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Economic analysis of Fenton process in the slurry treatment

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Abstract: *The search for clean and highly efficient technologies, with high power of elimination of pollutants and reduced cost is becoming constant due to the increasingly rigorous legal requirements on the quality of liquid effluent disposal. In this scenario, the Advanced Oxidative Processes seem to be an alternative technique for the treatment of toxic and/or recalcitrant effluents and have been attracting great attention in the scientific and industrial area. This study aimed to evaluate the cost/benefit and the average reaction time of the slurry degradation process via Fenton, considered a source of environmental pollution in landfills. According to the results obtained in the Fenton process, there was a conversion of 80% of the effluent degradation, which corresponds to an average reaction time of 90 minutes. Stochastic model allowed a complete analysis of the experimental data in the cost/benefit analysis of the slurry treatment.*
Keywords: *Slurry, Degradation, Fenton, Stochastic Model, Advanced oxidative process.*

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I. INTRODUCTION

The final disposal of garbage in Brazil varies according to the region where it is collected, but on average, about 71% is destined to 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.

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.

Regarding the physico-chemical characterization, this type of effluent presents a high concentration of pollutant compounds if compared to the values allowed by the legislation. Its composition presents high organic load and requires proper treatment for the disposal in water bodies.

The conventional processes used in slurry treatment are based on physical-chemical (adsorption and flocculation) and biological processes, which have high purification efficiency (Hermosila et al., 2009). However, by the physic-chemical 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 (Freire et al., 2000), making their efficiency quite discussed.

In this context, 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 generation, which can lead to complete mineralization of organic compounds (carbon and water formation). It is considered as one of the most efficient processes of pollutants removal from the aqueous solution, which may contain soluble organic compounds that are toxic and recalcitrant (Esplugas et al., 2002, Wu et al., 2011). This work is justified with the oxidative Fenton process in the treatment of slurry, a complex mixture, being necessary most of the cases to employ two or more treatment technologies to obtain an effluent within the discharge patterns.

In the Fenton reaction, the hydroxyl radical is the oxidant species catalyzed by the iron ion in this system, capable of oxidizing several classes of organic compounds in a spontaneous reaction (Guedes, 2003), according to "equation 1"

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad k = 76\ L\ mol^{-1}s^{-1} \tag{1}$$

In the absence of a substrate or in the prevalence of high concentrations of Fe^{2+}, the formed hydroxyl radical can oxidize another ferrous ion to ferric ion, according to "equation 2"

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad k = 3.2 \times 10^8 L\ mol^{-1}s^{-1} \tag{2}$$

Ferric ions can decompose H_2O_2 to H_2O and O_2, which stages are pH-dependent, as evidenced in "equations 3 to 6":

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \quad k = 0.001\text{-}0,01\ L\ mol^{-1}s^{-1} \tag{3}$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \tag{4}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \quad k = 1.3 \times 10^6\ L\ mol^{-1}s^{-1} \tag{5}$$

$$H_2O_2 + {}_\bullet OH \rightarrow HO_2^\bullet + H_2O \quad k = 2,7 \times 107\ L\ mol^{-1}\ s^{-1} \tag{6}$$

Reactions show that iron acts as a catalyst, however, since Fe^{3+} reduction is generally much slower than Fe^{2+} oxidation, iron exists in solution, mainly in Fe^{3+} form (Cardeña, 2009). Fenton process depends on the conditions of the reagents, that is, the ratio of Fe^{2+}, Fe^{3+} and H_2O_2 concentrations and reaction characteristics (pH, temperature and quantity of organic and inorganic constituents). These parameters determine the efficiency of the overall reaction in terms of the production and consumption of hydroxyl radicals.

Taking this into consideration. this study aimed to evaluate the application of Fenton process in the degradation process of the slurry *in natura*, considered a serious problem of environmental pollution caused in landfills.

II. MATERIALS AND METHODS

2.1- Sample and preservation

The slurry used in the experiments is from Cachoeira Paulista Sanitary Landfill, located on Fiuta Municipal Road, Km 4, 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.

2.2- Experimental procedure

Analytical characterization of slurry *in natura* and after oxidative treatments were adapted, according to Standard Methods (Apha, 1999). COD determinations were performed with closed tube digestion, followed by spectrophotometric determination (spectrophotometer SP 1105) at 620 nm. The BOD_5 (Biochemical Oxygen Demand 5 days) determinations were incubated (SP 500) for a period of 5 days with inoculation of Seed-type microorganisms at 20±3ºC, with the oxygen measured, before and after incubation, by Winkler titrimetric method, modified by sodium azide. The organic carbon determinations were performed on a Shimadzu total organic carbon analyzer, model TOC-VCPH, based on high temperature catalytic oxidation and CO_2 determination by infrared spectroscopy. In order to determine the organic carbon, the calibration curve was prepared from a potassium biftalate standard, in the linear range of 0-1000 $mg.L^{-1}$.

Fenton process was optimized by a fractional factorial design (2^{3-1}), with triplicate at the central point and random duplicates, witj the following input variables: H_2O_2 concentration (%) (25; 50, excess), Fe^{2+} concentration (g/L) (1; 2; 3) and pH (2; 3; 4), according to Table 1. The response variables in this planning were percentages of total organic carbon (TOC) in the leached degradation.

Fenton process experiments were performed on a borosilicate glass reactor manufactured by Adonex. A wooden base fixes the tubular reactor of 42 cm and 4 inches of internal diameter, with volumetric capacity for 4 L. The reactor is composed of three entrances, two of the same side located in the points of 22 and 40 cm height for the access of hydrogen peroxide and effluent recycle. The other one is opposite, at 5 cm height, for aeration of the system. At the lower base of the reactor there is a faucet for collection of the treated effluent.

A metal clamp attaches the reactor to a cone-shaped cap with a polished escape at the top. This escape connects to the polished part of an arc-shaped glass tube that is connected to a plastic tube. This operational part has been developed to condense the foam, through the air access, and make this foam returns to the process to avoid reagent and effluent losses, Fig. 1. During the advanced oxidative process (Fenton), the reactor operated for 90 minutes at room temperature and 3L of the slurry were added *in natura*. $FeSO_4.7H_2O$ was dissolved in 50 mL of H_2O and sufficient amount of H_2SO_4 for dissolution. This solution was added to the slurry *in natura*. The pH of the solution was then adjusted with addition of H_2SO_4 to obtain the respective pH values shown in Table 1. The peristaltic pump was configured to add the entire volume of peroxide during the time of operation. For the aeration of the system, the air flow rate was 0.75 L/min. With the reactor operating, a sample was collected with 5 minutes and then samples were collected every 10 minutes, totalizing a reaction period of 90 minutes.

Table 1 - Control factors of the levels of slurry treatment from Cachoeira Paulista sanitary landfill – SP.

Factors	**Levels**		
	Low (-1)	**Medium (0)**	**High (+1)**
[1]H_2O_2 concentration (%)	25	50	excess
pH	2	3	4
[2]Fe^{2+} concentration (g/L)	1	2	3

[1]H_2O_2 volume = (low level: 66.9 mL; medium level: 83.7 mL; high level: 100.5 mL)
[2]$FeSO_4.7H_2O$ mass = (low level: 15.09 g; medium level: 30.19 g; high level: 45.29 g)

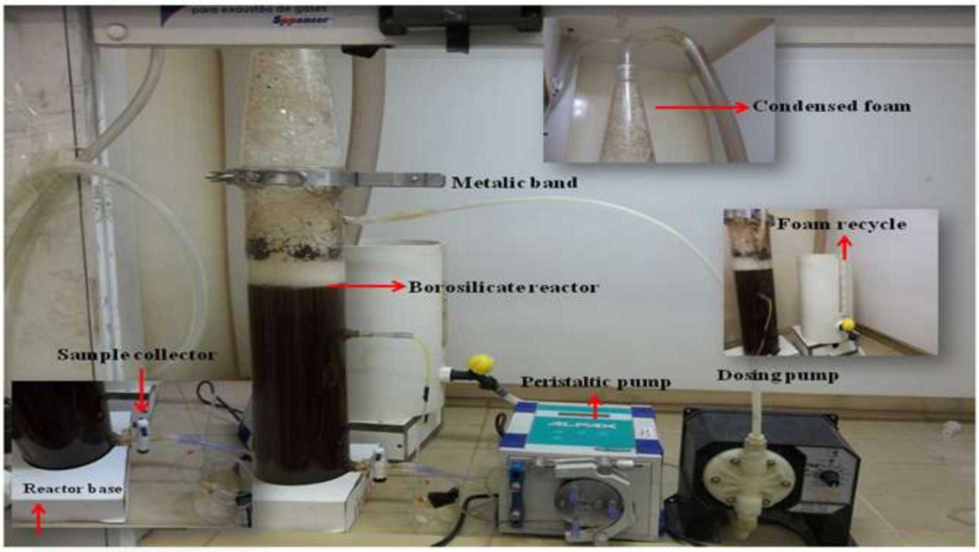

Figure 1— Fenton oxidative process reactor

III. RESULTS AND DISCUSSION

3.1- Evaluation of slurry chemical treatment regarding TOC

The results of TOC reduction percentages after 90 minutes of reaction are shown in Table 2. Based on the results presented in Table 2, a maximum degradation was obtained in assay 8, ie at pH 4 and using the highest concentrations of H_2O_2 and Fe^{2+}. In this assay, TOC degradation with the chemical treatment was 80.0% (from 1658.0 mg/L to 342.4 mg/L). The minimum degradation of TOC with the chemical treatment was 64.6% (from 1625.3 mg/L to 574.9 mg/L), in assay 6.

By means of a chemical evaluation, the analytical results of TOC ratio must be highlighted, since the final organic load was considered in function of the concentration of this parameter in the slurry treatment process.

Table 2- TOC reduction percentage in Fenton process

Experiments	pH	H_2O_2 (g)	Fe^{2+} (g)	TOC (%)
1	2	0.63	45.3	72.4
2	2	0.94	15.1	66.1
3	4	0.63	15.1	73.3
4	4	0.94	45.3	78.5
5	2	0.63	45.3	72.1
6	2	0.94	15.1	64.6
7	4	0.63	15.1	71.5
8	4	0.94	45.3	80.0
9	3	0.78	30.2	73.5
10	3	0.78	30.2	73.3
11	3	0.78	30.2	73.7

3.2- Evaluation of slurry chemical treatment regarding TOC

Advanced oxidative processes are used in laboratory scale for the treatment of different types of effluents and this technology is approached by scientific literature emphasizing its importance in reducing the environmental impact on the receptor bodies. Giménez et al. (2015) highlighted that the use of advanced oxidative processes implies in the analysis of the cost of each experiment in a laboratory and the need for prior designing.

In this study, the economic evaluation was performed in laboratory scale for Fenton process, based on reagent costs and energy consumption of the systems. The energy consumed by the equipment in Fenton process with a duration of 90 minutes is presented in Table 3, with the average energy consumption in kWh for each equipment.

Table 3- Energy consumption of the equipments (kWh) and their respective cost

Equipments	Consumption (kWh)	Cost US$
Pristaltic pump	0.03	0.005
Metering pump	0.02	0.003
pHmeter	0.002	0.0003

The energy consumption of the equipment was estimated by the direct measurement of the energy consumed by the ICEL ME-20500 (220V and 60Hz) equipment, certified according to the numbering (201111011512). The estimation of the reagents consumption was based on the levels of the worksheet of the Table 1, considering the following reagents and concentrations: H_2SO_4 (98% m m^{-1}), $FeSO_4.7H_2O$ (99% m m^{-1}), H_2O_2 (30% m m^{-1}), based on the quotation of Chemistry and Derivatives Journal (2017) and Cavalcanti et al., 2013.

The optimization of Fenton process in function of TOC conversion reduction was evaluated by mena s of the total cost for the conversion of 80% in the reaction medium regarding cost/benefit of each experiment, as presented in Table 4.

In Fenton process, the best cost/benefit is related to the experiment 4, in the Table 4. It was evaluated by calculating the total consumption (energy + reagent), in which the energy cost was estimated at US$ 0.075 and the reagent consumption at US$ 0.014, totaling US$ 0.089 for 3 L of slurry from the reactor, during 90 minutes of reaction. For the slurry treated with Fenton process, the cost per liter was estimated at US$ 0.029 and the cubic meter was predicted at US $ 29.67. The levels of the variables of the experiment with the best cost/benefit, considering 3 L of slurry were: pH 4, amounts of the reagents H_2O_2 with 100.5 mL and Fe^{2+} with 14.9 g. The results of the total cost for the conversion of a efficiency percentage of 80% in the slurry degradation show that the experiment 8 presented the lowest cost with the same levels of the variables related to the best cost/benefit.

In the Table 4, the comparative analysis shows an increase in the energy cost compared to the chemical cost in Fenton process. The stochastic model in this study was able to predict, depending on the variables of Fenton process, the reaction duration, in which it was obtained an efficiency of 80% of degradation of the slurry, according to Figure 2.

Table 4- Costs projection for Fenton process

Exp.	**Reagents**			**Energy**	**Total Cost US$**	**TOC (%)**	**[1][CT/ %Red.]×1000**	**Chemical Cost**	**[2]Time (min.) 80% conversion**	**Energy Cost**	**Total Cost for 80% conversion**
	pH adjustment	**Fenton Reagent**									
	H_2SO_4	**H_2O_2**	**$FeSO_4.7H_2O$**								
1	0.108	7.6×10^{-4}	0.009	0.075	0.097	72.4	1.34	0.022	125	0.104	0.126
2	0.013	9.2×10^{-4}	0.005	0.075	0.094	66.1	1.42	0.019	216	0.180	0.199
3	0.012	6.0×10^{-4}	0.015	0.075	0.102	73.3	1.39	0.028	125	0.105	0.132
4	0.009	6.0×10^{-4}	0.005	0.075	0.089	78.5	1.13	0.016	131	0.109	0.124
5	0.008	6.0×10^{-4}	0.005	0.075	0.089	72.1	1.23	0.013	145	0.121	0.135
6	0.108	$7.6\times10^{-}$	0.009	0.075	0.097	64.6	1.50	0.022	118	0.097	0.119

		4									
7	0.012	7.6×10^{-4}	0.009	0.075	0.098	71.5	1.37	0.022	125	0.104	0.127
8	0.009	9.2×10^{-4}	0.015	0.075	0.099	80.0	1.24	0.025	86	0.072	0.097
9	0.013	9.2×10^{-4}	0.005	0.075	0.094	73.5	1.28	0.019	185	0.154	0.173
10	0.012	6.0×10^{-4}	0.015	0.075	0.102	73.3	1.39	0.028	135	0.112	0.140
11	0.009	9.2×10^{-4}	0.015	0.075	0.099	73.7	1.34	0.025	93	0.078	0.103

[1]Factor to evalaute cost/benefit relation; [2]Reaction duration for conversion of 80% in the slurry treatment; US$ 1.00 = R$ 3.16, quotation of exchange UOL (2017)

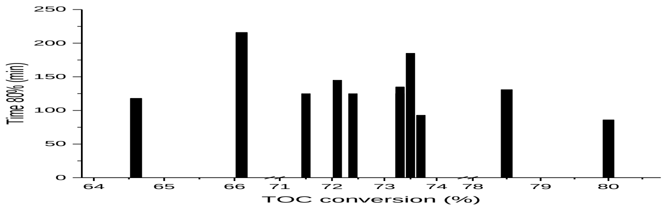

Figure 2- Reaction time to slurry degradation

IV. CONCLUSION

Fenton process for the chemical treatment of slurry reached a conversion of 80%, regarding to the degradation of the organic matters. In the evaluation of costs, for Fenton process, cubic meter was estimated at US$ 29.67, allowing a projection of chemical and energy costs involved in the reaction medium. Another important point was the use of the stochastic model to estimate the average time for the degradation process, till it reached a conversion rate of 80%. It favored an uniform comparison of the benefit of the degradation with the costs for the choice of the optimized route with the best cost/benefit of slurry treatment.

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