International Scholarly Research Network
ISRN Chemical Engineering
Volume 2012, Article ID 275371, 8 pages
doi:10.5402/2012/275371

Research Article

Heterogeneous Photocatalytic Degradation of Dairy Wastewater Using Immobilized ZnO

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Received 4 June 2012; Accepted 16 July 2012

Academic Editors: M. A. Oturan and I. Poulios

This work evaluated the efficiency and systemic application of heterogeneous photocatalytic degradation for dairy wastewater under advanced oxidation process (AOP) utilizing solar radiation and immobilized ZnO as measured by total organic carbon (TOC). The AOP system consisted of a semibatch reactor and glass tank operated with an initial volume of 3 L of dairy wastewater. ZnO was immobilized on a metal plate of 800×250 mm and used as a catalyst bed. Evaporation rate was considered when effective degradation of the photocatalytic system was determined. The AOP utilized Taguchi's L_8 orthogonal array. The entry variables were pH, reaction time, initial organic load in the effluent, and ZnO coating thickness on the catalyst bed. When optimized, an effective TOC degradation of 14.23% was obtained under variable values of pH 8.0, a metal-plate coating of 100 micrometers (μm) ZnO, and total reaction time of 180 min.

1. Introduction

Among food industries, the dairy industry produces the greatest volume of pollutants (generating 2.5 L of effluent per liter of processed milk) largely attributable to the elevated amounts of water consumed [1].

Dairy wastewater does not generally contain inherently toxic chemical substances. It does, however, host a substantial load of dissolved organic compounds such as proteins, lactose, fat, and minerals. There is also a disturbingly unpleasant odor due to decomposition of some constituents which may lead to an unsatisfactory civil situation impacting neighboring properties and commercial operations [2, 3]. The management and disposal of dairy effluent is, therefore, a pivotal concern in compliance with societal standards and environmental regulations.

All existent procedures for wastewater treatment are classified as chemical, physical, and biological processes. The combinative use of these processes, whether sequentially or concurrently, tends to produce a greater efficiency in reducing the pollutant aspects in liquid residues. Limitations in terms of implementation, efficiency, and cost are a factor, however [2]. Biological processes, as an example, have been widely used as the most promising alternative to dairy wastewater treatment. These processes present limitations that can potentially affect degradation efficiency through restrict pH range, abrupt organic-load variations, and also the effluent's physical-chemical characteristics leading to a physical overload of the system and sludge volume [4].

Among chemical methods, AOP is a type of process based on generating hydroxyl radicals, a highly reactive species, which promote organic compound oxidation. Some AOPs have been studied recently including combinative applications of complementary technologies for organic compounds degradation in effluents such as ozonation, Fenton and Photo-Fenton, electro-Fenton, UV/photoelectro-Fenton, electro-Fenton and peroxicoagulation, UV/ozone (O_3), UV/hydrogen peroxide (H_2O_2), UV/titanium dioxide (TiO_2), and UV/ZnO [5–9]. TiO_2 and ZnO are effective semiconductors, relatively cheap and nontoxic, both of which are being evaluated for respective photocatalytic efficiency [10–12].

The utilization of a heterogeneous photocatalyst, a widely accepted practice, includes redox reactions from adsorbed water, hydroxyl anions and oxygen molecules, or other substances [13].

With ZnO as a semiconductor, degradation processes are initiated by photoexcitation of the catalyst followed by the formation of a surface bandgap (1). The oxidation potential (h^+_{VB}) permits the formation of active intermediates by the direct oxidation of organic matter (2). Many reactive hydroxyl radicals can form either by decomposition of water (3) or by a bandgap reaction with OH^- (4). The hydroxyl radical, as described before, is a powerful nonselective oxidation agent leading to organic chemical compounds degradation [14–17]

$$\mathrm{ZnO} + h\nu \longrightarrow \mathrm{ZnO}\ (e^-_{CB} + h^+_{VB}) \quad (1)$$

$$h^+_{VB} + \text{organic matter} \longrightarrow \text{oxidation products (intermediates)} \quad (2)$$

$$h^+_{VB} + H_2O \longrightarrow H^+ + {}^\bullet OH \quad (3)$$

$$h^+_{VB} + OH^- \longrightarrow {}^\bullet OH. \quad (4)$$

The catalyst conduction band electron (e^-_{CB}) potentially reduces molecular oxygen to a superoxide anion (5). This radical can form organic peroxides in presence of organic matter (6) or H_2O_2 (7)

$$e^-_{CB} + O_2 \longrightarrow {}^\bullet O_2^- \quad (5)$$

$${}^\bullet O_2^- + R \longrightarrow R - OO^\bullet \quad (6)$$

$${}^\bullet O_2^- + HO_2^\bullet + H^+ \longrightarrow H_2O_2 + O_2, \quad (7)$$

where R: organic matter and $R - OO^\bullet$: organic peroxide.

Electrons on the conduction band are also responsible for producing hydroxyl radicals that lead to the mineralization of organic matter (8) [15, 17]

$${}^\bullet OH + \text{organic matter} \longrightarrow \text{organic matter degradation.} \quad (8)$$

Studies of semiconductors in photocatalyst processes use semiconductors in suspension [15, 16]. However, such practices may be more expensive when a scale-up process is anticipated since photocatalyst particle-recovery is not an easy task. This leads to an increase in process costs [18, 19]. A viable alternative technique is the preparation of photocatalyst layers in different substances without photocatalyst activity loss [20]. Few studies have used continuous flow reactors with fixed-bed photocatalyst [21–24].

Integral to this study was an examination of the efficiency of heterogeneous photocatalyst processes for dairy wastewater using immobilized ZnO to reduce organic load. The immobilization was carried out by the application of a coating containing the photocatalyst [5].

Solar radiation was used as UV source. To determine the process parameters, Taguchis L_8 experimental design was used to determine the process parameters. The efficiency of the process was evaluated in terms of TOC effective percentage degradation.

2. Materials and Methodology

2.1. Sampling and Conservation. The dairy wastewater samples used in this work were generously provided by *Cooperativa de Laticínios de Guaratinguetá*, in the city of São Paulo. It was collected in 25 L drums and refrigerated at 4°C while stored.

2.2. Total Organic Carbon Determination (TOC). TOC determinations were carried out in a Shimadzu Model TOC-VCPH analyzer using catalytic oxidation in high temperatures and CO_2 determination by infrared spectroscopy. Organic carbon (OC) analysis required a calibration curve derived from potassium biphthalate in a linear range from 0 to 500 mg/L. The analytical curve for inorganic carbon (IC) was derived from a mix of Na_2CO_3 and $NaHCO_3$ in a range from 0 to 500 mg/L. The detection limit for this method was 2 mg/L with a variation coefficient established for OC and IC analysis of 2%.

2.3. Preparation of Metal Plates. A ZnO p.a. sample from Merck was used.

Two identical 800 × 250 mm stainless steel plates with an area of 200 cm^2 were selected for these experiments [5]. The corresponding coating containing ZnO was applied to the plates by *DuPont do Brasil S.A.*, in Guarulhos, in the city of São Paulo.

2.4. Preparation of the Coating. A coating containing ZnO was diluted until obtaining a sliding viscosity of 24″ in Ford 4 viscometer. Viscosity adjustments were made using 100 g of the coating and 12.5 g of Solvesso 100 to attain the 24″ CF4. Typical plate coatings contain TiO_2 which required a viscosity compensation for the presence of ZnO. Temperature used to adjust the viscosity at 25°C corresponding to approximately 70 cPs (centipoises). The application of the coating was subsequently carried out over 30 min at 140°C. The same coating was applied to the two metal plates with variations in the thickness and/or amount of pigment employed.

A greater coating thickness was anticipated to allow deployment in a higher number of experiments since a double layer of paint tends to remain on the place surface longer. No studies, however, were conducted to verify how long the plates would last or if the surface coating would suffer any damage by use.

2.5. The Photocatalyst System (Solar Reactor). The experiment system consisted in a 200 cm^2 metal plate coated with immobilized ZnO p.a., a glass tank (280 × 205 × 260 mm), a fixed dairy wastewater volume of 3 L, a centrifugal pump (Bomax, model NH-30PX-T) with a nominal power of 10 W and a flow rate of 13 L/min. The effluent was pumped in an open system for solar UV radiation absorption between 9 AM and 5 PM.

The entire system was placed in a wooden structure that positioned the metal plate at 23° in relation to the Earth's

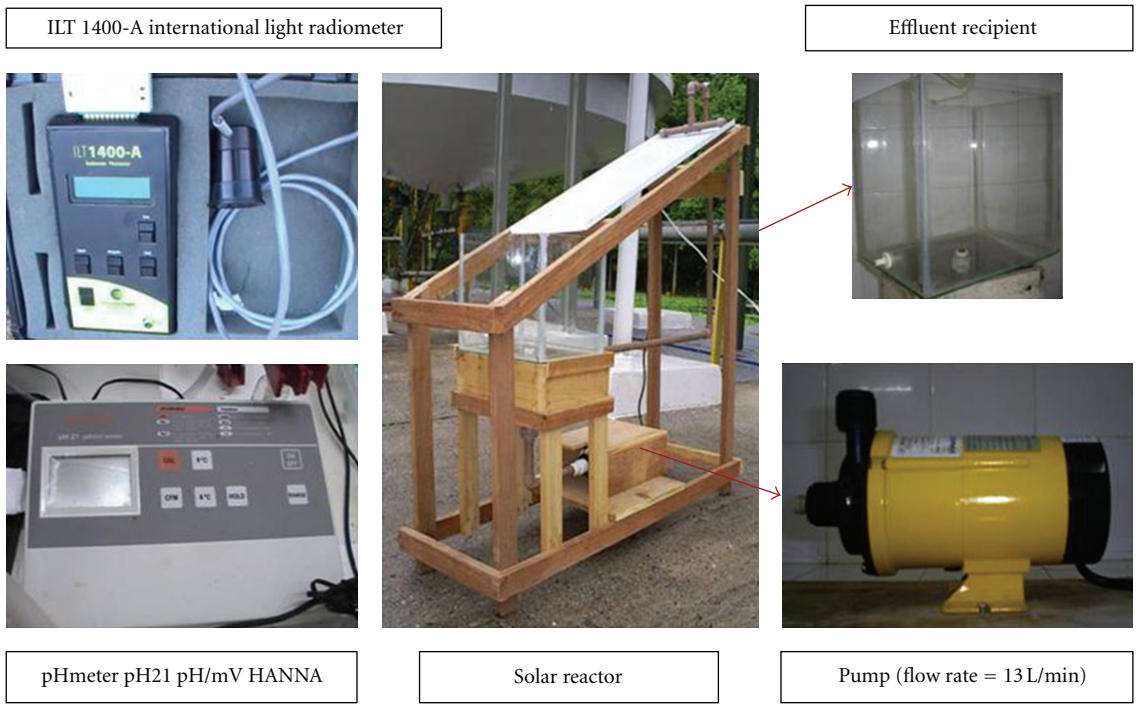


Figure 1: Schematic of the solar reactor with ZnO photocatalyst.

Table 1: Control variables and levels used on solar reactor experiments.

Control variables (factors)	Level 1	Level 2
A: reaction time (min)	120	180
B: thickness of ZnO (μm)	50	100
D: pH	6.0	8.0
G: effluent concentration	1 : 1 v/v	*In natura*

equatorial plane (Figure 1). This angular position corresponds to the geographical position where the experiments were conducted at the EEL/USP facility at 23° south latitude.

Effluent was pumped over the upper part of the plate and flowed evenly over the surface while receiving solar radiation. Radiation was measured using a ILT 1400-A International Light radiometer.

Using wastewater with elevated organic load and soluble solids, a thin homogeneous flow of effluent passed over the plate and was dispersed by the slope, flow-rate, and the geometry of the exit holes for the PVC nozzle assembly that was positioned at the top of the reactor to maximize exposure to solar radiation.

The effluent of this study had a homogeneous appearance and there were no indications of any type of solid deposition fouling.

2.6. Experimental Design. The experiments were carried out using Taguchis L_8 model of 2 levels and 4 factors. The variables of the process were reaction time, thickness of coating containing ZnO, pH, and concentration of effluent. These factors and levels are shown in Table 1. The experiments were conducted in a random order and with a parallel system omitting ZnO. This control plate is defined as "Control" consisting of an uncoated metal plate of the same dimensions as the experimental plate. The control plate surface was covered with 3 M highland tape.

Table 2 shows the Taguchi L_8 orthogonal design and requisite constituents for performing experiments in determination of the most significant and, consequently, optimal deployment of the AOP system (ZnO-UV_{solar}).

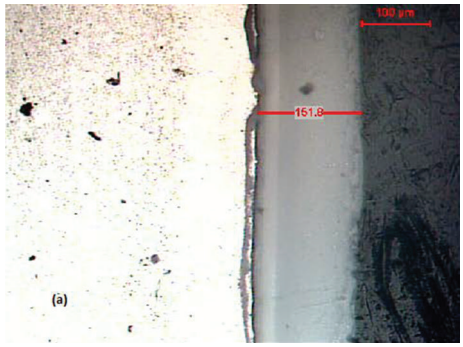
The orthogonal array for Taguchis L_8 model has 3 empty columns (C, E, and F) deliberately blank in correspondence to the interactions of the other factors [25].

According to the chosen design (Table 2), Experiment 1 was carried out under minimum conditions. Effluent was diluted first (1 : 1 v/v) then placed and homogenized in the glass tank with adjusted pH. The first sample was then collected and named Sample 1 with initial reference to zero time. The pH control was constant either by addition of H_2SO_4 or NaOH, both at 5 mol/L. This experiment was concluded after 120 hours of reaction resulting in a collected final sample.

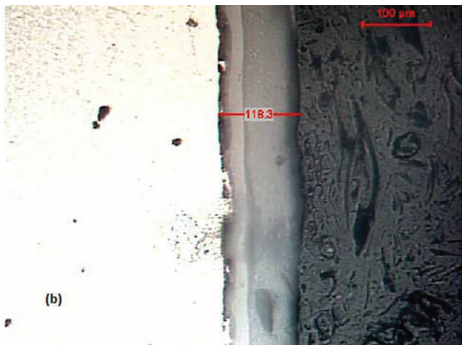
2.6.1. "Control" Procedure. A solar reactor was operated in parallel named "Control" using the same or similar methodologies noted above but without the coating containing ZnO. The blank experiment was designed to exhibit possible effects of photolysis in the system. Such effects could be attributed to a significant amount of organic matter being degraded by exposure to UV radiation, notable volume reduction through evaporation, and possible aqueous dilution resulting from additive compensations for evaporation. All samples were analyzed in terms of total organic carbon (TOC).

Table 2: Taguchi's L_8 orthogonal design for the experimental model of photocatalyst treatment of dairy wastewater.

Exp.	A Reaction time	B Thickness ZnO	C Interaction AB	D pH	E Interaction AD	F Interaction BD	G Effluent concentration
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2



(a)



(b)

Figure 2: Micrograph of plates of 100 μm (a) and 50 μm (b) of ZnO PA.

Table 3: Physical-chemical results for dairy effluent before and after AOP treatment in a reaction time of 3 h.

Parameters	Results		Percentage
	In natura	After AOP	
Actual color (Pt Co)	6523.5	3261.8	49.9
Turbidity (NTU)	2786	1919.6	31.1
pH	4.36	7.55	—
Odor	Pungent	Odorless	—
COD (mg L^{-1} O_2)	6032.5	4222.8	30
BOD_5 (mg L^{-1} O_2)	2218.7	1819.3	18
BOD_5/COD	0.368	0.431	—
TOC (mg L^{-1})	1010	692.9	31.4
Phosphorus (mg L^{-1})	208.5	156.4	25
N-NH_3 (mg L^{-1})	158.4	126.7	20
N-organic (mg L^{-1})	180.1	144.1	19.9
ST (mg L^{-1})	10720	5896	55
Oil and grease (mg L^{-1})	2002.1	801	60
Chlorine (mg L^{-1})	793.5	536.7	32.4
Iron (mg L^{-1})	91.53	61.8	32.5
Zinc (mg L^{-1})	5.0	5.0	—

3. Results and Discussion

3.1. Metal Plates Micrographic Analysis. A micrographic analysis of both plates used on these AOP experiments was carried out to verify the real thickness of ZnO on those plates as shown in Figure 2. Figure 2 apply to (a) shows the plate prepared with thickness of 100 μm of ZnO and Figure 2(b) shows the plate with 50 μm of thickness.

According to the micrographic analysis, the real thickness of ZnO on plates differ from the one initially proposed for this work. The one corresponding to 100 μm consisted of 151.9 μm. To the 50 μm plate, the real thickness consisted of 118.3 μm. It may be observed, however, that the original plates already have a layer of paint between the new coating and the metal. Thus, the actual values of plates (a) and (b) were of 118.5 μm and 84.9 μm, respectively, being the variation range of 34 μm between each other. This difference, however, was enough to determine the importance of the thickness of the semiconductor on this study as a variable in the orthogonal array used.

3.2. Dairy Effluent Characterization. Table 3 shows the physical-chemical results obtained in the AOP treatment using ZnO immobilized in a reaction time of 3 h.

The BOD_5/COD parameter is commonly used to verify the biodegradability of the effluent. The BOD_5/COD value for effluent *in natura*, or crude, is 0.368. This indicates that without proper pretreatment, the effluent is resistant or preventing biological treatment in an efficient manner. The relationship of BOD_5/COD reflects the effectiveness of oxidization in destroying certain constituents in the organic load. Biodegradability was evaluated as described by Jardim

Table 4: Degradation percentage of dairy wastewater by photocatalyst treatment using ZnO in relation of TOC.

Exp.	TOC degradation percentage samples	TOC degradation percentage blank	TOC removal percentage	Mean radiation rate (μW/m^2)
1	20.42	6.93	13.49	982.5
2	21.10	17.40	3.7	789.3
3	13.16	4.84	8.32	700.0
4	13.32	1.66	11.66	996.3
5	25.55	12.47	13.08	464.4
6	16.91	11.00	5.91	452.2
7	14.68	0.52	14.16	574.4
8	31.42	17.19	14.23	621.2

and Canela [26], noting a relationship BOD5/COD >0.4 as characteristic of biodegradable effluent. Thus, Table 3 shows results achieved by the immobilized ZnO photocatalytic process at a ratio of 0.431, showing that photochemical treatment increased the biodegradability of the dairy effluent.

Other parameters showed a reduction of approximately 20–30%, with the exceptions of oil and grease and total solids 60% and color at 50%. This indicates the process is significantly more effective for the removal of color, oils and solids, and high-concentration parameters making conventional biological process unnecessary. Thus, indications in this study show this process to be a valid pretreatment.

The analysis of zinc in the initial and final effluent serves to verify the concentration of zinc as the process proceeds and show the durability of the coated plate. As would be expected, the ZnO acts as a catalyst and does not influence the zinc concentration in the effluent.

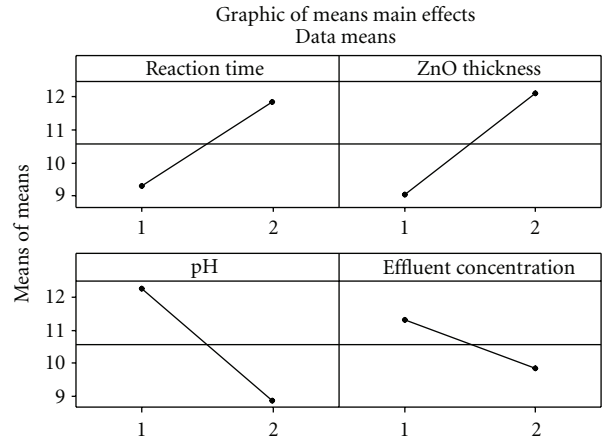


Figure 3: Main effects for the degradation of dairy wastewater by photocatalyst treatment using ZnO in relation to TOC.

3.3. Determination of TOC Degradation Percentage. The percentage of degradation is defined as the difference between the initial and final concentration of the effluent divided by the initial concentration when multiplied by 100 (9)

$$\text{TOC removal percentage} = \left[\frac{\left(\text{TOC}_0 - \text{TOC}_f\right)}{\text{TOC}_0}\right] \times 100, \tag{9}$$

where TOC removal percentage: percentage of organic matter degradation in TOC terms, TOC_0: initial total organic carbon (mg/L), and TOC_f: final total organic carbon (mg/L).

The effective degradation percentage is shown as the percentage difference between the experimental samples and the control samples. Experiments were analyzed only in relation to TOC in terms of percentage degradation as shown in Table 4.

Table 4 features significant effluent degradation in conditions 2, 5, 6 and 8 by nonrelated factors in the AOP used. According to these results, the highest degradation is due to the alkalinity of the medium rather than any photolysis effect. Among evaluated first-order parameters, effluent concentrations appeared less influential in the degradation efficiency. The highest effective percentage degradation of TOC was of 14.23% for condition 8, in which the parameters applied were reaction time of 180 min, thickness of plate containing ZnO of 100 μm, pH 8.0, and *in natura* effluent.

After statistical analysis of residual and experimental values, a new graphic was plotted of evaluated parameters as shown in Figure 3, displaying the optimal results for the experiments performed. Factors for reaction time and coating thickness should be used at maximum level.

Figure 3 shows that the longer the oxidation process is (referring to 180 min duration), the better degradation of organic matter will be. As a factor, the thickness of the ZnO coating as a variable shows that degradation noticeably improves at greater thickness (100 μm) due to a large contact area and the presence of small gaps and roughness make the effluent flow over the catalyst bed at a longer rate. However, the acid medium (pH 6.0) was more effective than the alkaline medium (pH 8.0). Particles of ZnO may also precipitate in an acid medium when it is used in suspension. Since the catalyst bed is fixed in position, there should be no significant interference in the experiment and, consequently, no promotion of degradation from the catalyst bed.

Table 5: Variance analysis of the polynomial model of first order for the dairy wastewater treatment by photocatalyst treatment.

	Coefficient	SE coefficient	T	P
Constant	8.852	8.558	1.02	0.382
Reaction time	3.765	2.850	1.32	0.278
Thickness of ZnO	1.835	2.850	0.64	0.565
pH	−4.600	2.850	−1.61	0.205
Effluent concentration	−0.260	2.850	−0.09	0.933

$S = 4.03031$, $R^2 = 61.4\%$, R^2 (adjusted) = 10.0%.

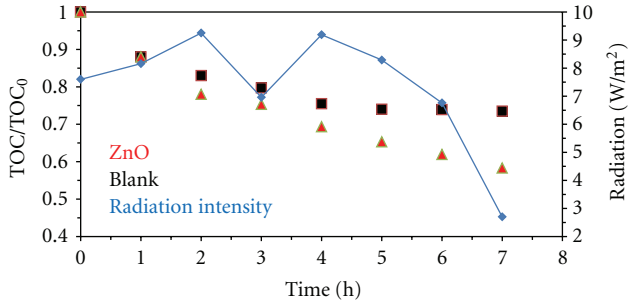


Figure 4: Test for long term degradation of photocatalytic process comparing to blank procedure and the equivalent radiation intensity during the reaction time of 8 h.

Results obtained from a regression linear model (coded) were adjusted as

$$\text{TOC degradation percentage} = 8.85 + 3.77\ \text{time} + 1.84\ \text{thickness} - 4.60\ \text{pH} - 0.26\ \ [\text{effluent}]. \quad (10)$$

Table 5 presents the variance analysis of the first-order polynomial model.

The value for TOC degradation in a linear model, without interactions, was recorded at 61.4%. A significant difference between R^2 and R^2 (adjusted) indicates that the model has been parameterized, that is, terms that do not contribute to the adjustment were included. According to the results, it seems probable that a significant difference between the values, via the linear model, may not accurately express the TOC variation.

The principal effects on photocatalyst degradation variables suggest that reaction time (72.2%) and pH (79.5%) were the most numerically significant with the initial effluent concentration to be the least expressive (6.7%).

Table 4 shows Experiments 2, 5, and 8 exhibiting elevated photolysis degradation and photocatalytic degradation values. Degradation efficiency, however, in Experiment 8 still presents the optimal results. A long duration experiment was carried out in order to verify the photocatalytic degradation process as well as the control procedures. Results for those two experiments, performed concurrently under the same conditions, are shown on Figure 4.

Figure 4 illustrates the importance of the 3-hour reaction time as a critical variable for the experimental work while the control remained unchanged. Degradation with ZnO follows linear behavior expressed in the TOC. The longer the exposure, duration, the greater the degree of degradation. At 8 h of solar exposure there was an approximate 50% degradation of organic matter.

The feasibility of implementing the process on an industrial scale will depend on two main factors: the anticipated percentage of degradation and the time available in system utilization.

Additionally, Figure 3 also shows the impact of solar intensity during an 8 h exposure period. It is apparent that even with variation peaks at 2 h and 4 h, the intensity is not sufficient to alter the efficiency of the process, suggesting that photoirradiation alone is sufficient to trigger the photocatalytic process. These intensity peaks related turbidity. Increases in radiation intensity were likely due to the actual time of day during which the processes were conducted. The 2 h- to 4 h -exposures occurred from 10:00 AM to 12:00 PM (noon).

Table 6 displays the cost in US$ for 3 h exposures and equivalent value.

Thus, for a reduction of about 30% of TOC, without considering the photolysis effect, the spent in running the process, was US$ 0.0164, which is cost effective for degradation percentages in contrast to other treatment systems and could be employed in dairy effluents treatment plants.

The comparison study of the electro-Fenton and the UV/photoelectron-Fenton processes led to a higher mineralization (>80% of degradation) using the latter at a low current within pH range of 2.0–6.0 at 35°C. UV light enhances the process; however, the UV lamp used, reaction time, and temperature control may influence directly in the energy consume of the process [8]. Both advanced electrochemical oxidation processes (AEOPs) show moderate energy costs, which increase with increasing electrolysis time and applied current [9].

When compared to another photocatalyst process using TiO_2, the cost of the process is basically the same in relation to energy and reagent consume. They differ, however, in terms of percentage degradation. Studies showed higher degradation using an initial concentration of the organic matter lower than the one used in this study [14, 15, 17, 19]. This may suggest that higher concentrations would have lower degradation percentages to photocatalyst studies and yet the results obtained by using ZnO are significant and could be employed in scale-up processes [14–16, 19].

4. Conclusions

The Taguchis L_8 orthogonal array used in the experimental design has shown a correlation to the thickness of the plate and pH resulting in a TOC degradation percentage of 31.42% and effective percentage degradation of 14.23% for all conditions at an optimal level.

Therefore, collected data results show a preference to use of solar photocatalyst processes in dairy wastewater pretreatment with possible applications to other types of

Table 6: Equivalent value related to the cost of 3 h of ZnO photoirradiated reaction.

Equipment and reagents	Quantity used (3 h)*	Cost for the process (3 h) (US$)*
Pump energy consumption (kW-h)	0.0287	0.008323***
Reagents H_2SO_4 + NaOH (g)	0.02	0.0008105**
Total cost:		0.0164

* US$ 1,00 = R$ 1.71; Cotações UOL.
** Quote N° 212712 from Labsynth Produtos of Laboratórios Ltda.
*** 1 kW-h = US$ 0.29; the third most expensive electricity in Brazil—Portal Business Brasil.

wastewater, especially due to its low cost in 3 operational hours (US$ 5.47 per m^3) and its relatively simplicity. Even though the degradation percentage was low, the treated effluent should not be thrown directly to superficial waters. However, the increase in biodegradability and improvement in physical-chemical characteristics important to the dairy effluent obtained with the oxidative process favor the viability of biological treatments with less hydraulic retention time.

Acknowledgments

The authors thank Companhia Siderúrgica Nacional (CSI) for SEM analysis and Cooperativa de Laticínios de Guaratinguetá, City of São Paulo (CLG) for the dairy wastewater sample used in this work. The authors also thank Marco Fernandes from DuPont in preparing the ZnO-coated plates and the Engineering School of Lorena University.

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