

Catalytic Ozonation Using Fe²⁺ in the Treatment of Dairy Effluent in a Semi-Batch Process with Recycle

*Raquel A. Messias, Hélcio J. I. Filho, Guilherme A. Ferreira, Otávio A. Silva,
Adriano F. Siqueira and Marco A. K. Alcântara**

*Escola de Engenharia de Lorena, Universidade de São Paulo, Estrada Municipal do Campinho, s/n,
Bairro do Campinho, 12602-810 Lorena-SP, Brazil*

This work describes the treatment of dairy industry effluent using catalytic ozonation with Fe²⁺ as its catalyst in a semi-batch process with recycle. A fractional factorial design 2⁴⁻¹ was used with a reduction percentage of total organic carbon (TOCred) as response. Optimal conditions were obtained by the reaction time of 30 min, ozonator power of 35 W, O₂ flow rate of 0.125 L min⁻¹, Fe²⁺ concentration of 1.0 g L⁻¹ and pH 4.0 for a 2 L raw effluent. TOCred of 64.03% represents a decrease in concentration from 473.0 to 170.1 mg L⁻¹, with an estimate cost of US\$ 0.03 L⁻¹ effluent. The treatment performed was not sufficient to discharge it directly on surface water; however, significant reduction of TOCred, among physical and chemical characteristics makes a better product to be proceeded into a biological treatment.

Keywords: dairy industry, catalytic ozonation, advanced oxidation processes

Introduction

Due to high consumption of water and large volume of effluent produced, dairy industry is considered the most pollutant in comparison to other food industries.¹ Treatment is, therefore, required since it is composed of high molecular weight and aromatic compounds that are not easily degraded, considered as pollutants.

Dairy effluents are composed of milk and processed products derived from milk as well as disinfectants, detergents, spices and essences (butter and cheese production) that are diluted in the washing process of equipment, pipes, floor and other facilities of such industry.²

Industries have currently used treatment alternatives based on physical and biological processes that although show restricted efficiency, have several limitations. These limitations generally include primary treatment for the removal of suspended solids and fat material, and a secondary biological treatment. Problems related to the secondary biological treatment are related to high foam production, low biodegradability of sludge, low resistance to load shock, difficulties in removing nutrients (nitrogen and phosphorus) and problems in the degradation of fat and other specific types of pollutants as dyes, apart from unpleasant odor.^{3,4}

Thus, efficient and economically viable technologies are required to treat these types of effluents.⁵ In this sense, advanced oxidation processes (AOPs) are technologies extremely efficient based on the oxidizing power of several radicals formed that are used in the destruction of organic compounds of difficult degradation (partial or total).^{6,7}

Catalytic ozonation may be considered as a homogeneous process based on ozone activation by metal ions present in aqueous solution. These reactions are characterized by single-phase development or as a heterogeneous process in the presence of metal oxides.⁸ Also, the transition metals form low solubility products under certain pH conditions.

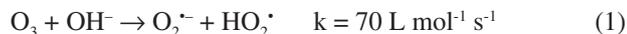
As pH is related to concentration of hydroxyl ions (OH⁻), it directly influences the decomposition of molecular ozone. In situations where a small concentration of hydroxyl ion is present (pH < 4), the reaction takes place predominantly by electrophilic addition of molecular ozone (direct reaction).⁹ In an alkaline medium, hydroxyl ions in high concentration may start the decomposition of molecular ozone leading to the formation of hydroxyl radical (indirect reaction).¹⁰

The reaction system becomes heterogeneous in an alkaline medium with Fe²⁺ ions in the catalytic ozonation processes producing a resultant precipitation of these ions. However, this precipitation does not prevent to work in this pH.¹¹ The removal rates of the organic load in alkaline

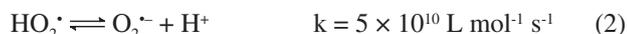
*e-mail: marko@usp.br

medium are not always satisfactory. Due to the complexity of environmental matrix, numerous compounds considered sequestrants of hydroxyl radical, such as HCO₃⁻, CO₃²⁻, CH₃COO⁻ and humic substances might be present resulting in decrease of the efficiency of the process.⁹

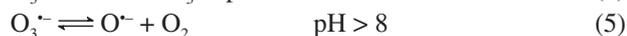
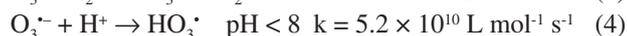
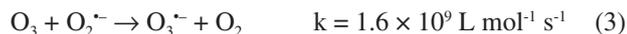
The reaction between the hydroxide anion and ozone leads to the formation of superoxide radical anions (O₂⁻) and hydroperoxide radicals (HO₂[•]), as shown in equation 1.¹²



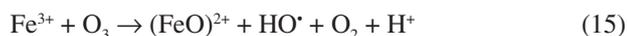
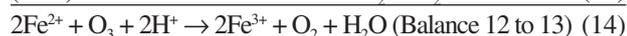
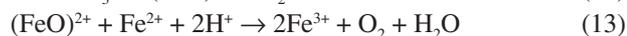
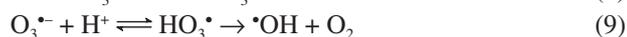
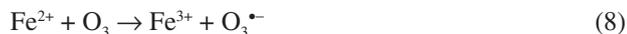
Hydroperoxide radical shows acid-base equilibrium (equation 2).¹²



The radical anion ozonide (O₃⁻) formed in the reaction between ozone and the superoxide radical anion (O₂⁻) quickly decomposes to form hydroxyl radicals. This formation of hydroxyl radicals may occur both in acid and alkaline media (equations 3 to 7).^{13,14}



Some studies¹⁵⁻¹⁷ show that Fe²⁺ catalyzes decomposition of O₃ to generate hydroxyl radicals following a distinct mechanism. In this case, the catalytic system O₃/Fe²⁺ involves direct reaction of Fe²⁺ with ozone. Equations 8 to 14 illustrate proposed reaction mechanisms of Fe²⁺ with ozone.¹⁸ Béltran *et al.*¹⁹ proposed reaction mechanisms between Fe^{III} and ozone with subsequent formation of hydroxyl radical, as shown in equation 15.



As shown in equations 8 to 15, the reaction mechanism is the transfer of electrons from the reduced metal to ozone,

forming Fe³⁺ ion and radical ion O₃^{•-} and so the hydroxyl radical. In the presence of excess Fe²⁺, hydroxyl radical can oxidize a second Fe²⁺ providing a stoichiometric ratio of 0.5 moles of ozone *per* mole of ferrous ion.¹⁸

Arslan²⁰ studied coagulation, ozonation and Fe²⁺ ions catalyzed ozonation (FeSO₄·7H₂O) in commercial textile dyes at different pH (3 to 13). The response variable was the percentage of color and chemical oxygen demand (COD) reductions. In the coagulation procedure, a range of Fe²⁺ concentrations (FeSO₄·7H₂O) from 0.25 to 5 g L⁻¹, at different pH values (3 to 13) was used. Largest reductions were obtained at pH 11 using 2.5 g L⁻¹ of FeSO₄·7H₂O, yielding 96.9% reduction in dye and 54% reduction of COD. At pH 3, color reduction was 72.9% and COD 6.5%, which is attributed to the fact that dyes tend to aggregate in alkaline medium, causing reduction in solubility and ionization. In the process of ozonation and catalytic ozonation, 3.5 g h⁻¹ of ozone mass flow was applied. After 10 min of ozonation and at different pH (3, 5, 8 and 11), in contradiction with coagulation experiments, the highest color and COD reductions were obtained at pH 3, with 77% color and 11% COD reduction, respectively. It should be pointed out that in an alkaline media, there is the decomposition ozone, occurring the formation of •OH radicals, waiting for an increase in the oxidation of pollutants. However, organic dyes, having polyaromatic structures and double bonds in their chromophoric groups, can react both in molecular pathway (acidic medium) as a radical •OH (alkaline medium). Considering the presence of acetic acid in the dye formulation, this will possibly compete with •OH alkaline solution, meaning that less •OH is available for dye oxidation. In the same study, ozonation tests were also conducted in the presence of Fe²⁺ ions as FeSO₄·7H₂O, applied in concentrations ranging from 0.025 to 1.0 g L⁻¹ at different pH (3 to 11). The color and COD removal efficiency was slightly higher in the presence than in the absence of Fe²⁺, showing the tendency to decrease with increasing pH, too. Increasing the concentration of Fe²⁺ to 0.5 and 1.0 g L⁻¹ at pH 3, showed an increase in the percentage of color and COD reductions. For 0.5 g L⁻¹ Fe²⁺ concentration, 76.2 and 25.2% color and COD reductions were observed, respectively. Increasing the concentration of Fe²⁺ to 1.0 g L⁻¹, 94.6 and 47.8% in color and COD reductions were achieved, respectively. However, it possibly works in alkaline medium using Fe²⁺ ions. COD and total organic carbon (TOC) removal rates do not depend only on catalyst, but also on the matrix to be treated.

Freire *et al.*²¹ applied the ozonation process for treating paper mill effluent by direct reaction (molecular ozone) and by indirect reaction (hydroxyl radical). These two processes were compared concerning TOC removal efficiency, total

phenols and effluent color. Sevimli and Kinaci²² compared the efficiency of Fenton process with ozonation and Fenton process concerning textile dyeing degradation. Balcioglu and Ötoker²³ compared pH and H₂O₂ concentration effect over the ozonation process, concerning COD efficiency removing of pharmaceutical effluents.

Some references found in literature compare the efficiency of the ozonation process in the degradation of different substrates via direct and indirect reaction. For this work, both acidic media (pH 4.0) and alkaline media (pH 10.0) were used.

This work aims an experimental design to evaluate the efficiency of a dairy effluent treatment system from a dairy industry, Cia. de Alimentos Glória, in the city of Guaratinguetá, state of São Paulo, Brazil. The technique used advanced oxidation processes with the use of catalytic ozonation, using Fe²⁺ as a catalyst in a recycling semi-batch process, besides a new reactor configuration due to the foam generated during the process.

This work aims a technological innovation since there is no scientific reference to scientific work about homogeneous catalytic ozonation in a semi-batch process with recycling for this type of effluent.

Experimental

Sampling and preservation

The effluent used was from the dairy industry Cia. de Alimentos Glória in the city of Guaratinguetá, São Paulo, Brazil. Samples were collected directly from the homogenizer tank of such industry in quantity enough to perform all of the experimental design planned; they were stored in plastic recipients and frozen down in order to minimize alteration in the physicochemical characteristics of the effluent. Analysis and experiments were conducted at Escola de Engenharia de Lorena (EEL-USP) in the Laboratories of Basic and Environmental Sciences Department (LOB) and Chemical Engineering Department (LOQ).

Methodology

A volume of 2 L of dairy effluent was used in each experiment, conditioned naturally to room temperature (23 ± 2 °C) before experiments. In order to minimize any intrinsic physicochemical alteration to this type of effluent, only the corresponding volume of effluent was thawed to be used in possible experiments of the day. After homogenizing the effluent, the volume was measured in a flask and transferred to a Becker. pH was adjusted

according to the experimental condition with commercial solutions of 98% m/m H₂SO₄ that were measured using a benchtop pHmeter. After the adjustment, the effluent was introduced to the reactor. After setting up all modules and adaptation of pumps and tubes, O₂ flow rate (99.50% of purity) for cylinder was adjusted using a valve according to each experiment. During this phase, the whole system was verified using only injection of O₂. Afterwards and concomitantly, the ozonator was started up at the specific power and the addition of FeSO₄·7H₂O began. This solution was previously solubilized with commercial 98% m/m H₂SO₄, being introduced to the reactor with a peristaltic pump during 20 min of the total reaction time according to design of experiment levels. Concomitantly, the aeration of the system was initiated for foam formation reduction.

In general, homogeneous catalytic ozonation application should be associated with some technique for the removal of metallic ions from the treated effluent. Toxic character of some metals may restrict the application of this type of process. Furthermore, the presence of ions like iron, although less dangerous from a toxicological point of view, may be associated with undesirable effects, such as the arising of blemishes in clothes, as well as an unpleasant taste and odor in water.¹¹

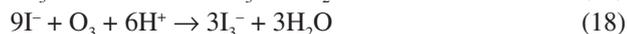
Liquid foam was drained into a reservoir that could be recycled to the oxidative process through a pulse peristaltic pump (started up at the beginning of the process), without compromising the initial volume of the reactor. With a gradual reduction of foam formation during the rest of the reaction, the air pump was shut down at the last 10 min of the process. After 30 min of reaction, an aliquot (30 mL) was taken to perform TOC analysis. It is imperative to explain that prior to TOC analysis, considering the heterogeneous catalysis, the final product (obtained after oxidation process) was filtered and pH was conditioned in an acidic media. Considering the homogeneous catalysis, the final product was conditioned in alkaline solution for Fe precipitation, and then, pH was conditioned in an acidic media.

Organic carbon determinations were carried out using a total organic carbon Shimadzu analyzer, model TOC-VCPH, based on the catalytic oxidation at high temperatures.

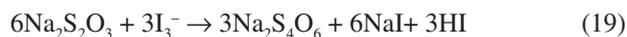
In the determination of TOC, the analytical curve of non-purgeable organic carbon (NPOC) was prepared using a standard solution of potassium biphthalate, linear range 0-1000 mg L⁻¹. To the TOC determinations, samples were diluted with deionized water according to their concentrations. Samples were prepared between pH 2.9 to 3.1, without any precipitate and after homogenization they were injected in the combustion chamber of the equipment of TOC determination.

Quantification of O₃ mass flow

Iodometric titration was used to quantify the concentration of O₃ that was bubbled in a KI solution in sulfuric medium that consists in an indirect titration process. The end point for titration was obtained using amido gum as an indicator.²⁴ The formation of tri-iodine ion (I₃⁻), stable and soluble reactional product, which possesses the same number of equivalents than ozone, was obtained as shown in equations 16 to 18.



The concentration of tri-iodine was dosed by using a standard solution of sodium thiosulfate as shown in equation 19.



It is relevant to emphasize that the combination among ozonator power and O₂ flow rate did not show linearity, and thus, the O₃ mass flow rate (mg min⁻¹) was quantified in all experiments of the experimental matrix. It was quantified the O₃ that was injected in the reactor, before the contact with the effluent. So, the products of the effluent do not interfere with this quantification.

Configuration of semi-batch reactor with recycle to the catalytic ozonation process of dairy effluent

The reactor used in this work was developed after some exploratory experiments. From an operational point of view, it is worth to emphasize that the configuration developed in this work gives the possibility to use the reactor under different systems: batch, semi-continuous with recycle and continuous one.

The reactor used in this work was idealized aiming effluent treatment that, besides promoting oxidation of organic matter, would concomitantly eliminate the foam formed during the treatment, without compromising the process or influencing the kinetics of degradation. The reactor was projected in borosilicate glass that can be operated in a batch or a continuous process (Figure 1). It consists of three main modules: reactor, cone (foam separator) and reservoir.

The inferior part of the reactor is 0.42 m high and of 0.10 m internal diameter with volumetric capacity of 4.0 L supported by a wooden base.

The oxidation process of the organic matter is carried out in the reactor (1). It consists, in all its extension, of a

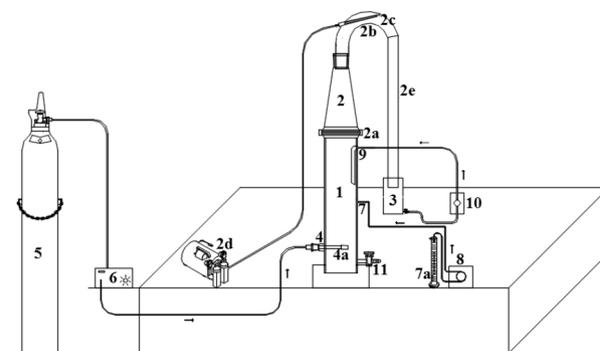


Figure 1. Components of the reactor: (1) reactor, (2) cone (foam separator) and (3) reservoir.

cylinder shape and that is where the input of O₂ + O₃ (4) from the ozonator (6), catalytic solution (7a), effluent feed (7) and sampling (11) occurs.

The O₂ + O₃ input is done at the base of the reactor (4) by micro-bubbles, using an air-stone (4a) for better adsorption of O₂ + O₃ and homogenization of oxidative system. The oxygen of the O₂ cylinder (5) is converted into ozone by the method of electric discharge that occurs in the ozonator, taking into account that the input is done at the inferior part of the reactor allowing an ascending flow.

The entry of the catalytic solution (7) is done at the opposite side of the O₂ + O₃ flow. The catalytic solution (7a) is previously prepared in sulfuric medium and introduced to the reactor by peristaltic pump (8) that is activated 10 s after the ozone input and remains active for 20 min of the whole reaction time of 30 min.

The effluent recycle entry, after the disruption of foam, is processed by the entry (9) through a pulse pump (10).

Sampling (11) was carried out manually with a kind of an open/close glass valve that allows fast sampling and closure of the system, without interference.

Module (2) is in the shape of a cone and it is attached to the reactor by a metal clip strap (2a). This is composed of a glass tube (2b) curved at 180°. This tube is comprised of an internal capillary tube with a narrower end (2c), projected in favor of the flow, in which atmospheric air is introduced by a centrifuge pump with the function of disrupting superficial tension of the foam (2c). The curved end of the tube allows a perfect fit to a hose (2e) for the transportation of effluent to the third module (3) (reservoir) that is connected to a pulse pump (10). This projects the liquid back to the reactional system through the entry (9) as recycling, completing the cycle of configuration of the reactor.

Experimental design for the degradation of the dairy effluent

In order to optimize the parameters to be tested, a 2⁴⁻¹ fraction type of factorial statistical design was carried

out, randomly, in duplicate with 3 central points, being the response variable the percentage of reduction of total organic carbon (TOCred) after 30 min of reaction. The independent variables (factors) proposed for this stage were ozonator power, O₂ flow rate of the cylinder, Fe²⁺ concentrations and pH. Table 1 shows the variables with respective evaluated levels.

Table 1. Factors and levels for the treatment of 2 L of the effluent during 30 minutes

Factor	Symbology	Level		
		(-1)	(0)	(+1)
Power / W	A	30	33	35
Flow rate O ₂ / (L min ⁻¹)	B	0.5	0.25	0.125
[Fe ²⁺] in the effluent / (g L ⁻¹)	C	0.5	0.75	1.0
pH	D	4.0	7.0	10.0

Estimate values of ozonator power were determined by experimental measurement using a power and energy consumption measuring equipment (ICEL, model ME-2500, 220 V and 60 Hz, conformity certifying number 201111011512). Feeding the ozone generator was carried out by using oxygen gas of high nominal purity of 99.50% and a valve attached to the cylinder with an adjustment from 0 to 2 L min⁻¹. Fe²⁺ concentrations were 0.5, 0.75 and 1.0 g L⁻¹, corresponding to 5.03, 7.55 and 10.06 g of FeSO₄·7H₂O with 99.0% of purity for 2 L of effluent.

After evaluating better experimental conditions, the physically and chemically treated product was analyzed to verify if the quality was in accordance with discharge limits to hydric bodies or if it should undergo a biological treatment as activated sludge treatment.

Results and Discussion

Analytic characterization of effluent *in natura*

Table 2 shows the results from the physicochemical characterization of the effluent *in natura* of the studied industry, along with data from pertinent legislation of discharge in hydric bodies: Article 18 of Environmental Control Agency of São Paulo State (CETESB),²⁵ an environmental agency in the State of São Paulo, Brazil, Resolution 357/05 of National Council of Environment (CONAMA)²⁶ and CONAMA Resolution 430/11 that complements and changes 357/05.²⁷

According to Table 2, there is a great variation in the analyzed parameters, which can be explained by different cleaning processes, physical and chemical characteristics of raw materials and processing type of products. The

variation is related to the collections made during the experimental period, not only in one day.

The dairy effluent is characterized as a white color type of effluent due to the physicochemical characteristics. The cleaning system “clean in place” (CIP), in which acidic and alkaline solutions are added, carries this cleaning water to the treatment plant resulting in a pH that can range from 2.0 to 12.0 in the homogenizer tank.³⁰

Gases produced by the fermentation of anaerobic bacteria cause the odor; suspended solids and/or emulsifiers cause turbidity. Suspended solids are derived from milk coagulants. The loss of fat from milk that corresponds to 90% of total fat material of the effluent,³¹ also contributes to the high concentration of solids.

The presence of nitrogen is related to high content of proteins but since milk is diluted in the cleaning process, this value is found under the limits of legislation concerning discharge in hydric bodies.

Although COD does not appear as one of the parameters of discharge in waters it is a factor of extreme importance for aiding in the determination of recalcitrance of a compound in relation to biochemical oxygen demand (BOD), indicating its biodegradability.³²⁻³⁴ High values of COD are due to substances present in the milk; spills, leaks, deficient operations of equipment, overload of tanks and loss in the process also contribute to the increase of concentration of the organic matter of the effluent.³⁵

Another important parameter to be analyzed is the relation between biochemical oxygen demand after five days incubation and chemical oxygen demand (BOD₅/COD) in which an estimate of biodegradability can be inferred.³²⁻³⁴ As in BOD, only the biodegradable fraction can be measured, the higher this value is close to COD, the easier the effluent can be biodegraded.^{36,37}

Raw liquid effluents of dairy industries show mean values of BOD₅/COD in the range of 0.50 to 0.70.⁴ The ratio BOD₅/COD has been used by several researchers to express biodegradability of effluents of environmental relevance, being used as a parameter in the selection of type of effluent treatment. According to results from raw effluents, the mean ratio of BOD₅/COD was 0.85. After the treatment by catalytic ozonation, this ratio reached the value of 1.27. The increase in BOD₅/COD obtained suggests that the chemical process may be used as a pre-treatment in order to improve biodegradability of the effluent. According to Balcioglu and Ötörker²³ the most biodegradable fraction of an effluent may be increased by ozonation, since it leads to formation of low molecular weight by-products that are readily biodegraded.

Thus, the use of biological processes for this type of effluent can be justified, something that had already been taken into account by the company. Although activated

Table 2. Physical and chemical characteristics of the effluent *in natura*

Parameter	Effluent <i>in natura</i>	Methodology ²⁸	LOQ ²⁹	CETESB (Article 18) ²⁵	CONAMA (357/05) ²⁶ and (430/11) ²⁷
True color (Pt-Co)	39.0-46.0	SM 2120 C Spectrophotometric method	3.0	–	75
pH	5.0-11.0	Potentiometric method	–	5.0-9.0	5.0-9.0
Turbidity / NTU	39.23-45.7	SM 2130 B Nephelometric method	0.1	–	100
COD / (mg O ₂ L ⁻¹)	2100-2800	SM 5220 D Closed reflux, colorimetric method	3.0	–	–
BOD ₅ / (mg O ₂ L ⁻¹)	1800-2300	SM 5210 D Respirometric method	0.5	Up to 60% or minimal removal of 80%	Minimal removal of 60%
TOC / (mg L ⁻¹)	470-790	Catalytic combustion with detection by infrared spectroscopy	3.0	–	–
N-NH ₃ / (mg L ⁻¹)	4.56-6.30	SM 4500 B Preliminary distillation step and spectrophotometric method (Nessler)	0.05	–	20.0
N-Organic / (mg L ⁻¹)	6.78-7.36	SM 4500 B Preliminary reduction of the N and distillation step and spectrophotometric method (Nessler)	–	–	–
Phosphorus / (mg L ⁻¹)	7.15-11.05	ICP-OES	0.005	–	0.02
ST / (mg L ⁻¹)	2700-2910	SM 2540 B Total solids	2.0	–	–
STF / (mg L ⁻¹)	1900-2105	SM 2540 G Total, fixed and volatile solids	2.0	–	–
STV / (mg L ⁻¹)	800-805	SM 2540 G Total, fixed and volatile solids	2.0	–	–
Surfactant / (mg L ⁻¹)	0.71-1.58	SM 5540 C Anion surfactants as MBAS	0.03	–	–
Oil and grease / (mg L ⁻¹)	2100-2290	SM 5520 DE Soxhlet extraction method	5.0	100	50

–: Not specified; LOQ: limit of quantification; COD: chemical oxygen demand; BOD₅: biochemical oxygen demand after five days incubation; TOC: total organic carbon; N-NH₃: ammoniacal nitrogen; N-organic: organic nitrogen; ST: total solids; STF: fixed total solids; STV: volatile total solids; surfactant: extracted with chloroform and methylene blue in a separation funnel and determined by visible spectrophotometry at 655 nm; oil and grease: determined by solvent extraction method (Soxhlet method); SM: standard methods; ICP-OES: inductively coupled plasma optical emission spectrometry; MBAS: methylene blue active substances.

sludge process is widely used, it can be observed that in several visits to the company there was a strong and characteristic odor, high sludge production, consumption of nutrients and hydraulic retention time in the effluent treatment.

Besides all of the above mentioned, biological processes have some limitations, as a narrow range of optimal conditions (pH, temperature, nutrient concentration, residence time). Among several other restrictions, it can be cited the inability of biological processes to metabolize recalcitrant compounds.³⁸

Several studies have been conducted in order to develop technologies that minimize industrial effluents volume and toxicity, aiming to allow not only the removal of contaminant substances, but also the complete mineralization. Toxicity associated with industrial effluents may be intimately associated with the presence of recalcitrant or refractory compounds.³⁹

Recalcitrant or refractory compounds are not biodegraded by organisms that normally exist in treatment of biological systems, considering hydraulic retention times usually applied. However, they are frequently disposed on aquatic bodies.¹¹

In this situation, chemical processes appear as a promising alternative for degradation of these pollutant chemical species.⁴⁰

For the parameter oils and fat, it can be observed that its concentration is high due to the content of fat present in the raw effluent from processed raw material and the process adopted by industry.³¹

Evaluation of experimental matrix and TOCred in the design of semi-batch process with recycle

With the purpose of increasing efficiency in the ozonation reactions, especially in the removal of

organic matter with ozone consumption inferior to the direct ozonation, the catalytic process was used. Some considerations have to be taken into account, however, as for the employment of catalytic process: (i) solubility of catalyst in the reactional media; (ii) difficulty in reusing the catalyst used; (iii) need of using ion removal techniques due to its toxic characteristics and/or unwanted adverse effects.¹¹

Ferrous ions were selected as catalysts for this work. Therefore, there is no definition of the type of catalysis of the process because in acidic pH, ferrous ions are soluble (homogeneous), but in pH 7 and 10, there is a formation of a product less soluble with Fe²⁺ ion (heterogeneous). The maximum concentration of Fe²⁺ in this work was 1.0 g L⁻¹, because in higher concentrations it was verified a little reduction on the percentage of TOC reduction (TOCred).

The maximum power of the ozonator in this work was 35 W. There was a notorious and characteristic odor of ozone when pure oxygen from the cylinder was used. This could be determined qualitatively by O₃ indicator paper that darkened quickly under power higher than 35 W. Maximum and minimum flow rates were inverted during the treatment, being the flow rate at the low level of 0.5 L min⁻¹ and high level of 0.125 L min⁻¹, which does not compromise the statistical evaluation of the process. To this extent, atmospheric air was injected through a silicon hose attached to the tube containing a capillary tube, enabling the disruption of superficial tension of the foam. In all

experiments and at the first 10 min of oxidation reaction, there was an intense formation of foam, possibly based on the fast degradation and respective mineralization of effluent to CO₂. Some different causes may be considered to explain this foam formation. The wastewater may contain various substances used for cleaning equipment and factory items, such as alkaline phosphates, acids, surfactants and complexing compounds.⁴¹ The presence of large quantities of O₂ + O₃ could also enhance the foam formation. Furthermore, the foam formation could be favored by the fast degradation and respective mineralization of effluent to CO₂. However, hypotheses investigation were not performed in this work.

Table 3 presents the percentage of TOCred and mass ratio of O₃ by oxidized carbon.

Overall, it was observed that replicates showed low deviation, which indicates good repeatability and good control of random errors.

An analysis based on results showed that the best average for TOCred (61.29%) was obtained with experiments in duplicate 1 and 19, suggesting that the ozonator power (A) must work at its highest level (35 W), O₂ flow rate (B) must be at 0.125 L min⁻¹, Fe²⁺ concentration (C) in 0.5 g L⁻¹ of effluent and pH (D) 4.0.

Due to the ozonator power and O₂ flow rate, the average ozone mass rate could be determined for the experimental design, being the O₃ mass rate of duplicates 1 and 19 (3.85 mg min⁻¹). The best result for the O₃ mass relation

Table 3. Percentage of TOCred and O₃/oxidized carbon mass ratio

Experiment	Factor ^a				Mass O ₃ flow / (mg min ⁻¹)	TOCred / %	mg O ₃ /mg C _{oxid.}
	A	B	C	D			
1	+1	+1	-1	-1	3.85	61.26	0.09
19	+1	+1	-1	-1		61.32	0.09
2	+1	-1	+1	-1	7.26	56.91	0.23
13	+1	-1	+1	-1		55.89	0.24
3	0	0	0	0	4.32	55.70	0.12
8	0	0	0	0		56.36	0.13
15	0	0	0	0		56.31	0.12
4	-1	+1	-1	+1	2.36	45.97	0.08
17	-1	+1	-1	+1		46.26	0.08
5	+1	+1	+1	+1	3.85	55.84	0.11
10	+1	+1	+1	+1		55.28	0.12
6	-1	-1	+1	+1	4.38	49.37	0.15
7	-1	-1	+1	+1		50.20	0.14
9	-1	-1	-1	-1	4.38	55.55	0.14
12	-1	-1	-1	-1		56.01	0.14
11	+1	-1	-1	+1	7.26	44.90	0.28
16	+1	-1	-1	+1		44.56	0.28
14	-1	+1	+1	-1	2.36	51.07	0.08
18	-1	+1	+1	-1		51.46	0.08

^aA: Power (W); B: O₂ flow rate (L min⁻¹); C: [Fe²⁺] in the effluent (g L⁻¹); D: pH.

by carbon degraded (TOC) was 0.09, which indicates that the ozonator power and O₂ flow rate selected were pertinent to the proposed process. Considering economical and safety aspects, it is important because O₃ in excess can compromise the process.

It is not possible just through the analysis of the results of Table 3 to evaluate and optimize the best experimental conditions. However, all of the TOCred reduction responses were assessed for statistical analysis generated by Minitab 16.

First, the graphic of probabilities of percentage reduction of each output variable (TOCred) was generated, to verify the normality of experimental data of this planning. Figure 2 shows the graph of normal probability in terms of percentage of TOCred. The points in the figure correspond to the 19 experiments of the exploratory factorial matrix fractional 2⁴⁻¹, conducted in duplicate with three central points.

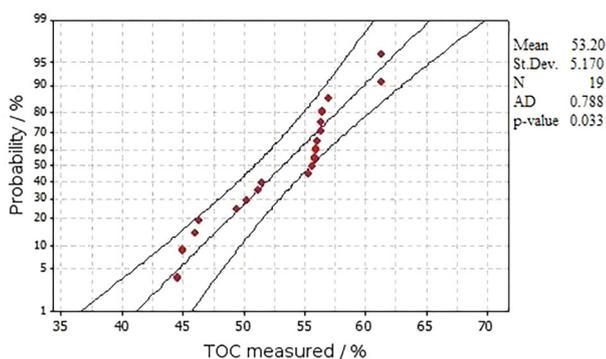


Figure 2. Normal probability on percentage of TOCred, considering 95% confidence interval.

It can be seen in Figure 2 that the graph does not follow a normal distribution with a *p*-value of 0.033. Even though data is aligned, 95% of data points are within the limit of experimental error for a 95% level, showing confidence to experiments. The various effects of variables may be seen

Table 4. Analysis of variance from the mean values of percentage reduction in TOCred array 2⁴⁻¹ for the treatment of dairy wastewater by catalytic ozonation

Term	Effect	Coef	SE Coef	T	<i>p</i> -value
Constant	–	52.616	0.09037	582.24	0.000
Power	3.759	1.879	0.09037	20.80	0.000
Flow O ₂	1.884	0.942	0.09037	10.42	0.000
[Fe]	1.274	0.637	0.09037	7.05	0.000
pH	–7.136	–3.568	0.09037	–39.48	0.000
Power × Flow O ₂	5.976	2.988	0.09037	33.07	0.000
Power × [Fe]	1.696	0.848	0.09037	9.39	0.000
Power × pH	–1.564	–0.782	0.09037	–8.65	0.000

%TOCred = (Constant) + (Coef × Power) + (Coef × Flow) + (Coef × [Fe]) + (Coef × pH) + (Coef × Power × Flow) + (Coef × Power × [Fe]) + (Coef × Power × pH).

in Figure 3 and Table 4 (analysis of variance, ANOVA) and in Figure 4 (Pareto chart).

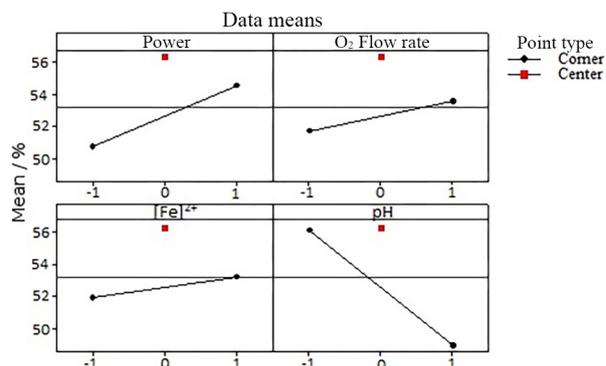


Figure 3. Main effects for percentage of TOCred variation measurements.

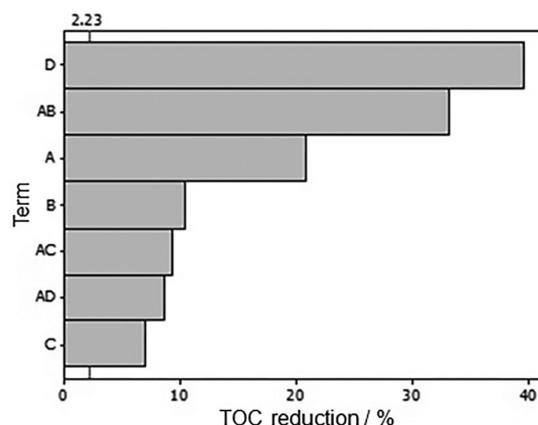


Figure 4. Pareto chart of the standardized effects considering $\alpha = 0.05$. (A) Ozonator power; (B) O₂ flow; (C) Fe²⁺ concentration and (D) pH.

Figure 3 shows the main effects of parameters for percentage of TOCred. It can be seen that for the highest percentage of TOCred, the best condition is found with factors A, B and C adjusted in the central point (33 W; 0.25 L min⁻¹ and 0.75 g Fe²⁺ L⁻¹ respectively), while D factor was at low level (pH 4.0).

The analysis of variance consists in a group of statistical models such as least squares for the evaluation of total sample variance that can be attributed to different factors of experimental error. Figure 3 shows that the best and highest percentage of TOCred is working with the power flow, and $[\text{Fe}^{2+}]$ at the central point, or 33W power, the O_2 flow rate 0.25 L min^{-1} and $[\text{Fe}^{2+}] 0.75 \text{ g L}^{-1}$ effluent, obtaining reductions getting TOCred above 56%.

Table 4 presents factors of analysis of variance (ANOVA) involved in the catalytic ozonation process.

Through ANOVA (Table 4), it can be observed that all studied variables were significant on the studied process with p -value, which is approximately zero (since we showed only three digits on the table, it appears as being "0.000"). A p -value ranges from 0 to 1. The p -value is calculated from the observed sample and represents the probability of incorrectly rejecting a null hypothesis that is true indeed (type I error). Minitab 16 automatically displays p -values for most hypothesis tests. These results were also confirmed by a Pareto diagram with 95% confidence, presented in Figure 4.

To the variable response TOCred, the factor power (A) was more significant than the interaction power-iron (AC) which indicated that the direct ozonation is more reoccurring.

Based on the design of experiment used, a statistical model was proposed in order to predict the behavior of the catalytic ozonation process. Equation 20 represents the model obtained (considering ANOVA in Table 4), having the response factor percentage of TOCred.

$$\begin{aligned} \% \text{ TOCred} = & 52.616 + 1.879 \times [\text{Power}] + 0.942 \times \\ & [\text{Flow}] + 0.637 \times [\text{Fe}] + (-3.568) \times [\text{pH}] + 2.988 \times \\ & [\text{Power} \times \text{Flow}] + 0.848 \times [\text{Power} \times \text{Fe}] + (-0.782) \times \\ & [\text{Power} \times \text{pH}] \end{aligned} \quad (20)$$

The mathematical model obtained does not demonstrate lack of adjustment and presents an R^2 of 99.73% of variations around the mean. Therefore, the optimization of variables can be found at power (35 W), O_2 flow rate (0.125 L min^{-1}), Fe^{2+} concentration (1.0 g L^{-1}) and pH (4.0), with 64.26% of TOCred.

The best experiment with variables at the optimized level were carried out obtaining a mean value (triplicate) of 64.03% in the TOCred, which is close to the theoretical one, 64.26%.

Economic evaluation of semi-batch process with recycle

Estimate values of energetic consumption of equipment were determined by experimental measurement considering the time of 30 min. Table 5 shows the estimated cost of experiments for the experimental planning used.

Overall, Table 5 shows that the best result of the process is also the one with lower cost/TOCred ratio. As it can be observed in experiments 1 and 19 of design 2^{4+1} , in which the mean was 61.29% of degradation of TOCred concentration and its cost/TOCred ratio (0.50), the ratio is the lowest of all the other experiments.

According to the statistical modelling, the optimization of variables shows 64.03% of TOCred with a cost of US\$ 0.03644 L^{-1} of effluent, in which the change happens only with the Fe^{2+} concentration factor. Even with the change in ferrous concentration, the estimate is relatively the same (US\$ 0.03 L^{-1} of treated effluent), being the best cost/TOCred ratio of the catalytic ozonation process the one in which optimized variable conditions were ozonator power (35 W), O_2 flow rate (0.125 L min^{-1}), Fe^{2+} concentration (1.0 g L^{-1}) and pH (4.0).

Loures *et al.*⁴⁴ carried out a study of the application of photo-Fenton process followed by a biological treatment in

Table 5. Values of energy consumption and reagents *per* liter of dairy effluent treated by catalytic ozonation process of duplicate and triplicate experiments

Experiment	Factor level				Energy consumption / (US\$ L^{-1})	Reagent consumption / (US\$ L^{-1})	Total value / (US\$ L^{-1})	Mean TOC reduction / %	Ratio US\$/% reduction ($\times 10^3$)
	A	B	C	D					
1 and 19	+1	+1	-1	-1	0.00253	0.02831	0.03084	61.29	0.50
2 and 13	+1	-1	+1	-1	0.00253	0.09943	0.10195	56.40	1.80
3, 8 and 15	0	0	0	0	0.00223	0.05256	0.05479	56.12	0.97
4 and 17	-1	+1	-1	+1	0.00193	0.02762	0.02955	46.11	0.64
5 and 10	+1	+1	+1	+1	0.00253	0.03323	0.03575	55.56	0.64
6 and 7	-1	-1	+1	+1	0.00193	0.09874	0.10067	49.78	2.02
9 and 12	-1	-1	-1	-1	0.00193	0.09382	0.09575	55.78	1.71
11 and 16	+1	-1	-1	+1	0.00253	0.09313	0.09566	44.73	2.14
14 and 18	-1	+1	+1	-1	0.00193	0.03392	0.03585	51.26	0.70

US\$ 1.00 = R\$ 2.576;⁴² 1 kWh = US\$ 0.11837.⁴³

dairy effluents. Best experimental conditions had percentage of TOCred as response variable and they were: temperature at 30 °C; pH 5.0; concentration of peroxide of 0.255 mol L⁻¹; Fe²⁺ concentration of 0.0108 mol L⁻¹; UV irradiation of 15 W and time of 60 min. Under these conditions, they obtained 54.96% of TOCred. Results showed high efficiency with biological treatment after the AOP where COD, BOD₅ and TOCred were 91, 74 and 91%, respectively. The total estimate cost of photo-Fenton treatment was US\$ 0.0893 L⁻¹ of effluent with a cost/TOCred ratio of 1.62.

Salazar and Izário Filho⁴⁵ studied the heterogeneous photocatalytic process to reduce the organic matter of dairy industry effluent. Titanium dioxide (TiO₂) was used as the semiconductor with solar radiation. Best conditions of the treatment step having percentage of reduction of COD were: time of reaction of 180 min, TiO₂ anatase and pH 5.0 obtaining 54.77% of COD reduction.

In addition, Samanamud *et al.*⁴⁶ studied the heterogeneous photocatalytic process on dairy effluent treatment. In this study, ZnO was employed as the semiconductor using solar radiation. Degradation was measured in terms of percentage of TOCred, the highest efficiency was found at pH 8.0 with a TOCred of 14.23% of degradation with a reaction time of 180 min. The photocatalytic treatment had an estimate cost of US\$ 0.0055 L⁻¹ of effluent, but with a cost/TOCred ratio of 0.39.

It can be observed that in the heterogeneous catalysis with UV radiation, the reaction time to obtain a significant reduction of organic content is higher when compared to homogeneous catalytic processes.

Conclusions

The designed reactor showed efficiency in disrupting the superficial tension of foam, without compromising the volume, and, possibly, the kinetics of the reaction.

The optimization of the variables of the process via mathematical model showed a TOCred of 64.03%, ozonator power of 35 W, O₂ flow rate of 0.125 L min⁻¹, Fe²⁺ concentration of 1.0 g L⁻¹ and pH 4.0, with an estimate cost of US\$ 0.03 L⁻¹ of effluent.

The treatment performed was insufficient to guarantee direct discharge to superficial water. However, significant reduction in TOCred concentration makes that the chemically treated product (catalytic ozonation with ferrous ion), with significant cost/TOCred ratio, shows better characteristics prior undergoing a biological treatment, reducing hydraulic retention time, risk of overloading and oscillations in the organic matter content. However, other characteristics, as pH and residual ozone should be considered, too.

Acknowledgements

The authors thank Cia. de Alimentos Glória, Guaratinguetá, São Paulo for the dairy effluent sample provided for this work, as well as the laboratories used for this study. Likewise, thanks to the Coordinating Agency for Advanced Training of Graduate Personnel (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES) for financial support of this Master's study. FAPESP Process 2009/17650-2.

References

1. Vourch, M.; Balannec, B.; Chaufer, B.; Dorange, G.; *Desalination* **2008**, *219*, 190.
2. Nirenberg, L. P.; Ferreira, O. M.; *Tratamento de Águas Residuárias de Indústria de Laticínios: Eficiência e Análise de Modelos Matemáticos do Projeto da Nestlé*; Goiania: Universidade Católica de Goiás, 2005, 18 p.
3. Cammarota, M. C.; Freire, D. M. G.; *Bioresour. Technol.* **2006**, *97*, 2195.
4. Machado, R. M. G.; Freire, V. H.; Silva, P. C.; Figuerêdo, D. V.; Ferreira, P. E.; *Controle Ambiental nas Pequenas e Médias Indústrias de Laticínios*, 1ª ed.; Segrac: Belo Horizonte, 2002, p. 223.
5. Rey, A.; Faraldos, M.; Casas, J. A.; Zazo, J. A.; Bahamonde, A.; *Appl. Catal., B* **2009**, *86*, 69.
6. Ferreira, I. V. L.; Daniel, L. A.; *Eng. Sanit. Ambiental* **2004**, *9*, 335.
7. Moraes, J. L.; Sirtori, C.; Peralta-Zamora, P. G.; *Quim. Nova* **2006**, *29*, 20.
8. Bacioglu, I. A.; Arslan, I.; *Water Sci. Technol.* **2001**, *43*, 221.
9. Kasprzyk-Hordern, B.; Ziólek, M.; Nawrocki, J.; *Appl. Catal., B* **2003**, *46*, 639.
10. Von, G. U.; *Water Res.* **2003**, *37*, 1443.
11. Assalin, M. R.; Durán, N.; *Analytica* **2007**, *26*, 76.
12. Beltrán, F. J.; *Ozone Reaction Kinetics for Water and Wastewater Systems*; Lewis Publishers: Boca Raton, 2004, p. 358.
13. Langlais, B.; Reckhow, D. A.; Brink, D. R.; *Ozone in Water Treatment: Application and Engineering*; 1st ed.; Lewis Publishers: Chelsea, 1991, p. 569.
14. Hoigne, J.; Bader, H.; *Water Res.* **1976**, *10*, 377.
15. Sauleda, R.; Brillas, E.; *Appl. Catal., B* **2001**, *29*, 135.
16. Piera, E.; Calpe, J. C.; Brillas, E.; Doménech, X.; Peral, J.; *Appl. Catal., B* **2000**, *27*, 169.
17. Arslan, I.; Balcioglu, I. A.; Tuhkanen, T.; *Water Sci. Technol.* **2000**, *42*, 13.
18. Legube, B.; Leitner, N. K. V.; *Catal. Today* **1999**, *53*, 61.
19. Béltran, F. J.; Rivas, F. J.; Gimeno, O.; *J. Chem. Technol. Biotechnol.* **2005**, *80*, 973.
20. Arslan, I.; *J. Hazard. Mater.* **2001**, *B85*, 229.

21. Freire, R. S.; Kubota, L. T.; Durán, N.; *Environ. Technol.* **2001**, *22*, 897.
22. Sevimli, M. F.; Kinaci, C.; *Water Sci. Technol.* **2002**, *45*, 279.
23. Balcioglu, I. A.; Ötoker, M.; *Chemosphere* **2003**, *50*, 85.
24. Vogel, A. I.; *Vogel's Qualitative Inorganic Analysis*, 7th ed.; Prentice Hall, Englewood Cliffs, 1996, p. 300.
25. Environmental Control Agency of São Paulo State (CETESB); *Prevenção e o Controle da Poluição do Meio Ambiente*, Decreto No. 8,468, de 8 de Setembro de 1976, Artigo 18, <http://www.cetesb.sp.gov.br/Institucional/documentos/Dec8468.pdf> accessed in April 2015.
26. Ministério do Meio Ambiente, Conselho Nacional do Meio Ambiente (CONAMA); *Dispõe sobre a Classificação dos Corpos de Água e Diretrizes Ambientais para o seu Enquadramento, bem como Estabelece as Condições e Padrões de Lançamento de Efluentes, e dá outras Providências*, Resolução No. 357 de 17 de Março de 2005, <http://www.mma.gov.br/port/conama/res/res05/res35705.pdf> accessed in April 2015.
27. Conselho Nacional do Meio Ambiente (CONAMA); *Dispõe sobre Condições e Padrões de Lançamento de Efluentes, Complementa e Altera a Resolução No. 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente - CONAMA*, Resolução No. 430 de 13 de maio de 2011, <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646> accessed in April 2015.
28. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF); *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; APHA: Washington, D.C., 1998.
29. Thompson, M.; Ellison, S. L. R.; Wood, R.; *Pure Appl. Chem.* **2002**, *74*, 835.
30. Tetra Pack; *Dairy Processing Handbook*; Tetra Pack Processing System AB: Lund, 1995, <https://www.docenti.unina.it/downloadPub.do?tipoFile=md&id=282957> accessed in April, 2015.
31. Hansen, A. P.; Saad, S.; Jones, V. A.; Carawan, R. E.; *J. Dairy Sci.* **1977**, *59*, 1222.
32. Malato, S.; Blanco, J.; Richter, C.; Fernández, P.; Maldonado, M. I.; *Sol. Energy Mater. Sol. Cells* **2000**, *64*, 1.
33. Malato, S.; Blanco, J.; Fernandez-Alba, A. R.; Aguera, A.; *Chemosphere* **2000**, *40*, 403.
34. Reuschenbach, P.; Pagga, U.; Strotmann, U.; *Water Res.* **2003**, *37*, 1571.
35. Tommaso, G.; Ribeiro, R.; Oliveira, C.; Stamatelatos, K.; Antonopoulou, G.; Lyberatos, G.; Hodúr, C.; Csanadi, J. In *Novel Technologies in Food Science: Their Impact on Products, Consumer Trends and the Environment*; Sobral, P. J. A.; McElhatton, A., eds.; Springer: New York, 2011, p. 381.
36. Hu, Z.; Grasso, D. In *Encyclopedia of Analytical Science*, 2nd ed.; Worsfold, P.; Poole, C., eds.; Elsevier: Oxford, 2005.
37. Aquino, S. F.; Silva, S. Q.; Chernicharo, C. A. L.; *Eng. Sanit. Ambiental* **2006**, *11*, 295.
38. Freire, R. S.; Pelegrini, R.; Kubota, L. T.; Durán, N.; Peralta-Zamora, P.; *Quim. Nova* **2000**, *23*, 504.
39. Almeida, E.; Assalin, M. R.; Rosa, M. A.; Durán, N.; *Quim. Nova* **2004**, *27*, 818.
40. Álvares, A. B. C.; Diaper, C.; Parsons, S. A.; *Environ. Technol.* **2001**, *22*, 409.
41. Chipasa, K. B.; Mechzyeka, K.; *J. Ind. Microbiol. Biotechnol.* **2006**, *33*, 635.
42. <http://economia.uol.com.br/cotacoes/noticias/redacao/2014/12/02/dolar-sobe-067-e-atinge-r-2576-apesar-de-atuacao-do-banco-central.htm> accessed on December, 2014.
43. <http://www.aneel.gov.br/493.htm> accessed on December 8, 2014.
44. Loures, C. C. A.; Izário Filho, H. J.; Samanamud, G. R. L.; Souza, A. L.; Salazar, R. F. S.; Peixoto, A. L. C.; Guimarães, O. L. C.; *Int. Rev. Chem. Eng.* **2013**, *5*, 280.
45. Salazar, R. F. S.; Izário Filho, H. J.; *Augm Domus* **2009**, *1*, 27.
46. Samanamud, G. L. R.; Loures, C. C. A.; Souza, A. L.; Salazar, R. F. S.; Oliveira, I. S.; Silva, M. B.; Izário Filho, H. J.; *Int. Rev. Chem. Eng.* **2012**, *2012*, 1.

Submitted: January 26, 2015

Published online: May 12, 2015

FAPESP has sponsored the publication of this article.