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Fenton-adsorption process for leachates from two landfills (karstic-clays)

Proceso Fenton-adsorción para lixiviados de dos rellenos sanitarios (karstico-arcilloso)

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Abstract

The nature of leachates depends on many factors, which makes them highly complex and difficult to treat, since they can be very different from one site to another. Tests were carried out to analyze the efficiency of organic matter removal by Fenton/adsorption treatment of leachate from two landfills. The Fenton process was optimized by finding the conditions of pH, contact time, $[COD/H_2O_2]$ and $[Fe^{2+}/H_2O_2]$ ratios of the reagent Fenton with which the highest amount of COD and color was obtained. The treatment was tested in leachate from the city of Tuxtla Gutiérrez, Chiapas, Mexico (clays) and compared with the removals previously obtained in the leachate from the landfill of the city of Mérida, Yucatán, México (karstic). In both, removals higher than 99% were obtained in chemical demand for oxygen, total organic carbon and color. In this research, it was found that the optimization of the Fenton process depends directly on the concentration of organic matter measured as chemical oxygen demand.

Keywords: Fenton, adsorption, leachate, landfill, physicochemical treatment.

Resumen

La naturaleza de los lixiviados depende de muchos factores lo que los convierte en líquidos altamente complejos y difíciles de tratar, ya que pueden llegar a ser muy diferentes entre un sitio y otro. Se llevaron a cabo pruebas para analizar la eficiencia de la eliminación de la materia orgánica mediante el tratamiento con Fenton/adsorción en lixiviados de relleno sanitario. El proceso Fenton se optimizó encontrando las condiciones de pH, tiempo de contacto y relaciones $[COD/H_2O_2]$ y $[Fe^{2+}/H_2O_2]$ del reactivo Fenton con las que se obtuvo la mayor cantidad de remoción de DQO y color. El tratamiento se probó en lixiviados provenientes de la ciudad Tuxtla Gutiérrez, Chiapas, México (arcilloso) y comparado con las remociones obtenidas previamente en el liviado del relleno de la ciudad de Mérida, Yucatán, México (karstico). En ambos casos se obtuvieron remociones superiores al 99% en los parámetros demanda química de oxígeno, carbono orgánico total y color. Con base en los resultados se concluyó que la optimización del proceso Fenton depende directamente de la concentración de materia orgánica medida como demanda química de oxígeno.

Palabras clave: Fenton, adsorción, lixiviado, relleno sanitario, tratamiento fisicoquímico.

1 Introduction

The leachates are the result of liquid percolation through the waste in the process to be stabilized (Méndez *et al.*, 2009; Naveen *et al.*, 2017; Khan *et al.*, 2020). There are many factors that affect the quality and quantity of the leachate, for example: seasonal climate variation, filling techniques, stacking method and compaction, type and composition of the wastes, filling structure, etc.; its composition depends on the age of the filling (Wu *et al.*, 2010; Brennan *et al.*, 2016; Zhao *et al.*, 2018).

The leachate biodegradability fraction (known as biodegradability index BI -BOD_5/COD-) of a young landfill (less than 5 years old) is approximately >0.4, while for a medium one (5-10 years old) it is <0.2 and for a mature one (older than 10 years) is 0.1 (Corsino *et al.*, 2020), and even less. COD and pH vary from >1000 mg/L and <6.5 in young to <4000 mg/L and >7.5 for mature, and ammonia nitrogen from <400 (young) to >400 mg/L (mature) (Detho *et al.*, 2020). The composition of the leachate varies not only with the age of the landfill, but also from one site to another, so the representative parameters are not always the same (Luo *et al.*, 2020).

In previous studies, different physicochemical treatments have been tested in leachate, including membrane filtration (Costa *et al.*, 2019), coagulation-flocculation, flotation, adsorption, Fenton oxidation (Méndez *et al.*, 2009; Aftab and Hur, 2019; Smaoui *et al.*, 2019, Zhang *et al.*, 2019), Fenton/coagulation (Wu *et al.*, 2010; Luo *et al.*, 2019), heterogeneous Fenton and electrofenton (Sruthi *et al.*, 2018), electrocoagulation with fiber filtration (Li *et al.*, 2017), electrofenton with different doses of H_2O_2 and Fe^{2+} (Mohajeri *et al.*, 2019) and using of sodium sulphate with H_2O_2 in an advanced oxidation process (Hilles *et al.*, 2016), among others. However, there is no treatment or treatment set have been found that achieve satisfactory removal in leachates and residue generated that being disposed under the applied normativity and are also economically feasible. In México, Mexican Official Standard NOM-001-SEMARNAT-1996 (DOF, 1998), which establishes the maximum permissible limits of pollutants in the discharge of wastewater into national waters and goods.

In México, the rapid production of waste, the difficult collection and the non-classification has caused greater attention to control this problem (Jiménez-Rodríguez *et al.*, 2020). Since 2002, there have been various studies in the literature on the characteristics and composition of the leachate generated in the Mérida city sanitary landfill, which was inaugurated in 1997 initially with eight cells. Subsequently, in 2011 the provision of new cells was announced, which would extend the period of operation of the landfill until 2027-2030 (Ayuntamiento de Mérida, 2020; Gobierno del estado de Yucatán, 2020). Currently, the sanitary landfill in the city of Tuxtla Gutiérrez Chiapas has 7 planned cells, a leachate lagoon and an emergency lagoon. However, prior to this, the final disposal of waste was carried out in the municipal garbage dump (from 1995)

until 2008, when the current sanitary landfill was implemented, so the dump was closed. This sanitary landfill is the only one in the state of Chiapas that operates under the corresponding regulations, since there are 118 clandestine dumps distributed in the rest of the municipality (Nájera *et al.*, 2009).

An important aspect to take into account is the type of soil where the sanitary landfills are located, since the type of construction to be carried out depends on it and this also contributes to the composition of the leachate. In addition, the impact of leachates on the soil is also different, since pollutants can migrate in porous, fractured, saturated and unsaturated media. (Quintero-Ramírez *et al.*, 2017). The Yucatecan karstic soil is heterogeneous and the processes of decontamination, retention, mineralization, adsorption, among others, cannot be carried out, with which the aquifer is exposed to all kinds of compounds that could be on the soil surface (Aguilar-Duarte *et al.*, 2016). On the other hand, in Tuxtla Gutiérrez clay-type soil predominates, which with the increase in water content tends to expand and contract when it decreases (Castellanos *et al.*, 2016). This could mean that if the soil is violated by pollutants, it will retain them, allowing their advance whenever the water content varies, which occurs according to the seasons of the year and the climate.

The leachate from the landfill in the city of Mérida has been treated with different processes, but it is Fenton-adsorption that has proven to have the best pollutant removal efficiency, higher than 99% in COD and color (San Pedro *et al.*, 2015). The leachate from the closed area of the landfill in the city of Tuxtla Gutiérrez has been treated with the coagulation-flocculation processes (Nájera *et al.*, 2009), coagulation-flocculation-Fenton and coagulation-flocculation-Fenton-anaerobic reactor (Nájera, 2011), reaching 67%, 70% and 95% COD removal, respectively. The treatability of these leachates has recently been tested with the Aged Refuse Filled Bioreactor (ARFB) system, with removals of 80% in COD and color (Bautista-Ramírez *et al.*, 2018), and 85-88% in BOD, COD and color removal, in addition to TN and TP with removals of the order of 98% (Nájera-Agular *et al.*, 2019).

Several methodologies for leachate treatment are reported in the literature; however, little is known about the repeatability of these treatments in other leachates (different geographic region, type of soil, type of fill, etc.). An ideal treatment would be one that can be adjusted to the chemical diversity that the nature of each leachate possess. For these reasons, it

is important to carry out a comparative study under standardized conditions for each region. The objective of this work is to determine if the optimization of the Fenton-adsorption process of the Mérida leachate can be replicated in the leachate from Tuxtla Gutiérrez landfill.

2 Materials and methods

2.1 Leachate sampling

Leachate sampling campaign was conducted in the landfill evaporation lagoons from the city of Tuxtla Gutiérrez, Chiapas (October 2012). In Figure 1, the location of the Tuxtla Gutiérrez landfill and that the city of Mérida (with which it was compared in this study) is shown. In each sampling, 60 L of a composite leachate sample taken from different points of the lagoons were used, remaining in refrigeration (8 ℃) until the moment of the analysis.

2.2 Fenton process

Previously, Méndez *et al.* (2010a) established the optimal dose for the Fenton oxidation in the leachate from Mérida city: $(H_2O_2) = 600$ mg/L (using H_2O_2 30% w/w) and $(Fe^{2+}) = 1000$ mg/L (using $Fe_2SO_4 \cdot 7H_2O$). Based on that methodology, the leachate from Tuxtla Gutiérrez city was studied, starting the process with the optimal dose. Subsequently, the optimum conditions found in the experiments were used for the leachate, as described below.
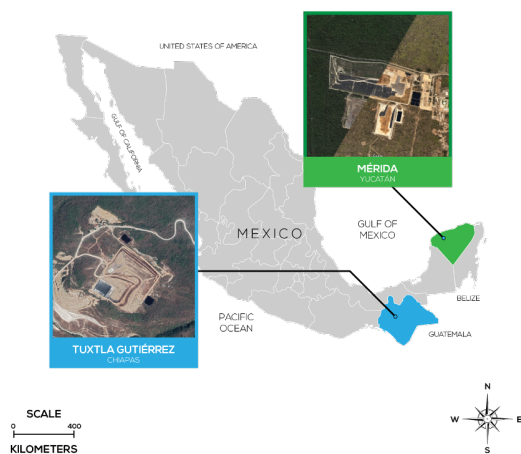

Fig. 1. Spatial location of landfills compared.

2.2.1 Optimal pH

For each sample of raw leachate, the pH was reduced to 2, 3 and 4 with concentrated sulfuric acid. Subsequently, the Fenton process was carried out using the jar tested equipment, with the above-mentioned dose (2 L, fast mixing at 320 rpm for 5 min). The parameters of COD and color were determined in the raw leachate and in the effluent of the Fenton process after an hour of sedimentation. All tests were done in triplicate.

2.2.2 Optimal contact time

The Fenton process was carried out the conditions described in 2.2.1, and was filtered at certain times (5, 10, 20, 40, 60, 80, 100 and 120 minutes of reaction). Then, COD and color were determined. The results obtained were plotted (time versus removal percent). The optimum value corresponded to the minimum time required to obtain the highest percentage of removal of COD and color.

2.2.3 Determination of the best ratios $[Fe^{2+}/H_2O_2]$ and $[COD/H_2O_2]$

In 2 L samples of raw leachate, using the jar test equipment, the pH was adjusted to optimal conditions and Fenton reagent was added (fast mixing at 320 rpm for 5 min, followed by the optimal contact time for the reaction without stirring). For determining the best ratio $[Fe^{2+}/H_2O_2]$ and $[COD/H_2O_2]$ of the leachate from Tuxtla Gutiérrez, a two-way analysis of variance was tested and the sources of variation were each of the following ratios: $[Fe^{2+}/H_2O_2]$ with values of 0.2, 0.6, 1.0, 1.4 and 1.8 and $[COD/H_2O_2]$ with values of 1, 5, 9, 13 and 17. Random trials were performed in triplicate. The color and COD were measured for both the raw leachate and the filtration effluent.

2.3 Adsorption with granular activated carbon

A 75 cm long, 20 cm diameter tube acrylic column was constructed, which was packed 60 cm with granular activated carbon. An adjustable speed peristaltic pump was used, and the up flow was maintained constant to have a contact time of 2 hours between the leachate and the activated carbon (flow rate 170 mL/min).

For the packing of the column, granular activated carbon (GAC) of the macroporous lignite type was used: Gama L brand with the following characteristics: mesh number: 8x30; surface area of 348.61 m^2/g,

relative density of 0.38 and a cross-section of the adsorption area of 0.162 nm^2.

2.4 Characterization of samples

These parameters were measured in all samples: chemical oxygen demand (COD), biological oxygen demand at 5th (BOD$_5$), pH, total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC), color, total solids (TS), total dissolved and suspended solids (TDS and TSS), total and ammoniacal nitrogen (TN and N-NH$_3$). Standard methods (APHA, 1995) were used for all analysis.

2.5 Statical design

To determine the optimal value of the relationships [Fe^{2+}/H$_2$O$_2$] and [COD/H$_2$O$_2$] of the Fenton process, the experimental results obtained were analyzed, using a two-way model of fixed effects:

$$y_{ij} = \mu + \alpha_i + \beta_j + \varepsilon_{ij}$$

where:
y_{ij} = Percentage of removal (expressed as COD and Color).
μ = Great mean of the response variable.
α_i = Effect of the relationship [Fe^{2+}/H$_2$O$_2$] on the response variable.

β_j = Effect of the [COD/H$_2$O$_2$] relationship on the response variable.
ε_{ij} = Random error (due to the variability of the leachate composition and laboratory errors).

For all statistical analyzes, the STATGRAPHICS program, version 5.1 for Windows, factorial variance analysis, and Fischer's least significant difference (DMS) method were used to contrast the means of each treatment.

3 Results and discussion

3.1 Leachate characterization

Table 1 shows the characterization of the raw leachates from Tuxtla Gutiérrez landfill. Despite the high COD, samples present characteristics of mature, old or stabilized leachates (Renou, *et al.*, 2008; Peng 2017; Lim *et al.*, 2016). This coincides with the characteristics reported in different studies on the Mérida leachate (Méndez *et al.*, 2010a; San Pedro *et al.*, 2015). The characteristics of the leachate depend on various factors such as the nature of the waste (which in turn depends on social and economic factors), the climate and the operations carried out in the sanitary landfill, among others.

Table 1. Concentration of the parameters analyzed in raw leachate.

Parameter	Mérida* (X±s)	Tuxtla Gutiérrez (X±s)
COD$_T$ (mg/L)	10193±263	9280±57
COD$_S$ (mg/L)	9958±151	9135±106
BOD$_{5T}$ (mg/L)	861±46	500±82
BOD$_{5S}$ (mg/L)	748±6	457±172
pH	8.31±0.1	8.48±0.2
Color 455 nm (u Pt-Co)	13667±870	8875±487
TS (mg/L)	19050±685	16304±146
TSS (mg/L)	360±47	544±21
TDS (mg/L)	18690±671	15760±84
TN (mg/L)	2113±210	2950±424
N-NH$_3$ (mg/L)	1797±479	2510±382
TC (mg/L)	5112±507	4114
IC (mg/L)	162±6	2010
TOC (mg/L)	4950±513	2104
BI**	0.084	0.05

*Reported by San Pedro *et al.*, 2015
**BI: biodegradability index (BOD$_5$/COD)

The leachates analyzed in this study come from a landfill with cells of different ages whose leachates are stored and mixed in stabilization ponds and are subjected to evaporation, and rainwater capture, as well as recirculation to the cells of the landfill. For this reason, the composition of the leachate combines characteristics of young and old leachates.

According to Bautista-Ramírez *et al*. (2018), BI for leachate from Tuxtla Gutiérrez, Chiapas, landfill in 2008 was 0.2; while for 2012 (in this study) its value fell to 0.05 as shown in Table 1. Sanitary landfills tend to undergo physical and chemical changes due to the degradation and complexity of the mixture of compounds that exist in them (Kamaruddin *et al*., 2017); the organic concentration (measured as COD, BOD and TOC) decreases as the filling age increases. The organic load measured as BOD decreases faster than COD, which remains in the leachate due to the presence of refractory organic material, as humic and fulvic acids, and heavy metals (Zhang *et al*., 2016; Liu *et al*., 2019). Over time, the biodegradable fraction of the organic contaminants of the leachate decreases; as a result, a high content of COD and ammonium, a low ratio of (BOD_5/COD), presence of inorganic salts and xenobiotic compounds (Poblete and Pérez, 2020) increase the difficulty in the biological treatment of leachates (Sang *et al*., 2008). For this reason, a physicochemical treatment such as Fenton-adsorption treatment is feasible.

As in the Mérida landfill leachate, the pH of the Tuxtla Gutiérrez leachate ranges between 7.7 and 8.8 (Table 1 shows that for 2012 the value was 8.48); regarding color, the Tuxtla leachate has a lower color intensity than Mérida leachate, however, the concentration of ammoniacal nitrogen is higher.

3.2 Optimization of the Fenton process

The results of the Fenton process of the color and COD removal efficiency for the Tuxtla Gutiérrez leachate are shown in Figure 2.

Optimal pH keeps iron soluble to interact with hydrogen peroxide and continue the reaction (Ahile *et al*., 2020). In Figure 2 is observed that the values of pH 3 and 4 are more efficient in the removal of color and COD than the leachates treated with pH 2, as mentioned in the literature for Fenton process (Wang *et al*., 2020). At pH lower than 3, the reaction becomes slower and less hydroxyl radicals are produced, making it less efficient for the removal of COD and color (Mohajeri *et al*., 2019). However, as shown in the Figure 2, there is no significant difference between the values of pH 3 and 4, so by economy the pH 4 is chosen for both leachates.

With the Fenton reagent, OH· radicals are released and react with organic substances, removing hydrogens from bonds with carbon, nitrogen or oxygen and bringing them to carbon-carbon bonds (in other cases also adding to aromatic compounds). It can reach mineralization (formation of CO_2, H_2O and inorganic acids), and even from low molecular weight acids such as acetic and formic (Seibert *et al*., 2019), favoring less toxicity and increasing biodegradability (Márquez-Ramírez *et al*., 2019).

The optimal contact time for COD and color removal was 5 minutes as shown in the Figure 3. The contact time depends on in turn the pH and the optimal dose, in the literature different experiences with Fenton process are reported where the reaction time varies from 5 min (Durai *et al*., 2020) to 3 hours (Zhang *et al*., 2018) in COD removal.

In Table 2, the results of the analysis are shown to optimize the [Fe^{2+}/H_2O_2] and [COD/H_2O_2] ratios, the first relation determines the oxidation rate due to Fe^{2+} acting as a catalyst and [COD/H_2O_2] determines the molar ratio between organic matter and oxidant.
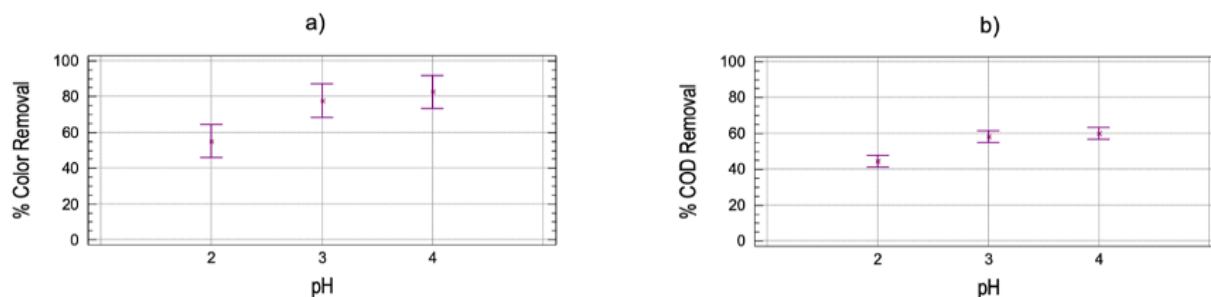

Fig. 2. a) Color removal of the leachate from Tuxtla Gutiérrez versus pH. b) COD removal of the leachate from Tuxtla Gutiérrez versus pH.
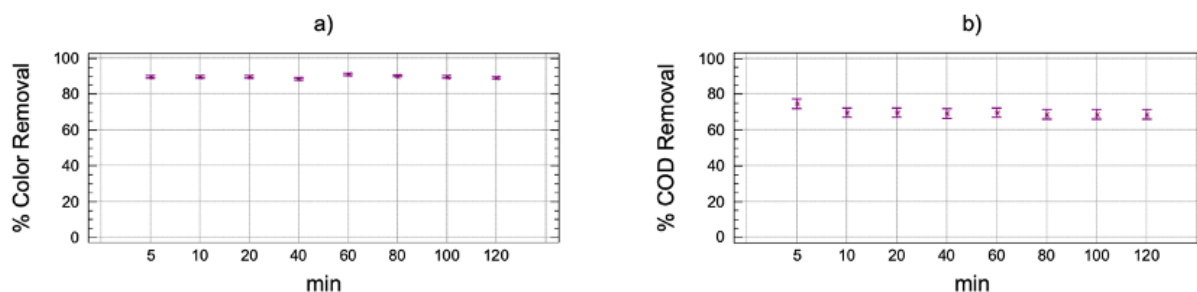
Fig. 3. a) Color and b) COD removal efficiency versus contact time of the leachate from Tuxtla Gutiérrez.

Table 2. COD and color removals obtained from $[Fe^{2+}/H_2O_2]$ and $[COD/H_2O_2]$ ratio.

| Experiment | Dose | | COD (mg/L) | Color (U PtCo*) |
	Fe^{+2}/H_2O_2	COD/H_2O_2		
1	0.2	1	1924±23	1660±113
2	0.2	5	3074±25	1335±92
3	0.2	9	3480±23	1280±85
4	0.2	13	3620±34	1830±127
5	0.2	17	5434±88	4780±424
6	0.6	1	2192±11	6830±580
7	0.6	5	1914±14	1485±120
8	0.6	9	2444±141	1370±85
9	0.6	13	2872±79	1280±85
10	0.6	17	3268±45	1190±14
11	1	1	2502±14	6750±283
12	1	5	1942±42	1640±28
13	1	9	2198±20	1280±85
14	1	13	2752±28	1015±35
15	1	17	3118±3	1235±64
16	1.4	1	2664±17	4900±394
17	1.4	5	1936±6	3270±1004
18	1.4	9	2400±34	1300±42
19	1.4	13	2762±3	1015±35
20	1.4	17	2900±11	1670±99
21	1.8	1	3176±57	2925±215
22	1.8	5	2064±68	2410±226
23	1.8	9	2642±31	1330±42
24	1.8	13	2796±11	1120±42
25	1.8	17	2900±74	1265±7

*Platinum and cobalt units

Finding the optimal dosage of Fenton treatment reagents is extremely important. Generally, the degradation of the substances increases with the concentration of iron, however, an excess of them means large amounts of iron salts, which increases the concentration of dissolved solids, affecting the effectiveness of the treatment. On the other hand, the degradation increases with the dose of H_2O_2, nevertheless, the excess not used in the reaction increases the COD (Göde *et al.*, 2019). Figure 4 shows the graph of means for the ANOVA results according to the color removal of the 25 different doses tested. It can be seen that the doses 1, 2, 3, 4, 7, 8, 9, 10, 12, 13, 14, 16, 15, 20, 21, 22 and 25 had the best color removal (86%). However, the best COD removal (78%) is only obtained with doses 1, 7, 12 and 19, according to Figure 5.
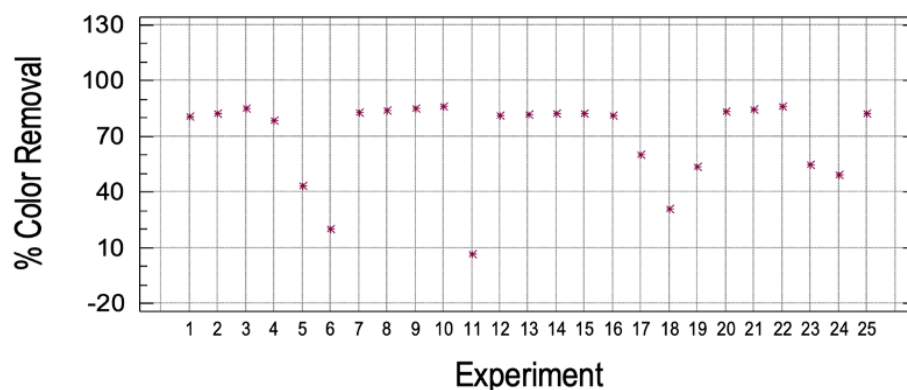
Fig. 4. Color removal efficiency versus the dose used for the leachate from Tuxtla Gutiérrez.
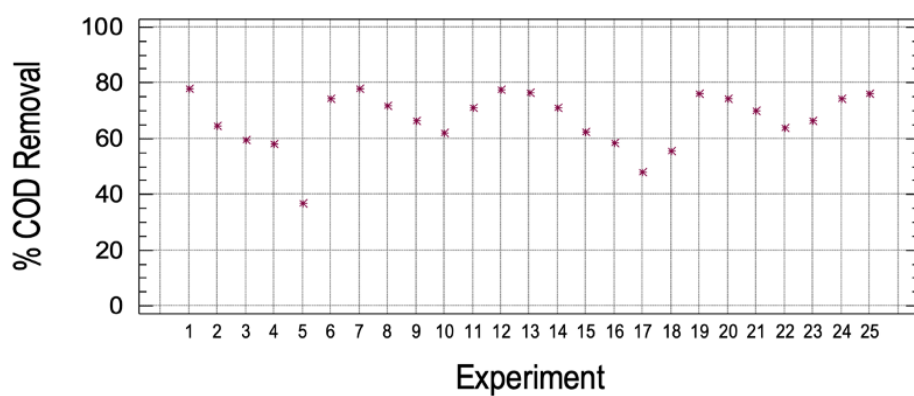

Fig. 5. COD removal efficiency versus the dose used for the leachate from Tuxtla Gutiérrez.

Table 3. Optimal conditions for the Fenton process.

Leachate	Dose optimum ratio			Contac time
	Fe^{+2}/H_2O_2	COD/H_2O_2	pH	(min)
Mérida	0.6	9	4	60
Tuxtla Gutiérrez	0.6	5	4	5

From experiment 7 (ratios: Fe^{2+}/H_2O_2 = 0.6 and COD/H_2O_2 = 5) coincides with the best removals of both COD and color, this was considered to be optimal.

In the study made by Méndez *et al*. (2010b), using the same experimental model, but the sample analysed was the leachate from Mérida landfill, found that the optimal relations in the Fenton process of this leachate were: Fe^{2+}/H_2O_2 = 0.6 and COD/H_2O_2 = 9.

Table 3 presents the optimum ratios found for the leachates of the two cities compared. Based on this information it is possible to observe that the organic load measured as COD is the main source of treatment variation, it depends on the amount of H_2O_2 necessary to generate enough radicals that will make oxidation possible when combined with Fe^{2+}. The amount of iron depends on the amount of peroxide used, always maintaining a ratio of 0.6. Furthermore, Table 3 also shows the optimal conditions of the process.

3.3 Fenton-adsorption treatment

The sample volume that was analysed for the adsorption effluent, was obtained at 10 minutes (volume of approximately 1.7 L). Table 4 shows the removals of the different parameters of the two leachates.

Table 4. Removal percentage of the parameters measured in the adsorption effluent of the treatment of studied leachates.

Parameter	Mérida leachate* (%)	Tuxtla Gutiérrez leachate (%)
CODT	99.96	99.58
CODS	99.96	99.83
BOD_{5T}	96.89	86.61
BOD_{5S}	96.88	90.82
Color	99.83	99.92
TS	97.95	64.38
TSS	79.65	64.75
TSD	98.36	50.51
TN	99.96	59.69
$N-NH_3$	99.97	50.5
TC	98.3	99.2
IC	95	100
TOC	99.3	99.2

*Reported by San Pedro *et al*., 2015.

As shown in Table 4, the best removal rates obtained by the Fenton/adsorption treatment for COD, TOC and color for both leachates are > 99%. However, the Fenton process was used under optimal conditions, the nature of each leachate is responsible for the removal of the other parameters vary from one sample to another. Cataldo & Angelini (2013) tested a combination of oxidation by ozonating and adsorption with activated carbon, obtained COD removals around 91% by the adsorption/ozonating process, and 98% when they invested the processes (ozonating/adsorption), values slightly lower than those obtained with Fenton/adsorption. Papastavrou *et al*. (2009) working with leachates previously treated with a biological treatment tested the coagulation/adsorption process with activated carbon, the best removals were 50% for coagulation and up to 80% for coagulation/adsorption. The difference between the last study with the study of Cataldo & Angelini (2013) and the present study is the latter was subjected to intense oxidation processes, in which the larger molecules are decomposed into others easier to adsorb. San Pedro *et al*. (2015) conclude that the adsorption with activated carbon, preceded by the Fenton process, is more efficient than the adsorption of raw leachate.

San Pedro *et al*. (2020) demonstrated that GAC is more efficient to remove organic matter measured as COD in leachates treated with Fenton because it has a greater capacity of adsorbing larger molecules, since in the Fenton process, molecules of diverse sizes have partially oxidized giving rise to smaller molecules that can be adsorbed by GAC.

Due to the quality of leachates depends on many factors, such as the climate, the structure of the landfill, the socioeconomic level of the population, etc. (Lopez *et al*., 2004; Pereira *et al*., 2016), some of the compounds presented may be more easily degraded than others. Thus, the quality of the waste is determined mainly by the composition of the waste deposited in the landfill and by the processes of biochemical reactions that take place. Oulego *et al*. (2016) report that leachates with high concentrations of humic acid have a positive effect on the removal of COD because this fraction is more easily oxidizable.

An important parameter to measure the organic load is the TOC, and as shown in Table 4, the removal of this for both leachates is also higher than 99%; however, it points out that the IC was completely removed in the leachate from Tuxtla Gutiérrez. This supposes that the remaining matter is of organic nature, although the concentration is very low. In addition, it should be mentioned that IC removal in the Tuxtla leachate occurred in the Fenton process stage.

The remaining organic matter can also be evaluated in terms of BOD_5, according to Table 4, for Mérida leachate removal is higher than 96%, while in Tuxtla Gutiérrez it is 86%. This could imply that, in a subsequent stage of polishing treatment, a biological process will be viable (which coincides with the increase in BI of the AE from Tuxtla Gutiérrez leachate to 3.75).

Table 5. Comparison of results from different samples treated with Fenton.

Treatment description	Fenton conditions	Removal	Reference
Fenton using as tertiary treatment of landfill leachate (Lages, Brasil)	pH = 3 H_2O_2 = 847 mg/L FeSO4 = 696 mg/L Time = 2 hours	Color 98%	Göde *et al.*, 2019
Fenton treatment for mature leachate (Madurai, India)	pH = 3 H_2O_2 = 30 mM FeSO4 = 30 mM Time = 5 min	COD 97.83%	Durai *et al.*, 2020
Fenton treatment for industrial textile wastewater (Kahramanmaras, Turkey)	pH = 3 H_2O_2 = 2.20 g/L Fe^{2+} = 0.10 g/L Time = 90 min	Color 97% COD 73%	Cetinkaya *et al.*, 2018
Fenton-adsorption treatment for petrochemical wastewater (petrochemical company, Mexico)	pH = 3 H_2O_2 = 13.65 g/L (H_2O_2/Fe^{2+}) = 0.27 Time = 3 hours	COD 70%	Contreras-Bustos *et al.*, 2019
Fenton-adsorption for mature leachate of karstic soil (Mérida, Mexico)	pH = 4 (COD/H_2O_2) = 9 (Fe^{2+}/H_2O_2) = 0.6= 0.27 Time = 60 min	COD 99% Color 99%	San Pedro *et al.*, 2015
Fenton-adsorption for mature leachate of clay soil (Tuxtla Gutiérrez, Mexico)	pH = 4 (COD/H_2O_2) = 5 (Fe^{2+}/H_2O_2) = 0.6 Time = 5 min	COD 99% Color 99%	This study

However, for this leachate the removal of N-NH_3 is only 50%, although, is low compared to the removal from Mérida leachate (> 99%), adsorption with activated carbon allows to remove between 50-70% of ammoniacal nitrogen (Abbas *et al.*, 2009). Only 50% of the N-NH_3 molecules from Tuxtla Gutiérrez leachate have been retained in the activated carbon, this can be due to the fact that the nitrogen is in high concentrations (higher than in the Mérida leachate). For this reason, it is suggested that the retention time in the adsorption column for the Tuxtla Gutiérrez leachate should be increased.

TSS concentrations in the effluents of the adsorption process are the result of the Fenton process, stage in which an increase occurs due to the intensive oxidation converts the dissolved solids into flocculated and little dense sludge which are not retained totally even when passed through a filter Press whose filter media has a very small pore (4μm). Another important amount of solids is retained on the adsorption column, however, the final concentration is high.

Table 5 shows the results of Fenton treatment for different samples. As can see, the methodology following in this study (and in the Mérida leachate)

is capable to reach high removal efficiencies of COD and color.

The conditions of the Fenton process for the treatment of contaminated effluents have been worked on in different ways according to the author; however, all conclude on the influence of the dose on the final results (removal efficiency). As mentioned above, the importance of optimum pH is crucial as it is the first step of the process and prepares the samples to interact with Fenton reagent. Next, establishing an optimal dose will allow the advance of the reaction (it will determine how far it can continue to generate OH· radicals), exceeding this optimal dose the limiting reagent and there will be no further removal organic matter. In the particular case of the leachates form Mérida and Tuxtla Gutiérrez, pH 4 was used (unlike the rest of the studies presented in Table 5), since it was found to have the same efficiency as with the pH 3, this represents a lower expenditure on acid (and therefore a lower addition of water to the system).

The removal of organic matter measured as COD allows the effluents from both leachates to reach the values required to accomplish with current Mexican regulations NOM-001-SEMARNAT-1996

(DOF, 1998). In the adsorption process, the pH increases from acid values (2.7) to alkaline (8.7), thus achieving with Mexican standards. The TSS content in the effluent is slightly above the limit, thus the maximum allowed in discharge waters is 60 mg/L. The BOD$_5$ value of the treated leachates is lower than that established by the Mexican Standard NOM-001-SEMARNAT-1996 for any type of receiving body. Simultaneously, the COD and color values obtained are lower than those established in the Federal Law on Rights (DOF, 2012). However, more detailed analyses of the remaining substances in the treated leachate should be carried out in order to ensure their safety for the environment. Finally, it is important to mention that the influence of the landfill soil type is also a considerable factor in the behavior of leachates over time. The effect of the karst cover material called sascab on the composition of the leachate is an increase in alkalinity and low concentrations of heavy metals, due to the fact that metals are solubilized at low pH (2 to 3) but the pH increases when passing through the strata of sascab. This effect is not appreciated in clay soils, so the novelty of the Fenton-adsorption treatment consists of the versatility to treat leachate with different chemical characteristics and obtain high percentages of removing organic matter.

Conclusions

The Fenton/adsorption process was efficient in the removal of organic matter, obtaining removals above 99.96% and 99.58% of COD, and 99.83% and 99.92% of color for the leachates from Tuxtla Gutiérrez and Mérida landfills, respectively.

The optimization of the Fenton process depends directly on the concentration of organic matter measured as COD. For the leachate from Tuxtla Gutiérrez the COD/ H$_2$O$_2$ ratio was 0.5 and the optimum Fe^{2+}/H$_2$O$_2$ ratio was 0.6; the pH with the best removal of COD and color was 4 and the contact time was 5 min.

These results show that the application of Fenton-adsorption process for the removal of organic matter in mature leachates generated in the Mérida and Tuxtla Gutiérrez landfills can comply with the discharge conditions established in the Mexican regulations.

References

Abbas, A. A., Jingsong, G., Ping, L. Z., Ya, P. Y., and Al-Rekabi, W. S. (2009). Review on LandWll leachate treatments. *Journal of Applied Sciences Research 5*, 534-545.

Aftab, B., and Hur, J. (2019). Unraveling complex removal behavior of landfill leachate upon the treatments of Fenton oxidation and MIEX® via two-dimensional correlation size exclusion chromatography (2D-CoSEC). *Journal of hazardous materials 362*, 36-44. https://doi.org/10.1016/j.jhazmat.2018.09.017

Aguilar-Duarte, Y., Bautista, F., Mendoza, M. E., Frausto, O., Ihl, T., and Delgado, C. (2016). IVAKY: índice de la vulnerabilidad del acuífero kárstico yucateco a la contaminación. *Revista Mexicana de Ingeniería Química 15*, 913-933.

Ahile, U. J., Wuana, R. A., Itodo, A. U., Sha'Ato, R., and Dantas, R. F. (2020). A review on the use of chelating agents as an alternative to promote photo-Fenton at neutral pH: Current trends, knowledge gap and future studies. *Science of The Total Environment 710*, 134872. https://doi.org/10.1016/j.scitotenv.2019.134872

American Public Health Association, American Water Works Association, Water Environment Federation (APHA). (1995). Standard Methods for the Examination of Water and Wastewater. 19th ed. *American Public Health Association, Washington.*

Ayuntamiento de Mérida (2020). Residuos sólidos. Available at: http://www.merida.gob.mx/sustentable/contacto/relleno-sanitario.phpx. Accessed: June 26, 2020.

Bautista-Ramírez, J. A., Gutiérrez-Hernández, R. F., Nájera-Aguilar, H. A., Martínez-Salinas,

R. I., Vera-Toledo, P., Araiza-Aguilar, J. A., Méndez-Novelo R. and Rojas-Valencia, M. N. (2018). Biorreactor empacado con materiales estabilizados (BEME), como pretratamiento para lixiviados de rellenos sanitarios. *Revista Mexicana de Ingeniería Química 17*, 561-571. https://doi.org/10.24275/10.24275/uam/izt/dcbi/revmexingquim/2018v17n2/Bautista

Brennan, R. B., Healy, M. G., Morrison, L., Hynes, S., Norton, D., and Clifford, E. (2016). Management of landfill leachate: The legacy of European Union Directives. *Waste management 55*, 355-363. https://doi.org/10.1016/j.wasman.2015.10.010

Castellanos, J. E., Martínez, J., Alonso, F. A., Grajales, J. F., Caballero, F., Cruz, J. J., and Samayoa, I. A. (2016) Estudio del comportamiento hidromecánico de una arcilla expansiva, caso de estudio, la arcilla de Tuxtla Gutiérrez, Chiapas. *Revista Pakval 37*, 5-9.

Cataldo, F., and Angelini, G. (2013). Municipal landfill leachate treatment using the combined action of activated carbon and ozone. *Ozone: Science & Engineering 35*, 55-62. https://doi.org/10.1080/01919512.2012.722045

Cetinkaya, S. G., Morcali, M. H., Akarsu, S., Ziba, C. A., and Dolaz, M. (2018). Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater. *Sustainable Environment Research 28*, 165-170. https://doi.org/10.1016/j.serj.2018.02.001

Collado, S., Núñez, D., Oulego, P., Riera, F. A., and Díaz, M. (2020). Effect of landfill leachate ageing on ultrafiltration performance and membrane fouling behaviour. *Journal of Water Process Engineering 36*, 101291. https://doi.org/10.1016/j.jwpe.2020.101291

Contreras-Bustos, R., Cardenas-Mijangos, J., Dector-Espinoza, A., Rodriguez-García, A., Montoya-Herrera, L., and Jiménez-Becerril, J. (2020). Treatment of wastewater from the petrochemical industry by a chemical Fenton process. *Revista Mexicana de Ingeniería Química 19*, 523-532. https://doi.org/10.24275/rmiq/IA637

Corsino, S. F., Capodici, M., Di Trapani, D., Torregrossa, M., and Viviani, G. (2020).

Assessment of landfill leachate biodegradability and treatability by means of allochthonous and autochthonous biomasses. *New Biotechnology 55*, 91-97. https://doi.org/10.1016/j.nbt.2019.10.007

Costa, A. M., Alfaia, R. G. D. S. M., and Campos, J. C. (2019). Landfill leachate treatment in Brazil?An overview. *Journal of Environmental Management 232*, 110-116. https://doi.org/10.1016/j.jenvman.2018.11.006

Detho, A. A., Daud, Z., Samo, S. R., Khan, Z., Memon, D. A., and Awang, H. (2020). Physicochemical Characteristics of Landfill Leachate from Simpang Renggam Landfill Site, Johor, Malaysia. *Quaid-E-Awam University Research Journal of Engineering, Science & Technology*, Nawabshah. 18, 82-88.

Diario Oficial de la Federación (1998). Norma oficial mexicana NOM-001-SEMARNAT-1996, que establece los límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales. Available at: https://www.gob.mx/cms/uploads/attachment/file/105139/Normas_Oficiales_Mexicanas.pdf. Accessed: September 12, 2013.

Diario oficial de la federación (2012). Ley Federal de Derechos. Available at: https://www.gob.mx/cms/uploads/attachment/file/120801/LFD_2012.pdf. Accessed: September 15, 2013.

Durai, N. J., Gopalakrishna, G. V. T., Padmanaban, V. C., and Selvaraju, N. (2020). Oxidative removal of stabilized landfill leachate by Fenton's process: process modeling, optimization & analysis of degraded products. *RSC Advances 10*, 3916-3925. https://doi.org/10.1039/C9RA09415F

Gobierno del estado de Yucatán (2020). Residuos sólidos. Available at: https://sds.yucatan.gob.mx/residuos-solidos/index.php. Accessed: June 28, 2020.

Göde, J. N., Souza, D. H., Trevisan, V., and Skoronski, E. (2019). Application of the Fenton and Fenton-like processes in the landfill leachate tertiary treatment. *Journal of Environmental Chemical Engineering 7*,

103352. https://doi.org/10.1016/j.jece.2019.103352

Hilles, A. H., Amr, S. S. A., Hussein, R. A., El-Sebaie, O. D., and Arafa, A. I. (2016). Performance of combined sodium persulfate/H_2O_2 based advanced oxidation process in stabilized landfill leachate treatment. *Journal of Environmental Management 166*, 493-498. https://doi.org/10.1016/j.jenvman.2015.10.051

Jiménez-Rodríguez, J. E., Martínez-Valdez, F. J., Estrada-Martínez, R., Monroy-Hermosillo, O., Saucedo-Castañeda, G., and Ramírez-Vives, F. (2020). Effect of incubation conditions on the aerobic pretreatment of the organic solid wastes and the volatile fatty acids production. *Revista Mexicana de Ingeniería Química 19*, 799-812. https://doi.org/10.24275/rmiq/Bio849

Kamaruddin, M. A., Yusoff, M. S., Rui, L. M., Isa, A. M., Zawawi, M. H., and Alrozi, R. (2017). An overview of municipal solid waste management and landfill leachate treatment: Malaysia and Asian perspectives. *Environmental Science and Pollution Research 24*, 26988-27020. https://doi.org/10.1007/s11356-017-0303-9

Khan, A., Khan, S. A., Saeed, Z., and Naz, B. (2020). Impact of Leachate Percolation on Groundwater Quality near the Municipal Open Dumpsite (Jam Chakro): A Case Study of Surjani Town, Karachi, Pakistan. *International Journal of Ground Sediment & Water 10*, 541-556. https://doi.org/10.5281/zenodo.4005959

Li, R., Wang, B., Owete, O., Dertien, J., Lin, C., Ahmad, H., and Chen, G. (2017). Landfill Leachate Treatment by Electrocoagulation and Fiber Filtration. *Water Environmet Research 89*, 2015-2020. https://doi.org/10.2175/106143017X15051465918976

Lim, C. K., Seow, T. W., Neoh, C. H., Nor, M. H. M., Ibrahim, Z., Ware, I., and Sarip, S. H. M. (2016). Treatment of landfill leachate using ASBR combined with zeolite adsorption technology. *Biotech 6*, 195. https://doi.org/10.1007/s13205-016-0513-8

Liu, X., Novak, J. T., and He, Z. (2019). Removal of landfill leachate ultraviolet quenching substances by electricity induced humic acid precipitation and electrooxidation in a membrane electrochemical reactor. Science of The Total Environment 689, 571-579. https://doi.org/10.1016/j.scitotenv.2019.06.329

Lopez, A., Pagano, M., Volpe, A., and Di Pinto, A. C. (2004). Fenton?s pre-treatment of mature landfill leachate. *Chemosphere 54*, 1005-1010. https://doi.org/10.1016/j.chemosphere.2003.09.015

Luo, K., Pang, Y., Li, X., Chen, F., Liao, X., Lei, M., and Song, Y. (2019). Landfill leachate treatment by coagulation/flocculation combined with microelectrolysis-Fenton processes. *Environmental Technology 40*, 1862-1870. https://doi.org/10.1080/09593330.2018.1432694

Luo, H., Zeng, Y., Cheng, Y., He, D., and Pan, X. (2020). Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. *Science of The Total Environment 703*, 135468. https://doi.org/10.1016/j.scitotenv.2019.135468

Márquez-Rámirez, E., Michtchenko, A., and Zacahua-Tlacuatl, G. (2019). Effects of radiation of CO_2 laser on natural dolomite for the degradation of azo dye reactive black 5 by photocatalysis. *Revista Mexicana de Ingeniería Química 18*, 555-569. https://doi.org/10.24275/uam/izt/dcbi/revmexingquim

Méndez, R., Castillo, E., Sauri, M., Quintal, C., Giacomán, G. and Jiménez, B. (2009) Comparación de cuatro tratamientos fisicoquímicos de lixiviados. *Revista Internacional de Contaminación Ambiental 25*, 133-145.

Méndez, N. R., García, R. R., Castillo B. E., and Sauri, R. M. (2010a). Tratamiento de lixiviados por oxidación Fenton. *Ingeniería e investigación 30*, 80-85.

Méndez, N. R., Pietrogiovanna, B. J., Santos, O. B., Sauri, R. M., Giacomán, V. G. and Castillo, B. E. (2010b). Determinación de la dosis óptima de reactivo Fenton en un tratamiento de lixiviados por Fenton-adsorción. *Revista Internacional de Contaminación Ambiental 26*, 211-220.

Mohajeri, S., Hamidi, A. A., Isa, M. H., and Zahed, M. A. (2019). Landfill leachate treatment through electro-Fenton oxidation. *Pollution 5*, 199-209. https://doi.org/10.22059/POLL.2018.249210.364

Nájera, A. H. (2011). Combinación de procesos fisicoquímicos y biológico anaerobio para el tratamiento de lixiviados maduros generados en el relleno sanitario de Tuxtla Gutiérrez. Tesis de Doctorado en Ciencias en Desarrollo Sustentable, Universidad de Ciencias y Artes de Chiapas, México.

Nájera, H., Castañón, J., Figueroa, J., and Rojas-Valencia, M. (2009). Caracterización y tratamiento fisicoquímico de lixiviados maduros producidos en el sitio de disposición final de Tuxtla Gutiérrez, Chiapas, México. 24 y 25 de septiembre, *II Simposio Iberoamericano de Ingeniería de Residuos*, Barranquilla, Colombia.

Nájera-Aguilar, H. A., Gutiérrez-Hernández, R. F., Bautista-Ramírez, J., Martínez-Salinas, R. I., Escobar-Castillejos, D., Borraz-Garzón, R., Rojas-Valencia, M. N. and Giácoman-Vallejos, G. (2019). Treatment of low biodegradability leachates in a serial system of aged refuse-filled bioreactors. *Sustainability 11*, 3193. https://doi.org/10.3390/su11113193

Naveen, B. P., Mahapatra, D. M., Sitharam, T. G., Sivapullaiah, P. V., and Ramachandra, T. V. (2017). Physico-chemical and biological characterization of urban municipal landfill leachate. *Environmental Pollution 220*, 1-12. https://doi.org/10.1016/j.envpol.2016.09.002

Oulego, P., Collado, S., Laca, A., and Díaz, M. (2016). Impact of leachate composition on the advanced oxidation treatment. *Water Research 88*, 389-402. https://doi.org/10.1016/j.watres.2015.09.048

Papastavrou, C., Mantzavinos, D., and Diamadopoulos, E. (2009). A comparative treatment of stabilized landfill leachate: Coagulation and activated carbon adsorption vs. electrochemical oxidation. *Environmental Technology 30*, 1547-1553. https://doi.org/10.1080/09593330903252240

Peng, Y. (2017). Perspectives on technology for landfill leachate treatment. *Arabian Journal Chemistry 1*0, S2567-S2574. https://doi.org/10.1016/j.arabjc.2013.09.031

Pereira, S. F., Gonçalves, A. L., Moreira, F. C., Silva, T. F., Vilar, V. J., and Pires, J. (2016). Nitrogen removal from landfill leachate by microalgae. *International Journal of Molecular Science 17*, 1926. https://doi.org/10.3390/ijms17111926

Poblete, R., and Pérez, N. (2020). Use of sawdust as pretreatment of photo-Fenton process in the depuration of landfill leachate. *Journal of Environmental Management 253*, 109697. https://doi.org/10.1016/j.jenvman.2019.109697

Quintero-Ramírez, A., González, Y. V., and Valencia, L. A. L. (2017). Variaciones geotécnicas en un suelo tropical causadas por los lixiviados de residuos sólidos urbanos: escala laboratorial. *Boletín de Ciencias de la Tierra 41*, 40-47.

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., and Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials 150*, 468-493. https://doi.org/10.1016/j.jhazmat.2007.09.077

San Pedro-Cedillo, Méndez-Novelo, R. I., Rojas-Valencia, M. N., Barceló-Quintal, M., Castillo-Borges, E. R., Sauri-Riancho, M. R., and Marrufo-Gómez, J. M. (2015). Evaluation of adsorption and Fenton-adsorption processes for landfill leachate treatment. *Revista Mexicana de Ingeniería Química 14*, 745-755.

San-Pedro, L., Méndez-Novelo, R., Hernández-Núñez, E., Flota-Bañuelos, M., Medina, J., and Giacomán-Vallejos, G. (2020). selection of the activated carbon type for the treatment of landfill leachate by fenton-adsorption process. *Molecules 25*, 3023. https://doi.org/10.3390/molecules25133023

Sang, Y. M., Gu, Q. B., Sun, T. C., and Li, F. S. (2008). Color and organic compounds removal from secondary effluent of landfill leachate with a novel inorganic polymer coagulant. *Water Science Technology 58*, 1423-1432. https://doi.org/10.2166/wst.2008.446

Seibert, D., Quesada, H., Bergamasco, R., Borba, F. H., and Pellenz, L. (2019). Presence of endocrine disrupting chemicals in sanitary landfill leachate, its treatment and degradation by Fenton based processes: A review. *Process Safety and Environmental Protection 131*, 255-267. https://doi.org/10.1016/j.psep.2019.09.022

Smaoui, Y., Mseddi, S., Ayadi, N., Sayadi, S., and Bouzid, J. (2019). Evaluation of influence of coagulation/flocculation and Fenton oxidation with iron on landfill leachate treatment. *Environment Protection Engineering 45*, 139-153. https://doi.org/10.5277/epe190111

Sruthi, T., Gandhimathi, R., Ramesh, S. T., and Nidheesh, P. V. (2018). Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes. *Chemosphere 210*, 38-43. https://doi.org/10.1016/j.chemosphere.2018.06.172

Wang, Y., Shao, Z., and Yi, X. (2020). Novel Fenton-biological combined process at neutral pH by virtue of endogenous acidification and fungal degradation: Performance and cost analysis in the lab-scale study. *Chemical Engineering Journal 399*, 125745. https://doi.org/10.1016/j.cej.2020.125745

Wu, Y., Zhou, S., Qin, F., Peng, H., Lai, Y. and Lin,Y. (2010). Removal of humic substances from landfill leachate by Fenton oxidation and coagulation. *Process Safety Environmental Protection 88*, 276-284. https://doi.org/10.1016/j.psep.2010.03.002

Zhang, A., Gu, Z., Chen, W., Li, Q., and Jiang, G. (2018). Removal of refractory organic pollutants in reverse-osmosis concentrated leachate by Microwave?Fenton process. *Environmental Science and Pollution Research 25*, 28907-28916. https://doi.org/10.1007/s11356-018-2900-7

Zhang, J., Gong, J. L., Zenga, G. M., Ou, X. M., Jiang, Y., Chang, Y. N., Gou, M., Zhang, C. and Liu, H. Y. (2016). Simultaneous removal of humic acid/fulvic acid and lead from landfill leachate using magnetic graphene oxide. *Applied Surface Science 370*, 335-350. https://doi.org/10.1016/j.apsusc.2016.02.181

Zhang, J., Wu, X., Qiu, D., Mao, J., and Zhang, H. (2019). Pilot-scale in situ treatment of landfill leachate using combined coagulation?flocculation, hydrolysis acidification, SBR and electro-Fenton oxidation. *Environmental Technology 40*, 2191-2200. https://doi.org/10.1080/09593330.2017.1329347

Zhao, R., Feng, J., Yin, X., Liu, J., Fu, W., Berendonk, T. U., Zhang T., Li X. and Li, B. (2018). Antibiotic resistome in landfill leachate from different cities of China deciphered by metagenomic analysis. *Water Research 134*, 126-139. https://doi.org/10.1016/j.watres.2018.01.063