Photocatalytic Oxidation Process (UV/H₂O₂/ZnO) in the treatment and sterilization of dairy wastewater

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ABSTRACT. Advanced Oxidation Processes (AOP) have attracted much interest of scientific and industrial communities. Therefore, this process was employed experimentally to determine its efficacy in treating dairy effluents. For this, it was employed an artificial light reactor using photolysis (UV), hydrogen peroxide (H_2O_2) as an oxidant, and zinc oxide (ZnO) as an alternative catalyst. The variables studied in the photocatalysis were: H_2O_2, ZnO, under different values of pH, both in relation to the interferences with the reaction rate and with the process efficiency. First order differential equations were applied in determining the degradation rate over the hydraulic retention time (HRT); the F-test and the signal: noise ratio comparison were used to test the significance of variables. The AOP using photolysis UV, H_2O_2 and ZnO was effective in COD removal with 80% efficiency. As for the sterilization, in terms of total and fecal coliforms the efficiency was 100%, with the most probable number of total and fecal coliforms (MPN 100 mL⁻¹) equal to zero. A catalyst/oxidant/pH ratio was observed at 1 g 30 mL⁻¹ 4⁻¹ for a better kinetic-chemical reaction, for 1 hour lighting.

Keywords: heterogeneous photocatalysis, chemical kinetics, wastewater treatment.

Desempenho do Processo Oxidativo Fotocalítico (uv/h₂o₂/zno) no tratamento e esterilização de efluentes de laticínio

RESUMO. Os Processos Oxidativos Avançados (POA) têm atraído grande interesse tanto da comunidade científica como industrial. Assim, esse processo foi empregado experimentalmente com o objetivo de determinar sua eficiência no tratamento de efluentes de laticínios. Foi utilizado um reator com luz artificial utilizando a fotólise (UV), peróxido de hidrogênio (H_2O_2) como oxidante e, como catalisador alternativo, o óxido de zinco (ZnO). Foram avaliados diferentes concentrações de H_2O_2 e ZnO em diferentes valores de pH, tanto em relação às interferências na velocidade de reação quanto na eficiência do processo. Nesta pesquisa, equações diferenciais de primeira ordem foram utilizadas na determinação da velocidade de degradação em função do tempo de detenção hidráulica (TDH), análise estatística como o teste F e comparação razão-sinal-ruído na significância das variáveis estudadas. O POA, utilizando fotólise UV, H_2O_2 e ZnO, demonstrou ser eficaz na remoção de DQO apresentando eficiência de 80%. Quanto à esterilização do efluente, no que tange aos coliformes totais e fecais, a eficiência foi de 100%, com o número mais provável de coliformes totais e fecais (NMP 100 mL⁻¹) igual a zero. Observou-se para melhor reação cinético-química, durante 1h de luminosidade, a relação catalisador/oxidante/pH de 1 g 30 mL⁻¹ 4⁻¹.

Palavras-chave: fotocatálise heterogênea, cinética química, tratamento de efluentes.

Introduction

Among the numerous agro-industries encompassed by the economy of Minas Gerais State, stands out the dairy industry. Wastewater disposed by this type of industry includes besides diluted milk, several other products derived from developed processes, such as cleaning products, lubricants, and even domestic sewage (CAMPOS et al., 2004), which if untreated can harm the environment.

The amendment of wastewater produced by different agricultural activities to environmental standards is essential for public health and combating pollution, which led to the development of treatment systems combining high efficiency and low costs for operation and construction (PEREIRA et al., 2010a and b, 2011).

In this context, Advanced Oxidation Processes (AOP) have attracted great interest of scientific and industrial communities. These processes are based on the formation of the highly oxidizing hydroxyl radical (OH⁻). Given the high reduction potential, this radical is able of oxidizing a wide array of organic compounds to CO_2, H_2O and inorganic ions

from any atom other than carbon and hydrogen, component of an organic molecule (heteroatoms) (OLIVEIRA; LEÃO, 2009). The radical hydroxyl is usually formed in reactions resulting from the combination of oxidants such as ozone or hydrogen peroxide with ultraviolet (UV) or visible (VIS) radiation and catalysts, such as metal ions or semiconductors. Depending on the structure of the organic contaminant, different reactions may occur such as the addition of some substance attracted by electrons, such as a cathion or a molecule whose atoms have electron deficiency, and tend to link by covalent link to a nucleophile, causing a electrophilic reaction with substances containing unsaturations and aromatic rings, electronic transference and radical-radical reactions (AGUIAR et.al., 2007).

Formed hydroxyl radicals are capable to oxidize organic compounds through hydrogen abstraction, generating thus organic radicals. Afterwards there is the addition of molecular oxygen to form intermediate peroxide radicals that begin chain thermal reactions that degrade until CO_2, water and inorganic salts. The reaction by hydrogen abstraction usually occurs with aliphatic hydrocarbons (OLIVEIRA; LEÃO, 2009).

In this way, this study aimed to: a) evaluate the use of advanced oxidative processes under ultraviolet light (UV) having hydrogen peroxide (H_2O_2) as oxidant and zinc oxide (ZnO) as alternative catalyst in the treatment of dairy wastewater and, b) estimate the coefficients that describe the oxidation kinetics of COD, in order to obtain parameters for scheduling the reactor.

Material and methods

The experiment

The photochemical treatment was performed in laboratory, using a UV-light photocatalytic reactor, H_2O_2 as oxidant and ZnO as catalyst. The continuous flow cylindrical reactor was constructed with plywood, with 0.885 L total volume, 0.23 m height, 0.07 m internal diameter, pump of 0.12 HP for pumping the flow and 250 W mercury vapor lamp. The internal capacity of wastewater to be treated was 0.177 L (Figure 1a and b).

The wastewater (1.3 L) was poured into the top reservoir of the reactor, and then recirculated by a peristaltic pump in the system (Figure 1). The pump was turned on and the first samples of the raw wastewater were collected at the outlet of the reactor. This protocol was applied to all experiments, obtaining the mean value of all samples without treatment to determine the initial concentration (Table 4). This was done to provide a greater homogeneity to the effluent, and to condition the

reactor to a hydraulic balance. Then, the pH was controlled until achieving the desired value, by adding PA sulfuric acid (H_2SO_4) for acidification and 1 N NaOH for alkalization. After, amounts of hydrogen peroxide (H_2O_2) and zinc oxide (ZnO) were added according to the values of the Table 1; the lamp was turned on and started the collection of photodegraded wastewater at the outlet of the reactor every 10 minutes.
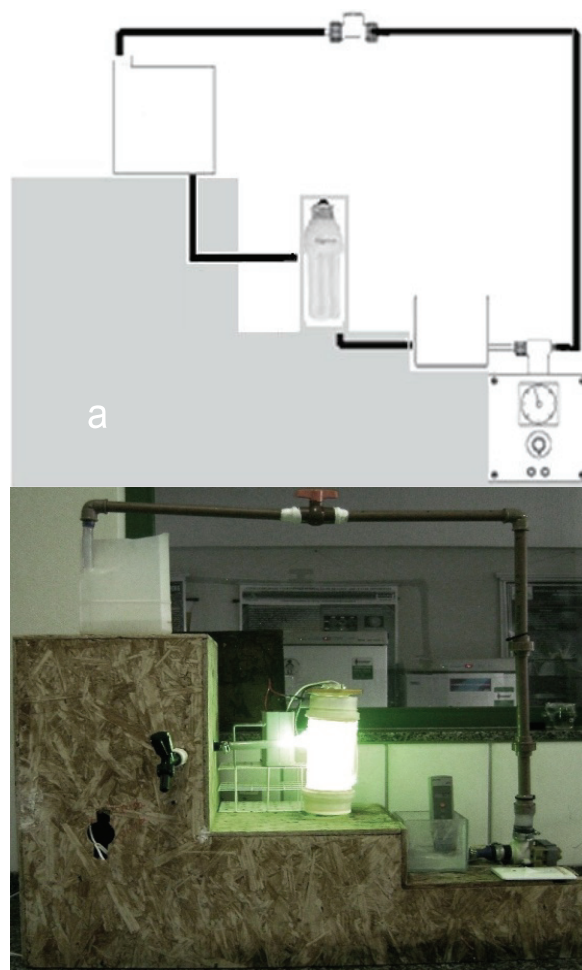

Figure 1. Diagram of the experimental unit (a), Photocalytic reactor (b).

Table 1. Experimental matrix for the experiment.

Levels	Levels of the controlled variables		
	H_2O_2 (35%)	Zinc oxide	pH
1	30 mL	0.5 g	3.0
2	50 mL	1.0 g	4.0
3	100 mL	1.5 g	6.0

The lamp was turned on, and seven samples were collected in series with 10-min. intervals. After collected, samples were preserved and analyzed according to the methodology presented in the Table 2.

Table 2. Tests, determinations, methods and frequency of physical and chemical monitoring.

Physical and chemical parameters	Reference
pH	APHA; AWWA; WPCF (2005)
Chemical oxygen demand COD$_{total}$	APHA; AWWA; WPCF (2005) (closed reflux digestion method)
Biochemical oxygen demand (DBO) total	Winkler modified method with azide iodide
Total solids (ST), Fixed total solids (STF) and Volatile total solids (STV)	APHA; AWWA; WPCF (2005)
Chlorides (Cl$^-$)	APHA; AWWA; WPCF (2005),
Oil and Grease (OG)	APHA; AWWA; WPCF (2005) (obtaining the extract using celite as filtering medium and Hexane).
Total Coliform (CT) and Thermotolerant Coliform (CTerm.)	APHA; AWWA; WPCF (2005) Multiple tubes method with series of three tubes
Electrical conductivity (CE)	Hach Conductivimeter

In order to study the process optimization, a systematic of simple experiments was performed, the Taguchi Experimental Matrix, using L9orthogonal arrays (Table 3).

Table 3. Taguchi Experimental Matrix – L9.

Peroxide concentration (H$_2$O$_2$)	Zinc oxide (ZnO)	pH
3	1	3
2	1	2
3	2	1
3	3	2
1	1	1
2	2	3
1	3	3
1	2	2
2	3	1

1= low level; 2= medium level; 3= high level.

Results and discussion

Characterization of the fresh wastewater

The fresh wastewater was characterized based on the principal parameters set by the current environmental legislation (BRASIL, 2005) and by Regulatory Determination Copam/Cerh-MG #1, from May 5th, 2008 considering the disposal of wastewater into water bodies (Table 4).

According to the parameters established by Conama and Copam, the dairy wastewater evaluated herein cannot be discharged directly into the environment, requiring previous treatment to reduce the pollution potential

Photodegradation

The time for total reaction of experiments was 1h, being gathered aliquots for COD analysis every 10 min., for the study of the degradation rate with varied chemical conditions of the medium (pH, catalyst and oxidant). Equations that describe the reaction speed (k) over time were found using the degradation rates relative to the initial concentration for the different situations, according to the model below:

$$\frac{dC}{dt} = -kC$$

$$\int \frac{dC}{dt} = \int -kdt$$

$$C = Co \cdot e^{-kt}$$

where:

C: remaining COD$_{total}$ concentration (mg O$_2$ L^{-1});

Co: initial COD$_{total}$ concentration (mg O$_2$ L^{-1});

k: degradation rate of COD$_{total}$ (mg COD removed L^{-1} min.$^{-1}$);

t (contact time): as it was the time of collection of the wastewater and the process was continuous with constant rate, it is adopted *t* as the contact time between radiation and wastewater.

With the described model, using the data found and ignoring the initial time to remove the punctual effect of catalyst and oxidant, the Table 5 was elaborated with maximum, medium and minimum efficiencies in relation the influent concentration (fresh) of 2,388 mg L^{-1}, and concentrations of the effluent collected every 10 min.

The highest initial speed was achieved when used the smallest volume of oxidant and intermediate amount of catalyst (Table 6). Using this same table and considering that the function of the catalyst was to reduce the activation energy without being consumed or modified, and comparing the oxidant and pH to understand initial speeds: analyzing the experiments 1, 2 and 3 for the same volume of oxidant (greater amount studied – 100 mL), it was observed that by reducing the pH, the initial speed has decreased. For the other experiments, this relationship was not observed, because the pH at 4 was in different conditions of oxidant volume, the most suitable for optimizing the process, proving to be adequate for the occurrence of the reaction.

Using the values of *k* (Table 7) and correlating with corresponding time, we found equations that described the speeds presented in Table 6. After starting the degradation, there was a downward trend in the reaction speed between the oxidant and effluent over contact time (Table 7), leading to the oxidant consumption during the reaction and mineralization of organic matter estimated by the COD$_{total}$ removal efficiency (Table 5).

Table 4. Characterization of the fresh wastewater.

Parameters	Obtained values	Parameters	Obtained values
pH	5.56	STV	380 mg L^{-1}
CE	0.77 dS m^{-1}	OG	709 mg L^{-1}
Cl^{-}	128 mg L^{-1}	COD	2,388 mg L^{-1}
ST	2,460 mg L^{-1}	BOD	825 mg L^{-1}
STF	2,080 mg L^{-1}	CT and CTherm	1.4x10^{3} NMP 100 mL^{-1}

Table 5. Maximum, medium and minimum efficiencies of degradation, average degradation speed, and descriptive equation relative to the 9 experiments.

Experiment	Medium	Maximum	Minimum	Average k	Equation
1	83.31	85.53	78.21	0.08	C = 2,388 e$^{-0.08t}$
2	89.05	89.89	87.3	0.08	C = 2,388 e$^{-0.08t}$
3	85.4	87.61	82.86	0.07	C = 2,388 e$^{-0.07t}$
4	83.43	86.11	75.83	0.09	C = 2,388 e$^{-0.07t}$
5	94.21	97.35	90.84	0.12	C = 2,388 e$^{-0.12t}$
6	92.12	96.24	85.45	0.12	C = 2,388 e$^{-0.12t}$
7	91.38	95.21	84.53	0.13	C = 2,388 e$^{-0.13t}$
8	95.77	97.67	92.28	0.11	C = 2,388 e$^{-0.11t}$
9	94.23	95.31	90.79	0.13	C = 2,388 e$^{-0.13t}$

Medium–Medium efficiency, Maximum– Maximum efficiency, Minimim– Minimim efficiency. *All the parameters listed in this table were calculated using the values collected every 10 min.

Table 6. Conditions of reaction and initial speed of degradation.

Experiment	Reaction condition	Initial speed of reaction
1	100 mL H$_2$O$_2$, 0.5g ZnO and pH equal to 6	20.73
2	100 mL H$_2$O$_2$,1.0g ZnO and pH equal to 3	16.59
3	100 mL H$_2$O$_2$, 1,5g ZnO and pH equal to 4	17.93
4	50 mL H$_2$O$_2$,0.5g ZnO and pH equal to 4	31.2
5	50 mL H$_2$O$_2$,1.0g ZnO and pH equal to 6.	39.01
6	50 mL H$_2$O$_2$,1.5g ZnO and pH equal to 3.	38.03
7	30 mL H$_2$O$_2$, 0.5g ZnO and pH equal to 3.	38.94
8	30 mL H$_2$O$_2$, 1.5g ZnO and pH equal to 6	30.55
9	30 mL H$_2$O$_2$, 1.0g ZnO and pH equal to 4	44.54

Where k-reaction speed, i.e., amount of degraded matter in terms of COD per minute of reaction (COD deg. min.$^{-1}$).

Table 7. Behavior of the reaction speed over contact time.

Experiment	Reaction speed	Speed equation	R^2
1	k1	0.2219 e$^{-0.0374 t}$	0.9318
2	k2	0.2203 e$^{-0.0352 t}$	0.9163
3	k3	0.2164 e$^{-0.0369 t}$	0.9142
4	k4	0.2332 e$^{-0.0328 t}$	0.9451
5	k5	0.3595 e$^{-0.0406 t}$	0.8838
6	k6	0.3143 e$^{-0.0339 t}$	0.8763
7	k7	0.3803 e$^{-0.0391 t}$	0.9039
8	k8	0.3039 e$^{-0.037 t}$	0.87
9	k9	0.4094 e$^{-0.0381 t}$	0.9956

Analysis of microorganisms indicators of fecal contamination

Analyses of fecal coliforms showed positive results for all experiments; for the fresh wastewater, concentration of total and thermotolerant coliforms was on average 1.4 x 10^3 NMP 100 mL^{-1}, indicating that for the fresh wastewater all total coliforms were thermotolerant. After the treatment, for the nine conditions examined (Table 6) the heterogeneous photocatalysis promoted an efficiency of 100%, considering the critical values of pH and exposure to UV radiation.

Physical and chemical performance of the photocalytic reactor

In relation to the H$_2$O$_2$, significant reductions of COD were detected in three different levels,

varying the oxidant volume between 30, 50 and 100 mL. This indicates that for obtaining a favorable result, the hydrogen peroxide should be adjusted to the smallest volume (level #1 – 30 mL) because it presented the greatest decrease in COD (Figure 2).

Oliveira and Leão (2009) investigated H$_2$O$_2$ for treating textile industry wastewater and observed that the H$_2$O$_2$ collected with the effluent under reaction may be affected in the analyses based on oxidation processes, such as the COD analysis, which may use potassium dichromate that works as an optimal oxidant. However, under excessive H$_2$O$_2$, this will react with potassium dichromate and owing the presence of another oxidant, the H$_2$O$_2$ starts acting as a reducing agent, raising the value of COD.

Duarte et al. (2005) examined the performance of a chemical reactor, added 3 mL H$_2$O$_2$ into a sample of dairy wastewater whose initial COD was 1,000 mg L^{-1} and observed a reduction of COD estimated at 66%. But, there was still about 10% of unreacted H$_2$O$_2$.

In the analyses relative to the addition of zinc oxide (Figure 3), the first level presented a reduction of COD of 42%, in the second level, the reduction reached almost 50%, and on the third level it reached

the highest value exceeding 60% (p < 0.05). This great variation was caused by the influence of the amount of zinc oxide, i.e., it is required the highest level of zinc oxide (level 3) to reach the most effective result.
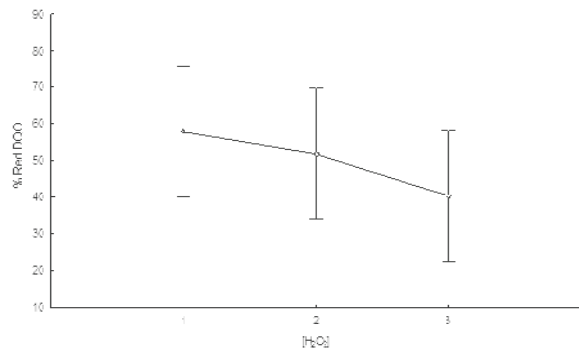

Figure 2. Influence of the volume of hydrogen peroxide in removing COD_{total} (levels 1, 2 and 3 cited on the horizontal axis are presented in the Table 1). % Red DQO- Reduction of COD.

Pascoal et al. (2007) verified that with the application of artificial and solar UV radiation in the photocalytic treatment, the catalysts also called semiconductors, at high concentrations may confer high turbidity, which can prevent the passage of light throughout the aqueous mixture.
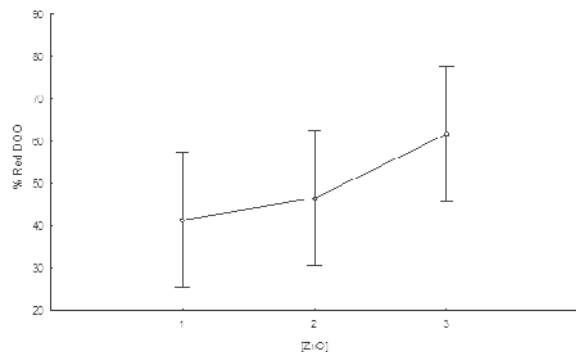
Figure 3. Influence of the mass of zinc oxide on the COD_{total} removal (levels 1, 2 and 3 cited on the x-axis are listed on the Table 1). % Red DQO- Reduction of COD.

Values of pH evaluated in the present study had no effect on the COD removal (p > 0.05). Duarte et al. (2005) observed that the revitalization of the thermal Fenton reaction occurred by Fe^{3+} photoreduction, resulting in more hydroxyl radicals in the reaction contributing to the efficiency under pH lower than 3.

The Figure 5 illustrates a model that relates the COD_{total} removal with Zn and H_2O_2. For an increase in the COD removal, it is required the use of smaller volumes of H_2O_2. On the other hand, to increase the COD removal, it is required to increase the mass of ZnO. The best results were achieved when using 30 mL H_2O_2 and 1.5 g ZnO.
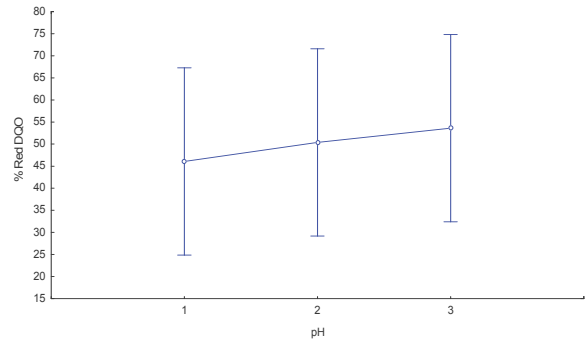

Figure 4. Influence of the pH on the COD removal (levels 1, 2 and 3 cited on the x-axis are listed on the Table 1). % Red DQO-Reduction of COD.
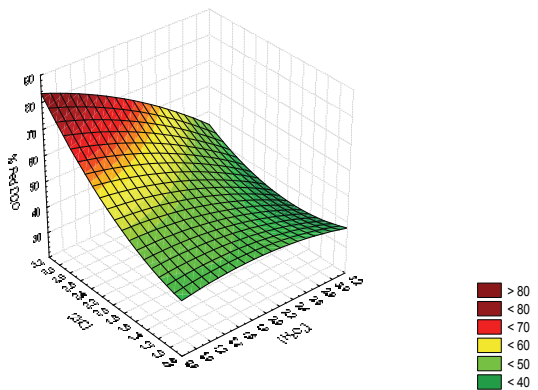

Figure 5. Correlation between the COD_{total} removal (% Red COD) and the amounts evaluated of ZnO and H_2O_2. % Red DQO-Reduction of COD. Optimization Equation: %Red COD = 30,706 + 14,1128 X +2,2198Y – 2,6782 X^2 – 6,0754 X.Y + 5,0245 Y^2.

The Figure 6 shows the COD_{total} removal efficiency as a function of the pH and the amount of oxidant (H_2O_2) used. It is necessary a smaller amount of H_2O_2 for a greater COD_{total} removal. Although the pH had not presented significance in the F-test (Figure 4), it evidenced a little change, with greater COD removal under higher values of pH.
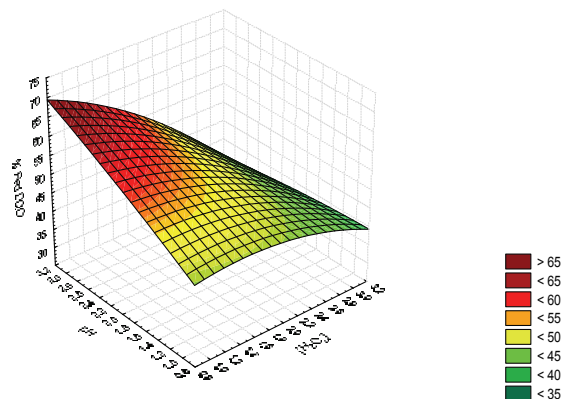

Figure 6. Correlation between the COD_{total} removal (% Red COD) and the pH values and amounts of H_2O_2 evaluated. % Red DQO-Reduction of COD. Optimization Equation: %Red COD = 30,2301 + 11,4855 X+ 15,4275 Y -2,6782 X^2 - 4,7617 X.Y – 0,534 Y^2.

The comparison of the three variables used in the experiment is presented in the Figure 7, as well as the efficiency of each to degrade organic compounds quantified as COD. The variable called by the Software as ghost variable is a control sample, i.e., without influence, once this is a symbology used to start the software and the construction of the graphs. The analysis on this graph was performed in relation to the average 50, and compared with the signal: noise ratio which is the direct relationship between what is measurable or not. As it is delimited the first line, established on the Figure 7, a great significance is observed to the hydrogen peroxide in the wastewater sterilization, this because the line is far from the average. The closer the variable is located in relation to the average, the less significant it will be in the process. This interaction can be observed in the representativeness of the pH.
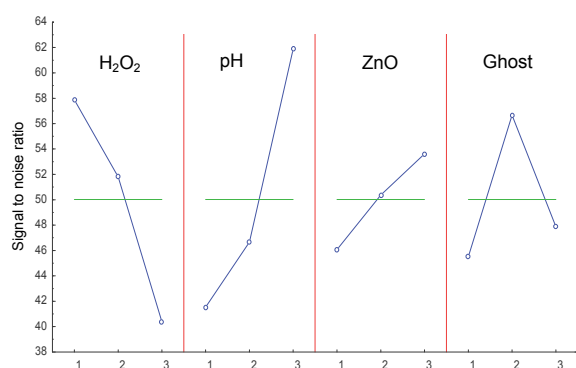

Figure 7. Comparative analysis relative to the experimental matrix determined for the nine experiments.

In the literature, there is a great variability of organic matter removal by biological processes.

Di Bernardo (1991) attained 60% of COD removal when evaluated a upflow anaerobic sludge blanket reactor at pilot scale in the treatment of dairy wastewater.

Afonso et al. (2001) treated dairy wastewater using batch-activated sludge and reached about 99% of COD removal. Campos et al. (2004) evaluated the performance of a upflow anaerobic sludge blanket reactor in laboratory and obtained, for different organic loads applied to the reactor, efficiencies between 24 and 52% in COD removal.

Comparing the COD removal efficiency herein observed with other studies using aerobic and anaerobic biological treatment, it was observed that only the aerobic process exceed the efficiency herein obtained. Authors working with anaerobic process justify the low efficiencies to the high concentration of oil and grease in the wastewater, which decrease the granulation of the UASB reactors, reducing the biodegradation efficiency. Therefore, with our

results it is verified the possibility and feasibility of combining chemical process (photocatalysis) with an anaerobic biological process in the treatment of dairy wastewater.

Conclusion

The Advanced Oxidation Process using UV photolysis, H_2O_2 and ZnO was effective in removing COD and total and thermotolerant coliforms from the wastewater, and can be successfully used to treat this kind of wastewater.

The best kinetic-chemical reaction for the duration time of 1h of lighting, concerning the catalyst, oxidant and pH ratio was 1 g ZnO / 30 mL H_2O_2 / pH = 4.

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