Hindawi Publishing Corporation
International Journal of Chemical Engineering
Volume 2013, Article ID 393467, 5 pages
http://dx.doi.org/10.1155/2013/393467

Research Article

The Application of a Surface Response Methodology in the Solar/UV-Induced Degradation of Dairy Wastewater Using Immobilized ZnO as a Semiconductor

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Received 30 May 2013; Accepted 15 August 2013

Academic Editor: Antonia Pérez de los Ríos

An Advanced Oxidation Process (AOPs) was carried out in this study with the use of immobilized ZnO and solar/UV as an energy source to degrade dairy wastewater. The semibatch reactor system consisted of metal plate of 800 × 250 mm and a glass tank. The reaction time was of 3 h for 3 L of dairy wastewater. Experiments were performed based on a surface response methodology in order to optimize the photocatalytic process. Degradation was measured in percentage terms by total organic carbon (TOC). The entry variables were ZnO coating thickness and pH, using three levels of each variable. The optimized results showed a TOC degradation of 31.7%. Optimal parameters were metal-plate coating of 100 μm of ZnO and pH of 8.0. Since solar/UV is a constant and free energy source in most tropical countries, this process tends to suggest an interesting contribution in dairy wastewater treatment, especially as a pretreatment and the optimal conditions to guarantee a better efficiency of the process.

1. Introduction

The use of ZnO as a semiconductor was studied for possible application in a photo-excitation-initiated degradation of the catalyst followed by the formation of a surface bandgap (see (1)). The oxidation potential (h_{VB}^{+}) permits the formation of active intermediates by the direct oxidation of an organic matter (see (2)). Many reactive hydroxyl radicals can be formed either by decomposition of water or by a bandgap reaction with OH^{-} (see (3) and (4)). The Hydroxyl radical is a powerful nonselective oxidation agent leading to organic pollutants degradation [1–3]. Consider that

$$ZnO + h\nu \longrightarrow ZnO\ (e_{CB}^{-} + h_{VB}^{+}) \quad (1)$$

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

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

$$h_{VB}^{+} + OH^{-} \longrightarrow {}^{\bullet}OH \quad (4)$$

The methodologies used in the design of experiments allow a similar result as the one obtained from conventional experiments with the advantage of the use of fewer experiments. Thus, a good design of experiments can provide sufficient results for an effective statistical analysis [4]. In order to obtain the optimized variables for the study of

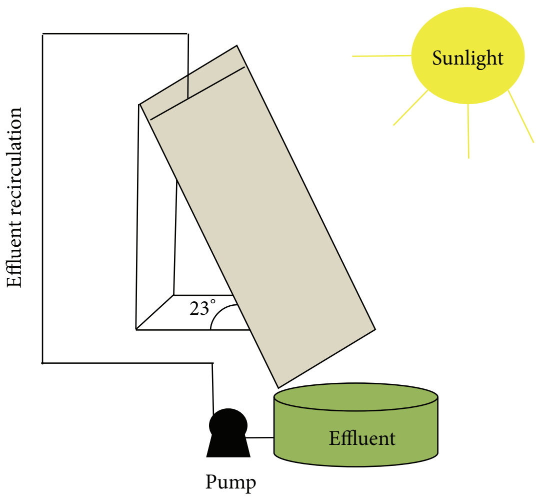

Figure 1: Schematic diagram of the solar reactor with ZnO photocatalyst based on [8].

dairy wastewater photocatalytic treatment, a surface response methodology was employed.

Dairy wastewater does not generally contain inherently toxic chemical substances, but it is composed of dissolved organic compounds that are not easily degradable by biological treatment without a prior treatment. In fact, this limitation affects the efficiency of the treatment through pH (depending on the type of dairy), overload of the system, and sludge volume. Moreover, dairy wastewater also produces an unpleasant odor and consists of a liquid with a significant color if the organic load is high enough [5–7].

2. Materials and Methodology

2.1. Sampling and Conservation. The dairy wastewater samples used in this work were generously provided by *Cooperativa de Laticınios de Guaratingueta*, state of Sao Paulo, and refrigerated at 4°C while stored.

2.2. Preparation of the ZnO Coating and Experiment Procedures. The immobilization of ZnO particles was carried out by the application of a coating containing the photocatalyst [8] by *DuPont do Brasil S.A.*, in Guarulhos, Sao Paulo. Two identical 800 × 250 mm stainless steel plates with an area of 200 cm^2 were used each with a different thickness (50 and 100 μm). The coating containing ZnO was diluted until obtaining a sliding viscosity as described in [8]. Difference in thickness was obtained by applying an extra layer of the prepared ZnO paint to the 100 μm plate.

The entire system was placed in a wooden structure that positioned the metal plate at 23° in relation to the Earth's equatorial plane (Figure 1).

This angular position corresponds to the 23° south latitude in order to enhance irradiation. The solar reactor was then placed to receive the solar UV responsible for the photoexcitation of ZnO particles. Solar/UV was monitored by Radiometer ILT1400-A. Figure 2 shows the scheme of UV-induced degradation, when a semiconductor as ZnO is used.

Table 1: Variables and levels based on the Surface response methodology (15 runs with replication) for the dairy wastewater photocatalytic process.

Control variables	Level −1	Level 0	Level 1
pH	6.0	8.0	10.0
ZnO coating thickness (μm)	0	50	100

The preparation of samples was carried out according to the surface response methodology designed for this study, and experiments were conducted as in [10] without the blank procedure.

2.3. Surface Response Methodology for the Dairy Wastewater of This Study. A design was developed using a surface response methodology with a central point as shown in Table 1. Response was measured in TOC percentage terms. Experiments were conducted in pairs at the same time except those with central levels that were conducted one at a time. The advantage of using a surface response methodology is that it is able to analyze three levels instead of two as it happens to other designs of experiments. The surface response methodology consisted of 2 factors in duplicate with the base run of 15, a total of 30 experiments.

2.4. Surface Response Matrix Procedure. According to Table 1 for the central point, sample was adjusted to pH 8.0 with the addition of NaOH 5 mol·L^{-1}. A metal plate with ZnO coating thickness of 50 μm was used in the solar reactor. The first sample was collected before the beginning of the experiment. The last sample was collected after 3 h. pH control was constant either by addition of H_2SO_4 or NaOH. The procedure for the other experiments was analogous to the one described previously and performed randomly to guarantee the statistical significance of the experiments and avoid any bias. The efficiency of the process was evaluated in terms of TOC effective percentage degradation. 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.

3. Results and Discussion

3.1. Characterization of the Dairy Wastewater. Table 2 shows the physical-chemical results obtained for the dairy wastewater before and after the photocatalytic process using immobilized ZnO and Solar/UV.

BOD, chloride, phosphorous, ammonia, TOC, and turbidity showed a reduction range of 20–35%. While the parameters color, oils, and total solids showed a more expressive reduction with the range of 45–63%.

The presence of chloride in the dairy wastewater samples is mainly because chloride is present in the cleaning steps of reactors in the dairy industry. Its removal is then expressive

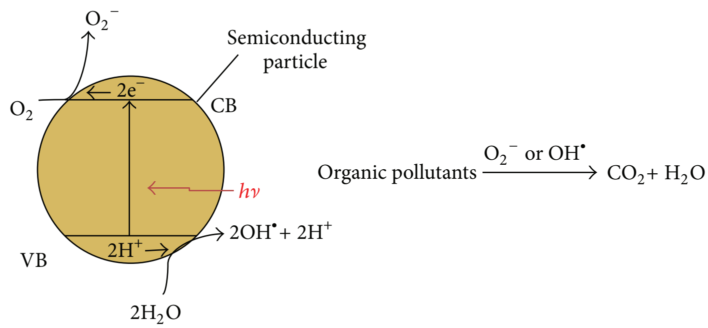

FIGURE 2: Schematic illustration of the UV-induced degradation of organic pollutants by semiconductors [9].

TABLE 2: Physical-chemical results for dairy effluent before and after AOP treatment.

Parameters	Results		Percentage
	in natura	After AOP	
BOD_5 (mg L^{-1})	2218.7	1775	20
Chloride (mg L^{-1})	793.5	526	33.7
Color (Pt Co)	6523.5	3260	50
N-NH_3 (mg L^{-1})	158.4	126.7	20
Oil and grease (mg L^{-1})	2002.1	750	62.5
Phosphorus (mg L^{-1})	208.5	156.4	25
TOC (mg L^{-1})	1010	690	31.7
Total solids (mg L^{-1})	10720	5886	45
Turbidity (NTU)	2786	1894	32
Zinc (mg L^{-1})	5.0	5.0	—

and could improve the biodegradability of the wastewater in a biological system.

The analysis of zinc before and after the treatment serves to verify the concentration of zinc as the process proceeds and shows the durability of the coated plate. No further studies were made to the coating plate in terms of longevity of the ZnO on the plate nor were biological studies conducted to verify the growth of any type of bacteria on the surface of the plate.

The results obtained indicate that the process is significantly more effective for the removal of color, oils, and solids. Thus, indications in this study show this process to be a valid pretreatment.

3.2. Optimization of the Photocatalytic Process by Using the Surface Response Methodology. Experiments were analyzed in terms of TOC effective percentage degradation as shown in Table 3.

Thus, the highest percentage of TOC degradation was of 31.6% for a ZnO coating thickness of 50 μm and a pH of 8.0, corresponding to the central point of the matrix.

It is possible to visualize the optimized parameters when using a surface response methodology through a 3D graph. This is shown in Figure 3.

As it can be seen in Figure 3 (acquired by the software Minitab v. 15), surface maximum peak leans towards pH 8.0 as its optimal variable. In terms of thickness, Figure 2 shows an increase as thickness is raised. Thus, a coating of 100 μm seems to perform better results than a coating of 50 μm. This difference, however, is not as expressive as it is shown for pH. This can be due to the relative small difference in thickness

TABLE 3: Surface response methodology matrix using 2 factors and 15 runs in duplicate and TOC effective percentage degradation of the dairy effluent after the AOP treatment.

Experiments	pH	Thickness (μm)	TOC effective percentage degradation
1	8.0	50	31.6
2	10.0	100	5.4
3	6.0	100	5.7
4	6.0	0	7.9
5	10.0	0	13.6
6	10.0	0	6.8
7	6.0	100	9.3
8	6.0	0	1.3
9	8.0	50	31.5
10	10.0	100	10.6
11	6.0	100	4.6
12	6.0	0	0.5
13	10.0	0	11.7
14	10.0	100	7.5
15	6.0	0	7.2
16	10.0	100	13.6
17	10.0	0	6.6
18	8.0	50	26.4
19	8.0	50	28.7
20	6.0	100	5.4
21	10.0	100	10.5
22	8.0	50	26.6
23	6.0	100	6.1
24	6.0	0	2.4
25	6.0	100	7.1
26	8.0	50	25.9
27	10.0	100	13.9
28	10.0	0	4.4
29	10.0	0	7.5
30	6.0	0	4.4

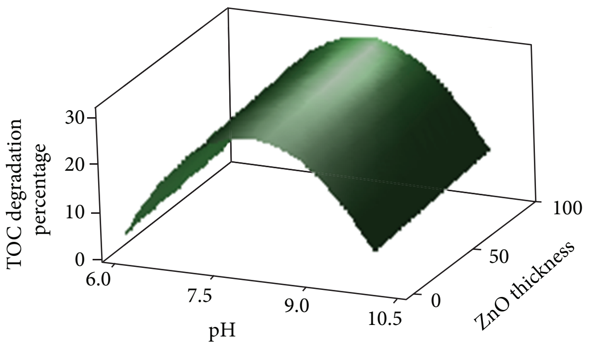

Figure 3: Surface Response graph in terms of TOC percentage removal by ZnO coating thickness and pH.

Table 4: ANOVA of surface response methodology for the photocatalytic process of dairy wastewater.

	Coefficient	SE Coefficient	t-value	P value
Constant	29.597	1.377	21.490	0.000
pH	1.798	0.746	2.409	0.025
ZnO coating thickness	1.283	0.746	1.719	0.100
pH ∗ pH	−22.639	1.567	−14.452	0.000
pH ∗ thickness	0.072	0.746	0.097	0.924

Where: $S = 3.37352$, Rsq. = 91.08%, Rsq.adj. = 89.45%, Rsq.pred. = 86.73%.

between both metal plates. The ANOVA of this methodology is shown in Table 4.

The model of this study can express 91% of TOC percentage degradation. Predicted value was 86.7% that corresponds to a difference of 5% from the model. The adjusted value was 89.5%, and therefore it shows a difference of 1.8% from the model value. Thus, values were not parameterized, and the data included are significant.

Results showed that pH was significant ($P < 0.05$), ZnO coating thickness was less significant in the process ($P = 0.1$), and the interaction of both variables was not significant ($P = 0.93$).

After statistical analysis, the optimal conditions for the AOP using ZnO photoirradiated are pH 8.0, a value that was mentioned in [11], and ZnO coating thickness higher than 100 μm.

A new experiment was conducted with the optimized parameters from this study and the ones found in [10], that is, pH of 8.0, ZnO coating thickness of 100 μm, reaction time of 3 h, effluent concentration in natura, average radiation of 584.0 $\mu W/cm^2$, reaction temperature of 31°C, and average evaporation rate of 0.17 L/h. The TOC percentage removal was of 32% as obtained by [8, 12, 13], though the authors employed TiO_2 with lower organic load.

Something that must be taken into consideration is the cost of the process for 1 h of reaction. For this experiment, the cost of reagents is not high since there is only pH control during the whole process. pH values, however, tend to remain constant during the process once it is adjusted at the beginning of the process.

The energy source chosen for this study requires sun exposition only, preventing the use of lamps and hence minimizing the energy consumption of lamps.

There is no water consumption during the process because the effluent is directly treated; that is, no dilutions are required for the effluent of 1010 $mg{\cdot}L^{-1}$ in this study.

4. Conclusion

Optimal values of the variables were pH 8.0 and a ZnO coating thickness plate of 100 μm. When optimized, an effective TOC degradation of 31.7% was obtained.

Since solar/UV is a constant and free energy source in most tropical countries, this process suggests an elevated potential contribution to dairy wastewater treatment, especially as a pretreatment.

Subsequent studies may explore and enhance solar/UV collecting and diminished vaporization. Results from this study show that the photocatalytic degradation contributes to the organic load removal of effluents, and studies related to economic viability may expand the process.

In addition, nanometric ZnO can be used not only for dairy wastewater treatment but also for other types of industrial wastewater even to a scale-up level. There was 50% of color removal in the dairy effluent, which can also be used in the treatment of dye industry effluents.

The AOP using ZnO photoirradiated can be associated with membranes and be an instrument in H_2O treatment for industries' own water reuse, especially those like dairy industries in which water consumption is extremely high.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors thank Cooperativa de Laticınios de Guaratingueta, in the state of Sao Paulo (CLG), for the dairy wastewater sample used in this work. The authors also thank Marco Fernandes from DuPont for preparing the ZnO-coated plates and Dr. Messias Borges Silva from the University of Sao Paulo.

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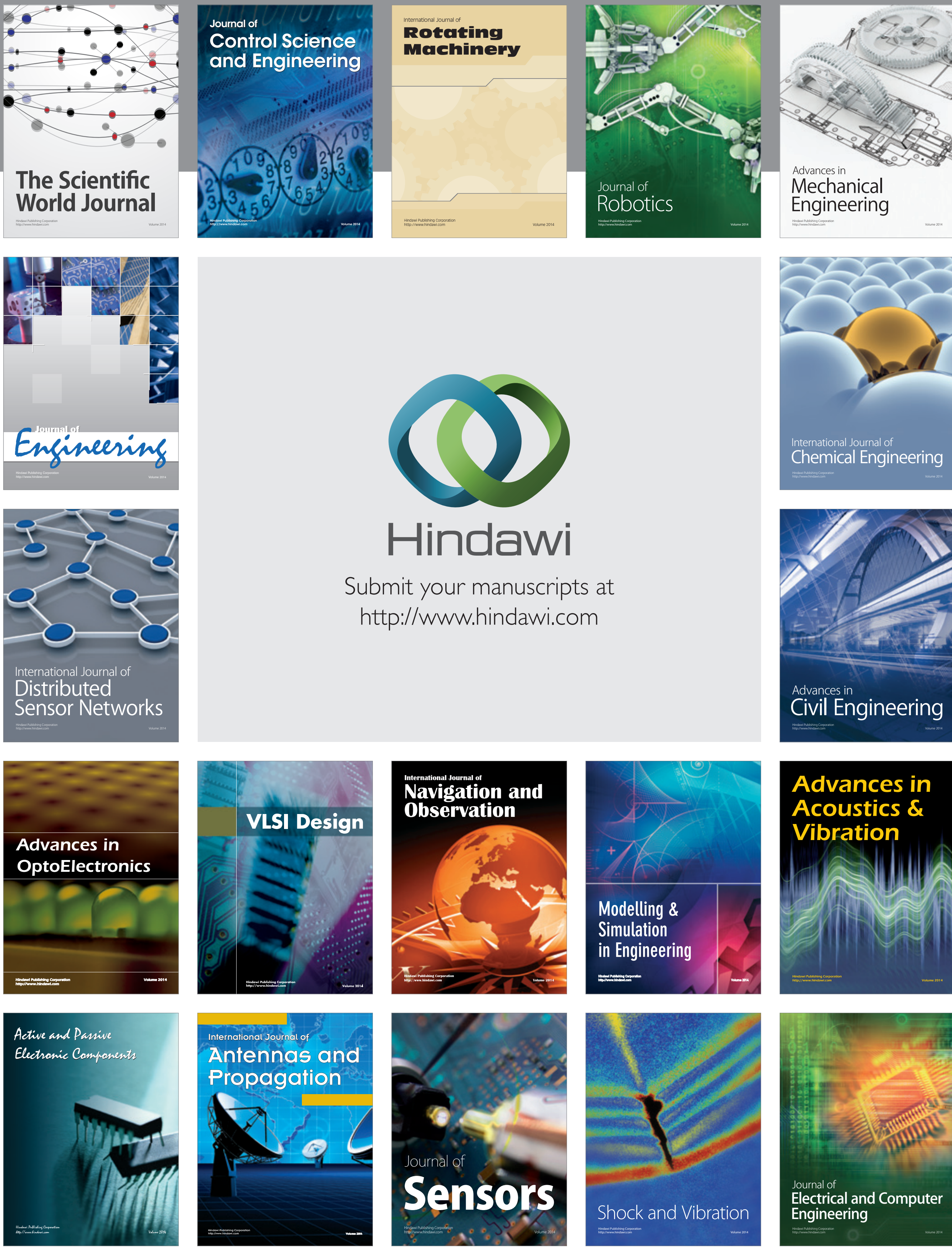
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