

# Application of Heterogenous Catalysis with TiO<sub>2</sub> Photo Irradiated by Sunlight and Latter Activated Sludge System for the Reduction of Vinasse Organic Load

Juliana Sanches Carrocci<sup>1</sup>, Rodrigo Yuji Mori<sup>2</sup>, Oswaldo Luiz Cobra Guimarães<sup>3</sup>,  
Rodrigo Fernando dos Santos Salazar<sup>4,5</sup>, Marcos Fernandes de Oliveira<sup>6</sup>,  
André Luís de Castro Peixoto<sup>7</sup>, Helcio José Izário Filho<sup>8</sup>

<sup>1</sup>Construfer Engenharia, Guaratinguetá, Brasil

<sup>2</sup>OXITENO, Tremembé, Brasil

<sup>3</sup>Departamento Básico, Escola de Engenharia de Lorena EEL/USP, Lorena, Brasil

<sup>4</sup>Departamento de Química, Universidade Federal de São Carlos (UFSCar), São Carlos, Brasil

<sup>5</sup>Unidade Cruz Alta, Universidade Estadual do Rio Grande do Sul (UERGS), Cruz Alta, Brasil

<sup>6</sup>DuPont do Brasil S/A, Guarulhos, Brasil

<sup>7</sup>Instituto Federal de Educação, Ciência e Tecnologia (IFSP), Capivari, Brasil

<sup>8</sup>Departamento de Engenharia Química, Escola de Engenharia de Lorena EEL/USP, Lorena, Brasil

Email: carrocci@hotmail.com, mori856@hotmail.com, oswaldocobra@debas.eel.usp.br, r.f.s.salazar@gmail.com, marcosfernandes1@yahoo.com.br, alpeixoto@ifsp.edu.br, helcio@dequi.eel.usp.br

Received September 13, 2011; revised October 20, 2011; accepted October 30, 2011

## ABSTRACT

Vinasse is the main residue generated during alcohol, sugar and blue rum production by fermentation process. This residue is effluent that could cause serious environmental pollution due to high organic load when is not treated adequately. The aim of this work consists of evaluating the efficiency and application of heterogeneous photocatalysis with TiO<sub>2</sub>, followed by a biological treatment (activated sludge system) to reduce organic load in the referred effluent. Complete factorial designs indicated the best experimental conditions subsequent to photocatalytic and biological treatments providing a reduction of non-purgeable organic carbon (NPOC) as a variable response. After the photocatalytic process, the sample from the best experiment condition was treated by a biological process in order to verify the degradation efficiency of the effluent organic matter studied according to the hybrid system (Advanced Oxidation Process—Activated Sludge System). This system, which presented more efficiency, had a photochemical treatment of 180 minutes carried out in aerated solutions, pH 9 and effluent *in natura*, while the biological treatment was performed at pH 8 and sludge concentration of 5 gL<sup>-1</sup>. The reduction of biochemical oxygen demand (BOD) was >80%.

**Keywords:** Heterogenous Catalysis; Activated Sludge; Organic Load

## 1. Introduction

Vinasse is the main residue resulted in the production of alcohol, sugar and brandy, being considered an effluent of high pollutant power and fertilizer. Without adequate treatment, poured in a river it compromises the survival of several aquatic species and when used as a fertilizer, the non treated effluent can contaminate groundwater and affect human beings. Recent studies [1] indicate that the potential market (internal and external) for the Brazilian ethanol and sugar will utilize ~685 million tons of sugar cane (2012-2013) making use of approximately 7 million hectares or ~of 2% of all the country's arable area [2,3].

That massive production of ethanol will generate as by-product of 300 billion liters of vinasse. That amount of effluent is justified due to the fact that for each alcohol

liter produced results in 10 to 15 liters of waste [4,5]. Also known as stillage, restil or distillery syrup, vinasse is characterized as an effluent of pollutant power due to its low pH, high corrosivity, high values of biochemical oxygen demand (BOD), besides an elevated temperature at the output of the distillers [6]. Due to its wealth of organic material and nutrients, this effluent has been used as a fertilizer in sugar cane crops. However, it is noticed the increasing concern of the scientific community with the risk that this material causes to water flows (rivers, lakes, springs and floodplains) and to groundwater, through the percolation until underground waters, causing an incompatible salubrity for human and animal feeding [7,8].

The purpose of this work consisted in evaluating both the efficiency and the application of heterogeneous photo-

catalysis with  $\text{TiO}_2$  followed by biological treatment (activated sludge) for the reduction of the organic load of the effluent.

## 2. Materials and Methods

For the development of this project supplies of effluent were furnished by small brandy producers in Guaratinguetá—São Paulo.

Past the destillation phase and cooling of the effluent, samples were previously filtered in cotton fabric and stocked in 50 liters drums during 5 days. After homogenization a single sample was kept at  $4^\circ\text{C}$ .

For the degradation of the effluent, as a pretreatment, was used heterogeneous photocatalysis with  $\text{TiO}_2$  fixed on a metallic plate and exposed to solar radiation. This phase aimed to better guaranty the biodegradability to the biological treatment, so that the final characteristics of the effluent were in agreement with the Article 18 of Decree nr. 8468/76 (São Paulo State) on legislation dump (**Schedule A**).

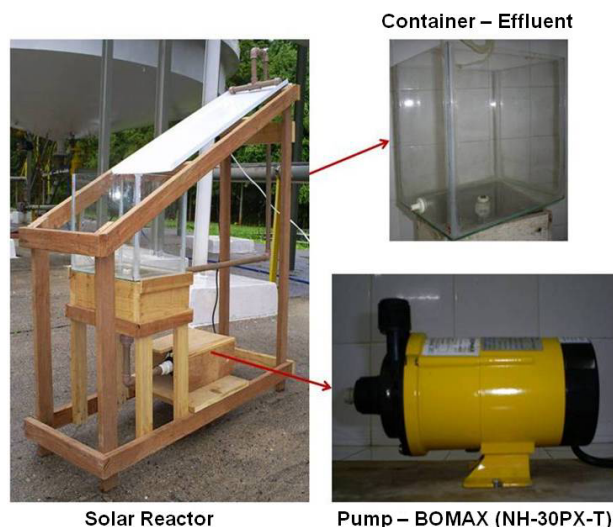
The studies, employment and implementation of processes based on solar radiation are interesting in the Paraíba Valley region (southeastern Brazil) due to the geographic coordinates and presented high average incidence of ultraviolet radiation ( $5500 \text{ Wh/m}^2$ ).

In order to conduce the photocatalysis process a fixed-bed solar reactor was used. System proposed was based on a batch process and bench scale, containing a continuous and decreasing system of the effluent percolation on the catalytic bed. During the reaction, water volume was maintained constant (3 liters) by continuous addition of water (minimizing loss by evaporation) and the flow ( $2 \text{ L}\cdot\text{min}^{-1}$ ) of the effluent. Preliminary studies demonstrated do not occur several interferences due to effluent dilution or photolysis reactions [9].

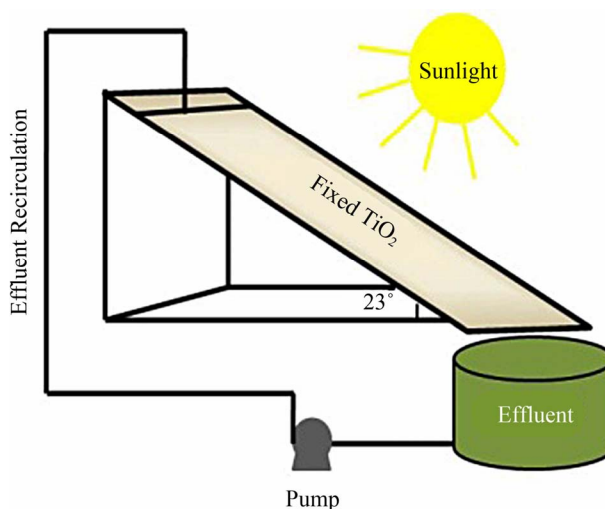
This system (**Figure 1**) consists basically of a glass container ( $28 \times 20.5 \times 26 \text{ cm}$ ), a centrifugal pump (BOMAX, model NH-30PX-T) and a metal plate coated with  $\text{TiO}_2$  anatase (25 cm wide and 75 cm in length).

A wooden structure was made for adaptation and support of the metallic plate allowing the correct sense of direction in Ecuador with an inclination angle of  $23^\circ$ , as shown in **Figure 2**. The effluent was pumped to the top of the plate, covering it in a uniform laminar layer while receiving solar radiation [10].

A pigmented coating with high  $\text{TiO}_2$  anatase concentration was formulated and applied by DuPont Brazil SA. Part of this formulation is registered and protected by law. This coating was selected and prepared from a fraction solution by adding an isocyanate activator in specific proportions. The mixture was subsequently diluted to a viscosity of 24 seconds of sliding in a Ford 4 viscometer (4 mm orifice) at a temperature of  $25^\circ\text{C}$ . A diluting sol-



**Figure 1.** Solar reactor with metallic plate coated with  $\text{TiO}_2$ , showing in detail the glass container and the centrifugal pump.



**Figure 2.** Scheme of a solar reactor with  $\text{TiO}_2$  as photocatalytic.

vent comprising a mixture of esters and aromatic hydrocarbons was the last component added. After the application of this coating, the plates were dried at  $140^\circ\text{C}$  for 30 minutes.

The mass of  $\text{TiO}_2$  over the distributed area was also determined by DuPont to contain  $0.025 \text{ g/cm}^2$  of titanium dioxide in the coating. A parallelepiped formula at a 50-micron thickness was used to determine the volume.

To control the rate of evaporation, a phenomenon inherent in this type of open system reactor, an arrangement was necessary for the effluent reservoir. Adjusting a U-tube connection and after operating the process, it became possible to control and adjust the volume of the effluent (adding water if necessary) throughout the reaction period. In some experiments a similar system was

put in parallel, using a metal plate without the catalytic surface, to monitor the blank test and the evaporation percentage.

The control and pH parameter setting during the experiments was carried out by a pHmeter adapted to the reservoir and temperature measurement by a digital infrared thermometer (INCOTERM model MULT TEMP). The values of solar radiation that reached the region during the reaction period were obtained by a radiometer model ILT 1400-A made by International Light.

The characterizations of the catalytic film on the metallic plate (morphology, homogeneity and thickness) and the TiO<sub>2</sub> structure were performed by scanning microscopy techniques and X ray diffraction (XRD).

A Full Factorial (2<sup>4</sup>) planning was conducted (Table 1) in duplicate for the pre-treatment of the effluent through advanced oxidation process (AOP) taking as input variables the reaction time (120 and 180 minutes respectively), aeration (with and *in natura*), pH (5 and 9) and the filtered effluent concentration (1:1 v/v and *in natura*). The acidity of medium was maintained with 5.0 eq·L<sup>-1</sup> of NaOH or 5.0 eq·L<sup>-1</sup> of HCl.

Levels of each factor were chosen after comprising the preliminary experiments, mainly the effluent acidity and the reaction time. The process efficiency was evaluated in terms of reduction of non-purgeable organic carbon (NPOC) %. For the better condition determined it was carried out some analyses of biochemical oxygen demand (biochemical oxygen demand (BOD), the solid content (Total Solids, Total Fixed Solids and Total Volatile Solids) metallic elements, phenols and nitrogen (ammonia and organic).

Statistical analysis was processed by MINITAB 14, Origin 6.0 and Excel (Windows 2007) softwares.

### 3. Advanced Oxidation Processes

Advanced Oxidation Processes (AOP) are extremely efficient technologies for the mineralization of organic compounds that are difficult to traditional biological degradation; they can be considered clean technologies for when degradation efficiency is reached, there are neither any other solid by-product formations nor any effluent

phase transference being, thus, employed for treatment of several types of effluents leading to mineralized final products (CO<sub>2</sub>, H<sub>2</sub>O and inorganic anions).

Among the advanced oxidation process most studied, the heterogeneous photo catalytic technology presents an important role in relation to the emerging technologies for water treatment, for the technological maturity that this process reached ahead of other studied advanced oxidation process, due to the potential utilization of sustainable energy that Brazil possess, mainly in what refers to the use of solar energy as an alternative source of energy [9-12].

The use of heterogeneous photo catalytic process has been pointed out as one of the most promising process in the treatment of recalcitrant waste [12]. It is a photo chemical process in which a semiconductor type is irradiated for the promotion of an electron from the valence band to the conduction band. In this process, reduction and oxidation sites are formed capable of catalyzing chemical reactions, which can be used in treating Industrial and domestic effluents [11,13].

Semiconductors can actuate as catalyzers as they present two energetic regions: one, of low energy, in the region of the valence band (VB) where electrons do not have any free movement; the other, in the region of more high energy, the conduction band (CB), where electrons are free to move through the crystal producing electrical conductivity similar to metals. Between these two bands there is the band gap region, which is the minimum energy necessary to excite the electron and promote it from a lower energy band to another of higher energy [11,14]. Generally, substances that donate electrons to gaps in the valence band are hydroxyl ions or water, which are oxidized to hydroxyl radicals and the substance that receives the conduction band electrons is the molecular oxygen that is reduced to superoxide anion radical (<sup>•</sup>O<sub>2</sub>) and conduct to an additional formation of the hydroxyl radical [11,15].

Of the most used photo catalyzers pointed out to date is the large band metallic oxide semiconductor, in particular the titanic dioxide, which belongs to the family of the transition metal oxide. It is the semiconductor most used in photo catalysis due to its excellent proprieties (optical, mechanical and electrical) and also its chemical stability, making it apt to work in a large pH band. It is cheap and non toxic, being relatively excited by a minimum energy of 3.2 eV, that corresponds to UV-A radiation with wavelengths inferior to 387 nm, representing 3% of the solar spectrum [9-11,15,16].

One of the advantages of heterogeneous photo catalysis using TiO<sub>2</sub> as semiconductor is related to its photo activation, located in the UV region. Besides, it presents low toxicity, elevated specific area and resistant to photo corrosion [9-11,17].

**Table 1. Factors and levels of vinasse treatment by advanced oxidation process (AOP).**

FACTORS	LEVELS	
	Low (-)	High (+)
A—Time (min)	120	180
B—Aeration	Without	With
C—pH	5	9
D—Effluent Concentration (Filtered)	1:1 v/v	<i>In natura</i>

## 4. Results and Analysis

### 4.1. Chemical Treatment

For the photochemical treatment, the response factor used for the full  $2^4$ , factorial planning, performed in duplicate, was the percentage of non-purgeable organic carbon. All tests were conducted between January and March 2009. The results can be seen in **Table 2**.

One important factor that should be pointed out when using photo activated process by solar radiation is the heterogeneity of the UV radiation intensity, as can be observed in **Table 2**. Although processed at the same period of day, tests were carried out in distinct several days. Another important fact to be mentioned is the instability of vinasse *in natura*: whose effluent characteristics can be altered, even under refrigeration, in function of possible microorganisms, as remaining yeast fermentation that have growth temperature between 0°C to 47°C and pH between 2.2 and 8.0 [18].

Comprehensively one can observe (**Table 2**) variations between 14.5% to 39.0% in the reduction of non-purgeable organic carbon (considering the averages of experiments). However, experiments 1, 10 and 15 were those

which reached reductions above 30%.

The experiments carried out as blank (pH 5 and 9) also obtained a considerable non-purgeable organic carbon reduction, which may have influenced in the individual analysis of each experiment. This fact can be justified by the degradation of the organic matter in view of the photolysis action and evaporation of volatile compounds (alcohols, ketones, aldehydes and organic acids) initially present and/or formed during the effluent oxidation process, since the reactor operates in an open system.

Starting from the experimental values obtained for each experiment it was possible to evaluate the effect and the distribution of the residual response factor of this planning. **Figure 3** illustrates the result distribution for the non-purgeable organic carbon (NPOC) concentration.

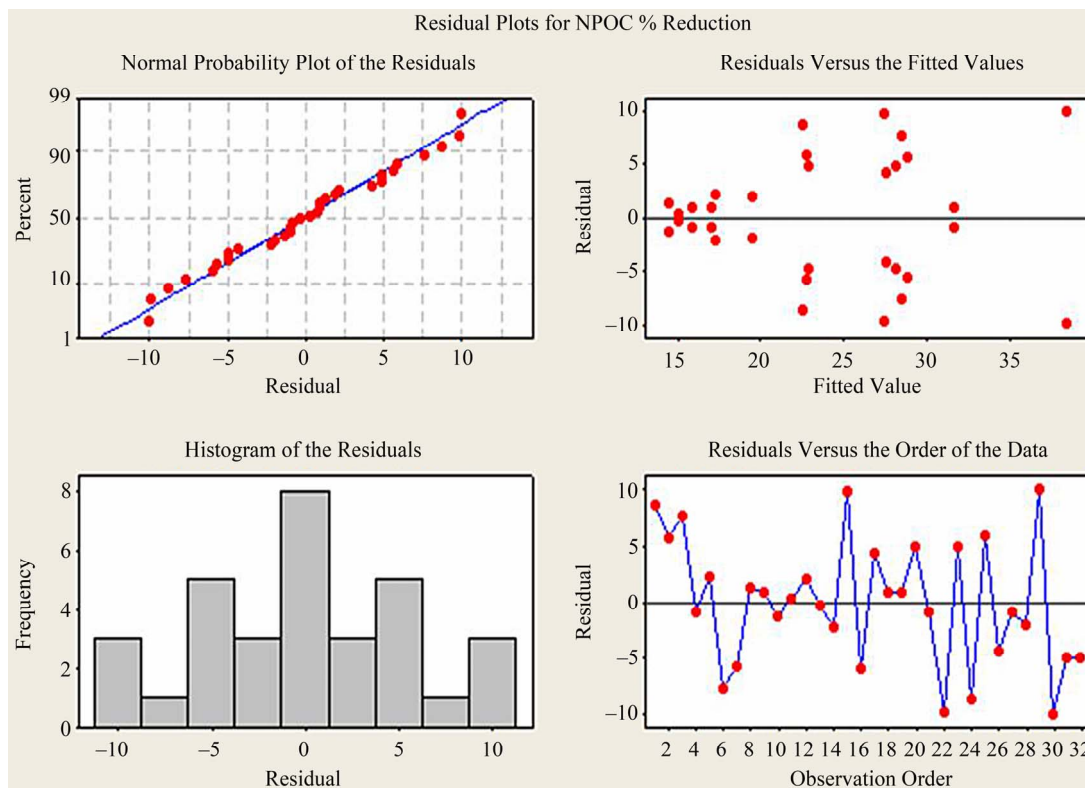
It appears that the residues of the experimental results for the non-purgeable organic carbon factor response follows a normal behavior, with symmetrical distribution around zero, indicating the quality of experimental data.

The statistical analysis of experimental and residual values resulted in the graphic of the 1<sup>st</sup> order factor effect of the evaluated parameter (**Figure 4**).

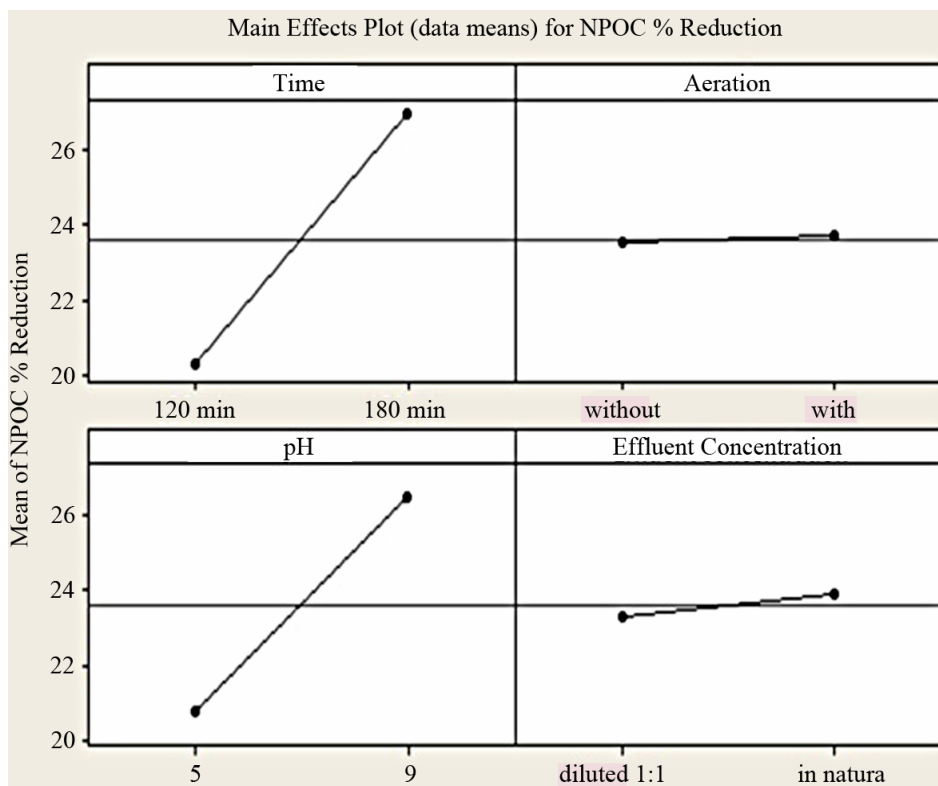
Graphics in **Figure 4** indicates the best result when the

**Table 2.** Average results (n = 2) of non-purgeable organic carbon (NPOC) ( $\text{mg}\cdot\text{L}^{-1}$ ) after photochemical treatment, indicating an average intensity of UV radiation and respective deviation standards.

Experiment	Factors	Measured UV ( $\mu\text{W}\cdot\text{cm}^{-2}$ )	Average and Deviation Standards		% NPOC Reduction
			NPOC Initial ( $\text{mg}\cdot\text{L}^{-1}$ )	NPOC Final ( $\text{mg}\cdot\text{L}^{-1}$ )	
1	+ + + +	798.1 ± 370.5	12802.5 ± 1219.8	7806.0 ± 1062.1	39.0
2	- + + +	687.5 ± 300.5	12785.5 ± 2679.2	9765.5 ± 1173.1	23.6
3	+ - + +	661.2 ± 154.2	13167.0 ± 3009.5	9357.0 ± 1248.8	28.9
4	- - + +	904.0 ± 65.1	10789.5 ± 976.5	9161.5 ± 775.7	15.1
5	+ + - +	784.3 ± 118.3	11972.5 ± 1212.7	9622.0 ± 640.6	19.6
6	- + - +	702.6 ± 108.3	12993.5 ± 3042.7	9878.5 ± 744.6	24.0
7	+ - - +	830.6 ± 128.5	12835.0 ± 2467.8	9225.0 ± 1004.1	28.1
8	- - - +	770.5 ± 98.3	12042.5 ± 1757.2	9972.0 ± 1015.4	17.2
9	+ + + -	920.9 ± 102.9	6766.0 ± 1780.5	4790.5 ± 352.9	29.2
10	- + + -	790.0 ± 458.2	6934.5 ± 1655.3	4857.5 ± 604.6	30.0
11	+ - + -	972.9 ± 118.2	6654.5 ± 1570.5	4677.5 ± 406.6	29.8
12	- - + -	493.9 ± 20.8	6529.5 ± 1358.4	4983.5 ± 504.2	23.7
13	+ + - -	868.7 ± 145.2	5092.3 ± 216.0	4354.8 ± 277.5	14.5
14	- + - -	899.1 ± 69.2	5676.0 ± 698.6	4781.5 ± 662.6	15.8
15	+ - - -	919.3 ± 155.0	6204.0 ± 1026.7	4246.5 ± 775.7	31.6
16	- - - -	670.5 ± 287.8	5979.0 ± 652.0	4956.0 ± 458.2	17.1
Exp. 1 (420 min)	X + + +	592.0	13,315	7355	44.8
Blank (pH 5)		601.4	11,475	9615	16.2
Blank (pH 9)		577.0	11,890	10,300	13.4



**Figure 3.** Residual plots of the obtained data for planned NPOC response factor full factorial ( $2^4$ ) in the photochemical reaction.



**Figure 4.** Effect of 1<sup>st</sup> order in relationship to % of NPOC reduction obtained in the full  $2^4$  factorial planning of the photochemical treatment.

reduction parameter non-purgeable organic carbon is reached in 180 minutes of reaction, with aeration, pH 9 and effluent in natura. The aeration factor had low significance as refers to non-purgeable organic carbon reduction.

The amount of dissolved oxygen in the untreated or aerated effluent was likely sufficient for an oxidation degradation processes with  $\text{TiO}_2$  with no subsequent gain in efficiency. This can be explained as a result of a compressor tank of small flow and low pressure having been used in the system. One can also consider that there was some aeration in the system during the experiments, due to the recirculation of the effluent in the glass reservoir, possibly interfering with this evaluated parameter.

For better understanding the effects and interactions of the obtained results (**Table 3**) a variance analysis of the photochemical process was made.

According to data generated by ANOVA (**Table 3**) it was observed that the time factor (A) is statistically the most significant for the non-purgeable organic carbon response, with confidence level of 97.3% ( $F = 5.91$ ), followed by the pH factor (C) (94.8%). Meanwhile, the aeration factors (B) and the effluent concentration (D) was not meaningful for having confidence level of only 7% and 18% respectively.

It has also been observed that the highest interaction (93.9%) occurred between the variables pH and Aeration; other minor values between the variables Time and Aeration (85.9%) and among Time, pH and effluent concentration (81.7%) in the photochemical reaction, which shows the importance of these parameters together.

These results, obtained after the photochemical treatment, can also be viewed through Pareto analysis, ob-

tained by Minitab software R14, with 95% confidence (**Figure 5**).

If was possible to confirm, referring to **Figure 5** and **Table 3**, that for the analyzed response the reaction time factor was the one that more influenced the reductions.

In consequence of the results of the statistical analysis and the reduction of non-purgeable organic carbon (NPOC) for test 1, it became necessary to repeat this experiment in order to maintain the effluent final volume (3 liters) to comply with all the necessary analysis of the photo catalytic and biological processes. The required analysis, according to Article 18 of Decree nr. 8468/76, was only obtained from the test (1) repeated samples.

**Table 4** presents data and physical characteristics of test (1) earlier conducted in duplicate and data of test 1 repeated as well.

Because of the need to repeat the best experiment (1) of the photo chemical planning, it became necessary to perform the non-purgeable organic carbon (NPOC) and chemical oxygen demand (COD) analysis once again. **Table 5** presents the results of test 1 previously performed in duplicate as well as the results of test 1 repeated.

In relation to the results of experiment 1 repeated it was possible to verify significant reductions for both parameters. Values of chemical oxygen demand and non-purgeable organic carbon differ from those obtained in the replicates as a result of different dates, temperatures and intensities of average solar radiation in relation to each reaction. It was also observed that for the non-purgeable organic carbon, the greater the intensity of solar radiation, the better was the results.

From the results of **Table 5** it is possible to verify the

**Table 3. Variance analysis for the obtained data referred to concentration of non-purgeable organic carbon (NPOC) of the photo catalytic process.**

Sources	DF	Seq. SS	Adj. SS	Adj. MS	F	P	S	R-Sq (%)
Time (A)	1	354.05	354.05	354.05	5.91	0.027	7.74020	59.38
Aeration (B)	1	0.40	0.40	0.40	0.01	0.936		
pH (C)	1	264.16	264.16	264.16	4.41	0.052		
Effluent Conc. (D)	1	2.93	2.93	2.93	0.05	0.828		
A × B	1	143.48	143.48	143.48	2.39	0.141		
A × C	1	18.73	18.73	18.73	0.31	0.584		
A × D	1	41.63	41.63	41.63	0.69	0.417		
B × C	1	243.43	243.43	243.43	4.06	0.061		
B × D	1	102.10	102.10	102.10	1.70	0.210		
C × D	1	14.58	14.58	14.58	0.24	0.628		
A × B × C	1	75.03	75.03	75.03	1.25	0.280		
A × B × D	1	18.39	18.39	18.39	0.31	0.587		
A × C × D	1	115.90	115.90	115.90	1.93	0.183		
B × C × D	1	0.71	0.71	0.71	0.01	0.915		
A × B × C × D	1	5.73	5.73	5.73	0.10	0.761		
Error	16	958.57	958.57	59.51				
Total	31	2359.82						

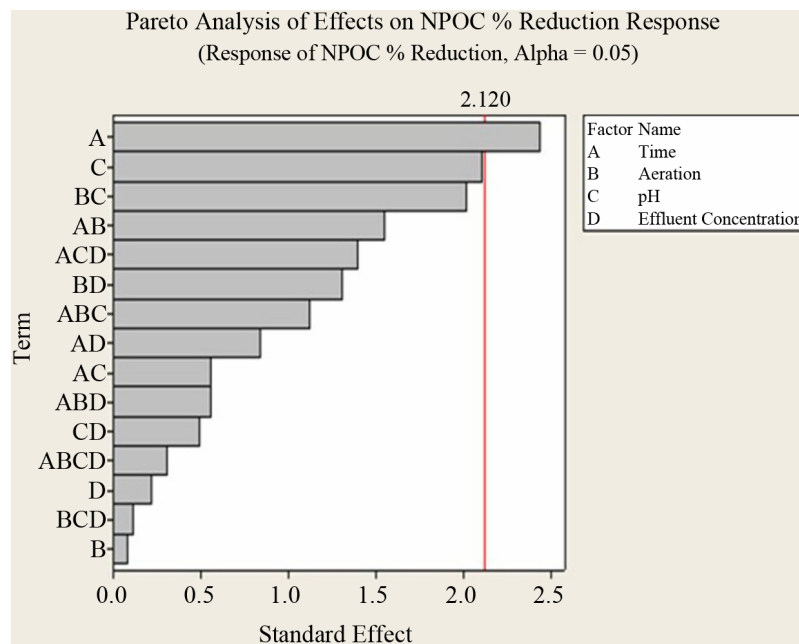


Figure 5. Pareto analysis for the effects that influenced the vinasse photo chemical reaction.

Table 4. Data and physical characteristics of the best planning experiment (1), according to parameters and the established levels for the photochemical treatment.

Experiment		Date of Experiment	Time (start/end)	Average Temperature (°C)	Average UV (W/cm²)	pH Initial	pH Final	V <sub>NaOH</sub> Added (mL)
Replicates	1.1	08/01/09	10:10/13:10 h	34.7	1060.0	3.5	9.0	60
	1.2	10/02/09	10:10/13:10 h	31.3	536.1	3.5	9.0	60
1 (Repeated)			10:10/13:10 h	31.7	668.6	3.5	9.0	60

Table 5. Results of chemical oxygen demand (COD) and non-purgeable organic carbon (NPOC) for the best experiment, reproduced once more, after the photochemical treatment.

Experiment	COD Initial (mg·L <sup>-1</sup> )	COD Final (mg·L <sup>-1</sup> )	% Reduction	NPOC Initial (mg·L <sup>-1</sup> )	NPOC Final (mg·L <sup>-1</sup> )	% Reduction
Replicates	1.1	38915.9	24138.0	13,665	7055	39.0*
	1.2	36377.6	26041.7	11,940	8557	
1 (Repeated)		23979.3	40.3	11,940	7780	34.8

\*Average of replicates (1.1 e 1.2).

effective degradation process occurred either in the chemical oxygen demand or in the non-purgeable organic carbon analysis as there were a significant reduction after the photo chemical treatment. In general, treatment by advanced oxidation process was not able to adjust the effluent disposal according to Article 18 of Decree nr. 8468/76 (<80% income).

In relation to biochemical oxygen demand analysis (Table 6), this was performed to evaluate the effluent load reduction after the photo chemical treatment. Another important factor to be analyzed is the relationship BOD/COD. According to Article 18 of Decree nr. 8468/76 (Schedule A), this relationship is different for several

Table 6. Result of biochemical oxygen demand (BOD) and the relationship BOD/COD of experiment 1 repeated after photochemical treatment.

Experiment	BOD (mg·O <sub>2</sub> ·L <sup>-1</sup> )			Relation BOD/COD Initial	Relation BOD/COD Final
	Initial	Final	% Reduction		
1	23,000	11,700	49.1	0.49	0.57

residues, changing with treatment, especially by the biological method. The relationship BOD/COD points out what kind of oxidation will be effective in the destruction of determined organic load. When the relationship BOD/COD is higher than 0.4 the effluent is readily bio-



degradable. If that relationship is between 0.4 and 0.2 the effluent will require care in the selection of the biological process so to have a desirable removal or organic load whereas if that relationship is greater than 0.2 then the biological process has very little chance of success [19, 20].

The result reveals that the obtained reduction achieved for this parameter was not sufficient to dispose the effluent as required by Article 18 of Decree nr. 8468/76. On the other hand, that result is important in the general process as it confirms the biodegradability of the effluent allowing it to be treated by the biological process (sludge activated).

In consequence of the results obtained in the analysis of metallic elements by atomic absorption for the effluent *in natura*, only the determinations that were outside the specifications such as copper, soluble iron and manganese were performed for the experiment 1 repeated. **Table 7** presents these concentrations in conjunction with the phenol concentration.

After the photo chemical treatment, concentration of manganese in vinasse was reduced to 27.3%, thus achieving less than the value required by legislation. That reduction can be occurred in view of possible precipitation of manganese oxide along the photo catalytic reaction. Levels of copper continued above the allowed by the regulatory environmental organs. Phenol concentration in

test 1 was reduced by 16.2%; however, this result is not sufficient as the phenol index constitutes an emission standard, being limited to  $0.5 \text{ mg}\cdot\text{L}^{-1}$  as Article 18 of Decree nr. 8468/76 and according to Brazilian environment Laws—CONAMA N° 357 [21]. As for the soluble iron concentration, reduction was also significant (19.72%), despite not having been sufficient to dispose the effluent as required by Article 18 of Decree nr. 8468/76.

For Nitrogen (ammoniacal and organic) and Solids (Total Solids, Total Fixed Solids and Total Volatile Solids), results are shown in **Tables 8** and **9** respectively.

Considerable reductions were observed in ammoniac and organic nitrogen after photo chemical treatment.

These values were greater in the analysis of organic nitrogen, showing the oxidation of nitrogenous species.

The results show that there has been a reduction in the value of total solids, fixed totals and volatile totals (this last with the greatest percentage of reduction) for experiment 1, proving the action of the catalytic process which partially mineralized the organic load of the effluent, possibly transforming it into a major fraction of volatile.

Analysis of color was also performed, bearing in mind the verification of the influence of solved solids present in the referred to effluent, in the heterogeneous photo catalytic process. In consequence of test 1 having been fulfilled in pH 9, after the addition of NaOH  $5 \text{ eq}\cdot\text{L}^{-1}$  it

**Table 7. Concentrations of copper (Cu), soluble iron ( $\text{Fe}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ) and phenol ( $\text{mg}\cdot\text{L}^{-1}$ ) obtained in experiment 1 repeated, after photochemical treatment.**

Elements	Maximum Allowed Concentrations ( $\text{mg}\cdot\text{L}^{-1}$ )*	Experiment 1 ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction
		Initial	Final	
Copper (Cu)	1.0	1.7	1.5	11.8
Soluble Iron ( $\text{Fe}^{2+}$ )	15.0	20.5	16.5	19.7
Manganese ( $\text{Mn}^{2+}$ )	1.0	1.1	0.8	27.3
Phenol	0.5	23.3	19.6	16.2

\*According to article 18 of Decree nr. 8468/76.

**Table 8. Results of nitrogen for experiment 1 repeated, after photochemical treatment.**

Experiment	Ammoniacal Nitrogen Concentration ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction	Organic Nitrogen Concentration ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction
	Initial	Final		Initial	Final	
1	48.3	31.6	34.5	87.5	39.9	54.4

**Table 9. Results of solids (total solids, total fixed solids e total volatile solids) for experiment 1 repeated, after photochemical treatment.**

Experiment	Total Solids ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction	Total Fixed Solids ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction	Total Volatile Solids ( $\text{mg}\cdot\text{L}^{-1}$ )		% Reduction
	Initial	Final		Initial	Final		Initial	Final	
1	12,200	10,100	17.21	4100	3700	9.76	8100	6400	20.99



was possible to observe a darkening of the effluent, which was gradually increasing due to the complex composition of vinasse with the presence of phenolic compounds and some other occurred oxidations.

#### 4.2. Cost Calculus

A simple and quick evaluation of costs was done involving the photochemical treatment of vinasse in bench scale.

In the photo catalytic process basically a centrifugal pump (0.013 CV-BOMAX, Model NH-30PX-T) and a metal plate measuring  $1875\text{ cm}^2$ , coated with  $\text{TiO}_2$   $0.025\text{ g}\cdot\text{cm}^{-2}$  thick were employed, besides a small sustaining wooden structure equipped with a distribution piping of the effluent on the plate.

For the manufacture of the metallic plate, both the price of the plate and the mass of titanium oxide applied onto it were taken into account. With respect to energy consumption a value of industrial kWh referred to October/2009 was used, besides the acquisition of the centrifugal pump above mentioned.

Considering a total of 4800 minutes used to conduct 32 experiments (planning of the complete  $2^4$  factorial experiments in duplicate) and as 3 liters of effluent were used for each experiment (total of 96 liters) it was possible to calculate the energy consumption by treated effluent liter.

From the values and spending related to the metal plate, centrifugal pump, wooden structure of the reactor and their pipes and considering a minimum annual fee (5%), annual depreciation for hydraulic equipments and electrical consumption results in US\$ 0.15 for each treated effluent liter. This value can be reduced through an expansion of scale and, consequently, the time used for the experiments.

Thus, one can say that the application of this process is financially viable, since the costs involved are low deployment and make possible the expansion of scale and consequently its application in plants.

#### 4.3. Biological Treatment

After the adjustment of the pH of the medium and the concentration of the digesting sludge culture, a full  $2^2$  factorial planning was carried out for the treatment of the sample that presented the best result as to the reduction of non-purgeable organic carbon after the photochemical treatment.

The time adopted for this treatment was 8 hours. The efficiency of the process was also evaluated in terms of reduction (%) of non-purgeable organic carbon. For the best test, analyses of biochemical oxygen demand, solids quality (Total Solids, Total Fixed Solids and Total Volatile Solids), metallic elements, phenol and nitrogen (am-

moniacal and organic) were fulfilled.

The biological treatment process with activated sludge (**Figure 6**) was conducted in containers with a capacity of 0.75 liters equipped with an air diffuser ( $Q_{ar} = 0.75\text{ liter}\cdot\text{min}^{-1}$ ).

The process of the vinasse biological treatment after applying the advanced oxidation process, samples of sludge collected at the Treatment Station of the Engineering School at Lorena-SP were brought to the laboratory for conditioning the microbial flora, necessary when the organic load comes from specific effluents. Parameters pH, morphology and identification of resistant microorganisms were evaluated, enabling the collection of data and the evolution of their culture.

After delivery of synthetic medium, as additional sources of nitrogen and phosphorus and continuous aeration, it was noted a growth of the culture (increase of flora mass by volume unit). On the following stage, for about 90 days, small aliquots were added to the vinasse sludge every 24 hours, gradually increasing the volume of effluent added so to adapt microorganisms to the vinasse sludge and, thus, start the biological treatment.

Referring to micrographs shown in **Figure 7**, we can observe the presence of important types of protozoa [ciliates (**Figure 7(a)**), rotifers (**Figure 7(b)**) and pedunculates (**Figures 7(c)** and **(d)**)] which start, thus, the biological treatment in function of the quality of microorganisms found in the sludge.

Before beginning the planned experiment tests for the biological degradation of the effluent by photochemical reaction a treatment was carried out with vinasse *in natura*, aiming to verify the importance of the advanced oxidative process as a pre-treatment. The dilution factor (f), applied to calculate the results were used due to different concentrations of sludge ( $3$  and  $5\text{ g}\cdot\text{L}^{-1}$ ) used both for these analysis as for the planning. **Tables 10** and **11** present the results of chemical oxygen demand and non-purgeable organic carbon obtained after the biological treatment.



**Figure 6.** System used in the aerated biological treatment.

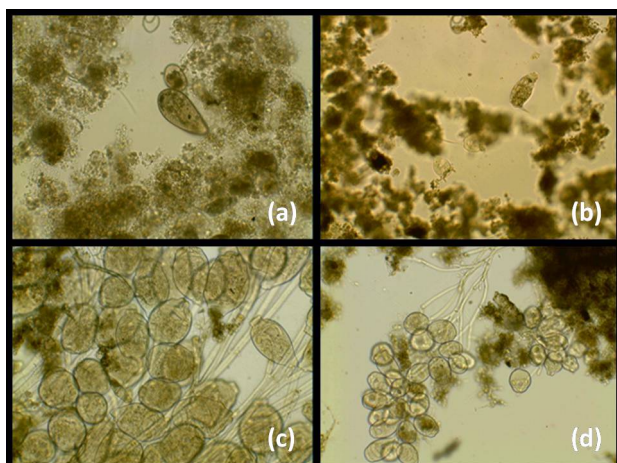


Figure 7. Micrographic photos of sludge using the biologic treatment (amplified 1000 $\times$ ).

Table 10. Results of chemical oxygen demand (COD) of vinasse in natura, after biologic treatment.

Sludge Treatment (g·L <sup>-1</sup> )	COD Initial (mg·L <sup>-1</sup> )	COD Final (mg·L <sup>-1</sup> )	COD Final $\times$ f (mg·L <sup>-1</sup> )	% Reduction
3	37964.1	25338.9	31752.9	16.4
5		24951.9	37691.6	0.7

Table 11. Results of non-purgeable organic carbon (NPOC) in vinasse in natura, after biologic treatment.

Sludge concentration (g·L <sup>-1</sup> )	NPOC Initial (mg·L <sup>-1</sup> )	NPOC Final (mg·L <sup>-1</sup> )	NPOC Final $\times$ f (mg·L <sup>-1</sup> )	% Reduction
3	9105	5877.8	7365.6	19.1
5		5015.0	7575.5	16.8

Table 12. Volumes of effluent and sludge (mL) used in the biologic treatment, according to sludge concentration of the experiment planning.

Sludge Concentration (g·L <sup>-1</sup> )	Effluent Volume (mL) Added to Test	Sludge Volume (mL) Added to Test	Total Volume (Effluent + Sludge) (mL)	Dilution Factor (f)
3	399	101	500	1.25313
5	331	169	500	1.51057

Table 13. Results of non-purgeable organic carbon (NPOC) in vinasse pre-treated by advanced oxidation process (AOP), after biologic treatment.

Photochemical Experiment	Biologic Experiment	A-Sludge Concentration (g·L <sup>-1</sup> )	B pH	Planning Experimental Conditions (A/B)	NPOC Initial (mg·L <sup>-1</sup> )	NPOC Final (mg·L <sup>-1</sup> )	NPOC Final $\times$ f (mg·L <sup>-1</sup> )	% Reduction
Experiment 1	1	5	8	+/+	7780	4393.5	6636.7	14.7
	2	3	8	-/+		5845.9	7325.7	5.8
	3	5	6	+/-		4759.5	7189.6	7.6
	4	3	6	-/-		5979.3	7492.8	3.7

It can be observed that the biological degradation of vinasse in natura presented 17% lower reduction when using 3 g·L<sup>-1</sup> sludge concentration and 1% lower reduction with 5 g·L<sup>-1</sup> sludge concentration for chemical oxygen demand. As for the non-purgeable organic carbon analysis these reductions were 19.1% and 16.8% for the sludge concentrations of 3 and 5 g·L<sup>-1</sup>, respectively. Thus, only the biological treatment was not sufficient to obtain proceeds to satisfy the law, whether the effluent should be treated previously by physical-chemical or chemically. Salazar (2009) also reported the importance of a pre-treatment for effluent with high organic load before aerobic biodegradation process [9,20,22].

The experiments of the full 2<sup>2</sup> factorial planning were carried out using as a sample test 1 repeated of the photochemical treatment.

The analysis obtained after the biologic treatment followed same analytic proceedings used for the samples treated by advanced oxidation process.

As a result of different concentrations of sludge (3 and 5 g·L<sup>-1</sup>) used in the experiments, according to proposed planning, the use of dilution factors were necessary for obtaining the results of the analysis as a result of effluent/sludge volume change in the tests being, thus, considered final calculi.

From the analysis of total solids in the acclimated sludge (14.8 g·L<sup>-1</sup>) it was possible to calculate the sludge and effluent volume used in each experiment, as per the values presented in Table 12.

After the biologic treatment in accord to planning, samples were allowed to settle the sludge sediment and from the supernatant (treated vinasse) was carried out the non-purgeable organic carbon analysis. Results are shown in Table 13.

Results of the experiments revealed that the biologic treatment was efficient due to the reduction of the sludge organic matter treated by advanced oxidation process. Experiment 1 had the best performance with 14.7% reduction with pH 8 and sludge concentration of  $5 \text{ g}\cdot\text{L}^{-1}$ .

As previously discussed, sludge used in this biologic treatment was adapted for this specific degradation, whose concentration conditions of the sludge and the environment, selected for the biologic planning, were estimated in optimized conditions for a domestic effluent treating plant since no information for this treating type was found for vinasse.

For the analytical characterizations after the biological treatment, all the experiments were evaluated in function of chemical oxygen demand. For other analytical parameters, only experiment 1 (1) was analyzed. **Tables 14** and **15** present the results for chemical oxygen demand and biochemical oxygen demand, respectively.

It was possible to observe significant chemical oxygen demand reductions (%) after biologic treatment; meanwhile, the best reduction (51.5%) was obtained in experiment 1 (1). As for biochemical oxygen demand, biological treatment was able to reduce to 73.3% the value of the initial concentration. This demonstrates that the organic load present in vinasse, after the photochemical treatment, was degraded by the microorganisms present in the conditioned activated sludge.

After the biological treatment, there was some increase in the relationship BOD/COD of the effluent in comparison to the previous relationship of the photochemical treatment for test 1 (BOD/COD = 0.57). This relationship is different in several residues and can be changed specially through the biological treatment.

For the analysis of elements and ions, only the determinations of copper, soluble iron and phenol were performed after hybrid photochemical/biological treatment (**Table 16**).

Levels of copper and soluble iron decreased significantly due to the fact that these elements are absorbed by microorganisms during the aerobic degradation process as they are metabolic nutrients. Results demonstrate that there was an increase of 13.3% in the concentration of phenol for test 1 (1). This fact can be justified by the absorption of the soluble phenolic compounds present in the activated sludge which, as analyzed, presented an equal concentration of  $18.9 \text{ mg}\cdot\text{L}^{-1}$ . In activated sludge systems, only concentrations of phenolic compounds in excess of  $50 \text{ mg}\cdot\text{L}^{-1}$  can cause inhibition and  $40 \text{ mg}\cdot\text{L}^{-1}$  are sufficient for the inhibition of nitrification [23].

Analysis of Nitrogen (ammoniacal and organic) and Solids (Total Solids, Total Fixed Solids and Total Volatile Solids) were also carried out for test 1 (1). Results are shown in **Tables 17** and **18**, respectively.

**Table 14. Results of chemical oxygen demand (COD) in vinasse pre-treated by advanced oxidation process (AOP), after biologic treatment.**

Photochemical Experiment	Biologic Experiment	A-Sludge Concentration ( $\text{g}\cdot\text{L}^{-1}$ )	B pH	Planning Experimental Conditions (A/B)	COD Initial ( $\text{mg}\cdot\text{L}^{-1}$ )	COD Final ( $\text{mg}\cdot\text{L}^{-1}$ )	COD Final $\times$ f ( $\text{mg}\cdot\text{L}^{-1}$ )	% Reduction
Experiment 1	1	5	8	+/+	23979.3	7697.6	11627.8	51.5
	2	3	8	-/+		13028.1	16325.9	31.9
	3	5	6	+/-		11885.8	17954.4	25.1
	4	3	6	-/-		13091.5	16405.4	31.6

**Table 15. Results of biochemical oxygen demand (BOD) in vinasse treated by advanced oxidation process (AOP) and after biologic treatment.**

Experiment	BOD ( $\text{mg}\cdot\text{O}_2\cdot\text{L}^{-1}$ )				Rel. BOD/COD Initial	Rel. BOD/COD Final
	Initial	Final	Final $\times$ f	% Reduction		
1 (1)	11700.0	2069.0	3125.4	73.3	0.49	0.27

**Table 16. Copper (Cu), iron ( $\text{Fe}^{2+}$ ) and phenol ( $\text{mg}\cdot\text{L}^{-1}$ ) in vinasse after photochemical/biological treatment.**

Elements	Max. allowed concentration ( $\text{mg}\cdot\text{L}^{-1}$ )*	Biological treatment			%
		Initial	Final	Final $\times$ f	
Copper	1.0	1.5	0.6	0.9	-40.0
Iron ( $\text{Fe}^{2+}$ )	15.0	16.5	3.9	6.0	-63.6
Phenol	0.5	19.6	14.7	22.2	+13.3

\* According to Article 18 of Decree nr. 8468/76.

**Table 17. Concentrations of nitrogen in vinasse after advanced oxidation process (AOP) and biologic treatments.**

Experiment	Ammoniacal Nitrogen Concentration (mg·L <sup>-1</sup> )				Organic Nitrogen Concentration (mg·L <sup>-1</sup> )			
	Initial	Final	Final × f	% Increase	Initial	Final	Final × f	% Increase
1 (1)	31.6	24.5	37.1	+17.4	39.9	32.7	49.4	+23.8
Sludge		20.1				290.9		

**Table 18. Concentrations of solids (total solids, total fixed solids and total volatile solids) in vinasse after advanced oxidation process (AOP) and biologic treatments.**

Experiment	Total Solids (mg·L <sup>-1</sup> )				Total Fixed Solids (mg·L <sup>-1</sup> )				Total Volatile Solids (mg·L <sup>-1</sup> )			
	Initial	Final	Final × f	% Increase	Initial	Final	Final × f	% Reduction	Initial	Final	Final × f	% Increase
1 (1)	10,100	7400	11,178	+10.7	3700	2350	3550	-4.1	6400	5050	7628	+19.2
Sludge		14,800				1300				13,500		

Referring to experiment 1 (1) it was observed an increase of 17.4% in the ammoniacal nitrogen concentration value and 23.8% for the organic nitrogen. This fact is due to the concentration of nitrogen (ammonia and organic), intrinsic to biologic sludge. It should be pointed out that this parameter is not limited by regulatory agencies for disposal but of great importance to control the parameters and full functioning of a biological treatment plant.

Results demonstrate an increase of concentration for both Total Solids and Total Volatiles for experiment 1 (1). For Fixed Total Solids reduction was 4.1%. As discussed above, referring to nitrogen, there was possibly a mass transfer of sludge to carry out this analysis or the sedimentation process was not efficient.

When characterizing vinasse in natura, it was verified that some of the parameters to be analyzed, as predicted by Article 18 of Decree nr. 8468/76 for disposal of effluents, disagreed with the established limits. In account to this fact, the efficiency of the hybrid system (Advanced Oxidation Process—Activated Sludge) was evaluated as for the reduction of organic matter in terms of reduction (%) of non-purgeable organic carbon, chemical oxygen demand and biochemical oxygen demand, in addition to adjustments in the concentrations of copper, ferrous ion and phenol. Solid (Total Solids, Total Fixed Solids and Total Volatile Solids) and nitrogen (ammoniacal and organic) reductions were also evaluated, parameters which are not restricted by regulatory agencies for disposal but are of great importance to functional control of a biological treatment plant.

Prior to biological degradation of the effluent treated by photochemical reaction, a treatment was carried out with vinasse in natura, in order to verify the importance of using a pre-treatment to Activated Sludge System in terms of reducing chemical oxygen demand and non-

purgeable organic carbon (**Table 19**).

After analyzing the results, it was noted a low efficiency of the system in reducing the organic load only by biological treatment. These results confirmed the need to perform a pre-treatment of vinasse that could allow a greater biodegradation when submitted to biological treatment.

After an adjustment of the biological system, the sample of experiment 1 brought from the photocatalytic treatment, was submitted to biological treatment. The efficiency of biodegradation of the organic load was observed for test 1 (1) in terms of reducing chemical oxygen demand, non-purgeable organic carbon and biochemical oxygen demand (**Table 20**).

By analyzing the hybrid system it was found an efficiency of 71.06%, 44.41% and 86.41% in the reduction of organic load for chemical oxygen demand, non-purgeable organic carbon and biochemical oxygen demand, respectively. These Figures are significant because of the complexity of the effluent and considering the high initial concentrations of the parameters discussed above.

With relation to copper and ferrous ion elements that were in disagreement with the regulatory limits after the photochemical treatment, when submitted thereafter to biological treatment the concentration values complied with the requirements.

As for the analysis of phenol, nitrogen (ammoniacal and organic) and solids (Total Solids and Total Volatile Solids) it was observed an increase of concentration after hybrid treatment (Advanced Oxidation Process—Activated Sludge). This fact is due to the concentration of phenol, nitrogen and solids in the intrinsic biological sludge from a sewage treatment plant (acclimated with vinasse), or as a result of the sedimentation process not being efficient.

Thus, it can be seen that the hybrid process (Advanced

**Table 19. Results of chemical oxygen demand (COD) and non-purgeable organic carbon (NPOC) in vinasse in natura after biological treatment.**

Sludge Concentration (g·L <sup>-1</sup> )	Fators	Initial Organic Load	After Biological Treatment
3	COD (mg·L <sup>-1</sup> )	37964.1	31752.9
3	NPOC (mg·L <sup>-1</sup> )	9105	7365.6
5	COD (mg·L <sup>-1</sup> )	37964.1	37691.6
5	NPOC (mg·L <sup>-1</sup> )	9105	7575.5

**Table 20. Results of chemical oxygen demand (COD), non-purgeable organic carbon (NPOC) and biochemical oxygen demand (BOD) of experiment 1 (I) for vinasse treatment in hybrid system: advanced oxidation process (AOP)—Activated Sludge.**

Factors	Initial Organic Load	After AOP	After Activated Sludge
COD (mg·L <sup>-1</sup> )	40185.1	23979.3	11627.8
NPOC (mg·L <sup>-1</sup> )	11940.0	7780.0	6636.7
BOD (mg O <sub>2</sub> L <sup>-1</sup> )	23000.0	11700.0	3125.4

Oxidation Process/Activated Sludge) proved to be feasible, since for biochemical oxygen demand the reduction achieved was above 80%, besides the adequacy of concentrations of elements and ions to comply with CETESB—Article 18 of Decree nr. 8468/76.

## 5. Conclusions

Despite not having a significant oversight by environmental control agencies regarding the disposal of vinasse and, on the other hand, an increased demand for products from cane sugar, the potential toxicity of this effluent is causing serious environmental damage, mainly by contamination of groundwater and surface water. To mitigate this environmental contamination, studies of new treatment processes appear as direct and effective alternatives.

This study was intended to show the feasibility of application of heterogeneous photocatalysis with TiO<sub>2</sub> anatase fixed on a metal plate for the treatment of vinasse, followed by biological treatment (Activated Sludge) so that the final characteristics of the effluent were according to Article 18 of Decree nr. 8468/76 environmental legislation after employing a hybrid treatment system.

Due to the use of a fixed-bed solar reactor in an open system in the photocatalytic process, periodic additions of distilled water were employed in a proportion of 215 mL·h<sup>-1</sup> of reaction, in order to correct the final volume, while minimizing the effects of pre-concentration during the photodegradation period.

The characterization of vinasse in natura and treated used spectrophotometric techniques, spectrometric and gravimetric methods for the determination of chemical oxygen demand, non-purgeable organic carbon, biochemical oxygen demand, metallic elements, some ionic species, phenol, nitrogen (organic and ammonia) and solids (Total Solids, Total Fixed Solids, Total Volatile Solids) being necessary some optimizations because of the complex characteristics of this residue.

From a full 2<sup>4</sup> factorial planning it was possible to determine the best conditions for the advanced oxidation process, with a response factor the reduction of non-purgeable organic carbon (NPOC). The experimental condition of the factorial planning presented as variables 180 minutes of reaction, with aeration, pH 9 and effluent in nature was the one with the best result of degradation of vinasse organic matter, resulting in a reduction of 39% to non-purgeable organic carbon (NPOC).

The experiments of the full 2<sup>2</sup> factorial planning were performed with a sample test 1 repeated of the photochemical treatment. It was found that the best analytical condition of the biological system to treat effluent pretreated with advanced oxidation process were: sludge concentration equal to 5.0 g·L<sup>-1</sup> and pH 8 during 8 hours of reaction, resulting in a reduction of 14.7% non-purgeable organic carbon (NPOC).

The efficiency of the hybrid system (Advanced Oxidation Process—Activated Sludge) was evaluated as for the reduction of organic matter, given in terms of reducing non-purgeable organic carbon (44.41%), chemical oxygen demand (71.06%) and biochemical oxygen demand (86.41%) besides the reductions in the concentrations of elements and ions according to the legislation. Due to the significant results obtained by combining the treatment of advanced oxidation process based on heterogeneous photo catalysis (TiO<sub>2</sub>/UV<sub>solar</sub>), with the biological system (Activated Sludge), one can say that this hybrid system has great potential application for the treatment of vinasse that, combined with the activated sludge biological process, can degrade the organic load within the performance values established by Article 18 of Decree nr. 8468/76 enabling its disposal.

According to the analysis of costs involved in the vinasse photochemical treatment in bench scale presented in this paper, we can conclude that the use of this process is financially feasible since deployment costs involved are low and make possible the expansion of scale and, consequently, its application in plants.

## 6. Acknowledgements

The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo, DuPont by technical support, and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for research funds and grants.

## REFERENCES

- [1] E. P. Carvalho, "Formulação de uma Estratégia para Garantir o Aumento da Produção," In: *Seminário "Uma Estratégia Para o Etanol Brasileiro"*, Casa do Brasil, Rio de Janeiro, November 2006.
- [2] União da Indústria de Cana-de-Açúcar (UNICA), 2009. <http://www.portalunica.com.br>
- [3] I. C. Macedo, "Situação Atual e Perspectivas do Etanol," *Estudos Avançados*, Vol. 21, No. 59, 2007, pp. 157-165.
- [4] Universidade Estadual Paulista—UNESP, "Termo de Referência para o Workshop Tecnológico—Vinhaça," 2007. [http://www.apta.sp.gov.br/cana/anexos/Termo\\_de\\_Referencia\\_Vinhaca.pdf](http://www.apta.sp.gov.br/cana/anexos/Termo_de_Referencia_Vinhaca.pdf)
- [5] G. A. Nascimento, "Aproveitamento de Bagaço em Usinas de Álcool e Açúcar—Venda, Queima ou Hidrólise," Universidade Estadual Paulista "Júlio de Mesquita Filho", Guaratinguetá, 2008.
- [6] W. J. Freire and L. A. B. Cortêz, "Vinhaça de Cana-de-Açúcar," *Agropecuária, Guaíba*, 2000, p. 203.
- [7] R. P. Barros, P. R. A. Viégas and F. S. R. Holanda, "Estudo dos Efeitos da Aplicação da Vinhaça na Qualidade de Solos em Cultivo de Cana-de-Açúcar (*Saccharum officinarum* L.), e o Uso de Indicadores no Sistema de Produção," 2009. <http://hdl.handle.net/2315/139>
- [8] M. T. Ludovice, "Estudo do Efeito Poluente da Vinhaça Infiltrada em Canal Condutor de Terra Sobre o Lençol Freático," Universidade Estadual de Campinas, Campinas, 1996.
- [9] R. F. S. Salazar and H. J. I. Filho, "Aplicação de Processo Oxidativo Avançado Baseado em Fotocatálise Heterogênea ( $\text{TiO}_2/\text{UV}_{\text{solar}}$ ) para o Pré-tratamento de Afluente Lácteo," *Augm Domus*, 2009, pp. 27-44. <http://revistas.unlp.edu.ar/index.php/domus/article/view/79/43>
- [10] R. F. P. Nogueira and W. F. Jardim, "A Fotocatálise Heterogênea e sua Aplicação Ambiental," *Química Nova*, Vol. 21, No. 1, 1998, pp. 69-72. [doi:10.1590/S0100-40421998000100011](https://doi.org/10.1590/S0100-40421998000100011)
- [11] X. Domènech, W. F. Jardim and M. I. Litter, "Procesos Avanzados de Oxidación para la Eliminación de Contaminantes," In: *Eliminación de Contaminantes por Fotocatálisis Heterogênea*, Rede CYTED, La Plata, 2001, Cap. 1.
- [12] G. R. S. Samanamud, C. C. A. Loures, A. L. Souza, R. F. S. Salazar, Y. S. Oliveira, M. B. Silva and H. J. I. Filho, "Heterogeneous Photocatalytic Degradation of Dairy Wastewater Using Immobilized  $\text{ZnO}$ ," *ISRN Chemical Engineering*, Vol. 2012, 2012, Article ID: 275371.
- [13] R. S. Freire, R. Pelegrini, L. T. Kubota, N. Duran and P. Peralta-Zamora, "Novas Tendências para o Tratamento de Resíduos Industriais Contendo Espécies Organocloradas," *Química Nova*, Vol. 23, No. 4, 2000, pp. 504-511. [doi:10.1590/S0100-40422000000400013](https://doi.org/10.1590/S0100-40422000000400013)
- [14] A. P. Davis and C. P. Huang, "Removal of Phenols from Water by a Photocatalytic Oxidation Process," *Water Science and Technology*, Vol. 21, No. 6-7, 1989, pp. 455-464.
- [15] R. L. Zioli and W. F. Jardim, "Mecanismo de Fotodegradação de Compostos Orgânicos Catalisada por  $\text{TiO}_2$ ," *Química Nova*, Vol. 21, No. 3, 1998, pp. 319-325. [doi:10.1590/S0100-40421998000300013](https://doi.org/10.1590/S0100-40421998000300013)
- [16] I. V. L. Ferreira and L. A. Daniel, "Fotocatálise Heterogênea com  $\text{TiO}_2$  Aplicada ao Tratamento de Esgoto Sanitário Secundário," *Engenharia Sanitária Ambiental*, Vol. 9, No. 4, 2004, pp. 335-342. [doi:10.1590/S1413-41522004000400011](https://doi.org/10.1590/S1413-41522004000400011)
- [17] J. Rodríguez, R. J. Candal, J. Solís, W. Estrada and M. A. Blesa, "El Fotocatalizador: Síntesis, Propiedades y Limitaciones," In: *Solar Safe Water, Tecnologías Solares Para la Desinfección y Descontaminación del Agua*, Proyecto FP6-510603 Del Sexto Programa Marco de la Unión Europea, Buenos Aires, 2006, pp. 135-152.
- [18] M. J. Pelczar, R. Reid and E. C. S. Chan, "Microbiologia," McGraw-Hill do Brasil, São Paulo, 1980, p. 576.
- [19] W. F. Jardim and M. C. Canela, "Fundamentos da Oxidação Química no Tratamento de Efluentes e Remediação de Solos," Instituto de Química (IQ), Universidade de Campinas, Campinas, 2004.
- [20] R. F. S. Salazar, J. S. Carrocci and H. J. I. Filho, "Employment of Factorial Design to Evaluate the Organic Loading and Aeration of Biological Systems in the Degradation of Dairy Wastewater," *Ambiente & Água*, Vol. 6, No. 3, 2011, pp. 98-109. [doi:10.4136/ambi-agua.522](https://doi.org/10.4136/ambi-agua.522)
- [21] Conselho Nacional do Meio Ambiente—CONAMA, "CONAMA No. 357: Disposição Sobre a Classificação dos Corpos de Água e Diretrizes Ambientais para o Seu Enquadramento, Bem Como Estabelecimento das Condições e Padrões de Lançamento de Efluentes," 2007. <http://www.mma.gov.br/port/conama>
- [22] R. F. S. Salazar, "Aplicação de Processo Oxidativo Avançado (POA) Como Pré-Tratamento de Efluente de Laticínio para Posterior Tratamento Biológico," Dissertação (Mestrado), Universidade de São Paulo, Lorena, 2009. <http://www.teses.usp.br/teses/disponiveis/97/97136/tde-25102012-134440/pt-br.php>
- [23] CETESB (Companhia de Tecnologia de Saneamento Ambiental), "Portal do Governo do Estado de São Paulo," 2009. <http://www.cetesb.sp.gov.br>



## SCHEDULE A

## CETESB—Discharge Parameters: Decree No. 8.468 of September 8, 1976—Art. 18

Effluents from any pollutant sources shall be discharged, directly or indirectly, into water collection must be subject to the following criteria:

- 1) pH between 5.0 and 9.0;
- 2) Temperature less than 40°C;
- 3) Sedimentable solids up to 1.0 mg/l in one-hour test into an Imhoff cone;
- 4) Substances soluble in hexane up to 100 mg/l;
- 5) 5 days DBO, 20°C maximum of 60 mg/l. This limit will only be exceeded in cases where the wastewater treatment system effluent reduces the pollutant load for approximately 5 days DBO, 20°C at a minimum 80% discharge;
- 6) Maximum concentrations of the following parameters:

1	Arsenic	0.2 mg/l
2	Barium	5.0 mg/l
3	Boron	5.0 mg/l
4	Cadmium	0.2 mg/l
5	Lead	0.5 mg/l
6	Cyanide	0.2 mg/l
7	Copper	1.0 mg/l
8	Hexavalent Chromium	0.1 mg/l
9	Total Chromium	5.0 mg/l
10	Tin	4.0 mg/l
11	Phenol	0.5 mg/l
12	Soluble Iron ( $\text{Fe}^{2+}$ )	15.0 mg/l
13	Fluoride	10.0 mg/l
14	Soluble Manganese ( $\text{Mn}^{2+}$ )	1.0 mg/l
15	Mercury	0.01 mg/l
16	Nickel	2.0 mg/l
17	Silver	0.02 mg/l
18	Selenium	0.02 mg/l
19	Zinc	5.0 mg/l