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Leachate and vinasse used in a biological process combined with Fenton's reaction: a green method for treatment of textile effluents

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Abstract: The production of textiles generates a large amount of liquid residues considered to be environmentally problematic and which, if discarded without due treatment, may cause eutrophication of water sources, the intoxication of living beings, and the blocking of light penetration. Some methods have been applied for the treatment of this type of waste, with the prominence of biological and physicochemical techniques. The combination of two or more techniques enhances the treatment's efficiency. This work investigated the use of bacteria derived from the leachate produced by the textile industry itself, fed with vinasse, a by-product of the alcohol industry, with subsequent application of Fenton's reaction. The biological method, optimized in terms of aeration and quantity of nutrients for the bacteria, combined with the physicochemical method optimized in terms of the amount of reagents, was efficient for the discoloration of the effluent in approximately 100 %, for toxicity reduction, for the degradation of organic matter in 80 %, and with acceptable acidity for disposal after only eight days of treatment. The method was considered of great efficiency and low application cost, without the production of hazardous waste.

Key words: color removal, environmental science, organic load reduction, sugarcane by-product, textile industry waste.

INTRODUCTION

The textile industry is one of the primary item sectors that most use water for their productions. The average volume for dyeing a ton of fabric is of approximately 100 m^3 of water. Among the chemical products used are fabric dyes, which are often present in residual waters of the textile dyeing process (Hussain and Wahab 2018).

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There are approximately eight thousand types of textile dyes, with a worldwide annual production of over 700 thousand tons. An astonishing 20 % of the total volume is discarded in water bodies as industrial waste, characterizing a severe environmental problem because many of such compounds are of difficult degradation and their residues, when discarded without due treatment, pollute the ecosystem (Beltrame et al. 2008). Dye residues may hamper the penetration of light in the water environment, jeopardizing the photosynthesis of autotrophic beings (Natarajan et al. 2018, Mendes 2016, Martins et al. 2011). Furthermore, they may be harmful if ingested by living organisms (Dusman et al. 2012). Some dyes are metabolized into cancerous agents and may be mutagenic when ingested by aquatic organisms (Dusman et al. 2012), and their effects may be observed for decades (Monteiro et al. 2008). Additionally, these industrial wastes may present an elevated content of organic load and inorganic salts. (Peixoto et al. 2013, Kamida et al. 2005).

Physicochemical methods such as adsorption, chemical degradation, electrochemical techniques, coagulation, flotation, sedimentation, ozonization, as well as biodegradation processes, are used for the treatment of textile effluents.

Biological processes gained prominence for resulting in little-polluting products and being economically attractive (Halasz and Tosato Jr 2012). This type of treatment is based on the correct choice of a group of degrading microorganisms and on the promotion of their activity by providing essential nutrients and other growth factors such as proper temperature and aeration. Sugarcane molasses has been used as a source of carbon, however, even though it is a cheap product, it is still a cost in the process. Under this viewpoint, an interesting alternative would be vinasse, a by-product of the alcohol industry and of the production of "cachaça". Its occurrence is abundant: eight liters of vinasse are produced for each liter of "cachaça" (Oliveira et al. 2009).

Sugarcane vinasse has high organic matter content and, when discarded improperly, may entail several problems to the aquatic environment for having a large amount of organic matter, as well as high Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD), and also provide an excessive amount of minerals. (Freitas et al. 2018). Thus, vinasse may cause eutrophication of water system and hamper the penetration of sunlight. Vinasse has been widely used as a soil fertilizer. The fertigation of sugarcane with vinasse is a regular agricultural practice in Brazil. However, the potential negative effects from long-term soil fertirrigation represent a major drawback regarding this practice, whereas the application of biodigestion represents an interesting method for reducing the polluting organic load and recovering bioenergy from vinasse (Fuess et al. 2018).

As a source of microorganisms for the biological treatments, an interesting alternative would be leachate, a dark and viscous liquid produced in the biodegradation of solid and pasty organic residues, considered to be an environmental pollutant and found mainly in landfills. If not adequately treated, it may cause severe environmental impacts primarily through the contamination of water tables (Bezerra et al. 2015, Yao 2017).

Among the promising chemical methods for treating liquid waste, the literature highlights the Fenton reaction technique for its discoloration capacity and potential of elevating the biodegradability of the effluent (Nogueira et al. 2007, Lucas and Peres 2006, Martins et al. 2011, Tony et al. 2009). The simplicity of its application also stands out, seeing that the reaction occurs at room temperature and pressure, does not require any particular reagent or equipment and may be applied to a wide variety of compounds (Nogueira et al. 2007). Fenton's reaction is an advanced oxidative process that generates and uses the free radical hydroxyl (•OH) as a potent oxidant to degrade compounds that cannot be oxidized by chlorine and permanganate, which are considered conventional oxidants. The •OH has a high oxidation potential (2.80 V) when compared to other strong oxidizing agents. The hydroxyl's action depends on the pH of the reaction medium, on the concentration of iron, and on the presence of hydrogen peroxide.

Combined techniques have been used for textile effluent treatment. Recently, Ong et al. (2008) investigated the feasibility of using granular activated carbon-biofilm in the decolorization of azo dye Acid Orange 7-containing wastewater. In 24 h, the biochemical film reached almost 100 % of decoloration.

In this work, we developed a method for treating liquid waste contaminated with dye residues from the textile industry, based on a biological process combined with Fenton's reaction. We observed the potential for degrading recalcitrant organic molecules derived from the textile dyes. In the biological treatment, we used leachate stemming from the textile industry residues themselves, as well as vinasse as a source of nutrients for microbial development. Both the biological and the physicochemical stage went through an optimization study before being combined, thus, summing their potentialities.

MATERIALS AND METHODS

This work's practical procedure followed this sequence: (i) *in situ* collection of the liquid textile effluent, (ii) characterization of the effluent, (iii) optimization of the biological treatment with vinasse and leachate, (iv) optimization of Fenton's reaction, (v) combination of the optimized treatments and verification of the efficiency of the process with the techniques combined.

Textile company Döhler S/A provided the textile effluent and leachate samples, while artisanal "cachaça" company Max Moppi provided the vinasse. Both companies are from Joinville, SC, Brazil. We obtained the molasses used in the reference sample for the development of the biological process from the local market.

BIOLOGICAL PROCESS

According to the residue treatment sector of the textile company which supplied the samples, there is a practical evidence that the microorganisms in the leachate have an effective action in degrading the dyes present in the waste precisely because they stem from the degradation of solid and pasty waste of the company itself. Molasses is a source of nutrients for the microorganisms; however, the company still has an expense with the molasses. Thus, we compared the efficiency of vinasse as a source of nutrients to that of the molasses (control). We also tested a mixture of vinasse and molasses. The treatment monitoring time was of fifteen days. The microorganisms received nutrients from molasses and vinasse on day 0 and day 8 in equal levels, as shown in Table I. The chosen proportions were based on information from preliminary tests performed at the company that supplied the samples.

Another variable of the process, besides the carbon source, was the intensity of agitation, which is proportional to the level of aeration of the mediums. We prepared four tests and their respective duplicates in 250 mL Erlenmeyer flasks under constant agitation (agitator table Orbital SL180/A at speed level 2), and four tests, plus duplicates, in containers with a broad rectangular base (35 x 20 cm, with a height of 15 cm) adapted from 5 L polyethylene bottles of commercial mineral water, geometrically reproducing the lagoon system originally used by the company. The assays under little agitation (1-4P, Table I) was manually agitated during 1 minute thrice a day, five times a week because the microorganisms require a minimum of aeration to growing.

We used vinasse and molasses diluted to 10 % due to their high organic matter concentration, which could result in an excessive dosage of nutrients for the bacteria or hamper the degradation action since there already is some amount of nutrients in the waste itself. We added to the samples only molasses (1A and 1P), vinasse in lower (2A and 2P) and higher (3A and 3P) concentrations, as well as molasses/vinasse in a 50-50 (v/v) proportion (4A and 4P) (Table I).

The biodegradation of the dyes was assessed by using chemical oxygen demand (COD) method, the absorption assess of the UV-Vis spectrum, and

TABLE I
Tests for the biodegradation of dyes from textile waste with microorganisms from leachate fed with molasses and vinasse.

Test*		Effluent (mL)	Leachate (mL)	Vinasse 10 % (mL)	Molasses 10 % (mL)
Little agitation	1P	800	160	-	12
	2P	800	160	4	-
	3P	800	160	12	-
	4P	800	160	6	6
Constant agitation	1A	125	25	-	3.75
	2A	125	25	1.25	-
	3A	125	25	3.75	-
	4A	125	25	1.87	1.87

*We added molasses for the 1P/A tests, vinasse in smaller quantity for the 2P/A tests, vinasse in a larger amount for the 3P/A tests, and equal amounts of molasses and vinasse for the 4P/A tests. We obtained samples 1-4P in rectangular-based containers under manual and periodic agitation, while samples 1-4A were packed in a 250 mL Erlenmeyer under constant agitation.

evaluation of the acute toxicity using *Vibrio fischeri* (*Photobacterium phosphereum*). We also monitored pH (MS Tecnopon Mpa210 potentiometer).

We determined the COD based on the Standard Methods for the Examination of Water and Wastewater (Baird 2017) at days 1, 8, and 15, along with the pH measurements.

Spectrophotometric evaluations were performed to verify the variation of the color intensity and tonality of the samples. We obtained the absorbance spectra (190 to 800 nm) with a UV-Vis spectrophotometer (Shimadzu UV-1800) at days 1, 8, and 15.

The purpose of the acute toxicity test with *Vibrio fischeri*, a luminescent bacterium of marine origin, is to indicate the degree of toxicity of sample. The bacterium's natural light emission is not changed in aquatic environments with dissolved oxygen concentrations over 0.5 mg/L. The test is based on exposing the bacterium to a sample of water or sediments for a given period and, in the presence of toxic substances to the bacterium, on verifying the decrease in luminescence, which is proportional to the sample's toxicity. Among the substances which are toxic to the bacteria are some metals, phenols, benzene and derivatives, and polycyclic aromatic hydrocarbons (Backhaus et al. 1997). We performed the *Vibrio fischeri* assays on the last day of the experiment (day 15).

We used Tukey's Test at the 5 % level to compare the means obtained in the analytical repetitions. We performed data analysis using software Sasm-Agri version 8.2 (Canteri et al. 2001).

FENTON'S PROCESS

In Fenton's reaction (Reaction 1), the oxidation of the target compound occurs due to the presence of ferrous salts and hydrogen peroxide, where the Fe^{2+} ion starts and catalyzes the decomposition of the hydrogen peroxide (Lucas and Peres 2006).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad \text{Reaction 1}$$

The hydroxyl radicals (•OH) formed in Fenton's reaction attack organic substrates, causing chemical decomposition by the abstraction of hydrogen and addition in unsaturated bonds (Lucas and Peres 2006). In the absence of a substrate, the hydroxyl radical formed may oxidize another Fe^{2+} ion (Nogueira et al. 2007). The Fe^{3+} ions originated in the reaction have the property of catalytically decomposing H_2O_2 into H_20 and O_2, with a pH-dependent occurrence. The formation of radicals and Fe^{2+} ions also occurs (Nogueira et al. 2007). The decrease in degradation efficiency according to the increase in pH is due to the fact that there occurs a transition of hydrated Fe^{2+} ions to ferric colloidal species $Fe(OH)_3$. This species catalytically decomposes the hydrogen peroxide into oxygen and water, preventing the generation of •OH, as well as the decrease of available catalysts for the formation of •OH (Rodrigues et al. 2017). Thus, Fenton's reaction must be performed with the pH of the reaction medium of at most 4.

Therefore, •OH formation is dependent on the presence of iron in the reaction. However, from a given concentration, the efficiency of the process becomes insensitive to this increase in iron content. This indicates that there exists an optimal amount of catalyzer to be used (Rodrigues et al. 2017). With the excess of H_2O_2 in the reaction, the concentration of Fe^{2+} ions becomes low relative to the concentration of Fe^{3+} ions because the reaction between Fe^{3+} ions and H_2O_2 is slow compared to the decomposition of H_2O_2 in the presence of Fe^{2+} ions. Hence, there probably also exists an optimal amount of peroxide to reach a higher efficiency of Fenton's reaction (Nogueira et al. 2007).

To determine these optimal values to reach the maximum efficiency of the treatment, we used the experimental planning with a central rotational composite design. The variables were the concentration of ferrous ion and the concentration of hydrogen peroxide, identified in coded form by X_1 and X_2, having as response the percentage of efficiency in color removal Y (Equations 1 and 2). We conducted the experiments following the planning matrix (Table III).

$$[Fe^{2+}] = 50X_1 + 100 \qquad \text{Equation (1)}$$

$$[H_2O_2] = 3300X_2 + 4950 \qquad \text{Equation (2)}$$

We chose the concentrations of the reagents from results obtained in the experimental planning performed in a previous work, which indicated the direction in which the displacement should be performed (a new factorial planning) for obtaining the optimal point.

The essays were performed randomly and in triplicate in a 250 mL Erlenmeyer flask containing 200 mL of the previously centrifuged effluent with its pH corrected with the addition of sulfuric acid (Sigma-Aldrich, St. Louis, USA) (initial pH = 3.0). We added the Fenton reaction's reagents to the flask containing the effluent under medium intensity agitation (300 rpm, agitator table Orbital SL180/A) in the concentrations established by the experimental design. We added the Fe^{2+} ions in the form of ferrous sulfate heptahydrate salt (Sigma-Aldrich, St. Louis, USA), and the hydrogen peroxide (Sigma-Aldrich, St. Louis, USA) using a 30 % H_2O_2 solution. The flasks were kept under constant agitation (80 min), with 1 mL samplings in pre-established times to follow the kinetic tendency, at 1, 5, 10, 20, 30, 40, 50, 60, and 80 min. We submitted the samples to absorbance reading. From the spectrophotometric measures, it was possible to monitor the color removing according to the time of the process.

The combined treatment first used the biological process and, in sequence, the physicochemical process. We then evaluated its efficiency.

RESULTS AND DISCUSSION

BIOLOGICAL PROCESS

We evaluated the biological process using the parameters pH, COD, *Vibrio fischeri* tests, and optic absorption measures.

The samples of textile waste with leachate, vinasse and/or molasses presented pH values between 7.29 and 9.35 (Table II). Beltrame et al. (2008) reported that, despite the great diversity of textile industry processes, raw materials, techniques, and equipment, in general, the wastewaters stemming from fabric stamping, dyeing, and washing present neutral or alkaline pH values, as was verified in this work.

TABLE II
pH[1] values for the tests of biological treatment of textile waste under more (A) and less (P) intense agitation, with leachate, and adding molasses (1), vinasse in lower (2) and higher (3) concentrations, and 50/50 molasses/vinasse (4). (See Table I).

Test	Day 1		Day 8		Day 15		Mean	SD
	pH[2]	SD	pH[2]	SD	pH[2]	SD		
1A	8.24^{B}	0.13	9.16^{A}	0.02	8.48^{B}	0.24		
2A	8.92	0.33	9.24	0.15	9.04	0.05	9.06	0.22
3A	8.67	0.05	9.04	0.21	9.02	0.04	8.92	0.21
4A	8.27^{B}	0.02	9.27^{A}	0.06	8.72^{AB}	0.16		
Mean	8.50	0.33	9.23	0.14	8.82	0.27		
1P	$7.78^{AB,b}$	0.04	8.22^{A}	0.12	$7.34^{B,c}$	0.07		
2P	$9.28^{A,a}$	0	8.75^{B}	0.08	$9.00^{AB,a}$	0.08		
3P	$9.14^{A,a}$	0.03	8.62^{C}	0.03	$8.88^{B,a}$	0.01		
4P	$7.70^{B,b}$	0.04	8.40^{A}	0.120	$8.23^{A,b}$	0.12		
Mean			8.50	0.23				

[1]Mean value of two repetitions ± standard deviation (SD). CV<5 %.
[2]Distinct subscripted letters, lowercase in columns and uppercase in lines, indicate a significant difference for Tukey's test (p≤0.05). When there was no difference, the mean ± SD are shown.

TABLE III
Design matrix and color removal rates, R[1].

Test	1	2	3	4	5	6	7	8	9	10	11
X_1	-1	1	-1	1	0	0	0	-1.41	1.41	0	0
X_2	-1	-1	1	1	0	0	0	0	0	-1.41	-1.41
R (%)	73.1	94.2	75.2	93.2	96.9	95.5	96.2	55.2	94.8	94.2	95.8

[1]Mean of three repetitions after 80 min of reaction. X_1 and X_2 are the coded concentration for the ferrous ions and hydrogen peroxide, respectively: -1 for $[Fe^{2+}]$ = 50 mg/L and $[H_2O_2]$ = 1650 mg/L; +1 for $[Fe^{2+}]$ = 150 mg/L and $[H_2O_2]$ = 8250 mg/L.

The raw effluent was alkaline (pH 10.3). The assays enriched with molasses and/or vinasse had their pH values decreased on the first day of treatment (Table II) because leachate (pH of 5.2), vinasse (pH of 3.3), and molasses (pH of 4.7) are acid. This is considered a positive action, considering that one of the necessities of the treatment is precisely the neutralization of the waste before its discard. Therefore, the use of the system with vinasse, molasses, and leachate would reduce the consumption of sulfuric acid, which is currently applied by the company.

In the systems under constant agitation (samples "A" of Table II), there was no significant difference among the pH values for the tests with molasses, vinasse, and molasses/vinasse when analyzing each day of treatment and their means. The samples with vinasse in systems under agitation did not have their pH values affected over time, remaining around 9 for the samples with lower (2A) and higher (3A) vinasse concentrations. The same behavior was not observed for the samples with vinasse in periodic agitation (2P and 3P), which had a behavior tending towards a decrease (day 8) and a mild pH increase (day 15). The best waste neutralization action was observed under little agitation and with molasses (1P) or molasses/vinasse (4P) (Table II). However, considering the last day of treatment (day 15) and samples with only vinasse, the agitation had little influence on the pH values, which remained around 9.

The COD ranged from 2.400 mg of O_2/L (sample 1P) to 550 mg of O_2/L (sample 2A). It is quoted that a moderate organic load for this type of waste varies from 300 to 3,000 mg of O_2/L

(Beltrame et al. 2008). Overall, the assays that presented the lowest indices of organic matter (lowest COD) were those enriched with vinasse (samples 2 and 3, Figure 1).

The amount of organic matter tended towards the reduction in the samples under constant agitation in the first eight days, whereas, in the samples under limited agitation, there was no significant variation of COD in this period (Figure 1). A more aerated system favored the development of the bacteria of the leachate, which are, therefore, mostly aerobic.

During the last week of analysis, observing the system under constant agitation, the amount of organic matter increased for the tests that contained molasses (1A and 4A); however, it did not change for the test with the higher concentration of vinasse (3A) and kept reducing for the test with the lower amount of vinasse (2A). It is worth emphasizing that on the eighth day, all tests received new doses of the products that contained nutrients (molasses and/or vinasse).

In the assays with higher amounts of vinasse (3A and 3P) and with vinasse/molasses under little agitation (4P), the COD remained constant between the 8th and 15th days. In the other experiments, there was an increase in COD in this period, except for sample 2A. This is because molasses has a more substantial amount of organic matter, given the larger COD results in the first day for samples 1 and 4. At the new addition of nutrients (on the 8th day), sample 2A, which did not contain molasses, was composed by a lower vinasse concentration, and was under continuous agitation; it was the only one that presented a COD reduction in the last week of evaluation. This behavior was observed because, in addition to the better conditions in terms of oxygenation, the sample 2A received a proper amount of nutrient - the vinasse in lower concentration - and the microorganisms were, therefore, able to use the available organic matter, without an excessive dosage. The COD variation of sample 2A was of 2.5 times between days 1 and 15, the highest found (Figure 1).

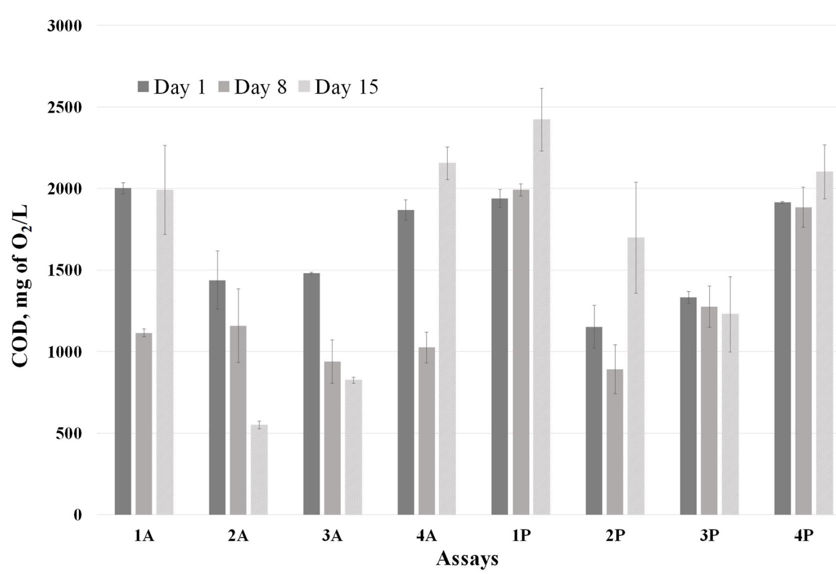

Figure 1 - Chemical oxygen demand (COD) for the tests of treating industrial textile waste with leachate and nutritional enrichment, under more (A) and less (P) intense agitation, with the addition of molasses (**1**), vinasse in lower (**2**) and in higher (**3**) concentrations, and 50/50 molasses/vinasse (**4**).

Therefore, considering that the best quality waste to be discarded into the environment must present low organic matter levels, tests under high agitation and with the enrichment of vinasse in the lowest concentration applied in this work would be the indicated treatment conditions.

The assays under limited agitation and with molasses or molasses/vinasse were visually more opaque. We confirmed this observation with the instrumental optic evaluation. In the test with higher vinasse concentration (Figure 2a), the continuous agitation did not allow an increase in absorbance, as occurred in the test with reduced agitation. Figure 2a also presents the spectrum of the raw effluent, which did not present a more intense color because it did not receive leachate nor a nutritive solution (molasses and/or vinasse). These products have pigments that contribute with absorbance in almost the entire interval of the analyzed spectrum. Therefore, the system under agitation would be the most indicated from the viewpoint of maintaining the light coloration of the liquid waste.

One may observe that, until the eighth day, there were no significant differences among the samples spectra between 300 and 800 nm (Figures 2b and 2c), the region of the predominantly visible. At 500 nm, the point of interest since the textile waste has a soft absorbance peak around this wavelength, the values did not present a significant statistical difference on days 1 and 8.

However, in the fifteenth day measures, the spectra of the different treatments showed discrepancies, as shown in Figure 2d. Considering that, the best treatment conditions would be the one which least presents color, i.e., with lower absorbance values in the visible region, the assay with a higher concentration of vinasse produced the best result, followed by the lower concentration of vinasse, molasses/vinasse, and molasses.

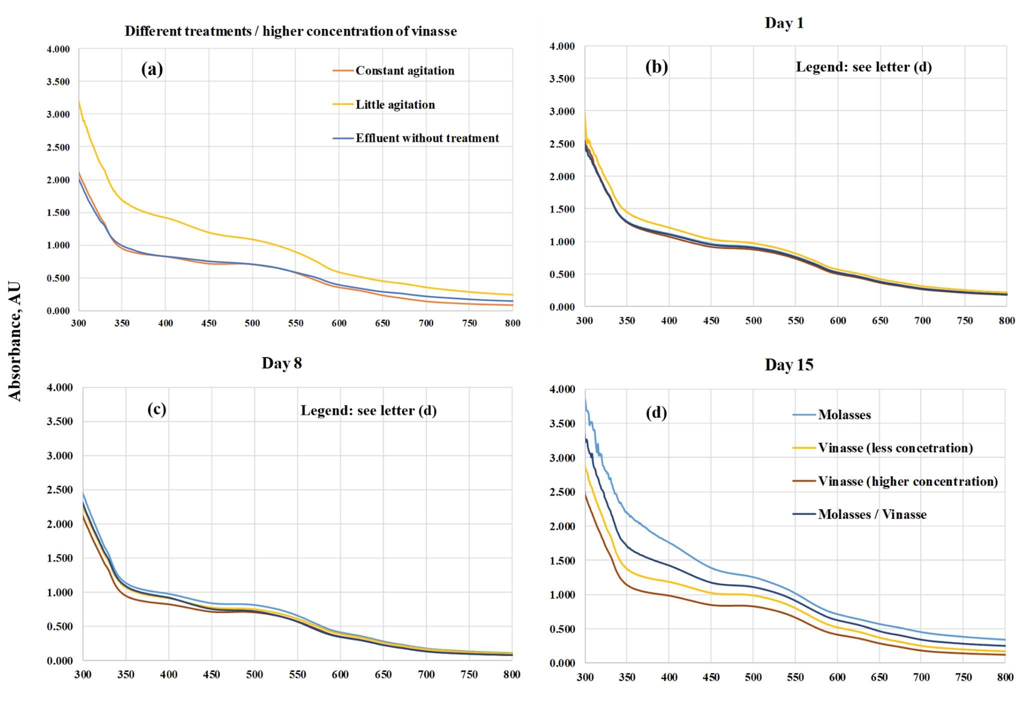

Figure 2 - UV-Vis absorbance spectra for the tests with textile industrial waste enriched with vinasse and molasses, under the action of microorganisms of leachate. Comparison of tests with vinasse in lower concentration relative to the other types of treatment **(a)** and comparison among tests with different sources of nutrients throughout the experiment **(b)**, **(c)**, and **(d)**.

Conchon (1995) stated that the activated sludge system (biological process) is the most efficient treatment for textile effluents operating in a prolonged timeframe for presenting high stability, low cost, with the removal of color in levels over 90 %.

Considering the exposed, regarding the optical measurements, the best condition for color removal was reached with fifteen days of treatment using only vinasse, in higher concentration, and under constant agitation.

We also performed the *Vibrio fischeri* test in a dilution factor of four according to the guidelines suggested by the sample supplier company, on the fifteenth day of the study. None of the samples under continuous agitation (1-4A, Table I) presented toxicity for the bacteria, a result that was observed only for sample 3P (highest amount of vinasse) among the tests conducted with limited agitation. It is important to highlight that wastewater samples from bleaching, rinsing and soaping of the textile factory may exhibit high acute toxicity and genotoxicity (Zhang et al. 2012).

Since samples 1P, 2P, and 4P presented a certain degree of inhibition of the bacteria's bioluminescence, we performed a serial dilution (4-8-16-32-64-128-256) to obtain the optimal dilution until be possible to classify them as a nontoxic waste. Samples 1P and 2P showed the highest degrees of inhibition, while sample 4P presented lower toxicity.

Therefore, under constant agitation, no treatment using the microorganisms from leachate with vinasse and/or molasses, in the tested proportions, may be applied with similar efficiency in terms of toxicity. The treatment under less intense agitation proved to be more efficient when using vinasse as the nutritional additive for the microbial flora, which is a positive factor in environmental terms.

In this first part of the work, we verified that it was possible to study the efficiency of the biological treatment of textile waste contaminated with industrial dyes under different conditions of nutrient supply and aeration. The leachate generated from textile industrial waste proved an interesting source of microorganisms for treating the waste. The system should preferably be continuously agitated, and the microorganisms would be fed with vinasse. The pilot-scale tests with *in loco* samples showed that this technology might be considered by the textile industry as an alternative for treating the waste it generates, also being an environmentally interesting destination route for leachate and vinasse.

FENTON REACTION TREATMENT

The spectra of the textile waste showed that the monitoring of color in the Fenton tests at 569 nm could be performed instead of analyzing the entire UV-Vis spectrum.

Equation 3 was used to determine the color removal parameter.

$$R = 100 \times [(Abs_o - Abs) / Abs_o] \qquad \text{Equation (3)}$$

where R is the color removal rate in percentage, Abs_o is the absorbance of the raw sample, and Abs is the absorbance of the treatment sample at 569 nm.

Table III shows the experiment's matrix and the color removal rates of the waste samples treated with Fenton's reaction under different conditions.

At 80 min of reaction, the maximum color removal was observed for all tests, ranging from 55.2 % (#8) to 96.9 % (#5). We analyzed the data with the aid of software Statistica® version 7 and evaluated a mathematical model for color removal characterized by Equation 4. For this model, the percentage of explained variation (R^2) was excellent, around 97.9 %.

$$R = 0.9622 + 0.1189 X_1 + 0.0044 X_2 - 0.1088 X_{12} + 0.0088 X_{22} - 0.0075 X_1X_2 \qquad \text{Equation (4)}$$

Despite the chemical complexity of the treated effluent, the parameters with p-values lower than 5 % ($p<0.05$) were considered significant.

For the studied range, only the linear and quadratic terms for the concentration of ferrous ions were relevant for the analyzed parameter. The H_2O_2 concentration or the interaction of this factor with the Fe^{2+} content was not statistically significant, having been incorporated into the residues for calculating the analysis of variance.

Despite the excellent quality of the obtained model, it is desirable for practical purposes that the adjusted model be the simplest possible, having the lowest number of parameters without losing the quality assured in the choice of the experimental planning (Rodrigues and Iemma 2009). Hence, we obtained a new reparameterized model, characterized by Equation 5 which represents the percentage removal of color in function of the variables coded for the reagent concentrations, considering only the significant effects in the studied range.

$R = 0.9539 + 0.1189\ X_1 - 0.1062\ X_{12}$ Equation (5)

The percentage of variation explained by the reparameterized model was also high, 97.5 %, which allows concluding that the model adjusts almost completely to the experimental data.

From the analysis of the contour curve generated by the model (Figure 3), we verified that the largest removal index, of 98.7 %, was obtained when $X_1 = 0.5598$, which is equivalent to approximately 128 mg/L of Fe^{2+}. Since the level of H_2O_2 did not present a statistical significance in the studied range, we suggest the use of the lowest concentration (297 mg/L or $X_1 = -1.41$), which is an important factor in economic terms and operational safety.

COMBINATION OF THE BIOLOGICAL AND PHYSICOCHEMICAL TECHNIQUES

We applied to the textile industrial waste the biological degradation treatment with microorganisms from leachate in mediums enriched with vinasse (3 %) under constant agitation, subsequently applying the Fenton reaction method with 128 mg/L of Fe^{2+} and 297 mg/L of H_2O_2.

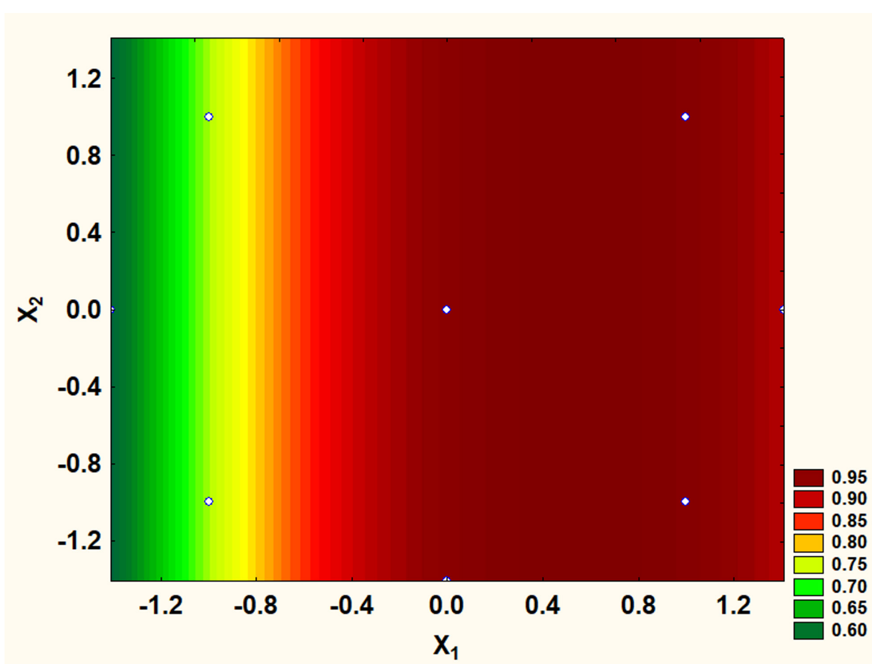

Figure 3 - Contour graph of ferrous ions and hydrogen peroxide concentrations for the color removal of the textile effluent. X_1 is the coded concentration for the ferrous ions and X_2 is the coded concentration for hydrogen peroxide.

The process was monitored by pH, COD, and absorbance parameters. At the end of the combined treatment, the pH of the effluent was of 8.0, which is an excellent value for the discarding of this type of industrial waste. According to the Conselho Nacional do Meio Ambiente (CONAMA 2011), the effluents of any polluting source may only be released in sewage systems with a pH from 5.0 to 9.0.

For all evaluated days, the COD of the effluent under treatment was lower than that of the raw effluent (1471 mg of O_2/L). This reduction stems from the effective degradation of the organic matter by microorganisms present in the medium.

Fenton's reaction showed an influence in the reduction of the COD, reaching 300 mg of O_2/L on the eighth day of the experiment, which represents a decrease of approximately 80 % of the effluent's organic matter.

For having dark colorations, the leachate and vinasse caused an absorption increase in the visible spectrum region when they were added to the solutions under analysis. At the end of the biological treatment, the color removal was of approximately 30 %. With the treatment combined with Fenton's reaction, the color removal reached around 100 % of efficiency. Combining chemical coagulation, photo-Fenton oxidation and biodegradation for the treatment of vinasse-rich wastewater, Rodrigues et al. (2017) highlighted that the second and third treatment approaches allowed to reach a nontoxic effluent, improved the biodegradability and led to a high global organics removal efficiencies, which allowed them to conclude that this combined method is a promising solution for treating this wastewater.

Therefore, we verified that the process of degrading color compounds and organic matter of textile waste is enhanced when the tested biological and physicochemical treatments are combined, accrediting the combined treatment as a potential method to be applied in the residue-treatment sector of textile companies.

CONCLUSION

We developed and optimized a biological process based on the use of leachate as a source of microorganisms and vinasse as a carbon source for the microbial action. Its action was enhanced when we combined it with a previously established physicochemical method based on Fenton's reaction, which contributed to the color removal and decreasing of organic matter of the textile waste. The combined method generated a high-efficiency process, with results of organic matter degradation of 80 % and a total color removal in only eight days of treatment, producing a little-toxic residue with acceptable acidity level.

The method may be considered promising for the use in textile residue treatment stations, given the great efficiency of the process, its low application cost, and the fact that it is ecologically interesting seeing that no hazardous residues are produced, besides also being a clean destination route for the leachate produced by the textile industry itself and for the vinasse, which is a by-product of the alcohol industry.

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AUTHOR CONTRIBUTIONS

Rafael Carlos Eloy Dias was the supervisor of microbiological analysis. Julio Lopes da Silva Junior managed the physicochemical assessments. Both researchers jointly coordinated the general project. The other authors contributed to the sample collection, lab procedures, data acquisition and discussion. The writing of the manuscript and the submission of the article were the responsibility of Rafael.

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