Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 No. 1 pp. 1-8 2019

Original Research Paper **Open Access**

Treatment of Leachates of a Controlled Landfill in Veracruz By Using the Fenton Method

Miguel Ángel López-Ramírez*, Olaya Pirene Castellanos-Onorio, Manuel Alberto Susunaga-Miranda**, Fabiola Lango-Reynoso*†, María del Refugio Castañeda-Chávez* and Jesús Montoya-Mendoza***
*Tecnológico Nacional de México/Instituto Tecnológico de Boca del Río, Carretera Veracruz-Córdoba 12, 94290 Boca del Río, Veracruz, México
**Tecnológico Nacional de México/Instituto Tecnológico de Veracruz. Av. Miguel Ángel de Quevedo 2779, Formando Hogar, 91897 Veracruz, Veracruz, México
†Corresponding author: Fabiola Lango-Reynoso

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 28-05-2018
Accepted: 02-08-2018

Key Words:
Controlled landfill
Leachate
Fenton Mehod
Chemical treatment
Contamination

ABSTRACT

Leachates are formed by the decomposition of solid waste contained in the final disposal site from liquids formed by precipitation or humidity in the area. Which, when filtered through waste, entrain substances in dissolved form and/or in suspension, creating a dark coloured liquid of variable characteristics and difficult to degrade, leading to contamination of soil and water bodies. Due to its variable characteristics, typical treatments such as evaporation, U.V. or recirculation are not suitable as chemical treatments. The Fenton process, being an advanced oxidation technique, has shown optimal performance in the treatment of young and mature leachates. Different parameters were tested during the Fenton oxidation-reduction process, which is consisted of treating the leachate with different combinations of hydrogen peroxide (H_2O_2) and ferrous sulphate ($FeSO_4$) under different acidic conditions, determining the optimal pH values, and doses of the Fenton reagent. Optimal conditions of the oxidation process were: contact time 1 hour, a pH value equal to 2, H_2O_2 concentrations of 250 mg/L and 75 mg/L of Fe^{+2}. The percentage of removal measured as BOD was of 96% at a final pH of 1.8.

INTRODUCTION

Leachate is the result of percolation of liquids through solid wastes in a stabilization process. That is, they are generated from the biochemical decomposition of waste or as a result of water infiltration from external sources, such as surface drainage, rain, groundwater and water from underground springs. Or, through waste in degradation processes, extracting dissolved or suspended materials generating a highly variable and toxic liquid. The organic matter load of leachate varies depending on the age of the landfill, from 2,000 to 3,000 mg/L in young fillings and from 100 to 200 mg/L in fillings considered as mature. Similarly, with the level of acidity that goes from 4.5 to 7.0 in young leachates and from 6.6 to 7.5 in mature leachates (Tchobanouglus 2000). Leachates, due to their physico-chemical characteristics, strongly variable in quantity and quality, are classified as one of the most polluting and difficult to treat waste, as indicated in Table 1.

The leachate, in terms of quality, contains heavy load of organic matter (high BOD), in addition to inorganic substances such as heavy metals (with its potential effect on aquatic ecosystems), high content of total and dissolved solids, presence of nitrogen in ammoniacal form, high concentration of chlorides, diverse organic compounds, as well as great pH variability. This depends on the nature of the waste (pH, age, temperature) and the stabilization phase in which they are located (Borzacconi et al. 1996a, El-Fadel et al. 2002).

Leachates are eventually removed from the landfills to be treated by physico-chemical and/or biological methods, thus avoiding soil, aquifers or surface water contamination through leaching, due to the runoff they generate. Treatment options include the reuse of leachates to maintain the moisture content of the landfills, on-site treatment (aerobic, anaerobic or physico-chemical), discharge to municipal treatment plants, or a combination of the above.

Several researchers have studied landfill leachate treatments obtaining promising results through different processes. These results indicate that the efficiencies of contaminant removal, obtained in a given leachate, are influenced by their chemical composition, which in turn is related to the characteristics and degree of sludge stabilization or the landfill age (Borzacconi et al. 1996b, Enzminger et al. 1997).

The controlled landfill of the city of Veracruz contains a type of sandy soil with particle sizes greater than 0.125 mm and smaller than 1.0 mm. In addition, it contains an average alkaline pH of 7.40, with an average conductivity of 1.40 dS/cm, resulting in a very slightly saline characteristic throughout the year. The fact that this landfill has a sandy soil, shows that it is not suitable because it retains less water than others; resulting in a leachate with an average BOD_5 of 74.140 mg/L and an average COD of 340.35 mg/L implying a biodegradability of 0.217. When the index of biodegradability is higher than 0.3, the leachate is considered biodegradable and is known as young leachate (typically less than two years old) (Deng 2007). For this reason, the first stage of treatment, always recommendable for young leachates, is the application of biological treatments; whereas physico-chemical processes are the best option for old leachates, as is the case of the one produced in the controlled filling of the city of Veracruz (Kurniawan et al. 2009).

One of the most promising physico-chemical treatments for leachates is the Fenton oxidation, which consists of the oxidation of the contaminant load with a combination of hydrogen peroxide and ferrous sulphate (Fenton reagent), typically at atmospheric pressure and temperature between 20°C and 40°C. This type of treatment is used generally in leachates considered old, in which the biodegradability index (BOD_5/COD) is low; therefore, biological treatments, whether aerobic or anaerobic, would be inefficient.

The optimal conditions of the Fenton reagent are obtained at acid pH values and with them, high removals of organic contaminants can be achieved. The Fenton process involves:

- A structural change of organic compounds that make possible a later biological treatment.
- A partial oxidation that results in a decrease in the toxicity of the effluent, and/or a total oxidation of the organic compounds in harmless substances that enable a safe discharge of the effluent without the need for further treatment.

The agent responsible for oxidation in the Fenton process is the hydroxyl radical (•OH), $Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \bullet OH$. This free radical is extremely reactive and is formed by the catalytic decomposition of hydrogen peroxide in an acidic medium (Kitis et al. 1999, Yoo et al. 2001, Lu et al. 2001). There is a wide variety of organic compounds that are possible to degrade with the Fenton reagent; some compounds are more refractory than others, requiring higher temperatures for oxidation. For example, benzene or phenol are oxidized relatively easily, while chlorinated derivatives are less reactive and require longer time or higher temperatures for their treatment. In many cases, an organic substrate, apparently refractory to the treatment can be oxidized by altering the conditions of temperature, pH or catalyst concentration.

There are numerous studies on the effect of the Fenton reagent on the removal of leachate contaminants from landfills. When a ratio of $[Fe^{2+}]/[H_2O_2]$ equal to or greater than 1.25 is used, the Fenton reaction can be divided into two processes. The first consists of an initial oxidation at low pH values, around 3. The second process, which follows the oxidation, is the coagulation-flocculation at high pH values (between 7-8). It was interpreted that the coagulation step in the Fenton process had a primary role in selective removal of contaminants, though the Fenton reaction is not coagulation. However, since the efficiency of organic removal in the Fenton reaction was higher than coagulation, the Fenton process in the landfill leachate treatment process may be called "a type of enhanced coagulation" (Yoo et al. 2001).

MATERIALS AND METHODS

Characterization of leachates: Samples were taken between the months of June 2017 and February 2018, where the following parameters were determined as per APHA-AWWA-WPCF (1998): pH, chemical oxygen demand (COD), ammoniacal nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN), organic nitrogen (org-N), total phosphorus (TP), fats and oils, settleable solids (SS) and total suspended solids (TSS). The samples were collected in a temporary oxidation lagoon located inside the controlled landfill of the city of Veracruz, where the leachates of different ages are mixed.

The leachate samples were homogenized with a Thermolyne Cimarec® 2 stirrer, at 600 r.p.m. In order to determine the optimum pH, concentration and dose conditions of Fenton reagent (peroxide and Fe^{2+}), and a contact time of one hour was proposed.

Determination of the pH: To this effect, the pH value of the leachates was adjusted to 2, 4 and 6, using concentrated H_2SO_4 (97% w/w oxidation tests, and a dose of 30% Fenton reagent (500 mg/L of hydrogen peroxide and 150 mg/L of ferrous sulphate) occupying a volumetric proportion of 25% according to the volume of the leachate to be treated.

Determination of concentration: The determination of the optimal concentration was obtained from the adjusted pH, with a concentration of 25%, according to the volume of the sample and with the concentrations of 30% Fenton reagent (500 mg/L of hydrogen peroxide and 150 mg/L of ferrous sulphate), 60% (500 mg/L of hydrogen peroxide and 300 mg/L of ferrous sulphate) and 90% (500 mg/L of hydrogen peroxide and 450 mg/L of ferrous sulphate).

Determination of optimal volume: The optimal dose is determined, based on the results obtained from the pH and the concentration of the Fenton reagent, by volume percentages of 25%, 50% and 75%.

Determination of the biochemical oxygen demand: To determine the biochemical oxygen demand (BOD) of the treated leachate, the procedures established in the Mexican standard NMX-AA-028-SCFI-2001 were followed. This standard establishes the determination of the biochemical oxygen demand in natural, residual waters (BOD_5) and treated wastewater - test method; the pH is then reduced to 8 with potassium permanganate so that the residual or residual peroxide does not affect the BOD readings.

RESULTS

Table 2 shows the results of the characterization of leachates, and Table 3 presents the treatments performed for the determination of the optimum pH, whereas Fig. 1 shows their respective results in the form of a removal percentage of organic matter measured as BOD.

Table 4 gives the treatments carried out to determine the concentration of the Fenton reagent and Fig. 2 shows the percentage results of the organic matter degradation obtained.

Table 5 shows the experimentation to determine the effective dose of the Fenton reagent in the leachates, and Fig. 3 shows the results measured in percentage of degradation of organic matter.

The controlled landfill of the city of Veracruz has a sandy soil, which is most prone to erosion by water and wind, as well as being the most porous. This is due to the large amount of water that filters out allowing larger particles to go through, thus maintaining a constant biochemical oxygen demand, since it does not act as a retention filter.

The pH of the leachate is alkaline, even though it does not come into direct contact with carbonates, calcium or magnesium bicarbonates, as reported by Méndez Novelo (2010) in the leachates of the landfill of the city of Mérida, being more similar to the value obtained in Hong Kong by Lau (2001).

Fig. 1 shows the removal percentages obtained in the different pHs treated in the sample, showing that pH 2 in treatments 1, 2 and 3 got better degradation results similar to those by Zhang et al. (2005), which was 2.5 units.

The results obtained, using a concentration of Fenton at 30% in treatments 10, 11 and 12, showed an 84% removal of organic matter (Fig. 2) that was higher than that reported by Cortez et al. (2011) in Portugal, with Fenton at 33% and a maximum efficiency of 44%. In addition, the coagulation-flocculation process was presented, in which several authors have reported high removals of organic matter as reported by Duran et al. (2002) with a maximum efficiency of

Table 1: Characteristics of young and mature leachate.

Characteristics	Units	Young leachate	Mature leachate
BOD_5	mg/L	2000-3000	100-200
COD	mg/L	3000-60000	100-500
Nitrates	mg/L	5-40	5-10
TSS	mg/L	200-2000	100-400
Ammoniacal nitrogen	mg/L	10-800	20-40
Total organic nitrogen	mg/L	10-800	80-120
pH	-	4.5-7.5	6.6-7.5
Total phosphorus	mg/L	5-100	5-10

Table 2: Characterization of the leachates of the controlled landfill of the Veracruz city.

Parameters	Units	Value
pH	-	8.500
COD	mg/L	340.35
BOD_5	mg/L	74.140
Ammoniacal nitrogen	mg/L	1.944
Total nitrogen	mg/L	3.058
Organic nitrogen	mg/L	1.112
Total phosphorus	mg/L	0.519
Fat and oil	mg/L	5.000
Sedimentable solids	mg/L	0.100
Total suspended solids	mg/L	15.000

Table 3: Treatments to determine the optimum pH.

Treatment	pH	Fenton	
		H_2O_2(mg/L)	Fe(mg/L)
1	2	500	150
2	2	500	150
3	2	500	150
4	4	500	150
5	4	500	150
6	4	500	150
7	6	500	150
8	6	500	150
9	6	500	150

Table 4: Treatments for determining the concentration of the Fenton reagent.

Treatment	pH	Fenton	
		H_2O_2(mg/L)	Fe(mg/L)
10	2	500	150
11	2	500	150
12	2	500	150
13	2	500	300
14	2	500	300
15	2	500	300
16	2	500	450
17	2	500	450
18	2	500	450

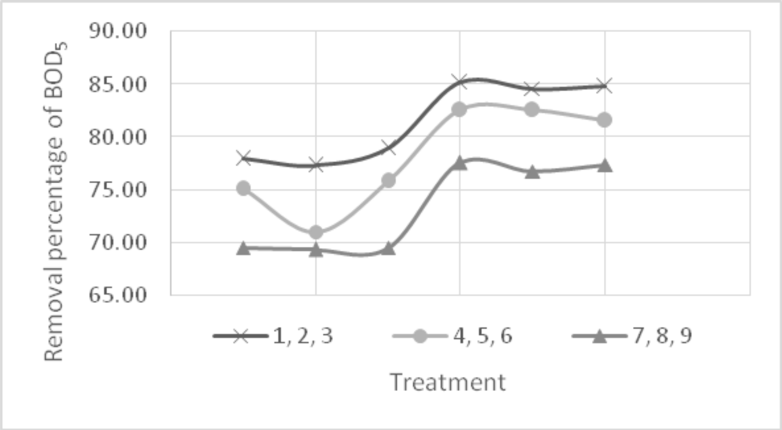

Fig. 1: Percentage of organic matter removal according to pH.

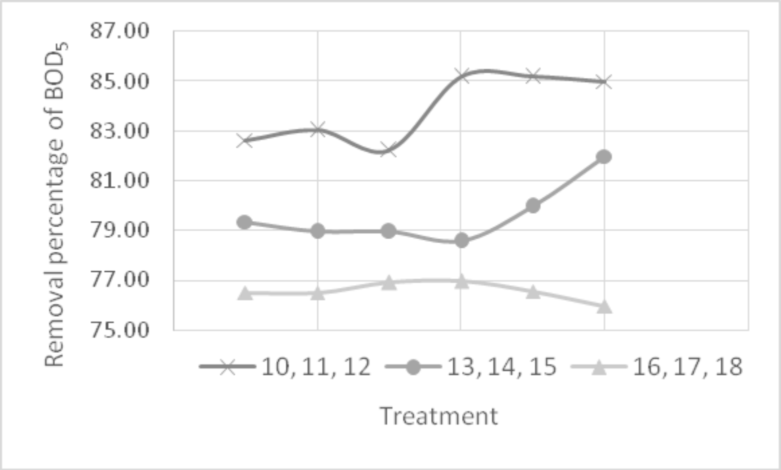

Fig. 2: Percentage of organic matter removal according to the concentration.

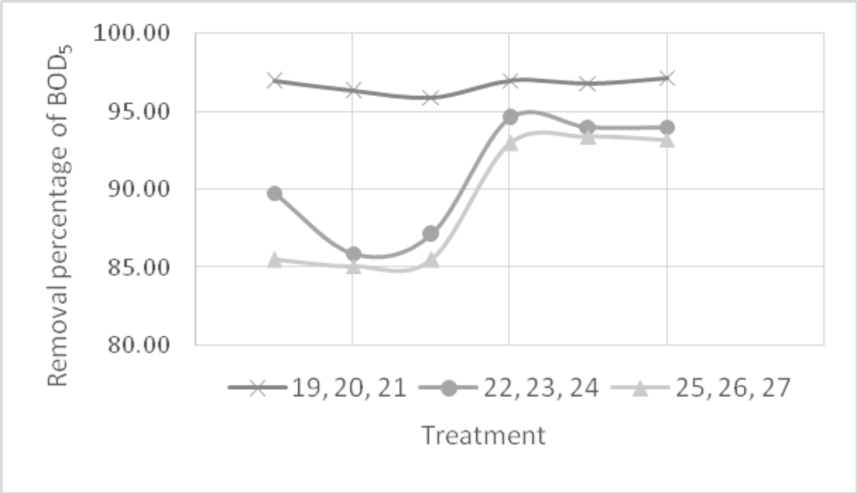

Fig. 3: Percentage of organic matter removal according to the optimal dose.

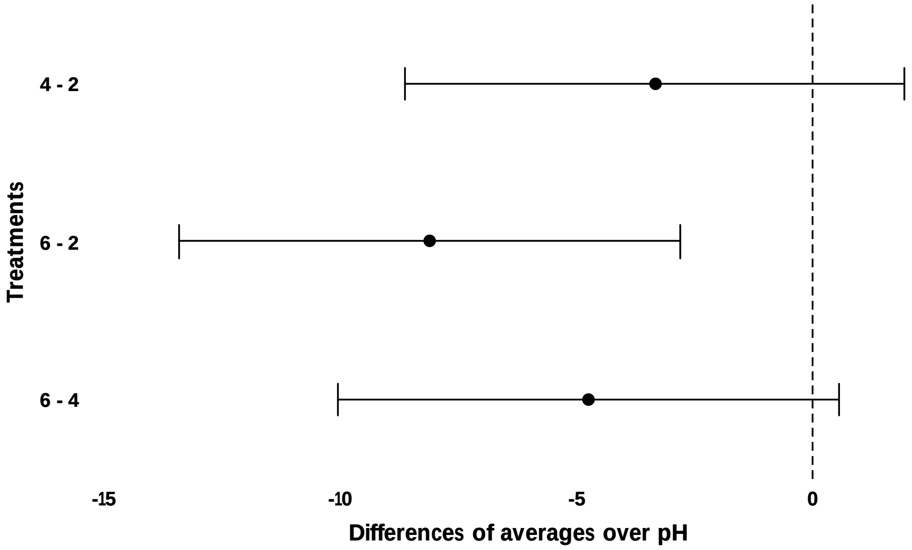

Fig. 4: A 95% ANOVA analysis for pH during the Fenton oxidation process.

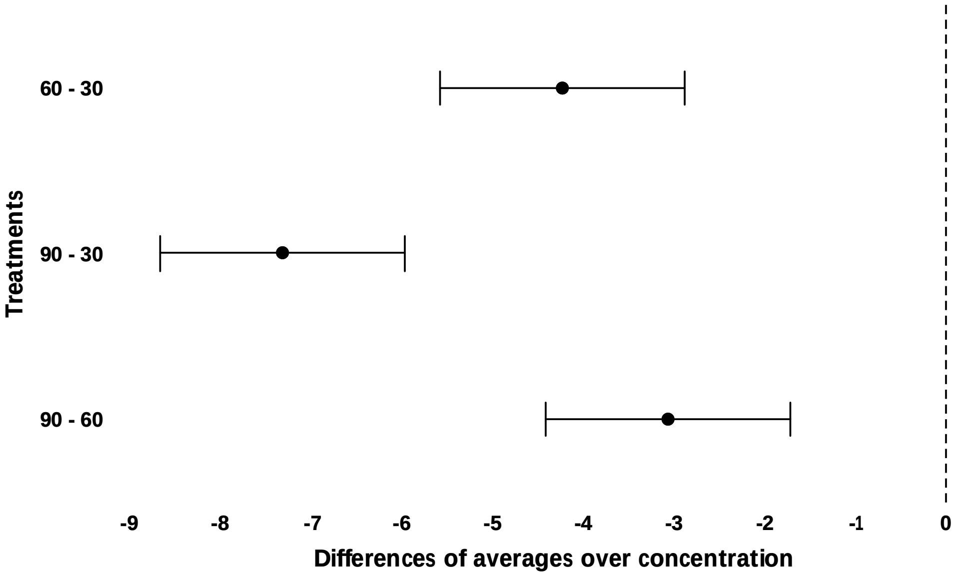

Fig. 5. A 95% confidence level ANOVA analysis for the effect of concentration.

78% and Ahn et al. (2002) of 83%, eliminating colloidal particles of small size that infer in the colour of the leachate.

Fig. 3 presents the removal results obtained from the dose of the Fenton reagent, according to the amount of effluent to be treated, with treatments 19, 20 and 21 showing the best results using a dose of 25% v/v .

As seen in Table 6, the efficiency of the Fenton reagent varies depending on the concentration of Fe^{+2}, because it acts as a catalyst in the oxidation reaction, ranging from 275 mg/L to 2792 mg/L. Due to the low presence of organic matter in the leachates, the concentration of the catalyst is 150 mg/L, in the same way, the hydrogen peroxide is 500 mg/L, while in the literature it varies between 200 mg/L and 34 000 mg/L, as given in Table 6.

DISCUSSION

The percentages of efficiency between the optimization treatments of pH and concentration, show characteristics, which differ among them, because the first results obtained

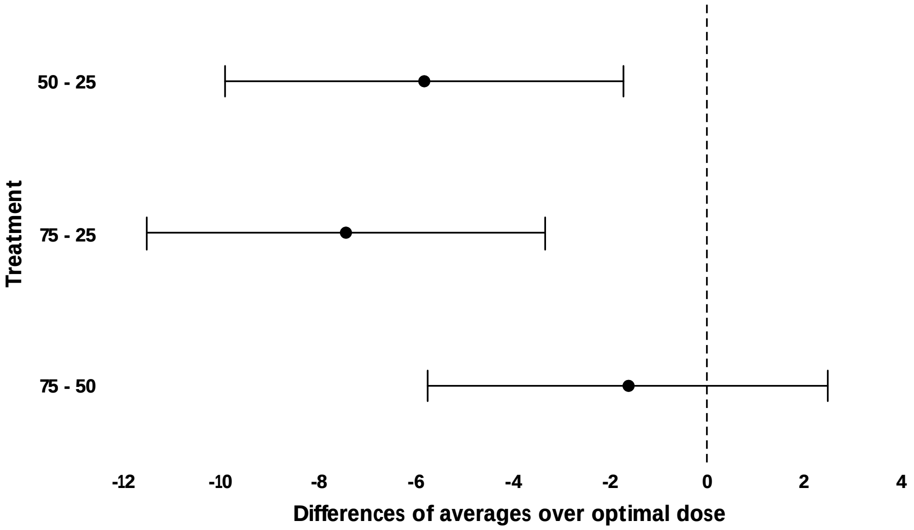

Fig. 6: A 95% ANOVA analysis regarding the optimal dose.

were collected during the rainy season and the following set of results during the North winds season, which can be noted by observing the valleys and crests formed in Figs. 1 and 2.

A 95% confidence level ANOVA analysis was carried out for the pH treatments during the Fenton oxidation process (Fig. 4) and it is concluded that the efficiency achieved in the use of the pH 2 and 6 is significantly different at the 95% confidence level. However, treatments with a pH 2 and 4 do not present a significant difference, as do treatments with a pH 4 and 6. Therefore, pH 2 is proposed as optimal, since it showed greater degradation of organic material.

According to the ANOVA analysis (Fig. 5), it was determined that the concentration of the Fenton reagent influences the efficiency in the degradation of organic matter, besides that it does not present similarities to each other.

According to the optimal dose, the ANOVA analysis (Fig. 6) showed that the optimal doses of 50% v/v and 75% v/v do not present significant statistical differences, whereas the 25% dose is different, besides that it presented a higher efficiency of BOD removal.

At the levels of optimum treatment for the degradation of organic matter, defined as Fenton 30% (500 mg/L of hydrogen peroxide and 150 mg/L of ferrous sulphate), with a volumetric concentration of 25% v/v and pH 2; the analysis does not present significant statistical differences between the seasons (rainy and north winds) (Fig. 7) previously described in the Fisher tests at 95% confidence.

Table 5: Determination of the effective dose of Fenton reagent.

Treatment	pH	Fenton	Volume (%v/v)
19	2	30%	25%
20	2	30%	25%
21	2	30%	25%
22	2	30%	50%
23	2	30%	50%
24	2	30%	50%
25	2	30%	75%
26	2	30%	75%
27	2	30%	75%

According to the characteristics of leachates from the controlled landfill of the city of Veracruz, which present low chemical and biochemical oxygen demands, they are classified as old leachates. Therefore, the use of the Fenton reagent as treatment in the degradation of organic matter is adequate.

The leachate collected in the controlled landfill of the city of Veracruz has a biodegradability index of less than 0.3; therefore, it is not susceptible to biological processes.

The optimum removal of organic matter measured as BOD reached percentages higher than the averages reported in Table 4 and similar to those obtained in Spain by Trujillo et al. (2006).

By decreasing the pH of leachates, the decrease in organic matter produces a greater efficiency in the degradation of organic matter.

By demonstrating average efficiencies of organic mat-

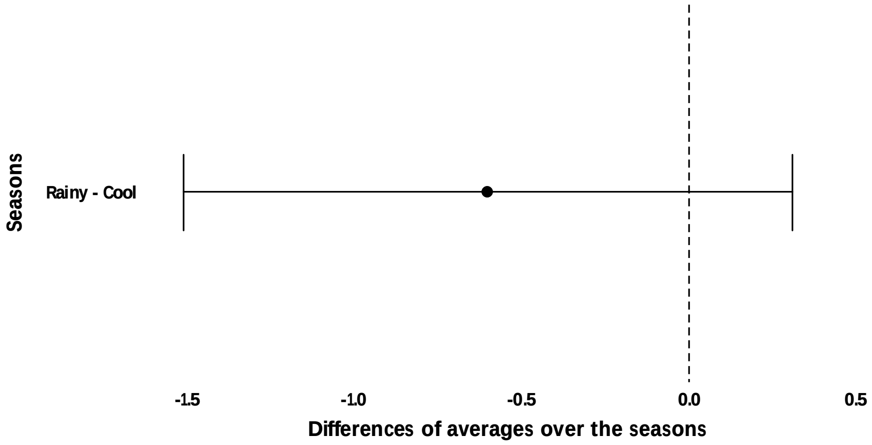

Fig. 7: A 95% confidence level ANOVA analysis for the efficiency between seasons.

Table 6: Comparison of leachate oxidation works by Fenton method.

Parameter	Unit	Veracruz a	Mérida b	Italia c	USA d	Hong Kong e	España 1 f	España 2 g	Estambul h			
pH	pH units	8.5	8.57	8.2	6.67	8.5	-	7.1	7.3			
Conductivity	mS/cm	10.7	21.83	45.35	-	-	-	47.1	-			
Alkalinity	mg/L	-	6115.96	21470	4050	-	-	-	9850			
BOD_5	mg/L	74.14	647	2300	0	75	475	3510	1220			
COD	mg/L	340.35	9080	10540	8596	1500	8100	6500	20700			
TOC	mg/L	-	2266	3900	2124	470	-	-	-			
BOD_5/COD	-	0.218	0.071	0.218	-	0.05	0.059	0.54	0.589			
Optimal values												
Reaction time	Minutes	60	20	120	120	30	40	-	60	5		
pH	pH units	2	4	3	3	2.5	6	3.5	3	3.5-4.0		
H_2O_2	mg/L	500	600	3300	10000	2550	200	34000	6500	2000		
Fe^{+2}	mg/L	150	1000	275	830	2792	300	558	650	1000		
Efficiency achieved												
COD	%	71	77	-	60	61	49	38	70	80	85	75
BOD_5	%	96.67	44	-	-	-	-	-	-	-	98	-
DBO_5/COD	-	-	0.100	0.5	-	-	-	-	-	-	-	-

a. Present study; b. Novelo et al. (2010); c. Lopez et al. (2003); d. Zhang et al. (2005); e. Lau et al. (2001); f. Rivas et al. (2004); g. Trujillo et al. (2006); h. Calli et al. (2005)
Total Organic Carbon (TOC)

ter removal of 96%, the Fenton reagent has shown to be an effective chemical procedure in the treatment of leachates from the controlled landfill of the city of Veracruz.

REFERENCES

Ahn, D.H., Chung, Y.C. and Chang, W.S. 2002 Use of coagulant and zeolita to enhance the biological treatment efficiency of high ammonia leachate. Journal of Environmental Science Health, A37(2): 163-173.

APHA-AWWA-WPCF 1998. Standards Methods for the Examination of Water and Wastewater. 20th Edition, USA.

Borzacconi, L., López, I. and Anido, C. 1996a. Metodología para la estimación de la producción y concentración de lixiviado de un relleno sanitario. In: XXV Congreso Interamericano de Ingeniería Sanitaria y Ambiental. México DF, Vol. 31.

Borzacconi, L., López, I., Arcia, E., Cardelino, L., Castagna, A. and Vinas, M. 1996b. Comparación de tratamientos aerobios y anaerobios aplicados a un lixiviado de relleno sanitario. In: XXV Congreso Interamericano de Ingeniería Sanitaria y Ambiental, 25: 1-8, AIDIS.

Calli, B., Mertoglu, B. and Inanc, B. 2005. Landfill leachate management in Istanbul: Applications and alternatives. Chemosphere, 59: 819-829.

Cortez, S., Teixeira, P., Oliveira, R. and Mota, M. 2011. Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments. Journal of Environmental Management, 92: 749-755.

Deng, Y. and Englehardt, J. 2007. Electrochemical oxidation for landfill leachate treatment. Waste Management, 27: 380-388.

Durán, P., Ramírez, Z.Y. and Durán, M. 2002. Bioadsorción de lixiviados viejosclarificados. Memorias del XIII Congreso Nacional de laFEMISCA, Morelia, pp. 455-460.

El-Fadel, M., Bou-Zeid, E., Chahine, W. and Alayli, B. 2002. Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content. Waste Manage., 22: 269-282.

Enzminger, J.D., Robertson, D., Ahlert, R.C. and Kosson, D.S. 1997. Treatment of landfill leachates. J. Hazard. Mater., 14: 83-101.

Kitis, M., Adams, C.D. and Daigger, G.T. 1999. The effects of Fenton's reagent pretreatment on the biodegradability of non-ionic surfactants. Wat. Res., 33(11): 2561-2568.

Kurniawan, T.A., Wai-Hung, L. and Chan, G.Y.S. 2006. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. J. Hazard. Mater., B129: 80-100.

Lau, I.W.C., Wang, P. and Fang, H.H.P. 2001. Organic removal of anaerobically treated leachate by Fenton coagulation. Journal of Environmental Engineering, 127(7): 666-669.

Lopez, A., Pagano, M., Volpe, A. and Di Pinto, A. 2003. Fenton's pre-treatment of mature landfill leachate. Chemosphere, 54: 1005-1010.

Lu, M.C., Lin, C.J., Liao, C.H., Ting, W.P. and Huang, R.Y. 2001. Influence of pH on the dewatering of activated sludge by Fenton's reagent. Wat. Sci. Technol., 44(10): 327-332.

Méndez Novelo, R.I., Pietrogiovanna Bronca, J.A., Santos Ocampo., B., Sauri Riancho, M.R., Giácoman Vallejos, G. and Castillo Borges, E.R. 2010. Determinación de la dosis óptima del reactivo Fenton en un tratamiento de lixiviados por Fenton-Adsorción. Investigación and Contaminación Ambiental, 26(3): 211-220.

NMX-AA-028-SCFI-2001. que establece la determinación de la demanda bioquímica de oxígeno en aguas naturales, residuales (DBO5) y residuales tratadas - Método de prueba. México, D.F., a 6 de abril de 2001.

Rivas, F.J., Beltrán, F., Carvalho, F., Gimeno, O. and Frades, J. 2005. Study of different integrated physical-chemical+adsorption processes for landfill leachate remediation. Industrial Engineering Chemical Research, 44: 2871-2878.

Tchobanouglus, G., Theisen, H. and Vigil, S.A. 2000. Gestión Integral de Residuos Sólidos. Volumen I. Editorial Mc Graw Hill, pp. 469.

Trujillo, D., Font, X. and Sánchez, A. 2006. Use of Fenton reaction for the treatment of leachate from composting of different wastes. Journal of Hazardous Materials, B138: 201-204.

Yoo, H.C., Cho, S.H. and Ko, S.O. 2001. Modification of coagulation and Fenton oxidation processes for cost-effective leachate treatment. Journal of Environmental Science and Health, 36(1): 39-48.

Yoon, J., Lee, Y. and Kim, S. 2001. Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment. Wat. Sci. Technol., 44(5): 15-21.

Zhang, H., Choi, H.J. and Huang, C.P. 2005. Optimization of Fenton process for the treatment of landfill leachate. Journal of Hazardous Materials, B125: 166-174.