IMPACT: International Journal of Research in Engineering & Technology (IMPACT: IJRET)
ISSN (P): 2347-4599; ISSN (E): 2321-8843
Vol. 5, Issue 8, Aug 2017, 9-16

SLURRY DEGRADATION ANALYSIS VIA FENTON AND PHOTO-FENTON BY STOCHASTIC DIFFERENTIAL EQUATIONS

DIOVANA APARECIDA DOS SANTOS NAPOLEAO[1], CAROLINA DE SOUZA RAMUNNO[2], HELCIO JOSE HIZARIO FILHO[3] & ADRIANO FRANCISCO SIQUEIRA[4]

[1,2]Basic Science and Environment, Department of Engineering, School of Lorena, University of São Paulo-Area I, Brazil

[3,4]Chemical, Department of Engineering, School of Lorena, University of São Paulo-Area I, Brazil

ABSTRACT

Advanced oxidation processes are based on the generation of free radicals OH, which have high oxidative potential, degrading several components that pollute the environment. These processes attract lots of attention due to the increase of complexity and difficulty in the treatment of the effluent, resulting in the search for new technologies that may solve the problem of the waste. This study aimed to investigate the slurry treatment by means of Fenton process and photo-Fenton and to evaluate the reaction duration with TOC and DQO stochastic modeling. According to the results, stochastic model allowed the evaluation of the rationale kinetics of Fenton and photo-Fenton reactions, identifying maximum degradation in TOC and DQO, besides optimizing H_2O_2 levels and pH in the experimental design, enabling the reduction of costs in the reaction process.

KEYWORDS: Slurry, Fenton, Photo-Fenton, Stochastic model, advanced oxidative process

INTRODUCTION

The final disposal of garbage in Brazil varies according to the region where it is collected, but on average, about 71% is destined for landfills (sanitary or controlled) and 26% for open garbage dumps. After being allocated in its final destination, the garbage goes through physical, chemical and biological decomposition processes, producing gaseous and liquid residual fractions. The liquid fraction is the result of the decomposition of the garbage, associated with: environmental factors regarding the rainfall regime, the landfill temperature and the composition of the waste. Acetogenic and methanogenic bacteria action accelerates the decomposition of waste, while the percolation of the rainwater carries the degradation products to the lower layers of the sanitary landfill. When waste comes to the landfill, it goes through a process of decomposition assisted by acetogenic bacteria, which will give an acid character to the slurry produced [1].

Over time, there is an increase in the concentration of methanogenic bacteria, leading to the production of slurry with basic characteristics, containing species much more recalcitrant than those produced in the preliminary stages of decomposition. The environmental problem that comes together with this type of percolation is associated with organic xenobiotic compounds, most of them with high toxicity.

The conventional processes used in slurry treatment are based on physical-chemical (adsorption and flocculation) and biological processes, which have high purification. However, by the physicochemical processes, the contaminating substances are not degraded, resulting the generation of highly contaminated solid phases (sludge). In the biological process (activated sludge), there is a need for long periods of residence and low efficiency in the removal of recalcitrant and colored compounds [2], making their efficiency quite discussed.

Advanced Oxidative Processes (AOPs) seem to be an alternative to solve or maximize the degradation of the slurry, since they are based on hydroxyl radical generative, which can lead to complete mineralization of organic compounds (carbon and water formation). They are considered as one of the most efficient processes of pollutant removal from the aqueous solution, which may contain soluble organic compounds that are toxic and recalcitrant [3]. The most know AOPs use ozone (O_3), ultraviolet radiation (UV), hydrogen peroxide (H_2O_2), Fenton or Photo-Fenton reagent, which uses Fe (II), H_2O_2 and photo catalysis with titanium dioxide (TiO_2) associated to UV radiation and oxygen.

Based on this context, this study aims to adapt the treatment of slurry, according to the norms of the legislation for disposal in recipient bodies, in a batch reactor using an advanced oxidative process via Fenton and Photo-Fenton, allowing the degradation of the organic constituents, making them biodegradable.

MATERIAL AND METHODS

Sample and Preservation

The slurry used in the experiments is from Cachoeira Paulista Sanitary Landfill, located on Fiuta Municipal Road, Km 4, and São Paulo. Two hundred liters of slurry were collected, homogenized and conditioned at 4°C, in a cold chamber in 50 L pumps, throughout the experimental period.

Photo-Fenton Process Foto-Fenton for Slurry Degradation

The oxidation reaction of the effluent was carried out in a Germetec tubular reactor (model GPJ-463/1), with a nominal volume of approximately 2 L, which receives the GPH-463T5L low pressure mercury lamp irradiation, emitting UV radiation at 254 NM and power of 15 W and 28 W (design with two levels of power), protected by a quartz tube. The tubular reactor for the photo - Fenton process is shown in Figure 1.

Figure 1: Tubular Reactor Used for Photochemical Treatment

For Photo-Fenton experiments, 2 L of the slurry in natura, previously conditioned at room temperature and homogenized, were used. The volume of Fe (II) salt solution and H_2O_2 (purity 32.33% w/v, technical grade) were then added during 90 min by means of a GG (SS model) and HH (model DD) metering pump. The pH was measured with a glass electrode, adapted to the reservoir, and connected to the Digimed digital potentiostat. The effluent flow between the tubular reactor (surface contact) and the storage tank was carried out with the aid of a centrifugal pump (BOMAX, which will be added Model NH-30PX-T - 13 L min^{-1}). The quartz tube that protects the lamp has a high transmittance value in the working spectral region, not dispersing the UV irradiation.

Experimental Design in Photo-Fenton Process

It will be considered a fractional factorial plan, composed of three factors at two levels and with three central points, in duplicate, to evaluate the significance and interactions of the parameters analyzed in the treatment of effluent by means of Photo-Fenton process. The independent variables (factors) proposed for these steps are air flow, Fe^{2+} concentration ($FeSO_4$ $7H_2O$ solution) and pH. Table 1 presents the variables with the respective selected levels for the treatment of the effluent with Photo-Fenton process.

Table 1: Factors and Levels for Experimental Design

Factors	Low level (-1)	Medium level (0)	High level (+1)
H_2O_2 concentration (%) [1]	22.3	24.5	26.8
pH	2	3	4
Fe^{2+} concentration (g/L) [2]	10	7.5	5
Ultraviolet	0	15	28

[1] H_2O_2 volume = [low level: 22.3 mL; medium level (10% excess): 24.5 mL; high level (20% excess): 26.8 mL].

[2] Fe^{2+} mass = (low level: 0.73 g/L; medium level: 0.98g/L g; high level: 1.47g/L); the calculation was estimated regarding the ratio H_2O_2/Fe^{2+}, for the following values: 10; 7.5 and 5.

Modeling of Degradation Processes of Oxidative Processes of Leach ate via Stochastic Processes

The study of stochastic differential equations (SDE) has been developed in the literature with the publication of articles by [4] and [5], presenting several practical applications. A precise model of stochastic differential equation that simulates the variation of chemical oxygen demand (COD) and the total organic carbon (TOC) ratio can be used for predictions and validations of optimal conditions defined in the experimental design study. Another important point is that from the identification of the most significant variables in the treatment of advanced oxidation process obtained from the planning of experiments, a systematic study can be developed to identify how the model parameters of the stochastic differential equation vary in function of the experimental conditions. This fact is useful to understand how the factors and variables studied influence the process of slurry degradation. For this, we will consider the functions f and g:

$$f, g : [t_o, T] \times R \longrightarrow R$$

It will consider the Wiener Process W (t), with a mathematical description of the Brownian movement, proposed

By Norbet Wiener. Wiener Process was defined as a continuous Gaussian process with independent increments, equation 1:

$$dx_t = f(t, x_t)dt + g(t, x_t)dw_t \quad \textbf{(1)}$$

E (W (t)) = 0 and Var (W (t)-W(s)) = t-s, t > s. The probability distribution of W (t) -W (s) is a normal with zero mean and variance t-s. According to KLEBANER (1999), in equation 2 the function f can be interpreted as a mean value of the variable cost and g a mean of the standard deviation of the variability of cost. From the experimental data obtained by the oxidation process of the slurry, a proposal for stochastic differential equations was presented by SIQUEIRA et al.

(2013), regarding the study of TOC variation, expressed in equation 2.

$$dx_t = \left(a + \frac{bk}{e^{kt}} \right) dt + \frac{c}{(t+1)^p} dw \quad (2)$$

The constants a, b, c, k and pare the model parameters dependent on the experimental conditions. The parameter cost is the conversion of TOC at the instant of time t, expressed in minutes. According to SIQUEIRA et al. (2013), the cast presents the normal distribution with mean and variance presented in equations 3 and 4.

$$E(x_t) = a.t + b(1 - e^{-k.t}) = \mu_t \quad (3)$$

$$Var(x_t) = \frac{c^2}{2p-1}\left(1 - \frac{1}{(t+1)^{2p-1}}\right) = \sigma_t^2 \quad (4)$$

Parameter a is related to the inclination to the degree that the reaction reaches after the fast initial conversion reaction, parameter b marks the mean initial conversion value of the process and parameter k is related to the time that the reaction spends to reach the rational conversion. Based on an auxiliary model, it is possible to estimate how much time the reaction spends to reach the conversion degree (t_R), according to parameter k, using the equation 5:

$$t_R = \frac{2.\ln(10)}{k} \quad (5)$$

RESULTS AND DISCUSSIONS

Analytical Characterization of Slurry in Natura

Table 2 presents the results of the physicochemical analyzes of the slurry in nature from Cachoeira Paulista-SP and the values of discarded allowed by the legislations established in Article 18 - CETESB and CONAMA. The result found in COD value (5335.84 mg/L) is considered high and must be related to factors such as the type of waste, climate and final disposal of the waste, as well as the time of operation of the landfill.

Table 2: Values of the Analytical Parameters of the Slurry of the Sanitary Landfill From Cachoeira Paulista - SP

Parameters	Values	CETESB Article 18	CONAMA 357/05 and 430/11
DQO (mg O_2/L)	5335.8	_	_
TOC (mg C/L)	2300.6	_	_

Based on the results, a maximum degradation of TOC and COD was obtained with pH 5, the highest H_2O_2 concentration, the higher mass of $FeSO_4.7H_2O$ and the highest power in the process (TOC from 2300.55 to 380.61 mg/L, corresponding to 83.45% and COD from 5335.84 to 1677.6 mg/L, corresponding to 68.6%).

Analysis of Parameters A and B Associated to the Conversion of TOC in Fenton and Photo-Fenton Processes

Taking into consideration the estimations of the parameters in several experimental conditions involved in the slurry treatment process, it was possible to study the influences of the input variables in each of the parameters of the stochastic model. Applying the technique proposed by [6] and [7], it is possible to obtain the equation 6 for parameter a:

$$a = 0.00494963 - 0.0009914\ A + 0.001728\ B*B \quad \textbf{(6)}$$

According to the stochastic model, the values obtained for R^2 were 74.34% and adjusted R^2 were 67.93%, evidencing a good adjustment of the predicted model for the experimental conditions analyzed.

Table 3 presents the regression coefficients from a to the model.

Table 3: Regression Coefficients for Parameter A

Terms	Coefficients	[1]t	[2]p
Constant	0.442261	26.6543	0.000
[3]B*B	-0.097220	-4.6219	0.002
[4]A	0.051423	4.6812	0.002

[1]t Student; [2]p-value; [3]B*B = H_2O_2*H_2O_2; [4]A = pH

For parameter b, relative to TOC degradation process, the auxiliary model was described by equation 7:

$$b = 0.442261 + 0.0514228\ A - 0.0972197\ B*B \quad \textbf{(7)}$$

The values obtained for R^2 was 84.4% and the adjusted R^2 was at 80.5% for parameter b, showing an adjustment to the experimental conditions for the conversion of TOC in the Fenton and Photo-Fenton slurry degradation process. Table 4 presents the regression coefficients of b for the model.

Table 4: Regression coefficients for parameter b

Terms	Coefficients	[1]t	[2]p
Constant	0.442261	24.6543	0.000
[3]B*B	-0.097220	-4.6219	0.002
[4]A	0.051423	4.6812	0.002

[1]t Student; [2]p-value; [3]B*B = H_2O_2*H_2O_2; [4]A = pH

In Figure 2, based on the stochastic and auxiliary models, it was observed that the TOC degradation process can be optimized with the following operational conditions described below:

Steps 1 - The first 12 min of the reaction should occur with pH at the highest level and H_2O_2 at the central point,

Steps 2 - After 12 min of reaction the pH and H_2O_2 should be considered at the low level.

Analysis of Parameters A and B Associated With COD Conversion in Fenton and Photo-Fenton Processes

With the studies carried out by [6] and [7] and applying the proposed technique, it was obtained the equation 8, related to parameter a:

$$a = 0.0035415 - 0.00274525\ B*B \quad \textbf{(8)}$$

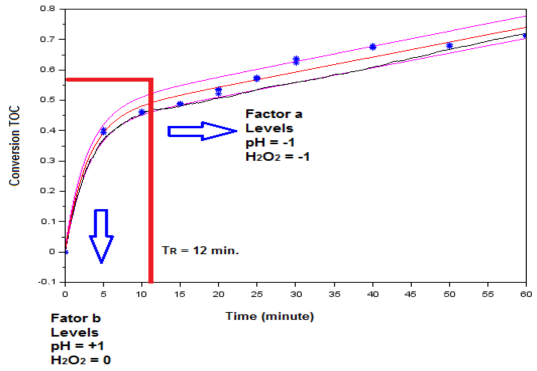

Figure 2: Optimized Process of Slurry Treatment by Stochastic Differential Equations

According to the stochastic model, the values of R^2 calculated were 63.11% and adjusted R^2 were 59.02% correspondent to the regression model. Table 5 shows the coefficients of the regression of parameter a.

Table 5: Regression coefficients

Terms	Coefficients	^{1}t	^{2}p
Constant	0.0035415	5.93623	0.000
^{3}B*B	-0.0027452	-3.92423	0.003

^{1}t Student; ^{2}p-value; ^{3}B*B = H_2O_2*H_2O_2

Based on the p-value presented in Table 5, the interaction H_2O_2*H_2O_2 influences the inclination of the degree. Equation 8 shows that the value of the parameter is related to the interaction of H_2O_2*H_2O_2 at the low level. The auxiliary model for parameter b related to COD degradation process was described in equation 9

$$b = 0.430593 + 0.20016\ B*B \quad \textbf{(9)}$$

According to the auxiliary model, the values obtained for R^2 were 38.87% and for the adjusted R^2 were at 32.08%. Table 6 shows the regression coefficients of parameter b.

Table 6: Regression Coefficients for Parameter B

Terms	Coefficients	^{1}T	^{2}P
Constant	0.430593	6.03505	0.000
^{3}B*B	0.200160	2.39244	0.040

^{1}T Student; ^{2}P-value; ^{3}B*B = H_2O_2*H_2O_2

It was observed in equation 9 that the value of parameter b is associated with the interaction of H_2O_2*H_2O_2 at the low level.

Figure 3 shows that COD degradation process can be optimized with the following operational conditions described below:

Step 1 - The first 14 min of the reaction must occur with H_2O_2 interaction at the lowest level,

Step 2 - After 14 min of interaction reaction of H_2O_2 should be considered at the medium level.

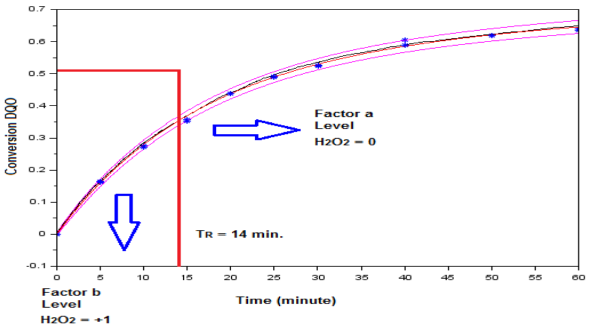

Figure 3: Optimized Process of Slurry Treatment By Stochastic Differential Equations

CONCLUSIONS

The use of stochastic model allowed to reproduce the variations of the experimental data for the conditions studied in the conversion of TOC and COD. According to the equations of the auxiliary model, a maximum degradation of TOC (78%) was observed in the reduction of the carbonaceous substance of the slurry and the varying pH and H_2O_2 must be on the lower level. In the COD degradation (68%) for slurry treatment, the interaction of H_2O_2 must be at the medium level. For Fenton and Photo-Fenton processes, it was evidence that there was an increase in the efficiency of the reaction medium with the aid of stochastic modeling, in which the process could occur with a lower amount of H_2O_2 and pH 4 for TOC. For COD, H_2O_2 reduction was observed, possibly due to the slower reaction kinetics, being considered relevant information for the reduction of costs in the slurry treatment process.

ACKNOWLEDGMENTS

The authors would like to thank the Foundation of Support for the Research of São Paulo - FAPESP for the financial support for the accomplishment of this project (Proc. 2014/21364-3). The Hydric and Environmental Analysis Laboratory, Basic Sciences and Environmental Department – Debas at Engineering School of Lorena which contributed to the development of this paper.

REFERENCES

1. Pacheco, J. R., Peralta-Zamora, P. G., Integração de processos físico-químicos e oxidativos avançados para remediação de percolado de aterro sanitário (chorume). Eng. Sanitária Ambiental, 9 (4), 306-311, 2004.
2. Freire, R. S.; Pelegrini, R.; Kutota, L. T; Duran, N.; Peralta-Zamora, P.; Quim. **Nova**, 23, 504, 2000.
3. GOGATE, P. R.; PANDIT, A. B. A review of imperative technologies for wastewater treatment II: hybrid methods. Advances in Environmental Research, v. 8, p. 553-597, 2004.
4. DURRETT, R. Stochastic Calculus: **A Practical Introduction.** CRC Press LLC, Florida, 1996.
5. KLEBANER, F. Introduction to Stochastic Calculus with Appications. Imp. College Press, London. 1999.

6. Siqueira, A. F, Cobra, O. C. G., Filho, H.J.I., Giordani, D. S., Silva, M. B.; Modeling the photocatalytic process of variation of chemical oxygen demand via stochastic differential equations. Open Chem. Eng. Journal, v. 7, p. 1-8, 2013.

7. Siqueira, A. F., Hizário Filho, H. J., Alcântara, M. A. K., Loures, C. C. A., Teixeira, L. A. B. M., Guimarães, O. L. C., Gabas, A. L., Napoleão, D. A. S. Modeling total organic carbon variation in a photocatalytic process via stochastic differential equations, v. 33, n. 8, Environmental Engineering Science, 2016.