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2013

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Environmental assessment of residues generated after consecutive acid-base pretreatment of sugarcane bagasse by advanced oxidative process

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Abstract

Background: Biofuels produced from sugarcane bagasse (SB) have shown promising results as a suitable alternative of gasoline. Biofuels provide unique, strategic, environmental and socio-economic benefits. However, production of biofuels from SB has negative impact on environment due to the use of harsh chemicals during pretreatment. Consecutive sulfuric acid-sodium hydroxide pretreatment of SB is an effective process which eventually ameliorates the accessibility of cellulase towards cellulose for the sugars production. Alkaline hydrolysate of SB is black liquor containing high amount of dissolved lignin.

Results: This work evaluates the environmental impact of residues generated during the consecutive acid-base pretreatment of SB. Advanced oxidative process (AOP) was used based on photo-Fenton reaction mechanism (Fenton Reagent/UV). Experiments were performed in batch mode following factorial design L_9 (Taguchi orthogonal array design of experiments), considering the three operation variables: temperature (°C), pH, Fenton Reagent (Fe^{2+}/H_2O_2) + ultraviolet. Reduction of total phenolics (TP) and total organic carbon (TOC) were responsive variables. Among the tested conditions, experiment 7 (temperature, 35°C; pH, 2.5; Fenton reagent, 144 ml H_2O_2+153 ml Fe^{2+}; UV, 16W) revealed the maximum reduction in TP (98.65%) and TOC (95.73%). Parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), BOD/COD ratio, color intensity and turbidity also showed a significant change in AOP mediated lignin solution than the native alkaline hydrolysate.

Conclusion: AOP based on Fenton Reagent/UV reaction mechanism showed efficient removal of TP and TOC from sugarcane bagasse alkaline hydrolysate (lignin solution). To the best of our knowledge, this is the first report on statistical optimization of the removal of TP and TOC from sugarcane bagasse alkaline hydrolysate employing Fenton reagent mediated AOP process.

Keywords: Sugarcane bagasse, Environment assessment, Advance oxidative process, Photo-Fenton reaction, Total phenolics, Total organic carbon, Taguchi experimental design

Background

In the last few decades, studies on viable process for second generation ethanol production from lignocellulosic biomass have gained significant momentum worldwide. Deployment of cellulosic ethanol as an alternative of gasoline may provide unique environmental, economic and strategic benefits over to fossil fuels [1,2]. However,

concerns like environmental pollution and cost economics of ethanol production technologies are required in-depth analysis for the establishment of biorefineries [3].

Sugarcane bagasse (SB) is the preferred choice of raw material for ethanol production in countries like Brazil, India and China where it is generated in plentiful amount every year [4,5]. SB like any other lignocellulosic material is a complex polymer which is consisted of three major constituents such as cellulose, hemicellulose and lignin. In order to utilize carbohydrate fraction of SB for ethanol production via microbial fermentation, it

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is necessary to use appropriate pretreatment method for lignin removal. Recently, consecutive acid-base pretreatment process has been found successful for the efficient removal of hemicellulose and lignin leaving cellulose for the cellulolytic enzymes action for its conversion into glucose [6,7].

During the dilute acid pretreatment of SB, hemicellulose is converted into various sugars primarily xylose and some other compounds such as furfurals, phenolics, acids and metals. This acid pretreated SB so called cellulignin when further exposed to dilute sodium hydroxide based pretreatment, considerable fraction of lignin is removed [8]. Alkali-mediated pretreatment methods degrade the lignin and release phenolic compounds, aromatic alcohols and aldehydes which strongly inhibit the microbial metabolism [9-11]. Compounds derived from hemicellulose and lignin during pretreatment, if discarded in open environment, heavily pollutes the land and water. Furfurals, acids, and phenolic compounds (p-hydroxybenzoic acid, m-hydroxybenzoic acid, vanillic acid, syringic acid, p-hydroxybenzaldehyde, vanillin, cinnamic acid, syringaldehyde and others) [12,13] contribute a huge environmental damage due to high toxic content, bioaccumulation in different food chains even at low concentrations [14].

An efficient treatment method is required to overcome the contamination of phenolic compounds, furans and weak acids. In this line, several methods have been investigated such as adsorption on activated carbon, photo-catalysis using TiO_2, activated carbon post-treatment, anaerobic treatment; autohydrolysis and organosolv process and several types of advanced oxidation processes (Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton) [15-20]. Amongst them, advanced oxidative process (AOP) has shown promising results for the reduction of total phenolics and organic matter from various waste liquors. AOP are defined as potential processes that are capable of producing hydroxyl radicals (•OH), highly oxidative species, in high amounts for mineralizing organic materials to carbon dioxide, water and inorganic ions. Majority of AOP processes are performed at lower temperatures which use energy to produce highly reactive intermediaries with high oxidation or reduction potential. The hydroxyl radicals may be obtained from powerful oxidants, such as H_2O_2 and O_3, combined with irradiation. These processes have shown a great advantage to degrade the pollutants [21-25].

Advancing the AOP process, Fenton reagent has been shown to be very efficient for oxidation of organic compounds which are toxic and non-biodegradable [26]. The Fenton reaction is defined as a catalytic generation of hydroxyl radicals from a chain reaction between ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) in an acid medium. H_2O_2 is a powerful oxidative agent, when it is catalyzed by ferrous sulfate, it produces the free radical •OH (hydroxyl) which has 60% higher oxidation power than the peroxide.

In addition, this radical has the ability of degrading the organic material of effluents in a more efficient way [27]. With a high oxidative potential, these hydroxyl radicals are the responsible for oxidation of organic compounds present in waste waters. The radical Fe^{2+} is the reaction catalyst. Nowadays, this process is used for treating a wide variety of toxic organic compounds that do not respond to biological treatments, or even in rehabilitation of contaminated land [28,29]. This study aims to evaluate the environmental impact of residues generated during the consecutive acid-base pretreatment of sugarcane bagasse. Advanced oxidative process (AOP) was used based on photo-Fenton reaction mechanism (Fenton Reagent/UV) for the elimination of total phenolics in lignin solution in conjunction with reduction in BOD/COD ratio.

Results and discussion
Characteristics of lignin residue
The lignin residue was characterized based on the physico-chemical parameters, such as pH, color, TOC, COD, BOD, turbidity, COD/BOD ratio and TP amount. Table 1 shows the physical and chemical characteristics of alkaline hydrolysates (native lignin solution) [30]. The COD/BOD ratio in native lignin solution was 0.03 lower than the standard value (0.2) revealing that the substances present in lignin solution residues are resistant to biological oxidation [31]. The color and turbidity analysis demonstrate that the effluent has intense color and turbidity. The presence of phenolic compounds in the alkaline hydrolysates shows the important characteristic of lignin solutions. During the photo-Fenton reaction of lignin solution, extensive amount of foam was generated. Excessive foam causes interference during the photo-Fenton reaction. Therefore, it is necessary to strictly control the foam generation. During the photo-Fenton reaction, all amount of hydrogen peroxide was consumed.

Statistical analysis of L_9 Taguchi experimental design
Changes in total oxygen concentration (TOC)
Table 2 demonstrates the percentage change in the TOC of lignin solution after photo-Fenton reactions in each

Table 1 Physical and chemical characteristics of residual lignin

Parameters	Characteristics	Standards[*]
True color (PtCo)	3621.33	Absent
Turbidity (NTU)	50.8	Absent
pH	7 – 8	5 – 9
COD (mg/L O_2)	5870.25	8
BOD (mg/L O_2)	169	60
COD/BOD	0.03	-
TOC (mg/L)	2053.0	-
Total Phenol (mg/L)	10.64	0.5

[*]Effluents standards in hybrid bodies - Article 18 [31] and [32] respectively.
(-) Unspecified.

Table 2 Profile of percentage reduction of TOC values in all 9 experiments (photo-Fenton reaction) performed as per L_9 Taguchi matrix

| Exp.	TOC range (%)		Average	S_i^{2*}
	1° Data set	2° Data set	(%)	(%)
1	91.92	93.68	92.80	1.55
2	90.21	92.90	91.56	3.62
3	91.96	93.49	92.73	1.17
4	90.49	90.40	90.45	0.00
5	93.97	94.60	94.28	0.20
6	92.30	92.92	92.61	0.19
7	95.18	96.28	95.73	0.60
8	91.82	93.58	92.70	1.55
9	92.08	94.70	93.39	3.43

*S_i^2 = variance.

Table 3 Average value of TOC percentage reduction in lignin solution using photo-Fenton after in all 9 experiments designed as per L_9 Taguchi matrix

Exp.	Temperature (°C)	pH	Fenton (mg L^{-1})	UV (W)	TOC average (%)
1	1	1	1	1	92.80
2	1	2	2	2	91.56
3	1	3	3	3	92.73
4	2	1	2	3	90.45
5	2	2	3	1	94.28
6	2	3	1	2	92.61
7	3	1	3	2	95.73
8	3	2	1	3	92.70
9	3	3	2	1	93.39

experiment carried out as per the L_9 orthogonal design of experiments. As can be observed from Table 2, experiment 2 and 9 only have the higher values of standard variation (S_i^2) showing 3.62 and 3.43 respectively. Different modifications in AOP have shown the satisfactory results for the treatment of the lignin solution. For example, Ninomiya et al. [33] recently studied the sonocatalytic-Fenton reaction for the degradation of lignin. Sonocatalytic-Fenton reaction showed synergistically enhanced •OH radical generation. The •OH radical generation was applied to lignin degradation and biomass pretreatment. Lignin degradation ratio by sono-catalytic-Fenton reaction was 60.0% at 180 min. Ma et al. [32] studied photo-catalytic degradation of lignin with the use of catalysts TiO_2 and Pt/TiO_2. The results showed that application of UV irradiation alone has almost no effect on the reduction of dissolved organic carbon (DOC). However, the addition of TiO_2 and Pt/TiO_2 reduced the original DOC (251 mg/L) by more than 40% within 30 minutes of treatment. Makhotkina et al. [34] also used Fenton and H_2O_2 photo-assisted reactions for and observed 85% lignin oxidation, at 0.1 M concentration under UV-radiation at pH 8.3.

Table 3 presents the average percentage change in TOC in all nine experiments carried out according to Taguchi L_9 orthogonal design. Experimental run 7 (temperature 35°C; pH 2.5; Fenton concentration 144 mL H_2O_2 + 153 mL Fe^{2+}; UV range 16W) showed the 95.73% TOC reduction. On the other hand, experimental run 4 (temperature 30°C; pH 2.5; Fenton concentration 120 mL H_2O_2 + 120 mL Fe^{2+}; UV range 28W) showed the minimum percentage change in TOC value (90.45%). This positive effect of UV radiation on degradation reaction was attributed to the reduction of Fe^{3+} to Fe^{2+} which in turn reacts with H_2O_2 allowing for the continued Fenton reaction. The absorbance of ferric ions may extend into the visible region, depending on the pH

because the pH influences the formation of hydroxylated species, which have higher absorption in the visible [35]. It is interesting to note that pH around 3.0 proved to be more effective for the reduction of organic matter present in the residue using photo-Fenton process. Several studies have confirmed this behavior [35-38]. Higher concentration of the Fenton's reagent was more effective for the reduction of organic matter due to the generation of hydroxyl radicals in greater amount. The extensive degradation of lignin was possibly due to the oxidative properties of the Fenton's reagent [39].

The effect of individual parameters on TOC reduction during photo-Fenton reaction has been shown in Figure 1. It is clear from the Figure 1 that pH had no significant effect on the TOC percentage reduction. The Fenton reagent (144 mL of H_2O_2+ 153 mL of Fe^{2+}) and temperature showed high impact in the process. It can be observed that the UV irradiation presence (16 W) or absence has a better contribution in the percentage TOC reduction. One of the possible explanations for this fact is the intense color of the residue, which interferences UV irradiation process. It can also be observed that the higher temperature (35°C) has a great significance (Table 3).

High Fenton reagent level majorly influenced the percentage TOC reduction. Table 4 presents the ANOVA of involved factors in both lignin residue treatment and photo-Fenton process, according to L_9 Taguchi experimental matrix. ANOVA presented in Table 4 clearly demonstrates that the Fenton reagent concentration was the most significant effect factor in the TOC percentage reduction, with F equals 6.8 and p-value equals 0.0156, followed by temperature (F = 3.5) and UV irradiation (F = 3.1) as already shown in Figure 2. The effect of pH was not found significant in TOC reduction (F = 0.02). The effect of Fenton concentration in percentage TOC reduction was more pronounced (almost twice) than temperature and UV irradiation variables and six times
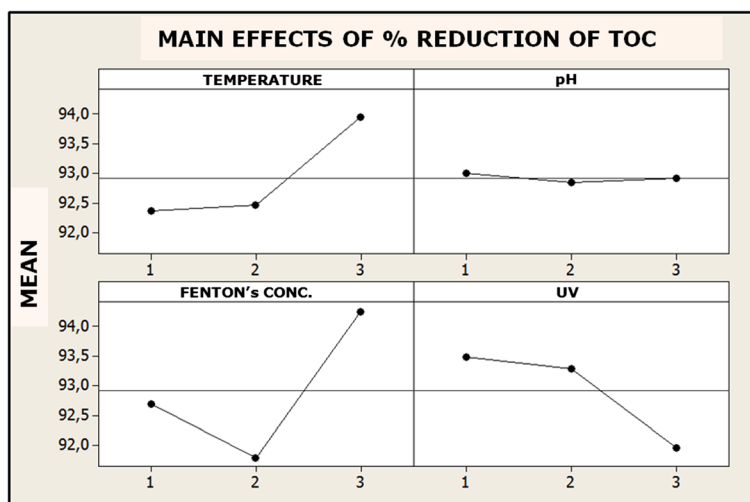
Figure 1 Main effects of different process variables (temperature, pH, H_2O_2 concentration and UV radiation) on TOC percentage reduction in lignin solution treated by photo-Fenton process.

more than pH variable. Figure 2 reveals the variability of the process parameters by average answers graph according to the signal-to-noise ratio (S/R). The best pool of conditions (temperature 35°C, 144 mL of H_2O_2 and 153 mL of Fe^{2+}) was found for percentage TOC reduction in lignin solution after AOP. Figures 1 and 2 clearly reveal the influence of UV irradiation on the percentage reduction of TOC at lowest and highest value. At the highest level of UV irradiation, a remarkable decrease in TOC was observed.

Changes in total phenols concentration

Table 5 shows the average reduction percentage of phenol compounds obtained from double process of experimental conditions in lignin residue treatment, according to L_9 orthogonal design. The maximum reduction in TP level from lignin solution was 98.65% in experiment 7 (Table 5). Figure 3 shows the main effect of four process variables (temperature, pH, Fenton reagent concentration and UV radiation) on percentage reduction of TP concentration in lignin solution.

The experiments 6 and 8 have shown similar phenolics degradation behavior, with around 97% of average

reduction of TP. The experimental conditions which were studied for both experiments demonstrated the temperature range was 30-35°C, pH between 3,0-3,5, low level of Fenton reagent for both experiments (96 mL of H_2O_2 and 87 mL of Fe^2) and irradiation presence in UV (16 - 28W) were not so effective as compared with the experiment 7. Experiment 7 (temperature 35°C, pH 2.5, Fenton reagent H_2O_2 144 ml + Fe^{2+} 153 mL and UV irradiation 16W, proved maximum reduction in TP (98.65%). This combination has shown the best degradation result in the phenol compounds from lignin residue. Table 6 presents the percentage range, the average percentage and the variance (S_i^2) in TP concentration in lignin solution after AOP in all 9 experiments performed according to L_9 matrix. It is clear from Table 6 that experiment 7 and 9 showed the higher values of standard deviation, 2.06 and 2.04 respectively. Table 7 shows the ANOVA of each process variables involved in lignin residue treatment using photo-Fenton process, according to L_9 Taguchi experimental matrix.

It can be observed that all the factors were significant for the studied process parameters in L_9 Taguchi matrix. The most significant factor was UV irradiation with F value of 404.00 followed by Fenton reagent concentration (F = 218.80) and temperature (F = 203.1). It can also be observed from the Table 6, that the experiments where UV irradiation were used (experiments 2, 3, 4, 6, 7 and 8) showed an average 95% of removal of phenolic compounds from the lignin solution. Fenton reagent concentration was the second most influence factor (Table 7). Fenton reagent at the concentration (96 mL of H_2O_2 and 87 mL of Fe^{2+}) with UV presence and pH range (3.0-3.5) has shown about 97% removal of total phenolics from lignin solution. Fenton reagent concentration at an

Table 4 Analysis of variance (ANOVA) for the average values of TOC percentage reduction in the photo-Fenton process based experiments as per L_9 orthogonal design of experiments

Factors	Sum of square	Degree of freedom	Average sum of square	F	p-value
Temperature	9.50	2	4.70	3.50	0.0763
pH	0.10	2	0.03	0.02	0.9766
Fenton Concentration	18.60	2	9.30	6.80	0.0156
Residual	8.40	2	4.20	3.10	0.0962
UV	12.30	9	1.40	-	-
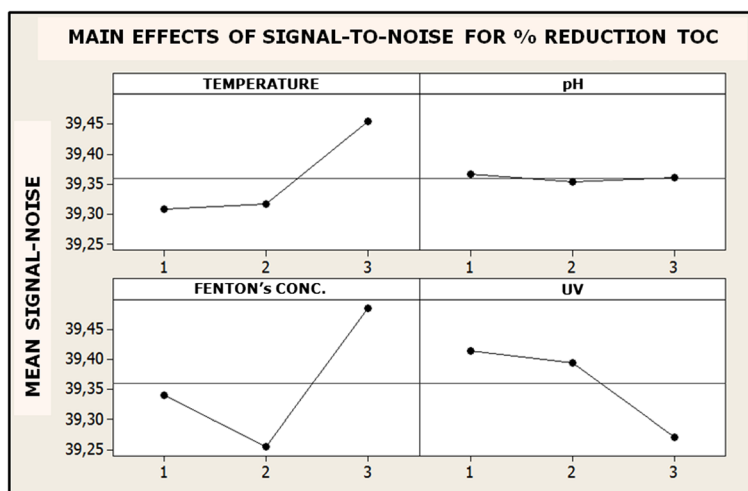
Figure 2 Effect of independent variable on the percentage reduction of TOC in terms of S/N ratio (the larger is the best) by photo-Fenton process according to L$_9$Taguchi matrix.

intermediate level (120 mL of H_2O_2 and 120 mL of Fe^{2+}) in the UV presence, showed average 89% of removal of phenolic compounds. In experiment 9, where the Fenton reagent were used at an intermediate level, the average of phenolic compounds removal was about 67% probably due to the UV absence in the reaction medium. UV promotes the larger production of •OH radicals which facilitates the large organic material degradation. Figure 4 shows the influence of process variables showing the S/N ratio. Clearly, the greater total phenol reduction percentage (larger signal) is the better. It is clear from the figure that temperature at level 2 (30°C) was more effective than level 1 (25°C) and level 3 (35°C). The effect of pH on percentage TOC reduction was not significant. Concentration of Fenton at level 3 showed remarkable percentage reduction in total phenolics concentration. Similarly, UV ranges at level 3 (28W) showed pronounced effect on total

phenolics concentration. Summarizing the effect of these parameters on total phenolics concentration according to L$_9$ Taguchi matrix design of experiment, it can be concluded that the larger S/N ratio (the larger is the best) had the strong influence on total phenolics percentage reduction.
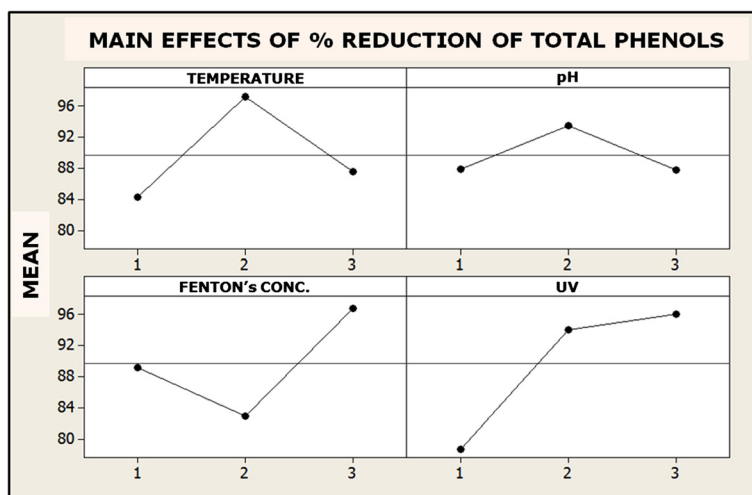
Materials and methods
Raw material
Sugarcane bagasse was acquired from Santa Fé S/A Plant, Nova Europa/SP city. The sugarcane bagasse was used in this experimental as it was obtained from sugarcane processing mill. The processing unit milled the bagasse before sending to laboratory. However, it was not further milled. Thus, sugarcane bagasse was non-uniform in size. It was sun-dried prior to acid hydrolysis in order to remove the extra water. Prior to use in experiment, the moisture content of sugarcane bagasse was analyzed. The total moisture level in bagasse was 10%. This humidity was taken into consideration in acid hydrolysis experiment.

Dilute acid hydrolysis
The dilute acid hydrolysis of SB was carried out in a hydrolysis reactor of capacity of 350 L located at the Engineering School of Lorena (EEL)-USP, Lorena, Brazil. For the hydrolysis of the SB, H_2SO_4 (98% of purity) was used as catalyst in a ratio of 100 mg of acid/g of dry matter, during 20 min at 121°C, using a ratio of 1/10 between the bagasse mass and the volume of acid solution. The hydrolysate obtained was maintained at 4°C. The recovered solid residue so called cellulignin was washed with running tap water until the neutralized pH, sun-dried to remove the moisture and was subsequently used for delignification experiments.

Table 5 Average value of total phenols percentage reduction in specific factors and levels to L$_9$ Taguchi experiments after lignin residue treatment using photo-Fenton process

Exp.	Temperature (°C)	pH	Fenton (mg L^{-1})	UV (W)	Average of total phenols (%)
1	1	1	1	1	71.10
2	1	2	2	2	84.78
3	1	3	3	3	95.98
4	2	1	2	3	94.08
5	2	2	3	1	96.49
6	2	3	1	2	97.02
7	3	1	3	2	98.65
8	3	2	1	3	97.30
9	3	3	2	1	66.99

Figure 3 Main effects of independent variables (temperature, pH, Fenton reagent concentration and UV irradiation) on total phenols percentage reduction from lignin solution by photo-Fenton process, according to L_9 Taguchi matrix design of experiment.

Dilute sodium hydroxide pretreatment of cellulignin

Cellulignin recovered after dilute acid hydrolysis was submitted to alkaline hydrolysis to recover the lignin solution. For the alkaline hydrolysis, sodium hydroxide (1M) was mixed with cellulignin in the ratio of 1:10. Alkaline hydrolysis was performed in rotatory reactor of capacity 50 L. The reaction was performed at 121°C for 10 min. After cooling the reaction mixture, the liquid fraction (soluble lignin) was separated and subsequently was used for advanced oxidation process (AOP).

Color determination

Color of lignin solution after alkaline hydrolysis (native) and after AOP was determined by UV-visible spectrophotometer (Bel Photonics, Italy), by using interpolation of an analytical calibration curve as a function of

absorbance measurement at 400 nm of wavelength using platinum-cobalt standards [30].

Turbidity determination

Turbidity measurement of lignin solution after alkaline hydrolysis (native) and after AOP was determined by using a turbidity meter with a precision of 2% (Tecnopon TB 1000). For the calibration of the equipment, standards of 0.1 to 1000 Turbidity Unit of standard solution (Formazin at different dilutions) were used.

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) analysis

All analytical determinations were performed according to the Standard Methods of Examination of Water and Wastewater [40]. The COD determination is based on the oxidation of organic matter by reduction of potassium dichromate in an acidic medium containing catalyst at elevated temperature and subsequent reading absorbance at a wavelength of 620 nm [41].

Table 6 Percentage reduction values of total phenol concentration lignin solution in all 9 experiments carried out as per L_9 Taguchi matrix

Exp.	Total phenol range (%)		Average	S_i^{2*}
	1° Data set	2° Data set	(%)	(%)
1	70.60	71.60	71.10	0.50
2	85.30	84.25	84.78	0.55
3	96.00	95.95	95.98	0.00
4	94.15	94.00	94.08	0.01
5	96.17	96.80	96.49	0.20
6	97.03	97.00	97.02	1.46
7	97.79	99.50	98.65	2.06
8	97.80	96.80	97.30	0.50
9	65.98	68.00	66.99	2.04

* S_i^2 = variance.

Table 7 Analysis of variance (ANOVA) obtained from average values of total phenols percentage reduction from L_9 orthogonal design to lignin residue treatment using photo-Fenton process

Factors	Square sum	Degree of freedom	Average square sum	F	p
Temperature	542.35	2	271.2	203.10	0.0000
pH	127.92	2	64.0	47.90	0.0000
Fenton concentration	584.42	2	292.2	218.80	0.0000
Residual	1078.91	2	539.5	404.00	0.0000
UV	12.02	9	1.30	-	-
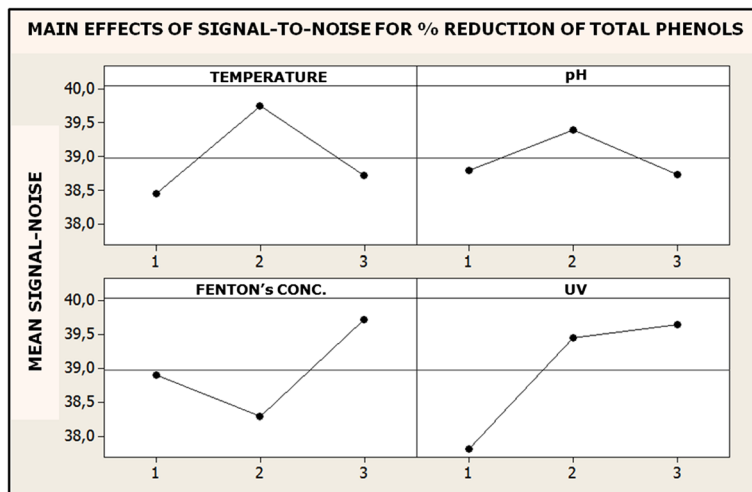
Figure 4 Main effects of process variables (temperature, pH, Fenton reagent concentration and UV radiation) on total phenols percentage reduction from lignin solution by photo-Fenton process, according to L$_9$ Taguchi matrix design of experiment. S/N ratio (the larger is the best) to total phenol percentage reduction.

In this procedure, the sample was heated for 2 hrs with potassium dichromate in a closed system. During this reaction, oxidizing organic compounds reduce with the conversion of dichromate ion into chromic ion green. The reagents used also contain mercury and silver ions. Silver is a catalyst, and mercury is used to control interference chloride. To determine the accuracy of the method, potassium bi-phthalate (850 mg/L) was used as a standard [42].

In the digestion flasks, 2.0 mL sample, 0.5 mL of digesting solution and 2.5 mL of the catalyst solution were mixed. The mixture was heated at 150°C for 2h. After the cooling to ambient temperature, absorbance was read at 620 nm. The O$_2$ concentration of the sample was obtained by interpolating the data obtained from the calibration curve performed with a standard solution of potassium bi-phthalate. Standards were prepared of standard values of COD (20-1065). The BOD test is based on the amount of oxygen needed by microorganisms to for the degradation of organic compounds. Organic compounds that were not biodegradable were considered to have BOD value as "zero" [30].

Total organic carbon (TOC) determination
TOC in lignin solution after alkaline hydrolysis (native) and after AOP was detected by TOC analyzer (TOC-VCPH, Shimadzu, Japan).
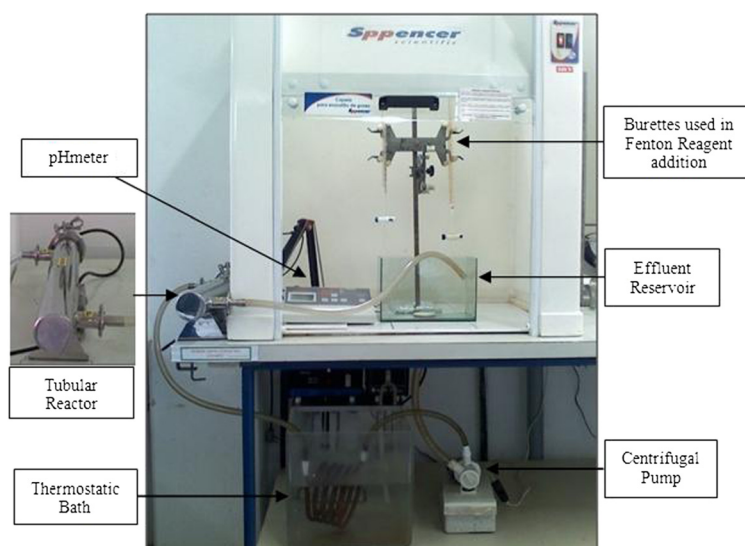
Figure 5 Lay-out of the experimental procedure to the treatment step of lignin residue using AOPs.

Total phenolics (TP) estimation

TP amount in lignin solution (native) and after AOP was analyzed by the colorimetric method using ferricyanide and antipyrine without extraction (0 - 5.0 mg/L) [30].

Advanced oxidative process (Fe^{2+}/H_2O_2 and UV irradiation)

AOP of alkaline hydrolysate of sugarcane bagasse (lignin solution) was performed in a tubular photochemical reactor (GPJ-463/1, Germetec S/A, Brasil) with a volume of approximately 1L at the irradiation of low pressure mercury lamp (GPH-463T5L, Germetec S/A, Brasil), emitting UV radiation at 254 nm with potentials of 16 and 28W, protected by a quartz tube. The reactor configuration as shown in Figure 5, was used for AOP using 3L of lignin solution. The photochemical treatment was carried out in a batch mode. For the Fenton reaction, the volume of the reagents (H_2O_2, 30% and $FeSO_4.7H_2O$, 0.18 mol/L) were added. H_2O_2 was added first as drops followed by the addition of $FeSO_4.7H_2O$ in the lignin solution. AOP was continued up to 2 hrs and the samples were withdrawn after every 10 min. These aliquots were previously adjusted to a pH between 7.0 and 8.0 for precipitation of iron salts and then subjected to analysis of COD, color, turbidity and TOC.

Experimental design

To optimize the effect of process variables (pH, temperature, H_2O_2 and Fenton's Fe^{2+} concentrations and UV radiation potential), a factorial statistical design (L_9 Taguchi orthogonal array design of experiments) was performed. Percentage reduction in total phenolics concentration and TOC reduction after AOP were the responsive variables (Tables 8 and 9).

Economic feasibility of the process

Two things are needed for any technology to be suitable for use in the industry- the technical feasibility and the economic feasibility. Table 10 shows some examples of cost economic analysis of AOP process employed for the treatment of various kinds of wastes generated.

Table 8 Process variables and their ranges selected for the AOP with photo-Fenton process applied to lignin solution using L₉ Taguchi matrix

Factors	Level 1	Level 2	Level 3
Temperature (°C)	25	30	35
pH	2.5	3.0	3.5
Fenton Reagent * (m_{H2O2} g + m_{Fe+2} L^{-1})	96 mL H_2O_2 + 87 mL sol Fe^{2+}	120 mL H_2O_2 + 120 mL Fe^{2+}	144 mL H_2O_2 + 153 mL Fe^{2+}
Ultra-violet irradiation	None	16 W	28 W

*Both H_2O_2 and Iron II were used in solutions with concentrations of [H_2O_2], 30% m/m and [Fe^{2+}], 0.82 mol/L. These values are the proportional to the treated effluent volume of 3 L.

Table 9 Experimental plans considering L₉ orthogonal Taguchi design divided in 3 levels (low represented by 1, intermediary represented by 2 and high represented by 3), to the lignin residue treatment using photo-Fenton

Experiment	Temperature (°C)	pH	Fenton reagent	UV
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Conclusions

Second generation ethanol production based biorefineries generate high amount of lignin solution due to the alkali mediated delignification pretreatment step. Lignin solution is extremely of high recalcitrance with high BOD/COD ratio of 0.25. An ordinary biological pretreatment is not enough to degrade the phenolics amount and consequently bring down the TOC of lignin solution up to satisfactory levels. Therefore, the involvement of AOP is highly recommended to facilitate the phenolics degradation and consequently bring down the TOC levels in lignin solution, recovered from biomass pretreatment. This study clearly demonstrates that AOP mediated by photo-Fenton reaction is highly efficient for the removal of organic material in conjunction with bring down the levels of TOC from sugarcane bagasse

Table 10 Cost-economic analysis of some advanced oxidation processes used for various kinds of wastes

Type of process	Type of waste	Estimated cost for the process used	Reference
UV/H_2O_2 and UV/TiO_2	Synthetic water	Electricity costs were assumed fixed over the 15 yr at £0.09 per KW h and hydrogen peroxide fixed at £270 m^{-3}	[43]
H_2O_2/UV and Fe^{2+}/H_2O_2	Polyester and acetate fiber dyeing effluent	0.23 ($m^{-3}) and 1.26 ($m^{-3})	[44]
Fe^{2+}/H_2O_2	4-Chlorophenol and Olive oil	Fe^{2+} 0.2 and H_2O_2 10 (kg m^{-3}) Fe^{2+} 0.7 and H_2O_2 18 (kg m^{-3})	[45]
Photocatalysis	Phenol waste water	43.36 ($/L) for all the process	[46]
Photocatalysis	Sewage effluent	15.10 ($/L) for all the process	[47]
Fenton reagent	Phenol waste water	14.28 ($/1000 gallon)	[48]
Photo-Fenton	Tannery waste water	64.13 (US$ m^{-3})	[49]
Photo-Fenton	Pesticides	1.1-1.9 € m^{-3}	[50]

alkaline hydrolysate (lignin solution). Taguchi L_9 experimental matrix proved that UV irradiation was the most significant factor with F value of 404.00, which significantly removed 98.65% TP and 95.73% of TOC reduction. The results have proved the efficiency of photochemical technology (AOP) in the treatment of residues generated during the alkali mediated delignification pretreatment of SB.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

ISO carried out the experimental work. ISO, AKC and MBS designed the study and were involved in all discussions, interpretation of data and writing the manuscript. SSS coordinated the overall study, analysis of results and finalizing the manuscript. All authors suggested modifications to the draft and approved the final manuscript.

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