 for the initial effluent – Fig. 6b)). The results presented allow establishing the pH of 3.0 as the best one for operation of the coagulation/flocculation process. 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 charge neutralization mechanism (Duan and Gregory, 2003).

3.2.2. Effect of coagulant dose

Once decided upon the pH that maximizes the removal of

organic matter, the concentration of Fe^{3+} was progressively varied from 50 mg/L to 500 mg/L. Fig. 7a) shows the results obtained for the reduction of turbidity and TOC from the effluent for different doses of the coagulant. It can be seen that the higher the concentration of Fe^{3+}, the higher is the removal of organic matter, reaching a maximum TOC removal of 30.5% using 500 mg Fe^{3+}/L, which corresponds also to the lower turbidity obtained (85 NTU). Similarly, the highest removal of BOD$_5$ (27.9%) and COD (43.6%), as well as the highest value of the BOD$_5$:COD ratio (0.39), were reached at the same dose – see Fig. 7b). The inhibition of *Vibrio fischeri* after coagulation/flocculation is shown in Fig. 7c). It is noted that the higher the concentration of Fe^{3+}, the lower the toxicity of the final effluent. So, the same dose of coagulant ([Fe^{3+}] = 500 mg/L) maximized simultaneously the removal of organic compounds, provided lower turbidity and toxicity and increased the biodegradability of the sugarcane vinasse.

Günes (2014) reported the Fe^{3+} concentration of 830 mg/L (equivalent to 2.4 g/L of FeCl$_3$) for the treatment of landfill leachate with an organic load similar to the vinasse used herein. Zayas et al. (2007), for treating a similar biodigested vinasse (although with a slightly higher COD of 8525 mg/L), reported an optimum dose of 20 g of FeCl$_3$/L.

The cost of chemicals for this treatment is relatively low, since it refers only to the FeCl$_3$ doses employed, reaching a maximum value of 5.7 R$/m^3 – 1.4 €/m^3 (see Table 1) for the maximum and selected dose of Fe^{3+} (500 mg/L). In general, it can be seen that in the coagulation/flocculation the efficiencies of organic matter reduction achieved were lower than when vinasse was treated by Fenton's oxidation, and provided also an effluent with a lower
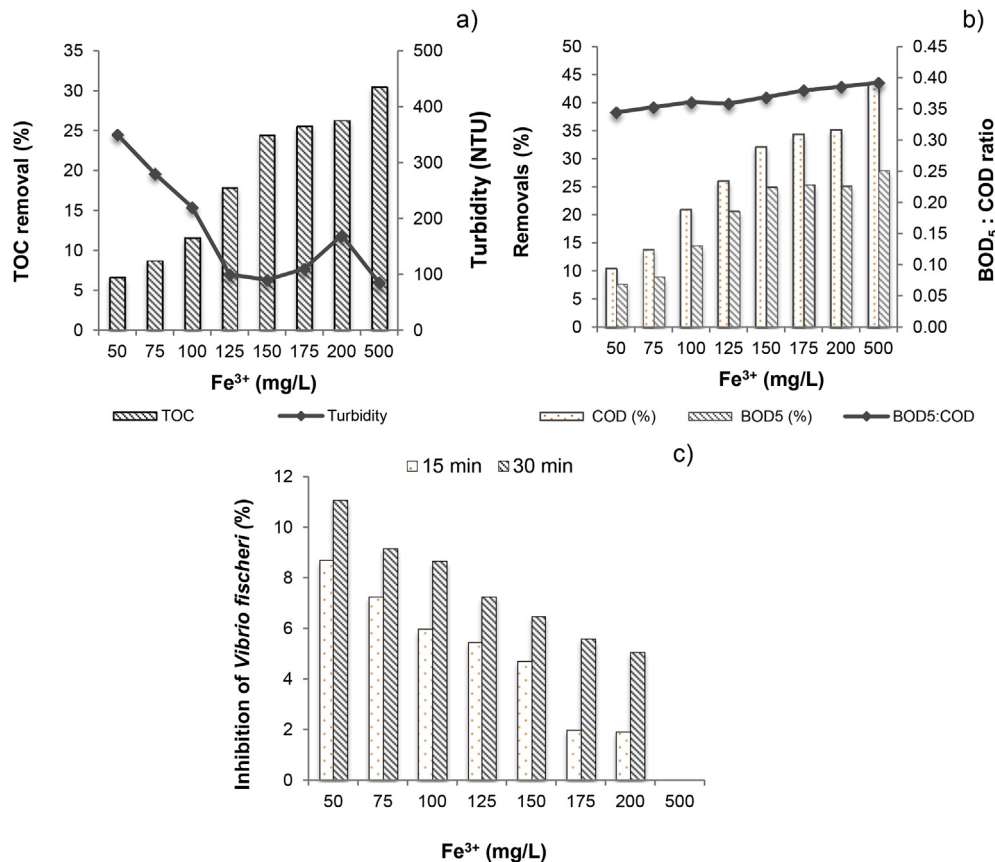
Fig. 7. Influence of Fe^{3+} dose in the removal of TOC and turbidity of the effluent (a), removals of COD, BOD_5 and BOD_5:COD ratio value (b) and inhibition of *Vibrio fischeri* (c) during the coagulation/flocculation process ($v_{coagulation}$ = 150 rpm, $t_{coagulation}$ = 3 min, pH = 3.0, T = 25 °C, $v_{flocculation}$ = 20 rpm, $t_{flocculation}$ = 15 min).

BOD_5:COD ratio. However, the treatment costs are much lower. Therefore, the coagulation/flocculation may be used as a pretreatment of the Fenton process, as will be presented in Strategy 3, in order to reduce the overall cost; this way the amount of organics to be oxidized in the Fenton's stage are reduced, thus requiring less chemicals, namely hydrogen peroxide. Moreover, in the chemical oxidation step one will make use of the iron salt as catalyst that remains dissolved in solution after the coagulation process, further reducing the operating cost.

3.3. Chemical coagulation/flocculation plus Fenton's oxidation (Strategy 3)

As above-mentioned, using coagulation/flocculation before the Fenton process aims at reducing the organic load of the biodigested sugarcane vinasse in order to decrease the amount of reagents required in the following process, lowering the treatment costs. Therefore, the effluent was previously treated at the optimum conditions of coagulation/flocculation found in Strategy 2 (pH = 3.0, and $[Fe^{3+}]$ = 500 mg/L), and then submitted to Fenton's oxidation at the optimum values of pH and temperature achieved in Strategy 1 (pH = 3.0 and T = 55 °C). The dose of hydrogen peroxide was varied while the catalyst used was only the dissolved iron (270 mg/L) that resulted from the previous coagulation/flocculation stage.

3.3.1. Effect of initial H_2O_2 dose

The concentrations of H_2O_2 in the Fenton oxidation step varied between 4.5 and 18.0 g/L. As previously observed for the raw biodigested sugarcane vinasse, the TOC removal occurs very

rapidly in the first 30–60 min of reaction (Fig. 8a)) for all hydrogen peroxide concentration tested and at the same time there is a slightly faster pH decrease (see Fig. 8b)). After this period the increase of TOC removal (and pH decrease) proceeded at a slower rate until 150 min; afterwards TOC remained nearly constant.

At the end of the chemical oxidation stage, the best values of TOC, COD and BOD_5 removals and higher value of BOD_5:COD ratio were all obtained using 14.5 g/L H_2O_2 (see Fig. 8c)), corresponding to removals of TOC = 40.2%, BOD_5 = 24.6% and COD = 45.4%, BOD_5:COD ratio = 0.54 and no inhibition of *Vibrio fischeri*.

The combination of the two processes (coagulation/flocculation followed by Fenton's reaction) reached global reduction efficiencies of TOC = 51.6%, COD = 69.2%, BOD_5 = 45.7% and total phosphate = 100%; a small reduction of magnesium (9.4%) and calcium (1.4%) content was also observed. This strategy generated a non-toxic effluent and considerably improved the biodegradability (from 0.31 to 0.54 before and after treatment, respectively); turbidity was substantially reduced (from 1500 to 1.3 NTU). The concentration of sulphate increased because sulphuric acid was added for adjusting the value of pH – see Table 1. The efficiencies obtained with the combination of processes are similar to those reached when treating the sugarcane vinasse by Fenton's oxidation alone, but upon combination of coagulation/flocculation with Fenton's oxidation less hydrogen peroxide was consumed (optimum dose decreased from 18.0 to 14.5 g/L), and consequently there is a reduction in the cost of chemicals from 86.6 to 75.3 R$/m^3 (from 21.2 €/m^3 to 18.4 €/m^3).
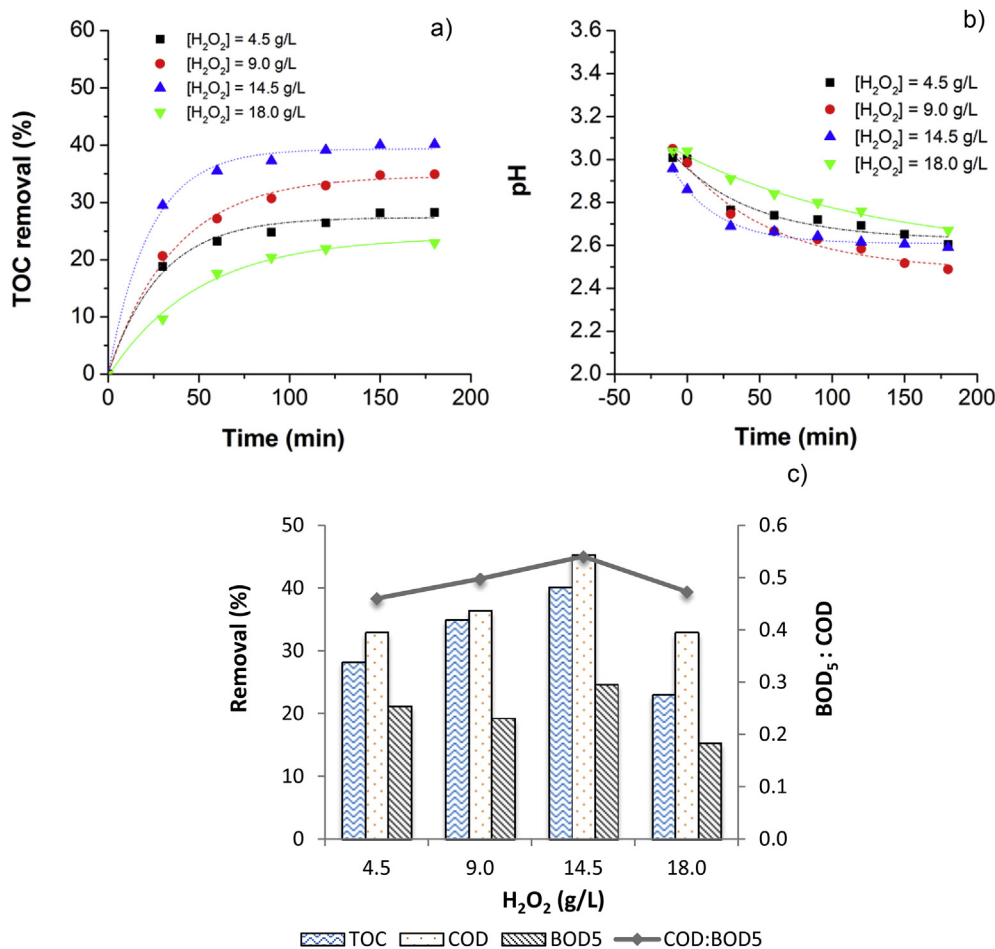
Fig. 8. TOC removal along the reaction (a) and pH along the Fenton reaction (b) and COD and BOD$_5$ removals and BOD$_5$:COD ratio after 180 min of reaction (c) in vinasse pre-treated by coagulation/flocculation (pH = 3.0 and T = 55 °C).

3.3.2. Hydrogen peroxide added incrementally over the reaction

In an attempt to further reduce the treatment costs, it was decided to apply the optimal dose of H$_2$O$_2$ (14.5 g/L) gradually and also a lower dose of 9.0 g/L. As detailed in Section 2.2.2, in these runs the same dose of oxidant was added gradually to the reaction mixture, i.e., every 5 min until 150 min of reaction. The gradual addition has a positive effect on the organic load decrease, as shown in Fig. 9a). This behaviour can be attributed to the reduction of parallel reactions between H$_2$O$_2$ and the hydroxyl radicals (scavenging effect) that prevail when the oxidant is present in solution in large excess at $t = 0$. Comparing the results, it can be observed that the gradual addition achieved better removals than the total addition at the beginning of the reaction. The TOC removal values after 3 h of reaction were 40.5% for a H$_2$O$_2$ dose of 9.0 g/L and 44.1% for 14.5 g/L, both exceeding the removal of 40.2% obtained when the optimal dose of 14.5 g H$_2$O$_2$/L was entirely added at the beginning of the reaction.

Fig. 9b) compares the removals of COD and BOD$_5$ and the BOD$_5$:COD ratio for total peroxide addition mode (all peroxide is added at $t = 0$) versus the gradual/continuous addition mode. The gradual addition of 14.5 g H$_2$O$_2$/L (Fig. 9b)) provides again an increase in the removals of BOD$_5$ (from 24.6 to 28.8%) and COD (from 45.4 to 50.6%), providing a non-toxic effluent. However, it was verified that there was a decrease in the BOD$_5$:COD ratio (to 0.35). The same trends were observed for the dose of 9 g/L (see Fig. 9c)) — when hydrogen peroxide was added gradually, COD removal

increases from 36.4 to 49.6% and BOD$_5$ from 19.3% to 24.8%; the effluent does not exhibits inhibition towards *Vibrio fischeri* and the BOD$_5$:COD ratio value is only 0.33. The decrease in the value of BOD$_5$:COD ratio is possibly related to the intermediate compounds formed when H$_2$O$_2$ is added gradually; it is suggested that these compounds are less biodegradable than those resulting from the assay where the same amount of oxidant is entirely added at the beginning. Moreover, a non-toxic effluent was generated for the two H$_2$O$_2$ doses tested. Therefore, the gradual addition of the oxidant is the best strategy to be adopted if it is desired to maximize organics removal before discharge.

Considering the economic viability of the process and the efficiency of treatment, the dose of 9.0 g H$_2$O$_2$/L gradually added in the Fenton step, subsequent to the coagulation/flocculation stage, is suggested. This strategy reduces considerably the costs of chemicals to 48.9 R\$/m^3 — 11.9 €/m^3 (comparatively to 75.3 R\$/m^3 — 18.4 €/m^3 — when all H$_2$O$_2$ is added at the beginning of reaction — Table 1) and improves the removal of organic compounds. However, because a lower BOD$_5$:COD ratio was reached, it is not yet clear if the effluent can be or not recirculated back into the high rate anaerobic reactors. This will be the aim of future work, i.e., assess the impact of the peroxide addition mode on biogas production.

4. Conclusions

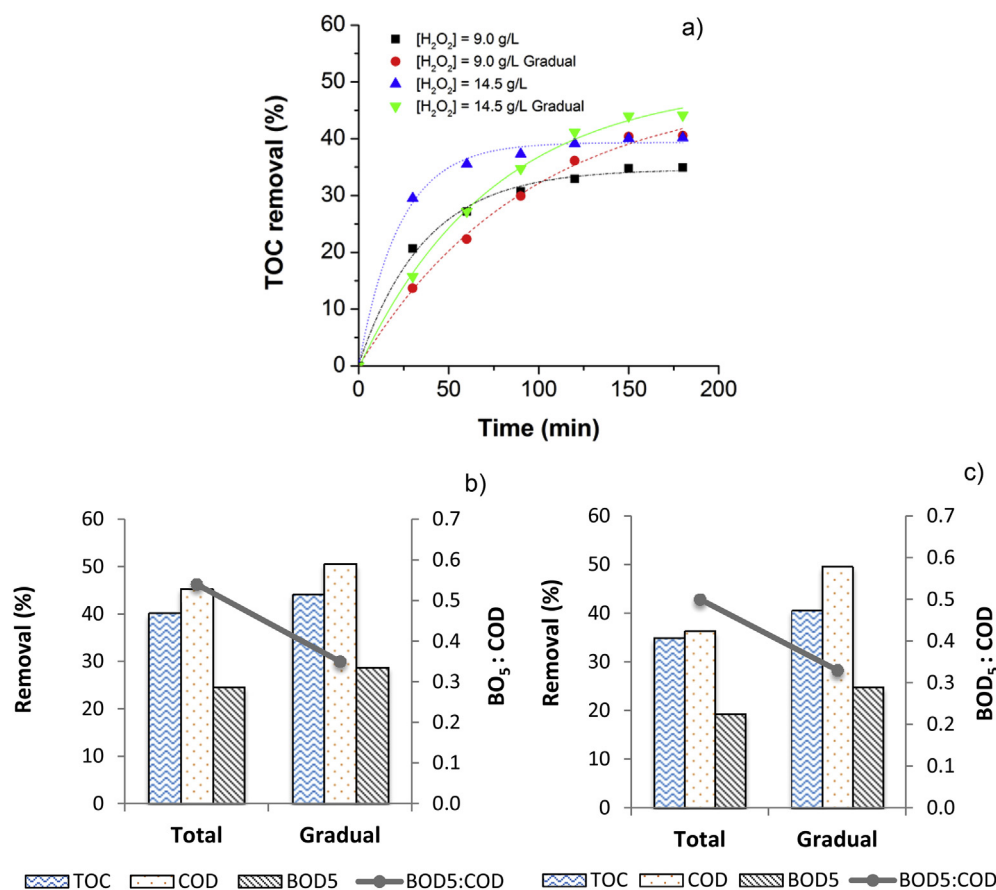It can be concluded from the analysis of the biodigested

Fig. 9. TOC removal along the reaction (a), percentages of COD and BOD_5 removals and BOD_5:COD ratio value after 180 min of reaction in gradual and total addition modes of H_2O_2 in effluent pre-treat by coagulation/flocculation with an oxidant dose of 14.5 g/L (b) or 9.0 g/L (c) (pH = 3.0 and T = 55 °C).

sugarcane vinasse that it is characterized by high load of organic matter, low biodegradability (BOD_5:COD = 0.31) and toxicity. Thus, the biodigested vinasse requires prior treatment for i) its recirculation back to the anaerobic reactors (to increase the production of methane) or ii) disposal in the environment. The present study demonstrated the applicability of isolated and combined coagulation/flocculation and Fenton's processes in the treatment of such biodigested sugarcane vinasse. It was found that:

i) The Fenton's oxidation can be operated at high values of pH (ca. 5) because the addition of catalyst decreased the pH of the solution down to 2.5–3.0. When used per se, this oxidation process allows obtaining high efficiencies in reduction of organic compounds (TOC = 53.7%, COD = 63.2% and BOD_5 = 36.9%), yielding a non-toxic effluent (0.0% inhibition of *Vibrio fischeri*), with small turbidity and providing significant improvement of the effluent biodegradability (BOD_5:COD ratio increased to 0.53). However, the operation cost is high (86.6 R\$/m^3 – 21.2 €/m^3);

ii) Coagulation/flocculation under optimised conditions allows to achieve moderate organic matter removal (30.5% for TOC, 43.6% for COD and 27.9% for BOD_5), considerable reduction of wastewater turbidity, but at a much smaller cost of treatment (5.7 R\$/m^3 – 1.4 €/m^3);

iii) To optimize the organic matter removal at a lower cost, the coagulation/flocculation was coupled to Fenton's oxidation, which in fact revealed to be an interesting strategy. With a H_2O_2 concentration of 14.5 g/L and without adding ferric ions

to that already present in solution after coagulation/flocculation, high global removals of TOC (51.6%), COD (69.2%), BOD_5 (45.7%) and a greater BOD_5:COD ratio (0.54) were reached, providing also a non-toxic effluent with very low turbidity (1.3 NTU). The corresponding cost is 75.3 R\$/m^3 (18.4 €/m^3).

iv) It was possible to further reduce the cost with chemicals (from 75.3 R\$/m^3 to 48.9 R\$/m^3 – from 18.4 €/m^3 to 11.9 €/m^3) by reducing the H_2O_2 dose to 9.0 g/L and making the addition of oxidant gradually along time, while keeping the efficiency almost the same (TOC = 56.0%; COD = 49.6% BOD_5 = 45.8). The final effluent still remains non-toxic.

If the main objective is to maximorganics reduction, coagulation/flocculation followed by Fenton oxidation with continuous addition of the oxidation is the best strategy; however, if the vinasse it to be recirculated back to the anaerobic reactor, it seems to be preferable to add the peroxide in a single dose (once at reaction start), because a more biodegradable effluent was obtained.

Acknowledgments

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