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Research article

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

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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.

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

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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):

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

$$HO^{\bullet} + RH \rightarrow H_2O + \text{intermediates} \quad (2)$$

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.

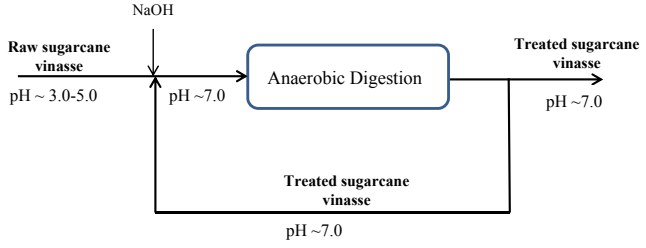

Fig. 1. Scheme of sugarcane vinasse treatment by digestion anaerobic.

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